SYMPOSIUM BI01

Materials Data Science—Transformations in Interdisciplinary Education
December 2 - December 3, 2019

Symposium Organizers
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Symposium Support
Bronze
Citrine Informatics

* Invited Paper

SESSION BI01.01: Data Science in Materials Education and Methods Development
Session Chairs: Raymundo Arroyave and Elizabeth Dickey
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 205

1:30 PM *BI01.01.01
Data Science—The New Critical Capability for Every Materials Scientist Kristen Brosnan; GE Global Research, United States

At GE Research, our mission is to develop innovative technologies and turn those into real products and solutions in the aerospace, power generation, healthcare, additive manufacturing, transportation, and oil and gas industries. Today, we are combining “physics” with artificial intelligence (AI) and machine learning (ML) to invent new materials, revolutionize manufacturing design, processing and inspection across our industrial portfolio. In this talk, I will provide examples of how data science methods are critical to materials discovery, how we are helping to train our work force, and my thoughts on the critical skills needed for today’s Materials Scientist.

2:00 PM *BI01.01.02
Transforming the Science of Materials through the Science of Information—A Pedagogical Perspective Krishna Rajan; University at Buffalo, The State University of New York, United States

This presentation will provide a perspective on how materials informatics can affect how one trains materials scientists and engineers. I will put this in the context of how we have established an entirely new materials department based on building the foundations of materials science through the lens of information science. The pedagogical foundation of MDI is founded on a data intensive perspective of materials science for the study of materials theory, characterization, synthesis, processing and computational and simulation techniques. Our novel pedagogical framework allows students to learn from that data by deriving information that may be outside the models on which they are based, and use this learning process in order to efficiently and robustly explore the information space that cannot be done by existing models

2:30 PM OPEN DISCUSSION

3:00 PM BREAK

3:30 PM *BI01.01.04
Open-Source Tools for Materials Informatics—Atomate, Matminer and Matscholar Anubhav Jain; Lawrence Berkeley National Laboratory, United States

In this talk, I will present our group's work in developing and disseminating three open-source tools for materials informatics: the atomate software (https://atomate.org) for running high-throughput calculations, the matminer software (https://hackingmaterials.github.io/matminer/) for data mining structure-property relationships, and the matscholar software (https://github.com/materialsintelligence/matscholar) for searching and analyzing text data. I will describe usage of these tools and their impact in helping users learn and perform materials informatics studies. For example, atomate makes it possible for users to generate data with high-throughput density functional theory using a high-level software framework. Matminer implements many of the feature extraction routines reported in the materials informatics literature, making it possible for users to rapidly test many different such algorithms for their study, and also collects together sample data sets for testing new algorithms. Matscholar makes it possible for researchers to search for information across millions of published abstracts. Finally, I will discuss usage of these tools with the Materials Project database and their past and potential future role in educational curricula.

4:00 PM BI01.01.05
Materials Software Workshop and Outreach at DOE Materials Genome Innovation for Computational Software (MAGICS) Center Ken-ichi Nomura, Aiichiro Nakano, Priya Vashishta and Rajiv Kalia; University of Southern California, United States

Emerging exascale computing will have a profound impact on materials simulations and machine learning (ML) to enable faster and more targeted material discoveries. This requires a new approach to computational materials science that integrates materials simulations with ML techniques. This interdisciplinary integration, along with the ever-tighter coupling between experiments and simulations, will provide a new platform for ML-enabled materials discovery. Here education and training programs on ML-based methodologies for the materials research community are urgent needs for future scientists and engineers to be competitive in the emerging field.

At the DOE Materials Genome Innovation for Computational Software (MAGICS) Center, we develop open-source materials simulation software, ML tools, training courseware that run on desktops to exascale supercomputers. Center software and databases provide function-property-structure relationships in functional materials to help synthesis and characterization of a wide class of materials. We have provided three hands-on trainings in Center-developed materials software databases so far (106 users from 55 universities, national labs and research institutions), and plan to continue the outreach program at annual MAGICS software workshops. In this talk I will discuss the MAGICS software suite and training courseware, and lessons learned from the software workshops.

This work was supported as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC0014607

4:15 PM *BI01.01.06
Incorporating the Principles of Compressed Sensing/Inpainting and Machine Learning into the Implementation of Advanced TEM Methods Nigel Browning¹,²,³, B. Layla Mehdi¹,²,³, Houari Amari¹, Heath Bagshaw¹, Matthew Bilton¹, Andrew Stevens² and Christopher Buurma³; ¹University of Liverpool, United Kingdom; ²Pacific Northwest National Laboratory, United States; ³Sivananthan Laboratories, United States

Transmission electron microscopy (TEM) is a widely used method to observe and quantify the atomic scale structure, composition, chemistry, bonding, electron/phonon distribution and optical properties of nanostructures, interfaces and defects in many materials systems. In addition to observing static structures, in-situ gas and liquid stages now permit dynamic experiments to be performed inside the TEM to observe complex structural and chemical transformations. In all of these cases, the goal in designing and implementing the TEM experiments is to acquire the most information about the sample while the least amount of damaging electron dose is delivered to it—a modern TEM experiment must therefore first determine the “optimal sampling” conditions for the material being studied. In addition, as many TEMs now have direct electron detectors capable of recording 100-1000 images per second or more (resulting in terabytes of data for each experiment), data compression and the use of automated analytics play a key role in interpreting the results of these experiments. The use of compressed sensing and inpainting methods is now being taught as part of the regular senior undergraduate/graduate student course structure.
in advanced TEM methods. In addition, the use of machine learning to improve the analysis of the sub-sampled datasets and data analytics to extract key parameters from a series of images are also key parts of the course. The sub-sampling/inpainting methodology for optimal sensing is hardwired into the acquisition mechanism of the microscopes used for the practical aspects of these microscopy courses, allowing students to directly modify the means by which images are acquired and test its effect on the speed, resolution and precision of the images obtained/reconstructed/analyzed during their training. In this presentation we will discuss the use of TEM images, and in particular obtaining the best TEM image for the lowest dose, to teach the concepts of compressed sensing, inpainting and machine learning as part of a core materials science method. Overall, we have found that the direct atomic scale images of the structure permit students to quickly get a grasp of the main mathematical and data concepts and how to best implement them in their experimental design. Here we will also discuss the application of these same methods onto other materials characterization techniques (and imaging tools in general), the way that users are trained on those methods, and the precision of the results that are obtained.

4:45 PM BI01.01.07
Semantic Exploration of Nanowires Technological Trend and Scientific Advancement  Vasilii Kaliteevskii; Lappeenranta University of Technology, Finland

Within the fast-growing field of nanoscience and nanotechnology, observing and understanding the relation between physical and chemical properties of nanostructures and their potential applications plays a critical role in fueling and channeling future innovations and future perspectives of the field. Nanowires, in particular, have been shown to be excellent object of study to explore new fundamental physical phenomena, yet their integration into working devices has not been progressing at the same rate. The potential commercialization of nanowires could hardly be reliant only on a simple count of growing scientific publication. Therefore, it is necessary to expend the view towards patent publications, with a goal to perform detailed comparative analysis of both technological and scientific knowledge. Patent documents are a superb source of technical information that is not published elsewhere, but at the same time are not peer-reviewed documents. For this reason, separate analysis of knowledge stored in scientific literature or patent databases might lead to an invalid path/picture of current nanowire technology development.

Here, we present possibilities of technologies such as the Natural Language Processing and Machine Learning used in the framework of patent and scientific publications search to support heuristic stage of design of new products and technologies. As a result, the content analysis, together with profiling results can shed a light on the overlap or possible gap between scientific discoveries and technological innovations. Finally, the implementation of heuristic methods such as TRIZ, which are proven to be effective tools for problem solving for classical physics and engineering could inspire combination of different methods, approaches and technologies in the field of nanowires, leading towards inventive solutions in the potential new devices, concepts and technologies, especially at the conceptual design stage.

BI01.02.01
Development of Data Scientists for Interdisciplinary Environments Such as Materials Science  Kazunori D. Yamada¹, Samy Baladram¹, Takuro Nakayama¹, Yinxing Li¹, Roger H. French² and Mitsuyuki Nakao¹; ¹Tohoku University, Japan; ²Case Western Reserve University, United States

Rapid advances in information technology have been drastically changing the world. Informational innovations are affecting people's lives divergently and comprehensively, and data sciences, a foundation to utilize these enormous and diverse data, are of increasing importance. Thus, there is an urgent need for educational institutions to train both experts in data science and to train all types of scientists to have data science skills. Tohoku University has made specific efforts on the education in data science. The “International Joint Graduate Program in Data Science
(GPDS)” and “Data Sciences Program (DSP)” designated for the international students are data science education programs running in Tohoku University. The former targets current students in the university while the latter recruits overseas students and these programs are operated in a coordination. The foundation of data science is undoubtedly statistical analytics and computer science. However, because of the highly-diversified nature of real-world problems, a data scientist cannot be successful with only a focus in a specialized field such as computer science alone. It is expected that data scientists should be easily able to cooperate with experts across many fields in diversified team research projects. In this regard, GPDS and DSP are operated both internationally and interdisciplinarily, in cooperation with overseas universities and other graduate schools in the university.

GPDS and DSP has been focusing on three in important abilities for data scientists. 1) Problem-finding: ability to find a problem from a transdisciplinary perspective and to create a process of solution. 2) Data analysis: ability to analyze the big data to extract the essential information for the problem-solving across diverse fields such as Materials Science and Life Science. 3) Technology architecture: ability to appropriately organize the technological infrastructure necessary for the problem-solving. Based on this direction, GPDS and DSP have been offering lectures, which cover from basic analysis methods to state-of-the-art research topics of data science. Besides the lectures, the educational programs has practical, step-wise training courses. First one is a start-up exercise for beginners of the computer programing, where students learn how to use Linux and Python. Second one is an intensive class based on drills in data analyses, from basic numeric calculation to specialized methods, such as approaches using complex machine learning models. Students successively work out problems, while instructors inspect the answers and codes from each student. By this process, instructors are able to detect weak and strong points of individual students, and to guide a student toward an efficient learning approach. The last one takes project-based learning (PBL) approach. Students are grouped into interdisciplinary teams and each team has heterogeneities in ability in computer programming, fields of specialty and degrees. In the course, students solve realistic problems using real-world data. In previous cases of this PBL training, students with computer skills tended to play a leadership role in a team. For these advanced students, the training course could be an opportunity to fulfill their ability throughout solving complicated real-world problems and to strengthen their expertise by guiding other un-trained team members. Solving a problem in coordination with other team members is definitely an important skill for data scientists and the course give meaningful experience for all students.

In these courses, students deal with various kinds of data from diverse fields, which include material informatics, materials science, natural language processing, plant engineering, blockchain, advertising, biology, bioinformatics and etc. An essential aspect of this learning is the combination of real-world, messy, datasets, and domain scientists, such as Materials Scientists, as critical team members.

B101.02.02
Pathway toward Sustainable Development of Next Generation Photovoltaics Focused on Materials—A Detailed Study on Research Trends through Bibliometrics Jun-Seok Yeo; Korea Institute of Science and Technology, Korea (the Republic of)

The development of sustainable power sources has attracted significant attentions because of the unsustainability of the traditional energies. Among the next-generation power sources, solar energy with photovoltaic (PV) has been considered as a viable alternative. In particular, hybrid organic-inorganic perovskite solar cells (PeSCs) have been intensively explored due to their high performance, high cost-effectiveness, and broader feasibility. In this study, we investigated the research trends and the collaboration networks with the bibliometric methods based on the scientific publications. For the systematic investigations, all the publications were classified by the publication years and the commercialization factors. From publication years of 2009 to 2018, a total of 6,581 documents were investigated. The commercialization factors were categorized by considering the LCOE and the environmental impact of the PeSCs; cost, efficiency, stability, scaling-up, and public acceptability. In addition, multiple bibliometric methods were used in this study: (1) ‘statistical analyses’ of publication output, (2) ‘topic modeling’ based on the publication abstracts, and (3) ‘social network analysis (SNA)’ of co-authorships at institute level. This strategic analysis will provide various aspects of scientific findings, and facilitate further discussion on the direction of the PeSC research.

B101.02.03
Designing Laboratory Activities for Undergraduate Synthetic Materials Chemistry Course Brandon J. Burnett; Weber State University, United States

Creating robust, simple, and safe material synthesis laboratory activities at an undergraduate level is becoming increasingly important as more undergraduate programs are adopting materials chemistry classes and programs. This
presentation will focus on efforts at a PUI to highlight core materials chemistry concepts through hands-on synthetic laboratory activities, including solvothermal syntheses, sol-gel, chemical vapor deposition, powder annealing, synthon design, and computer modeling. We will also discuss opportunities to collaborate with physics departments to incorporate structural and property analyses, for a cross-disciplinary education.

**B101.02.04**
**Developing Selective Absorbers for Solar Water Heating as a Holistic Materials Undergraduate Research Experience** Kristin Rabosky, Corey Collatz and Colin Inglefield; Weber State University, United States

The process of developing new thin film materials can be a rewarding experience as an undergraduate research project exposing students to recipe design for material growth, the intersection of multiple characterization techniques, and incorporating films into useful devices. Additionally, this project is useful in teaching students how to manage and analyze larger data sets garnered from a variety of samples. We are using a series of cermet based selective solar absorbers (SSAs) made with varying ratios of Mo and SiO2 as a platform to teach students about the many pieces in electronic materials development. These SSAs are tested with several characterization techniques to determine film quality and are then incorporated into a prototype water heater to verify optimization of light absorption and heat retention. We have found this project to be a successful platform for teaching students about the iterative cycle of new materials development.

**B101.02.06**
**From Stored Data to Data Stories—Jupyter and R Notebooks for Reproducible Materials Informatics** Paul J. Kowalczyk; Solvay, United States

Literate computing weaves a narrative directly into an interactive computation. Text, code, and results are combined into a narrative that relies equally on textual explanations and computational components. Insights are extracted from data using computational tools. These insights are communicated to an audience in the form of a narrative that resonates with the audience. Literate computing lends itself to the practice of reproducible research. One may re-run the analyses; run the analyses with new data sets; modify the code for other purposes.

This presentation will take one through the steps associated with literate computing: data retrieval; data curation; model construction, evaluation, and selection; and reporting. Particular attention will be paid to reporting, i.e., building a narrative. Examples will be presented demonstrating how one might generate multiple output formats (e.g., HTML pages, presentation slides, PDF documents) starting with the same code base.

As a specific example, a data narrative will be built showing how one might build predictive models for the prediction of band gap energies. Reports will be presented as (1) an HTML file, (2) a PDF document (in a format acceptable for journal submission), and (3) a slide presentation.

The presentation will have three main foci:
1. infrastructure: instantiating the computational environment; loading packages; loading data
2. computation: data curation, transformation, and analysis; model construction and evaluation
3. communication: creating tables, charts, and graphs; weaving all components into data narrative

At the presentation’s conclusion attendees will have walked through exercises that may serve as templates to be used with their data as they build their data narratives.

The R and Python ecosystems will be used throughout. All data, code, and text will be made available.
Graduate education is poised to undergo significant changes as we consider how best to prepare students for a dynamically shifting workforce. Areas of high national need often require scientists and engineers that can work in interdisciplinary/convergent spaces with strong, career-aligned skillsets. This presentation will focus on two National Science Foundation programs within the Division of Graduate Education that support new educational models and approaches. The National Science Foundation Research Traineeship (NRT) program was designed to broaden graduate student career pathways and preparation, foster lasting institutional changes in graduate training, and support interdisciplinary to convergent STEM research. The program currently supports 68 projects across 33 states and territories; each project has a budget of approximately $3,000,000. The Innovations in Graduate Education (IGE) program supports studies to test new approaches and generate the knowledge to identify best practices in graduate education. IGE awards are focused, educational research projects with budgets ranging from $300,000-$500,000. Taken together, these programs are testing new models and approaches that will train inclusive cohorts of STEM graduate students with the appropriate career-aligned skillsets to productively move into diverse career pathways. The presenter is the Lead Program Director for both NRT and IGE. PIs interested in learning more about these funding opportunities are encouraged to attend. Program objectives and exemplary projects will be discussed, and time will be included to answer programmatic questions.

The Materials Genome Initiative (MGI) calls for the acceleration of the materials development cycle through the integration of experiments and simulations within a data-aware/enabling framework. To realize this vision, MGI recognizes the need for the creation of a new kind of workforce capable of creating and/or deploying advanced informatics tools and methods into the materials discovery/development cycle. To meet this need, an interdisciplinary team at Texas A&M University has developed an interdisciplinary program that indeed goes beyond the prescriptions set forth by the MGI as it incorporates the discipline of engineering systems design as an essential component of the new accelerated materials development paradigm.

The Data-Enabled Discovery and Development of Energy Materials (D3EM) program, funded by the NSF Research Traineeship (NRT) program out of the Division of Graduate Education has enabled the creation of an interdisciplinary graduate program at the intersection of materials science, informatics, and design. The program consists of an interdisciplinary curriculum consisting of cross-disciplinary components in the three fields of materials, informatics and design, followed by an interdisciplinary integrative course that has, as its goal, the solution of a real-world materials discovery/development problem motivated by industry or national laboratories. In addition to the technical component of the curriculum, the D3EM program includes a comprehensive professional skill development syllabus that includes career path planning, communication skills, collaboration, leadership as well as an intensive technical writing program based on the POWER method pioneered by the College of Education and Human Development of Texas A&M University.

The D3EM program was created a partnership between TAMUs Center for Teaching Excellence and six departments across the Colleges of Science (Chemistry and Physics) and Engineering (Mechanical Engineering, Chemical Engineering, Electrical Engineering and Materials Science and Engineering) and is at its mid point in its time frame. In this talk I will discuss in detail the pedagogical model underpinning the curriculum as well as different aspects of the program as they relate to fostering interdisciplinarity not only within student participants but also among the entire student cohort and participating faculty.

International Data Corporation predicted that 60% of organization in 2021 will use machine learning approaches for
more extensive data analysis and insights. However, traditional materials engineering education on the undergraduate and graduate levels falls short to address this need. In this talk, I will discuss how NCState response to this shortcoming. For graduate education, we introduced the a graduate certificate which is designed for interdisciplinary graduated education at the intersection of materials science, engineering, and data science with the aim of preparing the next generation of materials engineers given the growing demand for data-science skills and knowledge of the artificial intelligence. The skills and knowledge obtained here will serve as foundation for the understanding of materials informatics and high throughput materials discovery that will improve a student’s career prospects. To address the immediate knowledge gaps in graduate and undergraduate education, we introduced a general hands-on introductory class on Materials Informatics with the aim to introduce the emergent field of materials informatics and current approaches that employ informatics and computational data to accelerate the process of materials optimization, discovery and development. The goal of our efforts was to prepare students to move into career positions that require a basic comprehension of data science techniques as applied to materials science and engineering problems.

9:45 AM BI01.03.04
Challenges and Opportunities in the Development of Data Science Skills in Undergraduate Materials Education—A Perspective from Mexico
Yareli Rojas-Aguirre, Yara C. Almanza-Arjona, Jesús S. Alejandro-Cruz, Lorena Meza-Puente and Marlene Covarrubias-Sánchez; Universidad Nacional Autónoma de México, Mexico

Nowadays, the term nanotechnology is strongly present in many areas of science and engineering. Nanotechnology can be defined as a set of disciplines focused on the study, manipulation, and control of matter at the atomic and molecular level, in order to exploit the properties that it presents in the nanoscale, to generate functional materials with physical and chemical attributes that exceed those we know today. However, after several decades of such research efforts, which are the actual industrial applications of nanomaterials? Which nanomaterials are industrially relevant? What should academic materials nanotechnology research focus on? Which are the main aspects that should be addressed by materials undergraduate students in the field? Despite its popularity in both, academics and the mainstream media, nanotechnology is not sufficiently addressed in the classrooms of Chemical Engineering, Chemistry and other Materials Sciences related undergraduate programs. Materials education and related disciplines have evolved slowly in Mexico because the discipline curriculum remained with no significant changes for almost four decades. One of the primary challenges in current undergraduate materials courses is to incorporate topics, such as Materials Data Science, which are related to several technologies that have enabled the massive production, analyses, and management of scientific data.

The fourth Industrial Revolution (IR4.0) is a technological shift driven by the emergence of robotics, Big Data, Internet of Things (IoT), Smart Manufacturing and Cloud-based Manufacturing. The most important elements of this technological era are machines, devices, sensors, and people, to be in communication with each other through the Internet. Hence, artificial intelligence (AI) and digital-physical frameworks make human-machine interfaces regularly present in our daily life. This new scientific and technological landscape demands a transformation in materials education as new concepts, methods, and technologies not previously taught in college are meant to either substitute or complement the current syllabus. This evolution in materials education is particularly important to learn, discover and design data-driven techniques that will allow future materials scientists and engineers to discover new materials through materials informatics and develop materials by means of machine-learning in order to reduce the time and cost of materials design and deployment.

This work describes the case of study of undergraduate chemical engineering students at the Institute of Materials Research, UNAM, Mexico who engaged in a Technology Intelligence (TI) research project as a learning strategy to analyze the potential applications of nanomaterials at industrial scale through the development of basic Data Science Skills. The objective of the project was to conduct data mining within the cycle of TI in order to collect information, validate and curate data in order to answer the research questions mentioned earlier. The data analysis and visualization enable the students to identify nine areas of the potential application of nanomaterials worldwide at an industrial level in the last 10 years (2009-2019): agriculture, biomedicine, construction, cosmetics and healthcare, electronics, energy, food technology, optics and optoelectronics, and textiles.

By engaging undergraduate students in a data-driven project, students developed basic research and data science skills and transformed their attitude and perception towards the conception of nanotechnology, into a novel and attractive approach by linking fundamental knowledge with state-of-the-art research. Additionally, this educational experience allowed them to acquire other important abilities as decision making, data mining, data curation, data
analyses, data visualization, detection of relevant correlations and communication of results.

10:00 AM BREAK

10:30 AM *BI01.03.05
Data-Driven Materials Design—Educational Needs to Harness Legacy Data for New Materials Development
Jennifer L. Carter; Case Western Reserve University, United States

Data-driven materials design informed by legacy data-sets can enable the education of a new workforce, promote openness of the scientific process in the community, and advance our physical understanding of complex material systems. The performance of structural materials, which are controlled by competing factors of composition, grain size, particle size/distribution, residual strain, cannot be modeled with single-mechanism physics. The design of optimal processing route must account for the coupled nature of the creation of such factors, and requires students to learn machine learning and statistical modeling principles not taught in the conventional undergraduate or graduate level Materials Science and Engineering curricula. Therefore, modified curricula with opportunities for experiential learning are paramount for workforce development. Projects with real-world data provide an opportunity for students to establish fluency in the iterative steps needed to solve relevant scientific and engineering process design questions.

Exploratory data analysis (EDA) coupled with data-driven modeling allows new researchers to quickly orient in a field and gain insight into how and why decisions were historically made. The alloy development in 9-12wt% Cr martensitic steels has been of ongoing for thirty years. EDA quickly highlights the trade-off between short-term strength and long-term creep stability with increasing chromium concentration [1]. Though this knowledge can be gained from careful study of the literature, EDA allows the researcher to gain this institutional knowledge in short order without having to know what or where to look for first in the literature. This reduces the training cycle time and has implications to all R&D sectors facing knowledge transfer challenges as the “Boomer” generation retires.

Data-driven process|structure|performance (P|S|P) modeling provides insights into the oft-competing mechanisms that must be considered and optimized in the design of processing routes for new materials and design performance requirements. P|S|P modeling requires a foundation in statistical principles to assess the significance and quality of the findings. The constraints of different modeling techniques allow researchers to infer different physical qualities from the models [2].

Limitations of legacy data teach students the importance of statistical study protocol development. How to design the next study to mitigate issues of uncertainty and leverage prior knowledge to optimize inference gained from the modeling efforts? This goes hand-in-hand with the development of high-throughput experiments for microstructural characterization and mechanical behavior. For example, the study protocol to deconvolute the time-temperature effects on the kinetics of precipitate formation requires multiple processing steps to extract useful metrics. Next, robust data-science algorithms for analysis of microstructure [3], and mechanical performance [4] are needed to efficiently probe the design space. The approaches are useful for establishing protocols for the procurement of new databases of structure and performance for the process development of alloys from conventional and additive manufacturing.


11:00 AM BI01.03.06
Student Inquiry of Precipitate Morphologies Using an Online GUI for PRISMS-PF Susan Gentry¹, Stephen DeWitt² and Mingwei Zhang¹; ¹University of California, Davis, United States; ²University of Michigan, United States
The morphologies of precipitates in metal alloys can often be complex due to competing mechanisms such as anisotropic interfacial energy and misfit strain energy. For these systems, multiphysics computer simulations can be powerful tools since researchers can artificially “turn off” individual mechanisms while holding all other variables constant. For instance, this approach has been used by investigators to elucidate the effects of misfit strain, interfacial energy, and anisotropic growth rates on experimentally observed precipitate morphologies in magnesium-rare earth alloys. Unfortunately, the inherent complexity of these computer simulations often makes them inaccessible for novice learners.

For educational uses, we have published a tool on nanoHUB that simulates two-dimensional equilibrium morphologies of an isolated precipitate within a matrix. The simulation tool, available at https://nanohub.org/tools/prismspfmisfit, is implemented using a black-box approach with a graphic user interface (GUI). To run a simulation, a user only needs to provide material parameters such as anisotropic interfacial energies, anisotropic misfit strains, elastic moduli, and Poisson’s ratios for the system. Underlying the simple GUI is an application built using PRISMS-PF, an open-source phase field framework that uses the finite element method to solve phase field equations to predict microstructural evolution. The nanoHUB tool launches a finite element simulation for a precipitate in a matrix, which is then evolved until it reaches equilibrium. The equilibrium precipitate morphology is output to the user, along with the dimensions of the precipitate and the volume fraction, for further analysis.

We use this online tool to help materials science and engineering students develop expert knowledge on the fundamentals of precipitate morphology. One trait of a subject-matter expert is the many deep connections between the facts they have learned, such as the interplay between interfacial energy and misfit strain energy. To develop these connections in novice students, we have developed an inquiry-based teaching module. Students are presented with a micrograph of metallic precipitates and are prompted to explain the shape and the aspect ratio based on misfit strain energy and anisotropic interfacial energy. Using the PRISMS-PF tool, students run simulations that vary the misfit strain and anisotropy to build mental models of these effects and ultimately identify the dominant mechanism(s) in the precipitate morphology. Finally, we present an evaluation of metacognitive questions that are used for formative assessment of this activity.

11:15 AM *BI01.03.07
Microstructural Analysis in Python for Materials Data Science Daniela Ushizima¹,², Silvia Miramontes-Lizarraga¹,², Michael Macneil¹ and Dilworth Parkinson¹; ¹Lawrence Berkeley National Laboratory, United States; ²University of California, Berkeley, United States

The growth of X-ray brilliance and extremely quick snapshots allied to advances in machine learning create new opportunities to streamline the description of materials structures as part of the design of new compounds. From industry to national laboratories, X-ray imaging has become fundamental to measure the function and resilience of new materials and for probing dynamic properties. However, the analysis of these rich datasets at scale requires further research in automation that combines computational and experimental methods.

A major challenge is to couple increasing data rate experiments to new data science algorithms in support of quantitative image analysis that can automatically drive the scientific discovery. Our efforts in deep learning applied to image representation and structural fingerprints have made sample sorting and ranking possible, allowing automated identification of special materials configurations from million-sized databases. These complex networks recognize events from data gathered in two regimes: experimentally and by simulation. While such methods successfully bypass hand-engineered features, their full extension to three-dimensional imagery seldom meets standards that are comparable to manual curation. Additionally, labeling large datasets of 3D data is practically impossible.

For example, the inspection of material deformation using X-ray attenuation contrast data from microtomography often generates two thousand cube voxels per volume. The issue is that the creation of millions of labeled volumes means manually handling eight billion voxels per time step for one experimental setting. Therefore, our research efforts also include the creation of the next generation curation tools based on advanced computer vision algorithms addressing fundamental problems, such as multiresolution algorithms for image segmentation (e.g. graph-based
classification and convolutional neural networks), stereological analysis, and enumeration of particles within microtomography imagery.

The contributions of our team include: (a) the development of numerical schemes to analyze data that stem from physical experiments; (b) the construction of new software tools to empower materials scientists and constrain parameter space, particularly given prior knowledge from experimental settings; and (c) the reproducibility of experiments by recognizing the importance of open-source codes and availability of benchmark datasets of scientific images coming from advanced instruments.

This talk will present computational tools for recognition of patterns that occur in scientific images, both coming from synchrotron-based X-ray instruments and simulation through HPC codes. This talk will include scripts for visual analysis and interaction with extracted 3D geometries to be shared with the audience, which will be illustrated on scientific imagery from open-data projects. Use-cases will demonstrate our advancements on inspection of hierarchical materials that consist of many individual strands, bundled within a matrix to achieve high-strength mechanical properties and durability.

11:45 AM BI01.03.08
Nucleation and Growth of AlN—A Case Study of the Challenges in Blending Materials Science and Data Science in an International Collaboration
Masayoshi Adachi¹, Benjamin G. Pierce², Ahmad M. Karimi², Laura G. Wilson², Roger H. French², Jennifer L. Carter² and Hiroyuki Fukuyama¹; ¹Tohoku University, Japan; ²Case Western Reserve University, United States

Aluminum nitride (AIN) is a promising substrate material for AlGaN-based ultra-violet light emitting diodes. In the Fukuyama group at Tohoku University, AIN crystal growth methods have been developed [1] with a recent focus on solution growth using a Ni-Al alloy. In order to design this technique, a fundamental study for the AIN formation on a Ni-Al droplet was undertaken. To understand the growth behavior and design an optimum crystal growth technique, an in-situ observation system for solution growth of AIN crystal using electromagnetic levitation [2] has been developed.

As part of the Tohoku University and Case Western Reserve University collaboration in Data Science for Life Sciences and Materials Science, an international and interdisciplinary research project started, focused on statistical significant quantification of AIN formation behavior, spanning nucleation, growth and coalescence so to design and define an optimum crystal growth technique.

The materials science goal was to profile the nucleation and growth rates of AIN crystals on the spherical liquid Ni-Al droplet. The study protocol, representing the details of how the experiments are to be run, including varying the temperature, the Ni-Al composition ratio, the N₂ gas pressure, and the static magnetic field (which controls the solution flow in the molten droplet). This design space of the crystal growth predictors allowed us to encompass from high to low nucleation rates, and from hundreds of AIN crystalites on the sphere, to controlled single crystal growth. The high speed cameras recorded the droplet from the top and the side simultaneously, and the video images analyzed in this project encompass over 530,000 single frame images. With this large dataset, analysis was done in our distributed and high performance computing environment at CWRU [3]. Image analysis was performed using Python (v2.7) libraries including Matplotlib, Numpy, Scipy, Pandas, Seaborn, Trackpy with Skimage and OpenCV [4-7].

In addition to the technical details, the code development involved graduate and undergraduate students, distributed and high performance computing, data exchanges of large datasets and producing robust codes with a number of students that can be validated and are sufficiently modular so that the pipeline is multi-functional. For code development over a two year period involved 3 undergraduate (UG) and 3 graduate (GS) students who participated sequentially, so proper code styling, commenting, documentation and Git code versioning were essential. In addition, communication between the image analysis students from Materials Science, Mechanical Engineering and Computer Science departments, was enabled by the students all having taken Applied Data Science courses at CWRU, so that the basics of an Open Data Science tool chain, gave them a common framework for both tools and data analysis project structure.

The project goal of the synergistic process may be advanced by French’s teaching Applied Data Science this summer at Tohoku University, with the goal of establishing a “nuclei” of Materials Data Scientists here, which can “grow” into a robust local community of students applying these new and complementary tools to Materials Science problems.
SESSION BI01.04: Novel Experiential Learning and Best Practices in Data-Driven Materials Education  
Session Chairs: Roger French and Yaroslava Yingling  
Tuesday Afternoon, December 3, 2019  
Hynes, Level 2, Room 205

1:30 PM *BI01.04.01  
The Informatics Skunkworks—Undergraduate Research at the Interface of Data Science and Science and Engineering  
Dane Morgan; University of Wisconsin-Madison, United States

Recently there has been an explosion of interest in the application of informatics tools, particularly machine learning, to materials and other domains of science and engineering. A number of features make science and engineering domain specific machine learning applications exceptionally well-suited to undergraduate research. First, relative to many research problems, domain specific machine learning applications are often simple to understand and easy to explore with limited background. Second, research projects in this area develop skills of high-value for future employment or post-graduate education, including technical skills in data science, statistics, programming, and specific domains, as well as broader skills in project management, teamwork, and communication. Third, many problems require only a laptop and free software, or relatively inexpensive computing resources (e.g., a small amount of GPU time). Motivated by the above opportunities I initiated the Informatics Skunkworks. The group has a goal of engaging undergraduates in research dedicated to realizing the potential of informatics for science and engineering, with a focus on materials problems. We have had over a 100 participants since 2015, now with typically over 30 per semester. The projects have had significant impact on students, shown most quantitatively by a strong list of conference presentations, published papers, student awards, and student placement in top graduate programs and companies. Three major challenges we face are (i) how to give students enough information to enable research but not so much that they cannot learn it quickly, (ii) how to allow students to make progress quickly without extensive programming or machine learning expertise, and (iii) how to provide high-quality mentoring given constraints on mentor experience and time. To overcome (i) we have developed a set of modules on key machine learning issues (e.g., machine vision or how to use specific codes) targeted at undergraduates with no background who need to quickly getting a practical working knowledge of the material. To overcome (ii) we have developed the MAterials Simulation Toolkit – Machine Learning (MAST-ML) package, along with useful practice datasets, which allows full machine learning project workflows to be executed from a simple input file with no programming skills and limited machine learning background. To overcome (iii) we are exploring increased program structure and student co-mentoring, but are still far from robust solutions. Our teaching modules and MAST-ML tools allow students to make progress in even just a few hours, supporting not just extended research projects but also class projects and laboratory exercises in this area. In this talk I will describe the mechanics of how we structure the skunkworks, some of the projects we have explored (and their successes and challenges), the resources we have developed to enable this work, and ongoing challenges and opportunities. In particular, I will also discuss our vision for the future and efforts to expand the skunkworks across multiple institutions, and I hope this talk will help start collaborations with others with shared interests to develop integrated efforts going forward.


Final Program 1/13/2020  11
Hackathons Foster Collaboration between Materials and Data Scientists
Brian Reich, Ashleigh Wright, Ralph Smith and Elizabeth C. Dickey; North Carolina State University, United States

Materials science is increasingly turning to data science to extract meaningful inference from large data streams. However, collaborations between researchers within the materials and data-science fields face several challenges including language barriers and domain-specific norms and expectations. In this presentation we discuss our experiences with using a “hackathon” to bridge this gap. We discuss two hackathons models in which participants work intensely for a short time in small groups to develop data-science solutions to authentic materials-science problems. The first hackathon model was implemented in an international workshop with established scientists, while the second model was implemented in a local environment comprised mostly of graduate students. In both cases, we found that short periods of intense interaction resulted in productive interdisciplinary teams. In the talk we discuss the advantages of various formats, approaches that were and were not effective, and offer suggestions for future endeavors and best practices.

Teaching Machine Learning and Artificial Intelligence in Materials through Experiential Learning
Joshua Tappan; Citrine Informatics, United States

Josh Tappan, Citrine Informatics’ head of community, will share Citrine's approach to materials informatics education initiatives. Citrine has successfully run several hands-on, experiential programs with universities across the country.

Josh will share the details of Citrine’s NextGen fellowship, which, over the course of 3 years, has supported 50+ undergraduate students in materials informatics research projects across the United States, as well as the Mines Initiative for Data Driven Materials Innovation (MIDDMI), a partnership with the Colorado School of Mines, which helped 8 student groups incorporate machine learning and materials informatics techniques into their research. Additionally, he will discuss Citrine's approach to education and curriculum development in the industrial materials community.

Audience members will be able to access some of the open educational resources Citrine developed as part of these programs.

SonicAtomic—New Interactive Sonification Interface for Students with Visual Impairment Assisting Multi-Dimensional Scientific Data Analysis
Thomas Watts1, Ahlam Lee2, Roberto Myers3 and Jinwoo Hwang3; 1Cornell University, United States; 2Xavier University, United States; 3The Ohio State University, United States

We present a novel interactive sonification interface that allows people with visual impairments to perceive the multi-dimensional scientific data using their auditory sense. People with disabilities are traditionally underrepresented in science, technology, engineering, and math (STEM) fields. Developing new accommodation technology for them is therefore important to motivate their participation in scientific research and education, which could cultivate a diverse STEM workforce and ultimately meet the nation’s STEM workforce needs. The participation of people with disabilities in STEM fields that typically provide a higher-paying and more secure job will also enable them to join mainstream society and serve as role models for people with disabilities and many other underrepresented groups. In this regard, we focus on the people with visual impairment, whose participation in STEM research and education has been especially low because the majority of scientific data acquisition and analysis processes tend to heavily rely on visual perception. We develop a new digital interface that converts the multi-dimensional scientific data (e.g. electron microscopy images) to sound waves, a process called sonification, which allows individuals to perceive and understand the data using their auditory sense. We opted to develop our sonification software for the 6th generation of the Apple iPad. The first prototype of our iPad application is built to sonify a high-angle annular dark-field image of a β-Ga3O2 lattice. The image is converted to an intensity matrix whose entries are the pixel intensity of the image in 16-bit grayscale. A portion of the iPad’s screen is mapped to points on the image (e.g. entries of the intensity matrix). Based on the location of the user touch on the iPad’s screen, the associated point on the image is converted to sound through one of two modes of functionality. Our first
mode of sonification takes advantage of the human ability for acute pitch discrimination and leverages variations in pitch in order to give the impression of vertical location of the sound source. We elected to associate points of the image of higher pixel intensity to higher frequencies and points of lower intensity to lower frequencies. We conjecture that blind individuals would be able to trace their finger along the iPad’s screen and identify irregularities in the \( \beta\)-Ga_3O_2 lattice (e.g. crystallographic defects) that would appear as a distinct, underrepresented range of frequencies in the sonic space generated by the image. Our second mode of sonification utilizes the perceived loudness of a sound, through variations in amplitude, in order to give the user the impression that the sound, produced based on their touch input, is originating from some point in 3D space. This approach to sonification leverages the fact that blind users are more sensitive to “binaural sound-location cues.” We further conjecture that, through this second mode of functionality, blind users will be able to gain a spatial understanding of the \( \beta\)-Ga_3O_2 lattice and detect variations in the number of Gallium atoms per atomic column. Our hope is that this application will serve as a framework for more advanced sonification techniques may be built upon.

3:00 PM BREAK

3:00 PM *BI01.04.05
An Overview of Educational Efforts in Materials Data Science at Northwestern
Christopher Wolverton and Peter W. Voorhees; Northwestern University, United States

Data science and data-driven efforts are making substantial impact on the discipline of Materials Science and Engineering. The underlying techniques and research in this area need to be incorporated into educational efforts and curriculum in order to prepare MSE students to use these methods in their materials work. In this talk, I provide an overview of some of the educational efforts in Materials Data Science at Northwestern. There are substantial efforts in this area in faculty members’ research, and these topics naturally have entered the educational curriculum. There are many examples of the incorporation of computational tools into both the undergraduate and graduate curriculum. These are focused on both the tools themselves, but also on the data and databases that result, and the use of these databases in materials design and discovery efforts. In additional, the Center for Hierarchical Materials Design (CHiMaD) is a center of excellence for advanced materials research focusing on developing the next generation of computational tools, databases and experimental techniques in order to enable the accelerated design of novel materials and their integration to industry, one of the primary goals of the U.S. Government's Materials Genome Initiative (MGI). The research within CHiMaD also provides opportunities for educational impact as well. Finally, we discuss the Integrated Computational Materials Engineering (ICME) Master’s program, in which students participate in interdisciplinary courses and seminars where some integrate machine learning methods in materials projects in collaboration with Computer Science faculty.

3:30 PM BI01.04.06
Learnings from Developing a Materials Data Science Curricula for Undergraduates and Graduate Students
Roger H. French; Case Western Reserve University, United States

Data science arises from advances in computing, communication, and data resulting in the ability to develop data-driven models based on large petabyte scale datasets. These distributed computing approaches, complemented by the ease of acquiring large datasets at petabyte scale, is driving the digital transformations of industry, science and technology and society itself. These approaches, complement the “petaflop” computing characteristic of high performance computing, used in materials science such as the materials genome initiative and integrated computational materials engineering research. One challenge for materials data science is that typically materials science datasets have been small and sparse, in comparison to epidemiological studies in the life sciences. Data Science combines advances in statistics, computer science and domain science (such as materials science) to enable new understandings through the application of statistical and machine learning and most recently deep learning. Consider “pure” data scientists as specialists in the academic fields of math and statistics, and computer science. A need arises to develop broader data science skills across the workforce to produce T-shaped graduates, with deep skills in a domain science such as materials science, while at the same time having broad skills in data science[1].

In 2013 we launched a 1 year study to design an applied data science (ADS) undergraduate minor, available to students across our university. These ADS students learn programming, inferential statistics, exploratory data analysis, modeling and prediction and complete a semester long data science project[2]. The ADS minor, started in
2015, and has grown to include 100 undergraduate and graduate students last academic year. The ADS curricula is taught using an open data science tool chain focused on open and reproducible science, based on R/Rstudio, Python, Git, Markdown and LaTeX to produce, compilable data analyses. In R, for example, advances such as the TidyVerse package of pipes and pipelined code and GGPlot2 for the grammar of graphics for data visualization are major steps towards realizing Donald Knuth’s vision of literate programming and are well matched to today’s multi-disciplinary team research [3].

For materials data science, we now offer a data science concentration, focusing the ADS courses on materials problems while addressing the core challenges of integrating data science with the physical and chemical sciences foundations of Materials Science. Essential to adoption of data-driven modeling is demonstrating how they do not replace our physical and chemical theories, models, and experimental experience. Instead they are a new tool, adding statistical power and significance, with improved inference and prediction. And these analyses must be subject to robust validation, using training and testing splits of the data.

Materials data science is not only an educational challenge, but also calls for advancing how we perform our research experiments and acquire data for analysis. A study protocol, encompassing the samples, their exposures and the evaluations performed on them, constitutes the basis of the metadata, the predictors and the responses of the experiment. In many experiments, it is possible to augment the experiment with additional predictors measured in sufficient numbers to provide statistically sound results. Having materials scientists knowledgeable about these data issues is an important to advancing our research methods.


3:45 PM BI01.04.07
Experiences of MIT MechE Faculty Integrating Machine Learning into Teaching Tonio Buonassisi and George Barbastathis; Massachusetts Institute of Technology, United States

The accelerated maturation of data science and machine learning tools has stimulated their integration into university curricula. Herein, we summarize certain efforts within the MIT Department of Mechanical Engineering, including: (1) The design and delivery of in-class and online teaching modules to upskill MIT MechE graduate-student researchers in datasci/ML; (2) project-based learning activities, i.e., learning by doing; and (3) outreach beyond graduate and undergraduate curricula. We evaluate the hypothesis that the artful integration of these tools into curricula enhances students' intuition for problem framing and solving, especially in systems with manifold inputs and outputs. We hope that our sharing sparks dialogue about evolving expectations for university curricula, at the intersection between traditional disciplines and these new tools.

4:00 PM BI01.04.08
Intellectual Community as a Bridge of Interdisciplinary Graduate Education in Materials Data Science Chi-Ning Chang, Clint Patterson, Debra Fowler and Raymundo Arroyave; Texas A&M University, United States

Recognizing materials development was advancing slower than technological needs, the Materials Genome Initiative (MGI) advocated an interdisciplinary approach employing an informatics framework in materials discovery and development. In response, an interdisciplinary graduate program, funded by National Science Foundation, was designed at the intersection of materials science, materials informatics, and engineering design, aiming to equip the next generation scientists and engineers with Material Data Science. The curriculum spans three stages: disciplinary grounding, multidisciplinary courses, and an interdisciplinary course and research. Over a two year period, students work with faculty and students from multiple fields, such as Physics, Chemistry, Materials Science and Engineering, Chemical Engineering, Electrical and Computer Engineering, Mechanical Engineering, Aerospace Engineering, and Industrial and Systems Engineering. Envisioning challenges in this interdisciplinary learning environment, distinctive and blended faculty and student intellectual communities enhance interdisciplinary collaborations and communications.

To connect faculty members from different disciplines, a Faculty Community of Scholars offers a biweekly platform to share an interdisciplinary culture, appreciate and formulate interdisciplinary partnerships and collaboration, and
maintain a communication cadence between members. For students, the program facilitates various intellectual communities. *Student Learning Community* and *Writing Community* meet weekly throughout the first semester of the program. These two intellectual communities not only assist students in the development of transferable skills (interdisciplinary communication and collaboration, critical thinking, ethical behavior, organization and management, and writing), but also devote effort to reduce disciplinary barriers by providing opportunities for students to present their disciplines and research as well as reflect on the gaps among disciplines. Students lacking a solid background in Data Science prior to taking multidisciplinary courses (e.g., materials informatics) and an interdisciplinary course and research (materials design studio), can participate in *Statistics and Python Coding Boot Camp* led by a senior student. Once students begin exposure to Materials Data Science in materials informatics class and materials design studio, a *Peer-Mentoring Group* of senior students help students with statistical issues, disciplinary gaps, and interdisciplinary research. Additionally, a peer and senior student led *Writing Feedback Group* is available to students writing an interdisciplinary research paper. To overcome barriers in the teacher-learner connection, each faculty mentor can facilitate *Coffee Talks* where both faculty and students interact and learn anew. Students generate topics for collegial discussions about career paths, career preparations, academic publication, dissertation writing and defense, funding, teaching, and so on.

In this presentation, we will discuss the implementation of intellectual communities bridging the components of this interdisciplinary graduate program. We will also consider lessons learned from our unique and innovative amalgamation of learning and teaching strategies and ways in which other institutions can implement similar methods.

**4:15 PM BI01.04.09**

*Changes in the Number ofDoctoral Degree Holders inComputational Materials Science in Japan During the Last 50 years—Text Data Mining Analysis on the Difference between Research Universities and Education-Oriented Universities*  
Yayoi Terada and Tetsuo Mohri; Tohoku Univ, Japan

Progress in computational materials science (CMS) has recently accelerated the discovery of advanced and novel materials. However, there have been few quantitative analyses regarding the change in the number of doctoral degree holders (doctors) who support and promote CMS in Japan.

We estimated the change in the number of doctors in CMS in Japan during the last 50 years. We analyzed the subjects of more than 150 thousand doctoral dissertations in science and engineering (SE) found in a Japanese doctoral dissertation database using text data mining techniques. The number of doctors in SE rapidly increased during the 1990s due to a reorganization of the graduate school and peaked at approximately 2000. Then, it rapidly decreased due to the recent birthrate decline. However, we found that the number of doctors in CMS continued to increase until approximately 2010. In addition to that, the decrease rate of those after 2010 has been small. Therefore, the ratio of doctors in CMS to those in SE has continued to increase. This indicates that the importance of researchers in CMS has been constantly enhanced and recognized.

We also analyzed the differences and similarities between doctoral theses in research universities and those in education-oriented universities in Japan. As a result of the analysis, we found that research universities are leading the national trend of the number of doctors in SE and CMS and the ratio of the number of doctors in CMS to those in SE. On the other hand, at the education-oriented universities, new doctoral courses have been established since the 1990s. Change of number of doctors in SE (especially in engineering) in education-oriented universities followed those of research universities and national trend. It has increased rapidly, and then has dropped rapidly as same as research universities. However, the ratio of the number of doctors in the CMS to those in SE in education-oriented universities was almost constant.

We analyzed keywords in the title of theses in both universities. We found that keywords related to application and simulation appear more frequently in theses of education-oriented universities. On the other hand, the keywords related to theory appear more frequently in theses of research universities. This indicates that research universities foster the researchers who orient more fundamental research and education-oriented universities foster the researchers who orient more applied research and practical research.
Metasurfaces are arrays of subwavelength anisotropic light scatters (optical antennas) that can produce abrupt changes in the phase, amplitude, or polarization of light. Within last few years significant progress, design of metasurfaces that refract and focus light, enabling many unique properties and applications such as holograms, optical vortex generation/detection, ultrathin focusing lens, perfect absorber, etc.

This tutorial will cover the fundamental principles, advanced designs and technological applications of optical metasurfaces, particularly focusing on the topics of (I) the development of high performance metasurface components and systems, (II) the advancement of nano-electro-mechanical systems (NEMS) based tunable dielectric metasurfaces, (III) synthetic interfacial optics with metasurfaces and 2D materials, and (IV) the numerical design methods for high performance dielectric metasurfaces.

8:30 AM
**Creating Metasurfaces and Metadevices with Mie Resonators** Mark Brongersma; Stanford University

Semiconductor nanostructures are at the heart of electronic devices and systems. When properly sized and shaped, they can also support optical, Mie-type resonances that are capable of boosting light-matter interaction over bulk materials. By combining their desirable electronic and optical properties, it is possible to create new optoelectronic functionalities. In this tutorial talk, I will start with a discussion of the basic properties of Mie resonators and show how they have been harnessed to create a large variety of passive metasurfaces. One of the key application areas for passive metasurfaces is the realization of flat optical components that can replace more bulky traditional counterparts (e.g. lenses and gratings). One of the next frontiers is to realize active flat optics capable of dynamically shaping optical wavefronts to e.g. tune the focal length of a lens or to actively steer laser beams. I will illustrate different approaches to achieve such active functions. Another area of interest that I will highlight is the development of Mieresonant antennas and metasurfaces that enable real-time measurement of the wavelength, polarization state, angle of incidence and angular momentum of light.

10:00 AM BREAK

10:30 AM
**Synthetic Interfacial Optics with Metasurfaces and Transition Metal Dichalcogenide Monolayer** Cheng-Wei Qiu; National University of Singapore, NUS Suzhou Research Institute (NUSRI)

Metasurfaces and 2D materials have been developing as two important candidates in the interfacial engineering, providing a plethora of new possibilities in novel optoelectronic functions and applications. The synergies between
those two domains hold great promises in manipulating light-matter interaction. In this tutorial talk, I will review and report some of the most recent developments in this field of interfacial engineering, via the artificially constructed hybridized structures of ultrathin thickness compared to the wavelength. In particular, the low-dimension and high-frequency scaling may promise a lot more applications, while the challenges in design principle and fabrication capability will become critical limits. The atomic thickness of 2D monolayers provides many interesting physical properties, while also limits the sufficient interaction with the light. Hence, nano-patterned metasurfaces are deployed with 2D monolayers to modulate and structure novel light behavior. The following advanced functional optical devices, developed by our group, will be discussed: 3D meta-hologram, high-pixelated nanoprinting, dynamic OAM generation, and more interestingly, the 2D-material meta-lens of <1nm thickness, significantly enhanced SHG, PL, and tunable structural colors, by the coordinated hybridization between those two parties. Our work paves a roadmap to design sophisticated and advanced optical devices, with low dimension, miniaturization, randomness, and scaled-up capability.

1:30 PM
High Performance Metasurface Flat Optics: from Components to Systems Federico Capasso; Harvard University

Metasurfaces are leading to the emergence of new optical components that circumvent the limitations of standard refractive and diffractive one by enabling dispersion engineering, which also leads to entirely new functionalities based on the local control of phase amplitude and polarization. The formulation of the generalized Snell’s law for metasurfaces and the use of dispersion engineering has led to the demonstration of metalenses with correction of monochromatic aberrations and to achromatic single lenses across the entire visible spectrum. The planarity of flat optics will lead to the unification of semiconductor manufacturing and lens-making, where the planar technology to manufacture computer chips will be used to make CMOS compatible optical components for a wide range of applications. Instruments based on flat optics will be discussed such as ultracompact spectrometers, endoscopes for the detection of bronchial cancer, polarimeters and polarization sensitive cameras without moving parts and conventional polarization optics.

3:00 PM BREAK

3:30 PM
Nonlinear Optical Metasurfaces: From Enhanced Light-Matter-Interaction to Full Phase Tailoring Thomas Zentgraf; Paderborn University

For efficient nonlinear processes, the engineering of the nonlinear optical properties of media becomes an important task. The most well-known technique for spatially engineering nonlinear optical properties is the quasi-phase matching scheme for second-order processes like second harmonic generation. However, the widely used technique of periodic polling of natural crystals only provides a binary state for the nonlinear material polarization, which is equivalent to a discrete phase change of π of the nonlinear polarization. The continuous tailoring of the phase of the nonlinear susceptibility would greatly enhance flexibility in the design and reduce parasitic effects.

In this tutorial, we will discuss nonlinear metamaterials with a continuously controllable phase of the local effective nonlinear polarizability. We will focus on plasmonic metasurfaces with various designs for the meta-atom geometry together with different polarization states of the light. In particular for circular polarization states, the controllable nonlinearity phase results from the phase accumulation due to the polarization change along the polarization path on the Poincare Sphere (the so-called Pancharatnam-Berry phase) and depends therefore only on the spatial geometry of the metasurface. By using a fixed orientation of the meta-atom, the nonlinear phase can be spatially arbitrarily tailored over the entire range from 0 to 2π. In contrast to the quasi-phase matching scheme, the continuous phase engineering of the effective nonlinear polarizability enables complete control of the propagation of harmonic generation signals, and therefore, it seamlessly combines the generation and manipulation of the harmonic waves for highly compact nonlinear nanophotonic devices.

We will discuss the concepts of enhancing nonlinear processes with simultaneous phase engineering for the manipulation of second- and third-harmonic generation from metasurfaces and the restrictions with respect to
symmetry and geometry of meta-atoms. Nonlinear metamaterials have fundamental significance in nonlinear optics and for tailored nonlinearities, as they provide a further degree of freedom in the design of nonlinear materials.

SYMPOSIUM EL01

Emerging Material Platforms and Approaches for Plasmonics, Metamaterials and Metasurfaces
December 2 - December 6, 2019

Symposium Organizers
Wenshan Cai, Georgia Institute of Technology
Mikko Kataja, CSIC-ICMAB
Ho Wai (Howard) Lee, Baylor Univ
Yu-Jung Lu, Academia Sinica

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* Invited Paper

SESSION EL01.01: Low Dimensional Photonics I
Session Chair: Ho Wai (Howard) Lee
Monday Morning, December 2, 2019
Hynes, Level 1, Room 102

8:15 AM *EL01.01.01
Dynamic Two-Dimensional Optical Phased Array Metasurfaces—Connecting Nanophotonic and Array Architecture Design Harry A. Atwater; California Institute of Technology, United States

Over the last several years, there has been intensive worldwide effort to explore dynamic and reconfigurable nanophotonics, driven mainly by innovation at the component level. True two-dimensional optical phase array metasurfaces with reconfigurable elements represent a new opportunity for nanophotonics, and here we describe a design approach linking nanophotonic device and array-level architectural design. The results show a surprising ability to achieve near-ideal optical phased array performance for several functions, including beam steering and reconfigurable lens operation, even with the use of highly non-ideal individual nanophotonic devices. We will show experimental results for a ‘universal’ reconfigurable metasurface in which a single dynamically reconfigurable optical phased array aperture can be used to perform multiple functions.

8:45 AM *EL01.01.02
Strong Light-Matter Coupling in Atomically-Thin Semiconductors Deep M. Jariwala; University of Pennsylvania, United States

The isolation of stable atomically thin two-dimensional (2D) materials on arbitrary substrates has led to a revolution in solid state physics and semiconductor device research over the past decade. A variety of other 2D materials (including semiconductors) with varying properties have been isolated raising the prospects for devices assembled by van der Waals forces.1 A fundamental challenge in using 2D materials for opto-electronic devices is enhancing their interaction with light, ultimately responsible for higher performance and efficiency in the devices. In particular, for photovoltaics; inorganic materials (e.g., Si, GaAs and GaInP) can concurrently maximize absorption and carrier
collection. But thin film absorbers have lacked the above ability often due to due to surface and interface recombination effects. In contrast, Van der Waals semiconductors have naturally passivated surfaces with electronically active edges that allows retention of high electronic quality down-to the atomically thin limit. First, I will show our recent work on photovoltaic devices from transition metal dichalcogenides of molybdenum and tungsten such as MoS2, WSe2 etc.\textsuperscript{2,4} as well as more recent work on high open circuit voltage devices. Next we will focus on the subject of strong light-matter coupling in excitonic 2D semiconductors. Visible spectrum band-gaps with strong excitonic absorption makes transition metal dichalcogenides (TMDCs) of molybdenum and tungsten as attractive candidates for investigating light matter interaction and applications as absorbing media in opto-electronics.\textsuperscript{3,5} Further, the excitonic features become more prominent as the layers are thinned down and dominant in the monolayer limit where the TMDCs transition into direct band-gap semiconductors with strong photoluminescence. In addition, TMDCs are known to have very large values of optical constants which allows strong light trapping even in ultrathin samples.\textsuperscript{2} We will present our recent work on the fundamental physics of light trapping in multi-layer TMDCs when coupled to plasmonic substrates. We systematically demonstrate via calculations and matching experiments that the presence of strong excitonic resonances in multilayers (< 20 nm thickness) combined with surface plasmon excitations of the nearby metals can achieve strongly coupled modes with apparent voided crossings in reflectance spectra. Further, we explore additional light confinement by patterning 1D arrays of rectangular resonators of varying widths and periods (100 nm to 500 nm). We observe newer and higher order modes appear with increasing TMDC thicknesses and widths. Simulated field profiles suggest that these modes range from mainly plasmonic to even hybrid nature as well as guided modes for longer wavelengths and thicker TMDCs. Further, the plasmonic mode exhibit strong dependence on 1D array grating period.

References:

9:15 AM *EL01.01.03
\textbf{Ultracompact Active Plasmonic Nanocircuitry} Sergey I. Bozhevolnyi; University of Southern Denmark, Denmark

Plasmonic nanocircuits have the potential to open new routes in manipulating optical information beyond the diffraction limit and future quantum information processing technologies. For the realization of multi-functional plasmonic devices, it is of major importance to control properties of their supporting guided optical modes such as modal profiles, impedances and propagation constants. In this talk, several ultra-compact active plasmonic configurations are considered from the viewpoint of realizing important photonic functionalities, including on-chip detection of optical spin-orbit interactions and high-speed electrooptic switching and modulation.

9:45 AM BREAK

SESSION EL01.02: Metasurfaces I
Session Chair: Mark Brongersma
Monday Morning, December 2, 2019
Hynes, Level 1, Room 102

10:15 AM *EL01.02.01
\textbf{Meta-Optics—Meta-Lens for Imaging and Sensing} Din-Ping Tsai\textsuperscript{1,2,3}, Mu-Ku Chen\textsuperscript{2,1,3}, Ren Jie Lin\textsuperscript{1,2}, Cheng Hung Chu\textsuperscript{2} and Lin Li\textsuperscript{2}; \textsuperscript{1}National Taiwan Univ, Taiwan; \textsuperscript{2}Academia Sinica, Taiwan; \textsuperscript{3}The Hong Kong Polytechnic University, Hong Kong
Metalenses consist of a large number of optical nanoantennas which are capable of focusing the incoming wavefront of light [1-6]. We use a $60 \times 60$ dielectric achromatic metalens array to capture multidimensional optical information. The highest efficiency can be up to 74% at a wavelength of 420 nm, while the average efficiency is approximately 39% over the whole working bandwidth. The light field images and the depth information of objects can be determined by reorganizing the patches of sub-images and calculating the disparity of neighbor sub-images, respectively. The depth information can be used to optimize the patch sizes to render the all-in-focus images without artifacts. The smallest feature of objects that could be resolved in our system is 1.95 μm under the incoherent white light. Our work provides several advantages associated with light field imaging: elimination of chromatic aberration, polarization selectivity and compatibility of the semiconductor process. Considering the flexibility, the achromatic multiplexed metalens array with integrated functionalities may be promising for multifocusing microscopy, high-dimensional quantum technology, hyperspectral microscopy, micro robotic vision, nomen automobile sensing, virtual and augmented reality (VR and AR), drones, and miniature personal security systems [7].

References

10:45 AM *EL01.02.02
Color Print and Color Holography Using Single-Layer Silicon Metasurfaces Thomas Zentgraf; Paderborn University, Germany

Metasurfaces possess an outstanding ability to tailor the phase, amplitude and even spectral responses of light with unprecedented ultrahigh spatial resolution, thus have attracted significant interests for several applications in optics. Here, we propose and experimentally demonstrate a novel meta-device that integrates color printing and computer-generated holograms within a single-layer dielectric silicon metasurface by modulating spectral and spatial responses at the subwavelength scale, simultaneously. With our design, such a metasurface appears as a microscopic color image under white light illumination, while encrypting two different holographic images that can be projected to the far field when illuminated with red and green laser beams. The metasurfaces consist of two types of meta-atoms made by amorphous silicon, each of them acts as a color filter under white light and provides a color channel for a specific wavelength to independently manipulate phase distributions by utilizing their orientations angles. Both the phase and spectral responses can be defined at a subwavelength scale simultaneously and independently. For the hologram design, we developed a modified parallel iterative Gerchberg-Saxton algorithm, which obtains holograms for arbitrary shapes to adapt “color-printing” indexed pattern. Such an algorithm is the key to the wavelength multiplexing holograms by utilizing the color filter property (wavelength selectivity) of the two designed meta-atoms. The method can further extend the design freedom of metasurfaces. By exploiting spectral and spatial control at the level of individual pixels formed by the meta-atoms, multiple sets of independent information can be introduced into a single-layer device that requires only a single lithography step. The additional complexity and enlarged information capacity are promising for novel applications such as information security and anti-counterfeiting.

11:15 AM EL01.02.03
Electrically Reconfigurable Metasurfaces Based on Phase Change Materials Yifei Wang¹, Patrick Landreman¹, Kye Okabe¹, Umberto Celano¹-², H.S. Philip Wong¹ and Mark L. Brongersma¹; ¹Stanford University, United States; ²imec, Belgium

Active tuning of nanophotonic devices has many potential applications. Such tuning can be achieved by changing either the shape or material properties of a structure. Phase-change materials, such as Germanium Antimony Tellurium (GST), are of particular interest as they can exhibit large and non-volatile changes in their refractive index. Pulsed laser illumination has effectively been used to induce phase transitions in GST-based optical devices. Such changes can cause large changes in the optical scattering properties in the near-infrared. However, electrical tuning of GST-based photonic antennas and metamaterials has remained elusive.

Here we present optical antennas and metasurfaces combining phase-change material and plasmonic structures. By
inducing phase-changes electrically in optical antennas, we achieve reversible multi-level tuning of scattered light intensity by more than 30%. Metasurfaces, designed as a perfect absorber, show over a 3-fold enhancement of reflection in the visible wavelength range between phases. This work demonstrates a first GST-based active metasurfaces working in the visible wavelengths, showing the potential to develop randomly-accessible metamaterial platforms in which metamolecules can be individually controlled.

11:30 AM EL01.02.04
All-Optical Isolation with Nanoscale High-Q Chiral Dielectric Metasurfaces Jefferson Dixon, Mark Lawrence, David R. Barton and Jennifer A. Dionne; Stanford University, United States

Photonic systems promise larger bandwidths, increased speeds, and reduced power consumption compared to their electronic counterparts. An optical diode analogous to an electrical diode represents the most fundamental device needed to realize such photonic platforms. Current optical diodes rely on the relatively weak magneto-optical effect, which requires high magnetic field strengths and long optical path lengths (> 100 µm) to break reciprocity. In order to miniaturize optical nonreciprocity and develop an optical diode that is scalable with current electronics (< 1 µm), we present a scheme based on Stimulated Raman Scattering (SRS) and discuss the design of an intrinsically chiral metasurface that supports diode-like behavior when combined with SRS.

Optical chirality in a dielectric metasurface requires coupled, non-orthogonal electric and magnetic dipole moments. Using full-field electromagnetic simulations, we investigate a dielectric metasurface comprised of cylinders that allow for the individual tuning of electric and magnetic Mie resonances by modifying their diameter and height, respectively. For a Si metasurface with a cylinder height of 600 nm and diameter of 500 nm organized into a square lattice with a period of 1.2 µm, transmission approaches unity at a wavelength of 1830 nm – a result of the overlap of the electric and magnetic dipole moments. Next, we break the orthogonality of electric and magnetic modes by introducing a notch into the center of the cylinder. We sweep notch depths from 50 nm to 300 nm with a notch diameter of 80 nm. The effective electric current loop that defines the magnetic dipole resonance is perturbed by the introduction of the notch, thus resulting in nonorthogonal dipole moments and a resonance in transmission at 1830 nm. By offsetting the notch in different directions in neighboring disks, we break four-fold rotational symmetry for the entire unit cell both geometrically and optically. This geometry exhibits a significant chiral response. For a metasurface array with a lattice period of 1.2 µm, cylinder height of 640 nm, diameter of 500 nm, and optimized notch positions, the difference in transmittance between L-CP and R-CP exceeds three orders of magnitude at a resonant wavelength of 1895.5 nm. This resonance exhibits a Q-factor exceeding 10^4 and can be optimized for even higher Q-factors by shifting the magnetic dipole moment via the height of the cylinders.

Next, we show how this chiral response can enable all-optical isolation through SRS. The probe beam frequency is set to the chiral resonance defined at 1895.5 nm. The pump frequency is Stokes-shifted by the frequency of the optical phonon (15.6 THz in Si) and is set to 1725.3 nm. Importantly, the pump handedness is fixed to L-CP and the probe must also be L-CP to transmit with amplification; a R-CP probe would be orthogonal to the L-CP pump and would not experience amplification. With probe illumination from the backwards direction, a L-CP probe will not experience amplification due to its orthogonality with the rotation of the pump, and a R-CP probe will be reflected by the chirality of the metasurface. This system results in a highly-asymmetric response, where transmission is enhanced for only the L-CP probe in the same direction as the pump illumination, thus resulting in near diode-like behavior for pump powers > 2 MW/cm². For a pump power of 5 MW/cm², the L-CP probe in the forward direction experiences transmittance > 2x more than any other probe handedness and direction. This asymmetry in transmission can be further enhanced by optimizing a geometry that minimizes polarization conversion, approaching values comparable with electronic diodes. This work presents both a general exploration of intrinsic chirality in metamaterials and an entirely new scheme for achieving optical isolation at the nanoscale.

11:45 AM EL01.02.05
Anisotropic Metasurfaces as Tunable SERS Substrates for 2D Materials Vrinda Thareja¹, Pieter G. Kik²,¹, Majid Esfandyarpour¹ and Mark L. Brongersma¹; ¹Stanford University, United States; ²University of Central Florida, United States

The reflection of light from metallic mirrors results in a near-zero electric field at their surface. This precludes strong light-matter interaction between such mirrors and two-dimensional (2D) materials placed in direct contact with them. Patterning of metal surfaces with sub-wavelength grooves can produce anisotropic metasurfaces that...
offer robust enhancements in the magnitude of fields near the surface, and control over their direction. Here, we use this control to analyze the Raman tensor for vibrational modes of atomically-thin graphene.

To study metasurface-enhanced Raman scattering from 2D materials, we pattern sub-wavelength groove arrays into a gold surface by means of focused ion beam milling. Optical reflection measurements show clear absorption resonances associated with gap plasmon modes excited in the grooves, with a resonance wavelength that can be controlled by varying the groove depth. Metasurfaces with groove depths ranging from 30-210 nm were prepared, and monolayer graphene was transferred onto the patterned surfaces. Reference Raman spectra taken on a smooth gold film under 532 nm excitation show a weak Raman signal from the graphene G peak and 2D peak. Spectra taken on the nearby patterned region show clear enhancement of the graphene G peak and 2D peak, with maximum Raman enhancement occurring for a groove depth of 70 nm. Notably, a much larger enhancement factor of ~50 was observed for the 2D peak compared to a factor ~25 for the G peak. We show that this vibrational mode-dependent enhancement can be quantitatively understood by considering the anisotropic nature of the metasurface and the specific tensorial nature of the Raman polarizability of the graphene vibrational modes. Numerical simulations of the enhancement as a function of groove depth show remarkable agreement with the measured data. Our findings demonstrate that anisotropic metasurfaces can be used as reliable and tunable surface enhanced Raman scattering substrates for the investigation of the vibrational modes of 2D materials.

1:30 PM *EL01.03.01
High-Speed Quantum Photonics with Plasmonic Metamaterials Empowered by Machine Learning Simeon I. Bogdanov, Zhaxylyk Kudyshev, Alexander Kildishev, Alexandra Boltasseva and Vladimir M. Shalaev; Purdue University, United States

We outline future directions in the development of a platform for high-speed integrated quantum photonics, the use of plasmonics to outpace quantum decoherence and the application of machine-learning techniques for photonics designs and quantum optical measurements.

2:00 PM EL01.03.02
Propagation and Spectral Sorting of Single Photons in High-Index Dielectric Nanowires Mélodie Humbert1,2, Peter Wiecha2,3, Gérard Colas des Francs4, Aurélie Lecestre1, Guilhem Larrieu1, Christian Girard2, Vincent Paillard2 and Aurélien Cuche2; 1LPCNO, Toulouse University, CNRS, INSA, France; 2CEMES - CNRS, France; 3LAAS - CNRS, France; 4ICB, CNRS, Bourgogne-Franche Comté University, France

We show both experimentally and theoretically that dielectric nanowires made of Silicon (Si-NW) are efficient waveguides allowing the wavelength-dependent transfer of visible photons from broadband quantum emitters. We first study the photodynamics of single NV centers in nanodiamonds positioned in the vicinity of such high index dielectric nanowires. Then, we demonstrate that the 1D propagation of light can be efficiently controlled by the geometry of the wire. These emitter-nanowire hybrid structures might be good candidates as building blocks for the design of CMOS-compatible optical nanodevices operated in the single photon regime.

Discussion: For a couple of decades, nanoscale optics has mainly been driven by plasmonics since noble metal nanostructures sustain strong resonances that can be used to enhance, confine, propagate or redirect visible light. Such properties have led to numerous actual or potential applications in integrated optics, sensors, nonlinear optics, field-enhanced spectroscopies, or photovoltaics. Recently, an alternative to plasmonics emerged with high refractive index dielectric nanostructures, which offer the same range of applications as plasmonics by manipulating waveguide and Mie optical resonances instead of plasmonic ones [1]. These resonances can be efficiently tuned by modifying the size, shape, and material of those nanostructures (e.g. silicon, optical index n=4). Furthermore, high index dielectric nanostructures offer several advantages when
compared to their metallic counterparts: absorption losses are far weaker for wavelengths greater than the direct band gap, access to semiconductor (CMOS) technology for nanostructure fabrication, and presence of intrinsic strong electric and magnetic resonances [2,3].

In the context of quantum nanophotonics, which aims to combine the confinement and propagation of light at the nanoscale along with quantum properties of light, their appealing properties make Si nanostructures an interesting platform to investigate classical to quantum optics transition in coplanar devices. In this work, we first discuss the effect of high index dielectric nanowires on the spontaneous emission of NV colored centers in nanodiamonds. The emission rate of punctual emitters is driven by the presence of the nanostructure which tailors the local density of optical states (LDOS) [4]. With time-resolved photoluminescence acquisitions, we show that the photodynamics of the quantum emitters is modified in the vicinity of the Si wires. The experimental data are systematically compared to simulated decay rates and LDOS computed with the Green Dyadic Method (GDM).

In a second stage, we show that visible photons emitted by the broadband single emitters coupled at one extremity of Si nanowires are efficiently guided up to the second extremity, located several micrometers away. By performing image plane acquisitions on a set of emitter-wire hybrid structures, we observed that the geometrical parameters of the wires, and the related waveguide modes, determine the efficiency of the transfer. The experimental results are in good agreement with numerical experiments.

References:

2:15 PM  EL01.03.03
Subwavelength Raman Molecular Mapping with Electron and Light Induced Stimulated Raman Scattering (ELISR) Amr A. Saleh1,2, Daniel Angell1 and Jennifer A. Dionne1; 1Stanford University, United States; 2Cairo University, Egypt

Many plasmonic processes, from photocatalysis to photothermal therapy, rely on nanoparticle-molecule interactions. Mapping these interactions with high spatial resolution is essential to optimize system efficiency, but can be incredibly challenging due to the molecules’ small size and generally complex microenvironment. Here, we propose a new method capable of identifying and mapping nanoparticle-molecule with sub-10nm spatial resolution. Our method, Electron and Light Stimulated Raman Scattering (ELISR), utilizes in-situ optical spectroscopy within a transmission electron microscope (TEM). Unlike existing correlated optical and electron microscopy techniques, where a sample is first imaged in a fluorescence optical microscope and then sectioned for cryo-electron microscopy, our method enables simultaneous high-resolution microstructure visualization with protein identification through Raman scattering. In particular, our technique uses a laser source as the pump and the electron beam as the broadband Stokes excitation. The electron beam serves as a highly-localized Angstrom-scale source to locally excite the plasmonic resonances of individual nanoparticles whose resonance is red-shifted from the pump laser to resemble Stokes excitation. Accordingly, the Raman scattering is locally enhanced by the electron beam and the spatial resolution is determined by the electron beam spot size and the nanoparticle size. We theoretically model this process using boundary element method (BEM) calculations. Attention is given to gold nanorods (NRs) with plasmonic resonances between 800nm and 900nm; we assume 785nm laser illumination and 80keV electron beam excitation. We investigate the enhancement of the 992cm⁻¹ benzene line, showing that enhancement in the stimulated over spontaneous Raman can be up to six orders of magnitude under electron beam illumination, even with laser pump intensities less than 10mW/µm². Experimentally, we use aberration corrected environmental transmission electron microscope combined with light excitation. The setup uses two parabolic mirrors coupled to two optical fibers. We use one of the optical fibers to couple the 785nm pump laser into the TEM and the other fiber to couple the light scattered from the sample out of the TEM. The scattered light collected from the sample is then coupled into a spectrometer after filtering out the pump laser. To characterize the e-beam stimulated Raman we use a model system of colloidally synthesized gold and silver NRs functionalized with 4-Mercaptobenzoic acid (4-MBA) as a Raman reporter. The lengths and radii of the rods are 105nm and 12nm, respectively, with transverse and longitudinal plasmon resonances at 510nm and 830nm, as confirmed with cathodoluminescence. Upon electron
beam excitation of the NR plasmon modes, we observe a significant increase in the Raman intensity of the 1570 cm\(^{-1}\) line of the 4-MBA. We locally map the stimulated Raman enhancement upon electron-beam excitation as a function of electron beam position and nanorod material and arrangement, including nanorod dimers. Our results demonstrate the promise of Raman spectroscopy with electron microscopy to enable single nanometer resolution molecular mapping, with simultaneous imaging of the nano-to-atomic-scale structure of the sample.

2:30 PM EL01.03.04
**Excited-States in Nanophotonic Chemistry—First Principles Approaches to Strong Light-Matter Coupling**
Johannes Flick\(^1\), Nicholas Rivera\(^1,2\) and Prineha Narang\(^1\); \(^1\)Harvard University, United States; \(^2\)Massachusetts Institute of Technology, United States

In recent years, research at the interface of chemistry, material science, and quantum optics has opened new possibilities to study strong light-matter interactions for nanophotonic chemistry [1,2]. In this new regime of nanophotonics, correlated electron, nuclear and photon interactions have to be treated on the same quantized footing. Towards this goal, we have introduced a general time-dependent density-functional theory [3] and variational QED framework [4].

In this talk, we demonstrate how these QED-derived frameworks are used to study strong-light matter coupling to change the chemistry of the system. As a concrete example, the effect of strong-coupling on photochemical reaction is studied for Formaldehyde. We construct the polaritonic excited-state potential-energy surfaces (PES) of a CO bond stretching that are modified under strong-light matter coupling [5]. We show how strong coupling can be exploited to alter photochemical reaction pathways by influencing avoided crossings. For CO2 molecules, we study the Rabi splitting and finite temperature effects [3] in vibrational strong coupling. Additionally, we study how strong vibrational coupling influences chemical reactions, recently observed in experiment. By using the variational QED framework, we demonstrate how we can calculate polaritonic observables for a wide range of coupling strengths [4]. Our work opens the important new avenue in introducing ab initio methods to the nascent field of nanophotonic chemistry with strong light-matter interactions and will enable a systematic search for potential new reactions that can be altered by these interactions.


2:45 PM BREAK

SESSION EL01.04: Nanophotonic Devices I
Session Chair: Mikko Kataja
Monday Afternoon, December 2, 2019
Hynes, Level 1, Room 102

3:15 PM *EL01.04.01
**A Strong Pockels Effect in Optical Devices on Silicon**
Jean Fompeyrine, Felix Eltes and Stefan Abel; IBM Research Zurich, Switzerland

An important building block in integrated optical circuits is an efficient link between the optical and electrical domain. Well-known examples of such links are integrated high-speed modulators to convert electrical signals into optical signals at very high-speed, and low-power tuning elements to compensate for variations in the device operation temperature and for device-to-device variations during fabrication. To enable such electro-optic links, the two most widely used physical effects are the plasma-dispersion effect and Joule heating. Although these effects are attractive to use due to their compatibility with standard photonic fabrication processes, their performance in integrated devices is intrinsically limited by high insertion losses and high-power dissipation.

Over the past decade, we established an alternative electro-optic switching technology by embedding a Pockels
material into silicon-based photonic devices. We reached this goal by developing a process to fabricate ferroelectric barium-titanate (BTO) thin films on silicon substrates using advanced epitaxial deposition techniques and by developing a BTO process technology. We correlated the electro-optical properties of the thin films with their structural properties such as porosity and crystalline symmetry to show guidelines for improving the functional properties [1]. By realizing integrated hybrid BTO/silicon devices, we demonstrated record-high, in-device Pockels coefficients of >900 pm/V [2]. The Pockels effect in BTO-based photonic devices indeed enables extremely fast data modulation at rates beyond >40 Gbps and ultra-low-power electro-optic tuning of silicon and silicon-nitride waveguides. We also show ways of how to integrate and use BTO in plasmonic slot waveguide structures for very compact optical devices. With the development of a wafer-level integration scheme of single-crystalline BTO layers to a 200 mm process, we could demonstrate a viable path to combine the BTO-technology with existing fabrication routes [3].

With major breakthroughs in the past years, BTO has emerged as a strong candidate for a novel generation of electro-optic devices. Major achievements of the BTO technology will be covered in the presentation, ranging from important materials aspects, device development, integration concepts, and novel applications in the area of quantum computing, high-speed communication, and neuromorphic optical computing.

Acknowledgements
The work discussed has received funding from the European Commission under grant agreement numbers FP7-ICT-2013-11-619456 (SITOGA), H2020-ICT-2015-25-688579 (PHRESCO), and H2020-ICT-2017-1-780997 (plaCMOS), from the Swiss State Secretariat for Education, Research and Innovation under contract number 15.0285, and from the Swiss National Foundation project no. 200021_159565 (PADOMO).

References

3:45 PM *EL01.04.02
Self-Stabilizing Photonic Levitation and Propulsion of Nanostructured Macroscopic Objects Ognjen Ilic;
University of Minnesota, United States

Light is a powerful tool to manipulate matter, but existing approaches often necessitate focused, high-intensity light that limits the manipulated object's shape, material, and size. Here, we discuss self-stabilizing optical manipulation of macroscopic objects achieved by controlling the anisotropy of light scattering along the object surface. In a scalable design that features silicon resonators on silica substrate, we identify nanophotonic structures that can self-restore when rotated and/or translated relative to the optical axis. Nanoscale control of scattering across a large area creates restoring behaviour by engineering the scattered phase, without needing to focus incident light or excessively constrain the shape, size or material composition of the object. These findings may lead to platforms for manipulating macroscopic objects, with applications ranging from contactless wafer-scale fabrication and assembly, to trajectory control for ultralight spacecraft, and even laser-propelled lightsails for space exploration.

4:15 PM EL01.04.03
Infrared Pixel Based on Seebeck Nanoantennas Francisco Javier Gonzalez1,2,3 and Robert E. Peale1,2; 1Truventic LLC, United States; 2University of Central Florida, United States; 3Universidad Autonoma de San Luis Potosi, Mexico

Many infrared imagers comprise a focal plane array of thermal detectors that convert incident infrared to heat and
thence to an electrical signal. The thermometric property of the well-established micro-bolometer is a change in resistance of a semiconducting element with temperature. These require a bias voltage and draw a current that consumes power, and the response of sufficiently sensitive bolometers is fairly slow. An opportunity is nano-scale thermocouples connected to planar antennas, which collect the incident infrared and drive a current that Joule heats the thermocouple junction. The antennas are wavelength specific, which has value for spectral sensing. The heated junction of dissimilar materials generates a thermoelectric voltage, which can be detected at the free ends of the thermocouple. The nano-scale junction can change temperature quickly due to small thermal mass, giving faster response than for traditional bolometers. The devices in principle require fewer processing steps and can use low-cost earth-abundant materials, potentially reducing the cost of infrared sensor systems in comparison to microbolometers. The thermoelectric elements generate their own output voltage without external bias, so that the only power required is that needed to operate the read-out circuit. We present results for a Seebeck nano-antenna pixel optimized for 10.6 micron wavelength radiation. Design and performance calculations are presented, together with experimental results for responsivity, noise, noise-equivalent power, detectivity, and time constant.

4:30 PM EL01.04.04
Nanoscale Aluminum Plasmonic Waveguide with Monolithically Integrated Germanium Detector Alois Lugstein1, Maximilian G. Bartmann1, Masiar Sistani1, Hamid Keshmiri1, Sven Barth1, Michael Seifner1, Martien Hertog2 and Minh An Luong3; 1Vienna Univ of Technology, Austria; 2NEEL CNRS/UGA, France; 3Univ. Grenoble Alpes, France

Surface plasmon polaritons have rapidly established themselves as a promising concept for emerging integrated ultra-compact photonic circuits rivaling electronics in both speed and critical feature sizes. Aside of effective sources, detectors and modulators, the overall performance of plasmonic networks critically rely on symmetry broken waveguides enabling the routing of signals within a circuit. We systematically investigated the guiding of plasmonic beams in ultra-thin (<50 nm) monocrystalline Al nanowires enwrapped by a passivating Al2O3 shell. The Al heterostructures were synthetized on 40nm thick Si3N4 membranes by a thermally induced exchange reaction of single-crystalline Ge nanowires and lithographically defined Al contact pads. Due to limited spatial resolution, optical methods are inappropriate to determine the short propagation length in ultra-thin metallic nanowires. Thus, we explored a well-tuned focused grating coupler to launch plasmons in the Al nanowire waveguides. To optimize the focussed grating coupler with respect to plasmon generation and coupling into the c-Al NW, numerical simulations based on the finite-difference time-domain (FDTD) method were performed.

Further we explored and a highly efficient electrical plasmon detector based on a monolithic quasi 1D metal-semiconductor-metal heterostructure device. Based on this system, we experimentally determined a plasmon propagation length of 140 nm for monocrystalline Al plasmon waveguides with diameters of only 40 nm. Further, our monolithic approach of plasmon generation, guiding and sensing enables us to examine bending losses of kinked Al nanowire waveguides.

This particular device allows a clear separation of the contributions of plasmon-induced and photo-excited carriers enabling to separately examine plasmon-induced hot electron injection and photoexcitation. The architecture features further precise control of the injection barrier at the abrupt metal-semiconductor interface, enabling selective probing the hot electron distribution from surface plasmon decay.

These systematic investigations of ultra-thin monocrystalline Al nanowires provide in general a platform for the evaluation of nanoscale metal based waveguides for transmission lines of next generation high-speed ultra-compact on-chip photonic circuits.

4:45 PM EL01.04.05
High-Speed Phase-Only Spatial Light Modulators with Two-Dimensional Tunable Microcavity Arrays Cheng Peng1, Ryan Hamerly1, Mohammad Soltani2 and Dirk Englund1; 1Massachusetts Institute of Technology, United States; 2Raytheon BBN Technologies, United States

Spatial light modulators (SLMs) are central to numerous applications ranging from high-speed displays to adaptive optics, structured illumination microscopy, and holography. After decades of advances, SLM arrays based on liquid crystals can now reach large pixel counts exceeding 10⁶ with phase-only modulation with a pixel pitch of less than 10 μm and reflectance around 75%. However, the rather slow modulation speed in such SLMs (below hundreds of Hz) presents limitations for many applications. Here we propose an SLM architecture that can achieve high pixel count with high-resolution phase-only modulation at high speed in excess of GHz. The architecture consists of a
tunable two-dimensional array of vertically oriented, one-sided microcavities that are tuned through an electro-optic material such as barium titanate (BTO). We calculate that the optimized microcavity design achieves a π phase shift under an applied bias voltage below 10 V, while maintaining nearly constant reflection amplitude. As two model applications, we consider high-speed 2D beam steering as well as beam forming. The outlined design methodology could also benefit future design of spatial light modulators with other specifications (for example amplitude modulators). This high-speed SLM architecture promises a wide range of new applications ranging from fully tunable metasurfaces to optical computing accelerators, high-speed interconnects, true 2D phased array beam steering, and quantum computing with cold atom arrays.

SESSION EL01.05: Poster Session I: Metamaterials, Metasurfaces and Nanoantenna
Session Chair: Ho Wai (Howard) Lee
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EL01.05.01
Gate Tunable Optical Properties in Organolead Halide Perovskite Heterostructures Teng Lam Shen¹, Meng-Ju Yu¹, Mriganka Singh¹, Chih Wei Chu¹ and Yu-Jung Lu¹,²; ¹Academia Sinica, Taiwan; ²National Taiwan University, Taiwan

In the past decade, lead halide perovskite material have received considerable attention to be a promising candidate for solar cells due to its excellent optoelectronic properties. Beyond of the remarkable power conversion efficiency. However, the optical dielectric constants (complex refractive index) are far less discussed, especially the dynamic control of refractive index in lead halide perovskite material has never been reported. Understanding and modulating the material properties could accelerate to the progress of applying perovskite in optoelectronic devices comprehensively. Here, we report electric field modulated dielectric permittivity in CH₃NH₃PbBr₃ film by using ellipsometry measurement. The designed device consists of Silver/Aluminium Oxide/CH₃NH₃PbBr₃/PMMA/Silver and results in a metal-insulator- semiconductor-insulator-metal (MISIM) heterostructures. Under an applied electric field (~10⁶ V/m) crossing the two silver electrodes, 5% change in the refractive index is observed between 440 - 520nm. We believe the results open new avenues for the application of perovskite based optoelectronic devices such as in electro-optic modulator in the visible and active tunable transistor lasers.

EL01.05.02
Manipulating Chiral States of Quantum Emitters via Circular Dichroism Metamaterials Sangsoon Yoon, Young-Bin Kim and Sun-Kyung Kim; Kyung Hee University, Korea (the Republic of)

The properties (e.g., wave vector, polarization, spontaneous emission rate, and so on) of generated electromagnetic waves is inherently dictated by optical density of states that well-ordered structures create. For example, a one-dimensional metal/dielectric subwavelength periodic pattern, which serve as an artificial birefringent film, exhibits a hyperbolic (as opposed to ellipsoidal) material dispersion, thus being capable of generating linearly polarized light into specific direction.

More specifically, when an Al/ITO metal/dielectric metamaterial film designed for a quarter wave plate is evanescently coupled to a quantum emitter, the far-field distribution of radiation is vertically localized for one polarization and horizontally spread for its orthogonal polarization. The contrast of the polarization-selective far-field distribution is the most pronounced when a quantum emitter is positioned at which an interference condition is completely met. As a practical example, such artificial, birefringent films can be applied to organic light-emitting diodes (OLEDs) to attain polarized and vertically directed emitted light; according to electromagnetic simulation result, the maximum extinction polarization ratio is up to approximately 30.

Likewise, circular dichroism materials such as helical reactive mesogen (RM) can be chosen to manipulate the chiral states (e.g., circular polarization) of quantum emitters. A RM embedded film synthesized on a glass substrate shows highly selective reflectance for opposite circular polarization over a particular wavelength range; the wavelength range is readily tuned by the pitch of helical morphology within RM material. Such a circular dichroism layer can help quantum emitters inherently yield circular polarized light. We will discuss the polarization and wavelength
resolved far-field distribution of quantum-dot films when they are integrated with tailored circularly dichroism materials.

EL01.05.03
Dynamic Beamsteering with Nonlinear, High-Quality-Factor Dielectric Metasurfaces
David R. Barton, Mark Lawrence, Jefferson Dixon, Jung-Hwan Song, Jorik Van de Groep, Mark L. Brongersma and Jennifer A. Dionne; Stanford University, United States

Dielectric nanoantennas are capable of sculpting the amplitude and phase of light through resonant modal coupling. Properly designed, these structures promise to transform modern optics by replacing traditional optical components with miniaturized films with curated phase, amplitude, and dispersion relations to generate arbitrary transfer functions for incoming light. The inclusion of nonlinear optical responses into metasurfaces will be crucial for applications spanning optical and neuromorphic computing, optical communications, sensitive detectors and dynamic sensors, but the low nonlinear susceptibility of dielectric materials significantly challenges these applications.

Here, we introduce a route towards efficient nonlinear wavefront shaping and beam-steering using high quality factor (high-Q) resonances in dielectric phase gradient metasurfaces. Typically, metasurfaces operate based on phase pickup from Fabry-Perot-like or Mie-like modes in the propagation direction of interest. In our case, we exploit coupling to in-plane waveguide modes, which interfere with the far-field Fabry-Perot modes to produce extremely high-Q modes, with Q’s exceeding 1000. We use a silicon on sapphire platform and pattern spatially arrayed silicon beams with widths of 200 to 370 nm as metasurface elements. Our beamsteering structures efficiently diffract light to the +1st order with wavelengths between 1300nm and 1500nm. Including small periodic notches, with depths varying from 30nm to 150nm, into one Si beam provides the extra momentum to efficiently couple to a waveguide mode; the interference between the Fabry-Perot mode and waveguide mode leads to a resonant response in the scattered spectrum, which manifests as a resonant decrease in the first diffracted-order scattered intensity. Our experimental quality factors range from 1400-2500 with perturbation periods ranging from 530 nm to 610 nm along a particular Si bar.

The high, experimentally-observed Q factors indicate that the illuminating electric field can locally be enhanced by more than 50 times. We utilize this enhancement to induce nonlinear shifts in the scattered transmission spectrum, using a nanosecond Q-switched laser centered at 1534nm. Here, we exploit the nonlinear Kerr effect to induce modulations to the refractive index of individual silicon bars dependent on the incident laser power. As the incident power increases, the refractive index, and hence the scattered amplitude and phase, of the metasurface elements are modified. Including Silicon’s nonlinear susceptibility in simulation, we show laser powers of 83 uW/um² can shift the resonant feature by greater than a full width half max. Our approach represents a facile route to achieve nonlinear optical phenomena in metasurfaces, and can be readily extended to other common nonlinear schemes, including harmonic generation and parametric wavemixing. Our high-Q scheme is generalizable to almost arbitrary transfer functions and materials, laying a foundation for a range of nonlinear-based technologies in computing, sensing, and communications.

EL01.05.04
Dynamically-Controlled Nanophotonic Phased-Arrays and Displays with Microfluidic Cavities
Qitong Li, Jorik Van de Groep, Adam White, Jung-Hwan Song, Polly Fordyce, Stephen Quake and Mark L. Brongersma; Stanford University, United States

Ultra-compact, high-resolution, and low energy-consumption tunable phased arrays and displays play a critical role in future’s daily life as they provide an efficient and user-friendly access to information. Nanophotonic devices, made by judiciously engineered optical resonators, are capable of harnessing the amplitude, phase, and spectrum of its scattered light with subwavelength resolution. However, active tuning of these optical resonances is still in its infancy. Active tuning is challenging as the semiconductors and noble metals display a limited tunability due to the generally weak electrorefractive and electroabsorptive effects. Here, we demonstrate the large, fast, and repeatable tuning of optical resonances by tailoring the dielectric environment of silicon (Si) nano-resonators that operate in the visible spectral range. The dramatic tunability results from the strong dispersion and interference of various optical resonances supported by Si nano-resonators when embedded in different refractive-index materials. This working principle is then realized by integrating the nanophotonic device with a microfluidic cavity that can programmably
control the refractive index (n=1-1.7) by flowing different liquid in real time.

Active beam steering, dual-wavelength switchable holography, and wavelength-selective focusing and imaging are all demonstrated to show the power and flexibility of the design principle. We also demonstrate the possible use of these elements in display application by showing both a broadband (~100 nm) amplitude tuning and full-color tuning (from blue to red, reflection peak from 480nm to 580 nm) for individual pixels. This large tunability results from the interference between the symmetric (electric dipole mode, toroidal dipole mode, magnetic quadrupole mode) and anti-symmetric (magnetic dipole mode, electric quadrupole mode) modes supported by Si nanodisk arrays, as their resonant frequencies and bandwidths all depend on the refractive index of surrounding materials. The dielectric environment is programmed up to 20 Hz with microfluidic cavities to show practical multi-color display function.

Altogether, these results demonstrate the unprecedented tunability to control the dielectric optical resonators in practical applications, ranging from active beam steering, real-time holography, to fluorescence microscopy and reflective displays with color-tunable pixels. The successful integration with mature microfluidic cavity technologies further paves the way towards next-generation ultra-compact active optical elements.

EL01.05.05
Structural Color Systems with the Combinations of Silicon Nanowire Arrays and Ultra-Thin 1D Resonators
Gil Ju Lee¹, Yeong Jae Kim¹, Dong Eun You², Dong-Wook Lee², Il-Suk Kang² and Young Min Song¹; ¹Gwangju Institute of Science and Technology (GIST), Korea (the Republic of); ²Korea Advanced Institute of Science and Technology, Korea (the Democratic People's Republic of)

Structural colors, which can occur by the interaction between visible light and exceptional photonic structures, have rapidly emerged as a key alternative to the traditional dyes or pigments because of their conspicuous advantages as following: 1) outstanding spatial resolution, 2) durability under harsh environments, 3) versatile utilization, 4) compactness, 5) eco-friendly materials, and 6) spectral selectivity. With these strong points, various structural colors including plasmonic nanostructures, metal-dielectric multilayers, and photonic crystals have attempted to substitute with the conventional dyes and pigments. Among them, silicon (Si) nanostructures are considered as the most suitable candidates because of the low-cost/mature fabrication process and excellent optical constants (i.e., high refractive index and low absorption loss compared to metals). Using the aforementioned properties, multicolor generation by Si nanowire arrays (Si NWAs) has been successfully demonstrated for reflective/transmissive structural color filters. However, the restricted color presentation of currently-reported structural colors has hindered the wide spreading of the promising structural color printing.

Here we propose a new class of reflective color filters to enlarge color gamut by attaching a sticker form of Si NWA on ultra-thin one-dimensional resonators which are in nanoscale. To implement the sticker form of Si NWAs, we fabricate transferable Si NWAs (T-SiNAs) embedded in polydimethylsiloxane (PDMS) which is a visibly transparent polymer. The nanoscale structures of each photonic configuration allow an exceptional mechanical softness, hence it enables flexibility and reusability without mechanical failure. First, we design and fabricate the T-SiNAs to possesses optical resonances covering from visible to near-infrared (NIR) ranges (i.e., 400 to 1000 nm). The resonance dip positions are shifted from short to long wavelengths by increasing the diameter of T-SiNAs. The fabricated T-SiNAs have the optimized structural parameters as follows: height = 2 μm, diameter = 50 to 150 nm with 10-nm-step, and period = 1250, 900, and 600 nm. To demonstrate the widening ability in color gamut, we selected metal-insulator-metal (MIM; Ag-SiO₂-Ag) structure as ultra-thin 1D resonator. Generally, MIM structures exhibit subtractive primary colors such as cyan, magenta, and yellow. However, by transferring T-SiNAs on MIMs, we enlarge the pristine color gamut of MIMs and experimentally realize additive primary colors such as red, green, and blue. Furthermore, such intriguing optical and mechanical characteristics facilitate a novel optical anti-counterfeiting sticker.

EL01.05.06
Optical Camouflage—Tunable Coloration Accompanied by Optical Janus Effect
Yong-Sang Ryu, Eui-Sang Yu, Jong-Su Lee and Taehyun Kim; Korea Institute of Science and Technology, Korea (the Republic of)

Reflective asymmetric coloration in a metal–insulator–metal (MIM) structure is proposed to achieve direction selective message encryption through the manipulation of physical characteristic of the top metal and effective refractive index of the dielectric insulator layer. A semicontinuous top metal film with nanoapertures, adopted as a
transreflective layer for MIM resonator, allows to exhibit direction-sensitive optical effect (called Janus effect) as well as to tailor the nanomorphology of a dielectric layer, which plays crucial roles in recognizable color changes when exposed to external liquids. This new concept of direction sensitive distinct colorations, followed by color tuning with respect to liquid exposures were thoroughly analyzed by theoretical simulations and experiments. Our liquid permeable approached in color changes indeed provide dramatic color tunability, a real-time sensing scheme, long-term durability, reproducibility, and most importantly, exhibit direction sensitive message hidings (Optical Camouflage) in a simple and scalable manner.

**EL01.05.07**
**Boosting Photoelectrochemical Water Splitting with Large Area Nanophotonic Antenna Arrays** Rambabu Yalavarthi, Stepan Kment, Radek Zboril and Alberto Naldoni; RCPTM, Palacky University in Olomouc, Czechia

Integration of plasmonic metal nanostructures with semiconductor nanomaterials has been proposed as a promising strategy to achieve enhanced light absorption and solar energy conversion efficiencies. In the present work, we report the fabrication of platinum coated Ni pillar arrays integrated with CdS nanoparticle continuous layer (Ni/Pt/CdS pillars) for photoelectrochemical water splitting. We use several Ni/Pt pillar array with varying pitch and diameter to achieve a wide wavelength (visible to near-infrared (NIR)) light harvesting. Compared to CdS coated Ni/Pt planar film, the best Ni/Pt/CdS pillar array shows ~200% photocurrent enhancement. The same is confirmed by an incident photon to current conversion efficiency (IPCE) and electromagnetic simulations. We will discuss the effects enabling the photocurrent enhancement, distinguishing the contribution from increased surface area, photonic and plasmonic light concentration.

**EL01.05.08**
**Design and Fabrication of a Microwave Metasurface Beam-Splitter Reflector** Arben M. Gjonbalaj, Richard Williams and Brian M. Wells; University of Hartford, United States

Metasurfaces have recently gained attention due to their physical compact nature, versatility, and exotic electromagnetic properties in manipulating propagating waves. In this work we present the design, fabrication, and experimental verification of a beam-splitting metasurface reflector with arbitrarily chosen split beam directions. A beam splitter is an integral component in many optical devices such as interferometers and multiplexers. Traditional beam splitters are based on cubes or plates composed of glass and mirrors that are comparatively large and bulky. Being able to fabricate a metasurface beam splitter will prove to be extremely useful for a variety of applications.

The metasurface under investigation was designed to split a normally incident wave into two beams, one directed to 25 degrees and the other directed to 45 degrees, using the Fourier transformation method of array synthesis. This method is used to calculate the necessary metasurface reflection properties and High-Frequency Electromagnetic Solvers (HFSS) simulations are performed to determine the required surface pattern for fabrication. This method can easily be extended to any combination of splitting angles and operating frequency. The beam-splitting metasurface is fabricated using traditional silk printing techniques with conductive ink on selected substrates. For this work conductive nickel ink patches were printed on an aluminum-backed acrylic substrate. Measurements were performed at 10.5 GHz using a single frequency microwave transmitter and receiver, the receiver was scanned through 180 degrees and electric field intensity was measured. These measurements show excellent agreement with the scattering predictions.

**EL01.05.09**
**Novel Diffractive Optical Elements for on Chip Multi-Spectral Imaging and Infrared Spectroscopy** Yuyao Chen, Wesley Britton and Luca Dal Negro; Boston University, United States

The integration of imaging spectrometers with high-sensitivity photodetectors for spectroscopic identification of multi-band infrared (IR) signals is of great potential for a number of applications that range from infrared imaging to environmental monitoring and biochemical detection. In our recent work, we designed, fabricated, and characterize novel diffractive optical elements (DOEs) that integrate imaging and spectroscopic functions on the same silicon chip. In particular, we demonstrate multi-functional focusing gratings and multi-focal lens flat lenses based on the versatile axilens concept with engineered phase modulations over 100µm footprint dimensions. Using electron beam lithography and sequential etching processes we demonstrate a novel four-level multi-functional phase element that combines the phase modulation of a traditional axilens (i.e., a diffractive lens with a large and programmable
focusing depth) with the spatial dispersion behavior characteristic of a compact 2D periodic grating. Furthermore, we demonstrate that the operation spectrum of our designed devices doubles the one of a traditional Fresnel lens. A comprehensive analysis of the operation bandwidth and cross-talk ratio on the detection plane between targeted wavelengths across the long-wavelength IR range (LWIR) is performed demonstrating broad band operation with a 15% cross-talk figure. Device-level simulations are performed using the three-dimensional finite element method and show excellent agreement with predicted device performances based on the rigorous Rayleigh-Sommerfeld diffraction theory.

**EL01.05.10**

**Optical Rectification in a Reconfigurable Metal-Insulator-Metal Diode**

Richard M. Osgood¹, Yassine Ait-El-Aoud¹, Michael Okamoto¹, Sean Dinneen¹, Declan Oller², Gustavo Fernandes², Jin Ho Kim², Sergey Dizhur² and Jimmy Xu²; ¹US Army Combat Capabilities Development Command - Soldier Center, United States; ²Brown University, United States

Optical rectification (OR) is an optoelectronic phenomenon where an illuminating optical field is rectified by a nonlinear material to produce a DC voltage and, in a conductive material, a current which can be a combination of thermionic and tunneling current. OR has been difficult to observe in many systems, due to the need for tunneling junctions with exceedingly small capacitance and surface area.¹,² We report optical rectification in a nanoscopic Metal-Insulator-Metal (MIM) diode’s tunneling junction, which is voltage-reconfigurable via simple resistive switching, thus enabling tunable conductivity. The conductively-tunable resistive switching MIM diode we explore can be tuned, set, and reset via the application of DC electric fields, making it ideal for exploring optical rectification phenomena under different nonlinear conductivity conditions and for dynamically tuning the device’s responsivity. Other nonlinear junctions cannot be so readily set and re-set. The resistive-switching MIM diode that we research also has the advantage of being scalable to large areas, due to its simple fabrication. Using a relatively simple MIM diode consisting of a planar Al electrode (“passive electrode” or PE), a thin Al₂O₃ barrier layer, and an initially planar Ag counter-electrode (“active electrode” or AE), we demonstrate optical rectification. By applying a voltage, a metallic filament, having a cross-section as small as (10 nm)², grows within the dielectric layer, from the PE to the AE, resulting in a nanogap between metals, bridged by a barrier layer, and with tunneling resistance that exponentially depends on the distance between PE and PE, set by a voltage-tunable nanogap. We measure current-voltage curves and the response to a modulated visible laser beam, and compare to our analytical MIM diode model, which was derived for 2D junctions.³ The filament’s separation from the AE is controlled precisely by controlling the junction’s voltage and current. The tunability of this platform opens the possibility for adaptive ultrafast photon detectors, wireless power transmission, and energy harvesting systems, potentially useful for reconfigurable antennas useful for flexible electronics applications, and/or for neuromorphic computing.


**EL01.05.11**

**Employing the Insulator-to-Metal Transition of Vanadium Dioxide for the Use as Switchable Flat Lens in the THz Regime**

Florian Kuhl¹, Janine Lorenz¹, Martin Becker¹, Angelika Polity¹, Teng Wang², Jinwen He³,⁴, Jinying Guo², Xinke Wang², Shengfei Feng², Yan Zhang² and Peter J. Klar¹; ¹Justus Liebig University, Germany; ²Capital Normal University, China; ³Beijing Institute of Satellite Information Engineering, China; ⁴State Key Laboratory of Space-Ground Integrated Information Technology, China

The potential of THz waves for applications has become widely recognized in the last few years and the use of phase transition phenomena for reversibly tuning the properties of functional materials in devices is an attractive research area of materials science. We report on various kinds of designed and microfabricated metasurfaces for actively switching the wavefront of terahertz (THz) radiation based on the well known insulator-to-metal (IMT) phase transition of pure vanadium dioxide (VO₂) and its ternary tungsten (W) doped V₁ₓWₓO₂. The IMT is induced by a temperature change of the structured thin films and occurs at about 68 °C for the undoped bulk VO₂ while doping with W strongly influences the phase transition temperature Tc by about -12.6 K / (at.% of W) . The microstructures, based on metasurfaces of C-shaped slot antennas, are etched into the rf-sputtered thin films on c-sapphire substrates using micro- and nanofabrication methods, i.e. photolithography and ion beam etching. The C-shaped slot antennas are active only when the pure VO₂ or the V₁ₓWₓO₂ is in its metallic phase, i.e. at temperatures
Examples are temperature-switchable THz multi-focus lenses which focus impinging THz radiation into four focal spots or Airy beam generators. Using both materials, VO$_2$ and V$_{1-x}$W$_x$O$_2$, allows us to fabricate stacked lenses that can be switched on and off at different temperatures linked to the critical temperatures $T_c$ of the thin films. We characterized the function of the THz wavefront modulators over a broad frequency range from 0.3 to 1.2 THz. Such thermally switchable THz wavefront modulators with a capability of dynamically steering THz fields will be of great significance for the future development of THz active devices.

**EL01.05.12**

**Optical Metasurfaces by Periodic Gain-Loss Building Blocks Using Colloidal Self-Assembly**

Max J. Schnepf$^{1,2}$, Tobias A. König$^{1,2}$ and Olha Aftenieva$^1$; 1Leibniz Institute for Polymer Research Dresden, Germany; 2TU Dresden, Germany

In conjugated polymers, electronic excitations are coherently spread over the whole conjugated polymer, the individual transition dipole moments interact by dipole-dipole coupling. As this dipole-dipole coupling is a near-field effect, the interaction is limited to a small spatial region, and the participating quantum emitters cannot be addressed and probed individually. With a colloidal approach, we build a larger-scale analogue of a conjugated polymer to study coherent energy transfer. We will couple a small ensemble of quantum emitters with a plasmonic colloidal cavities [1] and a spatially extended hybrid plasmonic lattice mode [2] to study the weak and strong light matter interaction. The fluorescence enhancement (optical gain) is provided by a lattice of silver indium sulphide (AgInS) quantum dots fabricated by confinement assembly. The light annihilation (optical loss) is achieved using a gold particle lattice by soft lithography templates and directed self-assembly.[3] By stacking of those two components, geometrical parameters can be varied, which allows to study the coherent energy transfer systematically by time-correlated scattering and reciprocal space imaging methods. Due to the scalability of both fabrication methods, we can produce substrates with areas larger than 2 cm$^2$, which can be expanded even further. In the end, the stacked structures pave the way to a quantum simulator of the underlying conjugated polymer.


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**EL01.05.13**

**Scale Law of Far Field Thermal Radiation from Metasurface**

Jiayu Li and Sheng Shen; Carnegie Mellon University, United States

Although the far-field thermal radiation from the single nanoscale thermal emitter is now well-understood under the framework of Quasi-normal mode (QNM) theory and coupled-mode theory (CMT), the collective behavior of a set of closely packed emitters or metasurface is still vague. When the periodicity of the emitter array is large, the optical mode overlapping between adjacent emitters in the near field is negligible. Therefore, it is reasonable and safe to treat the array of sparsely packed emitters in the way of a single emitter. As the packing density keeps decreasing, the interaction between neighbor emitters is no longer negligible. In this scenario, a change of the far-field thermal radiation with respect to the packing density is expected. In this work, we demonstrate a new scale law of the far-field thermal emission by applying QNM to the metasurface consisting of densely packed emitters. The tight binding method is used to approximate the collective resonant mode of the emitter array. The thermal radiation from single emitter inside the array is suppressed by the adjacent emitters. Depending on the resistive and radiative loss of the single emitter, the overall thermal radiation can be either proportional or inversely proportional to the number of emitters coupled. This new scale law of thermal radiation could serve as a general guideline for designing metasurface with desired thermal emission properties.

**EL01.05.14**

**Reactive Magnetron Sputtering of Heteroepitaxial Titanium Nitride for Plasmonic and Metamaterial Applications**

Amber N. Reed$^1$, Hadley A. Smith$^1$, Zachary J. Biegler$^{1,2}$, Rachel L. Adams$^1$, Madelyn Hill$^1$, Krishnamurthy Mahalingam$^1$, Kurt G. Eyink$^1$ and Augustine M. Urban$^1$; 1Air Force Research Laboratory, United States; 2University of Dayton, United States
High temperature stability, chemical stability, low surface energy and mechanical robustness, combined with a zero-crossover wavelength in the visible region make titanium nitride (TiN) a promising material for plasmonic and metamaterial applications in harsh environments. In this work we demonstrate the heteroepitaxial growth of TiN on (0001)-Al2O3, (001)-MgO and (0001)-LiNbO3 substrates as well as incorporation of TiN in metal-dielectric stacks. We discuss the differences in growth and crystalline properties based on substrate material and growth conditions. Additionally, we discuss the relationship between TiN crystalline quality and optical properties. Coupled x-ray diffraction (XRD) of our TiN show high quality epitaxial growth on all three substrates, however, further structural characterization reveals differences in crystal defects, strain and surface morphology based on substrate crystal structure and lattice mismatch. Pendellosung fringes on the (111)-TiN diffraction peak for the coupled XRD of TiN on c-plane sapphire and LiNbO3 indicate uniform d-spacing and a pristine interface. 6-fold symmetry for the TiN grown on sapphire is seen in XRD pole figure scans, indicating the presence of stacking faults. These domains, which are further evident in atomic force microscopy (AFM) of the TiN surface, are attributed to different stacking within the TiN domains. XRD of the TiN on MgO show Pendellosung fringes on the (001)-TiN diffraction peak. Cross-hatching features similar to those on the bare MgO substrate are seen in the AFM of the TiN surface. Variable angle spectroscopic ellipsometry (VASE) shows that TiN behaves metallic on all substrates with a zero crossover wavelength between 470 nm and 490 nm. Differences in the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) permittivity for TiN on the different substrates are also seen in the VASE measurements.

EL01.05.15
Multifunctional Infrared Metasurfaces for Polarization Analysis Joseph Miragliotta, Andrew Strikwerda, David Shrekenhamer, Lance Oh, Luke Currano and Garret Bonnema; JHUAPL, United States

The emergence of metasurface technology and its accompanying design principles are enabling the development of optical components with multiple functionalities, e.g., polarization discrimination and focusing. In this report, we highlight our computational and experimental results associated with the design, fabrication, and experimental characterization of infrared (IR) metasurface optics that were designed for wavelength and polarization-specific analysis of infrared fields in the near and mid-wave IR region of the spectrum. For the former, we developed an all-dielectric metasurface that enabled polarization analysis of a 1.55 micron laser source. For the mid-wave metasurface, a reflective metasurface architecture was observed to exhibit polarization-selective imaging throughout the 4.5 to 5 microns region.

EL01.05.16
Dielectric Loss Compensation for Enhanced Optical Rectenna Conversion Efficiency Ayendra Weerakkody and Garret Moddel; University of Colorado, United States

Frequency-dependent losses associated with dielectrics limit the efficient operation of devices at mid-infrared (IR) wavelengths. These material losses were overlooked in certain research areas such as metal-insulator-insulator-metal (MI2M) diode based optical rectennas for mid-IR energy harvesting, due to the difficulty in measuring/characterizing material properties at these frequencies. Many researchers in this field have focused only on enhancing the rectification efficiency of the diode and the coupling efficiency between the antenna and the diode. In this work, we demonstrate a technique understand the role of dielectric losses at 28.3 THz in our rectennas, and to introduce an innovative solution by taking advantage of combined effects of geometric dependence of losses, high frequency voltage division and resonant tunneling to achieve an improvement in conversion efficiency. First, we measured the frequency dependent complex dielectric constants of the MI2M diode oxide stack, which consisted of NiO and Al2O3, by mid-IR variable angle spectroscopic ellipsometry. After performing physical characterization, we fabricated 6 different wafers of rectennas with varying NiO thicknesses. Then we measured their DC current-voltage (I(V)) characteristics, as well as their optical response under illumination with a CO2 laser. Since the MI2M diode I(V) characteristics vary with frequency [1], we extracted the high-frequency DC resistance of the diodes by considering the ratio of open-circuit voltage to short-circuit current. This resistance, along with the measured complex dielectric constants, is used to model the rectenna as a clamper circuit with shunt-capacitive and conductive losses in parallel with the diode resistance [2]. These material losses were found to depend on the thickness of the diode, with thicker oxides compensating for losses as the losses are inversely proportional to the thickness. Due to compensation of losses in combination with high-frequency voltage division and resonant tunneling, we were able to achieve diodes with a conversion efficiency ten times higher than uncompensated devices.

References:
Light displays a wide range of different possible interactions with naturally-occurring materials. Optical sensing and imaging applications capitalize on this fact to study such materials and structures of interest. Alternatively, it is possible to engineer new, nanostructured materials that only exhibit a strong interaction to light waves with specific properties, e.g. a specific incident angle, wavelengths, or state of polarization. We are interested in using such designer materials to realize new types of specialized photodetectors for angular sensing and spectropolarimetry. To achieve specific sensing functions, one typically combines a conventional photodetector with a set of bulky optical elements capable of filtering light waves with properties of interest. These can include lenses, gratings, apertures, prisms, and polarization filters. This strategy makes dense integration a significant challenge. To overcome this challenge, we proposed the use of different types of high-index semiconductor nanostructures that exhibit an optically resonant interaction with the light waves of interest. These resonances can boost light-matter interaction and enhance absorption and photocarrier generation. This ultimately facilitates the creation of compact, highly integrated photodetectors that do not require additional external elements.

Here, we illustrate our approach with a nanopatterned silicon layer that displays a high differential absorption for left and right-hand circularly polarized light. It achieves this function by engineering both Mie and guided mode resonances in dislocated silicon nanowire patterns. We will present the fabricated photodetector structures and their experimental characterization. The proposed structures could potentially be used in a wide range of applications, for sensing, imaging, and augmented/virtual reality.

Tunable Terahertz Complimentary Metamaterial Enabled by Phase Transition of Vanadium Dioxide
Xiaoguang Zhao¹, Xuefei Wu¹, Jacob Scalch², Guangwu Duan¹, Richard Averitt², Xin Zhang¹ and Chunxu Chen¹; ¹Boston University, United States; ²University of California, San Diego, United States

Metamaterials and metasurfaces have enabled myriad applications by breaking the limitations of natural materials, including negative refraction index, subwavelength imaging, near zero epsilon, metalens, and invisibility cloaking. Tunability in metamaterials has generally been achieved through inclusions of condensed matter systems in which a dynamic response is induced by external excitations. The tunability by this method is both the extension and restriction of the metamaterials capability as the limits of the tuning are defined by the dynamic range of the included material. Overcoming this limitation of tunable materials and achieving better performance in hybrid devices is a challenge that can lead to greater advances in these devices. Vanadium dioxide (VO₂) is a correlated electron material, which has been particularly well studied largely because the insulator-to-metal transition (IMT) occurs above room temperature at around 340K. Upon undergoing the IMT, the resistivity changes by four-orders of magnitude and across a broad spectral range making VO₂ a powerful dynamic material to be combined with metamaterials to introduce nonlinear responses, state switches, and modulators. The physics of the accompanying crystal transformation from monoclinic to rutile state has historically obscured the exact mechanism of the transition.

In this paper, we patterned a complementary metamaterial on a thin layer of vanadium dioxide films by direct laser writing technique and photolithography to explore the tunable terahertz (THz) response. The metamaterial exhibits a transition in THz transmission which is larger than of a pristine VO₂ film. The modulation enhancement of dynamic materials by metamaterial resonators provides a way to enhance the natural utility of VO₂ through metamaterial inclusions while the sensitivity of the complementary resonator provides a straightforward way to investigate the nature of mesoscopic transition phenomena in correlated electron materials. We characterize the phase transition response of the VO₂ film and the tunable metamaterial using THz time-domain spectroscopy. For the complementary metamaterial, the resonance peak occurs at 0.48THz with a peak transmission of 82.8% when the VO₂ is in insulator state at the temperature below 315K. As the temperature increases, the VO₂ thin film transits to the metallic state, thus the resonance peak vanishes. The modulation amplitude of THz transmission at 0.48THz is 68.3%. We measured the dynamic transition as a function of temperature for heating and cooling processes.
transmission of VO$_2$ CSRR during the heating process does not change until the temperature reaches 334K. A dramatic reduction of transmission occurs within a 2K span from 335K to 337K during heating. Upon cooling, the reverse transition occurs albeit at a lower temperature. The rapid onset of this transition coupled with the wide hysteresis presents an attractive feature for applications in THz switches and modulation devices.

**EL01.05.19**

**Hybrid Graphene/Metal Antenna Arrays for Terahertz Communications**

Arpit Jaiswal, Arjun Singh, Farah Vandrevala, Josep Jornet and Erik Einarssson; University at Buffalo, United States

There is a critical need for compact antenna arrays capable of transmitting and receiving information in the terahertz band (0.1-10 THz). In order to achieve this goal, control of the array response is essential. Here we report design, fabrication, and experimental characterization of a hybrid graphene/metal antenna array consisting of metallic elements fabricated atop graphene. The antenna design was developed through numerical simulations that were informed by experimentally obtained graphene parameters. Experimental characterization revealed a clear enhancement due to the array, and the presence of the underlying graphene affected the reflected intensity. Graphene’s Fermi energy can easily be tuned by electrostatic gating, which makes this structure promising for active, steerable THz reflectarrays.

**EL01.05.20**

**Unexpected Photonic Band Gaps in 3D Crystal Structures**

Rose Cersonsky, James Antonaglia, Bradley Dice and Sharon C. Glotzer; University of Michigan, United States

Photonic crystals are materials composed of mixed dielectric media that result in the reflection of all electromagnetic waves within a range of wavelengths commensurate with the length scale of the crystal. Such complete photonic band gaps allow for light to be controlled through materials design. Since first theorized in 1987, much effort has been made to define and synthesize photonic crystal structures. In the decades since, many photonic structures have been discovered, often by using naturally occurring crystal structures as templates for design. However, these studies have yet to answer the question: what features of a 3D structure will produce a complete photonic band gap? Here, we present data on over 150,000 potential photonic crystals, and show that complete photonic band gaps are possible for many unexpected structures that have yet to be explored. Our simulations suggest that when designing novel photonic materials, the toolbox of structural templates may be larger and richer than previously thought, widening the field of target crystal structures.

**EL01.05.21**

**All-Dielectric Metasurfaces Made of HfO$_2$ Nanopillars for Structural Coloration**

Omid Hemmatyar, Sajjad Abdollahramezani, Yashar Kiarashinejad, Mohammadreza Zandehshahvar and Ali Adibi; Georgia Institute of Technology, United States

We perceive the color of an illuminated object in our surrounding primarily since it selectively reflects certain colors and absorbs the others. Beside these mechanisms, colors can be generated resorting to another mechanism called structural coloration. In structural coloration, the interaction of incident light with nanoscale features in the illuminated object leads to specific resonances in the reflection light each associated to a specific color. In recent years, due to several advantages of structural colors over its counterpart such as resistivity to high-temperature, photobleaching and ultraviolet irradiation on one side, and huge advancement in the fabrication technology on the other side, a significant research has been done to generate artificial structural colors using sub-wavelength nanophotonics structures. To implement these structural colors, both plasmonic and all-dielectric metasurfaces (MSs) have been used due to their capability of manipulating the light-matter interaction at nanoscales. However, the intrinsic dissipative ohmic loss in metals used in plasmonic MSs significantly reduces the quality of generated colors by broadening and weakening the resonance peak of the reflection which leads to small color gamut with low color saturation. To circumvent this issue, all-dielectric MSs using high-index or transparent dielectric materials have been used as an alternative to plasmonic-based structural colors [1]. Here, for the first time to our knowledge, we designed and fabricated an all-dielectric MS comprising of hafnia (HfO$_2$) nanopillars (NPs) to generate colors. These NPs can support both electric dipole (ED) and magnetic dipole (MD) modes due to the low loss of HfO$_2$. The MD mode can be coupled to the reflected light resulting in a sharp Fano-type resonance in the reflection spectrum which is desired for generation of pure and vivid colors. In the design step, we first simulated a set of MSs with different design parameters using finite difference time domain (FDTD) solver in Lumerical. Then, we fed the corresponding
reflection responses as the training data to a pseudo-encoder module [2, 3, 4], within deep learning architecture, and found the periodicity of the unit cell of our MS as the most effective design parameter on the spectral properties of the sharp Fano-type resonances. Based on these results, we again simulated a set of MSs with optimized design parameters to generate colors with high saturation. Finally, the designed MSs were fabricated using atomic layer deposition which enables fabrication of nano-scale features with minimum surface roughness as required in our MSs. The experimental results are in good agreement with those of simulation.

References:

SESSION EL01.06: Low Dimensional Photonics II
Session Chair: Deep Jariwala
Tuesday Morning, December 3, 2019
Hynes, Level 1, Room 102

8:15 AM *EL01.06.01
Multipole Resonances in Transdimensional van der Waals Antenna Lattices Viktoriia Babicheva; University of New Mexico, United States

Novel van der Waals materials and their heterostructures are especially promising in an ongoing quest for suitable photonic materials that enable miniaturization of optical components. van der Waals materials possess high optical anisotropy as the strong covalent bonding within a specific layer and weak van der Waals forces between adjacent material layers result in highly anisotropic lattice vibrations along the in- and out-of-plane directions of the layered material. It is proposed to use optical antennas made out of natural hyperbolic material hexagonal boron nitride (hBN) as an alternative way of realizing efficient subwavelength scatterers and overcoming limitations of plasmonic and all-dielectric material platforms [1,2]. Transdimensional designed lattices of resonant hBN antennas in the periodic arrays can serve as functional elements in ultra-thin optical components and photonic applications. In this talk, I will show that the hBN antenna possesses different multipole resonances enabled by the supporting high-k modes and their reflection from the antenna boundaries. An electric quadrupole mode causes a resonant magnetic response of the scatterer because of wave reflections from its boundaries similar to the formation of magnetic resonance in high-refractive-index elements. The full range of the resonances is demonstrated for the hBN cuboid antenna, a decrease of reflection from the array, and highly directional resonant scattering from antennas pairs. Multipole resonances cause the decrease in the reflection from antenna array to zero, which can be ascribed to resonant Kerker effect satisfying generalized zero back-scattering condition for particles in the array [3]. Transdimensional hBN lattices include 3D-engineered nanoantennas supporting multipole resonances in hBN antennas and arranged in the 2D arrays to leverage collective effects in the nanostructure. The effect can be used in designing optical elements and metasurfaces based on hBN scatterers for applications in mid-infrared photonics. The work is supported by AFOSR grant FA9550-19-1-0032.
Oxides exhibiting extremely low thermal conductivity ($\kappa$) are essential for heat management technologies such as thermoelectrics and thermal barrier coatings. Fabricating artificial superlattices is an effective approach to minimize the $\kappa$ of oxides because of the Kapitza resistance (interface between two different phases). However, their practical applications are limited by difficulties and cost of the atomic-scale fabrication. Therefore, materials exhibiting natural superlattice structures are of great value. The $\kappa$ of some natural superlattice In$_M$O$_3$(ZnO)$_m$ ($M = \text{In, Fe, and Ga}$, $m = \text{integer}$) polycrystals have been reported, but it has been very challenging to examine the effect of the Kapitza resistance due to the randomly-oriented grains. Here we fabricated InGaO$_3$(ZnO)$_m$ single crystalline films by the reactive solid-phase epitaxy method and measured the $\kappa$ perpendicular to the natural superlattices. When the superlattice period ($d_{SL}$) was longer than 1.93 nm, the thermal resistivity increased proportionally with the interface density ($d_{SL}^{-1}$), indicating that the ballistic phonon transport was suppressed at the InO$_2$/GaO(ZnO)$_m$ interfaces, which exhibited the Kapitza resistance of 1.64 m$^2$ K GW$^{-1}$. The minimum $\kappa$ was 1.12 W m$^{-1}$ K$^{-1}$ ($m = 5$), which is approximately 1/3 of the polycrystalline ceramics and lower than the amorphous InGaO$_3$(ZnO)$_m$. These results would be useful for advanced heat management technologies.

Controlling Emission of WS$_2$ Monolayer with a Spherical Silicon Mie Resonator

Tatsuki Hinamoto$^{1,2}$, Yan Joe Lee$^2$, Søren Raza$^3$, Hiroshi Sugimoto$^1$, Minoru Fujii$^1$ and Mark L. Brongersma$^2$; $^1$Kobe University, Japan; $^2$Stanford University, United States; $^3$Technical University of Denmark, Denmark

Two-dimensional transition metal dichalcogenides (TMDCs) have emerged as novel quantum emitters. Achieving control of their radiation properties, such as excitation rate, radiation efficiency, and radiation pattern, is of importance for next-generation photonic and optoelectronic devices. Recently all-dielectric nanophotonics has been identified as a promising way to control such radiation properties at the nanoscale by coupling the emitter to Mie resonators. It has been experimentally and theoretically demonstrated that Mie-resonant silicon nanowires (diameter/length $\sim$ 100 nm/40 um) can provide directionality to the emission of monolayer MoS$_2$ emitters due to the interaction between the source dipole and the excited electric and magnetic dipole resonances.[1] In order to further reduce the dimensions of the resonator, we propose a spherical Mie resonator for control over the radiation pattern of monolayer TMDCs.

First, we theoretically analyze the optical coupling of a 100-200 nm silicon nanosphere and a dipole emitter by modifying the classical Mie theory for excitation with a point dipole. As for the case of a silicon nanowire, the interaction of the source dipole and the excited electric and magnetic dipole resonances results in directional emission. To demonstrate this experimentally, we dropcast colloidal silicon nanospheres (100-200 nm in diameter) [2] onto monolayer WS$_2$ coated silica substrates. After Ar$^+$ ion etching of WS$_2$ around the silicon nanospheres to remove uncoupled emitters, we measure the exciton photoluminescence intensity of WS$_2$ under single silicon nanospheres using objectives in the top and bottom direction. By studying the top-to-bottom PL ratio over many nanospheres, we demonstrate 8-fold directionality in emission for selected nanosphere sizes as expected from our theoretical analysis.

Metasurfaces for Augmented and Virtual Reality
Mark L. Brongersma; Stanford University, United States

Since the development of diffractive optical elements in the 1970s, major research efforts have focused on replacing bulky optical components by thinner, planar counterparts. The more recent advent of nanophotonic metasurfaces has further accelerated the development of flat optical elements through the realization that resonant optical antenna elements can be utilized to facilitate local control over the light scattering amplitude and phase. In this presentation, I will show how metasurfaces can start to impact Augmented and Virtual Reality applications. I will discuss the creation of free space optical beam tapping systems and high-efficiency metasurface-based optical combiners for near-eye displays. The proposed optical elements can be fabricated by scalable fabrication technologies, such as nanoimprint lithography, rolling optical lithography, and direct write optical lithography.

Meta-Optics and Metasurfaces with Mie-Resonant Dielectric Structures
Yuri Kivshar1,2; 1Australian National University, Australia; 2ITMO University, Russian Federation

Metamaterials---artificial electromagnetic media that are structured on the subwavelength scale---were initially suggested for the realization of negative index media, and later they became a paradigm for engineering electromagnetic space and controlling propagation of waves. However, applications of metamaterials in optics are limited due to inherent losses in metals employed for the realisation of artificial optical magnetism. Recently, we observe the emergence of a new field of all-dielectric resonant metaoptics aiming at the manipulation of strong optically-induced electric and magnetic Mie-type resonances in dielectric and semiconductor nanostructures with relatively high refractive index [1]. Unique advantages of dielectric resonant nanostructures over their metallic counterparts are low dissipative losses and the enhancement of both electric and magnetic fields that provide competitive alternatives for plasmonic structures including optical nanoantennas, efficient biosensors, passive and active metasurfaces, and functional metadevices [2, 3]. Here, we aim to summarize the most recent advances in all-dielectric Mie-resonant meta-optics including active nanophotonics as well as the recently emerged fields of topological photonics and nonlinear metasurfaces.

In addition, we also aim to review the physics of bound states in the continuum and their applications in metaoptics and metasurfaces [4]. First, we discuss strong coupling between the modes of a single subwavelength high-index dielectric resonator and analyse the mode transformation and Fano resonances when resonator’s aspect ratio varies [5]. We demonstrate that strong mode coupling results in resonances with high quality factors, which are related to the physics of bound states in the continuum when the radiative losses are nearly suppressed due to the Friedrich–Wintgen scenario of destructive interference. Our theoretical findings are confirmed by microwave and optical experiments for the scattering of high-index subwavelength resonators with a tunable aspect ratio. The proposed mechanism of the strong mode coupling in single subwavelength high-index resonators accompanied by resonances with high-Q factor helps to extend substantially many functionalities of all-dielectric nanophotonics that opens new horizons for active and passive nanoscale metadevices. Next, we discuss how bound states in the continuum can appear in the physics of metasurfaces. We reveal that metasurfaces created by seemingly different lattices of (dielectric or metallic) meta-atoms with broken in-plane symmetry can support sharp high-Q resonances that originate from the physics of bound states in the continuum [6]. We demonstrate a direct link between the bound states in the continuum and Fano resonances, and discuss a general theory of such metasurfaces, suggesting the way for smart engineering of resonances for many applications in nanophotonics and meta-optics.


11:00 AM EL01.07.03
Enhancing the Most Versatile and Time-Tested Radiative Cooling Metamaterial – Challenges and Opportunities with Paints Jyotirmoy Mandal1, Aaswath Raman2, Adam Overvig1, Kamal Krishna Mandal3, Yuan Yang1 and Nanfang Yu1; 1Columbia University, United States; 2University of California, Los Angeles, United States; 3Chittagong Medical College Hospital, Bangladesh

In recent years, research on passive daytime radiative cooling has seen a variety of metamaterial-based innovations, such as structured polymers [1], photonic designs [2-3], and polymer-dielectric composites [4-6]. However, paints, which combine the optical functionalities of pigments, dyes and polymers across the solar to thermal infrared wavelengths, remain a time-tested, versatile and by far the most established radiative cooling 'metamaterial'. With the rapidly rising global demand for cooling necessitating immediate solutions, it is therefore paints on which research advances stand to be most impactful.

In this presentation, we will provide a broad overview of paints as a versatile radiative cooling metamaterial platform with multiple avenues for exploration. We will first discuss how the individual components of paints, e.g. dyes, pigments and polymers, contribute to the solar reflectance and thermal emittance required for radiative cooling. By altering these constituents and their size, as well as the macroscopic morphology of paint coatings, their optical properties can be drastically altered. We will specifically discuss the optimization of reflective pigments to maximize broadband solar reflectance, ways of enhancing the ultraviolet reflectance, tailoring macroscopic morphology to simultaneously achieve color and high near-to-shortwave infrared reflectance, reducing the diffuse glare of white paints, and enabling optical switching. Associated non-optical aspects, like the durability of optical performance, will also be discussed. Commercial state-of-the-art, recent scientific advances, and outstanding questions on paints will be presented as windows for further explorations in this field.


11:15 AM EL01.07.04
Dynamic Flat Lenses with Nonlinear, High-Q Dielectric Metasurfaces Elissa Klopfer, Mark Lawrence, David Barton, Jefferson Dixon and Jennifer A. Dionne; Stanford University, United States

Conventional imaging requires long path lengths and bulky, multi-lens components. For applications including on-chip microscopy, lightweight space probes, LIDAR, and point-of-care diagnostics, metasurfaces promise high-fidelity imaging but in a highly reduced footprint. Metasurfaces, two-dimensional arrays of subwavelength nanostructures, precisely control the amplitude, polarization, and phase of waves in an ultrathin system. However, dynamically controlling their optical output in response to an applied bias remains an outstanding challenge. Here, we present ultrathin imaging metasurface which exploits the nonlinear Kerr effect to locally modulate the refractive index, and hence the focal intensity. Our metasurface lens consists of a series of 25 nanoscale silicon bars, 700 nm in height with a width varying from 100 and 400 nm, separated by 700 nm. The width of each individual bar imparts a phase shift, that in series can be designed to form a parabolically-varying phase profile to focus the incoming light between 4 um and 20 um away. Importantly, Silicon also supports inherent nonlinearities via the optical Kerr effect, which describes a change in a materials refractive index dependent on incident intensity. To achieve efficient
nonlinearities, we introduce periodic notches symmetrically on both sides of the 219 nm wide Si bars, which introduces a high quality factor (high Q) mode via a guided mode resonance near the lens’s designed operating wavelength 1500 nm. Our full-field simulations indicate Q factors spanning 10000 to over 100000 at 1473 nm for symmetric notches spanning in depth from 10 nm to 2 nm with a period of 650 nm in a 100 nm wide Si slab. We then utilize this high-Q lens to modulate the intensity of the focal spot with input power. In the nonlinear regime, as the power increases from 1 kW/cm² to 50 kW/cm², the resonance red-shifts from 1499.4 nm to 1499.7 nm and the normalized power at the focal spot decreases 4-fold. Importantly, this power-limiting meta-lens operates at optical frequencies, utilizes Si in a lossless regime, and can be readily extended for multi-wavelength operation by integrating additional notches into the adjacent Si bars. Our presentation will describe both the design and fabrication of this nonlinear imaging metasurface, as well as applications to dynamic imaging.

11:30 AM EL01.07.05
Inverse Design of Actively Tunable Metasurfaces for Beam Steering Applications Prachi Thureja¹,², Ghazaleh Kafaie Shirmanesh¹, Katherine T. Fountaine³, Meir Grajower¹, Ruzan Sokhoyan¹, Yury S. Tokpanov¹ and Harry A. Atwater¹; ¹California Institute of Technology, United States; ²ETH Zürich, Switzerland; ³Northrop Grumman NG Next, United States

The ability to comprehensively control the constitutive properties of light including wavelength, amplitude, phase and polarization is crucial to the development of novel technologies for sensing, imaging, flat optics and holography. In recent years, metasurfaces have enabled extraordinary advances in light manipulation through precise design of their subwavelength resonant elements. However, the static nature of passive metasurfaces does not allow for post-fabrication modifications to their optical response, which limit their utility. Active metasurfaces overcome this limitation by enabling real-time control of the properties of scattered light. The active control is achieved by applying external stimuli to tune the intrinsic properties of subwavelength antenna elements. While this greatly enhances the versatility of metasurfaces, active metasurfaces typically do not exhibit ideal phase-amplitude response, i.e. constant reflectance and a phase shift of up to 360°. In addition, experimental non-idealities result in discrepancies between desired and measured performance and often generate scattering in undesired directions.

We report an inverse design approach to achieve optimal beam-steering behavior for active metasurfaces that includes experimentally relevant non-idealities, such as limited phase response, non-unity reflectance and correlation of phase and amplitude. By evaluating several multi-parameter global optimization methods, we develop an approach to enable prediction of the amplitude and direction of the scattered light, enabling access to any arbitrary steering angle. Additionally, our approach successfully overcomes the challenge posed by an inherently high dimensional optimization space. The non-intuitive solutions generated by our algorithm show up to an 86% improvement in the directivity of the steered beam compared to previous ‘forward’ designs, which typically assume constant amplitudes and do not account for experimental artefacts.

In previous experiments we have demonstrated wide phase and reflectance tunability via carrier density and refractive index modulation in gated metasurfaces that employ a semiconducting indium tin oxide (ITO) active layer [1]. Our inverse design approach treats each nanostructured antenna as an individual metal-oxide-semiconductor element, by which phase profiles are generated on a flat surface with the goal of creating arrays suitable for applications in beam-steering devices or focusing metalenses [2]. Furthermore, we use these device geometries for experimental validation of the proposed inverse design approach and discuss the role of near-field coupling between nanoantennas and its effects on the far-field radiation pattern. Finally, we explore the capabilities of our algorithm by applying it to other active metasurface functions such as reconfigurable metalens focusing and simultaneous steering in multiple directions.


11:45 AM EL01.07.06
Perfect Absorption in All-Dielectric Photoconductive Metasurfaces for Fast Optoelectronic Switching Thomas Siday¹, Polina Vabishehevich², Lucy Hale¹, Charles T. Harris², Ting Luk², John L. Reno², Oleg Mitrofanov² and Igal Brener¹; ¹University College London, United Kingdom; ²Center for Integrated Nanotechnologies, United States

Perfect absorption at desired wavelengths enables efficient operation of optoelectronic switches. We develop and
demonstrate an all-dielectric metasurface consisting of a network of electrically connected nanoscale semiconductor resonators with perfect absorption at 800 nm. Our metasurface is designed to support two degenerate magnetic dipole modes with their effective magnetic dipole vectors in and out of the metasurface plane. To enable excitation of the latter mode, which is symmetry-protected from coupling to plane waves at normal incidence, we break the resonator symmetry using simple geometrical perturbations. As a result, two modes can be excited simultaneously, leading to perfect absorption at the wavelength of 800 nm. The broken symmetry design implemented in a thin layer of low-temperature grown GaAs allows us to switch the metasurface between conductive and resistive states with extremely high contrast on the time scale of ~1 ps using an unprecedentedly low level of optical excitation. This capability allows us to make fast and more energy efficient optoelectronic detectors with THz bandwidth.

SESSION EL01.08: Low Dimensional Photonics III
Session Chair: Pieter Kik
Tuesday Afternoon, December 3, 2019
Hynes, Level 1, Room 102

1:30 PM *EL01.08.01
Quasi-2D Plasmons in Optical Coatings—From Emission Engineering to NanoKirigami Nicholas Fang; Massachusetts Institute of Technology, United States

Recently, exciting new physics of plasmonics has inspired a series of key explorations to manipulate, store and control the flow of information and energy at unprecedented dimensions. In this talk I will report our recent efforts on controlling light absorption and emission process in quasi-two dimensional optical coatings. In the first example, we show how the coherent Coulombic interaction between the molecular dipoles within a molecular aggregate can be tuned by surface plasmons in close proximity. We demonstrate experimentally ultrafast quenching of 2D molecular aggregates at picosecond timescale. Our analysis reveals that the metal-mediated dipole-dipole interaction increases the energy dissipation rate by at least five times faster than that predicted by conventional models. Our results can offer novel design pathways to the light-matter interaction in a variety of photon-exciton systems with applications such as high speed visible light communication.

In a second example, I will introduce versatile 3D shape transformations of nanoscale structures by deliberate engineering of the topography-guided stress equilibrium of gold nanostructures. By using the topography-guided stress equilibrium, rich 3D shape transformation such as buckling, rotation, and twisting of nanostructures is precisely achieved, which can be predicted by our mechanical modeling. Benefiting from the nanoscale 3D twisting features, giant optical chirality is achieved in an intuitively designed 3D pinwheel-like structure, in strong contrast to the achiral 2D precursor without nano-kirigami. The demonstrated nano-kirigami, as well as the exotic 3D nanostructures, could be adopted in broad nanofabrication platforms and could open up new possibilities for the exploration of functional micro-/nanophotonic and mechanical devices.

2:00 PM *EL01.08.02
Empowering Bilayer MoS2 by Engineered Plasmonic Nanostructures for Optoelectronic Applications Ta-Jen Yen; NTHU, Taiwan

Recently, extracting hot electrons from plasmonic nanostructures and utilizing them to enhance the optical quantum yield of 2D transition-metal dichalcogenides (TMDs) have been topics of interest in the field of optoelectronic device applications, such as solar cells, light emitting diodes, photodetectors and so on. The coupling of plasmonic nanostructures with nanolayers of TMDs depends on the optical properties of the plasmonic materials, including radiation pattern, resonance strength, and hot electron injection efficiency. Herein, we present three cases of intensifying the light-matter interactions between nano-scale plasmonic structures and a large-scale, transfer-free bilayer MoS2. These methods include 1. unusual quadrupole gap plasmons (QGP) in the tailored nanoantennas, 2. four different morphology-controlled plasmonic nanoparticles, and 3. engineering the bandgap of the bilayer MoS2 with the localized strain from the plasmonic nanostructures. By introducing the plasmonic effects aforementioned into the large-scale, transfer-free bilayer MoS2, our experimental results demonstrate not only excellent optoelectronic response, but also practical applications in hydrogen evolution reaction, photodetection and others.
2:30 PM EL01.08.03
Mid-Infrared Radiative Emission from Bright Hot Plasmons in Graphene Laura Kim1, Seyoon Kim1,2, Pankaj K. Jha1, Victor Brar1,2 and Harry A. Atwater1; 1California Institute of Technology, United States; 2University of Wisconsin–Madison, United States

The decay dynamics of excited carriers in graphene have attracted wide scientific attention, as the gapless Dirac electronic band structure opens up relaxation channels that are not allowed in conventional materials. We report Fermi-level-dependent mid-infrared emission in graphene originating from a previously unobserved decay channel: hot plasmons generated from optically excited carriers. In infrared emission spectroscopy measurements taken under optical excitation with a Ti:Sapphire laser operating at 850 nm with 100-fs pulse duration, we have measured emission for several sample geometries: planar graphene, and non-resonant and resonant gold nanodisks (NDs)-decorated graphene. The Fermi-level dependence of the observed radiation under pulsed laser excitation rules out Planckian light emission mechanisms, and is distinctly different from that observed under CW laser excitation. Our experimental results are consistent with the calculated plasmon emission spectra in photoindverted graphene, which suggest that quasi-equilibrium ‘hot’ carrier distributions in graphene upon ultrafast optical excitation support bright mid-infrared plasmonic excitation. Evidence for bright hot plasmon emission is further supported by a large emission enhancement observed from graphene decorated with gold NDs, which serve as out-coupling scatterers and promote localized plasmon excitation. The spectral flux of spontaneously generated plasmons is found to be several orders of magnitude higher than blackbody emission at a temperature of several thousand Kelvin. In addition, calculations for our experimental conditions indicate that conditions for plasmon gain exist on the sub-100 fs timescale during which stimulated plasmon emission dominates spontaneous plasmon emission. These observations set a framework for exploration of ultrafast and ultrabright mid-infrared stimulated and spontaneous emission processes and bright infrared light sources.

2:45 PM EL01.08.04
Strong Structural Nonlinearity from Plasmonic Nanowire Metamaterials in the Infrared Regime Brian M. Wells1, Anton Bykov2, Giuseppe Marino2,3, Mazhar Nasir2, Anatoly Zayats2 and Viktor Podolskiy4; 1University of Hartford, United States; 2King’s College London, United Kingdom; 3Université Paris Diderot-CNRS, France; 4University of Massachusetts Lowell, United States

Nonlinear optics is essential for information processing, sensing, and optical characterization applications. There are well known strong nonlinear homogeneous materials available at visible frequencies and composite structures that can exhibit a strong nonlinear response already engineered at long-wave-IR frequency ranges, but there are few materials with strong second order nonlinearity that exist within the infrared frequency range. Over the past decade, metamaterials, composites with subwavelength (often, plasmonic) inclusions have emerged as a viable platform for engineering linear optical response. Nonlinear metamaterials, where the structure of the composite used to re-shape local fields and enhance the nonlinear response of the components, have also been proposed.

Recently, we have demonstrated the emergence of structural nonlinearity, where the bulk nonlinear response of the composite results from a nonlinear interaction of nano-shaped light and free-electron plasma in nominally non-second harmonic generation (SHG) active gold. For this work we explore the potential of structural nonlinearity in plasmonic metamaterials for the second harmonic response at infrared frequencies. We demonstrate the emergence of structural response in plasmonic nanowire metamaterials and analyze perspectives of structure-induced plasmonic nonlinearities for the infrared frequency range.

3:00 PM BREAK

SESSION EL01.09: Lasing and Emission Control I
Session Chair: Nicholas Fang
Tuesday Afternoon, December 3, 2019
Hynes, Level 1, Room 102

3:30 PM *EL01.09.01
Eigenmode Engineering of Nanolasers Ren-Min Ma; Peking University, China

Nanolasers generate coherent light at the nanoscale. In the past decade, they have attracted intense interest, because they are more compact, faster and more power-efficient than conventional lasers. The eigenmode of a nanolaser can be engineered in a controllable manner for novel inner laser cavity field and/or emission beam synthesis. Furthermore, ensembles of nanolasers operating in unison can provide a macroscopic response that would not be possible in conventional lasers.

4:00 PM E1.01.09.02
Thermal Emission by Nanoscale Transmission Line Resonators Bowen Yu, Jiayu Li and Sheng Shen; Carnegie Mellon University, United States

Thermal radiation with a narrow-band emission spectrum is of great significance in various applications such as infrared sensing, thermophotovoltaics, radiation cooling, and thermal circuits. Although resonant nanophotonic structures such as metamaterials and nanocavities have been demonstrated to achieve the narrow-band thermal emission, tuning their radiation power toward perfect emission still remains challenging. Here, based on the recently developed quasi-normal mode theory, we prove that thermal emission from nanoscale transmission line resonators can always be controlled by tuning the size and geometry of single resonator and the density of the resonator array. By use of nanoscale transmission line resonators as basic building blocks, we experimentally demonstrate a new type of macroscopic perfect and tunable thermal emitters. The transmission line resonator arrays are fabricated by standard E-beam lithography techniques and subsequent lift-off process. The emissivity of the samples is measured by using a FTIR spectrometer combined with an infrared microscope. Our experimental demonstration in conjunction with the general theoretical framework lays the foundation for designing tunable narrowband thermal emitters with applications in thermal infrared light sources, thermal management, and infrared sensing and imaging.

4:15 PM E1.01.09.03
Continuous-Wave Lasing from Single Quantum Dot integrated with Plasmonic Nanocavity Yu-Hung Hsieh1,2, Kang-Ning Peng2, Bo-Wei Hsu1, Hao-Wu Lin1, Ta-Jen Yen1 and Yu-Jung Lu2,3; 1National Tsing Hua University, Taiwan; 2Academia Sinica, Taiwan; 3National Taiwan University, Taiwan

Lead halide perovskites have recently received considerable attention as promising candidates for laser devices due to excellent material properties such as high optical gain coefficient and low non-radiative recombination rate. However, most of the lead halide perovskite lasers were operated in pulsed mode in order to reduce the thermal loss to achieve population inversion, which requires extra efforts to generate the external pulsed excitation source. Here, we demonstrate a continuous wave lasing from single lead halide perovskite (CsPbBr3) quantum dot integrated with plasmonic nanocavity with undetectable threshold (power density lower than 90 mWcm\(^{-2}\)) and ultra-sharp single mode lasing (linewidth of 1.4 nm) under a cryogenic temperature at 4 K. In our design, a silver nanocube was placed on a gold substrate, with a single CsPbBr3 quantum dot placed in between. By finite-difference time-domain simulation method to calculate the electric field distribution of the designed structure, we theoretically observed a strong localized optical confinement, plasmonic gap mode, formed between the silver nanocube and the gold substrate. The plasmonic gap mode acts as plasmonic nanocavity and contributes a large Purcell enhancement (Purcell factor ~200) which can be determined via time-resolved photoluminescence measurement. In order to avoid quenching effect, a 6 nm Al\(_2\)O\(_3\) spacer was used to separate the quantum dot and the gold substrate, and the silver nanocube was covered by 1 nm Polyvinylpyrrolidone to isolate the emitter. In order to measure the lasing threshold, the temperature dependent light-in-light-out curve was performed and we observed a very small lasing threshold (power density lower than 188 mWcm\(^{-2}\)) at 80 K. This work is the first demonstration of continuous wave lasing from single quantum dot integrated with plasmonic nanocavity. In the end, we will discuss the detail working mechanisms as well as the practical applications.

4:30 PM E1.01.09.04
Disordered Anderson Lasing from Plasmonic-Scattering Assisted Perovskite Microparticles Sangyeon Cho1,2, Andreas C. Liapis2 and Seek-Hyun Yun1; 1Massachusetts Institute of Technology, United States; 2Harvard Medical School and Massachusetts General Hospital, United States

The integration of plasmonic nanoparticles and optical gain materials has opened a new avenue in developing micro- and nano-lasers. Lead halide perovskite is as a promising semiconductor gain material with high optical gain and
solution processability. Here, we describe a technique to integrate plasmonic particles into perovskite-based matrices and demonstrate lasing from various micro-structures. In particular, our results suggest that photonic Anderson localization can be achieved owing to the combination of strong light scattering from the embedded plasmonic particles and high optical gain from perovskite nanocrystals. In this work, we used a spin-cast precipitation of perovskite precursors and metallic particles to produce spherical microshells, which comprises a Ruddlesden-Popper phase CsPb$_2$Br$_5$ matrix incorporating CsPbBr$_3$ nanocrystals and silica-coated silver spheres with a diameter of 100 nm. In a coherent-backscattering experiment, we measured the product of wavenumber and disorder length to be 0.7, satisfying the Ioffe-Regel criterion for strong transverse localization. We observed stable multimode Anderson lasing from the hybrid microparticles under nano-seconds optical pumping at room temperature. The smallest Anderson localized laser we observed has an outer diameter of 1.1 μm and a shell thickness of 210 nm containing about 15 silver particles, with a lasing threshold of 4 mJ/cm$^2$.

4:45 PM EL01.09.05
**Plasmon-Enhanced Up-Conversion Fluorescence at Short-Wave Infrared** Shengnan Huang, Ching-Wei Lin and Angela Belcher; Massachusetts Institute of Technology, United States

Optical imaging owns the privilege of high specificity and high sensitivity due to the spectral multiplexing for *in vivo* applications, but is always hampered by the tissue autofluorescence and scattering. One promising approach to preventing tissue autofluorescence for optical imaging is to use up-conversion fluorphores. However, traditional up-conversion nanoparticles emit in the visible range, where the emission signal is heavily absorbed by the tissue, reducing the signal-to-noise ratio. In this work, we developed an autofluorescence-free imaging probe with plasmon-enhanced up-conversion fluorescence in the short-wave infrared window (850-1700 nm). We find the up-conversion enhancement is more than 125 times compared to the free fluorophores. Thermodynamic studies show that the dependence of up-conversion emission intensity on temperature fits the Arrhenius equation. In addition, the up-conversion emission intensity increases linearly with the excitation power. These results reveal that the observed plasmon-enhanced up-conversion is thermally assisted. Moreover, the tunable width of the working optical window for the up-conversion probe is around 200 nm, providing high flexibility for *in vivo* applications. Finally, we find that in a tissue phantom the signal-to-noise ratio of the plasmon-enhanced up-conversion fluorescence is more than 4 times better than the corresponding down-conversion fluorescence. The above results demonstrate that our plasmon-enhanced up-conversion fluorescent probe is a promising candidate for high-contrast *in vivo* imaging at short-wave infrared.

Session Chair: Mikko Kataja
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

**EL01.10.01**
**Self-Assembled Ordered Three-Phase Au-BaTiO$_3$-ZnO Vertically Aligned Nanocomposites Achieved by a Templating Method** Shikhar Misra$^1$, Leigang Li$^1$, Di Zhang$^1$, Jie Jian$^1$, Zhimin Qi$^1$, Meng Fan$^1$, Hou-Tong Chen$^2$, Xinghang Zhang$^1$ and Haiyan Wang$^{1,1}$; $^1$Purdue University, United States; $^2$Los Alamos National Laboratory, United States

Complex multi-phase nanocomposite designs present a great opportunity for developing next generation integrated photonic and electronic devices. In this presentation, we demonstrate a unique three-phase nanostructure combining a ferroelectric BaTiO$_3$, wide band-gap semiconductor ZnO and plasmonic Au metal towards multifunctionalities. By a novel two-step templated growth, a highly ordered Au-BaTiO$_3$-ZnO nanocomposite in a unique “nanoman”-like form, i.e., self-assembled ZnO nanopillars and Au nanopillars in BaTiO$_3$ matrix, has been realized, and is very different from the random three-phase ones with randomly arranged Au nanoparticles and ZnO nanopillars in BaTiO$_3$ matrix. The ordered three-phase “nanoman”-like structure provides unique functionalities such as obvious hyperbolic dispersion in the visible and near infrared regime enabled by the highly anisotropic nanostructures.
compared to other random structures. Such self-assembled and ordered three-phase nanocomposite is obtained through a combination of Vapor-Liquid-Solid (VLS) and two-phase epitaxy growth mechanisms. The study opens up new possibilities in design, growth and application of multi-phase structures and provides a new approach to engineer the growth of complex nanocomposite systems with an increased control over electron-light-matter interaction at the nanoscale. Finally, in-situ Transmission Electron Microscope (TEM) heating studies is presented to determine the thermal stability of the three-phase nanocomposite.

EL01.10.02
Plasmon Driven Synthesis of Single Core@Shell Nanoparticles Rifat Kamarudheen\textsuperscript{1,2} and Andrea Baldi\textsuperscript{1,2}; \textsuperscript{1}Dutch Institute for Fundamental Energy Research, Netherlands; \textsuperscript{2}Technische Universiteit Eindhoven, Netherlands

Under illumination, noble metal nanoparticles such as Au, Ag and Cu can act as efficient sources of heat thanks to the decay of localized surface plasmon resonances, which are light-driven oscillations of their free electrons.\textsuperscript{1} Such heating effect is confined to the immediate surrounding of the particles and could therefore be used to locally activate chemical reactions with nanoscale spatial resolution.\textsuperscript{2,3} Here, we show how we can activate, control, and spectroscopically follow the growth of different semiconducting shells on individual plasmonic nanoparticles under laser irradiation. We first adapted a literature reported temperature-dependent colloidal synthesis of Au@CeO\textsubscript{2} core@shell nanoparticles in the dark\textsuperscript{4} and then perform the same synthesis at the single particle level at room temperature using plasmonic heating. We show that, under plasmon excitation, we can grow conformal metal oxide shells with growth rates that scale with the nanoparticle surface temperature. Furthermore, the shell growth can be monitored in-situ by tracking the photoluminescence spectra of the plasmonic nanoparticle under irradiation. We also demonstrate that such photothermally-driven synthesis of core@shell nanostructures can be extended to grow other semiconductors such as zinc oxide and zinc sulfide, illustrating the universality of our technique. The use of light as a tool to activate and control chemical reactions at the nanoscale can lead to the synthesis of shape- and size-controlled hierarchical nanostructures which are inaccessible with classical colloidal synthetic methods, with potential applications in nanolithography, catalysis, energy conversion, and photonic devices.

\textsuperscript{1} M.L. Brongersma, N.J. Halas, and P. Nordlander, Nat. Nanotechnol. \textbf{10}, 25 (2015).

EL01.10.03
Programming Plasmonic Superlattices via Monolithic Assembly of Anisotropic Nanoparticles Yuhyeon Jung\textsuperscript{1}, Yahong Chen\textsuperscript{1,2}, Zhi Zhu\textsuperscript{2}, Chaoyong J. Yang\textsuperscript{2}, Wei Sun\textsuperscript{1}, Lingdong Sun\textsuperscript{1} and Chunhua Yan\textsuperscript{1}; \textsuperscript{1}Peking University, China; \textsuperscript{2}Xiamen University, China

Controllable integration of plasmonic nanomaterials is a key foundation towards diverse applications in enhanced spectrosocopies, sensors and electronic devices. Using top-down lithographical methods, including electron-beam or focused-ion beam lithography, could fabricate metallic nanostructure arrays with prescribed shapes, dimensions, and long-range ordering. However, lithography-defined metal nanostructures are usually polycrystalline in nature, which scatters the electrons and lowers the quality of surface plasmonic resonance. Besides, limited by the lithographic resolution, it is still difficult for scaling the edge-to-edge spacing down to sub-5 nm, further hampering the plasmonic coupling strength.

Alternatively, bottom-up assembly that uses chemical interactions to direct the integration of single-crystalline nanoparticles could provide both atomic-smooth nanoparticle boundaries and sub-1 nm edge-to-edge spacings. Both features promote the surface plasmonic resonance and minimize the energy losses at grain boundaries. Particularly for anisotropic nanoparticles, such as nanorods and cuboids, they exhibit coherent electron oscillations perpendicular and parallel to the long axis (i.e. transverse and longitudinal LSPR). By tuning the chemical recognitions, large-scale assembled nanoparticles display different lattice morphologies, periodicities and compositions. To in silico design and selective prepare prescribed superlattice structures from the anisotropic nanoparticles, it further requires controlling the relative sliding and rotation of the nanoparticles. However, limited by the difficulties for precise calculation and modulation of different assembly modes (i.e. head-to-head or side-by-side), it remains challenging to assemble anisotropic nanoparticles into monolithic superlattices with prescribed plasmonic properties over centimeter scale.
We here report a general framework that could in silico design and selectively prepare monolithic superlattices from anisotropic gold nanoparticles. We discover that precisely designed surface patterns could direct both the surface positions and the assembly modes of anisotropic gold nanoparticles. By designing different surface patterns, anisotropic nanoparticles could be selectively assembled into five prescribed modes, including head-to-head and side-by-side conformations. Epitaxial growth further extends the structural programmability into 3D space. The assembled superlattices exhibit wafer-scale uniform orientations, structural parameters, and assembly morphologies. Complex alphabets, numbers, and polygon shapes could also be constructed using the aligned nanoparticles. Because the minimal edge-to-edge spacing is less than 2 nm, we observed strong plasmonic coupling, as evidenced by the dark-field scattering measurements and FDTD simulations. Additionally, we have revealed that the nanogap induced subwavelength “hot-spots” lead to dramatically enhanced signals for SERS and fluorescence within the superlattices. Using the assembled superlattices, we could further construct sensitive diagnostic platforms that sense multiplex disease markers at single-molecule resolution.

**EL01.10.04**

**Fabrication of THz Rectennas with Metamaterial Selective Emitters** Emily Carlson¹, Minsu Oh¹, Dante DeMeo¹, Corey Shemelya², Nicole Pfiester¹,³ and Thomas Vandervelde¹; ¹Tufts University, United States; ²University of Massachusetts Lowell, United States; ³The Ohio State University, United States

In the United States, 68.5% of energy consumed is lost as waste heat or transmission losses [1]. If we could harness even a small portion of that thermal radiation we could heat and electrify millions of American homes. Rectifying antennas, or rectennas, absorb EM radiation and convert it to a DC voltage using an antenna and a rectifying diode. In a rectenna system with an EM source, the signal is converted into electrical AC signal by the antenna array and AC voltage signal is rectified by the rectifying diode to generate DC. Rectennas with conversion efficiencies greater than 80% are achieved both by using high input power at 915 MHz and 2.45 GHz as in [2] and [3], or by harvesting ambient environment RF from 876 MHz to 2.48 GHz using a multi-band stacked RF rectennas [4]. To move rectennas toward the THz range using infrared radiation sources, we consider the broad-band emission from our sources approximated as a blackbody spectrum. However, a full spectrum IR blackbody source requires high frequency antenna materials. Additionally, using broad-band sources introduces challenges such as needing a broad-band antenna response and a broad-band transmission line. To address these concerns, we add a metamaterial selective-emitter to absorb the radiation from the source and emit a narrow range of photons towards the rectenna.

We designed a metal-insulator-metal (MIM) diode made of Al/Al₂O₃/Au, where the top gold metal consists of our antenna array pattern. The MIM diode was simulated in CST and our Al and Al₂O₃ layers are deposited using the AJA 3-gun Sputtering system at Harvard’s Center for Nanoscale Systems’ Nanofabrication Facility. The antenna pattern is rectangular rows of length 5.4 μm and width 1.2 μm separated by 1.2 μm and connected at one end by a 0.5 μm contact bar. To fabricate the antenna array and selective emitter, we are using the Maskless Aligner MLA150 to expose the pattern directly onto photoresist with a 375 nm laser. Using this tool we can write 1 cm² areas in under 10 minutes, which is significantly faster than writing patterns using electron beam lithography. Although the minimum advertised structure size for the MLA150 is one micron, we have successfully achieved sub-micron resolution by using contrast enhancing material to increase resolution and optical proximity correction to reduce corner rounding [5]. Characterization of the full rectenna device is forthcoming, and samples will be characterized by Vector Network Analyzer in the THz range.


**EL01.10.05**

**Design and Fabrication of Bio-Inspired Nanostructures Exhibiting Structural Coloration** Bianca C. Datta and V. Michael Bove; Massachusetts Institute of Technology, United States

Structural color phenomena exhibited by several organisms produce compelling and vibrant visual displays. These
impressive effects result from interference and diffraction of light incident upon multilayer nanostructures, in which color is broadly tuned based on surface structure and geometry. The wings of the *Morpho* butterfly are a well-studied example of a biological system exhibiting structural coloration and a high degree of wide-angle iridescence due to a non-negligible degree of disorder in the photonic nanostructure. Recent work has demonstrated fabrication of artificial, *Morpho*-inspired nanostructures that exhibit coloration via a variety of fabrication techniques, including multi-step deposition, etching, and assembly processes. However, existing work has largely focused only on replication of specific structures found in nature, with few methods incorporating both color replication and the role of disorder on effects like iridescence. Furthermore, many of the processes used to produce these structures are elaborate or time-consuming. Here we explore methods for generating structures to create desired effects, while proposing new approaches for designing structurally-colored surfaces that are physically producible with rapid prototyping.

We propose methodologies for combined design, simulation, and material fabrication to generate color through new structural surfaces that replicate functional properties of natural systems. We depict a design methodology based around computational inverse design for the formulation of nanostructures exhibiting structural coloration. We furthermore depict example design constraints and study convergence with respect to the design trade space. We use simulation to determine optical properties (such as reflectance, and spectral response) of potential photonic surface structures, and compare different simulation methods on the basis of accuracy, as well as computational complexity and speed.

Such intricate biological systems require advanced fabrication techniques, and replication of nanoscale features of this complexity has been difficult. Thus, our designs are constrained for realizable fabrication using a multitude of processing methods, including direct laser writing techniques such as two-photon polymerization. Such techniques provide amenable platforms for rapid prototyping of simulated optimized structures to test for practical fabrication and implementation that provide a cost- and time-effective alternative to traditional lithographic methods. We then evaluate optical properties such as spectral response, diffraction, and reflectance of fabricated photonic structures. Successful samples will passively produce robust, visible colors with wide angle viewability, and surfaces will be iteratively designed towards the goal of specifically tuned color outputs.

When combined with the design and optimization process presented here, these methods allow for the use of the *Morpho* structure as a baseline for iteration, both to incorporate tailored disorder, and to produce structures with functionality beyond existing systems. In doing so, we present a versatile approach to bio-inspired materials design and provide a platform with applications ranging from light harvesting and steering, to chemical sensing, high performance displays, responsive products and architecture. We aim to compare our simulations to fabricated structures using optical microscopy, scanning electron microscopy, and angular spectrometry to test for quantitative performance. These evaluated and characterized structures could eventually be adapted to roll to roll or imprint-based systems for scale-up and manufacturing on a commercial scale.

**EL01.10.06 Metals and Dielectrics for Transient Photonics**

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Materials that exhibit tunable photonic responses have found widespread application in displays, lasers, sensors, and other optical sources. The combination of inherent material properties and nanostructuring gives fine control of optical transmission, absorption, and reflection in terms of peak wavelengths and intensities. We fabricate thin film and nanostructured designs that apply the transient optical responses of Mg and MgO to produce display pixels that exhibit a color change in response to the chemical reaction between these materials and water [1]. This permanent reaction holds promise for use in data encryption and anticounterfeiting. Color pixels fabricated through both metal-insulator-metal Mg/MgO thin film and Mg nanorod array designs allow for transmission signals corresponding to any color within the sRGB gamut. FDTD simulations are used to verify the accuracy of experimental spectral data and offer new insight into future designs that incorporate both stable and transient elements using spectroscopic ellipsometry data. In order to determine the effects of temperature and deposition method on the transient nature of the optical response, we investigate the etching properties of Mg thin films and nanostructures. Variation of temperature between 10 and 80 °C allows for the tunability of distinct hues, besides the modification of the rate at which color changes for additional device control based on the desired application. Mg and MgO are low cost, earth-abundant, and environmentally friendly materials; and, in turn, ideal candidates for optical components in industrial-
scale devices. Research into their use in conjunction with other metals (e.g. Al, Ag, and Au) opens up a new opportunity for color pixels than can be tuned between multiple signals set through nanostructured geometry, as will be presented.


EL01.10.07

**Additive Manufacturing of Nano-Architected Titanium Dioxide for 3D Dielectric Photonic Crystals**

Andrew Vyatskikh, Ryan C. Ng, Bryce Edwards, Ryan M. Briggs and Julia R. Greer; California Institute of Technology, United States

Probing 3D dielectric photonic crystals in the visible and in the infrared range typically requires fabricating complex 3D architectures with sub-micron features out of low absorption, high refractive index materials. Nano-architecting transparent high refractive index materials in 3D is technically challenging and requires complex experimental procedures, including stacking of individually fabricated 2D layers or double-inversion of a 3D polymer template. We developed a template-free additive manufacturing (AM) process that is capable of producing complex 3D architectures with sub-micron features out of titanium dioxide (TiO₂). We synthesize a hybrid organic-inorganic precursor and use it to formulate a pre-ceramic photoresist that is shaped into a designed 3D structure using two-photon lithography (TPL). This architecture is then pyrolyzed in air at 900°C, which yields a replica of the structure with 70% smaller dimensions. Energy-Dispersive Spectroscopy (EDS) and Raman spectroscopy reveal such processed material to be predominantly rutile titania.

We fabricated titania woodpile structures with a 1.5 μm lateral period that are comprised of 560 nm x 640 nm beams. Transmission Electron Microscopy (TEM) reveals that the microstructure of individual beams is nanocrystalline, with a 110 nm mean grain size and <1% porosity. Fourier Transform Infrared (FTIR) spectroscopy shows a high reflectance and a low transmittance peaks centered at 2.9 μm, which agrees with the position of a full photonic bandgap predicted by Plane Wave Expansion (PWE) simulations. This titania AM process offers a promising pathway to fabricate complex 3D nano-architectures out of high-index materials for 3D dielectric photonic crystals in the visible and the infrared.

EL01.10.08

**Graphene Oxide Si Field Effect Phototransistors with Embedded Nanoscale Vacuum Channel**

Siwapon Srisonphan and Khomsan Ruangwong; Kasetsart University, Thailand

This work presents a hybrid photodetection platform that combines the 2D material graphene, placed on top of well-defined SiO₂/Si nanoscale etched trench structures with simple and cost-effective fabrication processes. The hybrid nanoelectronic devices are consisting of a graphene/Si (Gr/Si) heterojunction in conjunction with graphene/SiO₂/Si (GrOS) field effect structure. Additionally, the suspended graphene naturally placed between two device structure (Graphene/Si and Graphene/SiO₂/Si) enable the nanoscale vacuum electronics formation between two devices, allowing the photoelectron transport and interacting with each other in the quantum regime leading to exceptional characteristics.

In hybrid GrOS based on p-Si substrate, the photo-excited electrons are separated in Si and subsequently transferred to the SiO₂/Si interface to combine with the intrinsic two-dimensional electron gas (2DEG) confined in a quantum well. This will significantly increase the amount of 2DEG. Therefore, the localized 2DEG causes two important phenomena: (1) increasing the localized electric field, leading to carrier multiplication generation in confined 2DEG channels and thus amplifying the photocurrent in the devices and (2) reducing the potential barrier height via strong coulombic repulsion at the edge of the Si, enabling electron emission through the air to complete the electrical current circulation as similar to nanoscale vacuum electronics. The hybrid photodetector device exhibits ballistic transport of photoexcited hot carriers with carrier multiplication gain resulting in high quantum efficiency for photodetection characteristic. Two-dimensional (2D) hybrid nanoelectronic devices based on p-Si and n-Si provide fully and finely tunable sensitivity up to 1.2 and 0.45 A/W, respectively, corresponding to external quantum efficiencies (EQE) of 235% (~350% internal quantum efficiencies (IQE)) and 88% EQE (or ~132% EQE), respectively. The multiplication gain in the proposed hybrid device originates from the impact ionization initiated by photoinduced carrier injection into the self-induced localized electric field (up to ~10⁶ V/cm) distributed in a 2DEG region in Si. The tunable photocurrent was rising with three half-power voltage dependence as a supplied voltage which corresponds to the Child–Langmuir (CL) space charge limited current as electron transport in a vacuum.
Thus, the result suggests that the overall carrier transport associated with the electron emission process from the 2DEG is confined in an inversion layer of the GrOS field-effect structure, allowing the ballistic transport of photoelectrons through a nanoscale vacuum (air) channel within the mean free path distance (<100 nm) to be collected by the graphene electrode.

The ON/OFF ratios of proposed device is in the range of $\sim 10^2$–$10^5$. The hybrid GrOS-based p-Si photodetection has fully tunable responsivity and efficiency that is suitable for imaging applications requiring bright condition adjustments. Therefore, the proposed hybrid photodetection platform is architecturally Si and CMOS-compatible and thus highly promising for ultrafast, low-power, and tunable optoelectronic applications.

**EL01.10.09**

**Electrochemical Growth of InAs Nanoparticle Arrays at Room Temperature—Towards Inexpensive Manufacturing of Optoelectronic Devices**

Marco Valenti, Yorick Blei, Andrea Cordaro, Stefan Tabernig, Albert Polman, Esther Alarcon-Llado and Mark Aarts; AMOLF, Netherlands

III-V nanostructures have shown novel exciting (opto)electronic properties, making them interesting for a wide range of disciplines ranging from bioengineering to quantum information technology and energy conversion. In particular, their optical properties are not only tuned by chemical composition (e.g., in ternary compounds), but also by their size, shape and collective arrangement (e.g., quantum confinement, Mie resonances, collective optical resonances). However, their manufacturing suffers from expensive techniques due extreme operational conditions (e.g., high temperatures and ultra-high vacuum) and has restricted choice on substrate materials.

In this work we explore the combination of electrochemical deposition and soft conformal imprint lithography (SCIL) to grow InAs nanostructure arrays on diverse substrates, including silicon and transparent ITO. We have electrodeposited arsenic from a liquid electrolyte at room temperature onto patterned indium droplets, which spontaneously reacts into InAs. Raman microscopy characterization shows the high crystal quality of the grown InAs nanoparticles by analyzing the lineshape of the longitudinal optical mode. We explain the growth of highly crystalline InAs nanoparticles by a 3D diffusion-reaction model and facile strain release provided by the confined nature of the initial indium particle. We explore the nanophotonic properties of the fabricated InAs nanoparticle arrays, with particular focus on light scattering. By tuning the size and pitch distances we demonstrate the potential of the presented methodology to manipulate the reflection, transmission, absorption and diffraction of light.

While this work represents the first demonstration of crystalline III-V nanostructure growth on a transparent conducting substrate (ITO), combining SCIL and electrochemistry is a promising high-throughput nanofabrication methodology towards inexpensive III-V nanopatterns, with the potential of bringing emerging all dielectric III-V designs to the market.

**EL01.10.10**

**Direct Laser Writing of Polymeric Microcavity with Graphene Oxide**

Cleber Mendonca¹, Nathalia Tomazio¹, Kelly Tasso¹ and Miguel Andres²; ¹University of Sao Paulo, Brazil; ²University of Valencia, Spain

Whispering gallery mode microcavities stand out due to their unique features, such as narrow spectral linewidth, small modal volume and high power density, making them interesting for several applications in photonics. Microcavities made of polymeric materials offer additional advantages, such as the ease of processing and the flexibility for incorporating dopants that bring functionality to the structure. In this direction, femtosecond laser induced two-photon polymerization has proven to be a powerful tool for the microfabrication of 3D polymeric structures. In this technique, spatial confinement of the polymerization is achieved by the nonlinear nature of the two-photon absorption process.

In this work, whispering gallery mode microcavities containing graphene oxide are fabricated via two-photon polymerization on an acrylic-based resin. The produced structure exhibits good structural quality and smooth sidewall surfaces (undoped cavity Q-factor of $1\times10^4$ @ 1550 nm). Raman spectroscopy confirms the presence of graphene oxide in the doped structure. The microresonator modes were characterized by a coupling setup based on evanescent field from a tapered optical fiber, which uses a broadband source centered at 1530 nm as excitation. Light is coupled into the resonator using a 2 µm diameter tapered fiber in the overcoupling regime and the transmitted light is guided to an optical spectral analyzer. The transmitted spectrum exhibits sharp resonances with a free spectral range of 9.3 nm, which is in agreement with the expected value given the structure geometry and index of refraction. Interestingly, we have observed a substantial decrease in the number of modes in the transmission
spectrum for the graphene oxide doped microcavity in comparison to the undoped one, which we believe may be related to some thermal processes since saturable absorption of graphene oxide, whose saturation intensity is on the order of 500 MW/cm², is not expected to occur for the excitation level used here. Therefore, we have been able to demonstrate the use of two-photon polymerization in the fabrication of high performance optical microcavities doped with graphene oxide, which can be exploited for further developments in high performance optical microdevices.

EL01.10.11
Analog Computation Modeling of Memristive Synapse Crossbar for Deep Neural Networks Chanyeol Choi, Jaekang Song, Jaeyong Lee, Beomseok Kang, Subeen Pang, Peng Lin and Jeehwan Kim; Massachusetts Institute of Technology, United States

A memristor-based crossbar is one of promising candidates for in-memory computing since it features nanosecond switching speed, extremely small cell size, low energy consumption for matrix-vector multiplication and weight update, capability of both storage and computing, three-dimensionality, and many analog weight update steps. Although there have been intensive studies on the development of a large-scale memristor crossbar to implement neuromorphic hardware system for deep neural networks, only limited approaches, such as inference task, were suggested due to device and cycle variations and nonlinear/step-limited weight update properties. To handle those issues, a 1T1R (1-transistor/1-memristor) with a closed-loop or spike-based count methods have been used to possess more control on linear weight update. However, to fully exploit memristor-based crossbar in-memory computing without above temporal solutions, it essentially requires (1) linear/symmetric conductance change, (2) multiple-level conductance steps, (3) less spatial and temporal variations for weight values with more analog components involved.

Here, we developed a simulator which estimates the energy consumption and accuracy of inference/online training in multi-crossbar peripheral system to provide an insight on required specifications of memristor device. By introducing analog components, overheads from ADC/DAC are minimized. Also, we partitioned two types of crossbars for fully-functioning in-memory computing: (1) morphable crossbar for computing, (2) memory crossbar for memorizing values used for backpropagation. With our recommended device parameters as guideline, we achieved 97% and 81% accuracy on MNIST and CIFAR-10 datasets, respectively. Also, it performed approximately X 30 and X 12 better than RTX 6000 and TPU in energy savings.

EL01.10.12
Ultrafast Photophysics Dynamics in Phase Transition VO2 Thin Films Pan P. Adhikari1, Shikhar Misra2, Kanishka Kobbekaduwa1, Exian Liu1, Haiyan Wang2 and Jianbo Gao1; 1Clemson University, United States; 2Purdue University, United States

Transition metal oxides are of great research interest over the past decades because of dramatic changes in optical and electrical properties throughout the phase transition processes, which have potential applications in ultrafast transistors, ultrafast electrical switches, gas sensors and thermochromic smart windows. In particular, vanadium dioxide, VO2 is one of the scientifically fascinating and technologically promising transition metal oxides depicting a reversible first-order semiconductor to metal phase transition (SMT) at critical temperature Tc = 68°C (341 K) which is much higher than the ambient room temperature. However, carrier transport mechanism in ultrafast timescale and the effects of dopants on it has yet to be clearly understood.

In this talk, we fabricated VO2 thin films, VO2 doped with Au, and Pt nanoparticles by pulsed laser deposition (PLD). Integrated VO2 films with ultrafast photoconductor device structure, resulted in a sub-40 picosecond response time, we studied the carrier photo-physics dynamics such as carrier photogeneration, recombination, transport, trapping, and de-trapping. In addition to investigate the temperature dependent transport dynamics resulted from the phase transition, we revealed the novel effect of Au and Pt nanoparticles doping. These fundamental understanding paves the pathway to functionalize the VO2, leading to designing nanoelectronics devices.

EL01.10.13
A Three-Dimensional SERS Substrate Fabricated by a Facile Transfer Printing of a Carboxylic-Acid-Functionalized Graphitic Nano-Layer Designed for Protein Analysis Hyung Joon Park and Yeon Sik Jung; KAIST, Korea (the Republic of)
Proteins consisting of one or more polypeptides play vital functional and structural roles in human body. To be used in research involving early diagnosis, drug delivery and clinic therapy, determining structure and concentration of these proteins are extremely important. To date, conventional analysis tools including enzyme-linked immunosorbsent assay (ELISA), X-ray, nuclear magnetic resonance (NMR) and cryogenic electron microscopy (cryo-EM) have contributed significantly to the development of protein research. However, such tools require complex and costly sample preparation procedures as well as skilled experts to analyze the measurement results. SERS (Surface Enhanced Raman Spectroscopy) is considered as a promising alternative for such measurement methods. Raman spectra directly measured from molecular vibrations can provide crucial information on proteins’ conformation and concentration with minimal efforts compared to conventional analysis. However, obtaining reproducible and distinguishable Raman spectra is challenging due to proteins’ extremely small Raman cross section.

To overcome such limitations, and perform conformational studies and quantitative analysis of proteins using Raman spectroscopy, we present a 3D SERS substrate coated with a carboxylic-acid-functionalized graphitic nano-layer (SSCG). The fact that SSCG can perform both structural analysis and concentration determination in a single measurement is a unique advantage over conventional analysis methods and other SERS research reported thus far. SSCG features stacking of gold nanowire sheets, which form 3D nanostructures. Fine and dense gold nanowire arrays generate strong local E-fields, and enable to obtain characteristic Raman spectra of proteins to analyze conformational features. Furthermore, a carboxylic-acid-functionalized graphitic nano-layer is coated on top of the 3D SERS substrate, and used as an immobilization media by forming a peptide bond with analytes. These functional groups enable the analytes to be dip-coated, completely eliminating the coffee ring effect and obtaining a uniform analytes coating, which leads to the possibility of quantitative analysis.

The proteins used in this study are tau protein and beta-amyloid. Both proteins are associated with Alzheimer’s disease (AD), which is a representative illness causing human dementia. These proteins are present in the body fluids and are well-known candidates for AD biomarkers. Accurate identification and quantification of such biomarkers by SERS will enable early diagnosis of the disease, which is critical in delaying disease progression.

**EL01.10.14**

Gallium Arsenide Nanowires for Selective Light Absorption by Lithography-Free Process Gil Ju Lee¹, Kwangwook Park², Gun Wu Ju¹ and Young Min Song¹; ¹Gwangju Institute of Science and Technology (GIST), Korea (the Republic of); ²Korea Advanced Nano Fab Center, Korea (the Republic of); ³Korea Institute of Science and Technology, Korea (the Republic of)

Over the past few years, semiconductor nanowire arrays have been extensively studied for achieving intriguing optical, mechanical, and electrical features. In recent years, the use of nanowires has expanded from the conventional application fields (*i.e.*, electronics and photonics) to medical application such as artificial photoreceptor. This recently-developed nanowire-based artificial photoreceptors interface with blind retinas to restore the vision inability. Their highly ordered structure is more analogous to the architecture of photoreceptors, which allows for proficient photo-absorption and charge separation that is similar in photon-harvesting electronics such as solar cells and photodetectors. Based on these features, the nanowire-based photoreceptors can overcome the representative limitations of predecessors such as requiring an external power supply and low density. They can generate and carry photocurrent to depolarize neurons without an external power supply, and their high/uniform density of photo-responsive units allows an enhanced spatial resolution. However, the reported nanowire-based photoreceptors have not been optically optimized yet, showing a restricted absorption range (*i.e.*, UV range) and low wavelength selectivity and sensitivity.

Here we introduce the approach to the highly selective and sensitive light absorber, like retina, using highly populated III/V nanowire forests fabricated by lithography-free method. Theoretically analyses reveal the diameter-dependent selective photon absorption is allowed even in dense and disordered configuration. Self-catalyzed growth implements the nanowire forest with the high density (*e.g.*, mean nearest inter-distance = 192.4 nm) and high aspect ratio (*e.g.*, mean aspect ratio = 34.3). Also, the averaged diameter of 94 nm with 49 nm-standard deviations sufficiently covers and decomposes visible spectrum. Finally, we observe a selective light-absorbing behavior of the nanowire forests with three monochromatic colors such as red, green, and blue. Weak correlations between each response such as minimally 0.05 and maximally 0.28 demonstrate that the nanowire forest functions like the retina. This work suggests that the nanowire forests could be applied for next-generation optoelectronics and/or bio-compatible light-sensitive material such as retinal prostheses.
Additive manufacturing via two-photon lithography (TPL) has been demonstrated as an effective method to photochemically reduce metal ions to obtain metal structures. Thus far, only a few metals, such as Au and Ag, can be fabricated by TPL, whereas photochemical reduction (PCR) of other metals, such as Ni, Cu, and Ti, remains out of reach. In this work we demonstrate a localized photochemical reduction AM method that is applicable to metallic systems beyond silver and gold using the photoreductant tungsten(0) arylisocyanide, while investigating its reduction mechanism under two-photon excitation. A recent work by Sattler et al has shown that the excited state of tungsten arylisocyanide exhibits a reduction potential of -2.7 V, which can theoretically reduce a wide variety of metal ion species. In this TPL process, we employ an ultra-short pulsed laser that is tightly focused into a voxel, where the tungsten complex absorbs the two photons simultaneously, donates an electron to the metal ion present in the system and reduces it to a metallic atom. We demonstrate a successful reduction of copper in 2D structures, which are characterized by energy dispersive spectroscopy (EDS) to show a uniform distribution of copper. To investigate the reduction mechanism, quenching experiments are performed using time-resolved spectroscopy and an electron transfer rate of 2x10^9 M^-1 s^-1 is determined, which suggests a diffusion-limited process. This method enables direct reduction of metal ions to metal structures and potentially provides gateways to develop new metal composites and to fabricate rare non-native metals for various applications in microelectronics, photonics, medical implants, and microelectro-mechanical systems.

Transparent Conductive Oxides (TCOs) are appealing plasmonic material candidates due to their transparency, refractory character, CMOS compatibility and their ability for dynamically tuning their properties through the application of an electric field. An important additional asset of TCOs is that their optoelectronic properties depend strongly on the precise fabrication techniques and conditions. Specifically, adjustment of the target doping, deposition and post-growth processing conditions causes variations in the stoichiometry, crystallinity and donor states. These result in changes to the carrier transport properties and thus enable one to tailor the optoelectronic properties of TCOs towards specific device requirements. Such modifications of TCOs have been achieved through thermal annealing in controlled ambient compositions to increase the carrier mobility and adjust the carrier concentration by inducing activation of donor states and modulation of the oxygen vacancy concentration. However, thermal annealing of thin films suffers from long dwell times and high thermal budget, making the process expensive, cumbersome and unable to be utilized for cases where the characteristics of the substrate must be preserved (i.e. flexible displays or manufactured chips with heat-sensitive components). Excimer Laser Annealing (ELA) has been demonstrated to be able to overcome these limitations and offer an ultra-fast, scalable and low thermal budget post-growth processing technique to enhance the crystallinity of TCOs. ELA operates through the application of a highly localised heating (in space and time) and offers a significantly increased level of control over the processes by varying the pulse length, pulse frequency, pulse number, fluence, wavelength and environmental temperature, pressure and composition.

In this work, we couple the ability of the local environmental to probe the defect composition with the advantages of laser processing, via ELA of room-temperature sputtered Indium Tin Oxide (ITO), Aluminium-doped Zinc Oxide (AZO), Gallium-doped Oxide (GZO) and Fluorine-doped Tin Oxide (FTO) thin films within a UV-transparent pressurised cell where we can finely control the ambient composition and pressure of the contained gasses. Through the use of a range of reactive gasses which are: oxidising (O_2), reducing (5% H_2 in N_2) or intermediate (0-100% O_2 in N_2 or Ar), we alter the concentration of oxygen vacancies and activated donors within the lattice after processing and relate these laser-induced compositional modifications to changes in the morphological, structural and optoelectronic properties. Ellipsometry in the IR (1.6-40 microns) enables us to directly probe the free-carrier contributions to the permittivity and thus precisely determine the optoelectronic properties of the as-grown and laser processed films.
We report an ambient-dependent modulation of the plasma energy and damping coefficient with laser fluence and ambient composition after laser processing while preserving the amorphous nature of room temperature sputtered ITO and improving the crystallinity of AZO and GZO. Our results present ‘Reactive Ambient - Excimer Laser Annealing (RAELA)’ as a novel and powerful technique to control the optoelectronic properties of key TCO materials. This allows for the creation of recipes to improve the quality of these alternative material candidates as plasmonic components. Due to the fast and localised nature of RAELA, and the utility of IR ellipsometry, we also present the combination of these two techniques as a useful tool in further material science studies into the, still not fully understood, conduction mechanisms of TCOs.

EL01.10.18

Wedge-Shaped Fabry-Perot Cavities for Continuous Variation of the Photonic Environment  
Alvaro Magdaleno1, Nuria Gordillo1, Michel Frising1, Michael Seitz1, Beatriz H. Juarez2, Jose L. Pau1 and Ferry Prins1;  
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A number of powerful photonic strategies to study the influence of the local density of optical states (LDOS) on the dynamics of light emitters have been developed over the years [1-3]. One of the simplest approaches involves placing the emitters between two reflecting surfaces forming a Fabry-Perot cavity. To vary the LDOS in such a system, the key tuning knob is the cavity length. Typical Fabry-Perot cavities are fabricated as vertical stacks using thin film deposition. However, from a practical point of view, tuning the LDOS in such a vertical Fabry-Perot cavity requires the fabrication of many different geometries [4], thus limiting the ability to efficiently optimize the performance. Obtaining a large range of cavity lengths in a single structure is challenging, though some reports using more complex scanning probe methods have been reported [5-6].

Here, we present a method to produce a wedge-shaped cavity in which the full spectrum of cavity lengths can be obtained [7]. It is fabricated by mechanically clamping together two silver-coated microscope slides using a small spacer on one side. This allows for accurate control over the angle (< 1 degrees) between the two silver surfaces and generates a continuously tunable cavity length along the wedge. The simplicity of this technique provides the quick development of samples which can be analysed with single measurements including the thickness of the cavity as free parameter. This platform allows us to precisely align the cavity mode spectrum with the energy spectrum of the active layer. As a first example, we will present results on the fine-tuning of cavity resonances with excitonic excited states in quantum dot solids, and discuss the influence of the LDOS in modifying the excited state and spatial dynamics of these systems. Second, we will discuss the fine-tuning of strong light-matter coupling between cavity modes and molecular vibrational states [4].

Our simple architecture provides a powerful yet easily implementable strategy for the detailed mapping of LDOS in a variety of materials. This will aid the design of optimized cavity induced photonics.

References:

EL01.10.19

Large-Area Active 2D Metasurfaces Comprised of Magnetic Nanoparticles  
Guinevere Strack1, Yassine Ait-El-Aoud2, Richard M. Osgood2 and Alkim Akyurtlu1;  
1University of Massachusetts Lowell, United States; 2US Army Combat Capabilities Development Command Soldier Center, United States

In this work, we demonstrate the fabrication and characterization of active, switchable metasurfaces comprised of ordered magnetic nanoparticles (MNP). Metasurfaces can be comprised of periodic scattering structures with dimensions smaller than the operating wavelength. The magnetic and optical properties of MNP arrays are dictated by several factors, including composition, particle size, and spacing. Ferromagnetic particles have high permeability (µ>1) and net magnetic dipole moments in the absence of a magnetic field. Nanoparticles below a critical dimension, can exhibit paramagnetic behavior, i.e., a lack of magnetic moment in the absence of an applied field.
Superparamagnetic nanoparticles are similar to paramagnetic nanoparticles, but exhibit a rapid increase in magnetic moment in the presence of an applied field. MNP arrays that exhibit ferromagnetic ordering have novel applications, for example, switchable metasurfaces and magnetically enhanced antenna arrays. In addition, large-area 2-D MNP arrays on flexible substrates can be integrated onto lightweight platforms that enable multifunctional electronics and optics. Finally, large-area fabrication strategies present a path toward technological development or prototyping. Traditional fabrication approaches for nanoparticle (NP) arrays typically require costly equipment and highly trained personnel. Herein, we employ a scalable fabrication approach for MNPs—nanosphere lithography (NSL). First, a hexagonally-packed monolayer of polystyrene spheres (PS; d≤500 nm) is assembled on a flexible substrate, for example, Willow® Glass. Next, e-beam evaporation or sputter deposition is used to coat the PS layer with Co, Ni, or co-deposited Co and Au. The PS layer template is degraded by exposing the sample to high temperature (for example, 600 °C), leaving behind ordered NPs. The size and spacing of the NPs can be controlled by the size of the PS and the thickness of the deposited metallic film. Another approach is to remove the PS layer using solvent, which produces an ordered, quasi-triangular nanoarray. Total integrated diffuse and spectral scattering are measured using a spectrophotometer with an integrated sphere accessory to account for visible and near-IR scattering characteristics of the nanostructured arrays. The samples are also subjected to sensitive magnetometer measurements, (superconducting quantum Interference device (SQUID)) to establish if the MNP arrays exhibit magnetic properties, and if so, the type of magnetism, e.g., ferromagnetic or superparamagnetic. The optical and magnetic properties of MNP arrays with various sizes and shapes, and materials compositions, are compared. Establishing relationships between materials functionalities and MNP structure and composition can present a path toward developing flexible, lightweight electromagnetic devices, such as textile-based antennas, electromagnetic switches, and optical rectification.

EL01.10.20
Self-Assembled Monolayers on Gold Nanoparticles for Orientation Control in Surface Enhanced Raman Spectroscopy

Stephen F. Bartolucci1, John Burpo2 and Joshua A. Maurer1; 1U.S. Army CCDC-AC, United States; 2United States Military Academy, United States

Certain metallic nanoparticles display localized surface plasmon resonance (LSPR) when interacting with light. In this study, we synthesize gold nanoparticles with a variety of shapes and sizes, such as spheres, stars and other shapes that display strong LSPR. These particles are then functionalized with self-assembled monolayers for orientation-controlled surface enhanced Raman spectroscopy (SERS). Various SAM molecules with different end groups are used in order to tailor the interaction with molecules of interest for detection using SERS. End groups with partial positive, negative and zwitterionic charges have been attached to the gold nanoparticles and characterized with zeta potential and scanning probe microscopy. Improved proximity and orientation control between the nanoparticle and the molecules being detected could lead to improved SERS response.

EL01.10.21
Chiral Lattice Plasmon Generation from Three-Dimensionally Chiral Helicoid Gold Nanoparticles

Ryeong Myeong Kim, Hyo-Yong Ahn, Hye-Eun Lee, Yoon-Young Lee and Ki Tae Nam; Seoul National University, Korea (the Republic of)

Many researches about plasmonic materials with chirality has been carried out due to their intensive light-manipulating ability1. However, synthesis of plasmonic nanoparticles have difficulties in delicate structure-making. In an effort to solve the problems, we focus on nature materials which have delicate chiral nanostructure and their ability to transfer properties from starting organic material to inorganic material, and vice versa2. Previously, we presented a novel fabrication method for gold helicoid nanoparticles by peptide-assisted method3,4,5 which transfer intrinsic chirality of organic material (peptide) to inorganic achiral gold nanoparticle to manage their morphology and chirality. The synthesized gold helicoid nanoparticles had fine chiral nanostructure in nanoscale level. Based on this structure, they exhibit strong optical activity with Kuhn’s dissymmetry factor 0.2 in visible range under CPL(circularly polarized light). This intense optical activity also can be seen in polarization-sensitive color modulation in far-field transmission of randomly dispersed solution. In an extension of our newly developed synthesis strategy, now, we are doing research about coupling behavior from periodically arrayed Helicoid gold nanoparticles to see enhanced optical properties and apply our nanoparticles to appropriate field. Assembled chiral nanoparticles show collective resonance behavior and strong CD signal which called chiral lattice plasmon resonance. Also, We confirmed their resonance is tunable upon incidence angle of light and periodicity of array. We expect this strategy and template can be new break-through to colloidal chiral nanoparticles for being applied in
various field such as, chiral sensing, wave plate, etc.

References

EL01.10.22
Coherent Energy Transfer in an Asymmetric Colloidal Nanostructures Max J. Schnepf1,2, Fabian R. Goßler1,2 and Tobias A. König1,2; 1Leibniz-Institute for Polymer Research, Germany; 2TU Dresden, Germany

We present a film-coupled colloidal building-block, comprising of a plasmonic core surrounded by a dielectric shell containing a fluorophore emitter. Due to the small mode volume and the strong loss rate, fluorescent lifetime of the emitter is significantly reduced and the emission rate is enhanced while the energy of the emitted photons remains unaffected.[1] We systematically study the energy transfer mechanism on the single particle level by employing electron microscopy, scattering spectroscopy, fluorescence life-time imaging (FLIM) and time-correlated single photon counting on the same cavity.[2] Moving from single cavities towards periodically arranged gain and loss materials with periodicities close the optical wavelength range, unique properties result from the energetic coupling of those building blocks. In order to investigate the arising properties on a large scale, we fabricated novel quantum dot lattices and coupled them to periodic plasmonic nanostructures using self-assembly of colloidal particles as fabrication method.[2] By combination of the two lattices with different overlap and at different angles, energy transfer of the coupled structures can be studied comprehensively. This will help to fabricate large scale structures featuring optical band gap structures for unique light matter interactions.


Acknowledgement: This project was financially supported by the Volkswagen Foundation through a Freigeist Fellowship to Tobias A.F. König. The authors acknowledge the Deutsche Forschungsgemeinschaft (DFG) within the Cluster of Excellence ‘Center for Advancing Electronics Dresden’ (cfaed) for financial support.

EL01.10.23
Active and Passive Plasmonic Colloid-to-Film-Coupled Cavities for Tailored Light−Matter Interactions Fabian R. Goßler1,2 and Tobias A. König1,2; 1Leibniz-Institut für Polymerforschung Dresden e.V., Germany; 2Technische Universität Dresden, Germany

For large-scale optical metasurfaces, tailored active and passive subwavelength building blocks are required to modulate the refractive index.[1] Here, we introduce a colloid-to-film-coupled nanocavity whose refractive index can be tailored by various materials, shapes, and cavity volumes. With this colloidal nanocavity setup, the refractive index can be adjusted over a wide visible wavelength range. For many nanophotonic applications, specific values for the extinction coefficient are crucial to achieve optical loss and gain. Recently, we employed bottom-up self-assembly techniques to sandwich optically active ternary metalchalcogenides between a metallic mirror and plasmonic colloids. The spectral overlap between the cavity resonance and the broadband emitter makes it possible to study the tunable radiative properties statistically. For flat cavity geometries of silver nanocubes with sub-10 nm metallic gap, we found a fluorescence enhancement factor beyond 1000 for 100 cavities and a 112 meV Rabi splitting.[2] In addition, we used gold spheres to extend the refractive index range.


EL01.10.24
Metamaterial Device Quality VO2 Thin Films Fabricated by Pulsed Laser Deposition Devanshi Bhardwaj,
Vanadium oxides are the most interesting materials because of its varying oxidation states between V$^{2+}$ and V$^{5+}$, out of which, the most studied compounds being V$_2$O$_5$ and VO$_2$. VO$_2$ has an interesting semiconducting to metal transition (SMT) property where it changes its phase from low-temperature insulating state to high-temperature (T>68°C) metallic state [1]. Because of this, VO$_2$ is explored in the field of the metamaterial. Earlier in our group, tuneable metamaterial has been demonstrated on the VO$_2$ thin films fabricated by UNSPACM [2]. The roughness of the film was found to be ~2.1 nm, thereby making the film inappropriate for metamaterial applications. Thus, the aim was to reduce the roughness of the thin film with a single step synthesis process so that it can be employed as an efficient metamaterial. Pulsed laser deposition (PLD) has been used to fabricate vanadium oxide thin films for several applications. This method has several advantages including easily controllable film composition by deposition parameters, controlled stoichiometry of the target material in the films deposited on the substrate and epitaxial growth of thin films.

We report the synthesis of vanadium oxide thin films by PLD under different parameter conditions on Si/SiO$_2$ substrate using V$_2$O$_5$ target. The microstructure and crystal symmetry of the deposited films were studied with X-ray diffraction, scanning electron microscopy (SEM), and Raman spectroscopy. The film obtained were phase pure as determined from XRD and Raman data. The film roughness and surface morphology were examined by atomic force microscopy. Roughness was reduced to about 4 nm as compared to other synthesis processes used earlier in the group [2, 3]. SMT was studied by I-V measurements on different films where 3-4 orders of resistance change were observed for the best condition. Thus, we were able to successfully synthesize VO$_2$ thin films with reduced roughness making it suitable for metamaterial applications.

References:

EL01.10.25
Hybrid IR Phototransistor with 2D and 0D Nanomaterials Anindita Sahoo$^{1,2}$, Peter Reiss$^{3,2}$, Etienne Quesnel$^{1,2}$, Johan Rothman$^{1,2}$, Eric De Borniol$^{1,2}$, Patrick Demars$^{1,2}$ and Bérangère Hyot$^{1,2}$; 1CEA, LETI, MINATEC Campus, France; 2Univ. Grenoble Alpes, France; 3CEA, IRIG, France

There is a growing demand for IR detectors in the application fields such as building, thermal management or night assistance car driving. To overcome the limitations in sensitivity and cost of existing systems, alternative device architectures and technologies are needed which better match the market requirements in terms of cost/performance ratio in particular. With that respect, graphene has already been established as an interesting 2D material which can operate as a photodetector in a vast range of wavelength covering from ultraviolet to far-infrared and THz regime. However, low light absorption and absence of gain mechanism limit the responsivity of graphene photodetector. Introducing hybrid phototransistor with highly efficient light absorbing 0D quantum dots and 2D materials, opens up the possibility to transfer the photogenerated carriers from 0D materials into the high mobility 2D channel, which dramatically increases the responsivity and gain of the photodetector. In the IR range, this type of low dimensional phototransistor based on graphene/PbS QD hybrid was first proposed in literature in 2012 [1, 2] till the demonstration in 2017 [3] of a high-resolution broadband image sensor sensitive to ultraviolet, visible and infrared light (300–2000 nm).

In this study, the potential of similar phototransistors has been revisited and their underlying photodetection mechanisms were gradually investigated. We initially studied CVD-grown single layer graphene as a phototransistor device. In the NIR region, our device based on a low-doped Si substrate showed a responsivity of about 100 A/W, which is 10$^7$ orders of magnitude higher [4] than graphene phototransistor on conventional SiO$_2$/highly-doped Si substrate [5, 6]. We also observed an unconventional hysteresis in the transfer characteristics of graphene associated with the induced electric field at the interface of SiO$_2$ and low-doped Si substrate. In a second step, we synthesized...
the colloidal QDs absorbing in the NIR region and developed a layer-by-layer dip coating with simultaneous ligand exchange procedure in order to deposit homogeneous PbS QD layers on graphene sheet leading to a well fabricated hybrid phototransistor. The above mentioned hysteresis persists even after the dip coating of graphene with PbS QD layers. However, in the high absorbing IR range of the QDs, the effect of low-doped Si substrate on photoresponse is somehow screened and the measured photoresponsivity of our hybrid devices matches well with the reported one on graphene/PbS QD hybrids with highly doped Si substrate \[2\]. We achieved a significantly high responsivity of 10^5 A/W and a photoconductive gain of about 10^8 at 940 nm with irradiation power of 6.4 µW/cm^2.


EL01.10.26
Enhancement of Photosensing Characteristics for Indium Gallium Zinc Oxide Based Visible Light Phototransistor via Polydimethylsiloxane Residues

Kyungho Park, Jin Hyeok Lee, Jusung Chung, Dongwoo Kim and Hyun Jae Kim; Yonsei University, Korea (the Republic of)

Visible light communication is an emerging area for use in computer optical buses, light fidelity, etc., due to its low cost and high directionality. Recently, phototransistors have attracted attention because they connect objects and users through light. Amorphous oxide semiconductors (AOSs) based thin film transistors (TFTs) are considered as one of many types of promising electrical devices due to outstanding characteristics, such as high mobility, low-off current, high transparency compared to amorphous silicon-based devices. Despite these versatile advantages, AOSs have a serious limitation as visible light sensors because they cannot absorb visible light due to the wide band gap of around or more than 3 eV. Therefore, AOSs cannot be used for an active channel layer of phototransistors for visible light detection. In order to resolve this issue, researchers have tried to apply the additional absorption layer such as quantum dots, 2D materials, or nanowires on the device. However, these studies have a drawback that requires complicated processes.

In this work, we investigated the defect generation method that improves the light absorption characteristics of indium gallium zinc oxide (IGZO) phototransistors by forming polydimethylsiloxane (PDMS) residues on the gate insulator (GI). To fabricate IGZO phototransistors with PDMS residues, we deposited IGZO channel by radiofrequency (RF) magnetron sputtering after forming PDMS residues on silicon dioxide, used as the GI. Thereafter, IGZO channel was annealed at 300°C in the air for 1 h, and aluminum electrode was deposited by RF magnetron sputtering. In this process, we controlled the amount of PDMS residues by optimizing the degree of hardening of PDMS through thermal curing time. PDMS residues could be easily formed by exfoliating cured-PDMS made by heated PDMS on the GI. PDMS residues increase the surface roughness of the GI. Hence, PDMS residues form interface trap sites between the GI and IGZO channel. Additionally, since PDMS has a boiling point at 200°C and consists of (C2H6OSi)n chains, it becomes decomposed during the 300°C annealing of IGZO channel. Therefore, deep states could be formed by hydrogen diffused into IGZO channel. During this process, deep states were formed by diffused hydrogen into IGZO channel. These trap sites could reduce the energy needed for electrons excitation into the conduction band. Also, there were previous researches that showed these trap sites cause formation of subgap states within the band gap of IGZO, and thus light with wavelengths wider than 420 nm could be absorbed by IGZO. We confirmed formation of trap sites through the transfer characteristics that the subthreshold swing increases from 0.37 to 0.50 V/dec and the turn-on voltage was negatively shifted from -1.02 to -6.81 V by forming interface trap sites and deep states, respectively. IGZO phototransistors with PDMS residues showed the light absorption characteristics with the turn-on voltage change from -6.81 to -23.40 V and Iphoto/Idark of 1.79x10^6 under red light irradiation (wavelength of 635 nm, intensity of 5 mW/mm^2). On the other hand, there was almost no change in IGZO phototransistors without PDMS residues at the same condition. Also, photoresponsivity,
photosensitivity, and detectivity were improved compared with IGZO phototransistors without PDMS residues, from 34.78 to 359.08 A/W, from 7.64x10^3 to 4.63x10^7, from 1.58x10^8 to 6.26x10^11 Jones, respectively, under red light irradiation with intensity of 5 mW/mm^2. As a result, this study achieved improved photosensing characteristics of IGZO phototransistors with PDMS residues for visible light above the wavelengths of 420 nm.

EL01.10.27
Defects and Oxygen Vacancies in BaTiO3 Thin Films Resulting from Changes in Growth Conditions Ashley Wissel, Zachary J. Biegler, Madelyn Hill, Kurt Eyink and Shanee Pacley; Air Force Research Laboratory, United States

BaTiO3 (BTO), a perovskite ferroelectric material, has historically been used in capacitors, memory storage devices, and optical devices. At AFRL, we have investigated BTO for use in waveguides for electro-optic modulators. It has been shown that growth conditions used in epitaxial growth have influenced lattice strain in heteroepitaxial thin films resulting in defects. This study investigated how changes in growth parameters affect the types of defects and oxygen vacancies present in BTO films. Tetragonal BTO thin films (a = 3.9945Å, c = 4.0335Å) were grown on cubic SrTiO3 (STO) substrates (a = 3.9046Å) by pulsed laser deposition (PLD) with an excimer laser of wavelength 248nm. The chamber was evacuated to a base pressure of 10^-9 Torr and a 99.99% pure pressed BTO target was used as the source. STO substrates were chosen because it has been demonstrated that STO can be grown as a buffer layer on Si to help with the integration of BTO into current silicon electronic systems. BTO films were grown at oxygen pressures ranging from 10mTorr – 300mTorr, laser energies from 200mJ – 350mJ, and substrate temperatures ranging from 500 - 800°C. Films were characterized by high resolution X-ray diffraction (HRXRD) coupled 2θ-ω scans and rocking curves to examine film quality and lattice spacing. Results from HRXRD show c-axis interplanar spacings around 4.16Å for strained films and 4.08Å for relaxed films. HRXRD showed that decreasing laser energy during growth increased lattice parameter and improved film quality, as evidenced by higher peak intensities and smaller full width at half maximum. Atomic force microscopy showed root-mean-square surface roughness around 330pm over an area of 2x2µm. X-ray photoelectron spectroscopy was used to verify the stoichiometry of the films. Spectroscopic ellipsometry from 1.5 - 4.5eV was used to determine the relevant optical constants and look for defect bands which give evidence of oxygen vacancies. Lastly, Raman spectroscopy from 100-900cm^-1 was used to identify the types of defects present in the films.

EL01.10.28
Multispectral Infrared-Visible Camouflage Surface Utilizing Disordered Silicon Nanowire Array Injoong Chang1, Taehwan Kim2, Namkyu Lee1, Joon-Soo Lim1, Hyung Mo Bae1, Jihyuk Kim1, Juyeong Nam1 and Hyung Hee Cho1; 1Yonsei University, Korea (the Republic of); 2Samsung Electronics Inc., Korea (the Republic of)

Camouflage patterns are focused on the reduction of visibility by confusing the edge of target and background. The development of thermal observation device (TOD) is greatly threatening the survivability of the weapon systems which emit the infrared radiation at their hot parts where the radiation energy is much higher than surroundings such as tank engines or aircraft nozzles. Therefore, infrared thermal camouflage technology has to be applied to these surfaces for military operations. In addition, these surfaces should have visible camouflage performance, thus requiring a surface with multispectral camouflage capabilities of the infrared and visible wavelength range. Silicon nanowires arrays are well-known metamaterials by their high absorption performance in the visible to infrared range. The nanowire arrays made by metal-assisted etching method have highly disordered structures and the nanowire length is controlled by etching time. In this study, we realize the multispectral camouflage by applying the infrared camouflage pattern with the visible camouflage so as to obscure the interface between the energy emitted from the surrounding background and that from the target by patterning the nanowire array structures. Using the CCD Camera and IR camera, the silicon nanowire surface are captured and it shows that the shorter length nanowire array is dark color in visible range and low apparent temperature (low emissive energy) in infrared range, however, the longer length nanowire array is dark yellow color in visible range and high apparent temperature (high emissive energy) in infrared range. We also measure the optical emittance and reflectance of visible and infrared range to analyze the change of color in the visible range and emissive energy of infrared range. It shows that the reflectance in visible range and emittance in the infrared range goes higher with nanowire length longer.

EL01.10.29
A Submicron Perovskite Plexciton Laser Sangyeon Cho1,2, Yi Yang1,1, Marin Soljačić1,1 and Seok-Hyun Yun2,1; 1Massachusetts Institute of Technology, United States; 2Harvard Medical School and Massachusetts General
Surface plasmon polaritons (SPP) with high effective refractive indices offer a new avenue to build sub-wavelength lasers. Here, we present room-temperature plasmonic lasing using CsPbBr$_3$ perovskite crystals on a gold substrate with a 5-nm-thick poly-norepinephine (pNE) dielectric layer. We colloidaly synthesized high-quality CsPbBr$_3$ microcrystals using our recently-developed sonochemical synthesis. The pNE layer was prepared by solution dipping of the gold substrate. The photoluminescence spectra from such structures show distinct double peaks, which indicate strong coupling between electron-hole pairs (excitons) and SPP modes with a vacuum Rabi splitting energy of about 40 meV. Finite-difference time-domain simulation suggests that the SPP hybrid mode is a whispering gallery mode with a Q-factor of 44. The smallest plexciton laser we have observed is 580 nm in width and 270 nm in height, emitting a linewidth of 0.1 nm at 535 nm above the pump threshold at 2 mJ/cm$^2$.

SESSION EL01.11: Plasmonics I
Session Chair: Yu-Jung Lu
Wednesday Morning, December 4, 2019
Hynes, Level 1, Room 102

8:00 AM EL01.11.01
Hybrid Au-NP Dendrimer Plasmonics—Energy and Charge Transfer Systems Rigoberto C. Advincula; Case Western Reserve University, United States

The preparation of new polymers and plasmonic nanomaterials require hierarchical levels of ordering and structuring: from molecular to macroscopic. Au nanoparticle plasmonics phenomena enable demonstration in both localized and propagating plasmons which can be quantified spectroscopically in particles, nanostructures, and thin films. Dendrimers and other hyperbranched polymer systems are of interest for their functionality in catalysis, drug delivery, reactivity, etc. Of high interest are hybrid metal nanoparticle dendrimer functionality in electro-optical applications and photonics. This includes Hybrid NP-dendrimers capable of hierarchical ordering and self-assembly. We highlight the convergent synthesis of a variety of polymer-hybrid dendrimers and their electropolymerizability with electroactive monomer groups. The synthesis of precise dendrons is in the form of modular building blocks for functional dendrimers. Our group has reported a number of these hybrid nanoparticle systems and have reported the step-by-step routes towards structure-property relationships. Energy transfer and charge transfer properties can be observed as well as quenching phenomena. What is also important is the use of surface sensitive spectroscopic and microscopic analytical tools applied rationally to highlight evidence of order and function.

8:15 AM EL01.11.02
Infrared Propagating Electromagnetic Surface Waves Excited by Induction Jonathan Brescia$^1$, Robert E. Peale$^1$, Evan M. Smith$^{2,3}$ and Justin W. Cleary$^2$; $^1$University of Central Florida, United States; $^2$Air Force Research Laboratory, United States; $^3$KBRWyle, United States

Propagating electromagnetic surface waves called surface plasmon polaritons (SPPs) can be excited by free-space beams on corrugated conducting surfaces at resonance angles determined by corrugation period, permittivity, and optical frequency. SPPs are coupled to and co-propagate with surface charges. Electrical isolation of the conducting corrugations blocks charge propagation between them, and excitation resonances of traveling SPPs are absent. However, SPPs can be excited via electric induction if a smooth conducting surface exists below and nearby the insulated corrugations. The dependence of SPP excitation resonances on that separation is investigated here. We find that excitation resonances for traveling SPPs broaden and disappear as the dielectric thickness is increased beyond ~1% of the free-space wavelength. The resonance line shape depends on whether the dielectric SiO$_2$ or TiO$_2$ is used as the separating layer, but this dependence appears uncorrelated with differences in optical constants for SPPs at long-wave infrared frequencies where dispersion is strong.

8:30 AM EL01.11.03
Dynamically-Tunable Plasmonic Devices Based on Phase Transition of Vanadium Dioxide Ruwen Peng$^1$, Yongmin Liu$^2$ and Mu Wang$^1$; $^1$National Laboratory of Solid State Microstructures, Nanjing University, China;
Recently, tunable nanophotonic devices have drawn intense attention with great promise for practical applications. In this work, we have experimentally demonstrated several dynamically-tunable plasmonic devices based on phase transition of vanadium dioxide, which include dynamic plasmonic color generators [1], dynamically switchable polarizers [2], and dynamically tunable bowtie nanoantennas [3]. We have fabricated periodic arrays of silver-nanodisks on a vanadium dioxide film to realize different colors, relying on the excitation of localized and propagating surface plasmons. Based on insulator-metal transition of vanadium dioxide, the plasmonic colors can be actively tuned by varying temperature. This approach of dynamic color generation can easily realize diverse color patterns, which makes it beneficial for display and imaging technology. We have also designed a system consisting of anisotropic plasmonic nanostructures with vanadium dioxide that exhibits distinct reflections subjected to different linearly polarized incidence at room temperature and in the heated state. The composite structure can thus be used to realize a dynamically switchable infrared image, wherein a pattern can be visualized at room temperature, while it disappears above the phase transition temperature. Besides, we have made the dynamically tunable bowtie nanoantennas integrated on a vanadium dioxide thin film. The investigations here can be applied in dynamic digital displays, optical data storage, and imaging sensors.

References:

8:45 AM EL01.11.04
Dipole-Quadruple Coupling in Plasmonic Honeycomb Lattices Ran Li, Marc Bourgeois, Charles Cherqui, Jun Guan, Danqing Wang, Jingtian Hu, Richard Schaller, George Schatz and Teri W. Odom; Northwestern University, United States

In 2D lattices composed of metal nanoparticles (NPs), the localized surface plasmons (LSPs) of metal NPs couple to the Bragg modes to produce surface lattice resonances (SLRs). By exploiting the intrinsic size and material tunability of these LSP modes, we achieved dipole and quadrupole SLRs from visible to near infrared wavelength range. Our work shows that there is a new mode-mixing scheme, which we call hierarchical hybridization occurring in honeycomb lattices of plasmonic NPs. The non-Bravais nature of honeycomb lattice introduces in-plane quadrupole LSPs mixing with the dipole LSPs to create a sharp and strong SLR. Further, by changing the plasmonic material and engineering the plasmonic NP size, we leveraged the out-of-plane quadrupole and in-plane quadrupole LSP response of plasmonic NPs. Two distinct and simultaneously optimized band-edge states were achieved in a single honeycomb lattice. This work highlights the ubiquity of multipolar LSP coupling in non-Bravais plasmonic lattice systems with different plasmonic materials, which has important implications for the band structure engineering of 2D metamaterials.

9:00 AM EL01.11.05
Substrate-Induced Control of Hyperbolic Polaritons Thomas G. Folland1, Alireza Fali2, Samuel T. White1, Mingze He1, Song Liu1, Neda Aghamiri2, James H. Edgar1, Richard F. Haglund1, Josh Caldwell1 and Yohannes Abate2; 1Vanderbilt University, United States; 2University of Georgia, United States; 3Kansas State University, United States

The current state-of-the-art in materials used for infrared (IR) optical components (e.g. lenses, waveplates or prisms) suffers from significant material limitations, exacerbated by the long free-space wavelengths of light in the IR. Leveraging polariton modes such as surface plasmon polaritons (SPPs), surface phonon polaritons (SPhPs) or hyperbolic phonon polaritons (HPhPs) is one route to overcome these limitations. The class of HPhP modes occurring in anisotropic crystalline materials such as hexagonal boron nitride (hBN), are of particular interest. They
can be supported at extremely high wavevectors, and can shown exhibit phenomena such as hyperlensing. Recent studies show that the substrate plays a critical role in controlling the properties of hyperbolic polaritons, and can designed to produce in-plane refraction within hBN heterostructures on phase-changing materials.

In our work we systematically explore the role that the substrate plays in controlling hyperbolic polariton propagation, using a range of scattering-type scanning near-field optical microscopy (s-SNOM) and nano-Fourier transform infrared (nano-FTIR) spectroscopies. We consider propagation on suspended, dielectric and metallic substrates, reducing the thickness-normalized wavevector by up to a factor of 25 simply by changing the substrate. Moreover, by incorporating the imaginary contribution to the dielectric function in lossy materials, the wavevector can be dynamically controlled by small local variations in loss or charge carrier density, while higher-order modes show reduced sensitivity to substrate-induced losses. Finally, we discuss the potential implications for devices including sensors and refractive optics. Sensing HPhP modes out-perform SPhP modes under certain circumstances, and that the choice of substrate is critical for sensing applications. Furthermore, an optimized substrate produces phenomena such as mode sorting within hBN devices. This demonstrates that the choice of substrate choice is critical in determining the properties of propagating HPhP’s, unlike earlier results on localized HPhP resonators.

9:15 AM *EL01.11.06
Emerging Anisotropic 2D Layered Materials for Photonics, Plasmonics and Polaritonics Koray Aydin;
Northwestern University, United States

Two-dimensional layered materials have recently garnered burgeoning amount of interest due to their unique electronic, optical, thermal, mechanical properties emerging at the mono-to-few layer thicknesses. Over the past decade, we have witnessed significant research activity on the area of two-dimensional materials. Most of research has focused on conventional 2D materials such as graphene and 2D TMDCs, having isotropic electronic and optical properties due to their crystal symmetry. Recently, layered materials such as black phosphorus and hexagonal boron nitride investigated for anisotropic crystal structure. In this talk, I will present theoretical investigations on monolayer borophene plasmons at optical frequencies. Borophene has recently expanded the 2D materials family after its successful deposition on silver substrates. We theoretically investigate the plasmonic properties of nanostructured monolayer borophene using full-field electromagnetic simulations and demonstrate that borophene nanoribbon and nanopatch arrays can support localized plasmon resonances at visible and near-infrared wavelengths. Due to its puckered crystal structure and vacancy distribution in hexagonal lattice, borophene exhibits strong anisotropic in-plane properties which makes it an unconventional plasmonic material. In the second part of my talk, I will introduce α-MoO$_3$ as an anisotropic photonic and polaritonic material. α-MoO$_3$ is a layered material that exhibits both in and out-of-the-plane anisotropic polaritonic response at mid-IR wavelengths. We designed and experimentally demonstrated an anisotropic polaritonic absorber and showed that one can couple to all phonon modes and address them individually either using structural tunability or polarization control of incident infrared radiation. I will also discuss our experimental investigations of the birefringent optical properties of α-MoO$_3$ in visible frequencies. By constructing α-MoO$_3$ based Fabry-Perot resonator, we observed strong polarization-dependent tunability of the Fabry-Perot resonance due to different refractive index of MoO$_3$ for different crystal directions. Anisotropic plasmonic, photonic and polaritonic materials provide additional freedom in controlling polarization dependent properties and could find applications in wide range of fields where polarization control plays important role.

9:45 AM BREAK

SESSION EL01.12: Nonlinear Photonic Effects
Session Chair: Igal Brener
Wednesday Morning, December 4, 2019
Hynes, Level 1, Room 102

10:15 AM *EL01.12.01
Third Harmonic Generation in Magnesium Near the Metal-to-Insulator Phase Transition Harald Giessen;
University of Stuttgart, Germany
Harmonic generation in plasmonic systems has gained significant interest over the last few years. While the plasmonic near-field enhancement has been studied in great detail, little attention was paid to the origin of the nonlinear signals which in fact lie in the microscopic nonlinearity of the involved plasmonic metals. In order to predict wavelength-dependent nonlinear processes it is therefore crucial to understand these microscopic nonlinearities. Utilizing an optical parametric oscillator as a tunable broadband light source, we study wavelength-dependent third harmonic generation from metallic thin films made of gold, copper, and magnesium.

We find that the linear properties of the metallic films, that is their absorption, strongly influence the third harmonic generation efficiency. Optical transitions between the different bands lead to a resonant enhancement of the third order susceptibilities. Utilizing hydrogen to switch metallic magnesium to dielectric magnesium hydride [2] we can tune the nonlinearity of thin films and observe the metallic-dielectric phase transition in the linear and nonlinear regime. We find complex relations between the linear transmittance and the radiated third harmonic, which provide new insights into the phase transition. Particularly, the first few seconds after switching this metal-to-insulator phase transition show remarkable nonlinear responses. We suspect that the surface roughness could play a substantial role.

Complimentary measurements of magnesium films that are being hydrogenized and investigated with an in-situ s-SNOM setup [3] and a mid-IR laser that is tuned to the magnesium hydride phonons gives additional information about the relationships between local microscopic structure and optical properties.

Our results might be of great relevance for nonlinear sensing [4] and nonlinear hydrogen detection in the future.

References

10:45 AM *EL01.12.02
High Harmonic Generation with Semiconductor Metasurfaces and Epsilon Near-Zero Materials Igal Brener; Sandia National Laboratories, United States

Metasurfaces created from nonlinear III-V semiconductors and heterostructures used to create resonant optical nonlinearities enable nonlinear optics in a new regime, where many simultaneous nonlinearities lead to harmonics and mixing products of laser beams without the need of phase matching. I will present our latest work on optical mixing and harmonic generation in dielectric metasurfaces made from III-V semiconductors and semiconductor heterostructures.

Similar behavior can be obtained in epsilon near zero materials provided that the mobility of the carriers in the material is high enough; these conditions are met in highly doped CdO where we observe high harmonic generation from the infrared to the ultraviolet, and without the need of any patterning.

11:15 AM EL01.12.03
Transient Second-Order Nonlinear Media Enabled by Hot-Electron Transfer Mohammad Taghinejad¹, Zihao Xu², Kyu-Tae Lee¹, Tianquan Lian² and Wenshan Cai¹; ¹Georgia Institute of Technology, United States; ²Emory University, United States

Second-order optical effects are essential to the on-demand generation of spectral components as well as active control of light via nonlinear processes such as second-harmonic generation (SHG), sum/difference frequency generation, optical rectification, optical parametric amplification, and Pockels effect. These optical processes rely on the interaction of two optical fields through the second-order dielectric susceptibility $\chi^{(2)}$, of optical materials. The
portfolio of $\chi^{(2)}$ media, however, is rather limited as the inversion symmetry in most optical materials inhibits achieving a nonzero $\chi^{(2)}$ response, under the electric dipole approximation. In such materials, the atomic-scale disordered sites at surfaces and interfaces are limited domains where the termination of the bulk-like crystal structure allows for nonlinear light-matter interactions of second-order type, yet in an inefficient manner. Although the enhancement of the weak surface nonlinearity through the utilization of resonant structures has revealed promising potentials, developing symmetry breaking methods are still necessary to activate $\chi^{(2)}$-based nonlinear effects in the bulk of centrosymmetric media. Towards this goal, exerting external strain and applying direct-current electric fields are among the limited proposed approaches for breaking the inversion symmetry and inducing a notable bulk-like $\chi^{(2)}$ susceptibility. However, the current span of the literature lacks optical symmetry-breaking schemes and initial developments in this area are required. In this work, we present a fundamentally new scheme for breaking the crystal inversion symmetry and enabling $\chi^{(2)}$ processes via the generation and transport of hot electrons. The sub-picosecond kinetics of carriers enables the ultrafast conversion of statically passive dielectrics into transient second-order nonlinear media, immediately expanding the portfolio of $\chi^{(2)}$ media beyond the conventional crystals. The induced nonlinearity is accurately tunable using an optical switch that controls the density of generated hot electrons. As an example, we demonstrate that the transient nature of the induced $\chi^{(2)}$ response enables all optical control of the SHG process, proving the feasibility of dynamically tuning second-order light matter interactions through the optical breaking of the inversion symmetry.

11:30 AM EL01.12.04
Tuning Second-Harmonic Generation from Silicon Metasurfaces via Electrical Control Kyu-Tae Lee, Mohammad Taghinejad, Jiahao Yan, Andrew S. Kim, Devin K. Brown and Wenshan Cai; Georgia Institute of Technology, United States

The pursuit of chip-scale and compact data processing capacity in a CMOS-compatible fashion has promoted the investigation of silicon-based photonic platforms for active optical functionalities via the nonlinear light-matter interactions. The use of silicon in integrated photonics, however, is primarily focused on passive photonic components such as waveguides, gratings, and resonators, while the investigation of active silicon photonics is largely limited to the exploration of several specific processes like the free-carrier dispersion and the Raman effect. This restriction mainly stems from the absence of the bulk second-order nonlinear susceptibility, $\chi^{(2)}$, under the electric dipole approximation due to the centrosymmetric nature of the crystal structure of silicon. To address such a limitation, here we demonstrate the enhancement and tunability of field-induced optical nonlinearity of the second-order type in silicon metasurfaces, where strong magnetic Mie resonances are leveraged to intensify the nonlinear interaction of light with silicon at a prescribed spectral range. On top of the strengthened surface SHG from the silicon metasurface, as facilitated by the magnetic Mie effect, introducing an electrical signal to our silicon structure provides an additional route to the frequency-doubling of light via the EFISH process. Our experimental characterizations and numerical modeling reveal that the efficiency of the field-induced frequency doubling peaks in the spectral vicinity of magnetic behavior, substantiating the synergic role of Mie resonances on the nonlinear optical generation from the silicon platform. Our finding reveals a generic route towards the dynamic control of second-order nonlinear processes, such as sum/difference frequency generation, optical rectification, and Pockels effect, in electrically active silicon metasurfaces.

11:45 AM EL01.12.05
Engineered Epsilon-Near-Zero Optical Nonlinearity of Al-Doped Zinc Oxide Thin Films via Atomic Layer Deposition Technique Subhajit Bej1, Sudip Gurung1, Nicholas St. John1, Zhenhuan Yi2 and Ho Wai (Howard) Lee1,2; 1Baylor University, United States; 2Texas A&M University, United States

Strongly enhanced third-order nonlinear optical properties of transparent conducting oxide (TCO) thin films in their epsilon-near-zero (ENZ) region (i.e. the region where the real part of their dielectric permittivity approaches zero), have been reported recently [1-3]. Such giant enhancement can be attributed to the hot electron dynamics resulting from ultrafast laser assisted heating. Upon excitation of leaky ENZ modes, effective nonlinear optical properties of these meta-films can be further boosted. Since the response time of these nonlinear processes can be ~100 fs, the ENZ materials could open distinct functionalities to the path to revolutionary nanoscale nonlinear optics and ultrafast on-chip optical applications.

In this work, we present a method to engineer the nonlinear refraction coefficients ($n_2$) and the nonlinear absorption
coefficients ($\beta$) of Al-doped zinc oxide (AZO) ENZ thin films synthesized by atomic layer deposition (ALD) technique. Nonlinear optical properties of TCO films can be attributed to the free carriers which also contribute to linear absorption of the thin films. Furthermore, third order nonlinear optical signals have cubic dependence on the electric field confined inside the TCO films. Hence, to engineer the nonlinear optical properties, we design the linear absorption and electric field intensity enhancement (FIE) associated with leaky ENZ modes in these AZO nanolayers via control over the ENZ wavelengths and optical losses by ALD deposition parameters such as dopant ratio and the number of macrocycles. The dopant ratio determines the material dispersion and ENZ wavelength whereas the macrocycle regulates the film thickness.

We fabricate AZO films with ENZ wavelengths varying between 1400-1600 nm and their thicknesses ranging from 55 to 216 nm [4]. Nonlinear optical properties of the fabricated films are measured using standard open and close-aperture Z-scan technique using an ultrafast femto-second laser (pulse duration ~70 fs). The peak wavelength ($\lambda_p$) of the fs pulses can be tuned from 1200 to 1600 nm with an optical parametric amplifier unit. Measured $n_2$ and $\beta$ values of the films are evaluated upon fitting the experimental data. Experimental results suggest that nonlinear refraction and nonlinear absorption strengths of these ENZ AZO films can be engineered by controlling the ZnO to Al dopant layer ratios in the deposited AZO films, as well as the film thickness. We also observe an enhancement of the effective nonlinear properties due to excitation of leaky ENZ modes at oblique incidence while illuminating with TM polarized light. Measured values as large as $n_2^{(\text{eff})} \approx 10^{-8}$ mm$^2$/Watt and $\beta_2^{(\text{eff})} \approx -10^{-4}$ mm/Watt are obtained along with approximately an order of magnitude tunability via ALD parameters. Lastly, we present a way to achieve ultrastrong, dispersion-free ENZ nonlinearity which relies on engineering of material dispersion with a multi-layer structure and excitation of a broadband leaky ENZ mode. The giant $n_2$ and $\beta$ values of ALD AZO films in their ENZ region and their controllability will be important for efficient all-optical signal processing.


(This work is supported in part by the Young Faculty Award Program from Defense Advanced Research Projects Agency (grant number N66001-17-1-4047), Robert A. Welch Foundation (Award number: AA-1956-20180324) and the Office of Vice Provost for Research at Baylor University.)
Polymer-based metamaterials provide a lightweight, flexible and low-cost platform exhibiting new optical, thermal, and electrical multi-functionalities that provide structural coloration, visual and/or thermal camouflage, solar and thermal energy harvesting, and personal cooling/heating. We will discuss several examples of new metamaterials with tunable photon, electron and phonon transport properties achieved by either sculpting the internal structure of polymers or using polymers to sculpt the internal structure of inorganic solids or nanoparticle arrays. These include:

(i) composite organic-inorganic films with a varying degree of crystallinity and mesoscale internal structure fabricated via extrusion and solvent casting followed by polymer chain alignment, which exhibit new tunable transparency, haze, thermal conductivity, and dynamical tunability properties,

(ii) new types of composite organic-inorganic polymer-based network metamaterials grown on low-density porous scaffolds to sculpt their internal structure,

(iii) nanoparticle arrays on stretchable polymer substrates, designed for mechanical tuning and switching functionalities.

This work is supported by the US Army Research Office (via the CCDC Soldier Center and the MIT Institute for Soldier Nanotechnologies), Advanced Functional Fabrics of America (AFFOA), MIT International Science and Technology Initiatives (MISTI), and the UNSW-USA Networks of Excellence. The authors thank Dr. Richard M. Osgood III for useful discussions.

Controlling the Instantaneous Polarization State of Femtosecond Optical Pulses Using Dielectric Metasurfaces

Wenqi Zhu, Lu Chen, Henri Lezec and Amit Agrawal; National Institute of Standards and Technology, United States

Metasurfaces are ultra-thin, planar optical elements composed of sub-wavelength nanostructures, which can be engineered to modify the local characterizations of light. Recently, it has been demonstrated that dielectric metasurfaces can be implemented to simultaneously and independently manipulate of the phase and amplitude for a near-infrared femtosecond pulse having over 200 nm ultra-wide bandwidth while maintaining high spectral resolution of 0.3 nm. Extending the applications of dielectric metasurfaces in ultrafast optics holds great potential for applications ranging from fundamental light-matter interactions to ultrafast communications. In general, the electric field of a femtosecond pulse is a vectoral quantity defined by its phase, amplitude, and polarization. Further controlling the instantaneous polarization state of a single optical pulse as a function of time would largely expand the capability and impact of ultrafast optics.

Here, we offer the experimental demonstration of polarization shaping using dielectric metasurfaces to control the temporal polarization state of femtosecond optical pulses. The pulse shaper consists of a Fourier-transform setup with a dielectric metasurface positioned in the focal plane. Rectangular silicon nanopillars are fabricated on a fused-silica substrate, with the dimensions carefully designed to provide the targeted spectral phase for two orthogonal polarizations – for example, a quadratic phase shift for p-polarized component and a constant phase for s-polarized component. The input pulse is linearly polarized and orientated 45° with respect to the nanopillars, providing two equal polarization components. After passage through the metasurface, the shaped output pulse is characterized by direct electric-field reconstruction using spectral phase interferometry. The measured spectral phase matches with the targeted phase function for both polarizations: the time-domain signal reveals a stretched pulse for p-polarization due to the quadratic dispersion and a narrow pulse for s-polarization due to the constant phase shift. By stacking the polarization ellipses along the time axis, a three-dimensional representation of the femtosecond pulse can be reconstructed. Within a single femtosecond pulse duration, the polarization state evolves between different linear and elliptical polarizations with varying degrees of ellipticity.

In summary, we have demonstrated femtosecond polarization pulse shaping by controlling the spectral phase for two orthogonal polarizations using dielectric metasurfaces. With the large bandwidth, high resolution, and easy compatibility offered by the metasurfaces, such an approach opens up new possibilities in the field of ultrafast
science and technology.

2:30 PM BREAK

SESSION EL01.14: Metasurfaces IV
Session Chair: Koray Aydin
Wednesday Afternoon, December 4, 2019
Hynes, Level 1, Room 102

3:30 PM *EL01.14.01
Metaphotonics with 2D and 3D Engineered Optical Materials Andrei Faraon, Philip Camayd-Munoz, Hyonghan Kwon, MohammadSadegh Faraji Dana, Gregory Roberts and Conner Ballew; California Institute of Technology, United States

In the past decade we witnessed the development of optical metasurfaces that enabled diffractive optical elements with new functionalities. However, the number of optical modes in a metasurface is limited, which directly affects the functionality and performance that can be achieved with a single layer metasurface device. In this talk I will present how systems of stacked metasurfaces and fully three-dimensional dielectric structures with more optical modes open up a new optical design space with exciting applications in various imaging modalities, spectrum splitting and other applications.

4:00 PM EL01.14.02
Light Control with Phase-Cancellation Metasurfaces Amr M. Shaltout, Jorik Van de Groep, Yifei Wang and Mark L. Brongersma; Stanford University, United States

The concept of phase-cancellation metasurfaces is introduced which enables the attenuation of specific optical modes using destructive interference. This concept has been utilized to implement a broadband circular polarizer using dielectric metasurfaces. We design and implement a dielectric metasurface which induces a hybrid phase-shift composed of an accumulation phase component and a geometric phase component. The metasurface is composed of anisotropic Silicon based nanorods in which accumulation phase is controlled by the nanorod thicknesses, and geometric phase is controlled by their orientations. Each unit cell is composed of two sub-units which transmit in-phase left-circularly polarized (LCP) optical component, and out-of-phase right-circularly-polarized (RCP) component. RCP is attenuated as a result of destructive interference, and a broadband circular polarizer with high extinction ratio (>13dB) is achieved using a single metasurface layer. The concept of destructive interference using phase-cancellation metasurfaces can be extended to other applications. It can be utilized in dynamic metasurfaces in which high contrast optical switches is achieved by controlling the condition of phase-cancellation to modulate the action of attenuation between ON and OFF.

4:15 PM EL01.14.03
Ultraviolet Metasurfaces for Chiral Sensing and Separation Jack Hu, Michelle Solomon, Mark Lawrence and Jennifer A. Dionne; Stanford University, United States

Chiral light-matter interactions are a potentially efficient and versatile method to resolve enantiomers, improving the efficacy of chiral pharmaceuticals and agrochemicals. However, the chiroptical response of small molecules is weak, thus limiting light based detection and separation schemes. Emerging nanophotonic platforms have been shown to increase the interaction between circularly polarized light (CPL) and chiral molecules through a concentration of the local density of optical chirality, \( C \). We have recently shown that tailoring electric and magnetic Mie resonances in dielectric metasurfaces can locally enhance the magnitude of \( C \) over 100-fold compared to CPL in free space. However, both theoretical and experimental demonstrations of enhanced optical chirality have been limited to the infrared and visible, while the chiral absorption features of most industrially relevant small molecules are in the ultraviolet.

In this presentation, we design ultraviolet metasurfaces that overcome this band mismatch, enabling high optical
New plasmonic metasurfaces with high-Q electric and magnetic dipole resonances. Similar to the case of a symmetric metasurface, for the biperiodic lattice we can fix the enhancement of 50-fold. A diameter offset is then introduced which produces high-Q antisymmetric electric and magnetic dipole resonances, producing a maximized ratio allows for spectral overlap of low-Q electric and magnetic dipole resonances, producing a maximized C enhancement of 50-fold. A diameter offset is then introduced which produces high-Q antisymmetric electric and magnetic dipole resonances. Similar to the case of a symmetric metasurface, for the biperiodic lattice we can fix the lattice parameter a=200 nm and disk height h=60 nm, then sweep the center disk diameter from 100 nm to 120 nm to spectrally shift the electric and magnetic resonances in relation to each other. For a metasurface with a 10% offset between neighboring disks, the high Q modes overlap at a center diameter of 107 nm. At this diameter, we calculate a local C enhancement of 1000-fold at an excitation wavelength of 263 nm. Furthermore, the circularly polarized phase of the incident CPL is preserved in the near fields resulting in a C enhancement of a single handedness. Thus, regions of large optical chirality persist above the metasurface, yielding averaged C enhancements exceeding 100-fold in a volume extending 200 nm from the disks. We also show that adjusting the structural asymmetry through the diameter offset allows for tuning of the radiative Q factors and consequently the local C enhancements across four orders of magnitude. Our results demonstrate the first nanophotonic platform that increases C more than three orders of magnitude in the ultraviolet, paving the way for efficient all optical chiral resolution of small molecules.

4:30 PM EL01.14.04
High-Speed Thermal Photodetection with Plasmonic Metasurfaces Jon Stewart1, Jarrett H. Vella2 and Maiken H. Mikkelsen1; 1Duke University, United States; 2Air Force Research Laboratory, United States

Integration of thermally-sensitive materials with highly-engineered metamaterial absorbers has allowed for the creation spectrally-selective thermal detectors ranging across the MHz-THz frequency bands. However, the fastest detectors possess a millisecond-scale response time limiting their applicability for real-time, high-resolution imaging or time-resolved sensing techniques. Here we demonstrate a high-speed, spectrally-selective thermal photodetector operating at room temperature by integrating a colloidally-fabricated plasmonic metasurface with an aluminum nitride (AlN) pyroelectric film. The subwavelength, absorbing metasurface possesses a picosecond-scale thermal diffusion time, which produces a voltage in the underlying pyroelectric film proportional to its temperature change. Impulse response measurements of the metasurface-pyroelectric detectors show instrument-limited responses down to 500 ps, where finite-element simulations reveal the possibility of achieving 25 ps response times rivaling the carrier-limited response times of photodiodes. These scalable, inexpensive, and large-area devices show potential for realizing uncooled thermal photodetectors with high responsivities and GHz speeds without the spectral limitations of bandgap-reliant detectors.

4:45 PM EL01.14.05
Tunable Metasurfaces Based on a Hybrid Platform of Dielectric/Phase-Change Materials Sajjad Abdollahramezani, Hossein Taghinejad, Yashar Kiarashinejad, Omid Hemmatyar, Mohammadreza Zandehshahvar, Ali Eftekhar and Ali Adibi; Georgia Institute of Technology, United States

To spectrally, spatially, and/or even temporally manipulating optical wavefronts in the subwavelengthscale, plasmonic metasurfaces consisting of a planar array of patterned metallic nanostructures have gained extensive attention [1]. However, their low coupling efficiency as well as inherent ohmic losses coming with significant heat generation hinder many practical on-demand applications. The advent of all-dielectric metasurfaces, which employ optically induced electric and magnetic Mie resonances of subwavelength high-index nanoparticles, expedited the realization of miniaturized CMOS-compatible metadevices addressing the challenges associated with plasmonic counterparts [2, 3]. Nevertheless, the functionality of the implemented metadevices cannot be tuned postfabrication. To dynamically engineer the amplitude, phase, polarization, and/or dispersion of light for a wider range of applications, exploiting active functional materials is indispensable [4]. Here, we present a non-volatile active platform by hybridizing a high-index metasurface with phase-change alloy Ge2Sb2Te5(GST). The intrinsic high-index and drastic optical contrast of GST (upon conversion from amorphous to the crystalline in multiplestates) make multipolar Mie resonances of all-dielectric nanoresonators optically tunable. As a proof-of-concept, we demonstrate a small footprint, multi-wavelength, and multi-level optical modulator capable of modulating the light with high modulation depth in extreme states of GST. We also experimentally show how the structure takes advantage of the
interplay of electric and magnetic resonance modes, due to the induced intermediate states of GST, leading to a considerable phase shift of the transmitted light necessary for beaming applications. We leverage a new deep learning architecture to effectively design optimized metadevices considering the fabrication imperfections while the underlying physics of light-matter interactions is explained through a sheer mathematical platform [5, 6]. Our findings further substantiate active dielectric metasurfaces as promising candidates for the development of miniaturized energy harvesting modules, optical sensors, phased array antennas, and holograms.

References:

SESSON EL01.15: Poster Session III: Plasmonics and Low Dimension Photonics
Session Chair: Yu-Jung Lu
Wednesday Afternoon, December 4, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EL01.15.01
Spectroscopic Optical Imaging at Nanometer Scales Ze Zhang1, Joel Martis1, Brad Takasuka2 and Arun Majumdar3,1; 1Stanford University, United States; 2Silicon Valley Peripherals, United States; 3SLAC National Accelerator Laboratory, United States

Nanometer-resolution optical spectroscopic imaging offers fundamental insights of light-matter interactions that has significant bearing on understanding optoelectronic properties of molecules and inorganic nanostructures, surface chemical reactions, and defect engineering. Optical spectroscopy techniques like Raman, IR spectroscopy and UV-vis-NIR spectroscopy, are widely used for materials characterization. However, their spatial resolution is limited by the wavelength of the light used, which is on the order of hundreds of nanometers to microns. Past attempts to break this diffraction limit include using a scanning probe to locally enhance the interaction between the sample and light, using near field optics to reduce the effective optical spot size, or using super resolution techniques such as PALM, STORM, STED. Electron microscopy, on the other hand, can readily achieve nanometer or even atomic resolution, but surface-sensitive electron spectroscopy of molecules and inorganic nanostructure is difficult due high electron doses and due to the energy mismatch between the high energy (5-300 keV) electron beam and the low energy (5 eV or less) electronic or vibrational states.

We introduce a new imaging technique named PhotoAbsorption Microscopy using ELecron Assays (PAMELA), which combines the high spectroscopic selectivity of photo-excitation with nanometer-scale spatial resolution of electron beams. PAMELA relies on the largely unexplored coupling of light and electron beams within matter that produces unique signatures, which can be utilized for the purpose of nanoscale imaging. This new technique is...
demonstrated by obtaining optical images of inorganic nanostructures at <10 nm spatial resolution that exhibit spectroscopic selectivity based on photoabsorption. PAMELA provides a more general approach for characterizing materials as it relies on the inherent light absorption, without requiring subsequent fluorescence, luminescence or any specific modification of the sample. This will likely open new opportunities in fields such as surface chemistry, biomolecular imaging, and quantum materials.

EL01.15.02
Light Wrangler—Manipulation and Analysis of Molecules with Plasmonic Nanoantennas Michel Frising, Alvaro Magdaleno and Ferry Prins; Universidad Autonoma de Madrid, Spain

Inspired by previous theoretical\(^1\) and experimental work\(^2\) we will show experimental data and simulations of plasmonic nanopore antennas designed to enhance the Raman-scattered signal of molecules. Spectroscopy of single molecules can reveal details about the molecular structure that are inaccessible in ensemble measurements. The most prominent example is the DNA molecule. The knowledge of the exact sequence of the nucleotides in the DNA molecule contains the complete genetic information of an organism. However, the individual base pairs are spaced by only a few hundred picometers, requiring extremely high resolution to distinguish adjacent nucleotides. Recent studies using tip-enhanced Raman scattering (TERS) on single molecules have shown that sub-nanometer resolution can be achieved\(^3–5\). While in these studies the probe is brought to the sample, we are going to bring the sample to the probe to streamline the analysis while maintaining the resolution of the TERS technique. In particular, we are going to present the Raman-scattered signal from different molecules in the hotspot of the plasmonic antennas specifically designed to enhance the intensity of the Raman-scattered signal which can be used to identify different molecules. Further, the plasmonic antennas can be used at the same time to influence the spatial dynamics of the molecules present in the hotspot\(^7,8\), which could be exploited to manipulate the molecule. Such a technique this would pave the way for a lab-on-a-chip system to determine sequences of molecules\(^6\).

References

EL01.15.03
Near-Infrared Interband Hot-Carrier Generation with Au-Pd Nanoalloys Sara K. Figueiredo Stofela, Orhan Kizilkaya\(^2\), Tiago R. Leite\(^1\), Mohammad M. Taheri\(^3\), Jason Baxter\(^3\), William A. Shelton\(^1\), Phillip T. Sprunger\(^1,2\), Benjamin T. Diroll\(^4\) and Kevin M. McPeak\(^1\); \(^1\)Louisiana State University, United States; \(^2\)Louisiana State University Center for Advanced Microstructures & Devices, United States; \(^3\)Drexel University, United States; \(^4\)Argonne National Laboratory, United States

The hot-carrier generation in the near-infrared (NIR) in Au nanostructures has recently been explored for applications in photodetection and photocatalysis. While the nonradiative decay of surface plasmons via Landau damping is a pathway to generating hot carriers near the Fermi level, a more efficient mechanism involves direct transitions (interband). However, for Au (and all noble metals) these transitions require at least 2 eV to take place. Therefore, noble metals have a band structure that is not ideal for the generation of hot carriers in the NIR. One possible route to improving the efficiency of hot carrier generation in noble metals at NIR wavelengths, is to shift
their electronic density of states closer to the Fermi level via alloying with a transition metal. In this work, we show how alloying Au with Pd couple the individual metal benefits: an oxidation resistance, a longer carrier lifetime and a favorable band structure for NIR transitions. Grazing incidence x-ray diffraction (GI-XRD) and x-ray photoelectron spectroscopy (XPS) measurements support the formation of single-phase alloy and oxidation resistance in the thin films. While, ultraviolet photoelectron spectroscopy (UPS) data shows how the electron density of states (EDOS) increase near the Fermi level when adding Pd to Au with respect to Au. Ellipsometry measurements show that adding Au to Pd improves the plasmonic properties in the NIR with respect to pure Pd. DFT calculations show that Au-Pd alloys are expected to generate more hot carriers than pure Au under NIR. Using NIR-pump, THz probe transient absorption spectroscopy, we also provide evidence suggesting that alloying Au with Pd results in an increased distribution of hot carriers with respect to Au in the NIR.

EL01.15.04
Super-Resolution Mapping of Plasmon-Enhanced Processes Ruben Hamans1,2, Matteo Parente1,2, Gabriel Castellanos3, Mohammad Ramezani1,3, Jaime Gómez Rivas1,3 and Andrea Baldi1,2; 1Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands; 2Institute for Complex Molecular Systems, Eindhoven University of Technology, Netherlands; 3Institute for Photonic Integration, Department of Applied Physics, Eindhoven University of Technology, Netherlands

Plasmonic and photonic structures have dimensions that are typically smaller than the diffraction limit. Here, we use super-resolution microscopy to map the coupling between fluorescent molecules and metal nanoparticle arrays and to study catalysis on individual Au nanostructures.

First, we investigate the coupling between fluorescent molecules and a periodic array of metallic nanoparticles. Due to their ability to support surface lattice resonances, these arrays can enhance the emissive properties of fluorescent molecules across the whole unit cell of the array, instead of just in the vicinity of a nanostructure. By combining super-resolution microscopy with finite-difference time-domain simulations, we find that collective resonances have minimal influence on the spontaneous decay rate of an emitter, but instead can be exploited to enhance the directivity of the emission. Our approach of experimentally mapping emission enhancement with sub-diffraction resolution and numerically disentangling the underlying contributions can inform the rational design of optical devices based on plasmonic particle arrays [1].

Second, we study the effect of the decay of localized surface plasmon resonances on the catalytic properties of metal nanoparticles. As a test reaction we use the nanoparticle-catalyzed reduction of the weakly fluorescent molecule resazurin to the strongly fluorescent molecule resorufin. By using catalysts with a plasmon resonance spectrally separated from the absorption and emission of the reaction products and by controlling the polarization of the incident fields, we can study the different contributions to the total catalytic rate of plasmonic hot electrons, electromagnetic hot spots, and photo-thermal effects. Understanding the underlying mechanisms of plasmon-enhanced catalysis is fundamental for the development of a next generation of photo-catalysts that can efficiently harvest light to drive chemical reactions.


EL01.15.06
Overcoming Quantum Decoherence at Telecom Bands with Plasmonic Nanocavities Yue Luo1,2, Xiaowei He1, Younghee Kim3, Jeffrey L. Blackburn4, Stephen K. Doorn3, Han Htoon3 and Stefan Strauf1; 1Stevens Institute of Technology, United States; 2Harvard University, United States; 3Los Alamos National Laboratory, United States; 4National Renewable Energy Laboratory, United States

Indistinguishable single photon generation at telecom wavelengths from solid-state quantum emitters remains a significant challenge to scalable quantum information processing. Here we demonstrate efficient generation of indistinguishable single photons directly in the telecom O-band from aryl-functionalized carbon nanotubes by overcoming the quantum decoherence with plasmonic nanocavities. With an unprecedented single-photon
spontaneous emission time down to 10 ps (from initially 0.7 ns) in the coupling scheme, we show a two-photon interference visibility at 4 K up to 0.79 without post selection. Cavity-enhanced quantum yields up to 74% and Purcell factors up to 415 are achieved with single-photon purities up to 99%. Our results establish the capability to fabricate fiber-based photonic devices for quantum information technology with coherent properties that can enable quantum logic.

**EL01.15.07**  
**Propagating Dirac Plasmon Polaritons in Topological Insulators** Yong Wang and Stephanie Law; University of Delaware, United States

The properties of topological insulators (TIs) have been widely explored due to their unique band structure. The energy states at the TI surfaces exhibit linear dispersion and spin-momentum locking. Carriers occupying these states are therefore two-dimensional, massless, and spin-polarized. Dirac plasmons comprising these carriers can be excited in TI thin films. Because most TI films are much thinner than the wavelength of light, plasmons excited on the top and bottom surfaces couple, resulting in an acoustic and an optical plasmon mode. Due to the spin-momentum locking characteristics of the TI surfaces, the optical mode is predicted to be spin-polarized. Before the spin properties of TI plasmons can be measured, propagating plasmons must first be excited. There are a variety of ways to excite plasmons in TI thin films. The most common way is to etch the film into an array of stripes to create localized plasmons. Although this technique has been highly effective, these localized modes cannot easily be used to understand the spin properties of TI plasmons. To excite propagating plasmons, we instead choose to use a grating coupler fabricated on the surface of the TI film.

We first grew a series of 50nm Bi₂Se₃ films using a molecular beam epitaxy (MBE) system. The TI films had the following structures: a layer of 5nm BiInSe₃ (BIS) on the top, 50nm Bi₂Se₃ TI in the middle, and 50nm BIS between the TI and the Al₂O₃(0001) substrate. The BIS layer on the top serves as a protection layer to prevent surface degradation and charge redistribution caused by the grating metals. The BIS layer on the bottom serves as a buffer layer to optimize the quality of the TI growth. After growth, 100nm gold/10nm titanium gratings with different grating periodicity are lifted off of the surface of the film. The periodicity of the gratings ranges from 100nm to 700nm. TM polarized transmission spectra are then taken in a Fourier Transform Infrared Spectroscopy (FTIR) system. From the extinction spectra, we observe a series of absorbing peaks that shift with the grating periodicity. We have ruled out any source other than the plasmons that could have possibly caused the peaks to show up in the range. TM transmission spectra were taken on a bare sapphire substrate, a single layer TI film directly grown on sapphire, a single layer BIS film grown on sapphire, and a sapphire substrate with gratings on top. None of the spectra shows the same peaks as those we see in TI films with top gratings. Hence, we have successfully demonstrated the existence of the propagating Dirac plasmons in the TI Bi₂Se₃ and the tunability of the plasmon frequency with grating period.

The next steps will be to launch the plasmon and detect the spin wave dynamically. TIs are the only known single-material system where such spin-polarized plasmons can be observed. The observation of propagating Dirac plasmons in TI is significant not only because it proves the theoretical predictions of TI Dirac plasmons, but also creates possibilities in developing future technology. A frequency-tunable propagating spin-density wave could be feasible for better memory or computing systems.

**EL01.15.08**  
**Surface-Plasmon-Polariton-Driven Narrow Linewidth Magneto-Optics in Ni Nanodisk Arrays** Francisco Freire Fernández⁵, Mikko Kataja⁶ and Sebastiaan van Dijken¹; ¹Aalto University, Finland; ²Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Spain

The integration of plasmonics and magneto-optics has led to the emergence of a new research field known as magnetoplasmonics. The main goal of magnetoplasmonic is twofold. First, the use of magnetic materials in plasmonic structures enables active light manipulation at the nanoscale via field-controlled breaking of time-reversal symmetry [1,2]. Second, the excitation of surface plasmons in magnetic materials can be used to resonantly enhance and spectrally tailor their magneto-optical response [3-7]. Despite its promise, magnetoplasmonics faces a challenge of overcoming optical losses. This holds particularly true for nanostructures containing ferromagnetic metals, whose losses are significantly larger compared to noble metals. Here we exploit surface plasmon polaritons (SPPs) excited at the interface of a SiO₂/Au bilayer to induce strong magneto-optical responses on the Ni nanodisks of a periodic
array. Using a reference system made of Au nanodisks, we show that optical losses in Ni do not broaden the linewidth of the SPP-driven magneto-optical signals. Loss mitigation is attained because the free electrons in the Ni nanodisks are driven into forced oscillations away from their plasmon resonance. By varying the SiO2 layer thickness and lattice constant of the array, we demonstrate tailoring of intense magneto-optical Kerr effects with a spectral linewidth down to ~25 nm. Our results provide important hints on how to circumvent losses in magnetoplasmonics via the design of off-resonance driving mechanisms.


EL01.15.09
Chiral Light-Matter Interactions in a Plasmonic Nanocavity for Chiral Organic Optoelectronics
Hyungchae Kim, Kyung Ryoul Park and Changsoon Kim; Seoul National University, Korea (the Republic of)

In recent years, circularly polarized light (CPL) detectors and CPL emitters based on chiroptical effects arising from chiral molecules have attracted much attention as building blocks of advanced information technology. Their performances, however, have been shown to be severely limited by the trade-off between the external quantum efficiency ($\eta_E$) and the dissymmetry factor ($g$) that characterizes their asymmetric optical behaviors depending on the helicity of CPL. One way to overcome this is to utilize the supramolecular chirality, which translates a molecular chirality into a supramolecular system whose size is comparable to or larger than the wavelength of light. Although this approach can increase $g$ without necessarily decreasing $\eta_E$, it is not applicable to optoelectronic devices whose vertical (with respect to the substrate) dimension is smaller than the wavelength, such as organic light-emitting devices and photodetectors.

Here, we numerically demonstrate that a nanophotonic platform consisting of a chirally patterned metal layer–insulator layer–metal layer (cp-M/I/M) structure can induce a strong chiroptical response of organic molecules positioned inside the insulator layer, and that a CPL-sensitive organic photodetector with both high $g$ and $\eta_E$ can be realized using this platform. In this nanophotonic structure, plasmonic hot spots are excited at an optical frequency only for a helicity of the incident CPL matched to the twisted direction of the chiral nanopattern, which is attributed to a selective excitation of a mode arising from the hybridization of a plasmonic mode near the top electrode and that near the bottom electrode. For full utilization of the plasmonic hot spots possessing high photonic densities of states, we examine the dependence of $\eta_E$ and $g_A$ on the molecular orientations. A CPL-sensitive photodetector incorporating in the cp-M/I/M structure vertically-oriented molecules, i.e., molecules whose transition dipole moment is normal to the substrate, features $\eta_E = 24\%$ and $|g_A| = 1.6$, which are respectively 24 (or 240) and 1.7 (or 1) times larger than $\eta_E$ and $|g_A|$ of Schottky photodiodes using Z-shaped chiral nanostructures [1] (or helicene based photodetectors [2]).

References:

EL01.15.10
The Effect of Magnetic Fields on Plasmon Resonance Frequencies of Metal Nanostructures
Peter Novello1, Yael Gutiérrez2, Siyuan Zhu1, Fernando Moreno2, Pani Varanasi1,1 and Jie Liu1; 1Duke University, United States; 2University of Cantabria, Spain; 3U.S. Army Research Office—Materials Science Division, United States

The interaction of a magnetic field and the field generated by a localized plasmon resonance on Au nanorods is shown to be a measurable effect. Previously, the magneto-optical Kerr and Faraday polarization dependent effects have been observed on hybrid magnetic-plasmonic structures, and it has been theoretically demonstrated that under
high magnetic field strength (>10T) a splitting of the plasmon absorption band occurs with circularly polarized light. Here the surface plasmon absorption of Au nanorods is measured utilizing a magnetoo-spectrometer with a magnetic field force up to 1.5T and non-polarized light. It is found that as the magnetic field strength increases, the energy and the lifetime of the plasmon resonance are altered. Coupled with theoretical work, our findings suggest either the Lorentz force is acting on the electrons under a magnetic field effectively amplified by the localized plasmon resonance, or an alternative mechanism exists.

EL01.15.11
Atomic Layer Engineering of Epsilon-Near-Zero Ultrathin Films with Controllable Zero Index Field Enhancement Sudip Gurung1, Aleksei Anopchenko1, Subhajit Bej1 and Ho Wai (Howard) Lee1,2; 1Baylor University, United States; 2Texas A&M University, United States

Enhanced and controlled light absorption as well as field confinement in an optically thin material are pivotal for energy efficient optoelectronics and nonlinear optical devices. Highly doped transparent conducting oxide (TCO) thin films with near-zero permittivities, in their so-called epsilon near zero (ENZ) frequency regions, can support ENZ modes which may lead to perfect light absorption and ultra-strong electric field intensity enhancement (FIE) within the films. To achieve full control over optical absorption and FIE, one must be able to tune the ENZ material properties as well as the film geometries. Here, we report a nano-engineering of ultra-smooth aluminum doped zinc oxide (AZO) films with tunable ENZ wavelength (1500-1725 nm), low optical losses, and thickness as small as 22 nm by using atomic layer deposition (ALD) technique. The ENZ properties of the AZO thin films are controlled by deposition conditions such as dopant ratio, deposition temperature, and number of macro-cycles. We experimentally demonstrate engineered absorption and FIE of AZO thin films via control on their ENZ wavelengths, optical losses, and film thicknesses. Furthermore, we introduce a simple mathematical formula for quick and accurate estimation of FIE when ENZ modes are excited in classical Kretschmann-Raether configuration. Finally, we demonstrate that under ENZ mode excitation, though the absorption and FIE are inherently related, the film thickness required for observing maximum absorption differs significantly from that for maximum FIE. This systematic study on engineering ENZ materials related enhancement properties by optimization of ALD deposition process will be beneficial for the design and development of next generation tunable photonic devices based on flat zero-index optics.

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EL01.15.12
Approaching Ultra-Strong Polaritonic Coupling within CdO Bilayers Joshua R. Nolen1, Evan Runnerstrom2, Kyle P. Kelley3, Thomas G. Folland1, Angela Cleri4, Joshua Nordlander4, Edward Sachet2, Christopher Shelton2, Alyssa Livingood3, Jon-Paul Maria4 and Josh Caldwell1; 1Vanderbilt University, United States; 2North Carolina State University, United States; 3Oak Ridge National Laboratory, United States; 4The Pennsylvania State University, United States; 5University of Kentucky, United States

Epsilon-near-zero (ENZ) modes are supported in films of polaritonic materials with vanishing permittivity values and deeply sub-wavelength thicknesses. These novel optical excitations are associated with extreme electric field confinement, enabling control over light-matter interactions such as resonant perfect absorption and strong nonlinear interactions. Recent studies have demonstrated ENZ phenomena in doped transparent conducting oxides (TCOs). Unlike traditional metals that are not tunable in the IR and THz due to fixed, high carrier densities, TCOs allow for tuning of both carrier density and electronic mobility. One highly promising TCO is highly-doped CdO, which has been shown to achieve electron mobilities extending upwards to 500 cm²/V-s with carrier densities ranging from 10¹⁹ to 10²⁰ cm⁻³. Unique to this material is a range of carrier densities where increasing values result in increasing mobilities.
ENZ modes are unique for their strong absorption/emission and narrow resonant linewidths that can be achieved without the need for nanostructuring. This behavior has been utilized to achieve perfect absorption in thin films as well as thermal emissivity control. These modes are attributed with a nearly-flat spectral dispersion that consequently results in low group velocities and short propagation lengths, diminishing their utility. However, these limitations may be mitigated through hybridization with other polaritonic modes, such as surface plasmon polaritons (SPPs) which are also supported in doped CdO films. Unlike ENZ modes, SPP modes propagate at a much higher group velocity but are hindered by carrier scattering losses and highly sensitive to surface morphology. Careful control over the carrier concentration during film growth has opened the door to achieving multilayer CdO films. Here we show that epitaxially-grown bilayer stacks of CdO, with bottom and top layers supporting SPP and ENZ modes respectively, exhibit cavity-free strong coupling between the ENZ and SPP modes and overcome the deficiencies of each constituent mode. The combined ENZ-SPP dispersion of these bilayer films displays a prominent anti-crossing with a separation that is on the order of the mode frequency, giving clear evidence of strong coupling. The degree to which these modes are strongly coupled together is dependent on both the spectral and spatial overlap of the modes. By carefully controlling the plasma frequency of the two individual CdO layers, this spectral overlap and thus the ENZ-SPP dispersion, can be tuned. We also show that tuning the oscillator strength of the individual modes is another approach towards manipulating the ENZ-SPP dispersion. This is controlled geometrically, by tuning the ENZ layer thickness.

In more recent work we have extended our focus to other geometries, such as CdO films where the SPP and ENZ films are spatially separated by a dielectric spacer layer. The dielectric layer thickness modifies the spatial overlap of the constituent electric fields as well as alters the effective index of the region above the SPP layer, providing additional tuning to the ENZ-SPP dispersion. We also examine the hybridization between localized SPP modes and an ENZ layer imbedded within a perfect absorber structure to monitor the impact of nanostructuring upon this strong coupling phenomena and how this can be used as independent knobs for tuning the resonant absorption, and alternatively thermal emission, of the structures. By fabricating such hybrid materials into nanostructure arrays, direct control of the emission polarization, spatial coherence and divergence is also engineered through careful design of nanostructure geometry and periodicity. This approach may lead to the realization of spectrally tunable thermal emitters for narrow-band, polarized and spatially coherent IR sources.

**EL01.15.13**

**Probing Hot Carrier Dynamics in Alternative Plasmonic Materials** Ping-Hsien Ou\(^1\), Meng-Ju Yu\(^1\), Hye-Young Ahn\(^2\) and Yu-Jung Lu\(^1,3\), \(^1\)Academic Sinica, Taiwan; \(^2\)National Chiao Tung University, Taiwan; \(^3\)National Taiwan University, Taiwan

Transition metal nitrides have been considered as promising plasmonic materials due to the high thermal stability and tunable optical properties to replace noble metals. In this work, we used pump probe transient absorption measurements to study the ultrafast carrier relaxation processes in gold film (standard plasmonic materials) and alternative plasmonic materials, including sputtered titanium nitride, zirconium nitride, hafnium nitride and niobium nitride. The long lifetime of hot carrier in alternative plasmonic materials make it more beneficial than that in gold to cross the Schottky barrier between semiconductor and plasmonic materials, and further enhance the performance of plasmonic device. Here, we demonstrated that transition metal nitrides are possible to be utilized in efficient hot carrier extraction. With femtosecond Ti:Sapphire pulsed laser, we are capable of distinguishing various carrier dynamics within a nanosecond. Two relaxation mechanisms take place during the period hot electrons relax probing at photon energy of 2.58 eV. One is the combination of electron-electron and electron-phonon interactions which occurs at femtoseconds to several picoseconds, and slow phonon-phonon relaxation with a hundreds of picosecond comes after the first short relaxation. Moreover, we not only confirmed that the relaxation process in transition metal nitrides are one order magnitude slower than that in gold, but also proved that niobium nitride has the longest first fast decay time. The more slowly the carriers relax, the more possibly they are captured. In addition, the relaxation time could be tuned with respect to quality of materials, thickness and substrate. Besides, we theoretically calculated the band structure of transition metal nitrides by first principles in order to study the carrier relaxation time. We conclude that the slow carrier relaxation time strikes an opportunity for hot carriers in transition metal nitrides to be efficiently transferred to semiconductor as hot carrier donor due to the long hot carrier lifetime. Thus, we believe the results pave the way for the applications of high performance optoelectronic devices with high efficient hot carrier extraction.

**EL01.15.14**

**Electric-Field Tunable Magnetoplasmonic Gratings** Mikko Kataja\(^1\), Rafael Cichelero\(^2\) and Gervasi Herranz\(^1\);

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With the advent of integrated photonics, grating couplers offer a solution towards integrated optical isolation by coupling optic fibers to on-chip waveguides. In this context, we study the interplay between electro-optical and magneto-optical effects. The magneto-optical effect breaks the time-reversal symmetry and induces frequency shifts in the energy and angular spectra of plasmon resonances. As a result of these shifts, exceptionally large magneto-optic responses are can be achieved [1]. In optoelectronic devices modulation and switching capabilities can be accomplished by electric control of the amplitude and phase of electromagnetic waves, using architectures based either on Mach-Zehnder interferometers or micro-ring resonators. Combining the properties of the two aforementioned materials could enable the control of the properties of magneto-optically active devices by electric fields which is an attractive prospect for development of novel nanophotonic devices. Facing this challenge, we study a magneto-optically active Au/Co multilayer grating coupler fabricated on top of an electro-optically active substrate (BaTiO3) as the basic device to uncover how these two active properties influence each other. We used Fourier optics microscopy to obtain the plasmonic band structures of our gratings [2]. The Fourier spectroscopy approach can be adapted to the study of magnetoplasmonic gratings by reducing the beam spot size in the objective back aperture, so that diffracted modes can be analyzed independently, enabling the exploration of the interplay between plasmonic resonances and diffracted light. We used this approach to study selectively surface plasmon polaritons propagating along backward or forward directions, enabling us to easily assess their non-reciprocal magnetic modulation. To assess the magneto-optic response, we measured the transverse magneto-optic Kerr effect (TMOKE) amplitude of Au/Co magnetoplasmonic gratings, measured from the ARR maps, obtained through the expression \( TMOKE = \frac{I(H_+)-I(H_-)}{I(H_{avg})} \), where \( I(H_+), I(H_-) \) are the reflected or diffracted intensity detected at opposite saturated magnetizations of Co (taken at \( H_- \approx 150 \text{ Oe} \)), and \( I(H_{avg}) \) is defined as the average of the absolute value of \( I(H_+) \) and \( I(H_-) \). To find out how the electro-optical effects influence plasmon propagation and magneto-optic responses, we measured ARR maps under applied electric fields. In line with our previous results, large magneto-optic signals – two orders of magnitude larger than intrinsic responses– arise from the SPP excitation. We show that, due to the presence of the ferroelectric layer, plasmon propagation can be modulated by electric fields enabling reversing the sign of magneto-optics signals. Thus, the combined integration of magneto-optical and ferroelectric materials enables control over non-reciprocal device properties by application of external electric fields, rather than magnetic fields, which could greatly simplify their integration into multifunctional nanophotonic devices.


EL01.15.15
Influence of Plasmonic Metasurfaces on the Optical and Electronic Properties of Organic Semiconductor Thin Films
Zhongkai Cheng and Deirdre O’Carroll; Rutgers, The State University of New Jersey, United States

Organic semiconductors have attracted considerable research interest owing to their ease of processing and unique physical properties, such as compatibility with plastic substances, low temperature processing, large area coverage, mechanical flexibility and low embodied energy. Plasmonic metasurfaces, which are nanostructured metallic films capable of supporting and directing surface plasmons at visible wavelengths, have been shown to improve the performance of organic optoelectronic devices by, for example, enhancing light absorption in or emission from the active layer. However, large-area, low energy fabrication processes are required for plasmonic metasurfaces to be compatible with organic semiconductor device processing.

In this work, we describe a straight-forward fabrication process for Ag plasmonic metasurfaces based on thermally dewetting thin Ag films. We study the integration of plasmonic metasurfaces with the organic semiconducting polymer, poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT), and the impact on the optical and electrical characteristics of the semiconductor thin film. F8BT is a fluorene-based conjugated polymer, that is widely employed as an active material in organic optoelectronic devices, especially organic photovoltaics and organic light-emitting diodes, because of its high quantum and power conversion efficiencies. By varying the size of the Ag nanoparticles (AgNPs) on the plasmonic metasurfaces from 20 nm to 150 nm in diameter, we observe pronounced increases in the scattering, absorption and photoluminescence spectra from F8BT film coatings. From the optical images, the light scattering intensity of metasurfaces with 150 nm diameter AgNPs is highest because of the high albedo (ratio of scattering to total extinction) of the large AgNPs. The extinction spectra are attributed to absorption and scattering by the localized surface plasmon resonances of the AgNPs. From the UV-visible extinction spectra,
the extinction peaks of 20 nm- and 80 nm-diameter AgNP metasurfaces occur at a wavelength of 500 nm and the extinction peak of the 150 nm-diameter AgNP metasurface is around 550 nm. The red-shifted extinction of the larger AgNPs is due to their more extended and distributed dipole response to incident light which causes a lowering in the energy of the surface plasmon resonance. Similarly, the 150 nm-diameter AgNP metasurface caused the greatest enhancement in photoluminescence emission from F8BT film coatings because of the high albedo of the large AgNPs. In addition, using integrating sphere absorption measurements we find stronger absorption enhancement and red-shifted F8BT absorption spectra on metasurfaces with increasing AgNP diameter. Finally, we investigate the effects of plasmonic metasurface electrodes on electrical properties of F8BT hole-only devices. We demonstrate working F8BT hole-only devices with plasmonic metasurface electrodes containing a wide range of Ag nanostructure sizes in an inverted device geometry.

EL01.15.16
Enhanced Subwavelength Coupling and Nanofocusing with Fiber-Plasmonic Hybrid Probe Khant Minn¹, Ho Wai (Howard) Lee¹² and Zhenrong Zhang¹; ¹Baylor University, United States; ²The Institute for Quantum Science and Engineering, Texas A&M University, United States

For studies of molecular interaction with light such as tip-enhanced Raman spectroscopy (TERS), it is imperative that light be confined to a small space in the order of nanometers which can be achieved by means of localized surface plasmons.¹ In conventional TERS, which has seen dramatic advancements in recent years such as chemical mapping with atomic resolution,² surface plasmons are excited on the metallic probe by directly focusing the laser beam in free space in the vicinity of tip apex. Such excitation scheme has to overcome the inherent spatial mismatch between diffraction-limited, micrometer-sized focal spot and nano-scale tip-sample interaction volume, leading to low mode coupling efficiency and high background scattering in the detected field.³ Recently, studies have shown that optical fiber-incorporated plasmonic probes can be a platform for transporting electromagnetic energy in nanoscale with high efficiency.⁴ However, these devices rely on the higher order radial vector mode for coupling of photonic to plasmonic modes which requires a special type of fiber that maintains radial polarization and expensive radial polarizer in the excitation path.

In this work, we propose a fiber-plasmonic hybrid probe that efficiently couples linearly polarized fiber core mode to radial plasmons on gold tip for nano-scale confinement of light. Using finite difference time domain 3D simulations, we show that linearly polarized light can be utilized to create hot-spot at the apex of the tip by selectively exciting plasmons at only one side of the tip base from the optical fiber. The coupled plasmonic mode then propagates to the narrow apex where it gets localized and strongly focused. Then we discuss the polarization selectiveness of our excitation scheme by comparing two orthogonal source polarizations. We show that the enhanced field at the apex is due to the spiraling plasmons excited by the end-fire coupling of light from fiber core at the tip base. We also demonstrate the cavity-like resonant response of the device by spectrally mapping the field enhancement for varying tip sizes. The focusing efficiency of 900 nm long tip at resonant wavelength is 1.3%. In the collection mode, the radiated power from a dipole emitter is probed by the 800 nm long tip and 5.1% of the dipole radiation is transmitted through the fiber. The proposed device is highly desirable for a plethora of applications including medical procedures, biomedical imaging and near-field spectroscopy.

References

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EL01.15.17
Plasmonic Coupling in Topological Insulator/Band Insulator Layered Structure Zhengtianye Wang, Vishnuvardhan Mambakkam, Theresa P. Ginley, Greeshma Chandan and Stephanie Law; University of Delaware, United States

Topological insulators (TIs) are semiconductor materials, exhibiting topologically protected surface states that arise...
from strong spin-orbit coupling. These surface states form a Dirac cone band structure at Γ point, which exhibits linear dispersion. Electrons occupying these states travel at relativistic velocity and behave as massless Dirac fermions. In addition, these states demonstrate spin-momentum locking, which limits scattering from nonmagnetic perturbations. When perturbed with a sinuosoidal electromagnetic field, these surface states can house two-dimensional Dirac plasmons at room temperature. The Dirac plasmons in TIs are predicted to be topologically protected and spin polarized, which means spin of electrons can be optically manipulated.

Instead of the normal bulk plasmon mode that arises in three-dimensional films, electrostatic coupling between the top and bottom surface states of a single layer of TI thin film causes an optical plasmon mode and an acoustic plasmon mode [1]. However, only the optical mode can be observed by optical methods due to its non-zero optical dipole [2,3]. Interestingly, the frequency of the optical mode lies in the untapped terahertz (THz) range. A superlattice structure of TIs and normal band insulators (BIs) is expected to bring coupling of multiple surface states, generating multiple optical modes in the THz. These modes are tunable by changing the layer structure of the superlattice, which is easy to do with molecular beam epitaxy (MBE). In our system, Bi$_2$Se$_3$ and (Bi$_0.5$In$_0.5$)$_2$Se$_3$ (BIS) were used as the TI and BI materials, respectively. BIS is a topologically trivial alloy material of Bi$_2$Se$_3$ and β-In$_2$Se$_3$, both of which belong to the group and share close lattice constants: 2.866nm and 2.823nm, respectively. It was shown that by using BIS as a buffer layer between a sapphire substrate and the Bi$_2$Se$_3$ film, the carrier mobility increased and the overall carrier density was reduced by a factor of at least two, indicating a reduction in trivial carriers and a Fermi energy closer to the Dirac point. Using BIS, indium diffusion into the TI layers is less of a concern than it would be with pure β-In$_2$Se$_3$ as the BI layers [5]. In this talk, we will demonstrate the experimental evidence of Dirac plasmon coupling in BIS /Bi$_2$Se$_3$/BIS/Bi$_2$Se$_3$/BIS stacked layers grown on sapphire (0001). The film was patterned into nanoribbon arrays with varying widths to excite localized plasmon modes. Fano-shape extinction spectra containing two distinct plasmon modes were observed with all samples in the range of 1.5THz-8THz through Fourier-transformed Infrared (FTIR) spectroscopy measurements. A three-oscillator, double-Fano-resonance model was adopted to extract parameters of the high/low frequency plasmon modes and to explain the quantum interference between the plasmons and the bulk phonon (α phonon=2.01THz). A blueshift in frequency was observed for both the high/low frequency modes as the nanoribbon width narrows, similar to what has been observed in the single plasmon mode in a single layer Bi$_2$Se$_3$ [2,3]. Understanding plasmon coupling in a multilayer TI/BI structure will provide a deep insight to the many-body interaction in low-dimensional strong spin-orbit coupling systems. It also lays the cornerstone for future tunable THz devices for detection, security screening and advanced communication.

Reference


EL01.15.19

Use and Limitations of Titanium Nitride Thin Films for Next Generation Optoelectronic and Plasmonic Devices Ryan Bower$^1$, Daniel Loch$^2$, Qiaomu Yao$^1$, Papken Hovsepian$^2$, Arutiu Ehiasarian$^2$ and Peter K. Petrov$^1$; $^1$Imperial College London, United Kingdom; $^2$Sheffield Hallam University, United Kingdom

Titanium nitride has emerged as an alternative material to the noble metals gold and silver for optoelectronic and plasmonic applications due to its increased mechanical stability, thermal stability and spectral tunability. As the number of TiN-based optoelectronic devices increases it is necessary to develop an understanding of the applicability of TiN within a range of operating environments. Key factors to consider include temperature stability and compatibility with application specific materials.

In this work, we investigate the applicability of TiN in conjunction with a range of materials commonly used within plasmonic and optical devices. TiN thin films were deposited by radio frequency (RF) and High-power impulse (HiPIMS) magnetron sputtering onto a variety of semiconductor- and industrial standard substrates including Si, MgO, glass and steel. Optical properties were measured using spectroscopic ellipsometry and correlated with the crystalline structure and surface morphology of the TiN thin films. Additionally, the spectral tunability of these materials was investigated with respect to lattice-mismatch-induced strain and film texture. This work also reveals
the temperature range of applicability of the TiN based optoelectronic devices.


**EL01.15.20**

**Plasmonic Aluminum Nanohole Arrays as Transparent Conducting Electrodes for Organic Ultraviolet Photodetectors with Bias-Dependent Photoresponse**

Qiuming Yu, Monica R. Esopi and Shin-Ya Chen; University of Washington, United States

Metallic nanostructured films incorporated into optoelectronic devices such as photodetectors have attracted attention for their ability to support localized surface plasmon polaritons (LSPPs), which can enhance optical absorbance, internal electric field, and ultimately device performance. Metallic nanostructured films can also act as a device electrode, making them a cost-effective, flexible, high-performance alternative to the commonly used indium tin oxide (ITO), which is expensive and brittle. Photodetectors that are sensitive to UV illumination are important in a variety of applications including environmental monitoring, scientific research, imaging, and flame and missile detection. Despite their applicability, extension of plasmonic enhancement mechanisms to UV-selective devices has been relatively slow, because the common plasmonic metals of Ag and Au cannot support surface plasmon polaritons (SPPs) when illuminated by light with wavelengths shorter than about 350 nm. Al is well-suited to support and tune SPPs in the UV spectral range due to its carrier concentration and dielectric function, although oxide formation on the Al surface can interfere with and cause a redshift in its plasmonic properties. In addition, Al provides an attractive material option for UV photodetectors due to its relative abundance and low cost compared to Ag and Au.

In this work, Al nanohole arrays (Al-NHAs) were utilized as transparent conducting electrodes to optimize the UV-selectivity and response tunability of photodetectors having a conventional photodiode structure with organic active materials, which provide a low-cost, flexible alternative to inorganic materials. UV-selectivity was ensured through the material selection of Al, for plasmonic activity within the UV spectral range, and the polymer donor of poly(9,9-diocetylfluorene-alt-bithiophene) (F8T2), for strong UV absorption with a cut-off around 515 nm. The active layer was a 350 nm film consisting of F8T2 and the fullerene-derivative electron acceptor PC71BM, combined in a weight ratio of 100:4 based on previous reports. PEDOT:PSS and LiF were used as hole and electron transport layers, respectively, for an overall device structure of Al-NHA/PEDOT:PSS/F8T2:PC71BM/LiF/Al. 3-dimensional finite-difference time-domain (3D-FDTD) electromagnetic simulations were conducted to design the Al-NHA to produce strong UV absorption in the active layer and enhanced internal electric field intensity. Al-NHA electrodes were successfully fabricated using nanosphere lithography and incorporated into photodetectors, which produced two narrow photoresponse peaks with specific detectivity (D*) values of 4.0x10^9 and 4.6x10^9 Jones under 340 and 515 nm illumination, respectively, and -2 V bias, and one broad photoresponse peak with a peak D* of 8.8x10^9 Jones under 450 nm illumination and 2 V bias. Compared to control ITO-based devices, Al-NHA-based devices had similar response under reverse bias and superior response under forward bias, as ITO-based devices became unstable under forward bias. The bias-dependent photoresponse switching is believed to benefit from plasmonic enhanced internal electric field that increases the driving force for hole diffusion. The mechanism was further confirmed by the investigation of conventional devices with planar Al electrodes and hole-only devices with both planar Al and Al-NHA electrodes. This response switching improves the applicability of UV photodetectors through the incorporation of cost-effective, flexible, and performance-enhancing plasmonic Al-NHA transparent conducting electrodes.

**EL01.15.22**

**Observation of Atomic-Like Transition in Sapphire Crystal by a Deep UV Photoluminescence Spectroscopy**

Nikesh Maharjan and Mim Nakarmi; Brooklyn College and The Graduate Center of the CUNY, United States

Deep UV Photoluminescence (PL) Spectroscopy was employed to study optical properties of sapphire crystal. The sample was excited by the third harmonic of a Ti:sapphire pulse laser at wavelength ~ 266 nm which is a below bandgap photoexcitation. In the low temperature (12 K) PL measurements, we observed two sharp atomic-like peaks at 368.8 and 374 nm with line-width of 0.85 and 3.30 nm, respectively in the PL spectra. We also performed
temperature and power dependent PL measurements. We will present the properties of the atomic-like transitions observed in sapphire at different conditions. The origin of these emission lines could be due to the point defects or incorporation of rare-earth elements. We will also discuss our exploration on the origin of atomic-like electronic states in sapphire crystal. Atomic-like emission in the sapphire could have potential applications in quantum information technologies for the development of solid state single photon source in UV region.

EL01.15.23
Atomic-Like Transition in Hexagonal Boron Nitride Probed by a Deep UV Photoluminescence Spectroscopy
Nikesh Maharjan1, Neelam Khan2, James H. Edgar3, Eli Janzen3 and Mim Nakarmi1; 1Brooklyn College and The Graduate Center of the CUNY, United States; 2George Gwinnett College, United States; 3Kansas State University, United States

Bulk single crystal hexagonal boron nitride (h-BN) flakes were characterized by deep UV photoluminescence spectroscopy. We performed a comparative study of oxidized and unoxidized h-BN flakes at low and room temperatures. In the low temperature (15 K) PL of h-BN flakes, we observed strong phonon assisted band edge emission peaks at 5.451 and 5.755 eV. The sample was oxidized at 900 °C for 1 hour. The PL measurements of the sample after oxidation, in addition to the phonon assisted band edge emissions, we also observed a sharp atomic-like emission line at 4.082 eV along with its photon replicas at 3.88 and 3.68 eV which were not present in the unoxidized samples. The origin of the sharp atomic-like transition could be related to the incorporation of defect or impurity during the oxidation process. We will discuss the properties of these atomic-like transitions and its possible origins in the h-BN flakes. Our results could have potential applications in the solid state single photon source for quantum information technologies.

EL01.15.24
Extracting Fundamental Physics of Nanoscale Light-Matter Interactions Using Deep Learning
Yashar Kiarashinejad, Sajjad Abdollahramezani, Mohammadreza Zandelshahvar, Omid Hemmatyar and Ali Adibi; Georgia Institute of Technology, United States

In this paper, we introduce a new approach based on deep learning (DL) for understanding the fundamental phenomena of nanoscale electromagnetic (EM) waves and matter interactions. This method builds on the dimensionality reduction (DR) technique in which autoencoders are leveraged to reduce the dimensionality of a light-matter interaction problem with the minimal imposed error by using the strong correlation among its different features [1]. The DR approach highlights the most important features (e.g., design parameters, material state) of any linear or nonlinear EM structure that affects its functionality. This method provides priceless information about the role of nanostructure parameters responding to incident EM waves for a given functionality. Moreover, along with providing the analytical formulas, the DR technique converts a large-size problem into a smaller space which can significantly facilitate and reduce the computation of brute-force optimization and design techniques. To show the applicability of the proposed approach, here we consider two sophisticated design problems for implementation of a reconfigurable multifunctional metadevice enabling dual-band and triple-band absorption in the telecommunication window [2,3]. The metadevice consists of an array of supercells, where each supercell has 4 design parameters (i.e., height, widths, pitches, and crystallization levels of the phase-change material), so that the total number of design parameters become 10. The simulation and experimental results are in a good agreement justifying the effectiveness of our proposed approach in predicting the most critical design parameters in the design problem.

References:

EL01.15.25
Graphene-Mediated Surface Enhanced Raman Spectroscopy for Detection of Biomolecules and Monitoring DNA Hybridization Sanju Gupta and Alexander Banaszak; Western Kentucky University, United States

In this work, we prepared graphene-mediated surface-enhanced Raman scattering (G-SERS) substrates comprising few-layer graphene nanosheets decorated gold and silver nanoparticles for bio-nanotechnology. Raman spectroscopy is a surface-sensitive and nondestructive inelastic light scattering technique. SERS, a specialized form, is useful for rapid and precise identification of biological molecules, industrially relevant chemical dyes at ultralow concentration and monitoring DNA hybridization. This phenomenon is due to the enhanced Raman signals by several orders of magnitude on SERS-active surfaces. While the key point of SERS technology is the nanoscale metal particles, which generates localized surface plasmon resonances in response to laser excitation, the resulting electromagnetic enhancement of > 10^4, controlled diameter and interparticle gap of metal nanoparticles on graphene supports offer an advance toward sensitive G-SERS substrates via localized hybridization at graphene-metal interfaces. We have used thermal reduction technique to produce functionalized graphene and wet chemistry for size tunable gold and silver nanoparticles as cost-effective facile synthesis approaches for strategic G-SERS platforms. Simple and high-throughput arrays (‘biochips’) are developed by decorating graphene nanosheets with gold and silver nanoparticles as well as sandwiching gold and silver nanoparticle and few-layer graphene for cascaded signal amplification to differentiate among nucleotide bases (adenine; A, thymine; T, cytosine; C, guanine; G), DNA hybridization through complementary and probe single-stranded DNA and to detect beta-carotene and malachite green chemical dye.

EL01.15.26
Real Space Imaging of Hyperbolic Phonon Polaritons in Boron Isotopically Enriched Hexagonal Boron Nitride via Photothermal Induced Resonance Georges Pavlidis1, Jeffrey J. Schwartz2,1, Joseph Matson3, Thomas G. Folland3, Song Liu4, James H. Edgar4, Josh Caldwell3 and Andrea Centrone1; 1National Institute of Standards and Technology, United States; 2University of Maryland, United States; 3Vanderbilt University, United States; 4Kansas State University, United States

Hyperbolic phonon polaritons (PhPs) demonstrate great promise for the advancement of nanophotonics in applications such as subdiffraction focusing and flat optics. Due to the large optical anisotropy of hexagonal boron nitride (hBN), PhPs are intrinsically hyperbolic, meaning that they propagate with very large wavevectors, well below the optical diffraction limit. In comparison to plasmons, another class of propagating modes in metals, hyperbolic PhPs enable tighter confinement and experience lower losses in the mid-infrared regime. Isotopic enrichment of the polaritonic medium (e.g., hBN) has been shown recently to be an effective strategy to increase the propagation lengths and lifetimes of PhPs.

Photothermal induced resonance (PTIR) is a scanning probe-based technique that yields nanoscale IR absorption spectra and maps by transducing the light-induced thermal expansion of the sample with the probe tip. In this study, a novel tapping-mode PTIR measurement paradigm with heterodyne detection is implemented to measure PhP propagation and to determine the spectral dispersion in large flakes (up to 120 μm × 250 μm) of isotopically enriched hBN (10B). The high signal-to-noise ratio afforded by this measurement scheme enables imaging PhPs in real space over distances up to 40 μm. Such measurements, coupled with reciprocal space analyses, enables accurate evaluation of PhP propagation lengths, lifetimes, and in-plane wavevectors. Our results confirm for first time, experimentally, that isotopic enrichment provides over a eight-fold improvement in PhP propagation lengths and lifetimes, as predicted by theory. We believe that the measurement scheme developed here and the isotopic enrichment strategy will further foster the engineering and development of high performance PhP-based nanophotonic devices.

EL01.15.27
Graphene-Metal Optical Modulators Using Interband Transition Ziqiang Cai and Yongmin Liu; Northeastern University, United States

Graphene is a well-known 2D material, and its optical property can be tuned by changing its Fermi level [1]. This tunable property makes graphene useful to build novel optical devices, such as modulators. However, due to its atomically thin thickness, the interaction between pristine graphene and light is low, impeding its practical applications. To solve this problem, people have demonstrated that by combining graphene with plasmonic nanostructures, the interaction between light and graphene can be greatly enhanced, which significantly increases the tunability and efficiency of graphene-based optical devices. For photon energy larger or smaller than twice the
Fermi Level, the absorption of light in graphene falls into interband or intraband interaction. Up to now, most of graphene-based modulators utilize intraband transition, corresponding to mid-infrared or terahertz operating wavelengths (e.g. [2]). In contrast, few works reported graphene modulators based on interband transition, corresponding to near-infrared and visible wavelengths. Although in the interband region, graphene plasmons cannot be excited, and surface conductivity is much lower compared with intraband region, the interband interaction has its advantages of insensitivity to graphene quality and step-like change of its surface conductivity, offering the potential to push the working wavelength of graphene modulators into the near-infrared or even visible range. Based on the idea proposed above, we have fabricated a graphene-based modulator, in which graphene is hybridized with metal-insulator-metal (MIM) structures to confine the light intensity around graphene. The resonant wavelength is at 1.5 μm and theoretical modulation depth is 50%. The measured modulation depth is close to 15%, higher than the reported modulation depth of graphene modulator using CVD graphene at the near-infrared wavelength ([3], [4]). By further optimizing the structure design as well as fabrication process, we believe that our device can provide a practical platform for near-infrared tunable optical devices.


EL01.15.28
Exciton Dynamics in Monolayer MoS2 Synthesized by Metal Sulfurization Hsu-Sheng Tsai1, Yung-Hung Huang1, Po-Cheng Tsai1, Zong-Yi Chiao2, Yi-Jia Chen3, Hye-Young Ahn4, Shih-Yen Lin1 and Yu-Jung Lu4; 1Research Center of Applied Sciences, Academia Sinica, Taiwan; 2National Taiwan University, Taiwan; 3National Dong Hwa University, Taiwan; 4National Chiao Tung University, Taiwan

The exciton dynamics in layered transition metal dichalcogenides, pioneering the new family of 2D materials beyond graphene, has been attracting a great attention for several years. Actually, the as-photoexcited carriers in monolayer MoS2 are distributed non-thermally in the electronic bands, and then undergo the thermalization and cooling processes before the formation of excitons. Many works concerning this topic have been done, the MoS2 used in these studies were all obtained by either exfoliation from bulk or chemical vapor deposition (CVD). However, the thickness and area of exfoliated MoS2 cannot be precisely controlled. The optical microscope (OM) and/or atomic force microscope (AFM) images of MoS2 triangular flakes obtained by CVD growth indicate that the MoS2 films are non-continuous even if the dimension is larger than 100 μm. These non-continuous films totally limit the real applications for semiconductor industry. In this study, we report the exciton dynamics in monolayer MoS2 synthesized by novel metal sulfurization method, in which the measured carrier relaxation time is comparable to the exciton dynamics in exfoliated monolayer MoS2 or by CVD growth. The carrier dynamics of A/B excitons were studied by using pump-probe transient absorption spectroscopy with broadband white-light probe beam. It is important to note that the sulfurization growth method can achieve large-scale (1.5 cm x 1.5 cm), continuous, and uniform MoS2 thin films with controllable number of layers. We performed PL measurement, Raman spectroscopy and UV-Vis absorption spectroscopy to study the layer number dependent optical properties. The transient absorption pump-probe spectra of monolayer MoS2 varying with pump energy density and delay time will be discussed. Finally, we conclude the dominant processes of carrier relaxation in monolayer MoS2 are the exciton-exciton annihilation, the trapping of the excitons by surface states, and the interband carrier-phonon scattering. The carrier lifetimes of A/B excitons of the three relaxation processes mentioned above are around 600 fs, 8.7 ps, and 45 ps, respectively.

EL01.15.29
Tunable Exciton-Plasmon Coupling with Strained 2D Semiconductors Yan Joe Lee1, Colin Yule1, Ozgur Burak Aslan1, Yifei Yu2, Linyou Cao2 and Mark L. Brongersma1; 1Stanford University, United States; 2North Carolina State University, United States

Two-dimensional transition metal dichalcogenides (2D TMDCs) are a promising materials platform to integrate with nanophotonic structures due to their strong optical response in the visible spectral range. In particular, their strong
Exciton resonances are stable even at room temperature and allow facile coupling with resonant semiconductor and plasmonic nanostructures. Furthermore, the optical properties of 2D TMDCs are very susceptible to external stimuli because they are atomically thin. Their exciton resonance location (and hence the optical permittivity) can be controlled by methods such as electrical gating, dielectric screening, and strain. This paves the way towards the realization of practical and tunable nanophotonic devices.

In this work, we demonstrate a novel approach to tune the coupling of excitons in 2D TMDCs with plasmonic nanostructures using strain. By straining the monolayer TMDC, we can detune the exciton resonance location from the localized surface plasmon resonance. This then allows us to actively control the coupling between the two resonances and the resulting scattering spectra of the nanostructure. We study the spectral evolution and mode splitting of the coupled plasmonic-TMDC structure. Since we can control the scattering amplitude and/or phase of this coupled system, they act as building blocks for tunable nanophotonic devices and metasurfaces.

SESSION EL01.16: Plasmonic/Nanophotonic Sensing and Spectroscopy
Session Chair: Eyal Feigenbaum
Thursday Morning, December 5, 2019
Hynes, Level 1, Room 102

8:00 AM EL01.16.01
Plasmonic-Assisted Photo-Catalysis—Nothing More Than a Classical Thermal Effect Yonatan Sivan, Ieng-Wai Un and Yonatan Dubi; Ben-Gurion University of the Negev, Israel

Recent experimental studies demonstrated that chemical reactions can be accelerated by adding plasmonic metal nanoparticles to the chemical reactants and illuminate them at their plasmon resonance. It was claimed that the enhanced reaction rate occurs via the reduction in the activation energy driven by the plasmon-induced non-thermal ("hot") electrons [Brongersm, et al, Nature Nanotech (2015)].

In this breaking news, we show that these claims are extremely unlikely to be correct, and that instead, the faster chemical reactions are likely the result of mere heating. To do that, we derive a self-consistent theory of the electron distribution in metal nanostructures under continuous wave illumination [Dubi & Sivan, Light: Science & Application (2019)]. We show that only about one billionth of the energy provided by the illumination goes to creating non-thermal ("hot") electrons, and the rest goes to heating. Quite different from previous theoretical studies, we took account of the heat transfer from the illuminated nanoparticle to the environment via phonon-phonon coupling and ensured energy conservation in the electron-phonon-environment system (rather than just in the electron sub-system). This approach not only allows us to distinguish between the generation of high energy non-thermal ("hot") electrons and the regular heating of the nanoparticles, but also enables the determination of electron and phonon temperatures in a unique and unambiguous way. The theory is then used to compute the rate and energy distribution of electrons that tunnel out of the metal and can participate in a chemical reaction or enable photodetection [Sivan et al, Faraday Discussion (2019)].

Further, we develop a simple model based on the Fermi golden rule and the Arrhenius Law, which shows that the enhanced chemical reactions observed experimentally are highly unlikely to result from the generation of non-thermal non-thermal ("hot") electrons in the metal; instead, it is more likely originate from a purely photo-thermal effect [Sivan et al, Science (2019), Sivan et al, arXiv (2019)]. Specifically, we focus on a few of the seminal papers on this field and identify experimental errors in the temperature measurements that led the authors of these papers to underestimate the photo-thermal effect. Then, we show that the alternative theory of illumination-induced heating can explain the experimental data to remarkable agreement, with minimal to no fit parameters. Comprehensive thermal calculations (whereby we sum properly the heat generated by all particles in the system) confirm the temperature extracted from the experimental data, thus, showing that any claim in these papers related with "hot" electron action is not supported by the data.

Finally, we show that for sufficiently high temperature and/or illumination intensity, it is necessary to account for the thermo-optical nonlinearity due to the temperature dependence of the optical and thermal properties of the...
system [Sivan et al, arXiv (2019)]. We discuss the dominant contributions to the nonlinearity and the sensitivity to the various parameters of the sample and illumination. Our results provide the first ever comprehensive theory of plasmon-assisted photocatalysis and should become the basis for analysis of future experiments; it also reveals various routes for optimization of the chemical reaction acceleration. Our theory is also instrumental in quantifying experiments aimed to enable efficient photodetection.

Reference:
Dubi, Y. & Sivan, Y. Light: Science & Applications; accepted (2019).

8:15 AM EL01.16.02
Nanomechanical Plasmon Spectroscopy—Optomechanics as a New Plasmonic Transducer Daniel Ramos, Oscar Malvar, Javier Tamayo and Montserrat Calleja; CSIC, Spain

We experimentally demonstrate the effect of the localized surface plasmon resonance (LSPR) of a single gold nanoparticle (AuNP) of 100nm in diameter on the mechanical resonance frequency of a free-standing silicon nitride membrane by means of optomechanical transduction. The key effect to explain the coupling in these systems is the extinction cross-section enhancement due to the excitation of the LSPR at selected wavelengths. In order to validate this coupling, we have developed an interferometric readout system with an integrated tunable laser source, which allows us to perform the first experimental demonstration of nanomechanical spectroscopy of deposited AuNPs onto the membrane, discerning in between single particles and small clusters by the frequency shift and polarization sensitivity.

The use of plasmonic structures as sensors is widely spread in recent scientific literature; thus, during the last years we have been witnessing a rising interest in the research on increasing the sensitivity of devices. The most widely used sensor type is based on the concept of surface plasmon resonance (SPR) which is especially sensitive to refractive index changes of the medium surrounding the metal structure, eventually detecting changes in the refractive index of 10⁻⁷. Despite the low-quality factor exhibited by the broad optical resonances, plasmomechanical systems represent an attractive alternative when compared with other optical cavities in literature because the SPR are easily excited by free-space light beams. This issue is of crucial importance because the free-space optomechanical coupling largely decays when the size of the mechanical system is below the wavelength[1,2], which, is needed to achieve high mechanical frequency regime.

We demonstrate the optomechanical coupling that emerges in the plasmonic cavity formed by a AuNP onto a free-standing SiN membrane by means of the excitation of the LSPR, which is related with an enhancement in the extinction cross section of the nanoparticle at a selected wavelength. The extinction is the combination of the absorption and the scattering of the particle; therefore, it becomes a hot-spot on the membrane consequently tuning the mechanical resonance frequency through thermomechanical effects. The LSPR can be tuned by changing the particle diameter or by clustering the particles, which allows the harnessing of the collective plasmonic modes. This cluster coupling usually vanishes when the separation between the particles exceeds the exponentially decreasing distance in which the evanescent field expands, which usually is in the order of few nanometers. However, we demonstrate the use of a membrane to efficiently extend the range of applicability of the coupling between nanoparticles to hundreds of nanometers[3].

We calculated the temperature profile by FEM simulations for different absorption powers from 10nW to 10uW. This temperature profile is translated into a frequency shift by means of the non-released stress generated in the structure due to the thermal expansion and the temperature-dependency of the material Young’s modulus. For integration times of about 3s, we have an Allan variance of 1.1x10⁻⁸, which means that the noise of our fundamental mechanical resonance at 8.6MHz is of 95mHz, which implies that the minimum detectable power is 72pW. On the other hand, the minimum power detectable by the state-of-the-art photodetectors is 2.2nW. Therefore, the proposed optomechanical device is two orders of magnitude more sensitive than a commercially available photodetector.

Magneto-Optical Surface Plasmon Resonance Biosensors with Uni-Axial Magnetic Anisotropy

Mathias Dolci, Xiaokun Ding, Yannick Dusch, Sabine Szunerits, Rabah Boukherroub, Philippe Pernod and Nicolas Tiercelin; Université de Lille, CNRS, Centrale Lille, ISEN, Université de Valenciennes, UMR8520, France

Surface plasmon resonance (SPR) is a surface-sensitive analytical technique used in a variety of biological sensors. The main problem with classical SPR technology is associated with the existence of a lower physical limit of detection (LOD) with respect to fluorescence. Various approaches have been proposed to overcome this limitation by developing different sensing concepts including phase-sensitive detection schemes, use of metallic nanostructures, line gratings and others. More recently, the addition of active functionalities to the SPR based devices have been proposed to enhance the intrinsic sensitivity of the SPR system. A magneto-optical (MO) SPR sensor, based on a magneto-plasmonic modulation technique produced in multilayers of noble and ferromagnetic metals has been lately proposed.

The use of a trilayered thin film structure (e.g. Au/Ferro/Au) allows to provide a transverse magneto-optical Kerr effect(TMOKE) of the p-polarized light. This TMOKE signal exhibits an improved physical sensitivity over classic SPR measurements thanks to the non-reciprocal modification of the surface plasmon wave vector induced by the magnetization in the ferromagnetic layer which is controlled by the applied magnetic field. Beyond sensing techniques, this modulation of the surface plasmon wave vector in this kind of architecture allows for applications in active plasmonics such as optical switches.

Here, we propose a novel combination of metals based on exchange coupled ferrimagnetic multilayer thin films composed of TbCo2 stacked with FeCo providing a well-defined in-plane and uniaxial magnetic anisotropy thus giving rise to an easy and a hard magnetization axis in the layer. This specific structure adds a new behavior to exploit the active control of surface plasmon resonance. Simulationsof the Magneto-Optic SPR effect in our structures were performed using a finite element software. The dielectric tensor, including magneto-optical constants of the TbCo2/FeCo multilayers was measured by ellipsometry, whereas standard parameters were used for the noble metal. Experimental studies were made by coupling our architecture with a modified-SPR commercial setup equipped with an external magnetic field and controlled by a Labview program. Measurements show a significant increase of sensitivity when used in a magneto-plasmonic configuration. Moreover, the measured plasmonic properties perfectly reflect the magnetization characteristics along the easy and hard axes allowing an indirect local measurements of the magnetic properties of the sample, and confirm the performed simulations. Methods, simulations and measurements will be shown and discussed at the conference. The interest of this novel sensing device for the detection of cardiac biomarkers such as troponin I will also be shown.

suffers from a low absolute optical absorption of ~1-2% depending on the substrate. [1] This significantly limits its efficiency as surface-incident photonic devices. Here we demonstrate a semimetal-dielectric-metal (SMDM) cavity structure that synergistically integrates near-field absorption enhancement with a Fabry-Perot cavity to address this challenge. The SMDM cavity structure consists of self-assembled, close-packed ultrahigh refractive index semimetal Sn nanodots (n=8~9 at λ=1600–5000 nm [1]) on a SLG/SiO2/Al stack. The nanogaps (~10 nm) between Sn nanodots effectively funnel the incident light into the underlying SLG regions with >100x electromagnetic field enhancement, and scatter the incident light into oblique angles. SLG absolute absorption has already achieved 5-15% over the visible and near infrared light regimes without a SiO2/Al stack. Reflection by the backside Al layer and coupling into the SLG (high index and a 2D Dirac semimetal at room temperature)/SiO2/Al cavity further enhances the SLG absorption to up to 25% in a broad spectral regime of λ=500-2500 nm. The enhanced SLG absorption has also been confirmed by field-enhanced Raman scattering and significantly increased photo-conductivities. This is much advantageous over the conventional plasmonic approach which uses costly materials (typically Au or Ag) and has a narrow resonant peak, as well as the nanophotonic design which requires a complicated and precise lithography in nanoscale. [2, 3] Further tuning the thickness of SiO2 dielectric optical medium and the size/gap of Sn nanodots, our design even shows an optimal SLG absorption of 40-45% at λ=1500-2500 nm. This work offers a new approach for high efficiency, broad-band, nanoscale photon management in 2D photonics, which is also compatible with nano-fabrication foundries in terms of scaling up photonic device fabrication.


9:00 AM EL01.16.05
Tunable Hybrid Metal-Nitride Metamaterial Framework towards Plasmonic Sensing and Nanophotonic Device Integration **Xuejing Wang**1, Haiyan Wang1, Xinghang Zhang1, Lia Stanciu1, Ping Lu1, Xuedan Ma1 and Deirdre O’Carroll1; 1Purdue University, United States; 2Sandia National Laboratories, United States; 3Argonne National Laboratory, United States; 4Rutgers University, United States

The advance on hybrid metamaterial design using bottom-up fabrication technique brings multiple advantages towards sensing and large-scale nanophotonic device integration. In our work, a novel two-phase plasmonic framework with Au nanoantenna arrays being embedded inside a titanium nitride (TiN) matrix was demonstrated, with easy access of controlling the packing density or aspect ratio. Advantages include sub-10 nm nanoantenna arrays, high crystalline quality, inch-scale fabrication as well as high durability. Such geometrical flexibility brings tunable resonance frequency and anisotropic dielectric dispersion at optical regime. We demonstrate effective molecular sensing affected by the surface-enhanced plasmonic substrate with built-in Au antenna array. Our functional hybrid thin film template, as a first step, can be applied to many three-dimensional metamaterial designs, we will show some of our latest research progresses on nanostructures and applications using such hybrid template.

9:15 AM EL01.16.06
Direct and Simultaneous Absorption and Scattering Measurements of Single Plasmonic Particles Using Integrating Sphere Microscopy **Eitan Oksenberg**1, Andrea Baldi2 and Erik Garnett1; 1FOM Institute AMOLF, Netherlands; 2Differ - Dutch Institute for Fundamental Energy Research, Netherlands

The spectral behavior of localized surface plasmon resonances is often studied using ensemble spectroscopy techniques, which provide average values of resonance energies and broadened line-widths due to varying sizes and shapes of the nanostructures. Single particle measurements can offer a sharp and distinct spectral fingerprint of plasmonic nanostructures but they often probe only the scattering profile or a mixture of multiple light-matter processes. Here we introduce integrating sphere microscopy as a method to probe directly and simultaneously the scattering and absorption behavior of single plasmonic nanostructures. We use this technique to quantitatively characterize the energy, line-width and extinction cross-section of the localized surface plasmons of single nanostructures. Our measurements are compared with theory and used to trace hot-electron chemical reactions on the surface nanostructures. The realization of a direct measurement of the scattering and absorption of a single plasmonic entity allows to probe with superior resolution physical and chemical processes that are induced by localized surface plasmon resonances.
9:30 AM BREAK

SESSION EL01.17: Plasmonics II
Session Chair: Yu-Jung Lu
Thursday Morning, December 5, 2019
Hynes, Level 1, Room 102

10:00 AM *EL01.17.01
Metal Hydrides as a Platform for Reconfigurable Photonic and Plasmonic Elements Kevin Palm1 and Jeremy N. Munday1,2; 1University of Maryland, United States; 2University of California, Davis, United States

The ability to control the optical properties of photonic materials on demand is essential for the operation of a variety of devices ranging from active color filters and routers to switchable mirrors and sensors. Here we will present our latest work on actively controllable photonic devices using metal hydrides. We have developed an apparatus for in situ measurements of hydrogen content and optical and mechanical response. Using this apparatus, we will show the dynamically tunable optical properties of several metals and alloys over a broad spectral range (250 - 1690 nm) and discuss a number of devices including structures that have five orders of magnitude change in reflectivity, as well planar systems for physical encryption and counterfeit detection. Finally, we investigate the hydrogen-loading amounts for several metal alloys and find higher loading amounts when compared to previous measurements for alloys with low atomic percent Pd, resulting from film stress and microstructuring. These results have led to new insights in the dynamic behavior of metal-hydrides and will help in the design of next-generation hydrogen sensors and tunable photonic devices.

10:30 AM EL01.17.02
Unidirectional Excitation of Surface Plasmon Polaritons via a Meta-Grating with Parity-Time Symmetry Yihao Xu, Lin Li and Yongmin Liu; Northeastern University, United States

Over the past years, there has been rapidly growing interest in non-Hermitian photonic systems. In 2003, Bender et al. proved that a Hamiltonian is not necessarily Hermitian to have a real spectrum. For instance, a Hamiltonian with Parity-Time (PT) symmetry can show real spectrum below a certain threshold, known as the exceptional point, accompanied with novel phenomena above the EP. Thanks to the equivalence in mathematical forms between the Schrödinger equation in quantum mechanics and the paraxial wave equation in optics, we can conveniently explore unique phenomena and properties of PT systems in optics, which will accelerate the development of novel optical devices.

Here we propose a plasmonic meta-grating with PT symmetry to excite unidirectional surface plasmon polaritons (SPPs). The basic principle is based on the behavior of the PT system around the exceptional point, where only directional propagation mode of SPPs is allowed. We have designed realistic grating array consisting of passive gratings (i.e., without gain materials), which can significantly reduce the challenges in fabrication and optical experiments. In addition, instead of using ideal sinusoidal permittivity modulation in simulation in former paper, here we demonstrate in both simulation and experiment that using discrete grating array can also achieve excellent contrast between SPPs in opposite directions at the working wavelength around 1150nm.

In addition to the unidirectional excitation of SPPs, we have designed PT symmetric meta-gratings to realize other intriguing functionalities, such as a unidirectional plasmonic distributed Bragg reflector, that is, a plasmonic diode, that shows selective reflection/transmission for SPPs with high contrast. To achieve this function, we need to modify the 2nd order Fourier coefficient for permittivity modulation, which is proportional to the reflectance of SPPs incident from the left and right.

In summary, we have demonstrated a sub-wavelength plasmonic grating structure with PT symmetry for unidirectional excitation and transport of SPPs. These results can be potentially employed as a new approach to designing transformative nanoscale optical devices, such as low-loss plasmonic routers and isolators for efficient optical computation, communication, and information processing.

**10:45 AM EL01.17.03**

**Excitation of Epsilon-Near-Zero Mode in Optical Fiber Coated with Ultrathin Aluminum-Doped Zinc Oxide Film**

*Jingyi Yang*¹, Khant Minn¹, Aleksei Anopchenko¹, Sudip Gurung¹ and Ho Wai (Howard) Lee¹;² ¹Baylor University, United States; ²Texas A&M University, United States

Near-zero refractive index systems, i.e., with vanishing permittivity and permeability values, have been shown to exhibit unique and extreme optical properties. Ultrathin epsilon-near-zero (ENZ) layer can support plasmon polariton mode with enhanced and highly-confined optical field [1]. Recent studies on ultrathin transparent conducting oxide (TCO) ENZ film have proposed various optical applications such as broadband perfect absorber [2], enhanced ENZ nonlinearity [3] and electrically tunable meta-devices [4, 5], etc. However, most of the recent studies on ENZ materials are limited in planar structures or metasurfaces with a relatively short length of light-matter interaction and operation, which restricts the excitation platform for developing novel optical devices with advanced functionalities.

In this work, we report the first experimental demonstration of ENZ mode excitation in D-shaped optical fiber nano-coated with aluminum-doped zinc oxide (AZO) layer via atomic layer deposition (ALD) [6]. The ultrathin AZO layer possesses ENZ property (real part of permittivity crosses zero at a wavelength of 1546 nm) in near-infrared wavelength regime. The evanescent optical field of the guided core mode of D-shaped fiber interacts with the ultrathin AZO ENZ layer on the side-polished portion to excite the ENZ mode. Highly polarization- and wavelength-dependent transmission with on and off ENZ resonance difference of ~20 dB at a wavelength of ~1600 nm in ENZ regime is observed in a 1.7 cm-long ENZ-optical fiber with a 30 nm-thick AZO layer. The measurements show a good agreement with full-wave numerical simulation and phase matching condition between fundamental core mode of D-shaped fiber and ENZ mode supported by ultrathin AZO layer. Compared to the excitation of ENZ mode on the planar substrates, the hybrid ENZ mode on the optical fiber exhibits much lower loss and relatively long light-matter interaction length of a few centimeters. The hybrid ENZ-optical fibers provide a novel platform for zero-index photonic applications, for instance, studying enhanced ENZ nonlinearity in fiber, quantum emission in ENZ media, and subwavelength mode enhanced in-fiber optical- and bio-sensing.

This work was supported in part by the Young Faculty Award Program from Defense Advanced Research Projects Agency (grant number N66001-17-1-4047), Robert A. Welch Foundation (award number: AA-1956-20180324), and the Vice Provost for Research at Baylor University.

1. Liberal, I.; Engheta, N. *Nature Photonics* 2017, **11**, (3), 149.

**11:00 AM EL01.17.04**

**IR Plasmonic Thermopile via Epsilon-Near-Zero Plasmons Using Y:CdO/Au Junctions**

*Joshua Nordlander*¹, Angela Cleri¹, Kyle P. Kelley², Evan Runnerstrom³, Patrick E. Hopkins⁴, Brian Foley¹ and Jon-Paul Maria¹;² ¹The Pennsylvania State University, United States; ²Oak Ridge National Laboratory, United States; ³U.S. Army Research Office—Materials Science Division, United States; ⁴University of Virginia, United States

CdO thin films have generated interest due to high electron mobilities with tunable carrier concentrations via substitutional doping with Y (Y:CdO). This combination of mobility and carrier concentrations have been used to support plasmonics in the mid-infrared spectrum spanning from 2.5 µm to 8 µm in wavelength. As the thickness of a film is reduced far below the skin depth of the material, a plasmonic mode known as an epsilon-near zero (ENZ) mode becomes active. This plasmonic mode is highly absorbing and highly confining of the incident electric field. One can create a Y:CdO/Au thin film junction, where the work function difference results in a small EMF. Illuminating this structure with IR light at ωIR=ωENZ produces strong absorption and an increased Tε in Y:CdO. As
electrons equilibrate with the lattice, the Y: CdO temperature increases thus changing the junction EMF. Y: CdO films were fabricated via HiPIMS sputtering, and junctions were created via photolithography techniques. The thermopile output voltage increases with increasing incident laser power, and is linear with the number of thermopile junctions. 30 µV were measured between 10 junctions with an incident laser power of 350 mW without optimization of the illumination area.

11:15 AM EL01.17.05
Tunable Single-Electron Tunneling from Metal into PbS/InP Neuromorphic Computing Building Blocks
Richard M. Osgood1, Paulo Jarschel2,3, Jin Ho Kim2, Hao Peng2, Sean Dinneen1, Yassine Ait-El-Aoud1, Yassine Ait-El-Aoud1, Jimmy Xu2 and Bruno Granddidier2; 1Combat Capabilities Development Command - Soldier Center, United States; 2Brown University, United States; 3"Gleb Wataghin" Physics Institute, Brazil; 4Univ. Lille, CNRS, Centrale Lille, ISEN, Univ. Valenciennes, UMR-8520-IEMN, France

The field of plasmonics and metasurfaces has advanced by leaps and bounds in the last 10-15 years, but ohmic losses continue to slow technological advances and scientific understanding. There is a need for plasmonic metasurfaces with tunable conductivity, instead of relying on fixed conductivity of ohmic metals. Here, we explore a novel material – a crystalline PbS/InP heterojunction – that is voltage-tunable, exhibits single-electron tunneling (SET), and has possible applications to neuromorphic computing. A neuromorphic computing architecture would go beyond traditional von Neumann linear architecture to a bio-inspired (neural) network of non-linear devices and weighting elements responsible for data processing, allowing much faster computation [1,2]. We report on tip-based tunneling measurements and analysis of SET in self-formed oxide interfaces between the two materials, which exhibit single-electron Coulomb-blockade staircases along with memory and memory-fading behaviors. This gives rise to both short-term and long-term (seconds and hundreds of seconds, respectively) plasticities as well as a convenient non-linear response, making this structure attractive for neuromorphic computing applications. We predict typical behaviors relevant to the field, obtained by an extrapolation of experimental data in the SET framework. The estimated minimum energy required for a synaptic operation is in the order of 1 fJ, while the maximum frequency of operation can reach the MHz range. Comparatively, the human brain synapses consume more energy (~pJ) and operate at a slower rate (1 ms or 1 kHz) [3], which demonstrates the potential of the proposed structure for such applications.


11:30 AM *EL01.17.06
Plasmon-Enhanced Energy Transfer via Nanostructures
Alireza Rahimi Rashed, Mohsin Habib, Nekhel Das and Humeyra Caglayan; Tampere University, Finland

In this work, we have designed and fabricated an array of plasmonic nano-ellipses that interacts with different types of quantum emitters (QEs) in the visible range of wavelength. The proper geometry of our design provides such absorption-reflection properties which spectrally overlap with emission spectrum of the QE. Alongside such spectral overlap, a thin layer of the dielectric layer between the plasmonic structures and a gain medium provides the possibility of spatial overlap. The interaction between the strong subwavelength localized field at the edges of the gold nano-ellipses and QEs, enhances Purcell factor towards the modification of the fluorescence and decay time of QEs. This approach allows enhanced emission from different emitters embedded in hybrid quantum systems. In this work, we study the energy transfer between the fluorescent dye molecules and CdSe/ZnS hydrophobic QDs with the array of plasmonic nano-ellipses.
1:30 PM *EL01.18.01
Visualizing Conformational Changes of Biomolecules Using Optical Force Microscopy In Situ Yang Zhao¹, Yun-Sheng Chen¹, Jack Hu², David R. Barton², Michelle Solomon², John Abendroth², Keino Davis², Lisa Poulakos², Katherine Sytwu² and Jennifer A. Dionne²; ¹University of Illinois Urbana Champaign, United States; ²Stanford University, United States

Many biological processes are associated with conformational changes of macromolecules such as enzymes, proteins, and DNAs. Currently, these dynamic processes can be observed indirectly through techniques such as optical tweezers, Förster resonance energy transfer (FRET), and optical beacon or directly with ultra-high frequency atomic force microscopy (AFM). While the last example points to the promises using AFM to directly visualize the molecules of interest, it only limits to certain processes where the speed is slower or comparable with the mechanical scanning of AFM. In this talk, I will discuss a new approach to visualize the conformational changes of biomolecules in situ. We constructed the technique based on the force exerted by polarized light on biomolecules. To enhance the light-molecular interactions, we created a plasmonic cavity formed between the plasmonic AFM tip and a plasmonic nano-aperture. We have shown that the plasmonic nano-aperture can exert differential optical forces down to piconewton ranges when illuminated with circularly polarized light of opposite handedness. Here, instead of a nano-structured AFM tip, we functionalize DNA molecules on the plasmonic AFM tip with a controlled density. We investigate both single strand and double strand DNAs at 20-base pair length with various densities. We are able to measure the difference in optical forces with a sensitivity of ~2.1pN/100uW/um². This sensitivity is associated with the optical forces exerted on single strand and double strand DNA molecules embedded between the plasmonic cavity. In addition, by introducing denaturing agent to the solution, we observed in-situ dynamic conformational changes of the double-strand DNA molecules, directly measured with the optical force microscopy technique.

2:00 PM EL01.18.02
Energy-Tunable Hot Carrier Photocatalysis with Surface Plasmon Polaritons Wonmi Ahn¹, Igor Vurgaftman¹, Jeremy J. Pietron², Pehr Pehrsson² and Blake S. Simpkins²; ¹Excet Inc., United States; ²U.S. Naval Research Laboratory, United States

The decay of surface plasmons generates hot carriers that can be injected into semiconductors or molecular systems, opening a new pathway to drive photo-induced chemical reactions. Recent studies demonstrate that by tuning plasmon resonance of metal nanoparticles hot carriers may be injected into specific anti-bonding orbitals of an adsorbed molecule and therefore the product selectivity can be achieved. In this talk, we will demonstrate surface plasmon polariton (SPP)-induced hot carrier generation that has a potential for energy-tunable photocatalysis. Unlike metal nanoparticles that suffer from resonance inhomogeneity and limited spectral tunability, metal films support SPPs that are homogeneous in-plane and accessible by simply tuning an illumination angle in a broad spectral range. We measured electrochemical responses of a metal/semiconductor heterofilm (Ag/TiO₂) and a bare metal film (Au) that were contacted with a mixed solution of sodium hydroxide and methanol. A strong photon energy dependence in the photon-to-carrier conversion efficiency was obtained from the heterofilm and this was further confirmed by the hole injection efficiency calculated using a Schottky transport model. Hot carriers generated in the bare metal film were energetically positioned near the metal's Fermi level, and therefore, chemical reactions were controlled by tuning electrode potential or solution pH. Both of these results have important implications for plasmon-induced photocatalysis, especially for energy-tunable chemical reactions.


2:15 PM EL01.18.03
Hyperbolic Meta-Antennas—Arbitrary Control of Light Scattering and Absorption towards Thermo-Plasmonic Bio-Medical Applications Nicolo Maccaferri¹,², Yingqi Zhao², Tommi Isoniemi², Marzia Iarossi², Antonietta Parracino², Giuseppe Strangi² and Francesco de Angelis²; ¹University of Luxembourg, Luxembourg;
Besides its fundamental importance, manipulation of light at the nanoscale is of great interest for the prospect of real-life applications, such as energy harvesting and photovoltaics, wave-guiding and lasing, optoelectronics, biochemistry and medicine. Novel optical designs and architectures that modify the optical power flow through plasmonic nanostructures represent another crucial step towards a nanoscale manipulation of light-matter interactions. In this framework hyperbolic metamaterials (HMMs) have received great attention due to their unusual properties at optical frequencies that are rarely or never observed in nature [1-2].

Here, we report about unconventional optical properties of metal-dielectric meta-antennas supporting type II hyperbolic dispersion, which enable almost pure and spectrally separated absorption and scattering channels in the visible/near-infrared spectral range [3]. We demonstrate that the physical mechanism responsible for the control of scattering and absorption lies in the different nature of the plasmonic modes excited within the hyperbolic meta-antennas. We also show that scattering is the dominating electromagnetic decay channel, when an electric super-radiant dipolar mode is induced in the system, whereas strong light absorption occurs when a magnetic sub-radiant dipole is excited. Importantly, both modes can be excited directly by coupling with far-field radiation, thereby making the proposed architecture suitable for practical applications. In this framework, we demonstrate also that HMM meta-antennas could find promising applications in photo-thermal therapy. Our findings open the pathway towards novel routes for exploiting light to energy conversion channels beyond what is offered by current plasmon-based architectures, possibly enabling applications including thermal emission manipulation, thermoplasmonics-based theragnostic nano-devices, novel nano-antenna designs and plasmon-enabled enhanced molecular spectroscopy.


2:30 PM EL01.18.04
Visualizing Plasmon Photocatalysis on Individual Bimetallic AgPd Nanoparticles with Concurrent Optical and Electron Spectroscopy Daniel Angell, Briley Bourgeois, Michal Vadai and Jennifer A. Dionne; Stanford University, United States

Bimetallic nanoparticles have emerged as a promising class of photocatalysts for chemical processing, energy harvesting, and environmental remediation. By alloying multiple metals together within a nanoparticle, significant improvements in reactivity as well as product selectivity have been realized. However, to date, most measurements are conducted on particle ensembles, where limited spatial resolution and averaging effects conceal important details about the photocatalytic mechanisms and optical properties of individual nanoparticles. To improve the efficiency of bimetallic photocatalysts, it is crucial to understand how their nanoscale properties such as shape, size, crystallinity and composition, affect performance.

Here, we investigate the photocatalytic efficiency of individual bimetallic nanoparticles, focusing on the light-driven dehydrogenation of AgPd single crystalline prisms. The particles are synthesized through the reduction of palladium and silver salts by formaldehyde, resulting in monodisperse prisms with edge lengths of approximately 35nm. We systematically vary the concentration of Ag in the nanoparticle from 0% to 2%, 5%, 10%, 20%, 30%, and finally 40%. The particles are dispersed onto a SiO2 grid, and a combination of electron imaging, diffraction, and electron energy loss spectroscopy (EELS) are used to follow the photocatalytic transformation. First, using monochromated EELS, we determine how the Ag concentration affects the plasmonic modes in individual AgPd triangular prisms. For the corner, edge, and bulk plasmon modes, we see dramatic shifts in the plasmon resonance energies with increasing Ag composition: 7.5eV to 6eV for the bulk, 5.8eV to 4.1eV for the edge, and finally 3eV to 1.9eV for the corner mode, for a composition change of 0% to 30% Ag. Although resonance shifts are observed, we see minimal change in comparative extinction cross-sections. Next, we illuminate the particles on their plasmon resonances and follow the dehydrogenation of these individual nanoparticles in an environmental TEM. Our TEM setup consists of an optical fiber coupled to a parabolic mirror for in-situ sample illumination, while concurrently allowing gas flow to the sample. We introduce H2 gas at pressures of ~20Pa - 40Pa and observe the light-driven transformation of individual AgPd nanoparticles from the H-rich phase to H-poor phase. Using both direct imaging of the propagating grain boundary defect, as well as the change in bulk plasmon resonance via low-loss EELS, we show that the phase transformation progresses to minimize the planar defect area at the phase boundary. While the dark-
state kinetics decrease with increasing Ag concentration, illumination on resonance can lead to an order-of-magnitude increase in reaction kinetics. Importantly, the transition speed is linear in time and is therefore not limited by hydrogen diffusion but rather by surface-reaction-rates. Furthermore, the speed is correlated with excitation of the edge plasmon mode. We discuss how the transformation kinetics and mechanism vary with illumination wavelength and power, and we can correlate these changes with an individual nanoparticle’s specific plasmonic modes and chemical composition. Our results help elucidate the combined roles of electronic and chemical contributions to bimetallic catalysis, informing optimized alloy concentration and nanostructure for record efficiency.

Highly Frequency-Selective Light Redirection for Optical Eye Tracking in Rainbow-Free Guided-Mode Resonance Diffractive Optical Elements with Near-Unity Transmission Jung-Hwan Song, Jorik Van de Groep and Mark L. Brongersma; Stanford University, United States

Augmented Reality (AR) is a technology which superimposes information or optical images onto the real-world environment of an observer. It is challenging to create optical elements that can seamlessly overlay images on top of a real scene and offering high transparency across the visible spectrum. Typically, bulky optical systems are required, but recent advances in holographic diffractive optical elements (DOE) have precipitated new approaches to realize high-performance AR displays. Unfortunately, high-diffraction-efficiency DOEs tend to produce undesired rainbows and image distortions. Many of the same opportunities and challenges hold true for eye-tracking systems. Here, we demonstrate an ultracompact, near-unity transmission, and rainbow-free optical eye tracking DOE based on a guided-mode resonance structure. To realize this optical element, we first prepare an anti-reflection coating on a quartz substrate by depositing a 200-nm-thick Si₃N₄ slab capped with a 100-nm-thick SiO₂ layer. This dielectric stack affords high transmission (~90%) over the entire visible spectrum. The nitride layer also serves as a waveguide that support a single transverse electric and transverse magnetic mode in the frequency range of interest. For this reason, this system can be turned into a guided-mode resonator by placing 3-nm-thick Si gratings between the Si₃N₄ and SiO₂ layers with 1-μm-long periodicity. Upon the planewave incidence, the scattered light from the Si grating elements can couple light into quasi-guided modes supported by the nitride layer. This guided light is primarily absorbed or diffracted, depending on the frequency of the incident light. We observe a high quality (Q~1000) guided-mode resonance at 870 nm wavelength and rigorously characterize the dispersion properties with a home-built angle-resolved confocal spectroscopy microscope. The spectrally sharp (<1 nm) resonant diffraction with a high peak diffraction efficiency (≈13%) to first-order diffracted beams is also directly measured under the normal incidence illumination. In contrast, across the visible spectrum the guided-mode resonance is dampened severely due to light absorption by the Si grating. This achieves the successful suppression of visible rainbows and diffraction efficiencies into the diffracted-orders are below 0.1% across the visible spectrum.

As a prototype eye tracking device, we fabricate a 2-cm-wide guided-mode resonance glass and attach it to a regular eyeglass frame. A small 870 nm light-emitting diode (LED) suspended on the eyeglass frame illuminates an artificial eye in front of the glasses. The scattered light from the eye is redirected by the optical element into a 1.6-mm-wide endoscopic camera located at the temple arm of the frame. The images formed by the diffracted rays allow the endoscopic camera to capture the full front-view of the eye even viewing at an oblique angle (60°). We also mathematically formulate all the relevant physics of the image formation with this element. We anticipate that our guided-mode resonance platform opens a promising route to realize new types of AR optical devices and elements for three-dimensional holography.

Durable Meta-Optics for Powerful Lasers Applications Eyal Feigenbaum; Lawrence Livermore National
The field of optical meta-surfaces is rapidly growing due to its great potential to enable thin optics implementation with relatively complex and flexible functions. In particular, high power laser systems could benefit from meta-optics that could implement beam shaping, e.g., for wave-front aberration correction, but with the advantages of smaller accumulation of nonlinearity and lighter weight. Additionally, meta-surface technology could enhance laser optics with improved anti-reflective layer designs.

Current meta-surface technology is limited with respect to high power laser optics, which requires both scalability and laser intensity durability. The principal challenge arises from the necessity of patterning sub-wavelength features (to control the local optical properties by modifying geometrical properties) while being able to modify the structural parameters on the large optics scale used in high power laser systems (e.g., National Ignition Facility, Laser MegaJoule). The current patterning methods are either limited in scalability (e.g., FIB, e-beam lithography) or limited in robustness due to the usage of soft-materials (e.g., nanoimprint).

We are developing novel technology capable of generating robust and scalable all-dielectric based meta-surfaces. In this talk we will describe the method, show results of fabricated meta-surfaces, and discuss the various levels of control that we have with this process. This method extends the current application field of interest for meta-surfaces to high power lasers, with the potential to stimulate meta-surface utilization in additional fields requiring large and robust optics.

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4:00 PM EL01.19.02
TiO$_{2-x}$ Enhanced IR Hot Carrier Based Photodetection in Metal Thin-Film-Si Junctions

Nicholas A. Güsken$^1$, Alberto Lauri$^1$, Yi Li$^{1,2}$, Takayuki Matsui$^1$, Brock Doiron$^1$, Ryan Bower$^1$, Anna Regoutz$^2$, Andrei Mihai$^1$, Peter K. Petrov$^1$, Rupert Oulton$^1$, Lesley Cohen$^1$ and Stefan A. Maier$^{1,2}$; $^1$Imperial College London, United Kingdom; $^2$Ludwig-Maximilians-Universität München, Germany

The extraction of hot carriers at a Schottky barrier interface has attracted enormous attention for example due to the possibility to create a photovoltage in a semiconductor/metal junction without being limited by the semiconductor bandgap energy. In particular the use of hot holes for these types of devices has not yet been studied extensively while recent studies predict an increase in extraction efficiency compared to their hot electron counterparts$^1$.

Here$^2$, we perform hot hole photodetection measurements on a simple p-Si/metal thin film junction using various metals such as Ti, Au and Titanium nitride (TiN). TiN is of particular interest as it constitutes a refractory alternative to other materials used for plasmonic applications where high field intensities exceeding the melting point of commonly used metals can occur. Resonantly excited plasmonic structures lead to strong fields in the vicinity to the metal surface which has been demonstrated to give rise to energetic and large hot carrier distributions.

We show that a backside illuminated p-Si/TiN system can be used for efficient hot hole extraction allowing for a responsivity of 1 mA/W at an excitation wavelength of 1250 nm and at zero bias. Our results unambiguously demonstrate that a few nanometer thin TiO$_{2-x}$ interfacial layer forming during growth at the Si/TiN interface allows for an increase in photoresponsivity of about one order of magnitude compared to a clean p-Si/metal interface. The direct comparison between a p-Si/Au and p-Si/TiO$_{2-x}$/Au further underpins this observation and additionally shows that the photoresponse dispersion relation of a TiO$_{2-x}$ thin film containing system deviates clearly from the response of a p-Si/metal system and thus from the commonly used Fowler description. Despite the fact that based on a bandgap energy of about 3.2 eV, TiO$_{2-x}$ is expected to act as a hole blocking layer, our results show a strong photoresponse. Thus, we propose a trap state mediated carrier transfer mechanism which is further supported by results obtained via electrical transport measurements.

References:

4:15 PM EL01.19.03
Quantum Dot Lasing from Plasmon-Based Nanocavities

Jun Guan$^1$, Laxmi Kishore Sagar$^2$, Ran Li$^1$, Danqing
Plasmonic nanolasers are important for fundamental studies of light-matter interactions and applications in on-chip photonic integration. Metal nanoparticle arrays supporting surface lattice resonances (SLRs) can provide optical feedback for directional lasing emission at room temperature. However, current SLR lasers rely on organic dye molecules as the gain media and show limited photostability. Colloidal quantum dots are promising gain materials because of their long-term stability, bright photoluminescence, convenient solution processing, and size-controlled spectral tunability. Here we show quantum dot lasing from SLR-based nanocavities. Our quantum dot-plasmon lasers exhibit low thresholds and engineered far-field properties. In addition, we demonstrated the energy transfer between excitons and plasmons by investigating the lasing dynamics.

4:30 PM EL01.19.04
Anisotropic Thermal Magnetoresistance in Radiative Heat Transfer
Antonio Garcia-Martin; Inst. de Micro y Nanotecnologia - CSIC, Spain

The possibility to create and manipulate nanostructured materials encouraged the exploration of new strategies to control the electromagnetic properties without the need to modify its physical structure, i.e. by means of an external agent. An approach is the combination of magneto-optically active and resonant materials (e.g. plasmonic modes), where it is feasible to control the optical properties with magnetic fields in connection to the excitation of resonances [1] (magnetoplasmonics). It has been shown that these nanostructures can be employed to modulate the propagation wavevector of SPPs [2], which allows the development of label free sensors with enhanced capabilities [3-5] or to enhance the magneto-optical response in isolated entities as well as films, in connection with a strong localization of the electromagnetic field [6-8].

Here we will show that they also play a crucial role in the active control of thermal emission and the radiative heat transfer (RHT) [9-11]. In particular Near Field RHT between two MO particles can be efficiently controlled by changing the direction of the magnetic field, in the spirit of the Anisotropic Magneto Resistance in spintronics [11]. This phenomenon, which we term anisotropic thermal magnetoresistance (ATMR), stems from the anisotropy of the photon tunneling induced by the magnetic field. We discuss this effect through the analysis of the radiative heat exchange between two InSb particles, and show that the ATMR can reach amplitudes of 100% for fields on the order of 1 T and up to 1000% for a magnetic field of 6 T. These values are several orders of magnitude larger than in standard spintronic devices. More importantly, this thermomagnetic effect paves the way for exploring heat transfer physics at pico- and even subpicosecond time scales, which are even shorter than the relaxation time of heat carriers. Moreover, we show that the heat flux is very sensitive to the magnetic field direction, which makes this effect very promising for the development of a new generation of thermal and magnetic sensors.

References:

4:45 PM EL01.19.05
Lead Halide Perovskite Based Plasmonic Upconversion Nanolaser
Yu-Jung Lu1,2,3, Teng Lam Shen1, Wen-Hui Cheng1, Chih Wei Chu1, Tsung-Fang Guo1 and Harry A. Atwater3; 1Academia Sinica, Taiwan; 2National Taiwan University, Taiwan; 3California Institute of Technology, United States; 4National Cheng Kung University, Taiwan
Organo-lead halide perovskite materials have recently received considerable attention for achieving an economic and tunable diode laser, owing to the use of solution-processable materials and the exceptional optical attributes of long carrier lifetimes and diffusion lengths, high fluorescence quantum yields, wavelength tenability, high optical gain coefficients, and promising two-photon absorption properties. However, reducing the volume of such lasers to the nanoscale is the challenge nanophotonics, with potential applications in arrays of ultra-compact lasers on a chip. Nanoplasmonic devices facilitate strong light-matter interactions at nanoscales, thus providing unique opportunities to control and manipulate radiative emission. Here, we report a novel plasmonic enhanced upconversion nanolaser consisting of a subwavelength organo-lead-halide perovskite nanocrystal on a 5-nm Al₂O₃ film on top of a plasmonic TiN film. A pump-probe transient absorption spectroscopy was used to study the photon-recycling-effect of perovskite nanocrystals as excellent optical gain media. Hence, we experimentally and theoretically demonstrated the localized strong optical filed enhanced single-mode lasing emission through two-photon absorption process in single perovskite nanocrystal coupled with plasmonic cavity. With the plasmonic cavity, the measured upconversion lasing threshold (200 nJ/cm²) was reduced by more than two orders of magnitude. Finally, we will discuss the outlook for upconversion plasmonic nanolasers in applications including, on-chip coherent light sources for bio-imaging, optical communication applications.

SESSION EL01.20: Poster Session IV: Novel Photonic Materials and Nanoparticles II
Session Chair: Ho Wai (Howard) Lee
Thursday Afternoon, December 5, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EL01.20.01
Seeded Growth Synthesis of Uniform Gold-Silver Alloy Nanoparticle and its Etching Study
Xingming Situ, Serene Bayram and Amy Blum; McGill University, Canada

Noble metal nanoparticles are one of the most interesting and well-studied nanomaterials because of their versatile preparation and their attractive electrical and optical properties. Alloyed noble metal nanoparticles have opened up new possibilities in applications such as in heterogeneous catalysis, electro-catalysis, imaging and surface enhancement Raman spectroscopy due to their tunable plasmonic properties. This tunability can come from controlling both the composition and the size in the synthesis of nanoalloys. Herein, we introduce a seeded growth synthesis of gold-silver alloy nanoparticles by chemical co-reduction in aqueous solution. Using gold acetate or gold chloroauric acid and silver nitrate as precursors and sodium citrate as the main reductant and stabilizer, we successfully synthesize stable gold-silver nanoalloys with diameters from 15 nm to 80 nm. The size of alloy nanoparticles can be controlled by the number of growth steps and the amount of precursor ions, which also determines the elemental composition of alloy nanoparticle. In addition, bis(p-sulfonatophenyl) phenylphosphane (BSPP) is utilized to etch the nanoalloys to obtain novel nanostructures, where smaller nanoparticles surround a larger "mother" nanoparticles of different composition. These novel nanostructures might be of significance in SERS since the periphery mainly contain silver on EDX-mapping.

Reference:

EL01.20.02
Thermal Effects—Alternative Mechanism for Plasmonic-Assisted Photo-Catalysis
Ieng-Wai Un1,2, Yonatan Dubi1 and Yonatan Sivan1,1; 1Ben-Gurion University of the Negev, Israel; 2National Tsing Hua University, Taiwan

Recent experimental studies demonstrated that chemical reactions can be accelerated by adding plasmonic metal nanoparticles to the chemical reactants and illuminate them at their plasmon resonance. It was claimed that the enhanced reaction rate occurs via the reduction in the activation energy driven by the plasmon-induced non-thermal ("hot") electrons.
In this contribution, we show that these claims are extremely unlikely to be correct, and that instead, the faster chemical reactions are likely the result of mere heating. To do that, we derive a self-consistent theory of the electron distribution in metal nanostructures under continuous wave illumination. We show that only about one billionth of the energy provided by the illumination goes to creating non-thermal ("hot") electrons, and the rest goes to heating. Quite different from previous theoretical studies, we took account of the heat transfer from the illuminated nanoparticle to the environment via phonon-phonon coupling and ensured energy conservation in the electron-phonon-environment system (rather than just in the electron sub-system). This approach not only allow us to distinguish between the generation of high energy non-thermal ("hot") electrons and the regular heating of the nanoparticles, but also enables the determination of electron and phonon temperatures in a unique and unambiguous way. The theory is then used to compute the rate and energy distribution of electrons that tunnel out of the metal and can participate in a chemical reaction or enable photodetection.

Further, we develop a simple model based on the Fermi golden rule and the Arrhenius Law, which show that the enhanced chemical reactions observed experimentally are highly unlikely to result from the generation of non-thermal non-thermal ("hot") electrons in the metal; instead, it is more likely originate from a purely photo-thermal effect. Specifically, we focus on a few of the seminal papers on this field and identify experimental errors in the temperature measurements that led the authors of these papers to underestimate the photo-thermal effect. Then, we show that the alternative theory of illumination-induced heating can explain the experimental data to remarkable agreement, with minimal to no fit parameters. Comprehensive thermal calculations (whereby we sum properly the heat generated by all particles in the system) confirm the temperature extracted from the experimental data, thus, showing that any claim in these papers related with "hot" electron action is not supported by the data.

Finally, we show that for sufficiently high temperature and/or illumination intensity, it is necessary to account for the thermo-optical nonlinearity due to the temperature dependence of the optical and thermal properties of the system. We discuss the dominant contributions to the nonlinearity and the sensitivity to the various parameters of the sample and illumination. Our results provide the first ever comprehensive theory of plasmon-assisted photocatalysis and should become the basis for analysis of future experiments; it also reveals various routes for optimization of the chemical reaction acceleration. Our theory is also instrumental in quantifying experiments aimed to enable efficient photodetection.

EL01.20.03
Three-Dimensional Plasmonic Nano-Composites Fabrication by Two-Photon Lithography Based 3D Printing
Qin Hu, Yaan Liu, Derek Irvine, Christopher Tuck, Richard Hague and Ricky Wildman; University of Nottingham, United Kingdom

Metal-containing nano-composites have numerous advanced optical, mechanical, electrical and photovoltaic properties. Thus, recent advancement in the diverse fields of plasmonics, metamaterials, flexible electronics, biosensors, artificial implants and solar cells have generated a significant demand for the fabrication of novel metallic nanoparticle containing nano-composites. However, the traditional techniques for the production of such nano-composites are either inherently limited to two-dimensional (2D) processing and/or involve multiple, time- and cost-intensive synthetic steps. Two-photon lithography based 3D printing technology has been shown to overcome these limitations and can fabricate arbitrary 3D micro/nano structures with resolution in the region of 100 nm. In this work, we report our progress in fabricating complex 3D gold-/silver-/copper-containing nano-composite structures by simultaneous two-photon polymerisation and photoreduction. The success of the two-photon induced (a) polymerisation is verified by Scanning Electron Microscopy (SEM) and Raman spectroscopy, and (b) metal salt reduction is verified using Transmission Electron Microscopy (TEM). This confirmed the presence of small metallic nanoparticles (diameter of gold nanoparticles: 4.3 ± 2.8 nm; diameter of silver nanoparticles: 5.8 ± 1.5 nm) embedded within the polymeric matrix. UV-vis spectroscopy defined that they exhibit the property of localised surface plasmon resonance (LSPR), whilst X-ray Photoelectron Spectroscopy (XPS) confirmed that they exist in the zero valent oxidation state. The capability demonstrated in this study opens up new avenues for a range of applications, including plasmonics, metamaterials, flexible electronics and biosensors.

EL01.20.04
Intermediate Coupling between Organic-Inorganic Perovskite Multi-Quantum Wells and Single Plasmonic Silver Nanoparticles
Franziska E. Muckel, Kathryn N. Guye, Yun Liu, Shaun Gallagher and David S. Ginger; University of Washington, United States
In quantum optics, different types of light-matter interactions are studied through the coupling of optical emitters to microcavities with the aim of developing high performance optoelectronic devices. In the weak coupling regime, when the coupling strength is less than the damping rate of emitter or cavity, the spontaneous emission rate of the emitter is enhanced, known as the Purcell effect. With increasing coupling strength, the scattered light of the systems starts exhibiting a Fano-like, coupling-induced transparency-dip in scattering, which grows into a vacuum Rabi splitting in the strong coupling regime, when energy transfer between the cavity and the emitter is reversible.

While plasmonic particles coupled to single emitters like dyes or quantum wells represent auspicious candidates for single photonic sources, systems with multiple emitters like quantum wells promise high coupling strengths, as the coupling strength scales with the number of emitters. Two-dimensional organic-inorganic perovskites, which grow naturally in multi-quantum well structures, combine large oscillator strengths with large exciton binding energies (> 250 meV), distinguishing them as promising emitters for use in cavity coupled systems. Two-dimensional perovskite have been successfully integrated into dielectric Bragg reflector cavities, but have not yet been integrated with plasmonic particles.

Here we study the coupling between solution processed, two-dimensional butylammonium lead iodide perovskite (BAPI) and individual silver nanoprisms. Consisting of defined layers of PbI$_4$ separated by organic spacers, the thin layer n=1 BAPI multi-quantum wells feature narrow excitonic absorption and emission linewidths (ca. 100 meV). Through sequential spin coating of nanoprisms and two-dimensional perovskite emitter, we are able to combine individual silver nanoprisms with BAPI multi-quantum wells. The area around individual nanoprisms exhibit an enhancement of the emission intensity in photoluminescence. Using single particle dark field scattering spectroscopy, we observed a suppressed scattering in the single nanoprism spectra corresponding to the excitonic feature of the BAPI, indicating a coupling between the cavity and emitter. The observed transparency dip induced a peak splitting of approximately 300 meV, approaching the strong coupling limit.

Additionally, by placing the BAPI layer between a gold mirror and the silver nanoprisms, we explored the effect of different geometries on the plasmon-perovskite coupling, further modifying the coupling interaction between the plasmonic cavity and the emitters.

**EL01.20.05**
**Accordion-Like Plasmonic High Density Silver Nanorod Array for Multiple Electromagnetic Responses**
**Mooseong Kim, Jungho Mun and Jin Kon Kim; POSTECH, Korea (the Republic of)**

We realized a high-density array of “accordion-like” plasmonic silver nanorods over a large area (~cm$^2$) exhibiting multiple electromagnetic responses in visible and near-infrared (NIR) wavelengths. This array of “accordion-like” silver nanorods was fabricated by confining lamellar-forming polystyrene-block-poly (methyl methacrylate) copolymer (PS-b-PMMA) inside cylindrical pores of aluminum oxide (AAO) template grafted by thin neutral brush layers. PS and PMMA lamellar nanodomains with the sizes of ~15 nm were alternatively stacked along the nanorod direction. After the AAO template was removed, a 5 nm thick layer of silver was thermally deposited on only PS nanodomains. Due to the multiple resonances exhibited in the visible and NIR regimes, the array could be used for multi-analyte detection. Furthermore, this concept of fabricating sophisticated nanoscale architectures by utilizing block copolymer self-assembly and incorporating plasmonic metals into one nanodomains could be applied to realize large-scale metamaterials working at visible and NIR wavelengths.

**EL01.20.06**
**Ultrathin Dielectric Shell Radiative Coolers on Semiconductor Substrates**
**Jin-Woo Cho¹, Sung-Jun Park¹, Soo-Gyeong Chang¹, Dukkyu Bae², Kyung-Jun Lee¹, Youngsuk Nam¹ and Sun-Kyung Kim¹; ¹Kyung Hee University, Korea (the Republic of); ²Hexa Solution, Korea (the Republic of)**

Thermal engineering in the pursuit of attaining radiative coolers, thermophotovoltaics, optical clocks as well as classical incandescent lamps is currently being studied intensively. An appropriate radiation spectrum must be engineered fitted for specific applications. In this study, we established a passive cooling strategy which tunes a spectral irradiance of objects in mid-infrared wavelengths (e.g., $\lambda = 2.5 – 30 \mu m$). For solar photovoltaics, the device temperature is much higher than an atmospheres temperature under direct sun light in daytime, which deteriorates the power conversion efficiency (e.g., 0.042%/K [1]). Therefore, a passive radiative cooling strategy without consuming external energy is considered a highly promising approach as a new environmentally friendly
technology.
For thermal radiation cooling, dielectric materials (e.g., SiO$_2$, HfO$_2$, Si$_3$N$_4$, Al$_2$O$_3$) are widely used due to the existence of phonon-polariton resonance at specific mid-infrared wavelengths. According to Kirchhoff’s radiation law, one needs to design a structure having large absorptivity over broadband mid-infrared wavelengths. Thus, we tailored a dielectric structure which is absorptive in considered mid-infrared wavelengths and also visibly transparent (e.g., $\lambda = 0.4 – 0.8 \mu m$).
We fabricated a two-dimensional array of micron optical cavities covered with dielectric shells on Si substrates using standard photolithography, in which hollow voids were conformally covered with thin dielectric layers. The dielectric shells were composed of 300-nm-thick Al$_2$O$_3$ and 500-nm-thick SiO$_2$ layers. Fourier-transform infrared spectroscopy equipped with an integrating sphere showed greatly enhanced, broadband absorptivity, although the total thickness of the dielectric shells is far below than the center wavelength of radiation (e.g., $\lambda \sim 10 \mu m$). We evaluated the thermal capability of developed radiative coolers through outdoor experiment in daytime and nighttime. Then, we observed a temperature drop of 8 K (daytime) and 5 K (nighttime) on a Si substrate.


EL01.20.07
Asymmetric Control of Scattering Behavior for Plasmonic Nanoparticle Assemblages Jonathon Mitchell; RCVA, Japan

In transparent or translucent films, similar transmissions in wavelengths are generally observed, however, plasmonic scattering of metal nanoparticles is known to alter the transmitted light. Likewise, nanospherical particles have been demonstrated to exhibit the same properties without the inclusion of metallised particles. Here we propose a design methodology for films which can exhibit asymmetric scattering behaviour via directed self-assembly. The results of two polymorphic approaches for nanospheres are reported, molecular-induced asymmetry and topological asymmetry.

In both cases we embedded the nanospheres within an ultra-thin a-Si:H or a-SiC:H layer, coated with TiO$_2$ thin film to match polarisation between samples. On one surface either a molecular-altered nanosphere or topological nanosphere was selected for front incidence, with either selected for rear incidence. To date we have experimentally prepared a series of different samples that scatter light of different wavelengths and to different degrees from the front and rear surfaces.

EL01.20.08
Development of Terahertz MEMS Imaging Sensor for Fast Measurement at Room Temperature Jonathon Mitchell; RCVA, Japan

The detection and measurement of THz radiation presents an ongoing challenge in many potential applications mainly due to the difficulty in building devices suited to detection within the THz region. In many devices some level of cryogenic cooling is required in order to obtain sufficient signal/noise ratio, or alternatively resolution is sacrificed by the use of a GaAs antenna. Given that most materials have properties in the THz range different to their properties in the visible range, THz-detection and imaging potentially opens up a vast range of applications. Therefore, development of a new micromechanical devices suitable for detection of terahertz radiation at or close to room temperature while offering significantly faster measurements than conventional thermal sensors is worthwhile.
In this study, a unique bridge design, adapted from our MEMS e-sensors, detects and measures the incident THz radiation by analysing the fluctuations in the mechanical resonance frequency of the bridge which result from thermal expansion under incident THz radiation. Three thin-layer coatings were tested on the bridges, Nickel-Chromium (NiCr), Silicon-Gold (Si-Au), and Silicon-Titanium (SiTi), for their distinct sensitivity to THz radiation and ease of fabrication. Standard semiconductor fabrication process are used to produce our MEMS e-sensors, as well as form the thin layer coating on the bridges. Our devices demonstrated high THz–induced thermal sensitivity, with electrical noise approximately 110pW/√Hz.
A hierarchical neural network was utilised to fingerprint spectra based on the variations in resonance for single bridge configurations and between parallel bridge configurations. Although at an early stage, this new approach has advantages over current alternatives for THz radiation detection and measurement. The thermomechanical sensor in this work operates uncooled while remaining sensitive to THz, ideally suited for real-world applications, for example real-time, non-destructive integrity testing of electrical wiring and electronic trace-lines.
EL01.20.10
Studying Hot-Electron Injection in a Gold-Nanoparticle Graphene Hybrid Structure by Raman Spectroscopy
Marcel Weinhold, Sangam Chatterjee and Peter J. Klar; Justus Liebig University, Germany

Plasmonic nanostructures provide enhanced light-matter interaction due to the excitation of collective free-carrier oscillations, so-called localized surface plasmons (LSPs). LSPs cause enormous electric-field enhancements in the near-field. They also may decay into energy-rich electron-hole pairs due to Landau-damping. These ‘hot-carriers’ are exploited in various applications including photocatalysis, photovoltaics, and optoelectronics in general. Consequently, combining such plasmonic nanostructures with two-dimensional layered materials that are discussed for next generation (opto)-electronic devices should drastically enhance their capabilities: such hybrid-materials could offer the unique and extraordinary properties known from 2D materials like graphene and benefit from the enhanced light focusing, large absorption cross sections, and hot-carrier generation provided by the plasmonic nanostructure. For instance, ‘hot carriers’ in graphene-based semiconductor-devices reportedly generate photocurrents or locally increase the electron density leading, for example, to the formation of pn-junctions. However, those plasmonic effects strongly depend on the particle’s dielectric environment and geometry mandating the investigation of individual structures. Here, we study the injection of hot-electrons that arise from non-radiative localized surface plasmon decay in a model system, i.e., a single gold nanoparticle, on a monolayer graphene substrate. We reveal the intricate interplay between hot-electrons injected from plasmonic nanoparticles into graphene and show how this induces a quantifiable altering of graphene's phonon dispersion relation. Spatially resolved micro-Raman spectroscopy is a virtually ideal tool for this study as the generation of hot-electrons due to the excitation laser and the detection of the corresponding Raman-spectra occur simultaneously. Furthermore, micro-Raman spectroscopy provides easy access to single particle measurements, which is desirable since the plasmonic properties of such particles vary drastically with the particle’s size and shape. In addition, we present an analysis procedure yielding further information on occurring temperature and strain distributions solely from the captured Raman shift maps. Raman-mappings on single spherical nanoparticles, either consisting of pristine gold or encapsulated by silica which are positioned on single-layer graphene on quartz substrates with different excitation wavelengths and under variation of the incident laser power have been carried out and will be compared in terms of hot-carrier injection and heating effects.

EL01.20.11
Hydrogenated Amorphous Silicon for Integrated Photonic Waveguides Juan E. Villegas¹, Boulos Alfakes² and Mahmoud Rasras¹; 1NYU Abu Dhabi, United Arab Emirates; 2Khalifa University, United Arab Emirates

The fabrication of thin dielectric layers is essential in the development of micro-photonic devices. The disposition of the layered materials is based on their refractive index contrast. This allows determined architectures (waveguides) to confine light and selectively transfer specific wavelengths through different types of on chip optical devices. Furthermore, future planar photonic platforms need the ability to construct stacked layers of such photonic devices. However, this has been proven to be economically restricted by the current methods of transferring crystalline Silicon layers. Therefore, it opens opportunities for other materials such as Silicon Nitrate (SiN) and amorphous Silicon (a-Si) to be deposited through standard CMOS processes.

In this work we present the fabrication of low loss hydrogenated amorphous silicon that can be used to build planar photonic devices. Thin films of a-Si were deposited through low temperature Plasma Enhanced Chemical Vapor Deposition (PECVD). Different levels of hydrogenation were used to passivate the deposited layers and both undoped and n-doped (with phosphorous) films were studied. Additionally, the films were optically and electrically characterized, their surface topology was analyzed through AFM, and their vibrational modes studied through Raman spectroscopy. Simple micro-ring resonators (with 15 µm in radius) were also fabricated in these films using e-beam lithography and Deep Reactive Reactive Ion Etching (DRIE) and used to study their propagation losses. We attained an optical loss of 15.88 dB/cm at 1537 nm for single mode waveguides with width and thickness of 500 nm and 200 nm, respectively.

EL01.20.13
Alumina-Based 2D Random Photonic Nanomaterials Mikhail Pashchanka and Jörg J. Schneider; Technical Univ-Darmstadt, Germany

Many researchers have extensively studied optical properties of porous anodic alumina in recent years. Apart from
the interference colors appearance due to the multiple reflection of the vertical and skew incident light.[1] Photonic
effects due to the light scattering and propagation into lateral directions have also gained much interest.[2] Although
considerable research has been devoted to the well-ordered porous alumina photonic crystal structures, rather less
attention has been paid to the systems with deliberately introduced tailored disorder. Such planar random photonic
alumina films, however, have numerous potential applications ranging from structural coloration, light entrapping,
to lasing and diverse optical devices. In any realistic experimental situation, anodic alumina will always naturally
contain intrinsic defects in nanopore layout. The challenge in preparation of alumina-based 2D random photonic
nanomaterials is, however, to introduce different predetermined degrees of disorder into highly ordered photonic
crystal by a controlled manner, gradually varying the experimental parameters. A number of approaches have been
developed in attempts to tune the nanopore and cell sizes and the degree of pore ordering independently, such as
imprint and electron beam lithography.[3] Such methods commonly rely on the artificial creation of pore nucleation
sites on aluminum and yield only limited nanochannel length due to the spontaneous rearrangement of pores during
the long-term growth. Here, we demonstrate the feasibility of preparation of mechanically stable and transparent 2D
photonic waveguides with predetermined degree of disorder introduced into alumina by pulse anodization method.
The resulting nanochannels have invariable diameters, length up to 166 µm, as well as clearly controllable and
predetermined randomness in their arrangement.

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EL01.20.14
High Performance Perovskite Photodetector Based on Nanopatterned Monocry stalline Thin Film Jinshuai
Zhang and Lei Su; Queen Mary University of London, United Kingdom

A new class of semiconductor materials, MAPbX₃ (where MA=CH₃NH₃⁺, X = I⁻, Br⁻ or Cl⁻), perovskites, has
emerged as a promising candidate for high-performance photovoltaic and optoelectronic devices, exhibiting a range
of excellent properties including strong light absorption, direct bandgaps, long carrier lifetime, high balanced hole
and electron mobilities, and long electron-hole diffusion lengths. Patterning has been proposed to form periodic
structures on the surface of perovskites, for applications such as improving the power conversion efficiency for solar
cells, enhancing photodetector performances, fabricating photonic crystals and distributed feedback lasers. Here we
report high-performance nanoscale surface patterned perovskite monocrystalline thin film photodetectors. The
nanopatterned metal-semiconductor-metal photodetectors demonstrate significantly improved performance
compared to the nonpatterned monocrystalline thin-film devices.

EL01.20.15
UV Plasmonic Behavior of Fluoride Thin Films with Metal Nanoparticles Fabricated by Pulsed Laser
Deposition and Evaporation Jan Lancok, Tomas Zikmund, Sergei Chertopalov, Jiri Bulir and Michal Novotny;
Institute of Physics CAS, Czechia

Fluorides exhibit unique optical features, such as low phonon energy and high transparency in UV region. Fluoride
doped by rare-earth (RE) makes them excellent for optoelectronics and photonics applications. Nano-structured
materials, where the metallic nano-particles (NPs) are distributed in a dielectric matrix, represent new type of
material with unique optical properties such as local surface plasmon resonance LSPR. Most of the plasmonic
research has so far focused on “classical” materials Ag and Au. However, other less used metals could bring
significantly new functionalities. For example Al NPs yield an LSPR within the deep UV optical range and by
tuning the size of NPs the resonance frequency could be shifted up visible spectral range. Despite potential and low
cost of Al, the exploitation of its plasmonics is very recent and still facing both scientific and technical challenges.
One of the crucial problems is the degradation of plasmonic properties induced by rapid oxidation. This problem
could be solved by using fluorides matrices, which will embed the Al NPs. In our work we demonstrated
successfully fabrication of Ag, Al as well as Rh and Bi NPs embedded by CaF2 and Eu⁺:CaF2 films fabricated by
Pulsed Laser Deposition techniques (NPs) with auxiliary Electron Beam Evaporation (fluoride) at UHV conditions.
By alternating of PLD and evaporation the photonic crystals consist of multilayers of metals nanoparticles and fluoride dielectric were fabricated. The fabrication of metallic NPs in UHV conditions embedded in fluoride matrix prevent the oxidisation, which could degrade of plasmonic properties of NPs. The size of the NPs was controlled by the number of the laser pulses focused on the metallic target and varied between 5 and 20 nm. The distance between them in perpendicular direction is easily controlled by laser triggering. The analysis of the measured date revealed an absorption band in the range from 200nm up to 450 nm corresponds to LSPR of incorporated metallic NPs depending on the metals and size, respectively. Results were compared and discussed with the results of analysis structural properties performed by SEM, TEM, AFM and XRD. The calculated absorption cross absorption effective cross-section will be compared with experimental results. The plasmonic behaviour of metal NPs will be compared with those presented for metal oxides nanocomposites. The effect of NPs on luminescence and down conversion properties of Eu3+:CaF2 films will be presented as a function of their structural properties.

**EL01.20.16**  
Scalable Plasmonic Gain and Loss Lattices by Laser Interference Lithography Templates and Colloidal Self-Assembly  
Fabian R. Goßler1,2 and Tobias A. König1,2; 1Leibnizinstitut für Polymerforschung Dresden e.V., Germany; 2Technische Universität Dresden, Germany

The emerging field of noble metal nanostructures has gained a lot of interest in the recent years. Their ability to induce localized surface plasmon resonances (LSPR) when excited by incident light shows much potential for various applications reaching from biomedical technologies over sensing to optical circuits. Plasmonic structures interacting with optically active materials like quantum emitters or J-aggregates can lead to light-matter interactions like strong coupling and fluorescence enhancement. [1] If such plasmonic systems are arranged in a periodic manner, coupling between the grid resonances and the LSPR can lead to coherent energy transfer and Surface Lattice Resonance (SLR) modes of high optical quality. Their properties can be tuned over a large spectral bandwidth by varying parameters like periodicity, composition and lattice structure. There was significant progress in both, manufacturing and tailored properties of such plasmonic nanosystems lately. Nevertheless, it still remains challenging to develop efficient and scalable ways to produce such devices. In this work, we show a procedure to generate plasmonic grids on transparent and flexible materials by using Laser Interference Lithography (LIL). This enables us to fabricate a square lattice of gold nanodiscs in a highly time- and cost-efficient way whose properties can be easily adjusted to meet the desired demands. The SLR of these periodic arrays can be coupled to gain materials to induce phenomena like coherent energy coupling on macroscopic scale. With this scalable approach based on LIL, nanophotonic devices can be moved closer to implementation in future optoelectronic devices.


**EL01.20.17**  
Thermally Induced Changes in Plasmonic Colors Based on Solid State Dewetting of Gold on a Paper Surface  
Nobuko Fukuda and Sakae Manaka; National Institute of Advanced Industrial Science and Technology (AIST), Japan

We have observed solid state dewetting [1-3] of gold formed by vacuum vapor deposition onto a paper substrate. Solid state dewetting occurs resulting in minimization of total free energy of the gold-air, gold-paper, and paper-air interfaces. We previously reported plasmonic color changes with solid state dewetting of gold nanoparticles on a coated paper surface [4]. In the case that the isolated gold nanoparticles are formed all over the paper surface just after deposition, coalescence of the nanoparticles proceeds even though ambient condition at room temperature. In the case that the gold nanolayer with defects is formed all over the paper surface, growth of the defects proceeds and finally the gold particles are formed. The shape changes of gold due to solid state dewetting bring about dynamic color changes.

In this study, we investigated the relationship between gold coverage on the coated paper surface and dynamics of solid state dewetting. A gold nanolayer with a metallic color was deposited on the coated paper with 1.0 Å/s for 10 nm. The gold coverage is about 90% on the paper surface according to analysis on the image collected with a scanning electron microscope. Heating of it at 40°C induces growth of the defects, resulting in formation of particles after 72 h. The surface color changes to magenta after 72 h. The growth of defects and the color change at 40°C proceed faster than at 80°C. We guess that the speed of the growth of defects might be determined by losing the
One of the most critical challenges to high-performance nanowire (NW) photodetectors is the detectability of weak signals that noise obscures. Cloaking is a proposed method to reduce the noise generated due to the probed field being disturbed by light scattered by the photodetector itself. Here we study and compare theoretically a traditional plasmonic material gold (Au) with an emerging plasmonic material zirconium nitride (ZrN) as a plasmonic cloak for silicon nanowire photodetectors, using Mie formalism for scattering and absorption efficiency and near-field contours of the electric field. Compared to Au, ZrN has real permittivity values similar in magnitude to common dielectric components, an ideal condition for generating a polarization vector in the shell that is antiparallel to that in the core, resulting in cloaking, and the cheaper availability of raw materials makes it a good replacement for the noble metal. We have predicted the performances across the entire visible spectrum, and have shown that though ZrN cloaks produce a significant decreasing the scattering, greater than 10 times compared to a bare nanowire, and twice as better compared to Au in the wavelength region of 400-500 nm, their performances become comparable at 550 nm, with Au providing twice as good a scattering cancellation as compared to ZrN over the wavelength region of 600-700 nm. By taking the absorption efficiency into account, we have defined a figure of merit (FOM) to determine the overall performance of the cloaked Si photodetector, and show that a ZrN cloak provides up to 3 times enhancement over the performance of a bare Si NW and a 60% improvement over a Au cloaked NW, in the wavelength region of 400-500 nm, while a cloaked Au NW shows up to 30 times improvement in the wavelength region of 600-700 nm over bare Si NW and up to a 4 time improvement over a ZrN-cloaked NW. We have also predicted the optimal dimensions for the cloaked NWs at various wavelengths between 400-700 nm.

References:
EL01.20.20
**Controlled Dewetting and Regrowth of Composite ErAs NP –GaAs(001) Interfaces** Kurt Eyink, Yuanchang Zhang, Madelyn Hill, Brittany Urwin and Krishnamurthy Mahalingam; Air Force Research Laboratory, United States

ErAs is a semimetallic rare earth monopnictide which has a plasmonic response in the IR-region. ErAs has a rock salt crystal structure and is known to grow epitaxially in zinc-blende GaAs. This ability has led to numerous potential application such as thermoelectrics, plasmonics, and photonics. In the case of plasmonics, patterning the ErAs is required in order to design particular resonances in a metasurface. However, Er oxidizes extremely easily in air which has prevented ErAs use in these application. Due to the difference in crystal structure of ErAs and GaAs, a high energy interface exists between ErAs and GaAs. ErAs nanoparticles form on the GaAs As surface via an embedded growth mode in which the ErAs NP are partially buried in the GaAs surface. We recently observed a dewetting of GaAs films from the ErAs NP-GaAs composite interface. In this presentation we study this phenomena as a vehicle for the formation of tunable plasmonic structures. Previously we have shown that the dewetting process depends on several variable such as ErAs NP concentration, the dewetting temperature, dewetting time, and the thickness of the GaAs cap. We explore the ability to form a patterned surface by controlling the thickness of the GaAs. Specifically we produce a cap covering an ErAs NP growth (0.5 monolayers) which is sufficiently thick to prevent the surface from dewetting. By ex-situ etching we thinned the GaAs cap back to a thickness between 2 and 5nm which will allow dewetting. We then perform in-situ cleaning followed by dewetting of the structure in an MBE chamber. We dewet at a temperature greater than 550°C for at least 15 min. We show that we can form dewetted regions of exposed ErAs NPs. Using a low flux growth process, we control the ErAs growth to only the exposed region and produce large areas with continuous ErAs. This demonstration is a first step in producing definable resonances in a metasurface composed of ErAs using this approach.

EL01.20.21
**Optical Properties of Individual and Ensemble Metamaterial Building Blocks—Rings of Plasmonic Nanoparticles** Dan Petrescu¹, Morgan Thinel¹, Amy Blum¹ and Klas Lindfors²; ¹McGill University, Canada; ²University of Cologne, Germany

Metamaterials interact with electromagnetic radiation to produce exotic resonant optical responses that arise as a result of meta-building block geometry and arrangement, rather than chemical composition alone. Such exotic optical responses include near-zero permittivity, negative permeability, and negative refractive index, which find applications in high resolution super flat-lenses, perfect absorbing super-flat antennae, and cloaking materials, among many others. In order for resonances to occur, the size of the meta-building blocks and the spacing between them need to be significantly smaller than the target radiation wavelength. Optical metamaterials therefore require the synthesis of highly uniform nano-sized building blocks as well as their 2D or 3D nano-scale arrangement. Currently, the large-scale synthesis of uniform nano-sized objects faces difficulties due to the costly and time-consuming nature of high-resolution lithographic techniques. Furthermore, the periodic arrangement of these nano-sized objects in 3D over extended length-scales presents yet another challenge. To address these challenges, we employed viral proteins that self-assemble into robust supramolecular scaffolds which can host a variety of plasmonic metallic nanoparticles for the preparation of nano-sized and uniform meta-building blocks. These building blocks were further assembled in 3D in a polyelectrolyte multilayer (PEM) system, using a layer-by-layer deposition technique.

One particular meta-building block, an annular ring composed of discrete plasmonic metallic nanoparticles, has previously been predicted to display a dominant magnetic dipole moment at optical frequencies. Once assembled in a 3D square lattice, these rings collectively displayed effective negative permeability resonances. Most excitingly, this material produced a negative refractive index at frequencies where the negative permeability and negative permittivity resonances overlapped. The permeability resonance frequency exhibited tunability across the entire visible regime, as a function of the number of nanoparticles in the ring. Our study investigated the optical properties.
of in-house fabricated rings as a function of the number of nanoparticles. Optical scattering spectra of individual rings were correlated with ring morphology and nanoparticle number via transmission electron microscopy (TEM)-correlated hyperspectral dark-field microscopy. In order to compare single-ring with ring-ensemble properties, polarization-dependent absorption measurements were investigated for solutions of rings as well as 3D ring assemblies in a PEM system. Finally, to probe the putative magnetic dipole moment of individual rings, Lanthanide complexes were chemically conjugated onto rings and employed as fluorescent magnetic moment reporters. Individual and ensemble measurements were also compared for fluorescence studies, using both TEM-correlated hyperspectral dark-field microscopy and solution-phase fluorescence.

**EL01.20.22**

Infrared Reflecting/Transmitting Smart Glass for Energy Efficient Windows

Mark C. Altwerger, Harry Efstathiadis and Yashashvini Andugula; SUNY Polytechnic Institute CNSE, United States

Low-emissivity (low-e) glass innovation is intended to decrease the loss of infra-red radiation produced from articles at the inside of a structure with an ambient temperature of 300 K. Consequently, the reflection characteristic for the low-e glass is appropriate to reflect ~72% of the radiation from around 3.5 μm and up to ~9.7 μm. However, claiming the reflectivity characteristic drops at wavelengths below 10 μm, about 28% of the radiation discharged is yet lost to the exterior. In addition, this glass covering isn't appropriate at all to reflect sun oriented NIR radiation. Practically 49% of sun-based vitality is appropriated in the range from 0.7-2.5μm for which the low-e glass-sheet reflectivity is beneath 10%. Along these lines, the advancement of a robust film that can reflect close infrared and infrared warmth radiation in the range 0.7-10 μm while transmitting over 90% of the obvious light power is highly desirable.

Metal oxides have been utilized to deal with the light reflectance over a constrained wavelength extend. In such materials, electron plasma recurrence characterizes the beginning of the high reflectivity routine. To move the plasma recurrence to higher energies (shorter wavelengths), the doping convergence of the metal oxide must be expanded over the dimension of 1x1021 cm-3. At these focuses, in any case, the dopant particles have been appeared to create transporters with heavier powerful mass, diminished portability, and more profound benefactor expresses that fundamentally decline the transmittance.

The metamaterial proposed circumvents the need for excessive dopant incorporation through field-enhancement of the electron concentration at the interface of the moderately doped ZnO thin film with SiO2. To achieve this, a structure was designed that alternates insulating and conducting layers that, when voltage biased, produces a 2-dimensional electron accumulation in a field-enhancement device (FED). The device structure deposited by magnetron sputtering may also find application in a variety of optoelectronic applications.

**EL01.20.23**

Monitoring the Release Process of Gold Nanoparticles from Gold-Incorporated Mesoporous Silica

Anthony Stender; Ohio University, United States

Because silica nanoparticles scatter but do not absorb light in the visible wavelength range, their spectral profile gradually increases in intensity with a decrease in illumination wavelength. Upon adding small gold nanoparticles (5-10 nm diameter) to a much larger mesoporous silica particle (100s nm in diameter), the latter gradually takes on enhanced optical properties that reveal the presence of the gold. In a series of experiments, the degree of gold loading into mesoporous silica was gradually increased, in order to characterize the optical effects. Two methods of gold loading were employed with slightly different end results. In the first method, gold was directly plated into the silica structure. In the alternative technique, gold nanoparticles were attached to the silica structure through molecular linkers. In an additional series of experiments, the optical signals of mesoporous silica particles were monitored in real time as molecularly-linked gold nanoparticles were removed from their surface. This was performed through the use of chemical cleaving agents in two different settings: a controlled experiment within a microchannel and naturally within an A549 cancer cell. All data were captured by means of filtered imaging via differential interference contrast (DIC) microscopy. These findings demonstrate that these dual-nanoparticle systems provide a valuable method for monitoring activities within dynamic environments.

**EL01.20.24**

Three-Dimensional Graphene Nanomaterials for Plasmonic Optofluidic Sensing

Kriti Agarwal, Chunhui Dai
Three-dimensional graphene architectures namely, graphene-based polyhedral pyramids, cubes, and hollow cylindrical tube, and cubes have recently been realized using a surface-tension self-folding mechanism. The spatial coverage of the plasmon-enhanced electric-field in two-dimensional graphene ribbons needs to be extended into the bulk space through volumetric enhancements to overcome the surface and edge-limited efficiencies induced in 2D nanoribbons currently used for conventional plasmonic devices. Unlike patterned 2D graphene where the conventional and coupled enhancement modes are isolated only to the edges of the materials, the self-assembled multi-faced polyhedral graphene exhibits hybrid plasmon modes caused by multi-dimensional coupling between the graphene vertices, edges, and surfaces over an extra spatial degree of freedom. While 2D graphene can only demonstrate bi-directional coupling through the two edges; the 3D nanomaterials benefit from fully-symmetric 360° coupling at the apex of pyramidal graphene, orthogonal four-directional coupling in cubic graphene, and uniform cross-sectional radial coupling in tubular graphene. Each of these coupling mechanisms exhibits a corresponding plasmonic enhancement mode with unique optical features and advantages. Here, we discuss the fabrication and characteristics of each 3D graphene nanomaterial and the corresponding advantage for plasmonic sensing mechanisms. 3D graphene nanomaterials induce bounded volumetric field that senses minute quantities of targeted substances even away from the graphene surface with almost a 60% shift in resonant frequency that is far superior to the 10% change exhibited by 2D graphene ribbons. The ease of incorporation of the 3D nanomaterials with microfluidic channels has the capability of delivering optofluidic sensing mechanisms that far exceed the performance constraints faced by current plasmonic sensors.

**EL01.20.25**

Chiroptical Kirigami Modulators for Terahertz Circular Dichroism Wonjin Choi, Gong Cheng, Theodore Norris and Nicholas A. Kotov; University of Michigan - Ann Arbor, United States

Circular dichroism (CD) is a spectroscopy method based on the differential absorption of left and right circularly polarized light, which enable identification and quantification of structures at molecular and nanometer scales. Until now, however, available spectral range for CD is physically limited by the development of dynamic polarization modulators. Among not yet fully explored region, of particular interest is the far infrared or terahertz (THz) region of the electromagnetic spectrum. This is because terahertz circular dichroism (TCD) could offer multifaceted spectroscopic capabilities for understanding mesoscale chiral architecture and low-energy molecular vibrations. Here we show that reconfigurable optical modulators fabricated from patterned sheets with periodic kirigami cuts enabled dynamic range of polarization rotation modulation in the THz region over thousands of cycles. Under mechanical application, the plasmonic stripes transformed into a topologically equivalent helix structure. We measured TCD spectra of several representative biological samples using kirigami modulators and found distinctive TCD peaks. Kirigami modulators will also play an indispensible role for other applications, such as polarization resolved THz imaging and phase-encrypted THz telecommunication.

**EL01.20.27**

Towards Applications of Plasma-Synthesized Plasmonic TiN Nanoparticles Alejandro Alvarez Barragan, Carla Berrospe Rodriguez, Giorgio Nava, Stephen Exarhos, Lorenzo Mangolini and Joseph Schwan; University of California Riverside, United States

The appealing capacity of plasmonic nanoparticles to efficiently harvest, scatter and emit light has recently garnered attention for application of these materials in plasmon-based photocatalysts, solar cells and thermo emitters. Gold and silver have been extensively used to successfully drive hydrogen dissociation and CO oxidation reactions by injecting hot electrons into molecules adsorbed to their surface. However, due to the low thermal stability and the high cost of both metals, the necessity of studying alternative plasmonic materials, that potentially will expand the field towards more ambitious and cost-effective applications, has been growing in the last years. Titanium nitride (TiN) is a conductive ceramic with high hardness and bulk melting point (2930 °C). Its plasmon resonance located in the visible-NIR region, low cost (relative to gold and silver), and the well-understood properties as a thin film in the semiconductor industry, make it a strong alternative to precious plasmonic metals.

The present work encompasses a comprehensive study of the plasma-based synthesis of TiN nanocrystals and highlights the potential for their in plasmonic-driven catalysis and as a high-temperature-resistant photothermal absorber.
TiN particles were synthesized via a scalable, modular, non-thermal plasma method. Titanium and nitrogen precursors were transported into a RF frequency plasma where TiN particles nucleate and grow. Platinum nanoparticles were subsequently deposited on the TiN by photo-induced reduction of an aqueous solution of chlorplatinic acid (H₂PtCl₆). The reduction of the precursor metal was driven by electron hole pair generation via plasmon decay. The addition of methanol as a hole scavenger increased the electron lifetime, obtaining metallic platinum. This reaction occurred at temperatures below 40°C under visible light illumination.

In addition, a novel TiN@SiOₓNy core-shell structure was produced by taking advantage of the modular capabilities of the non-thermal plasma synthesis method. The synthesized core-shell particles displayed a 60% higher plasmon peak in the extinction coefficient with respect to the uncoated TiN particles. To probe the potential of these heterostructures, core-shell and uncoated TiN particles were deposited on SiOₓ substrates by coupling the plasma reactor with a nozzle. This simple modification enables to deposit a thin film by jet impaction method. The emissivity (absorptivity) of both samples were measured under vacuum conditions, demonstrating the high temperature resistance of TiN@SiOₓNy core-shell films, as their optical properties at 700 °C remained stable. This simple experiment demonstrates the stark promise of this material to generate a tunable-band-like emission for applications in thermo photovoltaic systems.

This work strengthens the case for alternative plasmonic materials in fields dominated by precious metals, and heavily driven by materials cost.

**EL01.20.28**

*Nanofabrication of Improved Titanium Nitride Plasmonic Surfaces via Nanosphere Lithography*  
Spyridon Kassavetis¹, Stavros Panos¹, Despina Tselekidou¹ and Panos A. Patsalas²; ¹Aristotle University of Thessaloniki, Greece; ²Aristotle University, Greece

Plasmonic materials and devices have attracted enormous and multidisciplinary interest and efforts over the last decade. However there are few examples of plasmonic devices mainly due to materials issues, since gold and silver, the "traditional" plasmonic materials, are expensive, with limited possibilities to tune their plasmonic response across the spectra and low melting point, which makes them incompatible with CMOS growth and processing for application in microelectronics.

Transition metal nitrides (TMN) emerge as alternative plasmonic materials and principal candidates for plasmonic applications. The TMN are conductive ceramics with exceptional properties such as substantial electronic conductivity, high melting point (>3000 K) and tunable work function values. Consequently, they are particularly stable in hostile chemical environments, high temperatures, and strong electric fields, such as in lasers. These traits make them suitable for a wide range of applications from microelectronics to photonics and medicine. Among them, titanium nitride (TiN) is recently emerging as significant candidate for plasmonic applications (biosensors, catalysis and photochemistry, solar energy harvesting, photo-detection, and optical storage of information). In this work, TiN nanostructures with controlled spacing and tunable dimensions were fabricated using Nanosphere Lithography (NSL) and DC magnetron sputtering (MS) for the growth of TiN nanostructures. NL appears as a very promising approach, due to its rapid implementation and compatibility with wafer-scale processes. NSL combines the advantages of both top-down and bottom-up approaches and includes: (a) preparation of the nanospheres colloidal mask and (2) the deposition of the desired material in the empty space between the spheres. The mask is then removed and the layer keeps the ordered patterning of the mask interstices. Specifically, a suspension of monodisperse polystyrene nanospheres (diameter, d=552 nm) was spin coated onto the Si (001) substrate to form the mask. Subsequently, the selective growth of TiN was made by: (i) rf biased DC MS in Ar/N atmosphere by varying the TiN thickness from 10 to 30 nm. The arrays of ordered TiN nanostructures appear after the lift-off of the nanospheres mask. Atomic Force Microscopy showed the fabrication of relatively large scale (> 40X40 μm) and well-ordered plasmonic surfaces, where the TiN nanostructures with thickness lower than 20 nm form a honeycomb template over the Si (001). The optical response of the TiN plasmonic surface was examined by Optical Spectroscopy and Spectroscopic Ellipsometry.

EL01.20.29
Dopant Selection Strategy for High Quality Factor LSPR from Doped Metal Oxide Nanocrystals Bharat Tandon1,2, Sandeep Ghosh1 and Delia J. Milliron1; 1The University of Texas at Austin, United States; 2Indian Institute of Science Education and Research, Pune, India

Thin films of degenerately doped metal oxides such as those of Sn-doped In2O3 (Sn:In2O3) are commercially significant for their broad utilization as transparent conducting electrodes in optoelectronic devices. Over the last decade, nanocrystals (NCs) of Sn:In2O3 and other doped metal oxides have also attracted interest for localized surface plasmon resonance (LSPR) that occurs in the near to mid-infrared region. The suitability of this LSPR for some applications depends on its capacity to concentrate light in small regions of space, known as near-field hot spots. This efficiency to create near-field hot spots can be judged through an LSPR figure-of-merit such as Quality factor (Q-factor), defined as the ratio of LSPR peak energy to its linewidth. The free electron density determines the LSPR peak energy while the extent of electron scattering controls the LSPR linewidth and hence these factors together essentially dictate the value of the Q-factor. Here, we describe the properties of aliovalent cationic dopants that allow both high LSPR energy and low LSPR linewidth and, subsequently, high LSPR Q-factor. In this context, we identify Zr4+ as a model aliovalent dopant for high LSPR Q-factor in the In2O3 lattice. The resulting Zr-doped In2O3 NCs exhibit one of the highest LSPR Q-factors reported in the mid-infrared region while also performing equivalently to the recognized materials for either high dopant activation (Sn:In2O3 NCs) or low LSPR linewidth (Ce-doped In2O3 NCs), simultaneously.

EL01.20.30
Design of ZrB2 Patterns for Emissivity Enhancement with Adjoint Method Ali M. Kecebas1, Lina Irez1 and Ibrahim Sendur1,2; 1Sabanci University, Turkey; 2Center of Excellence for Functional Surfaces and Interfaces, Turkey

ZrB2, which belongs to family of ultra-high temperature ceramics (UHTC), is known in the literature by its high melting point, oxidation and ablation resistance, chemical reactivity and erosion resistance. These properties make ZrB2 a great candidate for applications in extreme environments, such as aeronautics and astronautics. In such applications, device temperatures can reach up to elevated temperature, therefore an effective cooling approach is required. Due to the unavailability of the conduction and convection heat transfer, task of controlling the radiative heat transfer becomes crucial. To improve the radiative heat transfer rate from the surface, effects of mixing and doping on the emissivity of the ZrB2 have been widely investigated. Improved emissivity is reported in these studies, by which heat transfer from the surface is increased.

As an alternative to mixing and doping, we investigated the effect of patterning of ZrB2 on the emissivity of it in 0.5 – 1.5 μm spectrum interval. As a starting point, we considered grating structures which are heavily utilized for coupling between incident waves and the surfaces. We found out that by arranging the periodicity of the patterns on the surface, emissivity is improved due to the increased coupling. Two resonant behaviors are observed as well as the broadband emissivity enhancement in the 0.5 -1.5 μm spectrum interval. Parametric analysis is carried out to optimize the emittance of the surface in broadband spectrum. Underlying physical mechanisms are investigated and source of broadband enhancement is explored. Initial findings yield that one distinct peak stems from the surface geometry and other one occurs due to dielectric function of ZrB2, which approaches to zero around the second peak wavelength.

After the parametric analysis, an initial design is determined. To further improve the emittance of that structure, we used adjoint method to optimize the topology it. In recent years, adjoint method is adapted to field of electromagnetics and utilized to design superior structures via computationally efficient topology optimization. When adjoint method is applied, final structure’s emissivity approaches to 1 around peak wavelengths and reaches up to 85 % in 0.5-1.5 μm spectrum interval. These findings show that emissivity of the pure ZrB2 can be improved by patterning. When parametric analysis is combined with adjoint method, very high emittance is obtained. Such high emittance demonstrates the possibility of an alternative approach for emittance enhancement, thus thermal management.

EL01.20.31
Tunable Graphene Plasmonic Devices Driven by Ferroelectric Domains Junxiong Guo1, Yu Liu2, Yuan Lin1, Wen Huang1, Xiaosheng Zhang1 and Jinxing Zhang2; 1University of Electronic Science and Technology of China, China; 2Tsinghua University, China; 3Beijing Normal University, China

Tunable Graphene Plasmonic Devices Driven by Ferroelectric Domains Junxiong Guo1, Yu Liu2, Yuan Lin1, Wen Huang1, Xiaosheng Zhang1 and Jinxing Zhang2; 1University of Electronic Science and Technology of China, China; 2Tsinghua University, China; 3Beijing Normal University, China
Graphene and related two-dimensional materials have attracted intensive attention for electronic and photonic applications due to their unique structures and band energy aligns over a wide wavelength range, despite being atomically thin. However, most of the existing active graphene devices suffer from low light-matter interactions, resulting in either slow responsivity or limited detectivity. Integrating graphene with the intelligent substrate to excite graphene surface plasmons offers a promising approach for improving the photoelectric performances of graphene-based devices.

Here, we demonstrated the graphene carriers can be easily modulated by ferroelectric domains and firstly proposed its potentials for tunable infrared photodetector and micro-spectrometer applications. Compared with the silicon-based graphene plasmonic devices using a complex process of micro-nano fabrication, our proposed devices provide the advantages of more convenient and controllable technique without the need of patterning graphene, and lower energy consumption due to nonvolatile properties of the ferroelectrics free of additional contact electrode. The simulated results show the photodetector features a tunable absorption peak, modulated by periodically polarized ferroelectric domains at nanoscale, with an ultra-high responsivity up to $6.72 \times 10^6 \text{ A W}^{-1}$ in the wavelengths ranging from 5 to 20 μm at room temperature. The potential mechanism for the prominent performances of the proposed photodetector can be attributed to the highly confined graphene surface plasmons excited by the local electrical field across the interface of graphene and ferroelectric layer resonant to the incident wavelength, which could be easily controlled by the features of the ferroelectric domains. The tunable spectral response and the ultra-high responsivity make the photodetector based on graphene plasmon tuned by the ferroelectric domains promising in practical applications of micro-spectrometer and other light sensing devices.

**EL01.20.32**

**A Plasmonic Platform with Lattice Manipulation of Metal Nanopatterns for Enhanced Upconversion Luminescence**

Byunghoon Kim and Doo-Hyun Ko; Kyunghee University, Korea (the Republic of)

Rare-earth activated upconverting nanoparticles (UCNPs) have been studied due to their energy conversion property based on multi-photon absorption process. Often, these nanoparticles are combined with plasmonic nanostructures to overcome the intrinsic limit, especially, low internal quantum efficiency. However, recent plasmonic structures suffer from complicated process and restricted resonance region. In this study, we demonstrated a novel plasmonic platform to manipulate resonance wavelength via lattice control method using sequential metal-contact nanolithography. The platform employed metal nanostructure-UCNPs embedded insulator-metal reflector (MIM), which exhibited various optical characteristics including confinement of near-infrared (NIR) light, and facile extraction of converted visible light through plasmonic resonance excitement. Consequently, we observed over 200-folded enhancement for upconverted luminescence. Unlike the previous research, which tends to enhance specific wavelength, the lattice-controllable plasmonic platform shows broadband enhanced upconversion luminescence providing a convenient and versatile application for photo-isomerization reaction.

**EL01.20.33**

**Giant Third-Harmonic Optical Generation from Topological Insulator Interfaces**

Yinxiao Xiang, Chenhui Yan, Fan Shi, Prakash Gajurel, Lian Li and Cheng Cen; West Virginia University, United States

Efficient nonlinear optical materials are rare yet critical platforms to enable photon coupling. Here, we report an anomalous third harmonic generation (THG) effect universally found in the epitaxial films of a family of V-VI chalcogenide topological insulators (TIs) with drastically different optical density of states. Unlike the regular scaling behavior and without any optical resonances, THG generated from these films decays exponentially as the film becomes thicker. At the minimum thickness required for the topological states at the top and bottom surfaces to remain decoupled, the THG intensity reaches its maximum which is almost four orders of magnitude stronger than current leading materials. We attribute this unusual effect to the topological bands with nonlinear dispersion velocities and nontrivial Berry connections. This discovery provides new insights into the connection between band topology and optical nonlinearity and also a unique venue for realizing strong nonlinear optical performances on chip.

**EL01.20.34**

**Direct Deposition of Plasmonic Nanoparticles via Sputtering Performed in Open Air for Easy Manufacturing of Plasmonic Nanocomposite Film**

Yoshiki Shimizu, Kazuto Hatakeyama and Yukiya Hakuta; National Institute of Advanced Industrial Science and Technology, Japan

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Nanocomposite film composed of plasmonic nanoparticles and matrix of metal-oxide semi-conductor is promising materials in future application for conversion of solar light into chemical energy with high efficiency. This background motivates the research on fabrication of noble-metal (Au, Pt, Ag, Pd) nanoparticles/semi-conductor metal oxide (TiO2, ZnO) nanocomposite film. Generally, the fabrication process employs one of the following conventional coating method; sol-gel, sputtering, vacuum evaporation. In these, sputtering and vacuum evaporation have an advantage of chemical wastewater free, while these require costly high-vacuum vessel. In this paper, we present the novel method based on sputtering performed in open air, which is expected to be alternative to the conventional sputtering and evaporation method. The method has the following features; 1. Non-use of harmful source for operation in open air, 2. Synthesis of nanoparticles of noble-metal with narrow size distribution, 3. Direct deposition of the synthesized nanoparticles on film surface. We have investigated its potential as a method for easy manufacturing of plasmonic nanocomposite film. Recently, we confirmed that the fabricated nanocomposite film reveals high photocatalytic activity for pollutant degradation under sunlight exposure. The detail of the developed method and the performance of the nanocomposite film will be presented in our presentation.

**EL01.20.35**

**All-Graphene-Electrode Electrically Driven Microdisk LEDs**

Ja-Hyun Ku, Sun-Wook Park and You-Shin No; Konkuk University, Korea (the Republic of)

Integrating micro-scale light sources with passive components in a single chip has been one of critical challenges in photonics and optoelectronics. In addition, driving the active optical elements by direct current injection has been a long-standing goal since it’s been great challenge to inject current into micro-sized optical devices without affecting the important optical characteristics. In this work, we use epitaxially grown III-V semiconductor compounds (AlGaInP) with vertical p-i-n junction including multi-quantum wells (MQWs) structures with central emission wavelength of ~680 nm, and successfully fabricate an individually transferrable microdisk (MD) array with diameters of 5 and 7 µm, respectively, which can serve as micro-scale light sources at visible frequency. In addition, we utilize the CVD-grown multilayer graphene (MLG) that shows high charge transmission and optical transparency at the given frequencies as the transparent electrodes to electrically pump the device. In fabrication, we first transferred the CVD-grown MLG on a Si3N4 device substrate using wet transfer method. Then we exploited PDMS micro-tip transfer technique to pick up the pre-fabricated MDs from the semiconductor wafer and transferred them onto the pre-transferred MLG on Si3N4 substrate. We used the electron-beam (E-beam) lithography and O2 plasma etching to pattern top- and bottom-MLG electrodes that are directly in contact with p-doped top and n-doped bottom layers of the MDs. A final metallization carried out on these MLG electrodes completed the fabrication of the electrically driven MD devices. We performed the electroluminescence (EL) experiment by applying pulsed currents with a repetition rate of 1MHz and duration of 19.5 ns. A clear EL emission from the device was captured by the charge-coupled device (CCD), and subsequently observed in the measured spectrum. We believe that our device can be essential building blocks for the compact integrated optical circuits.

**EL01.20.36**

**Generating Vibrant and High Contrast Structural Colors from Lossy Metals on Dielectric Gratings**

Youngji Kim¹, Kyungmin Jung¹, Jiung Cho² and Jerome Hyun¹; ¹Ewha Womans University, Korea (the Republic of); ²Korea Basic Science Institute, Korea (the Republic of)

Despite their unique properties including CMOS-process-compatibility, high chemical stability, catalytic activity, etc, lossy metals are generally shunned from use in structural colors because their damping loses compromise the color vibrancy. In this work, we demonstrate a strategy to create highly vibrant and high contrast color pixels from lossy metals (e.g., Pt and W). Our pixel is of the reflective type and consists of a metal substrate supporting a near-wavelength dielectric grating oriented 45 degrees to the input polarization. This allows the incident light to be decomposed into s-polarized (s-pol) and p-polarized (p-pol) light with equal strengths. The reflected signal is filtered by a cross-polarizer, cancelling the background signal and keeping the pixel contrast high. Each s-pol and p-pol component excites a resonance at different wavelengths through the coupled waveguide-array modes in the grating [1,2]. At each resonance, a phase difference between the s-pol and p-pol light arises, abruptly rotating the total polarization vector by π/2 over the wavelength. As a result, the cross-polarized filter transmits two spectrally distinct and sharp signals from the two resonances. We find that the metal loss severely degrades the p-pol resonance (i.e., surface plasmon polariton) due to the spatial overlap of the resonant field with the metal interface whereas its effect on the s-pol resonance, located between the grating and air interface, is relatively small. By measuring the cross-polarized reflection from gratings on lossy metals, we obtain spectrally pure and sharp signals.
translating to a high color vibrancy and large gamut range, as only the spectrally sharp s-pol resonance contributes to the reflected spectrum. In fact, W which is one of the lossiest metals, provides a larger gamut coverage than that of Ag. These results offer intriguing routes for realizing high-contrast structural colors from an expanded range of metals that host interesting chemical and physical properties [3].

References

EL01.20.37
Zeeman-Like Splitting of the Plasmonic Response of InSb Nanoparticles Raul Esquivel-Sirvent and Alonso Márquez-Hernández; Universidad Nacional Autonoma de Mexico, Mexico

We show that the plasmonic response of InSb spherical nanoparticles splits into two resonances when an external magnetic field is applied. This splitting is akin to a Zeeman splitting with the frequency separation of the satellite resonances depending on the magnitude of the applied magnetic field. InSb has a homogeneous dielectric function, and the extinction of the nanoparticle shows a resonance in the frequency range of THz. The application of the external magnetic field induces an anisotropy in the dielectric function. To understand the splitting of the plasmonic resonance, we show that the anisotropic sphere is topological equivalent to a spheroid with an isotropic dielectric function. The shifting of the plasmonic peaks is equivalent to having a spheroid of varying eccentricity. The plasmonic response and peak splitting also depends on the direction of the applied magnetic field. Finally, applications to active plasmonics will be discussed.

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EL01.20.38
Ultimate Light Trapping in a Free-Form Plasmonic Waveguide Juho Park1, Sanmun Kim2, Joongwon Lee3, Sangjun Han1, Ju Young Kim1, Junhyeong Kim1, Sergey Menabde1 and Min Seok Jang1; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2University of Cambridge, United Kingdom; 3Cornell University, United States

Slow light enables spatiotemporal manipulation of electromagnetic waves at the nanoscale and allows access to a plethora of nonlinear optical phenomena. Although the guided waves in plasmonic waveguides are known to inherently possess a slow energy velocity, their ultimate light-trapping performance remains unknown as the effect of the waveguide’s shape alteration has not been considered systematically so far. In this work, we search for the optimal geometry of a free-form metal-insulator-metal (MIM) plasmonic waveguide for light trapping, and reveal its unique properties that are significantly different from the conventional linear taper structures. We optimize the waveguide geometry by using three different numerical optimization algorithms combined with the transfer matrix method, and confirm the results with full-wave simulations based on the finite element method (FEM). The optimized light trapping structure possesses a dramatically enhanced quality factor, almost reaching the theoretical limit imposed by the material loss. Interestingly, it also exhibits a distinctive mode dynamics and a unique dependence on the material loss, both being fundamentally different from those of the conventional linear taper structures. Unlike linearly tapered waveguides, whose characteristic length (minimum necessary length to reach half of the maximum quality factor) is inversely proportional to the material loss, the quality factor of the optimized structure saturates at much shorter length, and its characteristic length scales logarithmically to the inverse material loss. Further, in order to demonstrate the feasibility of proposed design approach, we analyze the optimization results obtained with realistic materials at visible and mid-IR frequencies.
PLASMONICS ENHANCED PHOTODETECTORS HAVE BEEN WELL EXPLORATED IN VISIBLE TO THZ SPECTRUM. SEVERAL PLASMONICS MATERIALS HAVE BEEN GIVEN PROMISED RESULTS IN VISIBLE TO THZ REGIME, SILVER AND GOLD ARE THE MOST EXTENSIVELY USED NOBLE METALS FOR PLASMONICS APPLICATIONS. A WIDE RANGE OF ULTRAVIOLET SPECTRUM IS LESS DISCOVERED DUE TO THE LIMITATION OF THE INTRINSIC BEHAVIOUR OF THESE METALS. WHERE SILVER SUFFERS FROM RAPID OXIDATION AND POOR QUALITY FACTOR OF SURFACE PLASMON RESONANCE (SPR) AND LOCALIZED SURFACE PLASMON RESONANCE (LSPR) BELOW 350 NM BESIDES GOLD HAS AN INTERBAND TRANSITION AROUND 500 NM. TO EXPLORE THE PLASMONIC PROPERTIES IN ULTRAVIOLET (UV) REGIME, ALUMINUM HAS ENORMOUS POTENTIAL AND HIGH QUALITY FACTOR TO OPERATE IN THE DEEP UV TO NEAR UV SPECTRUM, SO WE PRESENT LOCALIZED SURFACE PLASMON RESONANCE DRIVEN UV PHOTODETECTION THROUGH ALUMINUM METASURFACE ON GALLIUM NITRIDE (GAN) SUBSTRATE. FOR THE GENERATION OF UV RANGE LSPR AND FORMATION OF SCHOTTKY CONTACT AT THE SURFACE OF GAN, THE SINGLE CRYSTALLINE ALUMINUM FILM IS GROWN BY PLASMA ASSISTED MOLECULAR BEAM EPITAXY (PA-MBE) METHOD ON UNDOPED GAN/AL2O3 SUBSTRATE. AS A METASURFACE, PERIODIC NANOHOLES WERE DESIGNED. CMOS COMPATIBLE TECHNIQUES ARE USED TO MAKE SUBWAVELENGTH METASURFACE AND SCHOTTKY DIODE. FURTHERMORE, FDTD SIMULATION AND MICRO UV REFLECTANCE MEASUREMENT WERE PERFORMED TO REALIZE THE BEHAVIOUR OF THESE PERIODIC NANOHOLES. THE HOT ELECTRONS GENERATED BY THE DECAY OF LSPR IN THESE PERIODIC SUBWAVELENGTH NANOHOLES AND ATOMICALLY SMOOTH METAL SEMICONDUCTOR INTERFACE CONTRIBUTE TO ENHANCE PHOTOEMISSION EFFICIENCY AND WIDE UV SPECTRAL ENHANCEMENT COVERAGE. THE ULTRAHIGH RESPONSIVITY (670 AMP/WATT) AND DETECTIVITY (1.48 × 1015 CM Hz-1/2 W-1) ARE OBSERVED AT 355 NM. THIS CMOS COMPATIBLE PLASMONICS BASED ULTRAVIOLET PHOTODETECTOR CAN REPLACE THE TRADITIONALLY GAN-BASED PHOTODETECTOR AND OPEN A NEW ERA IN ULTRAVIOLET DETECTION REGIME.

DIFFRACTION CONTROL WITH HIGH Q PHASE GRADIENT METASURFACES FOR NONLINEAR FREESPACE OPTICS

PHOTONIC MICRO-STRUCTURES, INCLUDING MICRONING RESONATORS, PHOTONIC CRYSTAL DEFECT CAVITIES, AND WHISPERING GALLERY RESONATORS, HAVE BEEN BY FAR THE MOST SUCCESSFUL PLATFORMS FOR BOOSTING LIGHT MATTER COUPLING, WHICH IS LARGELY THANKS TO THEIR HUGE QUALITY (Q) FACTORS, SPANNING THOUSANDS TO MILLIONS. THE ASSOCIATED LONG PHOTON RESIDENCE TIMES AND ENORMOUS AMPLIFICATION OF THE LOCAL LIGHT INTENSITY HAS LED TO HIGH-EFFICIENT LASING[1], FREQUENCY COMB GENERATION[2], OPTICAL SIGNAL MODULATION[3], OPTICAL ISOLATION[4], QUANTUM GENERATION[5], AND SINGLE MOLECULE BIOSENSING[6]. AT THE SAME TIME, NANOANTENNAS PROVIDE AN UNPRECEDEDENT LEVEL OF CONTROL OVER THE SCATTERING OF FREESPACE OPTICAL SIGNALS, ESPECIALLY WHEN ARRANGED INTO METASURFACE ARRAYS, ENABLING FLAT OPTICAL ELEMENTS SUCH AS BEAM STEERERS, LENSES, AND HOLOGRAMS[7]. HOWEVER, RESEARCHERS TYPICALLY FACE A TRADE-OFF BETWEEN ANTENNA SIZE IN RELATION TO WAVELENGTH AND RESONANT LIFETIME, WITH SUBWAVELENGTH STRUCTURES LIMITED TO QUALITY FACTORS (Q) LESS THAN 100, KEEPING MORE EXOTIC NONLINEAR PHENOMENA OUT OF REACH WITHOUT THE USE OF EXTREMELY HIGH POWER FEMTOSECOND LASERS.

BY UTILISING MIE AND GUIDED MODE RESONANCE (GMR) TO CONTROL THE SCATTERING PROFILE OF HIGH Q, Q>1000, RESONANT NANOARCHITECTURES, HERE, WE DEMONSTRATE EXPERIMENTALLY THAT THIS TRADE-OFF IS NOT IN FACT FUNDAMENTAL. WE SHOW THAT GMR IN ULTRATHIN DIELECTRIC METASURFACES CAN BE EMPLOYED TO BRING STRONG FIELD AMPLIFICATION TO A WIDE CLASS OF FREESPACE NANOPHOTONIC SYSTEMS, PRODUCING EFFICIENT OPTICAL NONLINEARITIES IN A NANOSCALE FOOTPRINT. COMBINING WAVEFRONT SHAPING WITH SUBTLE STRUCTURAL SYMMETRY BREAKING, ARBITRARY FREESPACE SCATTERING CAN BE ACHIEVED ALONGSIDE GMRS WITH LIFETIMES THAT CAN BE INCREASED ALMOST INDEFINITELY. AS A PROOF OF PRINCIPLE, WE PROVIDE THE FIRST THEORETICAL AND EXPERIMENTAL DEMONSTRATION OF TWO HIGH Q PHASE GRADIENT METASURFACE FUNCTIONS, ONE CAPABLE OF EFFICIENTLY STEERING AN INFRARED PLANE WAVE TO A PREDETERMINED ANGLE AND ANOTHER SPLITTING A PLANE WAVE INTO TWO BEAMS, WITH BOTH DEVICES SUPPORTING GMR Q FACTORS GREATER THAN 1000.

THE METASURFACES WERE PATTERED INTO A SILICON ON SAPPHIRE WAFER WITH A 600NM SILICON LAYER, USING ELECTRON BEAM
lithography followed by reactive ion etching. To realize the different metasurface phase profiles, nanowires of varying widths were arranged within a 2121nm supercell. Subwavelength periodic notches were also etched into particular nanowires, giving rise to GMRs with Q factors controlled via notch depth. Using a home built angle resolved microscope coupled to a grating spectrometer, we report efficient beam steering and beam splitting between 1350-1500nm, accompanied by GMRs with Q factors as high as 2500. To the best of our knowledge, this is the highest Q factor observed to date in a phase gradient device. We have numerically confirmed that the huge electric fields associated with these resonances can excite efficient nonlinearities, including the Kerr effect and stimulated Raman scattering, opening the possibility for novel functionalities such as subwavelength nonreciprocity. While our proof of principle demonstrations involve beam steering and beam splitting, the design principle we present could easily be extending to other types of wavefront shaping applications, such as lensing.


8:30 AM *EL01.21.03*

**Multifunctional Nanostructured Optical Surfaces for Industrial Applications** Juan Rombaut1, Bruno Paulillo1, Nestor Bareza1, Daniel Martínez1, Rinu Maniyara1, Kavitha K. Gopalan1, Prantik Mazumder2 and Valerio Pruneri1; 1ICFO, Spain; 2Corning Research and Development Corporation, United States

A wide range of optoelectronics applications require surfaces with specific properties, such as antireflection, self-cleanliness, electro-optic tuneability, etc. In this talk, we will review recent efforts from our group in developing optical structures based on ultrathin materials and nano-structuring, which offer unprecedented flexibility in molding light propagation, from the visible to the infrared range, and producing self-cleaning effects. In particular, we will show how to use graphene, ultrathin metals, scalable metal dewetting nano-patterning and nano-imprint lithography, to produce transparent surfaces for transparent electrodes, displays, optical windows and infrared sensing.

9:00 AM *EL01.21.04*

**Programmable Multiplex Optical Bandpass Filter via Laser Reshaping of Gold Nanostructure** Kyoungweon Park1,2, Jake Fontana3, Jason K. Streit1,2, Jamie Gengler1,2, Carl Liebig1 and Richard A. Vaia1; 1Air Force Research Laboratory, United States; 2UES, Inc., United States; 3U.S. Naval Research Laboratory, United States

Optical bandpass filters allow or reject the light within a specific wavelength range to prevent damage from unfiltered light or to utilize the quarantined light. The terrestrial atmosphere or complex biological fluids are among the examples which provide either broad or narrow transmission windows to accomplish certain functions. Metallic nanorods and their assemblies are a promising platform for optical bandpass filter due to their intense light-matter interactions with tunable optical cross-section greater than the particle volume. With our innovative synthetic strategy, we achieve to fabricate optical filters with independently tunable center wavelength and a variable bandwidth by carefully selecting the aspect ratio of a collection of AuNRs with narrow resonances that allow to create ideal flat top profile for targeted absorption and a sharp roll-off at the filter edges. Laser irradiation can be a simple tool to transcribe a transmission window at desired wavelength by reshaping a population in resonance with the LSPR. It is possible to write a single or multiple transmission window using polydisperse nanorods or nanowires with dense broadband spectral distribution over visible to mid-IR. We examine the impact of laser irradiation conditions on the spectral position, depth, and width of the transmission window and validate the results with theoretical study. The rational design can be achieved in various systems including solutions and nanocomposites to fabricate complex optical materials with properties not found in natural media.

9:15 AM *EL01.21.05*
Broadband Light-Trapping Layers for Thin Si Solar Cells Based on Dense Arrays of Silicon Mic Resonators
Nayeun Lee, Muyu Xue, Jiho Hong, Jorik Van de Groep and Mark L. Brongersma; Stanford University, United States

The high reflectivity of typical semiconductor is a major factor in deteriorating the efficiency of solar cells. The conventional approach to minimize these losses is to add a quarter-wavelength-thick antireflection coating with an optimized refractive index. However, this technique has limitations as single-layer antireflection coatings are relatively narrow band and do not trap light in the cell by redirecting it into the plane of the cell. New high-performance photon management approaches are required to achieve high-efficiencies with optically-thin and low-cost cells.

In this research, we propose and experimentally test the performance of broadband light-trapping layers for few-micron-thick Si cells using dense arrays of Si nanostructures. Light reflected from Si substrate can be canceled out by the scattered light from the array of Si nanostructures. While dense arrays of nanostructure can be viewed as homogeneous medium with a broad Fabry-Perot resonance, each individual nanostructure can also support Mie resonances of destructively interfering with the reflected light from the substrate. By judiciously optimizing the structure parameter of the Si nanostructures in an array, both broadband antireflection and light trapping can be achieved. The increased absorption of light is demonstrated experimentally with a 3 um thick solar cell. A 10.3% power conversion efficiency is achieved, representing a boost in the current density as well as enhancing cell’s efficiency over 48% compared to a reference cell without an antireflection coating.

9:30 AM EL01.21.06

Nanophotonic Refrigeration by Controlling the Chemical Potential of Photons Linxiao Zhu, Anthony Fiorino, Dakotah Thompson, Rohith Mittapally, Edgar Meyhofer and Pramod Sangi Reddy; University of Michigan, United States

Photonic cooling using coherent laser radiation has enabled reaching temperatures close to absolute zero, which plays a key role in identifying new states of matter, and led to novel strategies for solid-state refrigeration. The low entropy of laser radiation makes these cooling processes thermodynamically feasible. Recent theoretical studies have suggested the possibility of photonic cooling using incoherent light from semiconductor diodes. However, such photonic cooling using incoherent light has not been experimentally achieved. In this talk we will describe a first demonstration of photonic refrigeration by controlling the chemical potential of photons. Leveraging the large heat-transfer rates of near-field radiation and sensitive, high-resolution nano-calorimetry, we were able to experimentally observe net cooling of a planar object when it was separated from a reverse-biased photodiode by a nanoscale gap. Such cooling arises from a combination of a suppression of thermal radiation from photodiode at reverse bias, and an enhancement of photon emission from the planar device due to near-field tunneling. We will also describe the dependence of cooling power on gap distance and voltage bias. Finally, the competing effects of negative luminescence and radiative heating will be considered. Our study points to the new and promising direction of combining nanophotonics and optoelectronic devices for achieving solid-state refrigeration.

9:45 AM BREAK

SESSION EL01.22: Novel Photonic Materials and Nanofabrications I
Session Chair: Artur Davoyan
Friday Morning, December 6, 2019
Hynes, Level 1, Room 102

10:15 AM *EL01.22.01

Integration of Magnetooptical Materials for Photonic Devices Caroline A. Ross; Massachusetts Institute of Technology, United States

Thin film magnetooptical materials are enablers for integrated non-reciprocal photonic devices such as isolators and circulators, as well as magnetoplasmonic and magnetooptical heterostructures. Iron garnets, A12FeO12 where the A-site includes Y, Bi and Ce or a rare earth, offer particularly good magnetooptical figure of merit (Faraday rotation
(FR)/optical absorption) in the near-IR communications wavelengths, with FR and absorption both increasing at visible wavelengths. We describe the growth and magnetooptical properties of films of polycrystalline bismuth-, cerium and terbium-substituted yttrium iron garnet (BiYIG, CeYIG, and Tb,Bi,CeYIG), deposited on silicon substrates and waveguide devices using pulsed laser deposition. These materials were incorporated as cladding materials on Si or SiN waveguides to make integrated isolators based on both ring resonators and on Mach-Zehnder interferometers (MZIs). For TM-mode devices, isolation ratios and insertion losses are up to 40 dB and 3 dB respectively for a ring resonator and up to 30 dB and 6 dB for an MZI, with the latter having a significantly higher bandwidth of 20 dB isolation ratio over a 2 nm wavelength range. TE-mode devices, which require growth of the magnetooptical material on the sidewall of the waveguide, were also fabricated and tested. Garnet films are also useful in active photonic or magnonic devices based on the propagation of spin waves, and programmable spin wave logic devices have been demonstrated in YIG films. In BiYIG films capped with Pt, spin-orbit torque has been used to translate domain walls at velocities exceeding 4 km/s, enabling rapid magnetic switching or transmission of data. The potential of these complex oxides in enabling new types of photonic devices and structures will be assessed.

10:45 AM EL01.22.02
Surface Fermi Level Pinning and Surface Conduction in CdO Thin Films Angela Cleri¹, Joshua Nordlander¹, Evan Runnerstrom², Joshua R. Nolen³, Josh Caldwell³, John A. Tomko⁴, Patrick E. Hopkins⁴ and Jon-Paul Maria¹; ¹The Pennsylvania State University, United States; ²North Carolina State University, United States; ³Vanderbilt University, United States; ⁴University of Virginia, United States

Cadmium oxide (CdO) is one of the most promising candidates for low-loss mid-infrared plasmonics to date, as it demonstrates a tunable range of carrier concentrations (from $10^{18} - 10^{21}$ cm$^{-3}$), while maintaining mobilities between 300 cm$^2$/vs and 500 cm$^2$/vs over the entire range. These high mobility values lead to plasmonic structures with very low loss and very narrow frequency bands. Fully accessing the spectrum of plasmonic applications, including surface plasmon oscillations, epsilon-near-zero (ENZ) modes, and strong coupling phenomena requires that one maintains these appealing transport properties over a film thickness range spanning a few tens to a few thousands of nanometers.

Extensive CdO fabrication experiments using high-power impulse magnetron sputtering reveal a strong dependence of carrier density and mobility on film thickness, particularly when thickness values drop below 100 nm, a particularly interesting and important range for ENZ modes. For unintentionally doped material in this thinness range, mobilities fall and carrier concentrations rise, both of which can be attributed to surface donors. There is a widely reported surface accumulation phenomenon in CdO thin films that accounts for this phenomenon. Conversely, if CdO is donor doped to values where the Fermi energy is above the surface donor energy this effect can be reversed. In this case, as film thickness falls below 100 nm, carrier concentration drops due to surface depletion.

In this presentation, we demonstrate the reversal between surface accumulation and depletion in CdO by comparing thickness series sets of intrinsic CdO and In-doped material. Transport properties from this sample collection reveals a carrier concentration at which the thickness-dependence relationship is no longer present. At this carrier density, the bulk Fermi energy aligns with the surface defect energy so as to eliminate accumulation or depletion zones. Finally, we show how optical properties, i.e., perfect absorber ENZ layers are affected by these surface effects, and how they can be eliminated by sandwiching doped CdO layers between intrinsic (and lower doped layers), or by capping CdO surfaces to change the surface defect formation energies.

While surface accumulation has been reported in CdO thin films, this is the first demonstration of the reversal between surface accumulation and depletion at varying dopant levels, allowing for tunability of surface charge. This offers potential for tunable quasi-2-dimensional electron gas (Q2DEG) behavior at CdO surfaces.

11:00 AM EL01.22.03
Two-Photon Direct Laser Writing of Inverse-Designed Free-Space Near-Infrared Polarization Beamsplitter Wisnu Hadibrata, Heming Wei, Francois Callewaert, Vesselin Velev, Zizhuo Liu, Prem Kumar, Sridhar Krishnaswamy and Koray Aydin; Northwestern University, United States

Owing to high sub-diffraction limit resolution (~100 nm) and a true three-dimensional printing, two-photon polymerization (2PP) direct laser writing has opened the possibility of fabricating near-infrared complex 3D optical
components such as micro-lenses, micro-ring resonators and others. In this work, by combining 2PP direct laser writing and inverse design optimization methods, we have been able to demonstrate a compact, thin and broadband free-space polarization beam splitter working in infra-red range. We have optimized a 2λ-thick (in the direction of propagation) device capable of splitting parallelly and perpendicularly polarized light to be directed to the left by +θ° and right by -θ°, respectively. From our simulations, we observe a relatively large bandwidth operation ranging from 1.3 μm to 1.7 μm for the beam splitting behavior. In the experimental demonstration, we successfully fabricated the device using a commercial 3D direct laser lithography system based on a femtosecond laser at 780 nm. We have also performed optical characterizations for the fabricated device operating at 1.3 μm and 1.55 μm. The device exhibits good polarization splitting while also maintaining low transmission loss of 2 dB (1.3 μm) and 2 dB (1.55 μm).

11:15 AM EL01.22.04
Metal Oxide Perovskites—A Viable Platform for Mid to Far Infrared Nanophotonics? Ioannis Vangelidis1, James A. Hillier2, Elefterios Lidorikis1 and Nikolaos Kalfagiannis2; 1University of Ioannina, Greece; 2Nottingham Trent University, United Kingdom

In order to fulfil the promise of plasmonics, it has been viewed that one of the most disruptive technologies will be the “all dielectric plasmonics”. This, by itself, contradicts the definition of plasmonics (interaction of light with collective charge oscillations at metallic nanostructures). However, some interesting approaches can be exploited. In that respect, polar dielectrics can be used to couple an electromagnetic field to collective lattice oscillations, namely optical phonons. Those polar crystals can support optical modes that are confined either to the surface of the material or can be highly confined within or in the vicinity of sub-wavelength geometries, resulting in strong field enhancement. Similar to their metallic counterparts these oscillations are only supported when the real permittivity is negative and in the case of the polar dielectrics, this happens at the so-called Reststrahlen band. Naturally, the extent of this band defines the spectral range of operation.

In this work, we focus our attention to a family of very important technological materials; that of metal oxide perovskites. Metal oxide perovskites have been investigated for many years due to their excellent dielectric, piezoelectric, ferroelectric and optoelectronic properties. When a small number of electrons are introduced in the lattice (e.g. in oxygen-deficient samples or doped with metals, such as Fe or Nb) many other attractive properties arise such as superconductivity, ferromagnetism, high thermoelectric coefficient, blue and green light emission as well as accommodation of a two-dimensional electron gas. We present their exceptional capabilities, in terms of their bulk optical constants, which we have measured with an IR Spectroscopic Ellipsometer and which we compare with the most prominent polar dielectrics (h-BN, Sapphire, InP, GaN and GaP) and metals (such as Au) in an effort to establish a baseline for their performance. A particular focus is given to SrTiO3 which demonstrates a unique capability to maintain negative real permittivity for an extended spectral range due to an effective overall between two Reststrahlen bands and could throw it directly into centre stage for future infrared nanophotonic applications. We then calculate the localised modes on subwavelength structures and we: (i) clarify the fundamental nature of the modes, (ii) demonstrate an extraordinary tunability that SrTiO3 offers in the mid and far infrared wavelengths and (iii) we present a practical example of IR photodetection based on this material.

11:30 AM EL01.22.05
Nanoscale Manipulation of Carbon Nanotube Structure with Light-Matter Interaction Pingping Chen, Shuting Lei and Suprem R. Das; Kansas State University, United States

Carbon Nanotubes have been extensively studied in more than two decades for their physical and chemical properties, and more recently in their industrial applications, including wafer scale nano-electronic devices and nanocomposite structures. The interest in carbon nanomaterials has been greatly enhanced by the rise of graphene, the two dimensional analog of the one-dimensional tubes. Due to their extreme scaled-down geometry, particularly the diameter, a small perturbation in their structure could induce large changes in their electronic properties. However, such control of their structure is difficult to achieve due to processing complexity in a growth reactor. In this work, we use a fast, scalable and room temperature process to alter the nanotube structure by exploiting the light-matter interactions from a femto-second laser radiation. Multi-wall carbon nanotubes are irradiated with pulsed laser beam to modify the tube structures into ribbon-like geometry that may lead to unique electronic and photonic properties. In this work, we use scanning electron microscopy, atomic force microscopy and Raman spectroscopy to study the structural properties of these carbon nanomaterials that may be suitable for coupling with photons.
Controlling the micro- and nanostructure of metals offers the opportunity to investigate and engineer the properties of metal nanotechnologies, which are essential components in advanced optical and electronic systems. The electronic, optical, and thermal properties of these systems are closely related to the presence of strain, defects, and grain boundaries in the metal. Carrier transport, band structure, electromagnetic field enhancements, and thermoelectric properties are all dependent on crystal quality, but there is still an incomplete understanding of the role that individual crystal defects play.

Here, we report a study of the thermoelectric properties of thin-film gold single crystals and bicrystals on amorphous insulating substrates. The crystalline gold microstructures are created via rapid melt growth, which supports the high-yield, high throughput growth of thousands of single crystals and bicrystals on the wafer-scale [1,2]. Using the crystalline gold microstructures as a model system, we can enable systematic studies that reveal the relationship between the micro- and nanostructure of gold and its properties. We studied the spatial variation of the photothermoelectric voltage across the gold stripes using a focused scanning laser probe, which locally heats the metal via direct absorption and excitation of a plasmon resonance. In the bicrystals that each possess a single grain boundary, we observe a thermoelectric voltage distribution where the local Seebeck coefficient varies at the grain boundary, indicating strong carrier interaction with the boundary. Furthermore, variations in Seebeck coefficient along the length of the single crystal gold grains suggest that other crystal defects and strain play a role in determining the thermoelectric properties.

applications. GeOI based photonic components could have better performance than silicon-on-insulator (SOI) counterparts at this new spectral window, due to the superior optical properties of Ge over Si. High performance GeSn photo detector has been demonstrated on this platform. Ge has also been considered as a promising channel material to replace Si for high performance logics applications. This platform also enables the potential of integrating photonics devices with Ge CMOS devices.

2:00 PM EL01.23.02
Vertically Stacked Suspended SiGe Nanowire Meta-Photodetector for Visible Light with Active Tunability of Optical Coupling Junkyo Suh, Qitong Li, Jorik Van de Groep, Fenghao Xu, Krishna C. Saraswat and Mark L. Brongersma; Stanford University, United States

The ability to tune the optical spectra of nanostructures such as nanowires (NWs) through optical coupling is valuable for optoelectronic applications. The optical coupling of two Si NWs horizontally placed without active tunability has been studied. In this case, a part of optical resonant modes (symmetric mode) is only excited under top plane wave illumination. However, the optical coupling of vertically stacked suspended NWs has not yet been explored due to its difficulty to reliably fabricate the system. This configuration is particularly advantageous in that both symmetric and asymmetric modes can be simultaneously excited when illuminated because they naturally receive different phase information. Moreover, the active tuning of the system to engineer the strength of optical coupling has not been demonstrated. In this study, we demonstrate a novel method to fabricate vertically stacked (3D stacking) suspended SiGe NWs. Furthermore, photodetectors are realized with active tunability by electrostatic force applied between the two suspended NWs.

High quality pseudomorphic SiGe (30% Ge)/Si multilayers are epitaxially grown on Si substrate by chemical vapor deposition (CVD) and patterned by e-beam lithography. Then, the SiGe nanobeams are released by tetramethylammonium hydroxide (TMAH), followed by electrode formation on the SiGe NWs. Here, Ge composition in NWs can be increased by high temperature oxidation of the NWs. Electrostatic force applied between the SiGe NWs is used to modulate the spacing in between them. Spectral changes in both scattering and absorption through photocurrent measurement are monitored with various spacings ranging from 200nm to 50nm. As a result, the proposed meta-photodetectors with the active tunability pave a new way for the next generation CMOS compatible on-chip optoelectronic devices that can be monolithically integrated with nanoelectronics.

2:15 PM EL01.23.03
Guided-Mode Resonator Devices for Phase-Contrast Imaging Anqi Ji, Jung-Hwan Song, Qitong Li, David Miller and Mark L. Brongersma; Stanford University, United States

Phase-contrast imaging is an optical method which visualizes the optical phase differences that light acquires as it traverses structures with similar transparency. The inventor of phase-contrast microscopy, Frits Zernike, demonstrated successful imaging of unstained cells. The underlying key principle of this technique is to interfere the scattered light by a specimen with the high spatial-frequency content with an attenuated, 0.5π phase-retarded illumination containing the low spatial frequencies (i.e. DC component). This maximizes the intensity contrast in the interference images. Conventionally, this requires a set of bulky Fourier optics components for filtering and selective phase retarding elements, limiting its use in certain applications.

Here, we propose ultracompact phase-contrast Fourier optics elements with unprecedented high angular accuracy by using a planar guided-mode resonance structure. We designed 40-nm-thick, 160-nm-wide Si3N4 gratings on a 130-nm-thick Si3N4 slab waveguide with a lattice constant of 370 nm. The structure can be used to perform phase-contrast microscopy by interfacing the normally incident plane wave to the guided-mode resonance at a 645 nm illumination wavelength. This facilitates 90% amplitude reduction and 0.5π phase pickup for the DC incident illumination while leaving the scattered, non-DC Fourier components from a specimen passing through with near unity transmission. We deposit the Si3N4 waveguide on a quartz substrate by low-pressure chemical vapor deposition (LPCVD) and fabricate the grating with electron beam lithography and reactive ion etching (RIE). We also characterize the optical dispersion properties of the fabricated samples in a home-built angle-resolved-spectroscopy setup and observe the high quality guided-mode resonances (Q~100). This Q corresponds to ~0.5° angular accuracy in selecting the Fourier components for amplitude reduction and phase retardation. Our guided-mode resonance structures can be used in a conventional optical microscopes and we expect this opens a promising avenue for compact, flexible, and high-quality phase-contrast microscopy.

2:30 PM BREAK
3:00 PM *EL01.24.01
Photonic Materials for Deep Space Exploration Artur Davoyan; University of California Los Angeles, United States

In this talk we give an overview of our work on solar and laser sailing for deep-space travel in our solar systems and beyond. We will show that with the use of novel materials and lightweight photonic designs, radiation pressure forces may be harnessed to enable ultrafast maneuvering and travel. We will show that both solar and laser sailing may be used to enable revolutionary in-space propulsion. Hence, we will discuss conceptually new solar sail designs that making use of solar gravity assist and can be propelled to unprecedented >30 AU/year velocities. These sails maybe ideally fitted for interstellar probe missions. The close solar approach requires design of novel photonic materials capable of withstanding high solar flux. Laser sailing, on the other hand, may pave the way to near speed of light (20% of the speed of light with a ~100 GW laser) space travel enabling exploration of interstellar space and neighboring stars. We will highlight the conditions needed, discuss sail materials challenges, and provide a brief overview of problems such a mission might face. We will than show that with a smart photonic design many of the challenges facing laser propulsion may be alleviated.

3:30 PM EL01.24.02
Self-Assembly of Soft Matter in Porous Solids—From Multiscale Physics to Designing Metamaterials Kathrin Sentker, Manuel Brinker, Mark Busch and Patrick Huber; Hamburg University of Technology, Germany

Self-organized multiscale porosity in terms of precise pore size, shape, and orientation has been achieved in many base materials. Here we exemplify that in combination with self-assembly of soft fillings in pore space this provides particularly versatile pathways for the engineering of functional materials [1]. First, we present a nanoporous semiconductor/polymer hybrid with tunable electro-strain and will relate the macroscopic deformation to meso- and nanoscale electroactuation. Second, we show that embedding liquid crystals in nanoporous solids provides novel opportunities for subwavelength control of light-matter interactions on the single-pore scale and thus to fine-tune the optics of these materials. To that end we present reciprocal space mappings employing synchrotron-based 2D X-ray diffraction in combination with high-resolution birefringence experiments on disk- and chiral rod-like molecules confined in monolithic nanoporous silicon, silica and alumina. As a function of pore hydrophilicity and thus distinct molecular anchoring at the pore walls we observe a remarkably rich self-assembly behavior, unknown from the bulk state, such as a quantized formation of concentric discotic rings [2], a transition from axial to radial aligned discotic columns and the formation of pore-axis aligned supemolecular helices [3]. Intimately related with this surprising self-organization at the nanoscale the soft-hard hybrid materials exhibit novel metaphotonic functionalities encompassing optical anisotropy step-wise changing with temperature [2], enhanced light rotation and extremely fast electro-optically active Goldstone excitations typical of para-to-ferroelectric phase transitions [3]. Self-assembly of radial aligned rings and axial aligned columns of disk-like molecules in cylindrical alumina nanopores as evidenced by X–ray diffraction. This results in an either prolate or oblate ellipsoid of refractive indices (indicatrix) aligned to the pore axis direction. Thus, linear polarized light is split up by a parallel array of such pores into two beams with perpendicular polarizations and distinct propagation speeds. Their relative phase shift (retardation R) after passing the birefringent pore array is positive or negative, respectively, and vanishes upon heating to the isotropic liquid state.

**References:**


Beyond Solubility—Hyperdoped Silicon for Near-Infrared Plasmonics

Jura Rensberg\textsuperscript{1}, Kevin Wolf\textsuperscript{1}, Martin Hafermann\textsuperscript{1}, Sebastian Geburt\textsuperscript{2} and Carsten Ronning\textsuperscript{1}; \textsuperscript{1}Friedrich Schiller University, Germany; \textsuperscript{2}INNOVAVENT Laser Optics, Germany

The free charge carrier concentration of semiconductors, such as in silicon, is tunable over several orders of magnitude. Thus, the plasma wavelength of these materials can be adjusted over a wide spectral range by controlling the doping concentration. Comparable to noble metals in the ultraviolet/visible spectral region, highly doped semiconductors possess 'metal-like' optical properties but typically limited to the mid infrared region due to the solubility limit of dopants.

We demonstrate that the range of accessible plasma wavelengths can be extended far into the near-infrared region reaching the telecommunication wavelength by hyperdoping of silicon – doping beyond the solubility limit - using two non-equilibrium processes: high fluence ion beam doping and subsequent pulsed laser annealing. Laser annealing using high intensities over very short time scales leads to surface layer melting followed by rapid resolidification, which allows exceeding the solubility limit.

Further, we demonstrate how area selective activation of dopants by focused laser annealing can be used as a fabrication-friendly platform for flat optical and plasmonic devices. Detailed characterization of the optical properties of silicon is performed at various doping levels, and diffractive optical elements and plasmonic surfaces that operate in the near-to-mid infrared regime are presented. Our resulting devices are monolithic, flat, resilient to thermal and physical damage, and can be easily integrated into other silicon-based platforms.

Dynamic Nano-Optics Enabled by Stimuli-Responsive Polymers

Irina Zubritskaya\textsuperscript{1}, Alexandre Dmitriev\textsuperscript{2}, Sara Nocentini\textsuperscript{3}, Daniele Martella\textsuperscript{3}, Diederik Wiersma\textsuperscript{3} and Mark L. Brongersma\textsuperscript{1}; \textsuperscript{1}Stanford University, United States; \textsuperscript{2}University of Gothenburg, Sweden; \textsuperscript{3}University of Florence, Italy

Planar nano-optical elements beyond the diffraction limit are envisioned to replace the conventional refractive optics and are already providing needed functionalities to build lenses, beam deflectors, holograms and polarizing interfaces [1]. Their key elements are the nanoantennas that operate via plasmon or Mie-type optical resonances and are able to confine light on the nanoscale and modify its fundamental properties such as scattering, directionality, polarization and phase. However, a significant demand exists for the real-time steering of light in such optics. Here, we combine for the first time Mie-resonant and plasmonic nanoantennas and the light-responsive elastomers to create a fundamentally new dynamic / real-time tunable optical platform for reflected or transmitted light control.

We build a tunable optical platform based on nanoantennas and stimuli-responsive polymers, already well known to the fields of haptics and soft robotics, and also as artificial muscles, due to their strong yet soft actuation properties. For that, we employ liquid crystalline elastomers (LCEs) that are a special type of elastic polymers with self-organization and the ability to reversibly change their microscopic shape in response to the external stimuli such as temperature, irradiation with light or the electric fields (via resistive heating or piezo-like response) [2]. We further functionalize the LCE with photoswitchable molecules (azo-derivatives) incorporated to the molecular network, which makes elastomers light-responsive and capable of producing large mechanical strains upon illumination. By spacing the nanoantenna’s elements with LCE we change their mutual positioning upon actuation, thus providing the change in scattered light’s propagation, polarization and phase. We also demonstrate that the desired photomechanical strains and modified optical response can be programmed by careful chemical engineering of the molecular network. For that, we employ lithographic techniques such as direct laser writing (DLW) to produce high-resolution three-dimensional (3D) nano- and micro-scale structures and add the nano-mechanical functionality to optically resonant nanoantennas [3].

Phonon Polaritons and Biphasotropy in α-MoO₃
Sina Abedini Dereshgi, Xianglian Song, Akshay A. Murthy, Vinayak Dravid and Koray Aydin; Northwestern University, United States

Since successful demonstration of graphene as a monolayer 2D material, scientific community significantly expanded layered van der Waals materials family with different electronic, optical, mechanical and thermal properties which are pivotal in the quest for miniaturized photonics. Here, we investigate the optical properties of α-MoO₃ both theoretically and experimentally. Due to strong anisotropy of α-MoO₃ in all 3 dimensions, it is expected to show three distinct Reststrahlen (RS) bands in mid-IR wavelengths which can give rise to the excitation of phonon polaritons within these RS bands. Phonon polaritons have significant implications for optical device design due to their unique properties such as wavelength shrinking and low loss. The optical properties of α-MoO₃ can adequately be described using the phenomenological Lorentz oscillator model with parameters estimated in literature. Applying this relation, the complex dielectric constant of α-MoO₃ is calculated which is in turn used to obtain the dispersion relation of α-MoO₃ in x, y and z directions. After confirming our optical model, we propose a thin film multi-layer structure in order to experimentally examine the traces of the mentioned three RS bands through enhanced absorption as a result of phonon polariton excitation. The proposed structure, from bottom to top, is composed of thick Au, Ge and transferred α-MoO₃. In particular, two samples with two different thicknesses of Ge (400 nm and 800 nm) are fabricated. The reflectance (R) versus wavenumber measurements are carried out using FTIR to obtain the total absorption (A). Since the thick Au suppresses any transmission, the total absorption can easily be calculated using the R data. The FTIR results illustrate absorption peaks around 800 cm⁻¹ (12 μm) and 550 cm⁻¹ (18 μm) which represent the x and y direction (in-plane) phonons respectively. Furthermore, polarized incident light measurements in FTIR emphasize polarization-dependent absorption in α-MoO₃ which is an explicit outcome of perpendicular x and y phonons, where one of the in-plane resonance peaks is maximized only when the other one disappears. In order to explain the observed results in further depth, simulations are carried out using TMM and FDTD methods which are in agreement with the experiments. In order to have accurate simulation results, the thickness of α-MoO₃ flakes are measured by AFM and introduced to simulation. Our simulation results show Fabry-Perot (FP) effect in the Au/Ge/α-MoO₃ structure which enhances the absorption. Specifically, for the sample with 800 nm thick Ge, the FP resonance is intentionally designed to occur in the vicinity of the x-phonon peak. Therefore, the x-phonon peak is intensified which further supports our discussion. Since our measurement method relies on normal incidence measurement, there is no electric field component in z-direction. As a result, excitation of z-phonons is not viable. In order to circumvent this issue, we have designed and fabricated a new structure. A patterned layer of periodic Au nanodisks is added to the top of α-MoO₃ in Au/Ge/α-MoO₃ structure. When illuminated, the nanodisks diffract light and facilitate the coupling of radiation to the z-phonons of α-MoO₃. The absorption peak near 10 cm⁻¹ (10 μm) can be spotted in both experiments and simulations which justifies the observation of z-phonon polariton excitation. The electric field simulations are in line with the expected enhancement of z-component of the electric field. The outstanding anisotropy of α-MoO₃ in three directions can open new paths for mid-IR optics and it can provide unprecedented opportunities to engineer low-loss optical devices for the crucial mid-IR atmospheric window (8 – 12 μm).

Kerker-Conditioned Dynamic Nanoprints for Cryptographic Application
Jaehyuck Jang and Junsuk Rho; Pohang University of Science and Technology, Korea (the Republic of)

Metasurfaces are 2D metamaterials; they have exciting optical behaviors and interesting applications as ultrathin optical devices for nanoscale-resolution imaging, sensing, holograms and nanodisplay. Plasmonic metasurfaces, studied so far have inherent metallic-loss in the visible regime, so they have poor color saturation. Instead of plasmonic coloring, all-dielectric metasurfaces such as silicon metasurfaces offer an alternative way to generate colors by exploiting Mie resonances [1,2]. Nevertheless, for the next step toward real-life applications, the metasurface coloration demand a broad color spectrum as well as dynamic/tunable functionality which many of research are dealing with recently [3]. Therefore, we should consider three main aspects: material selection, structural design and the dynamic colour mechanism. All-dielectric materials are preferred to avoid optical losses that exist in conventional metals. The metasurfaces should be designed based on deep physical understanding of the
nanoantenna’s scattering behavior to achieve vivid and bright colours. Lastly, the dynamic colour mechanism requires a fast response and the compatibility to work with electrically driven devices. Here, we would like to introduce our significant effort which realize cryptographic nanoprints by metasurface coloration and thus will achieve a substantial step forward towards enhanced security printing applications [4].

1) Our hydrogenated amorphous silicon (a-Si:H) metasurfaces achieve diverse colours due to high refractive index and near-zero extinction coefficient of a-Si:H. 2) We deploy nanocuboid-antennas which is designed based on Kerker’s condition for tunable functionality. Unidirectional scattering tuned by the asymmetric nanoantenna’s spatial dimensions and polarization state enable a wide colour gamut and modulation range. 3) We design and experimentally demonstrate cryptographic nanoprints that contain encrypted optical information under unpolarized light, where the hidden information can be decoded under polarized light of a specific angle. This dual optical data storage enables doubly-secured QR codes as cryptography and microprints as steganography, respectively. We success to scan those QR codes with smartphone scanner. Consequently, we were able to connect nano planar optics with smartphone technology spread out all over the world. This research hastens the date when the meta-prints technology will be deployed on a commercial use.

References

SYMPOSIUM EL02

Molecular and Organic Ferro- and Piezoelectrics—Science and Applications
December 2 - December 4, 2019

Symposium Organizers
Kamal Asadi, Max-Planck Insitute for Polymer Research
Martijn Kemerink, Linkoping University
Katja Loos, University of Groningen
Tse Nga Ng, University of California, San Diego

* Invited Paper

SESSION EL02.01: Novel Applications and Analyses
Session Chair: Katja Loos
Monday Morning, December 2, 2019
Hynes, Level 1, Room 105

8:30 AM *EL02.01.01
Developing Ferroelectric Materials to Generate Giant Electrocaloric Effect Qiming Zhang; The Pennsylvania State University, United States

Electrocaloric effect (ECE) is the ability of a dielectric to change its temperature and entropy as an electric field is applied and released. ECE provides an effective means to realize solid-state cooling that is environmentally benign
and potentially highly energy efficient. During past several years, we have been investigating approaches in developing ferroelectrics which can generate giant electrocaloric effect over a broad temperature range. This talk will present these progress, especially, on how to generate a large ECE under low electric fields.

9:00 AM EL02.01.02
Reversible and Irreversible Pyroelectricity—Thermal Expansion and Ferroelectric Imprinting in P(VDF-TrFE) Christian Peter and Herbert Kliem; Electrical Engineering Physics, Germany

We investigate and discuss the pyroelectric response of poled and unpoled thin films of the ferroelectric co-polymer P(VDF-TrFE) at a composition 70/30 mol%. Having the films prepared in a low humidity environment reduces the dark current yielding polarization versus temperature hysteresis loops in unprecedented resolution. The loops are recorded between the glass transition temperature and the melting temperature. Poled and unpoled films are presented to exhibit clear first order Curie transitions. In poled samples we monitor a current in close vicinity to the Curie transition, which is assigned to detrapped charges released from the crystal-amorphous interface.

In the later sections of this work we show, that below the Curie transition, the pyroelectric response in poled films can be divided in reversible and irreversible contributions. The reversible contributions are a result of the thermal expansion of the non-ferroelectric amorphous phase in association with rigid ferroelectric crystallites. The irreversible contributions can be assigned to imprinting. Imprinting is an aging mechanism: Stray fields generated by the ferroelectric polarization in the ferroelectric crystallites, force the dipoles outside the ferroelectric crystallites to reorient anti-parallel to the ferroelectric polarization vector. According to that, the irreversible pyroelectric response is a current caused by dipole reorientation processes in the polymer due to internal fields. A consecutive annealing procedure below the Curie transition is used to experimentally separate the reversible from the irreversible pyroelectric response. Then, with the aid of numerical calculations, we model the current flow due to irreversible pyroelectricity. We show that above a certain temperature (Ta=45°C), the relaxation processes associated to imprinting / irreversible pyroelectricity stop being Arrhenius-like and start following a compensation law. We think that these relaxation processes take place at the surface of ferroelectric crystallites, in the so called defect-ferroelectric (DFE) phase. The DFE phase is postulated to be located at the boundary crystal-amorphous, so to say enveloping the ferroelectric crystallites. The conjecture that the relaxation processes associated to imprinting / irreversible pyroelectricity are located in the DFE phase is founded on two facts: First, the temperature Ta coincides with the onset-temperature at which the cell parameters of the DFE phase start to continuously expand with increasing temperature due to inclusion of defects. Besides, the DFE phase with fast changing cell parameters seems suitable to host non-Arrhenius-like relaxation processes. Second, both, the compensation law and the DFE phase depend substantially on the Curie Temperature. We conclude with the hypothesis, that there is an interphase at the crystal-amorphous interface, which hosts relaxation processes associated to imprinting.

9:15 AM EL02.01.03
LIMM Analysis and Geometry Depending Characterization of Novel Lead-Free Pyroelectric Materials for IR Array Detectors Sebastian Bette1, Stefan Tappertzhofer1, Simon Fichtner2, Thorsten Schmitz-Kempfen1, Bernhard Wagner2, Norman Laske3, Carl Van Buggenhout4 and Stephan Tiedke1; 1aixACCT Systems GmbH, Germany; 2Institute of Material Science, Christian-Albrechts-Universität, Germany; 3Fraunhofer Institute for Silicon Technology, Germany; 4Melexis Technologies NV, Belgium

New non-toxic biocompatible materials with piezoelectric and pyroelectric properties are developed for biomedical applications. Lead-free pyroelectric thin films are promising candidates for CMOS compatible and environmental-friendly miniaturized infrared sensors. Piezo responsivity of pyroelectric materials due to mechanical clamping makes the electrical response to transient thermal changes depended of geometrical properties of the pyroelectric material and its mounting. In this study, we report on the characterization of micro structured pyroelectric thin films. By measurement of the transverse effective piezoelectric coefficient, pseudo pyroelectrical contribution due to piezoelectric clamping can be separated from real pyroelectricity. Our novel IR-laser-based measurement setup is designed to record frequency dependent electrical response to spot wise intensity modulated IR irradiation of the sample surface and provides 2D responsivity maps. 3D information of the pyroelectric properties is extracted by LIMM (Laser Intensity Modulation Method). Therefore, the modulation of the IR source is swept up to high-frequencies while recording the sample’s electrical response (including absolute value and phase angle) by a lock-in amplifier. Thermal distribution inside the pyroelectric material is simulated to extract the material’s polarization distribution distribution out of the LIMM data. These results are complemented by microscopic techniques for fundamental
thermal analysis below the microscale. Our novel laser-based measurement setup is an essential step forward for precise material characterization with high spatial resolution for research and can be easily adapted for quality control on industrial scales to enable pyroelectric IR sensor arrays for mass-manufacturing.

9:30 AM EL02.01.04
Development of Functional Piezoelectric Polymers Based on Controlling Flexible Structure Takashi Nakajima1,2, Yoichiro Hashizume1, Takeo Furukawa3,1 and Soichiro Okamura1; 1Tokyo University of Science, Japan; 2Japan Science and Technology Agency, Japan; 3Kobayasi Institute of Physical Research, Japan

Vibrational energy harvesting using piezoelectric materials has been an emerging topic of a renewable energy technology. The technology has a possibility to establish a self-powering device for IoT system that do not depend on conventional power supplies such as batteries, which can deliver electric power only for limited-duration operations. Therefore, the technology is expected to apply to novel sensors for health care and intelligent buildings [1]. The inorganic piezoelectric materials such as Pb(Zr, Ti)O3 have been a promising material which shows highly efficient energy conversion owing to their high electromechanical coupling coefficients. From another point of view, power generation using piezoelectric polymers such as polyvinylidene fluoride (PVDF) are also attractive because of their prospective features of the robustness, flexibility and large scale production. Note that piezoelectric polymers are expected to generate high electric power under large deformation. For example, we designed the power generating systems which enable PVDF to induce large strain by applying a lever structure. The power generating floor generated 7 mW by human stamping [2], which is relatively large output using a piezoelectric material. However, the variety of the piezoelectric polymer is still limited. Thus, we have focused on developing the novel piezoelectric polymers which are more flexible, easy to install everywhere and eco-friendly. Firstly, we report on the self-polarization phenomenon observed in melt-crystallization process of VDF copolymer thin films. Ferroelectric polarization was spontaneously formed when Pt was used as the bottom electrode [3]. Thus, the poling process can be omitted by controlling the crystallization process, which has the advantage to avoid the breakdown. In addition, we also report on the recent progress of VDCN/VAc copolymer. VDCN/VAc is known as an amorphous polymer with great dielectric property and relatively large piezoelectric property. However, the mechanism of the piezoelectricity has not been understood yet. We have revealed that VDCN/VAc has nanoscale domains observed by scanning probe microscopy. Based on controlling the hierarchical structure of the polymer, we challenge to improve the energy conversion efficiency and formability for the fabricating process of the vibration energy harvesting devices.

References

9:45 AM BREAK

SESSION EL02.02: In Situ Characterizations
Session Chair: Qiming Zhang
Monday Morning, December 2, 2019
Hynes, Level 1, Room 105

10:15 AM *EL02.02.01
Nanoscale Switching Behavior of Molecular and Polymer Ferroelectrics Alexei L. Gruverman; University of Nebraska-Lincoln, United States

Piezoresponse Force Microscopy (PFM) has been used to investigate the switching behavior in ultrathin films of PVDF-TrFE. The mechanism of polarization reversal has been investigated via sub-10 nm real space imaging of domain pattern evolution under an applied electric field. The domain switching behavior revealed in PVDF-TrFE nanomesas is drastically different from that observed in inorganic solid-state crystalline ferroelectrics. The
nanoscale features of the switching process include remote domain nucleation and spatially nonuniform wall velocity. Local switching spectroscopy and domain dynamics studies relate the observed switching features to a random-bond type disorder associated with defects in conformation and molecular packing. The PFM approach has been also used for investigation of the static and dynamic behavior of ferroelectric domains in diisopropylammonium bromide (DIPA-B) microcrystals. It is shown that stable head-to-head or tail-to-tail domain configurations can be realized in DIPA-B. In-plane alignment of polarization allows investigation of the forward domain growth along the polar axis - a process that is difficult to attain in conventional ferroelectric switching studies. Using this sample geometry, we have directly measured anisotropy of the domain wall velocity for the forward and lateral growth and demonstrate the effect of the forming charged domain walls on morphology of the growing domains.

10:45 AM EL02.02.02
Mapping the Microscopic Electric Fields of a Self-Assembled Anti-Ferroelectric Material with Vibrational Spectroscopy Aaron Rury, Sydney Lavan, Cathleen Saraza, Adedayo Sanni and Kanwar Bhullar; Wayne State University, United States

The bulk polarizability of self-assembled anti-ferroelectric materials is central to the energy storage capabilities of these molecular solids. This polarizability critically depends on poorly understood electric fields on length scales smaller than constituent molecular units. In this study we use vibrational spectroscopy of single crystals of the anti-ferroelectric material 2-trifluoromethylbenzimidazole (TFMBI) to directly analyze these fields and how they change with temperature. Experimentally, we find cooling the material causes red-shifts of Raman-active peaks near 3100 cm\(^{-1}\) and blue-shifts of peaks between 900 cm\(^{-1}\) and 1600 cm\(^{-1}\). Density functional theory calculations provide assignments of these reporter vibrations. By comparing solid-state spectra to those acquired from molecules dissolved in different solvents, we are able characterize the direction and magnitude of changes to microscopic electric fields in TFMBI. We discuss how to relate the measured changes in the microscopic electrostatic structure of the material to temperature-dependent changes to its macroscopic dielectric properties. These results indicate vibrational spectroscopy may be a critical tool in assessing the microscopic electric fields central to the application of self-assembled materials in energy storage applications.

11:00 AM EL02.02.03
Correlation Microanalysis of Nanoscale Mechanical Property and Molecular Orientation of PVDF Based Copolymer Using Dynamic and Infrared Atomic Force Microscopy Wen Qian, Shuo Sun, Charles Nguyen, Stephen Ducharme and Joseph A. Turner; University of Nebraska-Lincoln, United States

Electrically active materials, such as Poly(vinylidene fluoride) (PVDF) and its copolymers, have the ability to harvest mechanical energy through mechanical vibrations and structural flexing. The ferroelectric phase of PVDF consist of long chains of the dipolar VDF (–CF\(_2\)-CH\(_2\)) monomer that crystallize in a quasi-hexagonal close-packed “β-phase” structure with the molecular dipoles aligned perpendicular to the chain axis, producing a switchable spontaneous polarization and consequently, a significant piezoelectric response. Due to the inherent nanoscale dependency of PVDF’s molecular structure, quantitative methods for nanoscale molecular structure and mechanical analysis are limited. In this presentation, we demonstrate the methods for investigating the local mechanical properties quantitatively. These properties include the elastic modulus and damping which are measured using contact resonance atomic force microscopy (CR-AFM). In addition, we have used nanoscale infrared (nanoR) spectroscopy with chemical mapping to probe the correlation between localized molecular structure and orientation on the nanoscale. The thin PVDF nanomesa studied here were made from a copolymer of 70% vinylidene fluoride and 30% trifluoroethylene, P(VDF-TrFe) using the horizontal Langmuir-Blodgett transfer technique. This nanomesa film was formed on a substrate of a p-type silicon wafer by a drying and fine annealing procedure. For CR-AFM, the height image, frequency map, and Q factor map are collected, which allows for the investigation of the local mechanical properties associated with the in plane and out of plane structure. In general, higher frequency value means stiffer and higher Q value reflects less energy dissipation. The orientation of PVDF’s molecular structure dependency was investigated by rotation of the sample stage. The distribution of the polymer chain axes was determined from the asymmetric frequency mapping -- which is attributed to the local stiffness of in-plane structure. The results demonstrate that CR-AFM can aid in the understanding of the fabrication process, to achieve high crystallinity and orientation with good mechanical properties. The nanoR mapping data were used to determine the crystalline orientation of an individual nanocrystal. By fixing the wavelength at 1078 cm\(^{-1}\) the C-C antisymmetric stretching absorption band can be mapped for the nanomesa crystal. In this way, we identified higher
signals when the IR laser was aligned with the C-C-C chain and lower signals were found when the IR laser was not aligned. A similar approach was used to determine molecular orientation, where the IR laser direction is changed to investigate the orientation dependency within the nanomesa structure -- which is consistent with the stage rotation done for the CR-AFM measurements. Through combination of CR-AFM and nanoIR, we are able to correlate the molecular structure and localized mechanical properties, to optimize the electroactive polymer organization. This approach can guide the design and fabrication of high-performance, flexible, energy-harvesting devices. [Research supported by the Nebraska Center for Energy Sciences Research].

11:15 AM EL02.02.04
Effect of Local Polar Environment and Phase Morphology on Organic Optoelectronics Aditi Khirbat1, Ilaria Bargigia1, Artem Levitsky2, Mark D. Losego1, Carlos Silva1, Gitti L. Frey3, Lee Richter3 and Natalie Stingelin1;
1Georgia Institute of Technology, United States; 2Technion - Israel Institute of Technology, Israel; 3National Institute of Standards and Technology, United States

Combining semiconducting and ferroelectric functions in a given architecture has been a long-time goal in the electronics community. Various approaches have been used1,2 to blend semiconductor and ferroelectric polymers for micro- and opto-electronic applications. Here we discuss model systems based on the archetypal semiconducting polymer poly(3-hexylthiophene) (P3HT) blended with the ferroelectric commodity polymer poly(vinylidene difluoride) (PVDF), to provide insights on the effect of the local environment and phase morphology, manipulated by the addition of PVDF, on the optoelectronic properties of P3HT. Unlike the phase separated structure generally reported in these blends1,3 we present signs of intermixing, with varying P3HT domain purity and crystallinity as a function of PVDF. We show strong influence of these structural effects, along with the blending induced effects of the ferroelectric β phase of PVDF, on the photo-physical processes of the semiconductor. We illustrate variations in the photoluminescence and charge dynamics of photo-induced absorption with blend compositions, suggesting localized enhancements of the polar, dielectric environment in the blend. Finally, a correlation between structure and relevant dielectric and semiconducting features is demonstrated, opening pathways to design new multicomponent material systems with multifunctional architectures for optoelectronic applications.

References

SESSION EL02.03: Molecular Ferroelectrics
Session Chair: Alexei Gruverman
Monday Afternoon, December 2, 2019
Hynes, Level 1, Room 105

1:30 PM *EL02.03.01
Highly Ordered Molecular Organic Ferroelectric Films by Soft Lithography Techniques Ilaria Bergenti1, Giampiero Ruani1, Silvia Milita2, Fabiola Liscio2, Franco Dinelli3, Xiaofeng Xu4, Indre Urbanaviciute5, Martijn Kemerink6 and Massimiliano Cavallini1; 1ISMN CNR, Italy; 2IMM CNR, Italy; 3INO CNR, Italy; 4Chalmers University of Technology, Sweden; 5Linkoping University, Sweden

Ferroelectric molecular compounds present great advantages for application in electronics because they combine the high polarization values, comparable with those of inorganic materials, with the flexibility and low cost properties of organic ones. However, some limitations to their applicability are related to the high crystallinity required for deploying the ferroelectricity. Highly ordered ferroelectric patterned thin films of disopropylammonium bromide have been successfully fabricated by lithographically controlled wetting technique. Confinement favors the self organization of ferroelectric crystals, avoiding the formation of polymorphs and promoting long range orientation of crystallographic axes. Patterned structures present high stability and polarization can be switched to be arranged in stable domain pattern for application in devices. The versatility of this methods allows to extend the results to the class of molecular ferroelectric materials.
Deuteration can be used as an effective probe for dynamic and structural properties of ferroelectric materials, especially those based on hydrogen-bond ordering, such as potassium dihydrogen phosphate (KDP) [1]. The diisopropylammonium halide (DIPA-X, X = Cl, Br, I) system is a ferroelectric material of interest due to its high room-temperature polarization, low coercive field, and low material cost [2]. The three DIPA halides all share similar structures and ferroelectric properties. In particular, on heating, the ferroelectric P21 phase gains a mirror plane to become the paraelectric P21/m phase. While the DIPA halides aren’t strictly hydrogen-bond-ordered ferroelectrics, they do contain NH–X hydrogen bonds, which form a continuous chain along the polarization axis. This hydrogen-bond chain plays an important role in crystal structure and may also influence the properties of the ferroelectric phase. The purpose of this report, therefore, is to address the role of deuteration on the properties of DIPA-X ferroelectric materials. We found that deuteration of the amine hydrogens in DIPA-X is easily carried out by recrystallization from heavy water. Like KDP, DIPA-Br exhibits a negligible change in lattice spacing on deuteration. Deuteration also lowered the temperature of the peak low-frequency dielectric constant associated with the ferroelectric-to-paraelectric transition by approximately 0.5 K in DIPA-Br. Further study with differential scanning calorimetry (DSC) revealed deuteration lowered the ferroelectric–paraelectric transition temperature and decreased the associated temperature hysteresis for all three DIPA halides. DIPA-I exhibited the largest shift with a decrease in transition temperature of 2.9 ± 0.4 degrees to its phase transition temperature, and DIPA-Cl the lowest with decrease of 0.5 ± 0.1 degrees. The temperature shift is downward, rather than upward, as is observed with most hydrogen-ordered ferroelectrics. For example, deuteration of KDP increases the transition temperature by 91 K [1]. The enthalpy of the transition, which ranged from 3.6 ± 0.1 J/kg for DIPA-Br to 4.2 ± 1 J/kg for DIPA-I, exhibited negligible change on deuteration.

This work was supported by the National Science Foundation (NSF) through the Nebraska Materials Research Science and Engineering Center (MRSEC) (DMR-1420645).

Therefore, the crystals transformed from the non-polar phase to the ferroelectric phase occurs without changing morphology or exhibiting significant internal stress, suggesting that the transition is continuous. This hypothesis is further supported by the relatively low enthalpy of the transition (1.3 J/g), and the small (1%) change in density [1]. The elastic modulus of approximately 10 GPa is the same in both phases (<10%) change in the elastic modulus, which is approximately 10 GPa for both phases, although the loss modulus of the ferroelectric phase, at 1 GPa, is approximately twice that of the non-polar phase. This work was supported by the National Science Foundation (NSF) through the Nebraska Materials Research Science and Engineering Center (MRSEC) (DMR-1420645) and by the Nebraska Center for Energy Sciences Research.


2:30 PM EL02.03.04
Molecular Organic Piezo- and Ferroelectric Coatings and Fibbers for Biodegradable and Biocompatible Platforms for Tissue Engineering Paula Maria Vilarinho, Nathalie Barroca, Ana Marote, Sandra Vieira, Maria Helena Fernandes, Odete Silva, Paula Marinho, Marisa Costa and Ana Gil; Univ de Aveiro, Portugal

Creating new tissues and organs and promoting the regeneration of damaged or diseased tissues and organs are the objectives of tissue engineering and/or regenerative medicine. In spite of the complexity of regenerating tissues major advances have been achieved. The potential of piezoelectricity-stimulated cell migration and growth unveils appealing opportunities in tissue engineering, as the use of devices allowing surface charges to be controlled in real time by simply applying a mechanical stimulus.

Poly (l-lactic) acid (PLLA) is an FDA approved biodegradable and piezoelectric polymer that has been object of extensive research, namely as a scaffolding material and drug delivery system. Here, we exploit the feasibility of using electrical polarization in PLLA coatings and aligned nanofibers and investigate the biological outcome of these electrically-induced poled PLLA platforms on neuronal relevant in vitro models. In addition we have carried out a metabolomics study of the effects of PLLA (either non-poled or negatively poled) on the metabolism of osteoblastic HOb cells, aiming at unveiling the metabolic cell adaptations to PLLA and its poled state. The presence of PLLA seems to trigger cell catabolism and anti-oxidative protective mechanisms in HOb cells, while directing them towards cellular growth. A qualitative tendency for negatively-poled PLLA to be more effective in sustaining cell growth than non-poled PLLA was suggested. Finally, the concept of a biological BioMEMs platform composed of piezoelectric PLLA and 316L stainless steel is proposed as an alternative to be used in the implant technology.

2:45 PM EL02.03.05
Molecular Ferroelectrics with Perovskite Structures Yu-Meng You; Southeast University, China

Molecular ferroelectrics with cheap, light-weight, flexible, wearable, and environmentally benign characteristics have been an attractive research topic in the past decades due to the potential applications in data storages, piezoelectric sensors, actuators, and nonlinear optical devices. Their intrinsic structure-property flexibility attracted particular interest for molecular design towards new materials with good ferroelectric performance at room temperature. Nevertheless, developing a reliable method to form polar structures and further tune the ferroelectricity is an imminent ongoing challenge.

In this talk, we present our recent achievements on molecular ferroelectrics in perovskite structures with new design strategies of selection of molecular building blocks and several new molecular ferroelectrics with exciting ferroelectric, optical and piezoelectric properties.

References:

3:00 PM BREAK
3:30 PM *EL02.04.01
Alternating Current Sensors, Memories and Displays with Ferroelectric Polymer Driven Sound Cheolmin Park and Jong Sung Kim; Yonsei University, Korea (the Republic of)

Visualization of human senses has been of great interest for developing an emerging interactive display that can artificially stimulate synesthesia with numerous unprecedented applications. Especially, visualization of various daily sound and music, which are much more complicated than human touch, in a form of flexible thin film devices can be a great challenge. In this presentation, we first present flexible artificial synesthesia devices that visualize continuous and complicated sounds. The device is made of a thin composite film of a piezoelectric polymer for sound generation and inorganic electroluminescence (EL) microparticles for direct visualization of input sound signals. Field-induced alternating current (AC) EL of the microparticles in the device depends upon the source sound wave, making their EL synchronized with sound arising from the piezoelectric actuation. Our device showed extreme mechanical tolerance that can be repeatedly folded and crumpled with visible sound, allowing a variety of unexplored applications including synchronous sound-lightings and wearable, on-body sound-vision systems to facilitate emotional interaction of human being with sound in a human-friendly form. We also demonstrate that piezo and ferroelectric sound is capable of sensing, monitoring, and storing the information of various liquids. Our platform utilises sound arising from liquid-interactive ferroelectric actuation, which is dependent upon the polarity of the liquid. Liquid-interactive ferroelectric sound (LIFS) is successfully developed when a liquid droplet is placed on a ferroelectric polymer layer across two in-plane electrodes underneath the ferroelectric layer under an external in-plane AC field. An AC field built up vertically between one of the electrodes and the liquid results in ferroelectric vibration of the device, leading to sound. The sound pressure level (SPL) of the device depends upon the polarity of the liquid, allowing for facile liquid sensing and identification. More importantly, as the SPL arising from LIFS of a liquid is correlated with non-volatile remnant polarisation of the ferroelectric layer, the information of a liquid is readily stored and retrieved even after the liquid is removed, resulting in a sensing memory of the liquid. By programming different LIFSs on a thin film pad, we can also identify the 2D position of a liquid droplet on the pad. Moreover, our device successfully monitored the flow of a human serum liquid passing through channels with their diameters ranging from millimetres to tens of microns and determined its velocity. Mechanically flexible and optically transparent tube-type LIFS AC devices allow for in situ analysis of the flow of a liquid in terms of SPL.

4:00 PM EL02.04.02
Fabrication of Piezoelectric Rubber Materials with Flexibility Tatsuya Ota and Shogo Mamada; Railway Technical Research Institute, Japan

Piezoelectric Rubbers prepared with mixing piezoelectric-ceramic particles and an elastic material have potential applications such as sensor and actuator due to the piezoelectricity and flexibility. In our previous study, in order to enhance the piezoelectricity, aligned-type piezoelectric rubbers in which piezoelectric particles were aligned in the direction parallel to the thickness by an electric field were fabricated. Since the piezoelectric rubbers previously fabricated had thinner shapes and large spring constants, it has not had the flexibility sufficient to use as vibration-isolating materials.

In this study, in order to lower the spring constants, the aligned-type piezoelectric rubbers with a thickness of more than 5 mm were prepared. For the thinner conventional aligned-type piezoelectric rubbers, piezoelectric particles precipitated in a molding were easily aligned by an electric field due to the thin shapes. On the other hand, it was difficult to align piezoelectric particles only by an electric field in the case of thicker rubbers because the piezoelectric particles used were submillimeter in size and they tended to precipitate to the bottom of the molding by gravity. Hence, in order to prepare the thicker aligned-type piezoelectric rubbers, a novel process in which the molding was inverted before applying an electric field was introduced. In the process, a precipitation layer of piezoelectric particles was set to the top of the molding before applying an electric field. The piezoelectric particles
gradually precipitated in an uncured rubber medium by gravity, which supported to align piezoelectric particles by an electric field.

To confirm the formation of particle alignments, numerical simulations on the process in which the molding was inverted before applying an electric field were carried out. As the results of the simulation study, piezoelectric particles were aligned from the top to the bottom in the molding even if the piezoelectric rubbers had more than 5 mm of thickness. Thus, the numerical simulations clarified that the particle alignments were affected by particle position before applying an electric field. Furthermore, in the experimental study, considering the case that piezoelectric particles comparably fast precipitated after inverting the molding due to the low viscosity of a medium, the viscosity of a medium was controlled by changing the period from starting to heat an uncured medium to inverting a molding and applying an electric field, which led to adjusting the speed of particle precipitation. Based on the actual experiments, the aligned-type piezoelectric rubbers with thicknesses of 5 mm and 10 mm were successfully fabricated for the piezoelectric particle volume of 10–30%.

The piezoelectric performance of the piezoelectric rubbers obtained in this study was comparable to previous ones. For the piezoelectric rubbers with a thickness of 10 mm, the spring constants as small as approximately 1/30 of the conventional piezoelectric rubbers were obtained. The thicker aligned-type piezoelectric rubbers newly fabricated have potential uses as anti-vibrating and sensing materials.

4:15 PM *EL02.04.03
Polymer Based Micromachined Ultrasound Transducers for Display-Like Applications David Cheyns; imec, Belgium

Traditional microphone units focus on human perceptible sound waves (between 20 Hz and 20 kHz). Acoustic development also includes the ultrasound region, compromising the frequencies above the detection limit of the human ear (from 20 kHz to several GHz). These sound waves can be used for a wide variety of applications, including medical imaging, therapeutic treatment, non-destructive testing, fingerprint detection, gesture recognition and mid-air haptic feedback. Nowadays, the ultrasonic transducer and sensor technology is largely based on rigid bulk piezoelectric ceramic materials, such as lead zirconate titanate or barium titanate. Classical techniques to grow such ceramic materials require high process temperature and dedicated substrates. Although this is a mature technology for discrete passive components, offering a reasonably wide bandwidth and sensitivity, it is not amenable to machine large two-dimensional (2D) transducer arrays. Monolithic integration with other electronic components such as signal processing electronics is hardly possible. For this, a display like process technology is required. During this presentation, I will give an overview of the recent developments at imec to use polymer based piezoelectric materials processed on glass substrates for large arrays of ultrasound transducers. Several challenges specific to organic material processing are tackled or under investigation: uniformity over larger substrate size, photo-lithographic based patterning, integration of the ultrasound elements with thin-film circuitry. Larger arrays of up to 64x64 elements are developed, which can be used to either emit ultrasound or to detect reflected acoustic waves. Using beam-forming techniques, the acoustic pressure can be focused on a single point in 3D space, which enables future application such as mid-air haptic feedback or local wound healing.

8:30 AM *EL02.05.01
Chain Dynamics Governing Phase Transition and Polarization Switching in Ferroelectric VDF-Based Polymers Takeo Furukawa¹, Hidekazu Kodama¹ and Takashi Nakajima²; ¹Kobayasi Institute of Physical Research, Japan; ²Tokyo University of Science, Japan

Ferroelectric vinylidene fluoride (VDF)-based polymers are overviewed with special interest on the chain dynamics governing phase transition and polarization switching phenomena. Their ferroelectricity originates in the large dipole moment of CH2CF2 unit. All-trans conformation and parallel packing induce alignment of all molecular dipoles to generate spontaneous polarization P_s that is switchable by action of high external electric field. The copolymer with trifluoroethylene (TrFE) containing 50-80mo% VDF exhibits Curie point T_c associated with...
transition into the paraelectric phase. As the VDF content exceeds 80 mol%, $T_c$ is overtaken by melting. For TrFE-rich copolymers, the paraelectric phase is preceded by the anti-ferroelectric phase consisting of randomly packed all-trans chains. Thus the phase behavior in VDF-based polymers is related to successive loss of intermolecular, intramolecular and crystalline dipolar order.

In the molten phase, VDF-based polymers assume a random mixture of three conformational states (TT, TG, TG’) and gain the conformational entropy of $R\ln 3$. That in the paraelectric phase is calculated to be $R\ln 1.6$. These values are consistent with the observed heat of transition at $T_m$ and $T_c$. Chain dynamics comprising such conformational disorder can be characterized by dielectric spectroscopy. One particular relaxation process has been found to exist near 1MHz at room temperature and to move toward higher frequency side to reach 1GHz on melting. Although the relaxation time shows down near $T_c$ in accord with dielectric anomaly, essentially the same chain dynamics govern the dielectric relaxation process. Below room temperature, the relaxation spectra split into two components. One is of VTF-type characteristic of segmental motion and the other is of Arrhenius type referred to a local mode. The latter is important because it lies on a linear extension to the molten phase with activation energy of 50kJ/mol. This is a clear demonstration of an elementary molecular motion governing the ferroelectric, paraelectric and molten phases.

The time domain measurements of polarization reversal using a step-wise electric field reveal another chain dynamics associated with 180-degree rotation of all-trans molecules about their chain axis. We have consistently examined the switching characteristics of VDF-based polymers from highly crystalline-thick to ultra-thin films. One of the common features is that the switching time obeys an exponential law that is transferred to a power law above 300MV/m. The fastest switching time was found to be limited to 1 ns at 800 MV/m. The time-resolved PFM confirmed that polarization reversal progressed via. nucleation-growth mechanism in respective crystalline grains filling VDF/TrFE thin film. The effect of high electric field in VDF-based polymers is not limited to polarization switching. It has been already established that extremely high fields lead to conversion among crystalline polymorphs of PVDF from nonpolar form II to ferroelectric form I via form IV and III. Another example is related to the observation that the VDF/TrFE films as prepared exhibit much reduction of dielectric constant after poling. This result is consistent with the reduction of lattice spacing and crystalline disorder. In the presence of dc field, $T_c$ moves to higher temperature side. Disorder induced by bulky TrFE in VDF sequence is a key factor for the appearance of $T_c$. Even if fully poled, there remains disorder inherent to ferroelectric instability. In VDF-based polymers, the elementary process observed dielectrically from molten phase to glassy state provides further information about such disorder.

9:00 AM EL02.05.02
Discovery of the Morphotropic Phase Boundary in Ferroelectric Polymers Yang Liu1, Haibibu Aziguli1, Bing Zhang2, Wenhan Xu1, Wenchang Lu2, J. Bernholc2 and Qing Wang1; 1The Penn State University, United States; 2North Carolina State University, United States

Significantly enhanced electromechanical responses are inherent to the piezoelectric materials at morphotropic phase boundary (MPB). However, this well-established physical concept has never been realized in organic materials. This work demonstrates the stereochemically-induced MPB in the ferroelectric copolymers. We reveal that compositionally tailored tacticity can lead to intramolecular order-disorder evolution in the crystalline phase and thus an intermediate MPB region allowing for simultaneous occurrence of competing ferroelectric and relaxor properties. Our first-principles calculations confirm the crucial role of chain tacticity in driving the formation of MPB via structural competition between trans-planar and 3/1-helical phases. The copolymer with the morphotropic composition exhibits significantly enhanced piezoelectric responses, approximately two times the state-of-the-art piezoelectric polymers. This finding (Y. Liu et al, Nature 562, 96 (2018)) not only enables the investigation of the mechanisms of MPB from a completely new perspective but also offers unprecedented opportunities for the development of scalable high-performance piezoelectric polymers that are promising for flexible, wearable and biocompatible applications.

9:15 AM EL02.05.03
Dipolar Doping of Organic Semiconductors to Enhance Carrier Injection Alexander J. Hofmann1, Simon Züfe2,3, Kohei Shimizu4, Markus Schmid1, Vivien Wessels1, Lars Jäger1, Stéphane Altazin1, Keitaro Ikegami2, Motiur R. Khan1, Dieter Neher1, Hisao Ishii4,4,4, Beat Ruhstaller2,3 and Wolfgang Bruetting1; 1Universität Augsburg, Germany; 2ZHAW Zürcher Hochschule für Angewandte Wissenschaften, Switzerland; 3Fluxim AG, Switzerland; 4Chiba University, Japan; 4Universität Potsdam, Germany
The strong dipole moment of polar organic semiconductor materials like tris-(8-hydroxyquinolate)aluminum (Alq3), if not oriented perfectly isotropic, will lead to the buildup of a giant surface potential (GSP), and thus to a macroscopic dielectric polarization of the organic film. Despite this being a known fact [1], the implications of such high potentials on charge transport and injection within and into an organic layer stack have only been studied recently. For example, we could explain and reproduce in silico the dependence of electron current in organic light emitting diodes (OLEDs) depending on the sign of the GSP of the electron transport layer (ETL)[2].

In this contribution, we will discuss the influence of the GSP of the hole transport layer (HTL) on hole injection into organic layers. Unfortunately, most hole conducting materials are either non-polar or show an isotropic orientation, hence we resort to the new concept of dipolar doping to tune the GSP of a hole conducting layer. Therefore, we chose the prototypical organic materials N,N’-Di(1-naphthyl)-N,N’-diphenyl-(1,1’-biphenyl)-4,4’-diamine (NPB) as host and Alq3 as dopant and varied the doping ratios to tune the GSP in the HTL of a prototypical OLED.

The mixtures are investigated in single-layer, monopolar devices with only the HTL as well as bilayer OLEDs with Alq3-doped NPB as HTL and neat Alq3 as ETL, respectively. The latter are treated as metal insulator semiconductor (MIS) structures following and applying our recently published method of charge extraction by linearly increasing voltage (CELIV) on polar OLEDs[3, 4].

Characterization is then done electrically using current-voltage characteristics, impedance spectroscopy, CELIV and time of flight, as well as optically with ultraviolet photoelectron spectroscopy. For all device types, we find an optimum in device performance and carrier injection for moderate doping concentrations of about 5%. By comparing all different methods with a focus on charge injection barriers, we reveal a complex relationship of carrier transport, substrate workfunction, modified injection and the effect of polarization, effectively manipulating charge carrier injection across the metal-organic interface and transport in the device.


9:30 AM EL02.05.04
Bulk and Interfacial Conductivity Switching in Organic Semiconducting Ferroelectrics Tim Cornelissen¹, Indre Urbanaviciute¹, Nicolas M. Casellas², Julia Guilleme², Tomas Torres², Miguel Garcia-Iglesias² and Martijn Kemerink¹; ¹Linköping University, Sweden; ²Universidad Autónoma de Madrid, Spain

Combining semiconductors and ferroelectrics is a promising strategy to realize novel non-volatile organic memories. While this has been demonstrated by blending ferroelectric and semiconducting polymers, we show that the same functionality can be incorporated in a single supramolecular material, solving amongst others phase separation and scaling issues. This unprecedented class of materials has a disc-like semiconducting core to which dipolar side groups are attached, making the materials both semiconducting as well as ferroelectric.

The ferroelectric and semiconducting properties are found to couple: the conductivity switches between a high and a low state when the ferroelectric polarization reverses. We show that there are two different switching mechanisms at play: bulk conductivity switching or injection barrier modulation. Depending on the material and the energy level alignment with the contacts, one of the two mechanisms will be dominant. Both mechanisms are rectifying, allowing for implementation in high-density, low-cost crossbar memory arrays.
Injection barrier modulation is the working mechanism behind the ferroelectric/semiconductor blends, and functions through a lowering of the injection barrier by the ferroelectric dipoles at the interface. The conductivity will switch from the low to the high state upon polarization reversal. This mechanism will be dominant when there is an injection barrier present.

In contrast, the bulk conductivity switching mechanism occurs when the energy levels of the material and the contact are well-aligned. Here the conductivity will switch from the high to the low state upon polarization reversal. Using a modified Marcus hopping model, we show that the asymmetric potential caused by the ferroelectric dipoles is responsible for the conductivity switching. Fitting the JV-curves to a combination of Ohmic and Space-Charge Limited current provides further proof for the conductivity switching being a bulk effect. This bulk conductivity switching is unique as in general conductivity switching mechanisms are caused by interface effects.

We have thus introduced a new class of materials that are both semiconducting and ferroelectric. The interplay of these two properties leads to rectifying and switchable conductivity. This makes these materials an excellent candidate for printable non-volatile memories.

9:45 AM BREAK

SESSION EL02.06: Ferroelectric Memories
Session Chair: Cheolmin Park
Tuesday Morning, December 3, 2019
Hynes, Level 1, Room 105

10:15 AM *EL02.06.01
Polymer Ferroelectric Non-Volatile Memories—Beyond the Single Bit Gerwin Gelinck1,2; 1TNO-Holst Centre, Netherlands; 2Technical University of Eindhoven, Netherlands

P(VDF-TrFE) based thin-film transistors and diodes have emerged as a promising storage technology for low-cost microelectronic applications on substrates such as plastic and paper. Items where today integration of a silicon chip is not economical, such as toys, cards, labels, badges, value paper, medical disposables, could be imagined to be equipped with electronics – with embedded memory functionality.

In this presentation, some of the higher-order integration aspects are discussed, as in almost all foreseeable applications, multiple memory devices are needed to store a multiple number of bits. An attractive architecture for exploiting the strengths of ferroelectric diodes for memory and logic is the cross-point array, without the need for transistors or other electronic components. In the context of memory, the memory cells are defined by patterning the top electrode into columns and the bottom electrodes into rows. The memory state is changed by addressing the corresponding row and column and applying a bias that will provide the desired ferroelectric polarization. To program all memory elements, each row is sequentially addressed. Large-size memory arrays – up to 1 kbit – will be demonstrated.

Other achievements reported here include multi-bit memory elements, via innovative schemes in fabrication as well as electric driving schemes; integration with relatively complex thin-film transistor addressing circuitry; and finally the combination with OLED pixels, resulting in non-volatile pixels.

10:45 AM EL02.06.02
Flexible Robust and High-Density FeRAM from Array of Organic Ferroelectric Nano-Lamellae by Self-Assembly Mengfan Guo, Yang Shen and Ce Wen Nan; Tsinghua University, China

Ferroelectric memories are endowed with high data storage density by nanostructure designing, while the robustness is also impaired. For organic ferroelectrics favored by flexible memories, low Curie transition temperature limits their thermal stability. Herein, we demonstrate a ferroelectric random access memory (FeRAM) based on an array of P(VDF-TrFE) lamellae by self-assembly. Written data shows enhanced thermal endurance up to 90 °C and
undergoes 12 thermal cycles between 30 and 80 °C with little volatilization. The promoted thermal stability is attributed to pinning effect at interfaces between grain boundaries and lamellae, where charged domain walls and charged defects are coupled. These results provide a novel strategy for improving robustness of organic flexible FeRAMs, and reveal an attracting coupling effect between different phases of ferroelectric polymer.

11:00 AM EL02.06.03
Ferroelectric Field-Modulation Imaging for Proton-Transfer-Type Organic Ferroelectric Thin Films Yohei Uemura1, Shunto Arai1, Jun’ya Tsutsumi2, Satoshi Matsuoka1, Hiroyuki Yamada2, Reiji Kumai3, Sachio Horiuchi2, Akihito Sawa2 and Tatsuo Haségawa1; 1The University of Tokyo, Japan; 2National Institute of Advanced Industrial Science and Technology (AIST), Japan; 3High Energy Accelerator Research Organization (KEK), Japan

The proton-transfer-type organic ferroelectrics are a novel class of ferroelectric materials composed of π-conjugated molecules that are linked by hydrogen bonding. The spontaneous polarization originates from the cooperative transfer of protons within the crystals as well as from the electric dipoles of π-conjugated organic molecules [1]. Many of the materials present room-temperature ferroelectricity with a much lower coercive field (10 – 20 kV/cm) than that of ferroelectric polymers (> 500 kV/cm). The soluble, lead-free, and rare-metals-free characteristics of the organic ferroelectrics allow us to expect that they could become useful components for printed electronics devices operating at low voltages [2]. Nonetheless, the appearance and dynamics of ferroelectric domains and domain walls in such a weak lattice-polarization coupling system are still unclear, although they primarily determine the ferroelectric switching characteristics.

Here we show that the variation in electro-optic response of π-conjugated organic molecules enables visualization of the ferroelectric domains and domain walls in organic ferroelectric thin films [3]. For this purpose, we adopt difference optical image sensing between the forward and reverse field applications with use of CMOS image sensor. We successfully demonstrate that highly sensitive and rapid visualization becomes possible by this technique which we call “ferroelectrics field modulation imaging (FFMI).” Based on the FFMI, we show that the unique optical-probe nature reveals the existence of two types of domain walls showing different three-dimensional orientations within the ferroelectric single-crystal films of Hdpzz-Hca: one type of domain wall is roughly perpendicular to the film plane, whereas the other is considerably tilted from the normal to the plane. We consider that both of the domain walls are neutral ones that are stabilized to generate substantial neutrality by being directed parallel to the direction of spontaneous polarization. We discuss and suggest that the FFMI technique opens a route for exploring the three-dimensional topological nature of domain walls in ferroelectric materials.

crystalline phases. In P(VDF-TrFE)-based polymers, nanoactuation is realized by the twisted-to-all trans conformation transformation. In polyamide-based polymers, nanoactuation is realized by the trans-to-twisted conformation transformation. This understanding will help us design new electroactive polymers for large electrostriction in practical applications.

2:00 PM EL02.07.02
Assessing the Individual Contributions of Dipolar, Trapped and Triboelectric Charges to Electrospun PVDF’s Electrical Response Valerie Rennoll, Ugur Erturun and James E. West; Johns Hopkins University, United States

Electrospun polyvinylidene fluoride (PVDF) has been widely investigated for energy harvesting and sensing applications due to its high sensitivity and flexibility. The electrical response of electrospun PVDF is largely attributed to the piezoelectricity of the polymer when poled and stretched to promote the β-phase. In this phase, dipolar charges are generated in the material when a force is applied due to the separation of hydrogen and fluorine atoms. However, when an air gap is present between the PVDF nanofibers and an electrode, the material can demonstrate an electrostatic response in addition to the piezoelectric response. This electrostatic response is created by surface and space charges that are trapped in the material during electrosprining, as well as triboelectric charges that are transferred between the electrode and material when in contact. The individual contributions of dipolar, trapped, and triboelectric charges in PVDF with an air gap present between the electrode and material remain unclear. In this work, each of these charge contributions is quantified and determined as a function of distance between the electrode and material, electrode material type, and duration, frequency, and load amplitude of the applied force. It is demonstrated that under certain conditions the piezoelectric response of electrospun PVDF is overwhelmed by the electrostatic response caused by trapped and triboelectric charges.

2:15 PM EL02.07.03
Unraveling the Electroactive Properties of Electrospun Silk Fibroin Vitor Sencadas1,1,2, Christopher J. Garvey3, Stephen Mudie4 and Gwenaël Gouadec5; 1University of Wollongong, Australia; 2Illawarra Health and Medical Research Institute, Australia; 3Australian Nuclear Science and Technology Organization (ANSTO, Australia; 4Australian Synchrotron, Australia; 5Sorbonne Université, France

Silk obtained from the formation of the cocoon during the larval stage of the Bombyx mori moth has been used in the textile industry for more than 5,000 years. This natural resource has found a wide range of applications, e.g. textiles, air cleaning filters, drug delivery, and tissue engineering [1, 2].
Silk fibroin (SF) is a copolymer made from heavy, light chains and a glycoprotein (P25) with a molecular weight of approximately 350, 26 and 36 kDa [1, 3, 4], respectively, linked together by a disulfide bridge [3]. While the heavy chain is predominantly made of alternating hydrophobic oligopeptides, the light chains are mainly hydrophilic and contain a high concentration of glutamic and aspartic acid residues [1, 2].
SF is known to have five different molecular structures: the metastable α-helix, also known as silk I; the trans-planar beta-sheets parallel to the fiber axis (silk II) with alternate amino acids chains projected to opposite sides of the sheet; turns and bends, beta strands and the polyglycine II, where the amino acids adopt a right-handed helix with three amino acids per turn [5].
SF presents a crystalline dimorphism, where the silk II crystals have a monoclinic unit cell [6, 7], while silk I crystallizes in an orthorhombic one [6]. The lack of center of symmetry on both crystalline units suggests that silk fibroin is piezoelectric, independently of the crystalline polymorphism present in the protein. Furthermore, the first quantitative measurements of silk piezoelectricity were made by Fukada [7] and reported a piezoelectric response of ≈1 pC.N⁻¹, similar to the piezoelectric constant of quartz crystal (≈2 pC.N⁻¹) [1, 7].
Here we will present our last findings in the understanding of the origin of silk piezoelectric properties. Silk fibroin processed by electrospinning has a high degree of orientation and is readily electrically poled. The electroactive properties of the protein were assessed by piezo-force microscopy (PFM) and correlated with its crystalline structure. A simple and cost-effective structure was fabricated to demonstrate the remarkable electroactive properties of this protein for energy scavenging and harvesting. The wearable nano-harvester device shows potential to be used in real-time monitoring of human physiological signals. Moreover, this work opens up new opportunities to explore silk fibroin materials as self-powered materials for biomedical and tissue engineering applications.

Acknowledgments
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References

2:30 PM EL02.07.04
Charge Accumulation and Polarization in Electrospun Piezoelectric Nanofibres Tobias Cramer1, Francesco Calavalle2, Oliviero Bocchi1, Davide Fabiani1 and Beatrice Fraboni1; 1University of Bologna, Italy; 2CIC nanoGUNE, Spain

Electrospinning is a versatile processing technology that offers a promising route to achieve large quantities of oriented nanostructured piezo- and ferroelectric materials. The processing conditions during electrospinning open the opportunity to impact on material morphology and to improve electromechanical material properties. As a consequence electrospun piezo- and ferroelectric materials have been employed in ferroelectric memory, strain and pressure sensors as well as energy harvesters. Despite this interest, the detailed mechanism of how nano-confinement and high electric fields during electrospinning impact on material properties is yet to be discovered. Here we prepare PVDF-TRFE nano-fibres at different electrospinning conditions. We compare macroscopic electromechanical response of fibre mats with microscopic analysis performed by PFM switching spectroscopy and electrostatic force microscopy on single fibres.1 Our results show that while electrospinning favors the formation of the piezoelectric b-phase in the polymer, the electric field is not strong enough to achieve piezoelectric domain polarization. Instead we observe accumulation of space charge in the polymer that explains the more electret like macroscopic electromechanical response.


2:45 PM EL02.07.05
Ultrahigh β-Phase Content PVDF with Relaxor-Like Ferroelectricity for High Energy Density Capacitors Nan Meng, Xintong Ren, Giovanni Santagiuliana, Haixue Yan, Mike Reece and Emiliano Bilotti; Queen Mary University of London, United Kingdom

Poly(vinylidene fluoride) (PVDF)-based dielectric materials are prospective candidates for electric high power density energy storage applications because of their ferroelectric nature, high dielectric breakdown strength and superior processability. However, obtaining a polar phase with relaxor-like behavior in PVDF, as required for high energy storage density, is a major challenge. To date, this has been achieved using complex and expensive synthesis of copolymers and terpolymers or via irradiation with high-energy electron-beam or γ-ray radiations. Herein, a facile process of pressing-and-folding (P&F) is proposed to produce ferroelectric β-PVDF with relaxor-like behavior, without the need of any hazardous gases, solvents, electrical or chemical treatments. This simple and scalable processing route generates unprecedentedly high β-phase content (~98%) and relaxor-like behavior in PVDF with
high molecular weights ($M_w$) (>534 kg mol$^{-1}$). An ultra-high energy density (35 J cm$^{-3}$) with a high efficiency (74%) is achieved in a P&F PVDF ($M_w$: 670-700 kg mol$^{-1}$), which is the highest value ever reported for a polymer-based dielectric capacitor.

3:00 PM BREAK

SESSION EL02.08: Sensors and Actuators II
Session Chair: Tse Nga Ng
Tuesday Afternoon, December 3, 2019
Hynes, Level 1, Room 105

3:30 PM *EL02.08.01
Flexible Hybrid Electronics Audio System David E. Schwartz, Robert Street, Ping Mei, Brent Krusor, Rene Lujan, Elif Karatay, Adrien Pierre, Siv Kor and Steve Ready; PARC, United States

Integration of piezoelectric materials into flexible electronics systems can enable enhanced functionalities in sensing and actuation. An example of this is the use of ferroelectric polymers to form flexible audio speakers. This talk will discuss the development of a flexible hybrid electronics (FHE) technology platform that combines printed interconnect, printed passive components, and discrete silicon chips with a bimorph PVDF-based speaker. The bimorph configuration is shown to produce increased sound pressure levels (SPL) over a single-layer device. The audio system has been demonstrated using two flexible circuits that include ink-jet-printed resistors developed for long-term reliability. One circuit amplifies the output of a portable music player and feeds it to the speaker. The second is a record-and-playback circuit designed around a dedicated audio integrated circuit. In both cases, the audio is clearly intelligible.

4:00 PM EL02.08.02
Roll-to-Roll Production of High Performance, Flexible and Transparent Piezoelectric Pressure Sensors and Loudspeakers Armen Yildirim, Rahim Rahimi and Mukerrem Cakmak; Purdue University, United States

The introduction of IoT (Internet of Things) has created an unprecedented demand toward the development of self-powered and high-performance sensors, among which piezoelectric materials are of great use in various important fields due to their unique properties such as high sensitivity, mechanical stability, energy harvesting and fast response time. Despite recent advances, the current state-of-the art solutions are still primarily based on brittle ceramic materials and hence cannot be easily incorporated into existing flexible electronic devices. In addition, the large-area processing of the modern advanced materials still poses a challenge.

Here, we report the roll-to-roll production of dual-functional high-performance piezoelectric pressure sensors and loudspeakers via electric field alignment of PZT (Lead Zirconate Titanate) and Graphene Nanoplatelets (GNPs) in a silicone-based polymer matrix. The alignment of particles in the thickness direction (“Z” direction) has not only shown to dramatically increase the piezoelectric performance, but also improves the transparency of the system by creating depletion zones where light can travel with less scattering. The ultra-sensitivity of the system has been demonstrated by the detection of a small bird feather (1.4 mg) dropped from a certain distance. The material can also generate up to 8.2 V signal when the pressure is applied by the touch of a fingertip.

Apart from its outstanding sensing capabilities and response time, the exact same system can also be used as a transparent, flexible and thin film loudspeaker when a voltage is applied across the material. To better understand the material’s performance and capabilities, sound pressure level (SPL) of the loudspeaker has been characterized across the entire range of human hearing (20 Hz-20 kHz) along with the sound directivity measurements at certain angles in an anechoic chamber. The potential applications of this system can range from built-in speakers (e.g., TV, computer or mobile phone screens) to active noise cancellation systems.

Finally, a large area sample (10 ft long and 6-inch-wide) has been produced to demonstrate the scalability of the manufacturing process via a novel custom-built 44 ft long roll-to-roll production line which was also designed by
Artificial touch and pressure sensing have become a critical technology. New generation neural implants with multifunctional, high resolutions minimally invasive brain-machine interfacing techniques made it possible to control external devices by assigning them to corresponding cortical networks in the brain. Researchers have shown that it is also feasible to interface a touch-sensitive pressure sensor with somatosensory cortex to transfer the touch feeling to the human brain. Such superior multi-disciplined studies converging both medical and engineering skills are the next milestones of technology shortly. State of the art technological requirements drives engineers to create robotic arms, skin-like functioning electronics and versatile sensors necessary to cure the disabilities and deformations in animals and human. Although researchers have shown a great success for mimicking the motion systems, they have yet to show the same performance to explore sensor tools entirely. Here, we developed piezoelectric fiber-based, large area, transparent, modular, and flexible devices for small pressure sensing and cardiac activity recording. Nano-structured piezoelectric fibers were produced using a two-step thermal size reduction (TSR) technique. In TSR, we start with designing a macroscopic preform which works as a template for the resulting fibers. Our initial preform contains a poly(vinylidene fluoride trifluoroethylene) (PVDF-TrFE) slab made from powders using a hot press at ~20 Barr pressure and above 90°C. This preform was embedded in polysulfone (PSU) protective cladding and drawn in fiber tower. Resulting fibers were between 10 µm to 1 mm. We stacked and stretched the first step fiber in a second PSU preform in order to obtain < 400 nm structure. TSR method simultaneously orients PVDF-TrFE molecules along the fiber length and creates dipoles perpendicular to the molecular chains. Piezoelectric characterizations have shown that the d33 constant of these fibers is exceptional (> 300 pm/V). This performance metrics have proved to be enhancing the performance of large area piezoelectric devices. We demonstrated a proof principle energy harvesting device, larger area electronic skin, an arterial pressure measurement system and an anthropometric artificial hand mimicking the human neural pressure measurement mechanism. We expect this work will find a broader range of application including smart and nano-textile, structural health monitoring, implantable high precision sensors.

Ferroelectric polymers from the PVDF-family have proven to be multifunctional and self-sustaining materials with a broad deployment in printed and flexible electronics. They can be used in large and flexible form factors for detecting mechanical excitations such as pressure variations, force touch and impact, for sensing human-body radiation and proximity, as vibration sensors for structure-borne sound detection and acoustics, as stretchable vital parameter sensors for movement, heart and respiratory rate monitoring, as well as piezoelectric energy harvesting elements, just to name a few [1]. Our multimodal ferroelectric polymer sensors are entirely fabricated by screen printing which is one of the most common techniques used in printed electronics, since it is highly tolerant to the type and form factor of substrates, the rheology of ink materials, provides sufficient alignment accuracy for multilayer printing and can be done in a sheet-to-sheet or roll-to-roll schemes. By optimizing the design, the printing and annealing process as well as the poling conditions and the source material, functional sensors with a yield of more than 98% with less than ± 5% deviation in the performance (e.g. remanent polarization) were demonstrated. It is also interesting to note that extended aging tests under definite climate and shock conditions revealed more than 98% preservation of the remnant polarization for high molecular weight PVDF-TrFE polymers. The sensors come in two versions; (i) either they have a sandwich-type structure of three layers that are printed onto a flexible or stretchable substrate (e. g. plastic films, paper and textiles) and response accurately, fast and reproducibly to pressure and temperature changes over large dynamic ranges or (ii) a two layer structure that is predominantly sensitive to lateral strain and vibrations and provides accurate direction sensitivity.
First a short overview of applications of printed PVDF-TrFE sensors will be given covering flexible 3D user interfaces [2,3], large-area force, impact and proximity sensors, ultrathin object-integrated microphones as well as medical patches.

One focus will be the realization of a concept for direction-sensitive and flexible strain sensors based on the ferroelectric copolymer P(VDF:TrFE) with a single layer of interdigitated embedded electrodes. The process employed for producing the embedded electrodes is based on a combination of (self-aligned) photolithography and electroforming or, alternatively, on capillary force driven filling of microfluidic channels hot embossed into P(VDF:TrFE) with conductive ink.

Finally, a novel printable nanocomposite material, which allows reducing the cross-sensitivity between the pyro- and piezoelectric sensing modes, will be presented. This material is composed of inorganic ferroelectric nanoparticles blended in a ferroelectric polymer matrix. By exploiting the fact that the piezoelectric coefficient in inorganic ceramics has an opposite sign to that one of the ferroelectric polymer either the piezo- or the pyroelectric activity can be suppressed by independently defining the poling direction of particles and matrix in a clever poling procedure [4].

EL02.09.03
Designing High-Capacitance Polymers Using Side Chain Sequence Control Anneliese Schmidt, Tara Meyer and Geoffrey Hutchison; University of Pittsburgh, United States

High dielectric and low energy loss polymers are of great interest for electrical components and energy storage devices, as they enable high power density and energy density while maintaining dielectric strength. While much of the work in this area has focused on ever increasingly complex donor and acceptor units in the backbone of polymers, this work incorporates the conjugated species, with highly polarizable end groups, as the polymers’ side chains. Synthesis of a flexible polymer with precisely sequenced phenylene vinylene pendant groups provides improved control over the side chains’ alignment, and the local dipole moment, while poling. Strategic control of the side chains’ sequence produces a material with tunable dielectric behavior and capacitance.

EL02.09.04
Role of Vertically Aligned and Randomly Placed Zinc Oxide (ZnO) Nanorods in PVDF Matrix—Used for Energy Harvesting Abhishek Anand; Indian Institute of Technology New Delhi, India

The nanocomposite of ZnO nanorods and ZnO vertically aligned nanorods with polyvinylidene fluoride (PVDF) are prepared via a solution casting method to make flexible and cost-effective piezoelectric nanogenerator. The structural and surface morphological studies of nanocomposite films have been carried out by X-ray diffraction (XRD) and Scanning electron microscopy (SEM) respectively. The crystalline polar β-phase of nanocomposite films has been evaluated by Fourier transform infrared spectroscopy (FTIR). The results showed enhancement in this phase from 53% in PVDF to 80.6% in PVDF-ZnO vertically aligned nanorods (VANRs) nanocomposite films, respectively. The electric polarization studies showed the maximum value of remnant polarization P_r is 0.2188 μC/cm² for PVDF-ZnO VANRs nanocomposite film, measured by Polarization-electric field (P-E) hysteresis loop. The value of output voltage for PVDF-ZnO VANRs is found to be 46.64 V which is more than seven times in comparison to PVDF-ZnO nanorods (NRs) based nanocomposite film generated by repeated human finger imparting on these nanocomposite films. The value of power density obtained for PVDF-ZnO VANRs is 45.87 μW/cm² at the load resistance of 15 MΩ, which can be used to drive energy to small-scale electronic appliances.

EL02.09.05
Systematic Optimization of Electrospinning Flow Rate for Preparing Highly β-crystalline Poly(vinylidene fluoride) Nanofibers Subramaniyan Ramasundaram, Ashiqu Rahaman, Abdelrahman Hussein and Byungki Kim; Korea University of Technology and Education, Korea (the Republic of)

Simultaneous application of uniaxial stretching and electrical poling made the electrospinning process as a suitable method for preparing poly(vinylidene fluoride) nanofibers (PVDF NFs) containing β-crystalline phase. To facilitate the rapid and large scale preparations, flow rate (FLr) of electrospinning must be optimized. In this regard, the efforts made in the literature were lacking in terms of systematic evaluation of crystalline composition, mechanical properties, and the assessing the role of residual solvents during annealing. In the present investigation, an attempt has been made to systematically evaluate the FLr on these properties. A 15% PVDF solution was used for this study. A 70:30 (v/v%) mixture of N, N’-dimethylformamide and acetone mixture was used as the solvent. First, at the FLr of 5 ml/h and the nozzle voltage of +20 kV, the voltage applied to collecting roller (CR) was optimized to control the loss of fibers due to web drifting. Application of -20 kV to CR was fully controlled the web drifting and favored the collection of nearly all fibers ejected from the nozzle. Primarily, NFs were prepared at the FLr of 2.5, 5.0, 7.5 and 10 ml/h. Field-emission scanning electron microscopic studies confirmed that the NFs prepared at 2.5 ml and above had the average diameter of 466 and 225 nm, respectively. The composition of crystalline phases were evaluated using the Fourier-transform infrared (FTIR) spectroscopy. The integral area under the characteristics peaks of α (975 cm⁻¹), β (1275 cm⁻¹) and γ (1275 cm⁻¹) were taken for consideration. The as prepared NFs, showed ~75% of β-phase, the rest 25% was shared by α- and γ-phases. Upon annealing at 150 °C, the NFs prepared at 2 ml/h found to be the best and contained 90% β-, 2.5% α- and 7.5% γ-phases. Differential scanning calorimetry, and X-ray diffraction studies were proved the composition of crystalline phases identified in FTIR studies. As observed in thermogravimetric studies, in as prepared NFs, the peak degradation temperature and residue content were higher for NFs prepared at 2.5 ml/h (466 °C and 32.5%) and the annealed NFs did not show any drastic change. Further, NFs will be prepared up to the maximum achievable flow rate (40 ml/h), the mechanical and piezoelectric characteristics of representative samples will be evaluated.
**EL02.09.07**

**Improved Energy Harvesting Characteristics by Structure Optimization of Flexible Modules Based on Lead-Free Piezoceramic Nanofibers** Sang Hyun Ji and Ji Sun Yun; Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of)

We optimized the module structure based on the lead-free piezoceramic nanofibers to improve flexible energy harvesting characteristics. Flexible lead-free piezoceramic nanofibers were prepared by the electrospinning process, and then flexible energy harvester modules based on piezoelectricity were fabricated through WIP process. The shapes, intervals and widths of electrodes in the flexible piezoelectric single modules were controlled, and the energy harvesting characteristics of the modules were investigated according to the oscillation frequency and the bending motion. Furthermore, the displacement and vibrational mode shapes of the flexible modules were analyzed using a laser scanning vibrometer. The flexible piezoelectric dual modules were fabricated according to x- and z-axis array arrangements of the single modules with the optimized electrode structures, and were connected to serial and parallel methods. The energy harvesting properties of the optimized dual modules were measured at various running speeds, after directly attached to the shoes. These results confirmed that the flexible piezoelectric modules can be applied as a sub-power source for wearable devices.

**EL02.09.08**

**Wearable Power Generation Biodevices on Body Surface** Taiki Takamatsu, Yin Sijie and Takeo Miyake; Waseda University, Japan

Wearable skin electronics is a next generation product that monitor biological signals from the human to the electronic devices. Numerical technological advances have been reported for thermal, strain and chemical sensors on the skin and for neuron-stimulated soft electronics on the brain. Even we could have a lots of wearable devices on the human skin, the final question is “the power supplies from where? on the skin”. To overcome this issue, we have developed two types of wireless power generation devices: one is enzymatic power generation from biofuels, especially glucose in sweat or blood, and the other is wireless power transfer system between an eyeglass/contact lens. To generate a power on the skin, we used two types of enzymes as biocatalysts and then developed enzyme/CNT hybrid electrodes: bioanode for glucose oxidation and biocathode for oxygen reduction. In contrast, the wireless power transfer system is based on two types of inductance(L)-capacitance(C) resonant circuits at the resonant frequency of 13.56 MHz. In the both cases, we demonstrated a LED lighting on the skin or on the eye surface.

**EL02.09.09**

**Kinetic Monte Carlo Simulations of Supramolecular Organic Ferroelectric Materials** Tim Cornelissen¹, Indre Urbanaviciute¹, Michal Biler², Mathieu Linares²,¹ and Martijn Kemerink¹; ¹Linköping University, Sweden; ²KTH Royal Institute of Technology, Sweden

Organic ferroelectrics can find application in a broad range of fields. They might, for instance, solve the ‘missing memory’ problem in printed electronics. However, a full understanding of their switching kinetics on all length and time scales is still lacking. A variety of computational models have previously been used to tackle this problem and to study different aspects of both inorganic and organic ferroelectrics. Unfortunately, these are usually restricted to idealized morphologies or short time scales.

In contrast, we have developed an electrostatic kinetic Monte Carlo model that can reproduce the static and kinetic ferroelectric properties for realistic 3D morphologies on experimental time scales. We apply this model to the prototype small molecular ferroelectric trialkylbenzene-1,3,5-tricarboxamide (BTA).

We simulate hysteresis loops, depolarization curves, and switching transients, and find good agreement with experiments. The simulations provide molecular-scale insight in the thermally activated nucleation-limited switching behavior that was also observed in experiments.

Specifically, we investigate the effect of structural disorder on the ferroelectric properties. When the disorder in the system is increased, the retention time decreases dramatically, while the coercive field remains mostly unchanged. This is due to different nucleation mechanisms: field-driven switching nucleation happens at the contacts, while for spontaneous depolarization nucleation occurs at disorder-induced defects. The switching transients become highly dispersive in the presence of disorder. We find that especially the presence of chiral defects has a retarding effect on the switching kinetics, suggesting chiral ferroelectrics might provide sub-µs switching times.

Our results thus provide a detailed insight in (the limiting factors in) polarization switching processes on
experimental length and time scales. Furthermore, we have shown that reducing the disorder can lead to an organic ferroelectric with moderate coercive field, long retention, and fast switching.

**EL02.09.10**

**Rational Design of Organic Supramolecular Ferroelectrics**  
Indre Urbanaviciute$^1$, Nicolas M. Casellas$^2$, Subham Bhattacharjee$^3$, Michal Biler$^4$, Tim Cornelissen$^1$, Mathieu Linares$^{1,5}$, Rint Sijbesma$^6$, Miguel García-Iglesias$^2$ and Martijn Kemerink$^1$; $^1$Linköping University, Sweden; $^2$Universidad Autonoma de Madrid (UAM), Spain; $^3$Eindhoven University of Technology, Netherlands; $^4$KTH Royal Institute of Technology, Sweden

With an increasing demand for cheap, efficient, lightweight and bendable electronics, a matching memory technology is required. Ferroelectricity-based memory devices assure non-volatility and low energy consumption, while organic materials, potentially used for this purpose, guarantee easy processability, low cost and advantageous physical properties including flexibility. A recently discovered class of organic self-assembling supramolecular ferroelectrics has emerged as a promising candidate for memory applications [1], [2], yet it lacked interest from a device perspective due to typically high operation temperature, modest remnant polarization and/or poor polarization retention. Here, we show that rational design and optimization of the molecular structure leads to advanced supramolecular materials that not only demonstrate excellent ferroelectric properties but also semiconductivity, opening new application possibilities arising from the hybridization of both phenomena [3].

The synthesized molecules are based on a C3 symmetry core-shell template, comprising three equally important structural units: a planar n-stacking core, to which three strong dipolar amide groups (O=C-NH) are attached, that are followed by flexible solubilizing alkyl (-CH$_2$-)$_n$ chains. While the conjugated cores and the hydrogen-bonding amide moieties are responsible for the axial self-assembly and stabilization of the columnar structure, the mesogenic sidechains separate the columns and provide sufficient molecular mobility to flip the columnar macrodipole, i.e. facilitate ferroelectric switching. Consequently, a charge transport channel is formed at the centre of the column, which is surrounded by directional and switchable polarization field.

To obtain structure-property relations we tested molecules with varied tail substitutions as well as different molecular cores, both experimentally and in computer simulations [4], [5]. We find that, and rationalize why, all key properties of the ferroelectric – remnant polarization, coercive field, operational temperature range, polarization switching time and data retention – depend strongly on these molecular modifications. As a result, ferroelectric and ferro-semiconductive materials with high remnant polarization (~60 mC/m$^2$), low electrical fatigue, temperature stability surpassing P(VDF-TrFE) and polarization retention exceeding the 10-year requirement for commercial memory devices even at high temperatures, are unearthed. The conclusions of this structural optimization study provide guidelines for further advancement in molecular engineering of self-assembling multifunctional materials.


**EL02.09.11**

**Porosity as a Tool to Increase the Power Output of Polymeric Nanogenerators**  
Mohammad Mahdi Abolhasani and Kamal Asadi; Max-Planck Institute for Polymer Research, Germany

Polymeric piezoelectric nanogenerators (PNGs) have emerged as a suitable candidate to harvest waste mechanical energy to power up portable electronic devices. Smart textiles, with piezoelectric functionalities integrated into the fabrics, have been envisioned. In this regards, numerous piezoelectric (nano-) generators based on PVDF or P(VDF-TrFE) nanofibers have been reported. However, the piezoelectric polymer (nano-)generators have typically shown low output energy densities; A the
common issue hindering their application. Introduction of porosity into the piezoelectric polymer has been proposed to increase the voltage output of PNGs. However, designing a process that allows the introduction of pores in polymer fibers with a typical diameter of the order 100 nm, would be a breakthrough in the field of PNGs. In this contribution, we discuss an elegant approach to tailor porosity in electrospun P(VDF-TrFE) nanofibers. The approach is based on the thermodynamics of polymer solutions, and solvent/non-solvent interactions with the polymer. We calculated the ternary phase diagram of P(VDF-TrFE)/non-solvent (water)/solvent, and experimentally verified it. Based on the phase diagram, a conscious amount of water is intentionally added into the P(VDF-TrFE) solution to induce porosity in the fiber. PNGs based on the porous electrospun P(VDF-TrFE) nanofibers show systematic increases of the output voltage with porosity. The output power increased from 0.1 mW/cm³ for PNGs with zero porosity to 7 mW/cm³ for PNGs with 50% porosity. Dielectric spectroscopy of the nanofibers attributes the enhanced output to the reduced dielectric permittivity of the fibers and that the voltage generation in the porous fibers is of the same origin as in neat piezoelectric P(VDF-TrFE) films and is due to the relaxation of segments within the restricted amorphous phase.

EL02.09.12
Analog Synaptic Transistors Based on Ferroelectric Hafnium Oxide Min-Kyu Kim, Youngjun Park, Dongshin Kim and Jang-Sik Lee; Pohang University of Science and Technology (POSTECH), Korea (the Republic of)

Neuromorphic computing has attracted much attention due to its power-efficient data processing. To realize efficient neuromorphic hardware systems, the development of reliable and robust synaptic devices is essential. However, the limited performance of the synaptic devices remains as a challenge for realization of neuromorphic hardware systems. Ferroelectric materials have a great potential to meet the requirements for synaptic devices. Here, we report analog memory characteristics in the ferroelectric thin-film transistor (FeTFT) based on oxide semiconductor and ferroelectric hafnium oxide layer [1]. The conductance of the oxide semiconductor channel is modulated by controlling the polarization of the ferroelectric hafnium oxide layer. Conductance modulation characteristics of FeTFT are used to demonstrate potentiation and depression characteristics. The desired synaptic device characteristics, such as linear weight update, small variation, and multiple states are achieved in FeTFTs. In addition, the possibility of FeTFT as a synaptic device in neural network is evaluated by artificial neural network simulation. In simulations, the neuromorphic system based on FeTFTs achieves 91% recognition accuracy for handwritten digits. This work can offer a possibility for FeTFT as a synaptic device to be used in neuromorphic hardware systems. In this presentation, analog memory characteristics of FeTFT for neuromorphic applications will be presented in detail.


EL02.09.13
In Situ Characterization of Active Polymers Using Terahertz Time Domain Spectroscopy Nha Uyen Huynh; San Diego State University, United States

The class of active polymers is gaining an increasing attention since it combines the appealing mechanical properties of polymers of strength and toughness to weight ratio with additional functionalities such electrical, magnetic, or luminescence. For example, a subset of electroactive polymers exhibit electromechanical coupling, where an application of electric field results in a mechanical deformation and vice versa. The latter coupling situates this class of materials for sensing and actuation applications. Despite the appealing attributes and potential application, characterization protocols are limited to the macroscale when it comes to the concurrent interrelationship between mechanical and electrical energies. Terahertz Time Domain Spectroscopy (THz-TDS), on the other hands, is capable of elucidating the simultaneous intrinsic electromechanical coupling since the energy below the activation energies of polymers that are also transparent to terahertz waves. In other words, the propagation of terahertz waves becomes intimate with the polymer continue, hence the reported frequency spectrum inherit the intermolecular vibrations resulting from either applying electrical field or mechanical stresses. In this presentation, the electromechanical response of standalone, ultrathin Poly (vinylidene fluoride-co-trifluoroethylene) film fabricated using spin coating technique. The frequency spectra of propagating terahertz waves are compared before, during, and after the application of varying electric field and mechanical stresses.

EL02.09.14
Tuning the Energy Storage Performance of Core-Shell Crumpled GO@BaTiO3 Nanoparticles Filled PVDF Nanocomposites by Interface Engineering Yan-Ge Yu1,1, Wen-Zhu Shao1,1, Cheng-Yan Xu1,1,2, Jing Zhong1,
Yang Li,1,1 and Liang Zhen,1,2; 1Harbin Institute of Technology, China; 2School of Materials Science and Engineering, Harbin Institute of Technology (Shenzhen), China

Ferroelectric polymer poly(vinylidene fluoride) (PVDF) and PVDF based polymer nanocomposites have received booming interest for film capacitor applications due to their relatively high permittivity at approximate. However, the addition of highly polarized fillers with a high proportion into PVDF leads to poor film processability and high energy loss, which significantly destroy the structural integrity of the film and limits the practical application of film capacitors. Herein, we prepared a unique core-shell structured GO@BaTiO3 nanoparticle by a simple and continuous process, and then obtained the nanoparticle filled PVDF films (GO@BTO/PVDF), which exhibited excellent energy storage performance. BaTiO3 nanoparticles were successfully wrapped in crumpled graphene oxide (GO), and the core-shell structured GO@BTO nanoparticles were well dispersed in PVDF film, which was demonstrated by transition electron microscopy (TEM) and scanning electron microscopy (SEM). Compared with PVDF films, the GO@BTO/PVDF films with a ultralow filler content of 0.8 wt% show a high discharged energy density at 225 MV/m, which is 40% higher than PVDF films, as well as a 15% enhancement of discharged efficiency at 225 MV/m. These superior performance is resulted from the interfacial engineering based on GO. GO is capable to reduce the huge difference between polymer and ceramic particles, making the film have less defective and present higher discharged efficiency. Moreover, the ultralow content of fillers can greatly improve the film processability, maintaining the structural integrity and performance stability of the films during stretching. This work provides an efficient strategy to enhance the energy conversion efficiency.

EL02.09.15
Hybrid Tribo-Piezo-Electric Nanogenerator with Unprecedented Performance Based on Ferroelectric Composite Contacting Layers Linards Lapēnskis, Kaspars Malnieks, Artis Linarts and Andris Šutka; Riga Technical University, Latvia

Triboelectric nanogenerators (TENG) are appealing mechanical energy harvesting devices that could power small portable devices and detectors. They can also act as self-powered sensors for mechanical displacement, chemical, acoustic sensing, and biomedical monitoring. The working principles of TENG devices are based on friction-related electrification – triboelectrification. Some of the recent works report that TENG output can be improved by using polarized ferroelectric films as the contacting layers. In the present work, porous polyvinylidene fluoride (PVDF) and BaTiO3 nanocomposite films (BaTiO3 content in a range from 0 to 35 vol%) have been prepared using spin-coating and consecutive immersion-precipitation. A clear correlation between the piezoelectric response of inversely polarized ferroelectric PVDF/BaTiO3 nanocomposite films and the performance of the TENG device based on these films is demonstrated. Nanocomposite films with the optimal composition (25 vol% BaTiO3) show a 48 pC N−1 piezoelectric coefficient, considerably higher than usually reported for such composites, and in TENG mode a record-high 2.7 kV open-circuit voltage is achieved. This observation is explained by magnified electrostatic induction that is driven by the piezoelectric charges and ferroelectric properties of these films. However, our results also indicate that piezoelectric charges cannot be solely responsible for great TENG performance; thus, a “double capacitor model” has been introduced. The mechanism involves interaction between two charged ferroelectric layers during contact–separation and contacted inversely polarized layers can be considered as capacitors connected in series. Air gap formation during separation rapidly decreases the total capacitance while the potential difference increases. The induced charge redistribution in the external circuit is registered as a current. Predictions of our model also hold true when experimentally obtained charge density (6.55 nC cm−2) values are compared with ones obtained from model calculations (6.60 nC cm−2). Furthermore, findings uncover the potential for vast improvement in the field of nanogenerators for mechanical energy harvesting as a significantly better piezoelectric performance of flexible nanogenerators has been reported elsewhere. As triboelectric research continues to thrive and expand, we anticipate that our work will help the TENG community to further improve the performance of ferroelectric-based TENG devices.


EL02.09.16
The Role of Intermolecular Forces in Contact Electrification on Polymer Surfaces Kaspars Malnieks, Andris
The contact electrification of polymer interfaces opens the possibility to harvest energy from triboelectric (nano)generators (TEG). The electron transfer between contacted-separated surfaces has been considered as the main electrification mechanism for polymers in TEG. The electron transfer mechanism requires to contact chemically different materials, as well as to increase specific contact area, which has been accomplished via nano-structuring. Here we show that contact electrification can be controlled by intramolecular forces in polymer bulk and adhesive forces at contact interface. Results also confirm covalent bond breaking as a mechanism for contact electrification of polymer insulators. By taking in account findings mentioned above, we produced a TEG device using soft thermoplastic styrene-ethylene-co-butylene-styrene (SEBS) block copolymer, which had shown the highest surface charging. We modified the surface of SEBS to make it more adhesive by treating the surface with hydrogen peroxide solution. As a result, we observed increase in separation stress by 38% from 2.97 N/cm² to 4.11 N/cm². The increased adhesion of peroxide treated SEBS surfaces can be attributed to formation of quasi-free ends of macromolecular chains. As expected, for modified SEBS surface charge increased 3.14 times from 0.92 nC/cm² to 2.89 nC/cm².

**EL02.09.17**

**Post-Annealing Process Dependent Electric Properties of (Hf, Zr)O₂ Thin Films Made by RF Sputtering Deposition Method**

Seung Eon Moon¹,², Yeriaron Kim¹,³, Jiyoung Woo¹, Jeong Hun Kim¹, Jong-Pil Im¹, Solyee Im¹ and Sung Min Yoon³; ¹ETRI, Korea (the Republic of); ²UST, Korea (the Republic of); ³Kyung Hee University, Korea (the Republic of)

To study the applications for ferroelectric non-volatile memory and ferroelectric memristor, etc, post-annealing process dependent electric the properties of (Hf, Zr)O₂ thin films by RF sputtering deposition method were investigated. The bottom electrode was TiN thin film to produce stress effect on the formation of orthorhombic phase and top electrode was Pt thin film by DC sputtering deposition. Post-annealing process, for example, post-annealing temperature, annealing gas, annealing time, etc, was varied along with the same other deposition conditions, for example, sputtering power, target to substrate distance. The structural and electric properties of the above thin films were investigated. As a result, it is confirmed that the electric properties of the (Hf, Zr)O₂ thin films depend on the post-annealing process which affects structural properties of the thin films, such as, structural phase, ratio of the constituents, etc.

**SESSION EL02.10: Theory and Modeling**

**Session Chair: Martijn Kemerink**

Wednesday Morning, December 4, 2019

Hynes, Level 1, Room 105

**8:30 AM *EL02.10.01**

**Modeling of Trialkylbenzene-1,3,5-Tricarboxamide (BTA) Molecules for Ferro- and Piezoelectric Applications**

Michal Biler¹, Patrick Norman¹ and Mathieu Linares²; ¹Royal Institute of Technology, KTH, Sweden; ²Linköping University, Sweden

Trialkylbenzene-1,3,5-tricarboxamide (BTA) is an archetypical amide-based liquid crystalline ferroelectric. It is a C₃ symmetry discotic molecule with a benzene core, to which three amide groups, having a dipole moment of around 3 Debye each, are attached. These amides form intermolecular N–H–O hydrogen bonds that induce molecular self-assembly into columns with a triple-helix H-bonded network. Microdipoles within this system add up to a net axial macrodipole in a cooperative manner. The π-π stacking of the benzene cores and packing of the tails further stabilize the molecular arrangement, which allows for unhampered dipole-flipping. When flexible mesogenic peripheral tails are attached, BTA enters a well-ordered liquid-crystalline columnar hexagonal phase, which facilitates rotation of the macrodipole and thus ferroelectric behavior. The length and the nature (linear or branched) of the tails can play a crucial role in the data retention as well as in the growth of the coercive field. Molecular simulations combining Density Functional Theory (DFT) and Molecular Dynamics (MD) are a precious tool to understand and rationalize the behavior of BTA liquid crystalline ferroelectric at the molecular level. We
were able to decipher the detailed nature of the switching of the amide groups under an electric field and how those changes between the different possible conformations influence the helicity of the stack. [1] Moreover, the influence of the side chains were investigated. We showed that morphological factors like improved packing quality and reduced disorder, rather than electrostatic interactions or intra/inter-columnar steric hindrance, underlay the superior properties of the branched-tailed BTAs in comparison with linear-tailed BTAs. [2] Finally, we were able to demonstrate a pronounced negative piezoelectric effect in the family of BTA molecules, which can be tuned by mesogenic tail substitution and structural disorder. [3]


9:00 AM EL02.10.02
Polar Mixed Molecular Crystals by Stereospecific Doping—Design Principle and Contributions to the Macroscopic Polarization Elena Meirzadeh1,2, David Ehre1, Igor Lubomirsky1 and Meir Lahav1; 1Weizmann Institute of Science, Israel; 2Columbia University, United States

Doping of molecular crystals is a promising avenue to design of functional materials. Stereospecific occlusion of guest molecules in host crystals reduces their symmetry by creation of polar domains, engendering macroscopic polarization and thereby inducing pyroelectricity and piezoelectricity. We have investigated the possibilities of stereospecific doping of non-polar molecular crystals comprising of molecules with a large dipole moment, in particular, crystals of amino acids: (i) asparagine monohydrate(ASN) doped with aspartic acid (ASP) and (ii) glycine (GLY) doped with L-alanine (ALA), L-threonine (THR), L-serine (SER), L-allo-threonine (ATH), L-phenylalanine (PAL), L-glutamic acid (GLU), and L-tyrosine (TYR).

We show that the macroscopic polarity in such crystals has two contributions: a) the polarity arising from the difference between the dipole moment of the guest molecule with respect to the dipole moment of the host molecule; and b) the polarity induced by distortion of the local environment pushing the host molecules out of perfect mutual compensation, leading for the case of zwitterionic amino acids (dipole moment of ≈14 D), to particularly large polarization.

For the case of ASN-ASP, the concentration dependence of the pyroelectric coefficient shows three distinctively different regions. Below 8 mol%, the pyroelectric coefficient, $a$, increases linearly with ASP concentration, $C$, indicating that the dopant molecules do not interact and their polarity is additive. This allows to introduce a pyroelectric coefficient per molecule $a_n=\frac{d(a)/d(C)}{(r×q)}=0.005$ pm/K, where $r$ is molecular density (cm$^{-3}$) and is the elemental charge. Between 8 and 12 mol% ASP, there is a sharp increase in the pyroelectric coefficient reaching at its peak 0.18 nC/(cm$^2$×K) and $a_n=0.016$ pm/K, indicating strong interactions between the polar domains. Above 12 mol% ASP, the pyroelectric coefficient decreases indicating anti-polar domain arrangement. The XRD data on macroscopic symmetry support the data on the pyroelectric coefficient. For the case of doped GLY, although dopant solubility is limited to <1 mol%, the pyroelectric coefficient reaches $a=0.02$ nC/(cm$^2$×K), leading to $a_n=0.001-0.005$ pm/K. Two substantially different types of temperature dependence of the pyroelectric coefficient were observed. For ALA, THR, ATH and PAL-doping, the pyroelectric coefficient remains negative with respect to the crystal growth direction in the range 0-100 °C. For SER, GLU and TYR-doping the pyroelectric coefficient changes from positive at 0 °C to negative at 100 °C. So far, this is the only example, not associated with a phase transition, when a pyroelectric coefficient crosses a zero point. We attribute this behavior to the different temperature dependence of the guest and host polarization.

Our experiments demonstrate that stereospecific doping of centrosymmetric crystals comprising polar molecules is a viable route to design functional polar materials.

9:15 AM *EL02.10.03
Computational Approaches for Studying Organic Ferro-, Antiferro- and Piezoelectric Materials Shoji Ishibashi1, Sachio Horuchi1, Reiji Kumai2 and Kiyojuki Terakura1; 1National Institute of Advanced Industrial Science and Technology (AIST), Japan; 2High Energy Accelerator Research Organization (KEK), Japan
We present examples of computational approaches for studying organic ferro-, antiferro- and piezoelectric materials. The first example is a study about the origin of exotic ferroelectricity in tetrathiafulvalene-p-chloranil (TTF-CA). As reported by Kobayashi et al. [1], its polarization (6.3 \( \mu \)C/cm\(^2\)) is more than 20 times larger than that expected by the point charge model (PCM), and their directions are opposite. TTF-CA is in strong contrast to typical inorganic perovskite ferroelectrics. Recently, we proposed a procedure to analyze the polarization mechanism within the framework of maximally-localized Wannier orbitals and applied it to TTF-CA as well as to perovskite transition metal oxides (BaTiO\(_3\) and PbTiO\(_3\)) [2,3]. For TTF-CA, only 2 bands below the band gap are responsible for the emergence of polarization, while, for BaTiO\(_3\) and PbTiO\(_3\), even relatively-deep states show significant contributions. The polarization has been decomposed into three contributions: (1) the PCM, (2) the local polarization (LP) and (3) the electron flow (EF) from cell to cell. It has been revealed that the EF term amounts to more than 100\% for TTF-CA, 68\% for BaTiO\(_3\), and 56\% for PbTiO\(_3\) of the total polarization. As for the LP term, it is nearly zero for TTF-CA or BaTiO\(_3\) while 12\% for PbTiO\(_3\). The valence top is derived from the anion (oxygen) states for BaTiO\(_3\) and PbTiO\(_3\) while it is from the cation (TTF) states for TTF-CA. Consequently, the EF term has the same sign as the PCM term in BaTiO\(_3\) and PbTiO\(_3\), whereas the EF term has the opposite sign to the PCM term in TTF-CA. For TTF-CA, as mentioned above, the predominant contribution to the polarization is from the EF term. This is the reason for the opposite polarization direction to that expected by the PCM in TTF-CA. Thus, the distinct polarization mechanism for TTF-CA has been figured out.

The second example is a simulation of the antiferroelectric-to-ferroelectric transition in squaric acid (SQA). Recently, in SQA, we observed experimentally, the transition from an antiferroelectric phase to a ferroelectric phase in the presence of a strong electric field [4]. Furthermore, we proposed two possible ferroelectric phases (FE-α and FE-β) with their molecular arrangements and space groups. The experimentally observed ferroelectric phase is thought to be the FE-α phase. On the other hand, the FE-β phase could not be practically achieved because of the dielectric breakdown of crystals. We simulate the antiferroelectric-to-ferroelectric transition [5] by computationally applying a static electric field [6]. Depending on the direction of the electric field, two different metastable ferroelectric (and piezoelectric) phases have been found. One of them corresponds to the experimentally confirmed FE-α phase, whereas the other corresponds to the FE-β phase, which has not yet been experimentally confirmed. The structural details of these phases have been determined as a function of the electric field. The spontaneous polarization values of the phases are 14.5 and 20.5 \( \mu \)C/cm\(^2\), respectively, and are relatively high among those of the existing organic ferroelectrics. Significant converse piezoelectric effects are observed for both the phases (~10 pm/V).

Some other examples (e.g. ferroelectrics based on proton tautomerism such as croconic acid and benzimidazoles [7]) will also be presented.


9:45 AM BREAK

10:15 AM *EL02.11.01
Photolithographic Patterning of Fluorinated Electroactive Polymers and Applications to Electronic Devices
Georges Hadziioannou; University of Bordeaux, France
Fluorinated electroactive polymers (FEPs) are materials of increasingly high interest due to their ferroelectric and relaxor-ferroelectric properties and find application in electronic devices such as sensors, actuators, organic field-effect transistors (OFETs) and electrocaloric devices. Before devices that use those materials find wider commercial applications, patterning issues need to be solved. Limited compatibility of those polymers with photolithography, which is the method of choice for large throughput electronics production, prevents their wider commercial realization. In this work we present a method to make those fluoropolymers cross-linkable upon UV irradiation by grafting photo-initiator groups directly on the fluoropolymer’s backbone. Such photo cross-linkable materials can be used as negative photoresists in conventional photolithographic patterning process for the fabrication of electronics. Main challenges of this approach, include the poor chemical reactivity of fluoropolymers as well as the negative effect that modification can have on the crystallinity and thus on the electroactive properties of the polymer.

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10:45 AM EL02.11.02
Polar Crystallization of Boron Nitride Nanotube-Polyvinylidene Fluoride Nanocomposites Dongwon Lee1,2,3, Sang-Hyon Chu2,3, Fuh-Gwo Yuan1, Catharine Fay2 and Cheol Park2, 1North Carolina State University, United States; 2National Institute of Aerospace, United States; 3NASA Langley Research Center, United States

A boron nitride nanotube (BNNT), an electrically-insulating counterpart of a carbon nanotube (CNT), is a great nanofiller candidate for ferroelectric polymeric nanocomposites due to BNNT’s exceptional properties in piezoelectricity, thermal stability, mechanical strength, and radiation shielding capability. Fast and high-yield polar crystallization of polyvinylidene fluoride (PVDF) was accomplished by incorporating BNNTs as a nucleating agent. As-fabricated BNNT-PVDF nanocomposites were characterized by Fourier-transform infrared spectroscopy (FTIR), wide-angle X-ray diffraction (XRD), and differential scanning calorimetry (DSC) to identify and quantify chain conformations. Besides, piezoelectric coefficients, \( d_{33} \), of BNNT-PVDF nanocomposites were measured and compared with that of a mechanically drawn \( \beta \) phase polar PVDF. The polar transformation due to BNNT incorporation has a great advantage over conventional \( \beta \) or \( \gamma \) phase transformation methods that require (1) mechanical drawing often resulting in defects or (2) high-temperature annealing for an extended time. In addition to the fast polar crystallization, BNNTs had a role of reinforcement of the polymer matrix. The improved Young’s modulus and electromechanical coupling coefficient of BNNT-PVDF nanocomposites indicated potential applications in energy harvesting under harsh environments such as large deformation, wide temperature cycles, and high radiation.

11:00 AM EL02.11.03
A Low-k Interfacial Layer Induced by Interface Trap Charge for P(VDF0.75-TrFE0.25) in Metal-Organic Ferroelectric-Semiconductor Device Yu-Chia Chen, Po-Han Chen and Chih-Ting Lin; National Taiwan University, Taiwan

The characteristics of high dielectric constant in poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) copolymer has attracted research attentions. However, previous literatures have shown that the dielectric constant would be decreased with film thickness reduced in metal-organic ferroelectric-metal device [1]. Furthermore, the metal-organic ferroelectric-semiconductor (MFS) device also has this phenomenon [2,3]. This phenomenon is caused by the capacitance of low-k interfacial layer (between P(VDF-TrFE)-metal or silicon) in series with dielectric capacitance. The molecular chains are constrained by the restrictive force from the substrate surface. It results in the low-k interfacial layer between the ferroelectric and semiconductor. The characteristics of semiconductors are more complex than metals. Therefore, it is necessary to explore whether there have the other causes that may cause the interfacial layer between P(VDF-TrFE) and silicon heterojunction.

In this work, we investigate the interface trap charges induced P(VDF-TrFE) dielectric characteristics which is study by a MFS device structure. To explore this effect, different interface trap density at P(VDF-TrFE)-silicon interface is generated. The generated interface trap density can be measured by a conductance technique at room temperature. The interface trap density of the two sample is approximately \( 4.1 \times 10^{11} \) – \( 2.2 \times 10^{12} \) and \( 1.3 \times 10^{12} \) – \( 2.6 \times 10^{12} \) eV\(^{-1}\)cm\(^{-2}\), respectively. The experiment results show that the lower interface trap density of MFS capacitor has lower...
interfacial layer effect. It is mean that the interface dipoles switching is influenced by the interface trap charge, which will lead to more significant interfacial layer effects. On top of that, we propose a mechanism to explain how the interface trap charge influences the interface dipoles switching.

References:

11:15 AM EL02.11.04
Crossover from Synaptic to Neuronal Functionality through Control of Polarization Dynamics in Organic Ferroelectric Tunnel Junctions Sayani Majumdar1,2, Hongwei Tan2 and Sebastiaan van Dijken2; 1VTT Technical Research Centre of Finland, Finland; 2Aalto University, Finland

Parallel information processing, energy efficiency and unsupervised learning make the human brain a model computing system for unstructured data handling. Oxide memristors, from filamentary to metal-insulator transition devices have been shown to emulate synaptic and neuronal functionalities in artificial neuromorphic circuits. However, challenges like non-linear conductance update, cycle-to-cycle and device-to-device variability and leakage current related issues in a dense crossbar structure are still not resolved. For neurons, often a circuit with multiple active or passive components are required which can complicate circuit designs in a large-scale neural network. Earlier, we found out that solution-processable ferroelectric tunnel junctions (FTJs) with P(VDF-TrFE) copolymer barriers on semiconducting bottom electrode can show analog memristive behavior with a broad range of accessible conductance states and low energy dissipation of 100 fJ for the onset of depression and 1 pJ for the onset of potentiation by resetting small tunneling currents on nanosecond timescales. Key synaptic functions like programmable synaptic weight, long- and short-term potentiation and depression, paired-pulse facilitation and depression, and Hebbian and anti-Hebbian learning through spike shape and timing dependent plasticity can be demonstrated.1 In our current work, we demonstrate that by manipulating the carrier concentration of the semiconducting bottom electrode in our FTJs, it is possible to control the dynamics of ferroelectric domain rotations and their subsequent relaxation in a way so that from synaptic devices they can act similar to neuronal devices.2 These results offer a promising outlook for the FTJ memristors on semiconducting bottom electrodes as both synapse and neuron devices in artificial neural networks by controlling carrier doping concentrations only.


1:30 PM *EL02.12.01
Tailoring Piezo- and Magnetoelectric Polymers Shape and Response for Specific Applications Senentxu Lanceros-Mendez1,2,3; 1BCMaterials, Spain; 2Ikerbasque, Spain; 3Universidade do Minho, Portugal

Electroactive polymer and polymer composites offer large application potential in areas such as sensors and actuators, energy generation and storage, filtration membranes and biomedical applications, among others. Many of
the applications rely both in the ability to properly tailor polymer properties, including microstructure, crystallinity and phase, and/or in the suitable choice of micro and nanofillers.

In this talk the main properties and characteristics of piezoelectric and magnetoelectric polymer will be presented. In particular, the main aspects for properly process materials with tailored shape and response as well the reasons and strategies for the development of specific magnetoelectric composites will be shown. Finally, some of the most interesting applications will be discussed, in which specific shape and/or materials response are particularly relevant. Finally, the main challenges and future directions in this research field will be outlined.

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2:00 PM EL02.12.02
Magneto-Mechano-Electric Characterization of Polarized 0-3 Terfenol-D/PVDF-TrFE Composites Scott Newacheck1,2 and George Youssef1; 1San Diego State University, United States; 2University of California, San Diego, United States

Conductive metallic particulate inclusions in an electroactive polymer matrix composite have been widely studied for enhanced sensitivity applicable to sensors, energy harvesters, electromechanical actuators, and high charge storage capacitors. Moreover, if the metallic particulates exhibit magnetostrictive properties, the domain of applications expands due to the direct and converse magnetoelectric coupling between electric displacement and magnetization by strain-mediation. One such composite has been analytically postulated to have a giant magnetoelectric coupling, namely Terfenol-D magnetostrictive particles embedded into PVDF-TrFE electroactive matrix, but has been proven difficult to experimentally polarize due to electrical breakdown and percolation. This presentation will discuss one method to synthesize Terfenol-D/PVDF-TrFE composites which are capable to become polarized by direct contact electrodes. The experimental protocol and results to elucidate the magnetic, electric, and mechanical properties of the composite is also discussed. First, it was observed that the ferroelectric polarization was improved with a small weight fraction of Terfenol-D particles, but the polarization was hindered as the weight fraction of the particles increased. Second, the permittivity of the composite rapidly increased with the addition of more Terfenol-D particles, which was attributed to the reduction in polarization of the PVDF-TrFE matrix and discussed through a modified Maxwell-Wagner model developed herein. Third, a notable phase delay was observed in the piezoelectric strain in response to a high frequency electric field, such a delay was directly proportionally to the addition of Terfenol-D particles. Fourth, the addition of the stiff Terfenol-D particles were found to enhance the storage modulus of the composite near glass transition but had negligible effect at the crystallization temperature. A modified thermomechanical model was used to fit the experimental data, which provided insights into the interrelationship between thermal transition and mechanical performance. Finally, microscale characterization using scanning electron microscopy (SEM) and magnetic force microscopy (MFM) were conducted on the polarized composite. SEM micrographs provided evidence to the complete enclosure of the magnetostrictive particles into the electroactive matrix, a perquisite for enhanced strain-mediated magnetoelectric coupling. MFM scans of the composite indicate that the Terfenol-D magnetic particles retained magnetic properties from synthesis process and are indeed dispersed within the matrix.

2:15 PM EL02.12.03
Voltage Controlled Molecular Spin State Switching in a Fe (II) Spin Crossover Molecular Complex Guanhua Hao1, Aaron Mosey2, Xuan Yuan Jiang1, Andrew Yost1, Keshab Sapkota3, George Wang3, Xin Zhang1, Jian Zhang1, Alpha T. N'Diaye4, Ruihua Cheng2, Xiaoshan Xu1 and Peter Dowben1; 1University of Nebraska–Lincoln, United States; 2Indiana University Purdue University-Indianapolis, United States; 3Sandia National Laboratories, United States; 4Lawrence Berkeley National Laboratory, United States

The spin crossover (SCO) phenomenon, in 3d transition metal compounds, has potential applicability in molecular spintronic devices for “flexible” memory. Voltage-controlled isothermal changes in the electronic structure of the spin crossover molecular system have now been achieved for the Fe (II) spin crossover complex \[ \text{[Fe[H$_2$B(pz)$_2$]$_2$(bipy)]}, \text{ where pz = tris(pyrazol-1-yl)-borohydride and bipy = 2,2'-bipyridine.} \] This isothermal voltage-controlled switching is evident in thin film bilayer structures where the molecular spin crossover film is adjacent to a molecular ferroelectric thin film (the tested examples being polyvinylidene fluoride
hexafluoropropylene or croconic acid (C₅H₂O₅)) [1]. These organic ferroelectric substrates appear to lock the spin crossover \([\text{Fe\{H₂B(pz)₂\}_2(bipy)\}}\) molecular complex largely in the low or high spin state depending on the direction of ferroelectric polarization [1,2]. This is clear evidence that a molecular multiferroic is possible. In both a planar two terminal diode structure and for a transistor structure, the voltage controlled isothermal reversible spin crossover switching of \([\text{Fe\{H₂B(pz)₂\}_2(bipy)\}}\) is accompanied by a conductance change, where higher conductance occurs at a high spin state while lower conductance is observed for a low spin state, and is seen to be nonvolatile, i.e. retained in the absence of an applied electric field. Nonvolatility arises from the interface between the SCO with nonconducting ferroelectrics which have a non-trivial coercive voltage and can be engineered to test and monitor the spin state of the film. The transistor structure fabricated with an interface between the SCO film and the ferroelectric polymer polyvinylidene fluoride hexafluoropropylene [1] is very different from other molecular spin transistors, a number of which have been fabricated, but are only functional at very low temperatures (i.e. below 10 K). The devices described in this talk are functional at room temperature and above. Like other spin crossover molecular complexes, voltage control of the \([\text{Fe\{H₂B(pz)₂\}_2(bipy)\}}\) spin state is possible, but the voltage control of the spin state becomes volatile when the net electric field from the adjacent ferroelectric is absent. With the very small gap between electrodes (around 160 nm), the ferroelectric fails to lock the changing conductance state of \([\text{Fe\{H₂B(pz)₂\}_2(bipy)\}}\) at zero applied voltage. Yet the conductance change is seen to be about 4 orders of magnitude. This suggests a large on/off ratio is possible. Because these molecular thin films are easily fabricated, and compatible with flexible substrates, there is the potential here for "inkjet printable" low cost molecular solid state memory from this next generation of molecular spintronic devices.


Materials with a negative piezoelectric effect demonstrate atypical, inverse strain-field and polarization-stress characteristics. While mechanisms driving the conventional — positive — piezoelectricity are transparent and manifest in a plethora of organic and inorganic materials, the negative piezoelectricity requires special conditions and is only found in few unique systems, which P(VDF:TrFE) is the most renowned example of [1].

Here, we investigate the piezoelectric activity in a family of small-molecular organic ferroelectrics – the liquid-crystalline BTAs (benzene-1,3,5-tricarboxamides) [2]. Curiously, both the large- and small-signal piezoelectric responses, measured interferometrically on solution-processed thin-film capacitors of BTAs, reveal a pronounced negative piezoelectric effect with \(d_{33}\) reaching values as high as \(-20\) pm/V for short substituted homologues [3]. The measured ‘inverted’ piezoelectric butterfly hysteresis loops are of close-to-ideal form with a well-expressed negative linear slope.

The dipolar disc-like BTA molecules self-assemble into hydrogen-bonded axial aggregates resulting in columnar macrodipoles that pack tightly in a hexagonal lattice. Considering a single ideal molecular stack, a positive piezoelectric response is expected due to the applied field stretching the macrodipole, as confirmed by DFT and MD simulations. However, in real device conditions, the columnar-hexagonal ordering is interrupted by zones of higher disorder. The negative \(d_{33}\) in such structures can therefore be explained by the so-called dimensional effect, which considers the ferroelectric layer as a set of rigid dipoles that are distributed in a deformable matrix. In BTAs this leads to a counterintuitive positive correlation between the large-signal piezoelectric constants and the structural disorder in the bulk, while the small-signal response remains unaffected. Comparison of the piezoelectric response under large- and small-signal conditions for different disorder further reveals that irreversible extrinsic polarization switching processes dominate the large-signal strain.

While the negative sign of the piezoelectric constants is determined by the dimensional effect, the linear strain-field trends in the short-tailed BTAs are caused by polarization-coupled electrostriction (or piezostriction). In longer-substituted BTAs quadratic stain-field relations can be observed due to the negative Maxwell strain starting to dominate because of their lower ferroelectric polarization and higher mechanical compliance. Strong modulation of the elastic constant upon polarization switching further leads to a unique amplification of the large-signal electromechanical response.

Due to their self-healing properties, flexibility and a large figure of merit for energy harvesting, BTAs may become relevant for a wide variety of applications like conformal and/or flexible sensors, energy harvesters and actuators for which rigid crystalline ferroelectrics are unsuited and can be outperformed.

performance of model polymer systems, which have been identified through rational co-design strategy based on advanced computational screening procedures. The proposed framework can augment screening procedures for identifying new polymer materials that are significantly better than the current state of the art.

4:30 PM *EL02.13.04
Design and Synthesis of Self-Assembled Organic Ferroelectrics Miguel García-Iglesias1,2, Nicolás M. Casellas1,2, E. W. (Bert) Meijer1, Martijn Kemerink4 and Tomas Torres1,2; 1Universidad Autónoma de Madrid, Spain; 2IMDEA Nanoscience, Spain; 3Institute of Complex Molecular Systems, Netherlands; 4Department of Physics, Chemistry and Biology (IFM), Sweden

Recent progresses in self-assembly and supramolecular chemistry have paved the way achieving control over the structure and function of organic and polymeric materials in an elegant and effective way. This bottom-up strategy, ubiquitous in biology, leads to dynamic and ordered nanostructures which function is directly related to the non-covalent interactions used to ensemble them. Therefore, a careful design of the building blocks and the resulting supramolecular interactions allows for the preparation of a great variety of macro- and nanoscopically ordered materials which combine different properties.1

Organic non-volatile memory devices based on ferroelectricity represent a promising approach towards the development of a low-cost, efficient and mechanically robust bendable memory technology.2 However, an important drawback of these materials is the utilization of insulating ferroelectrics, necessitating a destructive information read-out. In this context, the combination of ferroelectric and semiconducting properties in a functional material emerges as a valuable solution to this problem, resulting in a ferroelectric diode that retains the information when the power is turned off, and can be written, erased and non-destructively read. This bifunctionality was first achieved by blending distinct semiconducting and ferroelectric molecules in the bulk.3 Nonetheless, the possibility to combine these properties in a single molecular component is highly desirable since the interplay between the ferroelectric and the semiconducting nature would take place at the molecular level, diminishing phase segregation phenomena between dissimilar moieties.

Within this context, we present the synthesis of nanometer-sized self-assembled non-centrosymmetric architectures exhibiting intrinsic permanent polarization and, among others, ferroelectric properties or/and semiconducting properties.

These materials consist of disc-like organic molecules4 that (i) are semiconducting, (ii) possess dipolar side groups and (iii) can be organized into columnar morphologies that have sufficient long-range order to support both ferroelectric coupling between the dipolar groups and quasi-1D charge transport. In these materials the ferroelectric polarization is shown to couple strongly to the materials’ bulk conductivity, giving rise to switchable and rectifying current-voltage characteristics. The observed phenomenon is highly relevant for the fabrication of low-cost non-volatile rewritable memory devices.5 Moreover, making use of the previous design we envision the preparation of the next-generation of macro- and nanostructured organic photovoltaic devices (OPVs) using self-assembled donor-acceptor conjugates that demonstrate both a permanent dipole moment and light-harvesting properties. The use of non-centrosymmetric columnar aggregates in OPVs devices should promote fast photoinduced charge separation, as well as good electron transport and extraction features due to the extraordinary control over the internal structure and the presence of an intense permanent macroscopic dipole within the active layer.

References:

SYMPOSIUM EL03

Multiferroics and Magnetoelectrics
December 2 - December 6, 2019

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SESSION EL03.01: Multiferroics I
Session Chair: Sang Wook Cheong
Monday Morning, December 2, 2019
Hynes, Level 1, Room 101

8:30 AM *EL03.01.01
Potential of SrTiO3-Based 2DEG for Spin-Charge Interconversion
Agnès Barthelemy; Unité Mixte de Physique CNRS/Thales, France

While classical spintronics has traditionally relied on ferromagnetic metals as spin generators and detectors, a new approach called spin-orbitronics exploits the interplay between charge and spin currents enabled by the spin-orbit coupling in non-magnetic systems. We studied the potential of the bidimensional electron gases (2DEG) that forms at the interface between LaAlO3 and SrTiO3 [1] or by deposition of Al on SrTiO3 by sputtering [2]. We exploited the sizeable Rashba spin-orbit coupling of the gas to obtain a very large spin-current to charge-current conversion through the inverse Edelstein effect [2, 3]. The efficiency of the conversion, characterized by the Inverse Edelstein effect length, \( l_{\text{IEE}} \), is larger than the one measured for the topological insulator a-Sn or at Bi/Ag interfaces [4]. Moreover, this conversion efficiency can be highly modulated by a gate voltage. We used angle-resolved photoemission spectroscopy and Boltzmann calculations to map this peculiar gate dependence and linked it to the band structure. We will show that the conversion process is amplified by enhanced Rashba-like splitting due to orbital mixing, and in the vicinity of avoided band crossings with topologically non-trivial order [3]. This suggest that oxide interfaces have a strong potential for spin-based information readout in novel memory such as the magneto-electric spin-orbit transistor proposed by Intel[5].

[2]; D. C. Vaz et al., Nat. Mat. (2019)

9:00 AM *EL03.01.02
Chiral Domain Topology, Moire Patterns and Magnetism in Intercalated Transition Metal Dichalcogenides
Sang Wook Cheong and Kai Du; Rutgers University, United States
Transition metal dichalcogenides (TMDs) have been extensively investigated as 2D materials last decade. A large amount of transition metals (M) can be intercalated into the van der Waals gaps of a wide range of TMD materials, but a limited recent studies in intercalated TMDs have been reported. The limited examples include Fe$_{x}$TaS$_2$ crystals with $x=1/4$ and $1/3$, which exhibit intriguing configurations of antiphase and/or chiral domains related to the ordering of intercalated M ions with $2a \times 2a$ and $\sqrt{3}a \times \sqrt{3}a$ superstructures, respectively. In addition, Cr$_{1/3}$NbS$_2$ undergoes helical spin order below 133 K, and shows an interesting soliton-lattice behavior when in-plane magnetic fields are applied in the helical spin state. We have explored a series of chiral M$_{1/3}$Ta(Nb)S(Se)$_2$ to investigate the correlation among crystallographic symmetries, magnetic domain topologies and their physical properties. These results as well as Moire patterns with self-twisted TMDs induced by intercalation will be discussed.

9:30 AM *EL03.01.03
Multiferroics—Hidden Functionalities beyond Magnetoelectric Coupling Manfred Fiebig; ETH Zurich, Switzerland

Requirements to "good multiferroics" are tough. They are supposed to have a spontaneous magnetization and polarization, preferably parallel to each other, with a strong magnetoelectric coupling between them. Inevitably, this leads to a multiferroic state that is described by a very complex set of order parameters – complex enough to provide the symmetry degrees of freedom to fulfil so many requirements at once [1]. With the focus on electric-field-controlled magnetic order, it may go unnoticed that these degrees of freedom will permit many functionalities other than bulk magnetoelectric coupling. In my talk, I will describe the quest for such functionalities in our group. This includes inversion of a ferroelectric or a ferromagnetic multi-domain state in a homogeneous electric or magnetic field: In each domain, the direction of the order parameter is reversed but the domain pattern as such is left untouched [2]. In addition, a ferroelectric domain pattern on a uniformly magnetized background is transduced into a ferromagnetic domain pattern on a uniformly polarized background. Finally, a multiferroic bulk state is "condensed" into a multiferroic domain wall in a non-multiferroic environment.


10:00 AM BREAK

10:30 AM *EL03.01.04
New Concepts for the Direct Conversion of Heat to Electricity Using Multiferroics Richard D. James; University of Minnesota, United States

We describe recent progress on materials and devices for the direct conversion of heat to electricity applicable to the small temperature difference regime, 10-200 C. This regime includes abundant natural and waste heat sources, but there is currently no reasonable method to harvest the energy. We are pursuing an idea based on the use of first order phase transformations with either an abrupt change of magnetization or polarization at the transformation. In the ferromagnetic case the electricity is harvested by induction; in the ferroelectric case, by capacitance. It is a “direct” method in the sense that there is no separate electrical generator. We survey the theory of this method, the design of the materials and devices, and the analysis of various cycles. We compare theoretical predictions and the behavior of a prototype under cyclic heating/cooling. These devices provide interesting possible ways to recover the vast amounts of energy stored on earth at small temperature difference. They move heat produced by natural and man-made sources from higher to lower temperature and therefore contribute negatively to global warming. This lecture draws on work with Kanwal Bhatti, Ashley Bucsek, Xian Sherry Chen, Bharat Jalan, Bill Nunn, Yintao Song and Vijay Srivastava.

11:00 AM *EL03.01.05
Electric Field-Controlled Magnetism in (Bi,R)FeO$_3$ Solid Solutions Xiang Ming Chen$^1$, Jing Chen$^1$, Xin Xin Shi$^1$, Bin Xu$^2$, Ting Ting Gao$^1$ and Laurent Bellaiche$^3$; $^1$Zhejiang University, China; $^2$Soochow University, China; $^3$University of Arkansas, United States

BiFeO$_3$ has attracted the increasing scientific attention as the most important room temperature single phase multiferroic material. However, the weak magnetoelectric coupling in BiFeO$_3$ seriously obstructs its applications.
The cycloidal spin structure is actually a hint of the existence of the magnetoelectric coupling. In the present work, the magnetoelectric coupling has been realized by destroying the cycloidal state and switching it to the weak ferromagnetic state through symmetry modulation. Electric field-controlled magnetism is achieved in Bi$_{1-x}$R$_x$FeO$_3$ solid solutions by tuning the symmetry from polar $R3c$ to polar $Pna2_1$, where two morphotropic phase boundaries (MPB) are detected together with the greatly enhanced ferroelectric polarization and magnetism. The electric field-controlled magnetism is realized by an electric field induced structural transition from $Pna2_1$ back to $R3c$ which results in the magnetic transition from weak ferromagnetic state to cycloidal state, and this transition is shown to be reversible with additional thermal treatment.

11:30 AM  EL03.01.06
Coexistence of Multiferroicity and Metallic Conductivity in One-Dimensional Single-Component Radical
Yong Hu and Shengqiang Ren; University at Buffalo, United States

Multiferroics and metallic conductivity seem mutually exclusive and cannot be obtained in one material.[1] Dielectric property requires the localized charge and the electrical conducting behavior is based on the free charge carriers. The confined electronic structure in one-dimensional (1D) materials might break this long-standing contradiction. Electrons confined to a 1D chain exhibit various instabilities followed by symmetry breaking, such as superconductor,[2] topological insulator[3] and multiferroics[4]. Here we report the discovery of laser shock induced insulator-metal transition in K-TCNQ radical,[5] where the effect of antiferromagnetic spin ordering causes dipole ordering. The manipulation of spin exchange interaction with external laser shock wave, electric field and magnetic field is accompanied by insulator to metal transition, gigantic magnetoelectric and magnetocapacitance effects, respectively. Therefore, 1D systems with strongly coupled multiple degrees of freedom of electrons-spin, charge, and orbital-provide a new area to search for conducting magnetoelectric media. Our study opens the way for electron engineering, symmetry breaking and establish of self-organized electronic order from modular building blocks, permits the rational design of functional electronic materials that exhibit technologically useful behaviour.

Reference

11:45 AM  EL03.01.07
Spintronics with Magnetoelectric Antiferromagnetic Thin Films
Tobias Kosub and Denys Makarov; Helmholtz-Zentrum Dresden-Rossendorf e.V., Germany

Thin film magnetoelectric antiferromagnets (AF) have potential to revolutionize spintronics due to their inherently magnetic-field stable magnetic order and high-frequency operation. To explore their application potential, it is necessary to understand modifications of the magnetic properties and magnetoelectric responses of AF thin films with respect to their bulk counterparts.

Our approach is based on the electron transport characterization of magnetic responses of thin film antiferromagnets [1-4]. This task is difficult as minute uncompensated surface magnetization of antiferromagnets needs to be detected, which imposes strict requirements to the sensitivity of the method. We will outline our developments of zero-offset anomalous Hall magnetometry [3] applied to study the physics of insulating magnetoelectric Cr2O3 antiferromagnets. To build a reliable description of the material properties, the analysis of the transport data is backed up by structural characterization and real space imaging of AF domain patterns using NV microscopy [1,2]. Considering grainy morphology of thin films, we address questions regarding the change of the intergranular exchange [2], criticality behavior and switching of the order parameter [3].

The fundamental understanding of the magnetic microstructure of magnetoelectric α-Cr2O3 thin films and the possibility to read-out its antiferromagnetic order parameter all-electrically enabled the entirely new recording concept where a magnetoelectric memory cell can be addressed without using a ferromagnet, the purely antiferromagnetic magnetoelectric random access memory (AF-MERAM) [1]. In addition to the outline of the
memory concept, we discuss on the physics of the readout signal in α-Cr2O3 interfaced with Pt [4].


SESSION EL03.02: Magnetoelectrics I
Session Chair: Eckhard Quandt
Monday Afternoon, December 2, 2019
Hynes, Level 1, Room 101

1:30 PM *EL03.02.01
Recent Progress in Spintronics for Energy Efficient Systems Kang L. Wang, Armin Razavi and Hao Wu; University of California, Los Angeles, United States

Spintronic devices take advantage of the nonvolatility of magnetism and electrical control high energy efficiency, and thus offer promise to deliver next-generation systems in memory and computation as well as RF devices and systems. Spintronic devices offer the advantages of non-volatility, low switching energy (< fJ), high speed/frequency (<10 ns), and an almost unlimited endurance (>10^16). The development of this technology is especially crucial in the advent of big data and artificial intelligence, which demand fast access to large amounts of data at high processing speeds. In particular, recent advances on memory (magnetic random-access memory, MRAM) and logic devices have also drawn interest in memory-centric computing paradigms. In this talk, we will first provide an overview of the progress of magnetic materials for high spin orbit coupling (SOC) and spin orbit torque (SOT) applications. We will discuss SOC and magnetoelectric effects as two routes for energy efficient MRAMs. In SOT systems, a high spin-SOC material is used to create a transverse spin current to manipulate or switch the magnetic moment of an adjacent magnet through a torque in a magnetic tunneling junction device (MTJ). We will discuss recent advances in SOTs, including the applications of topological insulators surface states for increasing the switching energy efficiency. A major challenge for SOT switching is that it requires an additional inversion symmetry breaking to become deterministic, which is usually provided by applying an in-plane external magnetic field. We discuss the recent progress for realizing field-free deterministic SOT switching through symmetry breaking using various techniques, including antiferromagnetic materials and structural symmetry breaking.

Second, we will highlight progress in synthetic layered materials to achieve magnetoelectric effects for memory and logic devices using the voltage-controlled magnetic anisotropy (VCMA) effect, very much like multiferroic materials. In this case, a voltage is applied across the magnetic tunnel junction to reduce the anisotropy energy barrier to allow for the voltage controlled switching of the free layer in an MTJ but with a thicker MgO barrier layer, instead of of passing current through the MTJ. VCMA devices are two-terminal and have a much higher density compared to SOT structures which require three terminals for read/write. The reduction of energy barrier per unit voltage is characterized by the VCMA coefficient; to improve the effectiveness of voltage control and scaling to high densities, it is necessary to improve the VCMA coefficient > 1,000 fJ/Vm (first 1,000 challenge). We discuss the recent progress in this area, with a focus on interface and seed/spacer/insertion engineering. For this and related MTJ devices, the readout uses a tunneling magnetoresistance ratio (TMR). The state of the art TMR is of 200~300%. For improved read operation a large signal-to-noise ratio for readout in large arrays, TMR > 1,000%, is desirable and warrant as the second 1,000 challenge. We show strategies for enhancing TMR based on using materials with high spin polarization, such as Heusler alloys. Another challenge for VCMA devices is their high write-error-rate, which can be mitigated by using circuits-based approaches or new device concepts (such as skyrmion-mediated switching). The similar concepts may be applied to energy efficient RF systems. Lastly, for THz applications, ferrimagnetic and antiferromagnetic materials for enhancing the operation speed/frequency will also be briefly discussed.

2:00 PM *EL03.02.02
Thin Film Magnetoelectric Composite Sensors—Sensitivity and Bandwidth at Low Frequency
Dirk Meyners: Kiel University, Germany

Composite materials consisting of magnetostrictive and piezoelectric constituents are known for efficient strain mediated magnetoelectric (ME) coupling. Magnetic field sensors made out of such composites yield high sensitivity and low detection limits in the pT field range. Thin film ME sensors reach sensor performance similar to that of their bulk material counterparts provided that the frequency of magnetic field coincides with a mechanical resonance frequency of the sensor structure. In general this condition is not fulfilled. The measurement of e.g. biomagnetic signals requires extremely low detection limits at frequencies of few Hertz and a minimum bandwidth in the order of 20 Hz.

This presentation considers three different ME sensor concepts to enhance sensitivity to low frequency signals, i.e. magnetic frequency conversion (MFC), surface acoustic wave (SAW) sensors, and piezoelectrically driven sensors based on converse ME effect and inductive read-out by a surrounding pick-up coil. The focus is on designing the magnetostrictive phase, which must be tuned to the sensor concepts differing in underlying effects, utilized substrate, sensor size and thickness, as well as operating magnetic or piezoelectric excitation. In MFC the ME sensor structure is exposed to strong modulating magnetic fields changing the magnetization of the magnetostrictive film periodically with a frequency of about 1 kHz. In contrast to that, the converse ME effect sensors are piezoelectrically driven at comparably high frequencies (515 kHz). The SAW sensors are operated by means of interdigital transducer electrodes at 146 MHz leading to mechanical wave propagation at the device surface and thus through the magnetoelastic phase. Utilizing the ΔE effect, phase change between input and output signal serves as a measure of the applied field. With regard to the various concepts, the interplay between magnetic configuration, associated magnetic noise, and resultant ME sensor performance is investigated.

All sensors are fabricated by bulk micromachining. The sensors for MFC and converse ME effect are of Si cantilever type with 2 µm thick AlN serving as piezoelectric phase. The cantilevers are 350 µm thick and have lateral dimensions of 2.2 mm x 25.2 mm. Enabled through the thin film approach and magnetron sputter deposition, single FeCoSiB and complex multilayers comprising up to 80 individual layers form the magnetostrictive phase. The multilayers consist of repetitions of the stacking order unit Ta 5 / Cu 3 / MnIr 8 / FeCoSiB x [thickness in nm] with varying thickness x of the FeCoSiB layer. The total thickness of the FeCoSiB layers adds up to 1 µm, 2 µm, and 4 µm.

The SAW sensors are based on single crystal Quartz substrates with a 4.5 µm thick silicon oxide layer functioning as guiding layer for horizontal shear waves. Single FeCoSiB layers with a thickness ranging from 25 nm to 750 nm are deposited on the guiding layer and in between the transducers. SAW sensor sensitivity and insertion losses are investigated in dependence on the FeCoSiB layer thickness.

At current status, similar detection limits ranging between 60 pT/Hz1/2 and 150 pT/Hz1/2 are observed at 10 Hz frequency for all three kinds of sensor concepts. However, converse ME effect sensors and SAW sensors benefit from wider bandwidth of about 1 kHz and 1 MHz, respectively.

The presented work was conducted within the framework of the Collaborative Research Center CRC 1261, funded by the German Research Foundation (DFG).

2:30 PM NOVEL RF NEMS MAGNETOELECTRIC RESONATORS FOR SENSORS, NEVILLE SUN

3:00 PM BREAK

3:30 PM *EL03.02.04
Synthesis of Coaxial Nanofibers of Hexagonal Ferrites and Ferroelectrics and Studies on Strain Mediated Magneto-Electric Interactions
Ying Liu1,2, Peng Zhou2, Wei Zhang1, Tianjin Zhang2 and Gopalan Srinivasan1; 1Oakland University, United States; 2Hubei University, China

We report on the synthesis of coaxial nanowires of ferrimagnetic hexagonal ferrites and ferroelectric lead zirconate titanate (PZT) or barium titanate (BTO), assembly of nanostructures into superstructures with the aid of magnetic and/or electric fields, and studies on the nature of coupling between the magnetic and electric subsystems [1]. Such multiferroic nano-composites are expected to show strong strain mediated magneto-electric (ME) coupling due to very high surface area-to-volume ratio [2]. The efforts were on fibers of Y- or W-type hexagonal ferrite and PZT or BTO and their assemblies. Core-shell fibers with (Ni, Zn) Y-type or (Co, Zn) W-type hexaferrites and ferroelectrics were prepared by electrospinning. The choice of Zn-substituted ferrites with planar or uniaxial anisotropy was aimed at control of magnetic order parameters for ME studies at low frequencies and at resonance modes of electric and
magnetic subsystems and over a wide frequency range, from 1Hz to 110 GHz. The fiber synthesis was carried out by dispensing sol gels of ferrites and ferroelectrics through a coaxial syringe with a dual syringe pump. It was possible to control the core and shell diameters by controlling the gel viscosity, strength of the electric field and core and shell diameters of the needle. Electron-, scanning probe-, and scanning microwave microscopy of fibers annealed at 700-900 C showed fibers of shell diameter 200-800 nm and core diameter of 50-200 nm with well defined core-shell interface. Fibers were characterized in terms of magnetic, ferroelectric, and electromagnetic parameters. The magnetization for the fibers were in general agreement with values for bulk ferrites, but the polarization was one to orders of magnitude smaller than expected values. Investigations on ME effects were performed on 2D and 3D fibers assembled in a magnetic field and on discs of the fibers annealed at high temperatures. Low-frequency ME voltage coefficients (MEVC) for the films and discs were in the range 0.3 to 3 mV/cm Oe with the highest values measured for fibers of (Ni, Zn) Y and PZT. Magnetic field assembled films showed a higher MEVC than un assembled films. Polarization P vs electric field E measurements under an applied static magnetic field H on discs indicated a fractional change in the remnant polarization as high as 7% for H = 7 kOe. Magneto-dielectric measurements on films at 12-26 GHz showed 2-3 % fractional change in the dielectric permittivity for H = 7 kOe. The nanofibers studied in this work show strong ME coupling and are of interest for application in sensor and energy harvesting technologies.

The research was supported by a grant from the NSF (DMR-1808892)

4:00 PM EL03.02.05
Smart Magnetolectric Antennas for Magnetic Sensing and Energy Harvesting Mohsen Zaeimbashi1, Mehdi Nasrollahpour1, Xianfeng Liang1, Huaihao Chen1, Anthony Romano1, Ziyue Xu1, Ankit Mittal1, Nikita Mirchandani1, Gaurav Jha1, Isabel Martos-Repath1, Adam Khalifa2, Marvin Onabajo1, Aatmesh Shrivastava1, Sydney Cash2 and Nian Sun1; 1Northeastern University, United States; 2Massachusetts General Hospital, Harvard Medical School, United States

Recent progress in the field of magnetolectric (ME) materials have led to ultra-compact ME antennas with size of 2-3 order of magnitude smaller than that of conventional state-of-the-art compact antennas [1]. These miniaturized antennas could be suitable for Medical Implant Communications Service (MICS), in particular for wireless brain monitoring. A wireless implantable device should be able to perform multiple tasks in order to effectively monitor an individual’s condition. For instance, a wireless implantable device should harvest their required energy in order to power their circuitry systems. In addition, the implant needs to record the body’s information such as magnetic or electric fields in order to successfully track the changes the body. Finally, the implant should transmit the recorded data to the external antenna or device.

In this work we’re presenting an ultra-compact and smart magnetolectric antenna that can single-handedly perform all three above-mentioned tasks: energy harvesting, magnetic field sensing, and data communication. This complimentary combination makes ME antennas suitable for brain implantation where magnetic field recording is required to monitor the brain functionality. Fig. 1 shows the optical microscope image of fabricated ME antenna with AlN/FeGaB thin-film structure. AlN acts as a piezo-material and FeGaB as a magnetostrictive material. Proposed antenna has three parallel ME element, each with the size of 50×250 µm². Fig. 2a shows the architecture of energy harvesting setup. Fig. 2b shows the ME antenna concept and its functionality in receiving (energy harvesting) mode. Fig. 2c shows the S11 of ME antenna showing the resonant frequency of 2.25GHz. Fig. 2d shows the harvesting voltage from ME antenna, showing an induced voltage of 2.13mV when ME antenna is in presence of a 4.5nT RF magnetic field. Fig. 3a shows the ME antenna’s phase response in magnetic sensing mode. Here, ME antenna is in presence of a 1kHz magnetic field with 6.6µT strength. Fig. 3b is the zoomed-in version of Fig. 3a and shows the 1kHz phase peak which corresponds to the 6.6µT magnetic field under measurement. The limit of detection of this antenna is 917pT.


4:15 PM *EL03.02.06
Charge-Lattice and Spin-Lattice Interactions in Multiferroics and Magnetoelectrics Yimei Zhu; Brookhaven National Laboratory, United States

Topological structures and defects including ferroelectric and ferromagnetic vortices emerging near spontaneous symmetry-breaking transitions are ubiquitously observed in wide branches of science. They are invariant under continuous deformations, or perturbations, and protected by topology, thus are promising candidates as information carriers for future memory and logic devices. However, their controlled manipulation including creation and annihilation remains an important challenge towards practical applications. In this presentation I will give a few examples. 1) Structural transformation of sixfold ferroelectric vortex domains into crystallographically forbidden two-, four-, and eightfold vortices via a second topological defect in hexagonal manganites. Combining high-resolution electron microscopy and Landau-theory-based numerical simulations, we investigate the remarkable atomic arrangement and the intertwined relationship between polarization and topological defects. 2) Controlled evolution of helical and skyrmion phases in multiferroic oxides as function of doping, temperature, and magnetic field from direct imaging using in-situ Lorentz phase microscopy. We reveal that skyrmion channeling effectively suppresses the second skyrmion phase formation at low temperature, envisaging designing of skyrmion flow circuits based on multiferroic thin films for spintronics. If time allows, other material systems will also be presented.

Collaborations with S. Cheng, J. Li, and MG. Han at BNL and Jan Seidel at UNSW are acknowledged. Work at BNL was supported by DOE/BES-MSD under Contract DESC0012704.

4:45 PM EL03.02.07
Emission and Active Manipulation of Spin Waves in Multiferroic Heterostructures Huajun Qin, Sampo J. Hämäläinen and Sebastiaan van Dijken; Aalto University, Finland

Multiferroic heterostructures comprising strain-coupled ferromagnetic and ferroelectric layers can be exploited as programmable hybrids in magnonics. Attractive properties of multiferroic heterostructures include the imprinting of magnetic domain patterns with a regular modulation of magnetic anisotropy, the creation of abrupt anisotropy boundaries, strong pinning of straight magnetic domain walls, and electric field control of magnetic anisotropy, magnetic switching, and magnetic domain wall motion [1-3]. Here we show that these attributes provide an attractive platform for the emission of short-wavelength spin waves [4], the confinement of spin-wave modes in structurally uniform films [5], and the manipulation of spin-wave transmission [6]. In our studies, the multiferroic heterostructures consist of a ferroelectric BaTiO$_3$ substrate and a strain-coupled ferromagnetic film with a thickness of 20 – 50 nm. At room temperature, this material system comprises fully correlated stripe domains in the ferroelectric and ferromagnetic subsystems. Utilizing strong pinning of ferromagnetic domain walls onto ferroelectric boundaries, we demonstrate active manipulation of spin wave transmission from ~0% to ~100 % by non-volatile reprogramming of the domain-wall spin structure in a magnetic field [6]. We also present results on electric field control of spin wave transmission using local domain switching via lateral wall motion in perpendicular electric fields. Many of the magnonic concept realized in multiferroic heterostructures are extendable to other material systems with regular modulations of magnetic anisotropy.

EL03.03.01
Electronic and Magnetic Transitions in LaNiO$_{3-\delta}$ Nickelate Perovskites with Ordered Oxygen Vacancies
Yongjin Shin and James Rondinelli; Northwestern University, United States

Rare-earth nickelates perovskites (RNiO$_3$, with R=rare earth) are of high academic interest as they show sensitive variability in their properties with subtle structural changes. Unlike other RNiO$_3$ compounds, LaNiO$_3$ is the only compound showing no metal-insulator transitions with temperature as the relatively large size of La suppresses the distortive mode stabilizing insulating phase. Instead, LaNiO$_{3-\delta}$ exhibits interesting electronic/magnetic transitions with varying oxygen contents $\delta$. Specifically, the metal-semiconductor-insulator transition occurs concurrently with paramagnetic (PM)-ferromagnetic (FM)-antiferromagnetic (AFM) transition in bulk materials [1]. The origin of these transitions can be associated with ordered oxygen-vacancies in LaNiO$_{3-\delta}$, which transforms NiO$_6$ octahedra to NiO$_4$ square planer units along (110)$_p$ direction. As the square planar units are with different coordination environment and crystal-field splitting of d-orbital states, the assembly of two units results in unique electronic/magnetic structures.

In this work, we investigate the role of ordered-oxygen vacancies in LaNiO$_{3-\delta}$ by using first-principles calculations on LaNiO$_{3-\delta}$ phases with $\delta=0$, 0.25, and 0.5. The LaNiO$_{2.75}$ is composed of octahedral slabs separated by square planer plane, while LaNiO$_{2.5}$ is with a columnar arrangement of square planes and octahedra. We show that the magnetic properties of LaNiO$_{3-\delta}$ are mainly determined by octahedral units with limited connectivities, as Ni$^{2+}$ on square planar unit is with low-spin configuration and magnetically inactive. We also explain the structural distortions induced by insertion of square planar units, and conclude by connecting our findings to experimental bulk properties.


EL03.03.02
Enhanced Magnetoelectric Properties and Structural Phase Transition in BiFeO$_3$:YbEr Thin Films
Ricardo Martinez Valdes$^1$, Claudia Zuluaga$^1$, Blanca Y. Rosas$^1$, Javier Wu$^1$, Ram S. Katiyar$^1$, Shawn Zografos$^1$, Hannu Huhtinen$^2$, Wojciech Jadwisienczak$^3$ and Ratnakar Palai$^1$; $^1$University of Puerto Rico, United States; $^2$University of Turku, Finland; $^3$Ohio University, United States

Multiferroics materials are scientifically and technologically promising because of their potential applications in multi-state memory for data storage, magnetic recording, spintronics, quantum electromagnets, and sensors. BiFeO$_3$ (BFO) is one the rare single-phase room temperature multiferroics and shows ferroelectricity up to 820$^\circ$C and antiferromagnetism below 370$^\circ$C. However, high leakage current, weak magnetoelectric coupling, presence of cycloidal spin spiral, and critical structural stability of BFO are the bottlenecks for practical applications. Rare earths show many Interesting optoelectronic and magnetoptic properties. In order to enhance the magnetoelectric properties, we investigated Yb and Er co-doped BFO [Bi$_{1-2x}$(Yb$_x$Er$_{2-x}$)FeO$_3$] ($x = 0.05, 0.10, 0.15, 0.2$, and 0.25) bulk and thin film samples. We found that samples with $x =$0.1 and 0.15. Samples with 20 and 30% rare earth show significant improvement in magnetoelectric properties with very high polarization ($\sim 100 \mu$C/cm$^2$). The enhanced magnetic properties can be explained by the localization of 4f electrons and high effective magnetic moments of rare earth. A structural phase transition has been observed above 20% doping of rare earth. The effect of co-doping of rare earth on enhanced magnetoelectric properties and phase transition will be discussed in detail.

EL03.03.03
A Study on the Multiferroic Properties of Bi- and Tri-Layer Hydrogenated Graphene
Samuel Escobar, Rajesh Katiyar, Ernesto Espada, Vladimir I. Makarov, Brad Weiner, Gerardo Morell and Solimar Collazo; University of Puerto Rico at Rio Piedras, United States

Hydrogenated graphene has been of great interest for the scientific community due to properties like ferromagnetism and piezoelectricity that are not usually present in graphene; requiring subsequent functionalization after synthesis to obtain them. Hereby, we present a novel method for synthesizing hydrogenated graphene via a single-step process. Hydrogenated graphene was characterized primarily by Raman spectroscopy, X-ray Photoelectron Spectroscopy
(XPS), X-ray Diffraction spectroscopy (XRD) and Physical Properties measurement system (PPMS). Our Raman spectra confirms the presence of the 2930 cm⁻¹ peak associated with hydrogen functionalization, while the PPMS reveals the strongest ferromagnetism at room-temperature of a carbon-based material with a Curie temperature higher than 350 K. Preliminary research also suggests the presence of ferroelectricity within our material. These results are strong evidence of hydrogenated graphene’s capabilities for its implementation to spintronics & memory applications.

**EL03.03.04**
**Rashba Spin Splitting and Perpendicular Magnetic Anisotropy of Gd-Adsorbed Zigzag Graphene Nanoribbon Modulated by Edge States under External Electric Fields**
Zhengzhen Qin¹, Guangzhao Qin², Bin Shao¹ and Xu Zuo³; ¹Zhengzhou University, China; ²University of South Carolina, United States; ³Bremen University, Germany; ⁴Nankai University, China

The one-dimensional (1D) Rashba effect has become much important due to its key role in basic science to realize exotic electronic phenomena, such as Majorana bound states. Similar to the 2D or 3D systems, the modulation of Rashba effect in 1D matrix is the kernel of spintronics for manipulating electron spin. Herein, by investigating the effects of transverse and vertical external electric field (EEF) on the Rashba spin splitting and magnetic anisotropy energy (MAE) in a new type of highly flexible 1D system (Gd-adsorbed zigzag graphene nanoribbons) from first principles, we found that the Rashba spin splitting in such 1D system can be effectively regulated by the transverse EEF. Moreover, perpendicular magnetic anisotropy holds with either transverse or vertical EEF applied, despite obvious modulation of the MAE contributions in k-space as well as the Rashba spin splitting. Based on the analysis of the orbital-decomposed band structures and in-plane spin density under EEF, it is revealed that the MAE contributions along k-line as well as the Rashba spin splitting can be modulated by E_z due to the regulated coupling of Gd-5dₓ²-ᵧ² and dₓᵧ orbitals near E_f, which is driven by the edge states. The modulation of Gd-5dₓ²-ᵧ², dₓᵧ by C-pₓ orbitals of edge states is the key to manipulating the magnetic anisotropy, which even plays a decisive role on modifying the Rashba spin splitting in such 1D nanoribbon system. The MAE and 1D Rashba spin splitting are expected to be controlled through modifying the edge states in such systems via EEF or other means. Our study introduces a new strategy to manipulate Rashba spin splitting by edge states and provides new insight into the magnetic anisotropy in 1D Rashba system, which would revitalize further research in ZGNR-based systems within the spintronics and exotic electronic phenomena.

**EL03.03.05**
**Understanding the Origin of Magnetism in Anatase TiO₂ Using Free-Standing Membranes**
Sonu Devi and Thirumalai Venkatesan; NUSNNI-Nanocore, Singapore

Anatase titanium dioxide (TiO₂) is an important dilute magnetic semiconductor (DMS) as it exhibits room temperature ferromagnetism. However, even after a decade of research, the origin of ferromagnetism in this material system has not reached consensus. In this study, the magnetic properties of two systems, Ta-doped anatase-TiO₂ and undoped-anatase-TiO₂ had been studied in detail. To avoid the effects from a substrate and the interface we have fabricated free-standing membranes using water-soluble Sr₃Al₂O₆ sacrificial layer. A strong correlation between the observed ferromagnetism and Ta-doping has been observed. The magnetic centers and the exchange mechanism in the undoped-anatase TiO₂ have identified. This study proves the intrinsic nature of these dilute magnetic semiconductors.

**EL03.03.06**
**Dynamics of Phase Transition and Spin-Phonon Coupling in Ho₂Ti₂₋ₓO₇₋ δ**
Karuna K. Mishra¹, Ricardo Martinez Valdes¹, SM Koohpayeh² and Ratnakar Palai¹; ¹University of Puerto Rico, United States; ²Institute for Quantum Matter, Johns Hopkins University, United States

A₂B₂O₇ pyrochlores are of great scientific interest because of their interesting magnetic orderings (spin-liquid, spin-ice state, Neel-order) and crystal structure. Rare earth pyrochlores shows Ising-like spins, frustrated ferroelectricity, and multiferroic behavior. Pyrochlores also have the ability to immobilize actinides, thus could be used for the disposal of nuclear waste. We report on dielectric, electrical conductivity, magnetic behavior of pyrochlore Ho₂Ti₂₋ₓO₇₋ δ (x = 0.0 and ± 0.08) down to 5 K. For the better understanding of dynamics of phase transition and spin-phonon coupling, we employed micro-Raman spectroscopic studies of phonon spectra from 82 K- 700 K. Magnetic excitation induced phonon renormalization is evident in the low temperature magnetic phase. The presentation will
discuss the results in details.

**EL03.03.07**  
**Room Temperature Lead Palladium Titanate Nanoscale Multiferroic Thin Films**  
Karuna K. Mishra, Mohan K. Bhattarai and Ram S. Katiyar; University of Puerto Rico, United States

The discovery of single-phase magnetoelectric materials and their analysis of coupling mechanisms between spin and polarization is important from the point of view of next generation logic and memory devices. Herein, we report fabrication, dielectric, ferroelectric and magnetic measurement of a Pd-doped room-temperature magnetoelectric multiferroic PbPd₀.₃Ti₀.₇O₃ (PbPdT) thin film. Highly oriented PbPdT thin films were deposited on (LaAlO₃)₀.₃(Sr₂AlTaO₆)₀.₇ substrates by following laser ablation processes in oxygen atmosphere using pulsed laser deposition technique. Diffraction studies revealed that the film had tetragonal phase with (001) orientation. The surface morphology studies using atomic force and scanning electron microscopic techniques suggest a smooth and homogeneous distribution of grains on the film surface with roughness ~2 nm. The dielectric measurements as a function of temperature were carried out in Pt/PbPdT/LSMO metal-dielectric-metal capacitors that showed diffused behavior over a large range of temperatures at several frequencies, and exhibited a higher dielectric constant ~3200 at room temperature. The measured polarization hysteresis loops at room temperature were attributed to its ferroelectric behavior. A well-saturated magnetization \( M_H \) loop with remanent magnetization of 3.5 emu/cm² was observed at room temperature. The origin of magnetization is argued on the mixed oxidation states of Pd²⁺/Pd⁴⁺ in the PbTiO₃ matrix and complemented by x-rays photoelectron spectroscopic experimental results. These results suggest that our thin films are multiferroic (ferroelectric-ferromagnetic) at room temperature. The details will be presented in the meeting.

**EL03.03.08**  
**Electrical and Magnetic Properties of Thin Single Crystal Cr₂O₃ Films**  
Nguyen M. Vu¹, Xiangpeng Luo¹, Steve Novakov¹, Wencan Jin¹, Johanna Nordlander², Peter B. Meisenheimer¹, Morgan Trassin², Liuyan Zhao¹ and John Heron¹; ¹University of Michigan, United States; ²ETH Zürich, Switzerland

Magnetoelectric materials have been of great interest due to their potential for low-power spintronic devices via the electric field switching of magnetization. Antiferromagnet Cr₂O₃ is one of a very few room temperature magnetoelectrics and possesses unique properties such as uncompensated surface spins and perpendicular magnetic anisotropy. [1] Since the first demonstration of the electric field control of exchange bias in bulk single crystal Cr₂O₃ heterostructures [2], intense effort has focused the demonstration of magnetoelectric switching using Cr₂O₃ thin films at room temperature. [3,4] The existence of twin domains in thin films grown on metallic electrodes, however, leads to high leakage current and dielectric breakdown fields that can only be circumvented by growing rather thick films (250-500 nm). [4,5] By using an isostructural epitaxial oxide electrode, V₂O₃, recent studies have shown the reduction and even possible elimination of twin domains in Cr₂O₃ films. [3] Dielectric and magnetoelectric switching studies of 200 nm thick films show bulk like performance, however, for next generation logic and memory the films must be scaled down. [6]

Here we present an investigation of the electrical endurance and magnetic properties of very thin (30-60 nm) single crystal Cr₂O₃ films grown by pulsed laser deposition onto V₂O₃ buffered (0001) oriented Al₂O₃ substrates. Our results show that 60 nm single crystal thin film has bulk-like resistivity (10¹² cm) and significantly improved breakdown voltage (150-300 MV/m). Using magnetometry, we investigate exchange bias of thin film Cr₂O₃/ferromagnet heterostructure. The blocking temperature is found to be at 285 K which is higher compared to twinned films with similar or greater thickness in literature. [7] Further, Second Harmonic Generation confirms bulk magnetoelectric order of our single crystal thin film at room temperature. These results indicate the importance of crystallinity to realize bulk like properties in very thin films at room temperature.


Flexible Bismuth Ferrite Heteroepitaxy

Yu-Hong Lai\textsuperscript{1} and Ying-Hao Chu\textsuperscript{1,2}; \textsuperscript{1}National Chiao Tung University, Taiwan; \textsuperscript{2}Academia Sinica, Taiwan

In recent years, the multifunctional electric systems have a strong tendency toward flexibility because of the flourishing development of wearable and portable devices. As the candidate for non-volatile memory of next generation, Bismuth ferrite (BiFeO\textsubscript{3}), one of multiferroics, draws our attention due to its large ferroelectric polarization and antiferromagnetism with high transition temperature. This work presents a direct way to combine BiFeO\textsubscript{3} with muscovite in order to make it meet the requirement of the wearable device. In this study, we successfully fabricate high-quality BiFeO\textsubscript{3} thin film on muscovite through van der Waals heteroepitaxy via pulsed laser deposition. In analyses of X-ray diffraction, BiFeO\textsubscript{3} thin film has great crystallinity with the out-of-plane (111), which exactly is the direction of the strongest polarization. Through the PFM and the CV measurements, the results exhibit excellent ferroelectricity. Furthermore, the ferroelectricity does not show observable difference under bending test, which means its great stability against external stress. In the oncoming future, this innovative BiFeO\textsubscript{3}/muscovite system will be the most powerful elements in the application of electric technology.

Multiferroic Behavior in Na\textsubscript{0.5}Bi\textsubscript{0.5-x}Eu\textsubscript{x}TiO\textsubscript{3}

Ricardo Martinez Valdes\textsuperscript{1}, S. K. Behara\textsuperscript{2}, P. Kuruva\textsuperscript{2}, T. Thomas\textsuperscript{2}, Rattanakar Palai\textsuperscript{1} and Wojciech M. Jadwisienczak\textsuperscript{3}; \textsuperscript{1}University of Puerto Rico at Rio Piedras, United States; \textsuperscript{2}IIT Madras, India; \textsuperscript{3}Ohio University, United States

The complex perovskite Na\textsubscript{0.5}Bi\textsubscript{0.5-x}TiO\textsubscript{3} (NBT) is a promising lead-free piezoelectric with interesting ferroelectric (T\textsubscript{c} = 670 K) property and phase transition. The unusual A-site positional disorder and relaxor ferroelectric behavior in NBT makes it an important material for practical applications. Rare earth doped perovskites show interesting magneto-optic and opto-electronic properties. In order to develop a room temperature magneto-electric multiferroic material, we explored Eu-doped NBT Na\textsubscript{0.5}Bi\textsubscript{0.5}TiO\textsubscript{3} (NBT:Eu) with different concentrations. In this paper we report on optical, dielectric, ferroelectric, magnetodielectric, and magnetic properties NBT:Eu prepared by solid-state reaction. The as-synthesized NBT:Eu materials have Eu concentration between 1 to 20 at.% using A-site substitution in the general ABO\textsubscript{3} perovskite oxide are single phase, polycrystalline materials as determined by powder X-ray diffraction study\textsuperscript{[1]}. The luminescence intensity monitored at 617 nm increases linearly with the Eu concentration increase up to 20 at.% without indication of typically observed concentration quenching effect. The photoluminescence (PL) and cathodoluminescence (CL) spectra are dominated by sharp characteristic emission lines corresponding to Eu\textsuperscript{3+} intra-4f\textsuperscript{6} shell transitions centered at 593 nm (5D\textsubscript{0}→\textit{7}F\textsubscript{1}), 617 nm (5D\textsubscript{0}→\textit{7}F\textsubscript{2}) and 700 nm (5D\textsubscript{0}→\textit{7}F\textsubscript{4}), respectively. The PL excitation spectroscopy reveal that optically active Eu\textsuperscript{3+} ion centers can be effectively excited with photons between 325 nm to 550 nm via energy migration or direct resonant excitation processes. The electron paramagnetic resonance shows that characteristic electron spin resonance signal of Eu\textsuperscript{3+} ions are not observed in these material. The crystal field calculations and temperature dependent PL and CL studies have shown that the luminescence of Eu\textsuperscript{3+} ions occupying centro-symmetric and non-centro-symmetric sites; however corresponding luminescence temperature thermal quenching mechanisms are different for photon- and electron-excited spectra. Recently studied dielectric permittivity, dielectric loss, impedance, and phase angle of NBT:Eu as function of frequency\textsuperscript{[2]} were correlated with corresponding magnetic properties of the NBT:Eu subjected to up to 1 Tesla. It was found that material shows a novel room temperature ferromagnetic like behavior, which is unusual, but can be explained by the local structural disordering or phase coexistence. Finally, we will discuss the defects in NBT:Eu and their effect on observed optical, electric and magnetic properties of this novel multiferroic material.


Heterointegration of Complex-Oxide Epitaxial Films

Hyunseong Kum\textsuperscript{1}, Hyungwoo Lee\textsuperscript{2}, Sungkyu Kim\textsuperscript{1}, Shane Lindemann\textsuperscript{2}, Chang-Beom Eom\textsuperscript{2} and Jeehwan Kim\textsuperscript{1}; \textsuperscript{1}Massachusetts Institute of Technology, United States; \textsuperscript{2}Korea Advanced Institute of Science and Technology


To date, physical coupling of complex-oxide materials has been predominantly demonstrated through epitaxial means, which limits the breath of possible combinations of materials and restricted by lattice mismatch conditions between the epitaxial layer and substrate. Therefore, there is an increasing trend across all functional single-crystalline materials to lift-off the epitaxial layer from the substrate and transfer the membrane onto foreign substrates. This not only opens up immense amount of freedom to integrate various functional materials on one platform, it also potentially allows reuse of expensive and exotic substrates, expediting commercialization. To this end, we have developed a method to generate freestanding complex-oxide membranes by growing on top of graphene as well as precise cleaving at an epitaxial interface. This allows us to transfer and stack arbitrary complex-oxide membranes which was not possible by epitaxial means, allowing us to study new oxide interfaces and coupling phenomena.

We exfoliated several single-crystalline complex oxide films (e.g. SrTiO3, CoFe2O4, Y3Fe5O12 etc.) by growing them on top of graphene coated substrates. The graphene layer acts as a slippery exfoliation layer which allows crystal growth but also epitaxial lift-off. Additionally, we have found that it is possible to exfoliate single crystalline PMN-PT from STO surface with atomic precision. PMN-PT has one of the highest piezoelectric coefficients, and also shows exotic properties such as high pyroelectricity which has only started to be investigated. Not only were we able to exfoliate the films, we were able to reuse the substrate several times to continuously produce freestanding oxide membranes using a single substrate.

Using these films, we were able to fabricate a freestanding multiferroic bilayer laminate (CFO/PMN-PT), where CFO is a magnetostrictive material and PMN-PT is a piezoelectric material. We compared the magnetoelastic coupling of our freestanding device to a device not exfoliated from the substrate. An order of magnitude larger signal could be measured for the freestanding device compared to the device still clamped to the substrate, which demonstrate the applicability of our method.

Phase transitions in transition metal oxides, such as metal-Insulator transition, ferromagnetic, ferroelectric materials, are useful phenomena to realize novel electrical/magnetic switching and sensing devices. Among them, the strongly correlated electron system of VO2 exhibits an ultrafast metal-insulator transition (MIT) under external stimuli. If the MIT in VO2 can be controlled by a voltage, a field effect transistor (FET) could be demonstrated with ultrafast and ultralow power consumption switching properties. Here, to enhance the resistance modulation in VO2 FETs, we employ, as a gate insulator, a layered material of hexagonal boron nitride (hBN) which is atomically flat and has much fewer electron trap sites than the other gate oxides have. The VO2 thin film with a thickness of 10 nm was grown on TiO2 by the pulsed laser deposition method and, then, was etched down to 5 micrometer in width. The thickness of hBN was 30nm as top gate geometry. This VO2 thin channel undergoes a metal-insulator transition at around 325 K in the heating process. The transfer curve and gate leakage current of the VO2 FET was measured at 310 K (the drain bias V d is 1.0 V). The drain current increased clearly when applying the positive gate voltage (electron doping), while the current decreased under the application of the negative gate voltage (hole doping). We find no hysteresis and memory behavior in the VO2 FET under gating, indicating no chemical reactions and trapping at the interface. This gate-response speed was observed to be faster than the measurement limit of 400 ms. Namely, a slow response caused by the carrier trap at the interface was not observed. We also investigated the stability of the hBN gate insulator under gating. We can find that the drain current rarely changes during the application of the gate voltage for 3000sec. These observations show that hBN is a chemically and electrically stable material for the gate insulator application. The resistance of VO2 was modulated by up-to 1.2% at a gate voltage of 20 V, which is 4 times larger than in previously reported VO2 FETs with oxide gate insulators such as SiOx. This is likely because with hBN the interface carrier scattering is strongly suppressed. Our results indicate the advantage of use of h-BN as 2D material in order to demonstrate voltage control of transition metal oxides via electrostatic modulation.
Rashba spin texture is the property of inversion asymmetric systems to maintain a momentum-dependent spin splitting in the reciprocal space. This property has been predicted to support an electric-field control of spin degree of freedom promising for spintronic and magnetoelectric applications. Till now, its tunability is not so satisfactory. Here, we predicted that substantial modulation of Rashba splitting strength can be realized in the ferroelectric (FE) perovskite trilayers by reversing the FE polarization. Using first-principles calculations, we demonstrate that PbTiO$_3$/Bi$_M$O$_3$/PbTiO$_3$ ($M$=Al, Ga, In, Sc) heterostructures along [001] direction are promising candidates accessible experimentally. The middle layer supports large Rashba splitting at the CBM and the change of Rashba spin-orbit strength by FE polarization exceeds 80%. The splitting bands are locked at the band edge by carefully choosing the middle layer and are adjustable due to oxygen network. The designed structure improves the feasibility of utilizing Rashba effect in spintronic devices.

**EL03.03.16**

**The Magneto-Impedance and Magneto-Capacitance Effect in Different Magnetoelectric Composite Resonators**

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The magnetoelectric (ME) composite has recently attracted considerable attention both for ME effect and for its potential applications[1-2]. S.X. Dong et al. reported that the ME composite can detect a small DC magnetic field less than 10$^{-7}$ Tesla[2]. Especially, the ME effect based on magnetic sensor can be used to measure both DC and AC magnetic fields. In this report, we study the extracting equivalent circuit model and electrical impedance and capacitance dependence on dc magnetic field of magnetoelectric composite resonators. Our research exhibits that the equivalent circuit parameters are strong function of external DC magnetic field. The properties of magnetostRICTive materials dependence on external dc magnetic field lead to magneto-impedance and magneto-capacitance effects. Furthermore, the magneto-impedance and magneto-capacitance effects for FeGa/PZT, Terfenol-d/PZT, FeSiB/PZT and FeNiCoSiB/PZT composite resonators are presented. The experimental results show that the magneto-impedance and magneto-capacitance effects for the magnetoelectric composite resonator strongly depends on DC magnetic field ($H_{dc}$). 240% and 170% of the magneto-impedance can be achieved at anti-resonance frequency ($f_a$) of the FeGa/PZT and FeNiCoSiB/PZT resonator, respectively. The variation of magneto-capacitance for FeNiCoSiB/PZT composite resonator exceeds ~112% at anti-resonance frequency. This find represents another principle for design dc magnetic field sensors, MI devices, or tunable electronic devices.


**EL03.03.17**

**Electrostatically Tunable Mutual Inductance with Magnetoelectric Core for Wireless Power Transfer**

Changxing Sun$^1$, Wenrong Yang$^1$ and Nian Sun$^2$; $^1$Hebei University of Technology, China; $^2$Northeastern University, United States

Multiferroic composite materials with strong magnetoelectric (ME) coupling have led to many novel devices, such as information storage, sensors, energy harvester and tunable magnetic inductors. The capability of tuning magnetic properties by electric field makes such multiferroic composites have great potential for tunable magnetic devices application. Magnetic coupled resonance wireless power transmission whose energy is delivered from the transmitter (Tx) coil to the receiver (Rx) coil by mutual coupling has received considerable attention because of its use in applications in recent years. The mutual inductance is distance dependent when the coils have been designed, therefore the transfer efficiency of the magnetic resonance coupled wireless power transfer system decreases rapidly once the transfer distance is extended to the undercoupled region or the distance is shortened to the overcoupled region. High permeability materials, such as ferrite cores, are utilized to enhance the mutual inductance in the undercoupled region to achieve high transfer efficiency. In contrary, different coils configurations are presented with lower mutual inductance in overcoupled region to suppress frequency splitting to increase the efficiency. Mutual inductance...
should be enhanced by using magnetic core in undercoupled region and be reduced by using complicated loop structure in overcoupled region to achieve high transfer efficiency in. However, the mutual inductance value is usually determined in a previously built prototype, the transfer efficiency is decreased when the transfer distance is changed. The mutual inductance determined by coils configuration limits the transfer efficiency in the overcoupled region and undercoupled region for magnetic resonance coupled wireless power transfer system.

The tunable mutual inductance by electric field using multiferroic composite core has a potential application for efficient magnetic resonance wireless power transfer. Electrostatically tunable mutual inductance with multiferroic composite core consisting of two layers of Nanocrystalline ribbons and one slab have been demonstrated to tune the mutual inductance.

The multiferroic composite coil core consists of two layers of Nanocrystalline ribbons Metglas 1K107 (30μm thick each) and one PZT (0.5 mm thick) piezoelectric slab that was poled along its thickness direction were bonded together with ethyl cyanoacrylate glue. A control voltage ranging from 0 to 600 V, which results in an electric field from 0 to 12 kV/cm in the PZT slab, was applied across the thickness direction of the PZT slab.

The magnetic hysteresis loops of ME core is tested by VSM (Vibration Sample Magnetometer), the magnetic hysteresis loops is changed when the control voltage is applied on the PZT slab. Since the magnetic anisotropy is different under different electric field, the relative permeability of the matglas ribbons $\mu_{\text{eff}} = 4\pi M_s / H_{\text{eff}} + 1$ can be changed, where $H_{\text{eff}}$ is the total effective anisotropy fields in the magnetic ribbons, thus a tunable mutual inductance is expected.

Electrostatic tunable mutual inductance based on multiferroic composite core has been made and tested. According to the experiments results, the mutual inductance tunability, which is mediated by electric field controlled magnetic anisotropy and permeability, achieved a high value of 63.2% with minimum negligible power consumptions, which can be assumed to be a passive devices. The change of the magnetic anisotropy can also been observed in magnetic hysteresis loops. The mutual inductance tunability achieved in such coils based magnetoelectric core has a great potential for efficiency optimization of wireless power transfer in a large region of distance.

**EL03.03.18**

*Structural, Magnetic and Transport Properties of Nd$_2$CoFeO$_6$ and Pr$_2$CoFeO$_6$ Double Perovskites*  
Leonardo Oliveira and Jose A. Souza; Federal University of ABC, Brazil

Double perovskite (DP) compounds with general formula $A_2BB'O_6$ (where $A$ = alkaline-earth or rare-earth ions and $B$ = transition metal elements), belong to a family of materials that have attracted much attention due to their numerous fundamental physical properties. In these materials, the $d$ electrons at $BB'$ sites give rise to strongly correlated electronic and magnetic properties, such as metal-insulating transition, half-metallicity, large magnetoresistance, multiferroicity, long/short-range and frustrated magnetic ordering and many others. In this research, we obtained new DP compounds by traditional solid-state reaction method at 1300 K in air. Rietveld refinement of Nd$_2$CoFeO$_6$ and Pr$_2$CoFeO$_6$ indicates that both compounds crystallize in the orthorhombic $Pnma$ space group with similar lattice parameters, and with the $BO_6$ octahedral half occupied by Co and Fe ions at $4b$ Wyckoff site. Electrical transport measurements have shown a huge decreasing in the electrical resistivity from 10$^7$ Ω.mm to 1 Ω.mm as a function of temperature. DC magnetization of both compounds indicates a critical temperature around 220 K. Above this critical temperature and up to 380 K, the magnetic susceptibility does not follow the conventional Curie-Weiss law in the paramagnetic state. At higher temperature interval, from 380 K up to 700 K, we found a lower second slope in $\chi' \times T$ suggesting an unexpected increase in effective magnetic moment which are not predicted by taking into account the possible scenarios where one considers different valences and spin states for Nd/Pr, Fe and Co ions. Interesting, another peak in $dM/dT$ curve is observed at low temperature. In this context, we will discuss these results correlating the complex magnetic, electrical transport, and structural properties of these disordered double perovskite compounds.

**EL03.03.19**

*A Potential Multiferroic Material—Co Doped Hf0.5Zr0.5O2*  
Zimeng Zhang, Xiaoxi Huang, Vishal Thakare, Vishal Ravi, Yen-Lin Huang and Ramamoorthy Ramesh; University of California, Berkeley, United States

There is currently quite a bit of interest in multiferroics and magnetoelectrics for low power electronics. While there have been many new multiferroics added to the well-studied BiFeO$_3$ system, most of them have transition temperatures below room temperature. Thus, discovering new multiferroic and magnetoelectrics is desirable. Doped magnetic ferroelectrics (DMFE) are attracting attention in this regard since many of them have to potential to multiferroic/magnetoelectric property at room temperature. One such model system is BaTiO$_3$ doped with magnetic

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impurities. Our strategy is to take well known ferroelectrics, such as Hf0.5Zr0.5O2 (HZO) and introduce magnetic impurities, such as cobalt into the lattice. Prior work on Co-doping of TiO2 has revealed interesting magnetic effects and that forms the backdrop for our work. HZO is a simple fluorite showing robust ferroelectricity at the nanoscale and good compatibility with silicon and hence is a favored candidate for the next generation memory and logic devices. HZO has many phases, among which orthorhombic and rhombohedral phases possess ferroelectricity. Using epitaxy as the underlying driver, we have been able to demonstrate high quality HZO thin films in the 1-20nm thickness range. Doping with 5% Co does show the existence of a magnetic moment. We are presently studying the effects of Co concentration on the magnetic and ferroelectric stability. We demonstrated the existence of ferroelectricity by PFM and P-E loop measurements and tested the magnetic hysteresis loops. We will present results of this investigation on the role of HZO crystallinity and Co-doping on the magnetoelectric properties.

**EL03.03.20**

*Magnetodielectric Properties of Co/PZT/Co Spin Capacitor*  
Fernando Aponte, Roberto Masso-Ferret, Ricardo Martinez Valdes and Ratnakar Palai; University of Puerto Rico at Rio Piedras, United States

Spin capacitors have the potential to store both the electronic charge and magnetic spin that can produce conventional electric current and spin polarized current. The time evolution of spin polarized electrons injected into the piezoelectric material can be used for accurate sensing of magnetoelectric fields. To further study the application of multiferroic spin capacitors for future use in memory applications, Ferromagnetic/Ferroelectric/Ferromagnetic tri-layer artificial multiferroelectric structures in spin capacitor configuration were fabricated. Previous experiments were done by sputtering Iron (Fe) and Nickel (Ni) electrodes on lead zirconate titanate (PZT). In this paper, we report dielectric, magnetic, and magnetoelectric coupling in the tri-layer composite with Cobalt (Co) as the magnetic electrode sputtered onto PZT polycrystalline of different thickness. Various dielectric measurements were carried out, including: capacitance, impedance, loss coefficient, dielectric permittivity, and phase angle measurements done by a wide range of frequencies (100 Hz – 5 MHz) and magnetic fields (0 Tesla – 2.0 Tesla) at room temperature, and their interaction with the presence of the applied magnetic field (magnetocapacitance and magnetoimpedance) were analyzed. We also compared the magnetodielectric measurements of the Co/PZT/Co spin capacitor with Co/PZT/Ag and Ag/PZT/Ag tri-layers structures with their respective their behaviors. The magnetodielectric studies of different PZT layer thickness will be discussed in details.

**EL03.03.21**

*Charge Transfer and Hybridization Induced In-Plane Magnetic Uniaxial Anisotropy on the Co/NiO(110) Interface*  
Liang Yuhan and Yuanhua Lin; Tsinghua University, China

Emergent phenomenon is observed on the heterostructure interface, consisting of complex coupling of spin, orbital, lattice and charge. As a room-temperature stabilized G-type antiferromagnetic materials, the NiO is a favourable physic stage for investigating the interfacial magnetic coupling. Co/NiO interface has been investigated continually for its magnetic coupling and domain structure in (100) and (111) orientation, but few researchers focus on the in-plane orbital structure and related magnetic anisotropy in (110)-oriented Co/NiO interface. We find in-plane magnetic uniaxial anisotropy of polycrystalline Co films grown on the (110)-NiO, contrast to its isotropic crystallography nature. Depending on the X-ray linear dichroism spectrum(XLD) and X-ray circular dichroism spectrum(XMCD) shows, we found this uniaxial anisotropy emergent from the charge transfer of Co to Ni in the [-110] direction, and the hybridization of d-orbitals of Ni and Co. This work promotes the comprehension of the complex coupling of spin, orbital and charge, and provides possibilities for the NiO-based spintronics.

**EL03.03.22**

*Magnetic and Dielectric Properties of Potential Multiferroic GdCrO3*  
Jianhang Shi, Yanliu Dang, Steven L. Suib and Menka Jain; University of Connecticut, United States

Multiferroics materials have attracted a lot of attention due to their potential technological applications. GdCrO3 that belongs to the family of rare-earth chromites (RCrO3) has recently been reported to be a single phase magnetoelectric multiferroic. However, the origin or existence of ferroelectricity in GdCrO3 remains ambiguous. We have, therefore, examined the properties of bulk and thin film samples to explore their multiferroic properties. Magnetic measurements have revealed that it shows an antiferromagnetic transition with weak ferromagnetism below the Néel temperature $T_N$ of 169 K as well as spin reorientation, and giant magnetocaloric effect (MCE) at lower temperatures. In this work, structure, particle size, substitution effect, magnetic, and dielectric properties of this
family of material will be presented.

**EL03.03.23**

**Investigation of Interface Structure in Multiferroic h-ScFeO₃ Film**

Yosuke Hamasaki¹, Shintaro Yasui², Takahisa Shiraiishi³, Akihiro Akama⁴, Takanori Kiguchi³, Tomoyasu Taniyama⁴ and Mitsuru Itoh²; ¹National Defense Academy, Japan; ²Tokyo Institute of Technology, Japan; ³Tohoku University, Japan; ⁴Nagoya University, Japan

Polar iron oxides, which exhibit both ferroelectricity and (anti)ferromagnetism, are multiferroic materials, which promises potential application for new type memory devices. Hexagonal ReFeO₃ (Re = Rare earth element) with YMnO₃(YMO)-type structure exhibits ferroelectricity and weak-ferromagnetism. First principle calculation revealed that h-ReFeO₃ exhibits improper ferroelectricity (geometric ferroelectricity). Due to the strong magnetic interactions between Fe³⁺ cations, the higher magnetic order temperature in h-ReFeO₃ compared with hexagonal manganites is expected. A magnetic phase transition temperature of h-ReFeO₃ increases with decreasing ionic radius of Re cation. h-ReFeO₃ which consists of small ionic Re cation is a candidate for a high temperature multiferroic material.

Metastable h-ReFeO₃ were obtained by containerless melt crystallization process and crystallization from amorphous phase. Masui et. al. prepared Sc substituted LuFeO₃ by containerless process, and h-Lu₁₋ₓScₓFeO₃ was obtained in the range of x = 0 - 0.8. h-ReFeO₃ (Re = Tb, Lu, Y ) were stabilized on substrates such as YSZ(111) and Pt(111)/Al₂O₃(0001) in film form by pulsed laser deposition (PLD) and sputter techniques. Previously, we stabilized h-ScFeO₃ film on an Al₂O₃(0001) substrate using PLD technique. However, preparation of h-ScFeO₃ have not been reported yet. In this study, we attempted to prepare h-ScFeO₃ film on electrodes and investigated their physical properties and interface structure.

h-ScFeO₃ was deposited on various electrodes such as ITO, ZnO, SrRuO₃, and (La,Sr)MnO₃ by PLD technique. Single phase h-ScFeO₃ was obtained on La₀.₈Sr₀.₂MnO₃//SrTiO₃(111). Crystal structure of film was characterized by X-ray diffraction (XRD) and scanning transmission electron microscope (STEM). XRD measurements and HAADF-STEM observation revealed that h-ScFeO₃ with YMO-type structure was epitaxially grown with the relationships of ScFeO₃(0001)//La₀.₈Sr₀.₂MnO₃(111)//SrTiO₃(111).

The YMO-type ScFeO₃ film showed a ferroelectric P-E hysteresis loop with Pr ~ 4.9 μC/cm² and weak ferromagnetism with Tₘ = 195 K. The Tₘ value is the highest in hexagonal ReFeO₃ and ReMnO₃. Interface studies revealed that the monolayer consisted of two paired Sc cations connected to the YMO-type and perovskite structures. One of two paired Sc cations was displaced upward because of Coulomb repulsion from the Mn cations of La₀.₈Sr₀.₂MnO₃. We deposited ScFeO₃ film on various perovskite films or substrates. Single phase h-ScFeO₃ film was obtained on perovskite films or substrates with low valence B site cations. This results indicated that the valence of B cations in perovskite played an important role in the formation of the interface monolayer.

**EL03.03.25**

**Magnetic and Magnetocaloric Properties of Pd Doped in FeRh Alloy with Large Refrigerant Capacity**

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The B2-ordered intermetallic magnetic compound FeRh exhibits a thermodynamically first-order phase transition in vicinity of room temperature that makes it a highly intriguing subject for both fundamental and applied study. The structure, magnetic, and magnetocaloric properties of Pd doped in FeRh alloy have been investigated. Experiments revealed that there are same structures type FeRh (CsCl-type) with different lattice parameters and Fe₁₅.₇Rh (bcc-W type) phases coexist in FeRh₀.₉₅Pd₀.₀₅ sample. The wide phase transition temperature range is about 250 K, which is from 150 K to 400 K for this alloy. The maximum magnetic entropy change (-ΔSₘ) is 16.6 J/kg K for 0 - 30 kOe field changes and refrigerant capacity (RC) of 1347 J/kg was obtained due to the contribution of large transition temperature range. The excellent magnetocaloric performance indicates the applicability of FeRh₀.₉₅Pd₀.₀₅ as an appropriate candidate for magnetic refrigerant.

**EL03.03.26**

**Magnetic Properties of Co₃₋ₓNiₓO₄ (0 ≤ x ≤ 1.28) Particles Synthesized from Co₁₋ₓNiₓ(OH)₂: Precursors**

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Magnetic properties of cobalt nickel spinel oxides $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ (CNO) have been extensively studied over decades [1,2]. In the Co-Ni-O system, CNO is known to be metastable under atmospheric conditions as the rock-salt phase ($\text{Co}_1\text{Ni}_3\text{O}_4$) is stable when $T > 1173$ K while NiO and $\text{Co}_3\text{O}_4$ phase are stable when $T \leq 1173$ K [3]. Due to CNO’s metastability, it is believed to be difficult to chemically synthesize CNO for $X > 1$ through conventional process such as thermal decomposition and co-precipitation [2,4]. CNO thin films grown by physical vapor deposition for $X > 1$ [5,6], reportedly yield relatively low Curie temperatures ($T_C = -100$-200 K for $X = 1$) in contrast to higher $T_C$ for powder CNO ($T_C = -400$ K) [1]. Recently, it was reported that CNO samples for $X > 1$ can be synthesized by thermal decomposition of organic metal frameworks (MOF) for super capacitor electrodes applications [7]. In this case, CNO for $X > 1$ can be synthesized from Co-Ni MOFs where Co and Ni ions are uniformly mixed at an atomic scale. In this study, we report successful synthesis of CNO particles for $X = 0$-1.28 from $\text{Co}_{1.7}\text{Ni}_3\text{OH}_2$ precursors in which Co and Ni ions are uniformly mixed at an atomic scale, and the magnetic properties of the CNO at room temperature.

[Experimental] The $\text{Co}_{1.7}\text{Ni}_3\text{(OH)}_2$ precursors were prepared from a hydrochloric aqueous solution containing $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ by a uniform precipitation process. The were the annealed at 573-873 K for 3 hours in the air to transform into CNO particles. Their magnetic properties were investigated by vibrating sample magnetometry (VSM), electromagnetic resonance (EMR) spectrometry, and superconducting quantum interference device (SQUID) magnetometry at temperature from 5 K to room temperature (RT). [Results and Discussion] X-ray diffraction spectrometry (XRD) of the samples have shown that CNO particles are successfully synthesized for $X \leq 1.28$ without producing any other phases. The lattice parameter of CNO increases linearly with increasing $X$, yielding with Vegard’s law. The mean particle size of CNO estimated from XRD data using Scherrer’s equation is 8–33 nm. Magnetic measurements by VSM show that CNO particles for $X \geq 0.74$ possess remanent magnetization and coercivity at RT, it reveals that the CNO particles are ferrimagnetic at RT. Microwave absorption peaks are observed in the ENR spectra of CNO particles for $X \geq 0.74$. The EMR spectra of the CNO samples exhibit absorption peaks best fitted only by the Gaussian function. The peaks can generally be fitted by the Gaussian when it contains a ferromagnetic (ferrimagnetic) component and/or the Lorentzian when it has a paramagnetic one in the sample. Hence, it is suggested that the ferromagnetic CNO samples possess a fairly high crystallinity with few defects breaking magnetic interaction in the crystal. SQUID measurements of the samples shows that their saturation magnetization increases with increasing $X$ for $X < 0.74$ and decreases for $X \geq 0.74$. [References]

and Ho Co-Doping Jogender Singh, Ashish Agarwal and Sujata Sanghi; Guru Jambheshwar University of Science and Technology, India

Multiferroics having composition Bi_{0.80-x}Ba_{0.20}Ho_xFeO_3 (BBFO, BBHFO-5, BBHFO-10, BBHFO-15 and BBHFO-20 for x = 0, 0.05, 0.10, 0.15 and 0.20 respectively) were synthesized by method of solid state reaction. The crystal structure has been studied using X-ray diffraction technique. The X-ray patterns show enormous transform in crystal structure at concentration x=0.20. The Rietveld refinement of XRD patterns indicates that at concentration x=0 sample have rhombohedral structure with R3c space group while for the concentration x= 0.05, 0.10, 0.15 and 0.20, the mixed phase including rhombohedral R3c and triclinic P1 space groups were obtained with best fitting. This phase transformation in crystal structure is observed due to mismatching of ionic radii of doped ions and parent ions. Magnetic properties of all samples were carried out by using vibrating sample magnetometry. M-H hysteresis loops shows that with doping of Ba and Ho antiferromagnetic BiFeO_3 (BFO) transforms into ferromagnetic. The dielectric properties were carried out by impedance spectroscopy which shows that dielectric properties are enhanced with co-doping in comparison of the pristine BFO due to structure deformation and decrease in oxygen vacancies with higher concentration of Ho.

EL03.03.29
Probing the Ferromagnetic Resonance of the Si/Ge_{2}Sb_{2}Te_{5}/FeCoB Heterostructures Induced by Phase Change Yuyi Wei, Xinjun Wang, Jiawei Wang and Nian Sun; Northeastern University, United States

Over the past few decades, phase change materials (PCM) has received a lot of attention for its application such as novel non-volatile memory,[1-4] switches[5,6] and sensors.[7] Typically, PCMs exist in an amorphous and one or more crystalline phases, in which significant optical and electrical contrast can be observed. The change in state can be rapidly and repeatedly switched by inducing optical pulses or electrical (Joule) heating.[8,9] In 2011, F. Xiong et al. proposed a low power switching using GST with programming current of 1 to 8 µA and programming voltage of below 1V, indicating an energy loss of femtojoules scale.[5] This design not only brought a promising prospect to ultra-low power electronics and memory development but also proposed inspiration in voltage control of ferromagnetic resonance (FMR).

Here, a systematic study of the coupling effect in Si/Ge_{2}Sb_{2}Te_{5}/FeCoB heterostructures is presented. We investigated the FMR change in FeCoB film induced by crystalline phase change in GST film. A large shifting in FMR field of 15 mT in FeCoB film can be observed when GST is highly crystallized after annealing at 300 °C. And the uniaxial magnetic anisotropy field is also strengthened when Ge_{2}Sb_{2}Te_{5} is highly crystallized in hexagonal phase via interfacial coupling effect. With all these results, a novel structure using PCMs for voltage control of FMR is proved to be applicable. This structure can be predicted to have very low operation voltage as well as ultra-low energy consumption, showing an extraordinary advantage in the development novel fast response, energy efficient tunable microwave devices and non-volatile magnetic memory.

EL03.03.30
Two-Dimensional Transport in LaTiO_3 Thin Films Embedded in SrTiO_3 Jiyeon N. Lee and Mikk Lippmaa; University of Tokyo, Japan

Oxide materials with unexpected transport and magnetic properties at interfaces have generated great interest in multifunctional heterostructure design. One of the best-known systems is the interface between LaAlO_3 and SrTiO_3[1], exhibiting a two-dimensional electron gas in a strongly asymmetric quantum well due to possible switching or spintronic device application[2]. There is growing experimental evidence that the carrier accumulation in a quantum well at the interface leads to magnetic order that may be tunable or switchable if sufficient carrier density control can be achieved. However, except for limited tunability by electrostatic back-gating, it has proven to be difficult to control the carrier density in the electron gas.

In this work, we have chosen to use a similar electronic system consisting of a thin LaTiO_3 film, with a thickness of a few unit cells, embedded in SrTiO_3. While metallic conductivity at the LaAlO_3/SrTiO_3 interface appears abruptly when the LaAlO_3 film thickness exceeds 4 unit cells, the total carrier number in the LaTiO_3/SrTiO_3 system is continuously tunable over a wide range by changing the number of La atoms in the LaTiO_3 layer. Since the presence of a single LaO layer in the perovskite lattice is sufficient to induce metallic conductivity, a polar discontinuity does not arise, but carriers are still confined in a quasi-2D quantum well and form a high-mobility layer, similar to the LaAlO_3/SrTiO_3 interface. When the heterostructure is grown on a single crystal SrTiO_3 substrate and capped with a SrTiO_3 film that is grown at low temperature, the difference in the dielectric permittivities of the substrate and the
cap layer leads to an asymmetric quantum well, similar to the LaAlO$_3$/SrTiO$_3$ heterostructures. By using this specially designed heterostructure, we discuss how to determine the depth distribution of carriers while changing the LaTiO$_3$ or SrTiO$_3$ cap layer thickness and look at the effect of the carrier distribution on the magnetotransport characteristics. Our experiments show that a large negative in-plane magnetoresistance effect occurs at low temperature when the magnetic field is applied parallel to the current, in a qualitatively similar fashion to LaAlO$_3$/SrTiO$_3$ interfaces[3]. We also discuss the effects of back-gating on the magnetotransport characteristics and interpret the results in terms of carrier depth distribution changes in the heterostructure under electrostatic bias. We attempt to distinguish whether the observed negative in-plane magnetoresistance is related to carriers confined at the interface or those that distribute over a larger depth in the substrate-side tail of the quantum well and how such carrier redistribution affects the carrier density in the quantum well.

References:

**EL03.03.31**

Rare Earth Ortho-Chromate HoCrO$_3$—A Structure-Property Investigation into Its Multiferroic Nature
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Multiferroics are materials possessing different ‘ferroic’ orders such as ferro-magnetism, ferro-electricity, ferro-elasticity etc. Many rare earth ortho-chromates and ferrites were reported to exhibit multiferroic properties and magneto-electric coupling[1]. It was reported that in many of the rare earth chromates, the onset of polar ordering appears at temperatures slightly higher than their antiferromagnetic ordering[2]. Here we investigate the temperature evolution of structural and dielectric properties of Holmium based ortho-chromate, HoCrO$_3$. Polycrystalline HoCrO$_3$ was prepared by conventional solid-state synthesis route. Reitveld refinement of the synchrotron x-ray diffractogram at room temperature confirms the perovskite orthorhombic structure crystallizing in the Pbnm space group. Temperature evolution of synchrotron x-ray diffraction points to the presence of variation in unit cell volume around 242 K and 100 K. Magnetic measurement confirms the antiferromagnetic transition at 140 K. The compound exhibits a dielectric constant of 19.46 at 1.784 kHz at room temperature. Also, temperature variation of the real part of the dielectric constant reveals a typical relaxor-like behaviour with low temperature and high temperature plateaus along with two anomalies at 240 K and 140 K. Analysis of peaks in the loss tangent curves confirms thermally activated dielectric relaxation. The dielectric anomaly at 140 K indicates a possibility for magneto-electric coupling in the material. However, the peak at 242 K corroborates the volume change observed in synchrotron analysis, which is associated with a possible structural transition (Pbnm to Pna2$_1$), usually observed in similar rare earth based ortho-chromates having ferroelectric ordering. Two feeble features around 100 K and 242 K were observed in the temperature dependence of specific heat curve and these corresponds to the structural transitions observed in the unit cell volume derivative curve with respect to temperature. In the present work synchrotron x-ray diffraction technique was used for the first time to confirm the structural transition in HoCrO$_3$.

**EL03.03.32**

Investigation of Geometry Parameters Influencing the Performance of Cantilever Magnetoelectric Sensors
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Magnetoelectric (ME) sensors currently have attracted great interest due to their capability to detect magnetic fields in the picotesla regime at room temperature, showing a high potential in the biomagnetic field detection. Based on the magnetoelectric effect of ME sensors, the applied magnetic field induces a change in the strain of magnetotriective layer which will be transferred to the piezoelectric material via the mechanical coupling. An electrical voltage across the piezoelectric layer is thus generated and can be measured directly. However, for the application of non-invasive medical imaging like magnetoencephalography or -cardiography (MEG, MCG), a magnetic field sensor with a limit of detection (LOD) in the range of picotesla is required. To reach this goal, the LOD of ME sensors still needs to be further improved.
There are many approaches to improve LOD of ME sensors, either by increasing the sensitivity, or by decreasing the intrinsic noise level. A simple solution for improving the sensitivity is to optimize the geometry parameters of the ME sensor through a parameter study. Recent studies have investigated the influence of the geometry parameters of the individual layers and the substrate layer on the sensitivity of cantilever ME sensors using finite element model [1][2]. Here, an experimental model is built up for determining the basic parameters of the cantilever ME sensor.

In this study, we present cantilever ME sensors based on magnetoelectric composites with various geometry parameters. The cantilever contains poly-silicon layer, piezoelectric material (AlN) and magnetoelectric material (FeCoSiB) in sequence. The performance of the presented sensors is studied based on the sensitivity, voltage noise density, quality factor and LOD. Three different parameters including the cantilever length, the substrate thickness and the thickness ratio between the magnetostrictive and piezoelectric layers are analyzed to understand their effect on sensors’ performance. Since the devices were fabricated in 8 inch silicon technology, the availability of a relevant number of devices allows a statistical analysis. The results are used to identify the optimal geometry parameters for cantilever ME sensors and can be applied to develop next generation devices.

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EL03.03.33
Lead Free Multiferroic Nano-Heterostructured Films for Energy Storage Applications Mohan K. Bhattarai, Sita Dugu and Ram S. Katiyar; University of Puerto Rico, Rio Piedras, United States

Lead free environment friendly multiferroic perovskites thin films are of research interest due to its reduction in dimensionality leading to high energy storage and magneto electric behavior and hence are suitable for several electronic device applications. Herein, we report the tetragonal multiferroic heterostructure thin films fabricated by pulse laser deposition technique consisting alternate of Ba(Zr0.30Ti0.70)0.99 Fe0.01 O3 (BZTF) and Ba(Zr0.30Ti0.70) O3 (BZT) layers grown upon LSMO coated on MgO (100) substrate. X-ray diffractometry data analysis suggests phase purity of thin films oriented along (100) direction. Micrograph structural analysis using atomic force microscopy revealed a homogeneous distribution of grains with roughness ~ 3- 5 nm. Dielectric measurements on Au/BZT/BZTF/LSMO and Au/BZTF/BZT/LSMO metal insulator metal capacitors using a impedance analyzer as a function of temperature (100-650 K) and frequency (10^2-10^6 Hz) suggest their relaxor behavior. The slim P-E loop also corroborate relaxor behavior. The temperature dependent magnetic measurements using a physical property measurement system suggest the existence of magnetic nano clustures dispersed in a paramagnetic matrix and attributed to its super para magnetic behavior. A large energy storage density is estimated from our P-E loop data. These results suggest the present heterostructured thin films could be promising multiferroic materials for high energy density applications.

EL03.03.34
High Energy Density and Efficiency Achieved in Lanthanide-Substituted Bismuth Titanate Dielectric Films Shun Lan, Hao Pan and Yuanhua Lin; Tsinghua University, China

Dielectric capacitors with high electrostatic energy density, long-term stability, and environmental friendliness are strongly demanded in modern electrical devices. Here we fabricated Bi_{4-x}La_{x}Ti_{3}O_{12} (x = 0.75, 1.0 and 1.2) thin films by pulse laser deposition. It is revealed that the substitution of Bi by La leads to a continuous transition from ferroelectric to relaxor-ferroelectric and then to paraelectric with concurrently improved energy density and efficiency. Based on the transition, high energy densities of ~60 J cm\(^{-3}\), together with high efficiency(>80 %) as well as excellent cycling(~10^6 cycles) and thermal stability(-100~130'C), can be achieved in the Bi_{4-x}La_{x}Ti_{3}O_{12} films. These excellent performances should be ascribed to the paraelectric characteristics and suppressed leakage current of the film. The results prove the great potential of the Bi_{4-x}La_{x}Ti_{3}O_{12} films for electrostatic energy storage. More importantly, our findings show the advantage of paraelectrics as high performance energy storage dielectric materials.

EL03.03.35
Ferroelectric-Paraelectric Phase Transition in SnTiO\(_3\), a Lead-Free Putative Ferroelectric Rajesh K. Katiyar,
Karuna K. Mishra, Gerardo Morell, Brad Weiner and Ram S. Katiyar; University of Puerto Rico, San Juan, United States

The environmentally benign nature of Sn$^{2+}$ would make SnTiO$_3$ (SnTO) derived compounds an attractive alternative to lead-free dielectric material. Several theoretical studies suggested that the spontaneous polarization of SnTO is larger than that of classical ferroelectric PbTiO$_3$. Pure phase of SnTO is one of the challenging jobs due to often mixed oxidation states of Sn$^{2+}$ and Sn$^{4+}$ in perovskite titanates. The material was synthesized using a chemically route followed by a solid-state reaction method and were annealed it in a mixture ratio of 1:1 methane-hydrogen environment. The phonon spectra of tetragonal ferroelectric SnTO compound were measured as a function of temperatures in the range 82-1250 K using a micro-Raman spectrometer equipped with a CCD detector. Seven phonons are identified in the frequency range 100-1000 cm$^{-1}$ at the room temperature and are assigned as per the C$_{4v}$ point group symmetry. The reduced temperature dependent spectra were analyzed using the damped harmonic oscillator model to obtain the thermal evolution of the mode frequencies and their intensities. Upon increasing temperature, the optical phonon modes were found to be soften and their intensities decreases, as normally expected, due to involved multi-phonon scattering processes. At 823 K, the A$_1$(TO) phonon located at 441 cm$^{-1}$, exhibits anomaly and begins to harden upon further increase in temperature; in addition, the E(LO) mode at 827 cm$^{-1}$ disappear around 823 K, suggesting a tetragonal ferroelectric to a high symmetry paraelectric cubic phase transition. The nature of transition is found to be first order displacive type. The appearance of symmetry forbidden broad Raman bands in the high temperature cubic phase is attributed to contribution from phonon density of states. These studies on phonon behaviors on this putative green ferroelectric could provide insight about its structure-property relations and its thermodynamics properties as well. The detail results will be presented at the meeting.

EL03.03.36
Temperature-Induced Phase Transitions and Charge Transport in Ferroelectric [K NbO$_3$]$_{1-x}$[ (BaNi$_{1/2}$Nb$_{1/2}$O$_{3-δ}$)$_x$], Electroceramics Blanca Y. Rosas, Alvaro Instan, Karuna K. Mishra and Ram S. Katiyar; University of Puerto Rico, United States

Potassium niobate (KNbO$_3$) is a lead-free piezoelectric material, respectful of the environment and technologically very important. This is because it has excellent electromechanical properties and diverse applications in electronic and photonic devices. The electro-physical properties, such as the crystalline phase transition, the optical band gap, the dielectric constant, the Curie temperature, the electrical conductivity and the ferroelectric behavior of KNbO$_3$ can be tuned by suitable dopant, such as isovalent Ba in its A-site, and heterovalent Ni on B-site results in a single phase ceramic material with stoichiometric formula [KNbO$_3$]$_{1-x}$ [(Ba$_{1/2}$Ni$_{1/2}$)O$_{3-δ}$], for x = 0.1 and δ = 0.25 (KBNNO). The structural, optical, dielectric, charge transport phenomena and ferroelectric properties of this solid solution were systematically investigated. The ceramic material was prepared by the solid-state reaction method and calcined at 1198 K, using starting precursors as K$_2$CO$_3$ (99.5%), BaCO$_3$ (99.95%), Ni$_2$O$_3$ (99.9%) and Nb$_2$O$_5$ (99.9%). The orthorhombic ferroelectric phase formation of the synthesized samples is confirmed by using X-ray diffractometry and Raman spectroscopic analysis. Surface morphology study using scanning electron microscopy revealed well-sintered nature of the sample with grains are interconnected and densified. Temperature-dependent in-situ x-rays diffraction studies (300-873 K) revealed the phase transitions from room temperature orthorhombic to tetragonal to a cubic phase at elevated temperatures. The temperature dependent Raman spectra studies in the T-range 82-1000 K suggest that several bending and stretching phonon mode frequencies and their intensities exhibit anomalous changes across the phase transitions temperatures. These transition temperatures were corroborated with the DSC measurements. A direct optical band gap of 3.16 eV is estimated from the analysis of the diffuse reflectance spectra using Kubelka-Munk analysis. The dielectric properties of KBNNO were studied as a function of temperature between 80-500 K in a frequency range from 100 Hz to 1 MHz in a metal-ferroelectric-metal capacitor nanostructure. The dielectric constant and the loss tangent at 100 kHz were 280 and 0.01, respectively. The frequency dependence of the AC conductivity showed typical characteristics of the universal dynamic response. Our studies reveal the structure-property relation, fundamental physics and materials science of KBNNO electroceramics, and establishing its potential for ferroelectric device applications.
Tuesday Morning, December 3, 2019
Hynes, Level 1, Room 101

8:00 AM *EL03.04.01
Breaking Symmetries to Create a Robust Room-Temperature Ferrimagnetic Ferroelectric in LuFeO₃/CoFe₂O₄ Superlattices
R. Steinhardt¹, M. E. Holtz¹, P. Barrozo²,³,⁴, A. Coleman¹, I. Glushchenko¹, C. J. Fennie¹, D. A. Muller¹,⁵, Ramamoorthy Ramesh³,⁴ and Darrell G. Schlom¹; ¹Cornell University, United States; ²Federal University of Sergipe, São Cristóvão, Brazil; ³University of California, Berkeley, United States; ⁴Lawrence Berkeley National Laboratory, United States; ⁵Kavli Institute at Cornell for Nanoscale Science, United States

Materials that exhibit simultaneous order in their electric and magnetic ground states hold tremendous promise for use in next-generation, low-power memory and logic devices in which electric fields control magnetism. Such materials are, however, rare as a consequence of the competing requirements for ferroelectricity and magnetism, and until recently BiFeO₃ was the only material with this functionality at room temperature. Interface materials are a way to overcome these competing requirements, as was recently demonstrated for (LuFeO₃)₅/(LuFe₂O₄)₁ superlattices [J.A. Mundy et al. Nature 537 (2016) 523–527]. The rumpling imposed by the geometric ferroelectric hexagonal LuFeO₃ imposes a local distortion on the neighboring LuFe₂O₄—a distortion that removes the mirror symmetry that the LuFe₂O₄ layers would otherwise have. This breaking of symmetry enables the LuFe₂O₄ to become simultaneously ferrimagnetic and ferroelectric. This rumpling is distinct from strain engineering because no macroscopic strain is involved. In this presentation we extend this atomically engineered design methodology to LuFeO₃/CoFe₂O₄ superlattices producing a robust ground state that is simultaneously ferroelectric and ferrimagnetic at temperatures well above room temperature.

8:30 AM *EL03.04.02
Electric Field Control of Magnetism at Room Temperature
Ramamoorthy Ramesh; University of California, Berkeley, United States

There is currently a lot of R&D activity worldwide on two broad, systems level topics, both within the field of Microelectronics. One of them has to do with the emergence of the “Internet of Things”, which is the interconnectivity of microelectronics based sensing, communicating and information processing systems. The second has to do with the re-emergence of Artificial Intelligence/ Machine Learning, which is currently experiencing a worldwide explosion. Thus, the worldwide market for microelectronics is likely to go up significantly. A key side consequence of this is the total energy consumed in such applications, which could skyrocket towards 20-25% of primary energy and thus of concern. Indeed, in the field of AI, a “Computing Wall” driven by a “Memory Wall” has emerged as a key bottleneck in systems level applications, such as in “Connected Autonomous Vehicles” or driver-less cars. At the same time, the key driver for the field of Microelectronics, namely Moore’s Law, is reaching the end of size scaling and power scaling. As a consequence, there is a large amount of research activity focused on the new Moore’s Law that is instead focused on Energy Scaling. Thus, looking for a new generation of ultra-low power memories and switches is an area of significant current research. Complex perovskite oxides exhibit a rich spectrum of functional responses, including magnetism, ferroelectricity, highly correlated electron behavior, superconductivity, etc. The basic materials physics of such materials provide the ideal playground for interdisciplinary scientific exploration with an eye towards such applications. Over the past decade the oxide community has been exploring the science of such materials as crystals and in thin film form by creating epitaxial heterostructures and nanostructures. Among the large number of materials systems, there exists a small set of materials which exhibit multiple order parameters; these are known as multiferroics, particularly, the coexistence of ferroelectricity and some form of ordered magnetism (typically antiferromagnetism). The scientific community has been able to demonstrate electric field control of both antiferromagnetism and ferromagnetism at room temperature. Current work in our collaboration is focused on ultralow energy (1 attoJoule/operation) electric field manipulation of magnetism as the backbone for the next generation of ultralow power electronics. We are exploring many pathways to get to this goal. In this talk, I will describe our progress to date on this exciting possibility. The talk will conclude with a summary of where the future research is going.

9:00 AM *EL03.04.03
Magnetic Monopoles Hidden in Magnetoelastic Materials
Nicola Spaldin; ETH Zurich, Switzerland
In linear magnetoelectric materials, an electric (magnetic) field induces a magnetization (electric polarization) with a magnitude that is linearly proportional to the applied field strength. Here we use the prototypical magnetoelectric material, Cr$_2$O$_3$, to show that magnetoelectric materials with a diagonal magnetoelectric response host a hidden hedgehog-like magnetic order known as the magnetoelectric monopolization. We describe several consequences of this hidden order: First, we show that the magnetoelectric monopolization leads to a surface magnetization, independently of the choice of surface cut, that in turn should influence the exchange bias coupling in a heterostructure. Second, we show that a charge on the surface of such a magnetoelectric induces a divergent magnetic field above the surface, and describe an experimental search for this monopolar field using muon spin resonance spectroscopy [1]. Finally, we discuss the implications of an isotropic diagonal magnetoelectric response, and propose candidate materials for such behavior.


9:30 AM *EL03.04.04
Structure and Properties of Freestanding Two-Dimensional Oxide Perovskites
Dianxiang Ji, Songhua Cai, Haoying Sun, Yi Zhang, Wenpei Gao, Huaxun Huyan, Lu Han, Zhengbin Gu, Tula Paudel, Evgeny Y. Tsybalk, Peng Wang, Yuefeng Nie and Xiaoqing Pan, Nanjing University, China; University of California, United States; University of Nebraska–Lincoln, United States

Two-dimensional (2D) materials such as graphene and transition metal dichalcogenides reveal the electronic phases that emerge when a bulk crystal is reduced to a monolayer. Transition-metal oxide perovskites host a variety of correlated electronic phases, so similar behavior in monolayer materials based on transition metal oxide perovskites would open the door to a rich spectrum of exotic 2D correlated phases that have not yet been explored. Here we report the fabrication of freestanding perovskite films with high crystalline quality almost down to a single unit cell. Using a method based on water-soluble Sr$_3$Al$_2$O$_6$ as the sacrificial buffer layer, recently developed at Stanford University, we synthesize freestanding SrTiO$_3$ and BiFeO$_3$ ultrathin films by reactive molecular beam epitaxy and transfer them to diverse substrates, in particular crystalline silicon wafers and holey carbon films. We find that freestanding BiFeO$_3$ films exhibit unexpected and giant tetragonality and polarization when approaching the 2D limit. Our results demonstrate the absence of a critical thickness for stabilizing the crystalline order in the freestanding ultrathin oxide films. Furthermore, the systematic characterization of the cross-sectional samples by atomic resolution electron microscopy reveals that the crystal symmetry and physical properties such as local electrical polarization are strongly dependent on the local strain and boundary conditions of the film. The ability to synthesize and transfer crystalline freestanding perovskite films without any thickness limitation onto any desired substrate creates opportunities for research into 2D correlated phases and interfacial phenomena that have not previously been technically possible.

10:00 AM BREAK

10:30 AM DETECTION OF MAGNETICALLY LABELED CELLS USING MAGNETOELECTRIC MAGNETIC FIELD SENSORS, CHRISTINE SELHUBER

11:00 AM *EL03.04.06
Creating the Next Device for Moore’s Law with Room Temperature Quantum Materials
Sasi Manipatruni, Kepler Computing, United States

The nanoscale transistor is perhaps the most numerous man made object, exceeding $10^{18}$ transistors used in ubiquitous computing and communications devices. However, as we reach the hyper scaled dimensions for electronic transistors (smallest transistors reaching sub 10 nanometer dimension) [i], a search for identifying the next scalable transistor is ongoing. For use in ubiquitous computing, such a “transistor” not only needs able to operate at room temperature but also possess features commensurate with beneficial miniaturization (Moore’s law). We have studied >25 device topologies for new transistor technologies and have considered the use of nearly all the breakthroughs in materials science from the last 3 decades [ii]. We have come to the understanding that new materials and phenomenon enabled by quantum materials form the path to the next “transistor” that is suitable for consumer electronics and cloud computing.

The Technology Need: We describe the imminent need for a revolutionary new transistor for classical Boolean
computing based on a) The thermal power limit of the computers reaching the historic trigger point of 10 W/cm² (Figure 1), this has earlier led the conversion of computing from Bipolar to CMOS in 1980s. Another such trigger is imminent b) The exponential growth in energy demands due to proliferation of compute devices c) The continued need for classic computations that are described by a large variety of computational algorithms (e.g. Geometric, combinatorial problems, graphical processing, computational fluid dynamics, prediction of complex physical/biological phenomenon).

**A Quantum Materials pathway for new computing[iii]:** We will describe a fundamentally new scaling path for computing where we bridge the breakthroughs in quantum materials for creating the next general purpose, room temperature computing technology. The term Quantum Materials is used to describe a broad class of materials that exhibit strong interactions amongst the charge, spin, orbital and lattice degrees of freedom. Over the past 2-3 decades, since the advent of high temperature superconductivity in cuprates, there have been several classes of quantum materials that include i) the CMR manganites where new states of matter and exquisite tunability of such states with external stimuli are driven by the strong electron-electron correlations and the consequent mesoscale phase coexistence, and ii) topological insulators that are driven by strong spin-orbit coupling leading to unusual band topology and Dirac-like fermion behavior, as key examples.

**Magneto-electrics and Topological Conversion Pathway for Computing[iv]:** I will describe the concept device (named Magneto-electric Spin Orbit Logic) to drive high functionality materials in magneto-electrics and topological materials. In particular, the path to computing at 10-bit (~30X more energy efficient than advanced CMOS) with 10-20X relaxation of the interconnect requirements will be described.


11:30 AM EL03.04.07
**Stabilization of a New Antiferroelectric Phase of BiFeO₃ through Electrostatic Engineering in Oxide Heterostructures** Bastien F. Grosso, Quintin N. Meier and Nicola Spaldin; ETH Zürich, Switzerland

BiFeO₃ (BFO) is one of the most studied multiferroic materials because of the coexistence of magnetic and polar orders at room temperature. Here we show that previously unidentified structural phases of BFO, with functional properties different from those of the rhombohedral ferroelectric bulk structure, can be stabilized by exploiting the electrostatic boundary conditions in thin film heterostructures. This provides a complementary approach to the earlier successes in stabilizing some of the many low-energy phases that have been identified computationally, by using coherent heteroepitaxial strain [1,2]. Using density functional theory, we identify a new antipolar phase of BFO and find that the energy barrier to convert it into a ferroelectric phase is small enough for it to be a candidate antiferroelectric. According to our strain calculations and a simple electrostatic model, this antipolar phase can be stabilized with insulating non-polar electrodes for a certain thickness range of the BFO layer on a substrate imposing a small amount of compressive strain; the rhombohedral phase can be recovered by increasing the thickness. These predictions are consistent with a new antipolar phase recently observed experimentally in Laₓ,BiₓFeO₃/BiFeO₃ superlattices, which reveal a double hysteresis loop, characteristic of an antiferroelectric material [3]. Finally, we identify other new low-energy phases for BFO and propose possible ways to stabilize them experimentally.

References
Understanding Magnetoelectric Switching in Lanthanum-Doped BiFeO₃ Thin Films

Yen-Lin Huang¹, Rajesh V. Chopdekar², Chirs Addiego³, Xiaoqing Pan³, Heng-Jui Liu⁴, Ying-Hao Chu⁵ and Ramamoorthy Ramesh¹;
¹University of California, Berkeley, United States; ²Lawrence Berkeley National Laboratory, United States; ³University of California, Irvine, United States; ⁴National Chung Hsing University, Taiwan; ⁵National Chiao Tung University, Taiwan

The key to integrating the concepts of spintronics into conventional nanoelectronics lies with the ability to control the magnetic order in nanoscale devices. With the continuous shrinkage of integrated circuits, the energy efficiency required to control these tiny magnets as power dissipation becomes a determining factor below 7 nm node. Over the past decades, the oxide community has been exploring the materials that can provide opportunities to control magnetism. Among the large investigated materials, multiferroics might be one of the most promising material family. Multiferroics are defined as the materials which possess at least two order of parameters, particularly, the coexistence of ferroelectricity (P) and magnetism (M), and exhibit coupling from one to another. In this talk, I will discuss the magnetoelectric switching mechanism in lanthanum-doped BiFeO₃ thin films. BiFeO₃ is by far the best-studied multiferroic, which shows strong ferroelectricity (~100 \( \mu \)C/cm²) and G-type antiferromagnetism, above room temperature. It also shows weak ferromagnetism (Mₓ) induced by the canted spin configuration described by the Dzyaloshinskii–Moriya interaction (DMI). Moreover, these ferroic orderings, \( P \) and \( Mₓ \), are strongly coupled, thus one can switch the magnetism by an electric field. However, the strong spontaneous polarization in BiFeO₃ needs a large voltage to switch. Here, we introduce the chemical doping to modify the order parameters in BiFeO₃ and achieve an ultralow-voltage (< 500 mV) and non-volatile manipulation of ferromagnetism at room temperature. Moreover, while the lanthanum-doping increased, we observed a very different magnetoelectric switching pathway and magnetic anisotropy compare to pure BFO. This discovery leads to the enhancement of perpendicular magnetic anisotropy (PMA) on multiferroics thin film, which will be very attractive to the practical applications. Finally, I will conclude this talk with a summary of current challenges and future direction of multiferroics, especially BFO, toward the low-power electronics.

SESSION EL03.05: Magnetoelectrics II
Session Chair: Jeffrey McCord
Tuesday Afternoon, December 3, 2019
Hynes, Level 1, Room 101

1:30 PM *EL03.05.01
Multiferroic Self-Assembled Oxide Nanocomposites Incorporating BiFeO₃, YFeO₃ and SrFe₁₋ₓCoxO₃
Caroline A. Ross and Shuai Ning; Massachusetts Institute of Technology, United States

Self-assembled two phase epitaxial oxide nanocomposites, in which a magnetic phase and a ferroelectric phase are coupled via strain transfer at their interfaces, can exhibit multiferroic and magnetoelectric responses. Such nanocomposites hold promise for making new types of electrically-switchable magnetic devices. The most commonly studied nanocomposite consists of a perovskite matrix (e.g. BiFeO₃ (BFO)) surrounding vertical pillars of a ferrimagnetic spinel (e.g. CoFe₂O₄ (CFO)). An electric field applied to the BFO changes its strain state and hence the strain state and magnetic anisotropy of the CFO, promoting changes in magnetization and even reversal. We will first describe BFO/CFO nanocomposites including strategies for templating the pillar positions and the behavior of (110)-oriented nanocomposites with fin-shaped CFO exhibiting in-plane anisotropy, and compare the structure and properties of nanocomposites grown by sputtering vs. pulsed laser deposition. We then describe nanocomposites containing YFeO₃ (YFO) as the ferroelectric phase. Bulk YFO is not ferroelectric, but thin films of YFO grown on certain substrates exhibit a polarization that can exceed 100 \( \mu \)C/cm². Based on first principles calculations the polarization is attributed to epitaxial mismatch strain which promotes off-centering of the cations. YFO/CFO nanocomposites grown on SrTiO₃ (001) substrates show a magnetoelectric coupling in which the ferroelectric hysteresis is sensitive to an in-plane magnetic field. We also demonstrate the control of the magnetic properties of nanocomposites containing SrFe₁₋ₓCoxO₃ (SFCO) using ionic liquid gating. Single phase films of
SFCO are non-magnetic as grown and form either a perovskite or brownmillerite phase depending on deposition conditions and Fe:Co ratio. However, negative gating inserts oxygen and leads to a magnetization of up to 100 emu cm\(^{-3}\) and a structural change from brownmillerite to perovskite with an associated substantial volume change. This magnetic switching is reversible over multiple cycles and is also observed in nanocomposites of SrFeCoO\(_3\) codeposited with a spinel phase including Co\(_3\)O\(_4\) and CFO. The inclusion of new materials, SFCO or YFO, in nanocomposites therefore expands the palette of possible structures, properties and control strategies, enhancing the functionality of these magnetoelectric heterostructures.

2:00 PM *EL03.05.02
A Route to Low Noise Magnetoelectric Sensors—Controlling Magnetic Domain and Domain Wall Effects in Magnetoelectric Sensor Devices Jeffrey McCord; Kiel University, Germany

The role of magnetic domain formation and reorientation processes reveals fascinating physics and is of great relevance for technological applications. Especially the class of magnetic sensors that depend on magnetic thin film technology, rely on magnetic domain control for proper operation. Recent advances in thin film magnetoelectric (ME) composites offer a promising route for sensing ultra-low magnetic signals. Yet, one obstacle of achieving very low limit of detection is caused by magnetic domain activity, which is a well-known noise source in various magnetic field sensing applications. Irreversible and hysteretic magnetization changes from domain nucleation and other hysteretic domain effects impact the sensor’s performance. Moreover, the characteristics of magnetic domains reflect stress induced spatial alterations in the magnetic anisotropy distribution. Overall, due to the formation of magnetic domains in the piezomagnetic phase, the magnetization reversal in magnetic layers is complex. The role and relevance of magnetic domains and domain walls for the ME response will be discussed in detail. Domain effects in different types of ME devices, including magnetically and electrically modulated thin film devices as well as surface acoustic wave (SAW) devices will be discussed. Domain activity in operating devices is studied from low frequencies, in the hundred kHz range, and at 150 MHz. Domain investigations at the operational frequencies of modulated and SAW sensors are performed by time-resolved magneto-optical Kerr effect microscopy.

A direct connection between specific magnetic domain activities and the exhibited noise characteristics is obtained. Even minimal domain activity is restricting magnetic sensor performance. Magnetic noise density and not sensitivity is the main figure-of-merit for optimizing sensor performance. Controlling magnetic domain behavior is a key to improved sensor performance.

Support through the DFG through the Collaborative Research Centre SFB 1261 is highly acknowledged.


2:30 PM *EL03.05.03
Understanding the Magneto-Mechanical Response of Terfenol-D Micro/Nano-Structures Mohanchandra K. Panduranga\(^1\), Zhuyun Xiao\(^1\), Joseph D. Schneider\(^1\), Taehwan Lee\(^1\), Christoph Klewe\(^2\), Rajesh V. Chopdekar\(^2\), Padraic Shafer\(^3\), Alpha T. N'Diaye\(^2\), Elke Arenholz\(^2\), Rob N. Candler\(^1,3\) and Gregory P. Carman\(^1,3\); \(^1\)University of California, Los Angeles, United States; \(^2\)Lawrence Berkeley National Laboratory, United States; \(^3\)California
Nanosystems Institute, United States

The field of nanoscale strain mediated multiferroics has grown considerably during the last decade due to the promise offered for efficiently controlling magnetism in the small scale. Strain mediated multiferroics consist of piezoelectrics mechanically coupled to magnetoelastic materials. An applied voltage to the piezoelectric induces a strain in the magnetoelastic material reorienting the magnetic spin moments. This approach is contrasted with electrical current approaches to control magnetic moment such as to reorient small magnetic bits with spin transfer torque STT. For informational purposes the energy required to reorient a 100 nm magnetic memory bit using STT is on the order of 100 fJ with the promise that strain mediated multiferroic is less than 0.1 fJ, i.e. > 4 orders of magnitude improvement. While strain mediated multiferroic approaches promise substantial efficiency improvements, many research efforts focus on magnetic materials that are on moderately or weakly magnetoelastic due to fabrication related issues. In this presentation a review of progress on fabricating and testing Terfenol-D (Tb0.3Dy0.7 Fe1.92) small scale structures, i.e. one of the highest room temperature magnetoelastic materials, is described to help advance the multiferroic field. This work includes discussions of fabrication, magnetic spin assessment, thermal effects, corrosion properties, and application demonstrated work.

Polycrystalline Terfenol-D thin films (<100 nm) are produced using a DC magnetron sputtering process on Sapphire, Si and PMN-PT substrates. The crystallized Terfenol-D films are micropatterned with photolithographic methods using Ar etching. The continuous and micropatterned (<20 microns) structures are characterized with XRD, SQUID, MOKE, MFM, PEEM, and XMCD to evaluate magnetoelastic properties. For micro-patterned structures as large as 20 microns in diameter, magnetic single domain structures are observed (MFM and PEEM) which is unusually large for this soft magnetic material. The large single domain behavior is attributed to the residual stresses produced during fabrication to further stabilize the magnetic spin states along preferred magnetic easy axis. Furthermore, an absence of oxidation is observed in these small-scale structures. While there is a capping layer on the Terfenol-D films, one would expect stress corrosion cracking to arise along the micropatterned side walls but this is absent. We attribute the corrosion absence to both the capping layer as well as the residual stresses preventing stress propagation and arresting oxidation. XMCD results on elemental spin states in the Terfenol-D reveal that the magnetic moments predominantly arise from the Tb and Dy spin/orbital contributions with Fe magnetic spin pointing in the opposite direction, i.e. ferrimagnetic material. However, the main contribution for the Dy element arises from orbital moment rather than spin which is slightly unusual. Furthermore, the Dy elements spin orbital moment changes prominently as a function of temperature. We believe that the spin orbit moment coupling arising from Dy significantly contributes to the changes observed in the magnetocrystalline anisotropy as a function of temperature. Finally, demonstrations of a multiferroic PMN-PT/Terfenol-D (20 micron size microstructure) to capture and release magnetic particles attached to cells are presented for showing efficient control of magnetism in the small scale.

3:00 PM BREAK

3:30 PM *EL03.05.04
Materials for STT-MRAM Applications Guohan Hu and Virat Mehta; IBM T.J. Watson Research Ctr, United States

Spin Transfer Torque Magnetic Random Access Memory (STT-MRAM) is a type of emerging memory which holds the promise of high speed, high endurance, non-volatility, and good scalability. Since the theoretical prediction of the STT switching mechanism in 1996, significant progress has been made in the field, largely through materials innovations. In this talk, I will review the key materials discoveries that enabled the advancement of STT-MRAM technology. This includes the theoretical prediction and experimental realization of large tunneling magnetoresistance (TMR) with MgO tunnel barrier and the discovery of CoFeB based materials with interfacial perpendicular magnetic anisotropy (IPMA). This talk will also discuss our recent results at IBM on methods to lower the switching current of Spin-Transfer-Torque MRAM and achieve low write-error-rate by using optimized magnetic materials.

4:00 PM EL03.05.05
Efficient Energy Harvesting from Low Ambient Stray Magnetic Field Using Magnetoelectric Coupled Magneto-Mechano-Electric Generator Min Gyu Kang1, Hyeon Lee2, RamMohan SriRamdas1 and Shashank Priya1; 1Pennsylvania State University, United States; 2Virginia Tech, United States
Electrically modulated magnetoelectric AlN/FeCoSiB film composites for DC magnetic field sensing.

Smart infrastructure functionalized with Internet of Things (IoT) technology is driving need of the wireless sensor network system and its sustainable power source. Magneto-mechano-electric (MME) energy conversion is the most promising technology to supply a sustainable power into the IoT sensor devices as it efficiently converts low frequency stray magnetic field (50/60 Hz), which exists everywhere in modern infrastructure, into the electricity. However, currently reported MME generators produce relatively low power under low magnetic field ($\leq$300 $\mu$T), which commonly exist in infrastructure. In this work, we demonstrate magnetoelectric (ME) coupled MME generator to produce high output power from low amplitude magnetic field. Comprehensive energy conversion mechanisms of ME coupled MME generator, including structural factors and contribution of ME coupling on power output, are investigated in order to achieve high energy conversion efficiency in low amplitude magnetic field. Building upon the mechanism study, an optimum MME generator, producing milliwatt power below 300 $\mu$T magnetic field, is realized utilizing outstanding magnetoelectric composite cantilever. Exploiting the harvested power near a home appliance, sustainable powering integrated sensors and wireless communication system is demonstrated. The fundamental study performed in this work provides a direction to achieve the efficient magnetic field energy harvesting and this will enable practical implantation of the IoT devices into the smart infrastructure.

4:15 PM EL03.05.06
Electrically Modulated Magnetoelectric Thin-Film Sensors for Sensing Small Magnetic Fields
Patrick Hayes1, Sebastian Toxværd1, Phillip Durdaut1, Matic Jovičević Klug1, Dmitri A. Burdin2, Viktor Schell1, Yuri K. Fetisov2, Reinhard Knöchel1, Jeffrey McCord1 and Eckhard Quandt1; 1Kiel University, Germany; 2MIREA - Russian Technological University (MIREA), Russian Federation

Magnetoelectric (ME) thin film composites consisting of a sputtered piezoelectric (PE) and a magnetostrictive (MS) layer may be employed for measurements of magnetic fields passively, i.e. an AC magnetic field generates an ME voltage by mechanical coupling of the MS deformation to the PE phase, thus exploiting the direct ME effect. In order to achieve high field sensitivities a magnetic bias field, necessary to operate at the maximum piezomagnetic coefficient of the MS phase is used, using mechanical resonances further enhances this direct ME effect size. Despite being able to detect very small field amplitudes passively, by exploiting mechanical resonances, implies a limitation to available signal bandwidth, because of rather high Q factors. The requirement for a magnetic bias field along with the inability to detect DC magnetic fields makes practical implementation troublesome.

In the presented work the PE phase of such thin film ME composites is actively excited, thus exploiting the converse ME effect [1], remedying shortcomings of the direct ME effect. The experimental work makes use of surface micromachined thin film cantilever composites of mesoscopic scale (25mm x 2.5mm x 0.35 mm) of which a high frequency mechanical resonance at about 500 kHz, showing a mechanical quality factor of about Q~1000 is analyzed. This mechanical oscillation, being rigidly coupled to the magnetostrictive material, leads to a voltage induced in a pickup coil surrounding the sensor composite, giving rise to magnetoelastic interactions. Major signal components of bio magnetism lie in the range from DC to 500 Hz and amplitudes are of vanishingly small amplitude $\sim 50$ pT, this regime is targeted by this research. This entirely passive readout, combined with low spatial and power requirements makes the presented ME sensor system suitable for integration into arrays as anticipated for biomagnetic imaging. The converse ME voltage response with respect to small external fields shows sensitivities up to 40 kV/T, offering linearity up to a field magnitude of several $\mu$T, no external magnetic driving field is required. The sensor sensitivity scales nearly linearly with drive amplitude supplied to the PE phase, unfortunately the measured noise floor in the frequency regime of interest shows an abrupt increase as soon as an excitation threshold of about 200 mV is reached. Massive magnetization activity in the MS phase is presumably the dominant source of noise. High speed vibrometry measurements give insight concerning the high frequency mechanical oscillation mode, magneto optical imaging reveals magnetoelastic modulations of the MS phase.

Furthermore, we demonstrate the performance of electrically modulated thin film ME composites, using magnetron sputtered AlN and amorphous FeCoSiB films. This approach enables composite magnetoelectrics to detect low DC ($\sim 250$ pT/sqrt(Hz)) as well as AC ($\sim 75$ pT/sqrt(Hz) @ 10 Hz) magnetic fields without the need of an external magnetic AC or DC bias field. Finally, lower system noise is achieved using specially tailored antiparallel exchange biased MS layers thus inhibiting domain wall activity and even further improve the detection limit. Funding via DFG, SFB1261 “Magnetoelectric Sensors: From Composite Materials to Biomagnetic Diagnostics” is gratefully acknowledged.

References
Magnetostriiction makes it possible to drive a magnet into resonance using purely a voltage signal. In a piezoelectric-ferromagnetic bi-layer, an alternating voltage applied to the piezoelectric transforms into a pseudo alternating magnetic field for the magnet. Combined with an internal static field that comes from the magnetic anisotropy, this alternating magnetic field can put the magnet into resonance. We shall describe our recent experimental work that demonstrates this effect in a LiNbO3/Ni heterostructure. It was observed that a highly efficient transduction (>99.9%) is possible in this process. A magnet put into resonance in this way also shows potential for sensing very small magnetic fields (~pT/sqrt(Hz)). In addition, they can be used for locally driving two level quantum systems without needing an optical excitation. We shall discuss our recent progress regarding these applications.

EL03.06.01
Some Interesting Properties Associated to an Unusual High Iron Valence in the FeSr2YCu2O7.85 Superconducting Cuprate
Miguel Angel Alario-Franco, Sara Lopez-Paz, Xabier Martinez de Irujo-Labalde, Jorge Sanchez-Marcos, Clemens Ritter and Emilio Moran; Universidad Complutense, Spain

Iron containing perovskites have been intensively studied as potential functional materials with applications ranging from Solid Oxide Fuel Cell (SOFC) cathodes[1] and magnetoelectric multiferroics[2] to half-metallic magneto resistive[3] materials. On the other hand, high temperature superconducting cuprates are another example of correlated materials that are placed in the frontier between localized and itinerant electronic behaviour[4], with superconductivity emerging from a Mott insulating type material upon doping.

The title material combines two functionalities: magnetism and superconductivity, associated to the presence of separated Fe-O2 and Cu-O2 layers orderly stacked along the c-axis.

The formal presence of FeV cations resulted from ozone oxidation, leads to a long-range magnetic ordering, coexisting with the superconducting interactions (TN= 110 K > Tc= 70 K). The somewhat unexpected A-type AFM structure, with a μ(Fe) approximately 2 μB magnetic saturation moment, associated to the hypervalent iron sublattice, suggests an unusual low spin state for the iron cations; on the other hand, the low dimensionality of the magnetic structure results in a soft switching towards ferromagnetism under small external magnetic fields.

It is also interesting to mention the relatively high superconducting Tc in a highly overdoped cuprate [5]. The role of the crystal structure and the high charge concentration in the stabilization of this unusual electronic configuration for the iron cations is discussed.

Perovskite rare earth nickelates (RNiO₃), where R is a rare earth cation are well-known for the sharp metal-to-insulator transition (MIT) observed when decreasing temperature, at \(T = T_{MI}\) (R different than La) (1-3). Many studies have focused on manipulating the MIT for instance through strain (4), growth direction (5) and superlattice heterostructure (6). In this work, we use experimental and theoretical methods to design and study superlattices of two distinct rare earth nickelate oxides SmNiO₃ (SNO) and NdNiO₃ (NNO) that in bulk form show a MIT at two very different temperatures (400K and 200K, respectively). We find that these new complex oxide superlattices display different behavior than that of either bulk material, showing either a single MIT at an intermediate temperature, or two transition temperatures that converge asymptotically towards the strained bulk values of each material. This system allows the origin of the coupling at such interfaces to be studied. We show that the length scale of the MIT transition in the superlattices is set not by the length scale of the propagation of structural motifs across the two materials, which ab-initio calculations and TEM analysis suggest is minimal, but rather by the balance between the energy cost of having metallic-insulating domain walls (the cost of bending the order parameter across the metallic-insulating interface) and the energy gain of the bulk phases.

References:

EL03.06.03 Length Scales and Heterostructuring in the Metal-Insulator Transition of RNiO₃ Alexandru Bogdan Georgescu¹, Claribel Dominguez², Oleg E. Peil³, Jennifer Fowlie², Ankit S Disa⁴, Jean-Marc Triscone², Antoine Georges⁴,⁵ and Andrew Millis¹,⁶;
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The metal-insulator transition (MIT) of transition metal oxides is often associated with a simultaneous lattice and electronic symmetry breaking; however the relative roles of the electronic and lattice degrees of freedom is still an unresolved question. Further, the length-scale of the metal-insulator transition and what sets it is not well understood. Through the study of heterostructures of rare-earth nickelates (RNiO₃), we get insight into these questions. First, using a combination of first-principles, many-body computational methods and experiment [1,2,3,4], we study the effect of heterostructuring NdNiO₃ with the band insulator NdAlO₃. We find two competing effects: the effective lattice cost to disproportionate the NiO₆ octahedra increases due to resistance from the interfacial Al-O bonds. Separately, electronic confinement favors an insulating state by lowering the electronic kinetic energy. These effects combined lead to a higher MIT temperature than the bulk, accompanied by a lower signature of bulk disproportionation on the X-Ray spectra. To understand the length scales involved in the MIT we study superlattices of two nickelate materials that have the same type of transition but two different transition temperatures (NdNiO₃~150K and SmNiO₃~400K). We find that for thin enough layers of each material, a single transition at an intermediate temperature exists, while at higher layer thickness two MITs appear at temperatures that asymptotically tend to the bulk MIT temperatures with increasing layer thickness. We find that this behavior is set not by the gradual propagation of structural motifs, but by the competition between the domain wall energy cost at the interface between the metallic and insulating materials and the bulk free energy cost of the materials not being in their favored state. Our work thus opens new paths in the systematic study of complex oxide materials.

EL03.06.04
Ferroelectric Polarization-Switching Dynamics and Fatigue Behavior in Si-Doped HfO₂
Myeongseop Song and Seung Chul Chae; Seoul National University, Korea (the Republic of)

HfO₂-based ferroelectrics exhibits two regimes of “wake-up” and “fatigue” in which remnant polarization increases and decreases during electric field cycling, respectively. These two phenomena are considered as the effect of defect generation and diffusion including redistribution of oxygen vacancies. The structural transition in the wake-up stage has been focused in ferroelectric HfO₂ thin film. However, in order to operate a reliable device, it is necessary to understand the ferroelectric characteristics and dielectric properties in wake-up and fatigue processes.

Grimley et al. proposed that the variation of bulk defect concentration which constrains domain wall motion by defect pinning is the origin of fatigue behavior. However, Lou et al. suggested that the structure decomposition caused by charge carrier injection was the main reason for fatigue endurance. The mechanism of fatigue behavior of HfO₂ thin films is still unclear. So, understanding of the ferroelectric characteristics with respect to the fatigue behavior is required for practical device operation.

We report on the ferroelectric switching dynamics of fatigued 4.2% Si-doped HfO₂ thin film. Prior to the fatigue behavior, Si-doped HfO₂ thin films exhibited the wake-up behavior where the remnant polarization value increased with the repeat of external bias cycling. After the wake-up behavior, Si-doped HfO₂ film exhibited the degradation of the remnant polarization value alongside the sweep of external bias, i.e., fatigue behavior. The investigation of ferroelectric switching dynamics revealed the retardation and recovery of the characteristic switching time for ferroelectric nucleation coincident with the wake-up behavior and fatigue behavior, respectively. We analyzed the interface trap density with the capacitance-voltage characteristics and attributed the fatigue behavior to the increase of oxygen vacancies with fatigue behavior.

EL03.06.05
Unconventional Stability of Sub-Loop Behavior in Ferroelectric HfO₂
Kyoungjun Lee and Seung Chul Chae; Seoul National University, Korea (the Republic of)

Ferroelectricity with partial polarization switching is considered as one of a feasible candidate for an analog device in the form of the ferroelectric tunnel junction and ferroelectric transistor. However, deterministic control of ferroelectric polarization states with conventional ferroelectric materials have been met with accessibility problems due to the complex nature of ferroelectric switching mechanism and/or defect mediated uncertainty. Ferroelectric HfO₂ thin film has been investigated intensively as an alternative to perovskite materials in ferroelectric random access memory due to the advantages for nonvolatile memory applications, such as good scalability, compatibility with conventional complementary metal-oxide-semiconductor (CMOS) process technology.

Here, we report unprecedented stability of the sub-loop switching behavior in ferroelectric HfO₂. We suggest that the stable accessibility with robust stability of multiple polarization states in ferroelectric HfO₂ can be attributed to the large activation field for ferroelectric switching with small critical volume for the ferroelectric nucleation of HfO₂. The switching dynamics indicated a large activation field for ferroelectric switching. The temperature dependence of hysteresis and piezoresponse force microscopy measurements indicated a small critical volume for ferroelectric nucleation. The theoretical calculation demonstrated the stable switching energy landscape for single dipole flip in ferroelectric HfO₂. Monte-Carlo simulation demonstrated that the small critical volume for nucleation induces stable accessibility of multiple polarization states in ferroelectric HfO₂.

EL03.06.06
Electromechanical Performance of Core-Shell Structured Relaxor Ceramics and the Impact of Interfacial Stress
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The unique properties displayed by canonical relaxor systems, such as the electric field induced transformation from a pseudo-cubic relaxor state to a polar ferroelectric state[1], the associated huge strain [2] and the phase transition mediated polarization reversal mechanism [3], make these materials highly interesting objects for fundamental studies as well as versatile components for industrial applications.

Especially, the achievement of high strains has drawn significant attention, the origin of which is based on the reversibility of the phase transformation between the ferroelectric and the relaxor state [4]. Many relaxor-
ferroelectric systems exhibiting high actuating performance are located in the morphotropic phase region. They often exhibit multiple crystallographic phases arranged as core and shell within single grains and their ability to adapt the phase ratio depending on the external stimuli [5], is another important factor contributing to their exceptional electromechanical performance.

Here, we report on the development of interfacial stresses between different crystallographic phases in a multiphase \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-\text{BaTiO}_3\) relaxor ceramic as induced by thermal treatment. Upon electric field application, this system exhibits an “intrinsic core-shell structure” of a polar minority phase embedded into a polar majority phase. While the majority phase stays stable with increasing temperature up to the transition into the relaxor state, a gradual de-texturization of the minority phase is observed over the whole temperature range. The surface domain structure was found to decay already at significantly lower temperatures than expected from bulk observations. Development of interfacial stresses due to thermal expansion mismatch between majority and minority phases as well as differences in local stress state between surface and bulk are discussed as driving factors of the phase transition dynamics.

Tailoring of interfacial stresses through adaption of phase fractions opens up a pathway to optimize the strain performance of actuator materials and can become a useful tool for the stabilization of usually metastable crystallographic phases as well as for property tuning e.g. in piezotronics.


**EL03.06.07**

**Large Pyroelectric Energy Conversion Density in Lead-Free Relaxor-Ferroelectric Heterostructure**

Amrit Sharma, Makhes K. Behera, Sangram K. Pradhan, Bo Xiao and Messaoud Bahoura; Norfolk State University, United States

The need for efficient energy utilization is driving research into ways to harvest waste-heat which is ubiquitous, abundant and free. Thermal harvesting is a promising method for capturing freely available heat and converting it to a more usable form, such as electrical energy. Thermal harvesting for low power electronic devices using ferroelectric materials is one of the emerging areas of research because these ferroelectric materials possess spontaneous polarization and exhibit excellent piezoelectric as well as pyroelectric coefficients. These materials are unique as they only sense time-dependent temperature change to generate electric power. We have grown lead-free \(\text{BaZr}_{0.2}\text{TiO}_3\) (BZT)/ \(\text{Ba}_0.7\text{Ca}_0.3\text{TiO}_3\) (BCT) multilayer heterostructures and studied their structural, dielectric, ferroelectric, and pyroelectric properties. The BZT/BCT multilayer epitaxial heterostructures were grown on \(\text{SrRuO}_3\) (SRO) buffered \(\text{SrTiO}_3\) (STO) single crystal substrate by optimized pulsed laser deposition technique. The large angle x-ray scans showed only diffraction peaks from the substrate and pseudocubic reflections \((100)\) from the multilayer heterostructure, confirming that these films are phase pure, highly crystalline, and epitaxial in nature. The atomic force microscopy (AFM) studies indicate that the surface roughness is low and that film growth is of high quality. The ferroelectric phase transitions have been probed above room temperature with a relaxor behavior. The polarization versus electric field \((P-E)\) measurement shows that the multilayer heterostructure exhibits slim and well-saturated hysteresis loop with high saturation and low remnant polarization of 100 and 20 \(\mu\text{C/cm}^2\), respectively at 1.7 MV/cm. Solid-state, thin-film devices, that convert low-grade heat into electrical energy, are demonstrated from temperature dependent \(P-E\) loops using pyroelectric Ericsson cycles with energy conversion density of 1.61 J/cm\(^3\). Our findings suggest that the BZT/BCT multilayer ferroelectric thin film may be competitive with other thermoelectric materials for low-grade thermal harvesting.

**EL03.06.08**

**Ferroelectricity in BiNbO\(_5\)Cl Single Crystal Nanosheet**

Zhizhong Chen and Jian Shi; Rensselaer Polytechnic Institute, United States

While ferroelectric-field-controlled Rashba-Dresselhaus effect has long been proposed as a method to manipulate...
the valley and spin degrees of freedom in ferroelectrics with strong spin-orbit coupling, the experimental realization of such device concepts remains limited. Although ferroelectric two-dimensional (2D) materials with strong spin-orbit coupling have been widely investigated, most chalcogenide layered 2D or quasi 2D materials considered suffer from low band gap, low Curie temperature or high electrical leakage, rendering the electrical control difficult at room temperature, while the insulating nature of most ferroelectric (quasi-) 2D oxides with heavy elements limits their optical activity. In this work, we report the first experimental observation of ferroelectricity in a quasi-2D 10–100 nm thick nanosheet Sillen-Aurivillius semiconducting split-ion oxyhalide perovskite at room temperature. Optoelectronic, transport and temperature-dependent time-resolved photoluminescence studies show that Bi$_4$NbO$_8$Cl single crystal exhibits a direct band gap of 2.4 eV, decent optical quantum efficiency and carrier dynamics, making it promising candidate for photon-valley coupling. Electrical transport shows up to 100× I-V rectification in Bi$_4$NbO$_8$Cl single crystal nanosheet-based planar devices with symmetric graphite as electrodes. By electrical poling, the diode polarity becomes switchable, rendering repeatable rectified current. Such diode effect in Bi$_4$NbO$_8$Cl is attributed to the asymmetric Schottky barriers at Bi$_4$NbO$_8$Cl–graphite interfaces that could be adjusted by switchable ferroelectric dipoles. In the oxyhalide Bi$_4$NbO$_8$Cl, the combination of appropriate band gap from ion splitting, considerable visible light optical quantum efficiency, strong polarization and the possible strong spin-orbit coupling from Bi provides a novel design platform for realizing emergent spin-orbitronics.

EL03.06.09
Local Ferroelectric Properties of Free-Standing Single-Crystal Complex Oxides
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The last few decades have seen significant scientific discoveries in single crystal complex oxide materials including colossal magnetic resistance, superconductivity, voltage control of magnetism and many different ferroic orders, many of which could lead to completely new applications. However, integration of such oxides using direct synthesis on microelectronics-platforms such as Si, amorphous SiO$_2$, GaN, and unconventional flexible substrates has faced significant challenge due to various growth-related issues and the interface chemistry at high temperature. Therefore, the functionality and performance that are otherwise available for epitaxial, single-crystal, perovskite materials have remained unachievable in microelectronic devices for a long time. The recent invention of complex oxide layer transfer techniques (LTT) has opened a promising route to the monolithic integration of these materials with arbitrary substrates$^{[1][2][3]}$– thus offering a possible replacement to the rarely-successful direct growth techniques.$^{[4]}$

In LTT, complex oxides epitaxially grown on the lattice-matched substrate are made free-standing and then interfaced with arbitrary material on-demand. Although proof-of-concept devices such as field effect transistor and memory devices have already been demonstrated using such transferred complex oxide ferroelectric (FE) materials.$^{[1][2][3]}$ little is known about their ferroic properties, particularly at the mesoscopic length scale. In this work, we have studied free-standing, single-crystal PbZr$_{0.2}$Ti$_{0.8}$O$_3$ using piezoforce (PFM) and electrostatic force microscopy (EFM) and synchrotron X-ray nanodiffraction techniques. We find that the epitaxial strain imposed on the ferroelectric layers by the substrate during growth by pulsed laser deposition technique is alleviated when the layers are made free-standing. The reduction of elastic strain slightly widens the domain walls, reduces the spontaneous polarization and increases the piezoelectric response. We have studied ferroelectric properties of both the top layers and interfacial layers (which were in contact with the substrate) and found a negligible difference between them. This hints that the intrinsic dead-layer issues may not be the limiting factors for utilizing transferred epitaxial layers in electrostatically controlled devices.

Novel Epitaxial Strain Effects on the Hybrid Improper Ferroelectrics from First-Principles Xuezeng Lu and James Rondinelli; Northwestern University, United States

Epitaxial strain is a powerful tool to generate ferroelectricity owing to polarization-strain coupling. Local lattice degrees-of-freedom such as rotations of metal-oxygen octahedral also couple to strain, and can be used to tune a material’s oxygen rotational-related properties such as metal-insulator transitions and magnetic reconstruction by strain. Here, we first use electronic structure calculations to investigate the strain effects on (001) thin films of the hybrid-improper ferroelectric (HIF) A3B2O7 compounds. Surprisingly, other than the bulk polar Cm21 phase, we find a new nonpolar phase becomes the ground state under both experimentally accessible biaxial compressive and tensile strains, which is beyond the people’s believe about the rule of the polarization-strain coupling. Furthermore, the generality of the polar-to-nonpolar (N-NP) transition in HIFs (not only in A3B2O7 compounds) leads us to find a novel route to tune the physical properties that are classified as mechanical, optical and magnetic responses, which we also propose could be electric-field tunable, near the P-NP phase transition boundary. Our results may offer a route to search for new functionalities in hybrid-improper ferroelectrics.

EL03.06.11
Pure Piezoelectricity Generation by a Flexible Nanogenerator Based on Lead Zirconate Titanate Nanofibers Horim Lee, Hyeon Kim and Yongsok Seo; Seoul National University, Korea (the Republic of)

Lead Zirconate Titanate (PbZr0.52Ti0.48O3, PZT) alloy has been extensively studied to be used for piezoelectric nanogenerators to harvest energy from mechanical motions. In this study, PZT nanofiber-based nanogenerators were fabricated to test its true piezoelectric performance without triboelectric effect. Aligned PZT nanofibers were fabricated by sol-gel electrospinning process. The thickness, area, and orientation of the PZT textile made by electrospinning the PZT solution onto multi-pair metal wires or metal mesh were controlled to form a composite textile. After the calcination, the PZT textile mixed with polydimethylsiloxane (PDMS) was placed between two flexible ITO-PEN substrates. The performance parameters of the nanogenerators were investigated under the bending motion, which excludes the triboelectric effect. The assembled nanogenerator of an area of 8 cm² and a thickness of 80 mm could generate an electrical output voltage of 1.1 V and a current of 1.4 mA under the bending strain. The piezoelectric voltage depended on the thickness of the PZT textile, while the piezoelectric current depended on both the thickness and the area of the PZT textile. The electrical performance of the device was significantly affected by the orientation of the PZT fiber and the bending direction. The output voltage and the output current were strain-dependent, while the total integrated charge was independent of the strain rate. The properties of the flexible nanogenerator could be quantified to verify the pure piezoelectric performance of the device.

EL03.06.12
Polymorphic Phase Transition in BaTiO3 by Ni Doping Nguyen Xuan Duong1, Jong-Seong Bae2, Jongchul Jeon3, So Yeon Lim4, Soo Han Oh5, Aman Ullah6, Muhammad Sheeraz7, Jin San Choi8, Jae-Hyeon Ko9, Sang Mo Yang10, Kyou-Hyun Kim11, Ill Won Kim12, Chang Won Ahn13 and Tae Heon Kim14; 1University of Ulsan, Korea (the Republic of); 2Korea Basic Science Institute (KBSI), Korea (the Republic of); 3Korea Institute of Industrial Technology, Korea (the Republic of); 4Sookmyung Women’s University, Korea (the Republic of); 5Hallym University, Korea (the Republic of)

Hexagonal barium titanate (h-BaTiO3, P63/mmc), which is structurally non-perovskite and energetically stable above 1460 °C, can be an excellent platform for designing an exotic phase which does not exist in nature and for achieving new room-temperature multiferroics with high performance. Owing to the high synthetic temperature, a phase transition to the h-BaTiO3 and the related physical properties have not been studied in detail. In this work, we experimentally demonstrate a structural phase transition from perovskite BaTiO3 with tetragonal symmetry to non-perovskite hexagonal polymorph in Ni-doped BaTiO3 ceramics. Using various experimental techniques, we monitored the evolution of the structural, ferroelectric/dielectric, and electronic properties in our Ni-doped BaTiO3. We found that the reduction of Ti oxidation state by Ni doping plays a key role in the observed structural transition to h-BaTiO3. More details of our experimental results will be presented in conjunction with a discussion about the underlying mechanism of this polymorphic phase transition in BaTiO3.

EL03.06.13
Three-Dimensional Atomic Scale Electron Density Reconstruction of Octahedral Tilt Epitaxy in Functional
Perovskites Yanfu Lu, Yakun Yuan, Venkatraman Gopalan and Susan B. Sinnott; The Pennsylvania State University, United States

Octahedral tilts are the most ubiquitous distortions in perovskite-related structures that can dramatically influence ferroelectric, magnetic, and electronic properties; yet the paradigm of tilt epitaxy in thin films is barely explored. Non-destructively characterizing such epitaxy in three-dimensions for low symmetry complex tilt systems composed of light anions is a formidable challenge. Here we demonstrate that the interfacial tilt epitaxy can transform ultrathin calcium titanate, a non-polar earth-abundant mineral, into high-temperature polar oxides that last above 900 K. The comprehensive picture of octahedral tilts and polar distortions is revealed by reconstructing the three-dimensional electron density maps across film-substrate interfaces with atomic resolution using coherent Bragg rod analysis. The results are in excellent agreement with density functional theory. The study could serve as a broader template for non-destructive, three-dimensional atomic resolution probing of complex low symmetry functional interfaces.


EL03.06.14
Advanced Techniques in Ultralow Voltage Piezoelectric Characterization of Ferroelectric Thin Films with Piezoresponse Force Microscopy Aviram Bhalla-Levine1, Ryan Wu1, Sujit Das1, Roger Proksch2 and Ramamoorthy Ramesh1; 1University of California, Berkeley, United States; 2Asylum Research, United States

There is currently significant interest in ultralow power microelectronics for memory and logic functions. Recent reports have identified multiferroic systems as possible candidates for such applications, with the ultimate goal of reducing the switching voltage to below one hundred millivolts (translating to approximately one attojoule per unit operation). Thus, measuring the ferroelectric and piezoelectric responses of ultrathin ferroelectric layers at such low voltage scales is essential. Piezoelectric measurements are, in principle, easier to execute and analyze since the primary response arises solely from the ferroelectric state (unlike polarization based measurements that are susceptible to leakage and nonlinear dielectric effects). To understand switching at voltages on the order of one hundred millivolts, we are carrying out a careful study of the piezoelectric switching of five, ten, fifteen, and twenty nanometer thick lead zirconate titanate films as a model system. We specifically focused on characterizing the piezoresponse of such nanoscale thin films using very low alternating current voltages (down to ten millivolt excitations). Our research indicates that statistically credible piezoelectric switching information can be obtained at these voltages. We will report the results of these scaling studies using piezoresponse force microscopy (PFM) as well as pulsed polarization measurements.

EL03.06.15
New Lead-Free Materials on the Base of Sodium-Potassium Niobate and Sodium-Bismuth Titanate Perovskites Ekaterina Politova; Karpov Institute of Physical Chemistry, Russian Federation

New Lead-Free Materials on the Base of Sodium-Potassium Niobate and Sodium-Bismuth Titanate Perovskites E.D. Politova1, G.M. Kaleva1, A.V. Mosunov1, N.V. Sadovskaya1, S. Yu. Stefanovich1,2 D.A. Kiselev3, A.M. Kislyuk3, T.S. Ilina3,
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Lead-free materials are being intensively studied in order to replace widely used Pb-based ones. We study influence of cation substitutions and preparation conditions on structure parameters, microstructure, dielectric, relaxor ferroelectric, and piezoelectric properties of solid solutions in the systems based on (Na0.5Bi0.5)TiO3 (NBT) and (K0.5Na0.5)NbO3 (KNN) perovskites.

Ceramic samples in systems (Na0.5Bi0.5)TiO3 - BaTiO3 (NBT-BT) and (K0.5Na0.5)NbO3 – BaTiO3 (KNN-BT) with compositions close to Morphotropic Phase Boundaries (MPB) were prepared by the two-step solid-state reaction method at temperatures of 900 – 1500 K. To modify properties of the samples, in A- and B-sites of perovskite lattice Li+, La3+, Mn3+, Ni3+, Fe3+, Nb5+, Sb5+ and W6+ cations were added. To improve density of ceramics
overstoichiometric KCl and LiF additives were used. The samples were characterized using the X-ray Diffraction, Scanning Electron Microscopy, Second Harmonic Generation (SHG), Dielectric Spectroscopy (DS), and Atomic Force Microscopy in Piezoresponsive Force mode (PFM) methods. The unit cell volume changes were observed in modified KNN- and NBT-based ceramics depending on ionic radii of substituting cations. Ferroelectric phase transitions at ~ 400-500 and 600 – 700 K were confirmed using the DS and SHG methods. Phase transitions near ~ 400 K in NBT-based compositions revealed typical relaxor behavior due to the presence of polar nanoregions in a nonpolar matrix. At high temperatures > 700 K effects of dielectric relaxation were observed in ceramics studied caused by formation of oxygen vacancies in compositions with aliovalent substitutions. At the room temperature, non monotonous changes of the dielectric parameters and increase in the spontaneous polarization value was proved for modified ceramics. Using the PFM method ferroelectric polarization switching at nanoscale was observed, and in some KNN-based ceramics high values of effective $d_{33}$ piezoelectric coefficient up to 300 pm/V were observed. The results obtained confirmed prospects of new lead-free materials development on the base of modified KNN- and NBT-based compositions.

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EL03.06.16
Giant Polarization in Super-Tetragonal Ferroelectric Thin Films through a New Concept of Interphase Strain
Linxing Zhang; University of Science and Technology Beijing, China

Generally, the chemical or physical properties strongly depend on the change of lattice. The control of lattice strain, therefore, much affects the chemical or physical properties of functional materials, which has been widely used in superconductivity, giant magnetoresistance, multiferroics, catalysis and etc. Ferroelectrics are an important functional material, which has been widely used in the field of ferroelectric memories, tunable microwave devices, large-capacity capacitors, piezoelectric sensor devices, etc. The intriguing properties of ferroelectric materials utilize the basic functional primitive parameter of polarization. This team has realized this method, interphase strain, by creating a single-lattice-parameter epitaxial composite film on SrTiO$_3$ substrate from two tetragonal materials but with different lattice parameters, PbTiO$_3$ ferroelectrics and PbO non-ferroelectrics. The results show that the method improves the lattice distortion of PbTiO$_3$ to $c/a = 1.238$, compared to 1.065 in bulk. The remanent polarization is as high as 236.3 μC/cm$^2$, which is near twice the highest value of the known ferroelectrics. This composite ferroelectric thin film is very stable, and the super-tetragonal ferroelectric phase is stable up to 725 °C, compared to the bulk transition temperature of 490 °C.

The proposed “interphase strain” is a new concept for strain engineering to regulate lattice strain of ferroelectrics, and successfully achieved giant polarization in the super tetragonal PbTiO$_3$/PbO based ferroelectric thin films. The idea of "interphase strain" is as follows: if two kinds of materials with similar crystal structures, but different lattice parameters, are growing into a single-lattice-parameter epitaxial film, the material of the small lattice is inevitably subjected to the tensile stress from the large lattice material, thereby introducing a large lattice strain. The regulation of lattice strain can cause significant changes in the physical and chemical properties of the material. This new approach of interphase strain for strain engineering can be utilized to enhance the physical and chemical properties of other functional materials, such as superconductivity, giant magnetoresistance, multiferroic, and catalysis.


EL03.06.17
In-Plane Ferroelectricity in Epitaxial Dion-Jacobson CsBiNb$_3$O$_7$ Jie Jiang$^{1,2}$, Lifu Zhang$^1$ and Jian Shi$^1$; 1Rensselaer Polytechnic Institute, United States; 2Kunming University of Science and Technology, China

Conventional ferroelectric perovskite materials carry a debatable critical thickness below which the depolarization field is large enough to destabilize ferroelectricity. 2D ferroelectric materials are discovered to hold robust in-plane polarization down to a single unit cell, contending the continuous miniaturization of ferroelectric devices. However, due to the nonuniformity of the electrostatic field from quasi-2D metal electrodes, the in-plane intrinsic dipoles would experience a mismatched screening (screening frustration) making the in-plane polarization switching
dynamics complex. Until now there is rare direct experimental proof of the in-plane polarization switching in a 2D crystal. In this talk, for the first time, we will present the in-plane polarization switching in a Dion-Jacobson quasi-2D layered oxide. The coupling between the in-plane ferroelectricity and other physical properties, e.g. the switchable photo diode effect and the photon-induced domain switching, in layered materials may enable versatile applications down to the atomic scale.

**EL03.06.18**

**Nontrivial Topological Polarization Field Self-Ordered in Nanoporous Ferroelectrics—A Phase-Field Modeling**

Takahiro Shimada¹, Le Van Lich¹,², Takayuki Kitamura¹ and Hiroyuki Hirakata¹; ¹Kyoto University, Japan; ²Hanoi University of Science and Technology, Viet Nam

Topological objects or field textures, such as skyrmions, merons, and vortices, are intriguing features found in ordered systems with spontaneously broken symmetry. A plenty of topological field textures have been discovered, especially in magnetic and ordered soft matter systems, due to the existence of chiral interactions, and this has provided a fruitful platform for unearthing additional groundbreaking functionalities. However, despite one of the most important classes of ordered systems, ferroelectrics scarcely form topological polarization structures due to lack of such chiral interactions. Here, we show that a rich assortment of nontrivial topological polarization textures, including hedgehogs, antivortices, multidirectional vortices, and vortex arrays, can be spontaneously formed in three-dimensional nanoporous ferroelectric structures using the phase-field modelling based on the Ginzburg–Landau theory. We demonstrate that confining ferroelectrics to trivial geometries that are incompatible with the orientation symmetry may impose extrinsic frustration to the polarization field through the enhancement of depolarization fields at free porous surfaces. This frustration yields symmetry breaking, resulting in the formation of nontrivial topological polarization field textures. We also characterize the topological feature of polarization structures according to the topological theory of defects and homotopy theory. The results indicate that the nanoporous structures possess topological objects composed of two or more elementary topological polarization structures. This study therefore offers an intriguing playground for exploring novel physical phenomena in ferroelectric systems as well as a novel nanoelectronics characterization platform for future topology-based nanotechnologies.

**EL03.06.19**

**Frustrated Dipole Order Induces Noncollinear Proper Ferrielectricity in Two-Dimensions**

Ling-Fang Lin¹,²,³, Yang Zhang¹,²,³ and Shuai Dong¹; ¹Southeast University, China; ²The University of Tennessee, Knoxville, United States; ³Oak Ridge National Laboratory, United States

Within Landau theory, magnetism and polarity are homotopic, displaying a one-to-one correspondence between most physical characteristics. However, despite widely reported noncollinear magnetism, spontaneous noncollinear electric dipole order as ground state is rare. Here a dioxydihalides $MO_2X_2$ family (layered structure, where $M=Mo$ and $W$; $X=Cl$ and Br) is predicted to display noncollinear ferrielectricity, induced by competing ferroelectric and antiferroelectric soft modes. This intrinsic noncollinearity of dipoles generates unique physical properties, such as $Z_2 \times Z_2$ topological domains, atomic-scale dipole vortices, and negative piezoelectricity.

**EL03.06.20**

**Defect Complex and Hopping Mechanism in (Li, Al) Co-Doped ZnO Ceramics**

Dong Huang and Francis Chi Chung Ling; The University of Hong Kong, Hong Kong

Systematic studies on sintering temperature and Li:Al stoichiometry of Li and Al co-doped ZnO ceramic shows that the Zn$_{0.99}$(Li$_{0.1}$, Al$_{0.2}$)$_{0.03}$O sample exhibits a colossal dielectric constant (CDC) phenomenon with low dielectric loss ($\epsilon'' = 0.159$ at the frequency of 1 kHz) at the room-temperature. The CDC and low dielectric loss have good frequency stability. SEM and CL measurements show the grain boundary of the as-grown LAZ sample is accumulated with high density of V$_{O}$, and the spatial non-uniformity of V$_{O}$ concentration is removed after the O$_2$ annealing. With the impedance analysis, it is shown that the $R_{GB}$ (resistance of grain boundaries) is only $\sim$16 times larger than $R_g$ (resistance of grain), and the $CPE_{GB}$ is even smaller than $CPE_g$, implying that internal barrier layer capacitance (IBLC) effect is not likely the dominant source for the observed CDC of the LAZ samples. Dielectric spectrum analysis shows that the CDC is associated with two relaxation processes P1 and P2. Annealing the sample at 900 °C in oxygen leads to the drop of to 2250 but maintaining a low dielectric loss of $\sim 0.10$, while P1 vanishes and P2 persists. Comparing the synchrotron based hyperfine Al 2p X-ray photoelectron (XPS) spectra of the purely
Al-doped ZnO sample and the Li+Al co-doped ZnO sample shows that the electronic environment around the Al_{Zn} in these two samples are different, indicating that defect complex consisting of Al_{Zn} and Li_{Zn} is probably present in the Li+Al co-doped sample. Furthermore, after the Raman comparisons among the co-doped, singly Li- or Al-doped ZnO, it is shown the defect complex has altered the Zn-O bond’s local environment, which lead to the shift of A_1 stretching mode. This defect complex is possibly the electron pinning defect dipole responsible for the CDC associated with the P2 relaxation process. With the correlated barrier hopping model fitting, it is found that two energy level E_c~0.34 eV and E_c~0.87 eV are existed in as grown and O_2 annealed LAZ sample, causing the P1 and P2 relaxation, respectively. With two potential well model, we theoretically calculate the dielectric constant and loss against frequency for P1 and P2 relaxation, which are around ~7173 and ~2817.

EL03.06.22
Structure-Property Correlation in the Multiferroic (Bi_{1-x}Ba_{x})(Fe_{1-x}Ti_{x})O_3 System Arun Kumar and Dhananjai Pandey; Indian Institute of Technology (BHU), India

Magnetoelectric multiferroics offer the possibility of controlling the electric (magnetic) polarization by applying a magnetic (electric) field and have attracted significant interest in view of the interesting physics of coupling between magnetic and ferroelectric order parameters and potential technological applications in several multifunctional devices. BiFeO_3 is unique amongst various magnetoelectric multiferroics, as its ferroelectric and magnetic transition temperatures (T_C~1103 K, T_N~643 K) are well above the room temperature. In recent years, the (Bi_{1-x}Ba_{x})(Fe_{1-x}Ti_{x})O_3 (BF-xBT) system have received considerable attention due to large ferroelectric polarization, large remnant magnetization, linear magnetoelectric coupling and highest depolarization temperature for piezoelectric applications and considered to be alternative to toxic lead (Pb) containing piezoelectric ceramics like Pb(Zr,Ti)O_3 and (1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3. In the present investigation, we have carried out a comprehensive study on 0.3 wt% Mn-doped BF-xBT samples in the composition range 0≤ x ≤1.0. Our synchrotron x-ray diffraction results reveal two structural phase boundaries, one from rhombohedral (R3c space group) to cubic (Pm-3m space group) at x<~0.33 and other from cubic (Pm-3m space group) to tetragonal (P4mm space group) at x<~0.80. The composition dependence of the polarization and dielectric constant at room temperature exhibits a peak around x=0.33. This confirms the existence of morphotropic phase boundary at this composition due to a rhombohedral (R3c) to cubic (Pm-3m) phase transition across the morphotropic phase boundary. We also present a magnetic phase diagram of BF-xBT.

EL03.06.23
Phase-Field Simulation and High-Throughput Calculation of Resistive Switching Behavior in Random Access Memory Kena Zhang1, Jianjun Wang2 and Ye Cao1; 1The University of Texas at Arlington, United States; 2The Pennsylvania State University, United States

Metal-oxide based Resistive Random-Access-Memory (RRAM) which exhibits multiple resistive/memory states by the formation/dissolution of a conductive filament (CF), has potential to be the next generation memory technology. The performance of RRAM relies on the fast switching speed, large current on/off ratio, and minimized device variability, which are critically dependent on the ion (such as oxygen vacancies) migration driven by the concentration gradient, electrical bias, heat generation and dissipation. In this work we report that the mechanical stress induced by the growth and retraction of the conductive filament is equally important to the resistive switching dynamics. The stress inhibits the ion diffusion and segregation along the electric field direction and reduces the current on/off ratio and the switching time. To further understand the role of this mechanical stress in the resistive switching process, we developed a comprehensive phase-field model taking into account the electrical, thermal, and mechanical energy, and studied their relative effects on the RRAM resistive switching dynamics. We choose hafnium oxide as an example, and compare the simulation results with existing experimental results to validate the model. Based on this, high-throughput phase-field simulations for different oxides of different properties are performed to help selecting the potential candidates as the oxide switching layer materials with optimized switching speed, current on/off ratio and device uniformity. Our work thus provides fundamental insights into the resistive switching mechanism, and establishes a theoretical framework of materials selection and design for metal-oxide based RRAMs.

EL03.06.24
Symmetry Mismatch at Heterointerfaces and Photovoltaic Effect in BiFeO3/LaFeO3 Ferroic Superlattices Mimoun El Marsssi, Jamal Belhadi, Said Yousfi, Benjamin Carcan and Houssny Bouyanfif; University of Picardy,
France

Bismuth ferrite (BiFeO₃ or BFO) is the most studied multiferroic due to its robust ferroelectric state coexisting at room temperature with an antiferromagnetic order. Such coexistence and the possible cross coupling between both ferroic orders pave the way to so-called MagnetoElectric RAM combining advantages of the ferroelectric and the antiferromagnetic state. Similarly to the relaxor-ferroelectric systems a morphotropic phase boundary has been observed in La doped BFO (Bi,La)FeO₃ solid solution with peculiar nanoscale mixture. Emergence of such MPB is believed to arise from the competition between antiferrodistortive and ferroelectric instabilities. Our approach to investigate the structural interaction between BFO and LFO is based on superlattices that are ideal platforms for exploring antagonistic interactions at the origin of many exotic systems. For instance Cuprates combined with Manganites in superlattices were investigated to better understand the competition between magnetic and superconducting orders. Similarly to this strategy we grew series of SLs made of BiFeO₃ and LaFeO₃. Structural characterizations and Raman spectroscopy indicate an anti-polar structure in the BFO layers that is strongly dependent on the BFO thickness and temperature [1,2]. This antiferroelectric like structure very similar to the PbZrO₃ system cannot be explained by the nature of the induced strain but by the symmetry mismatch at the interfaces of the SLs. Compatibility of the octahedral tilt system seems to be the main driving force for this induced anti-polar state. Thickness-temperature phase diagram is constructed. We have highlighted a switchable PV effect in these artificial structures at room temperature. By changing the thickness of the BFO layer we have evidenced a change of PV characteristics from a positive Voc and a negative Jsc to an inverse effect. These results, compared to our results obtained on BFO single films [3], indicate different origin of the mechanisms of photo-carries separation in PV devices. Our results are promising and indicate the possibility to employing the vertical geometry of measurements for tuning the PV effect in multiferroic SLs.


EL03.06.25
Effect of Quadravalent Heavy Transition Metal Cations on Microwave Properties of Co₂Z Ferrites Piotr Kulik, Gavin Winter, Katherine Murphy, Jason Adams, Ogheneyunume Fitchorova and Vincent Harris; Northeastern University, United States

The demand for miniaturized and high performing broadband communication systems in the GHz frequency range is steadily growing due to severely crowded and rapidly changing modern commercial and military spectral environments. Hexaferrite composites have proven to be one of the few key enablers in providing miniaturized form factors due to their high permeability and permittivity as well as their capability to reach high resonance frequencies up to 100 GHz. In this work, a series of Z-type barium hexaferrites were prepared in which dopants of heavy transition metals, i.e., Mo⁴⁺ and Hf⁴⁺, were employed to modify structure and microwave properties. Through systematic measurements it was revealed that each dopant affected the hexaferrites’ properties differently by both shifting the resonant frequency and altering magnetic properties without strongly varying the hexaferrite crystallographic structure. Additionally, ε’ = μ’ was realized without any additives such as Bi₂O₃, which had been previously been used for tuning permeability and permittivity. Polycrystalline Co₂Z ferrites, having a nominal composition of Ba₃Co₂₋ₓHfₓFe₂₄₋₂ₓO₄₁ and Ba₃Co₂₋ₓMoₓFe₂₄₋₂ₓO₄₁, where x=0 to 0.05, were prepared by a solid-state process. BaCo₃, HfO₂, MoO₂, Co₃O₄, and Fe₂O₃ of high purity were mixed and calcined in oxygen for 5-8 hours at 800-1050 °C, which then were ball milled for 18-24 hours to reduce the grain size to under 1 µm. After ball-milling, ISOBAM was added as a binder and mixed for several minutes. Samples were then pressed to form toroids with an inner diameter of 3 mm and an outer diameter of 7 mm. The toroids were pressed by a cold isostatic press in order to maximize compaction before sintering in oxygen for 4-6 hours at 1000-1250 °C. Finally, samples were measured using the Agilent E864A PNA and a 7 mm precision airline, showing permeability and frequency changes. Results show that a nine-time reduction in size can be achieved while maintaining an impedance of 360 Ω close to that of free space over a broadband.

EL03.06.26
Insights into Magneto-Electric Coupling Using X-Ray Photoemission Electron Spectro-Microscopy Rajesh V. Chopdekar; Lawrence Berkeley National Laboratory, United States

Ferromagnetic-ferroelectric (FM-FE) heterostructures have been studied as a route to obtain strong room-
temperature magneto-electric interactions not commonly found in single-phase materials. In such composites it is critical to understand the role of charge- and strain- mediated interactions at interfaces of the constituent phases, and spatially resolved probes such as x-ray photoemission electron microscopy (XPEEM) at the Advanced Light Source PEEM-3 beamline can observe such interface interactions at the scale of a single FE or FM domain. Polarization-dependent soft x-ray spectro-microscopy as a function of temperature and applied electric and magnetic fields can offer unique insights into coupling at heterointerfaces with sub-100 nm resolution by exploiting the x-ray linear dichroism (XLD) and magnetic circular dichroism (XMCD) effects. I will present a detailed analysis of the magneto-electric coupling in model multiferroic systems (e.g. FM layers grown on FE single crystals, or single phase multiferroic epitaxial thin films) using XLD- and XMCD-PEEM imaging. While the 3D vector orientation of ferromagnetic domains can be mapped with XMCD imaging at different azimuthal orientations, anisotropic strain interactions between FE and FM phases can be mapped by XLD imaging in an analogous fashion. The anisotropic nature of the strain imprinted by the FE induces a local variation of the magnetic anisotropy of the FM phase due to large magnetoelastic anisotropy, and by varying applied electric fields or changes in temperature we can observe both the FM domain structure and imprinted strain state evolve due to such perturbations. Furthermore, we can compare spatially averaged electric-field dependent magnetometry to spatially resolved XMCD images in applied magnetic fields, and directly correlate a giant anisotropy rotation and change of anisotropy symmetry to the local tuning of magnetic anisotropy at the scale of single FE and FM domains. Similarly, PEEM-based mapping of multiple ferroic orders can offer insight into optical switching mechanisms of single-phase multiferroic materials. Thus, XLD- and XMCD-PEEM imaging offer a facile method to visualize magneto-electric coupling at the sub-micron scale by probing FE, FM, or antiferromagnetic domain evolution as a function of stimuli such as in situ applied electric or magnetic fields.


MoS₂ Negative Capacitance Field-Effect Transistor Based on PLD Grown Hf₀.₅Zr₀.₅O₂

Hae Won Cho, Seongin Hong, Junwoo Park, Sunkook Kim and Jeonghyeon Oh; Sungkyunkwan University, Korea (the Republic of)

Recently, the power consumption density has increased compared to the transistor which has increased exponentially per unit chip, making it difficult to store and process a large amount of data. Therefore, the development of low-power semiconductor technology is inevitable. In order to solve this issue on power consumption, research on a negative capacitance field-effect transistor (NCFET) is being actively conducted. In case of metal oxide semiconductor field-effect transistor (MOSFET), which is a conventional CMOS device, the subthreshold slope (S.S) value cannot fall below 60 mV/decade. NCFET, the next generation low-power device to replace MOSFET that encounters this limitation, can dramatically reduce power consumption density. Ferroelectric is negative capacitor in the gate structure of the NCFET, allowing channel surface potential to be amplified more than the gate voltage, enabling drive at less than 60 mV/dec S.S at room temperature. In this study, the ferroelectric Hf₀.₅Zr₀.₅O₂ (HZO) material in the gate structure was grown through pulsed laser deposition (PLD) process, and MoS₂ was used as a channel material to develop low power, high mobility 2D-NCFET. Conventionally, the ferroelectric HZO grown by atomic layer deposition (ALD), has been widely studied in electronic device development. In addition, research has been carried out focusing on HZO epitaxial growth at various substrates by PLD process. For the first time, we have introduced a new process to operate MoS₂; NCFET based on HZO, grown on Si substrate by PLD. The process conditions such as oxygen partial pressure were controlled during the experiment, and the Al₂O₃ (k~9) as bottom dielectric layer scaling resulted in a five-fold improvement in the subthreshold slope (S.S), operating the device at low power, from approximately 500 mV/dec to 100 mV/dec. To develop low power devices obtaining less than 60 mV/dec, the PLD process will further be optimized for the enhancement of ferroelectricity to obtain larger NC effect.

Anomalous Remnant Magnetization in Gadolinia Nanospindles at Room Temperature?

Parvez Akhtar, Sandeep Kumar and Madhusudan Singh; Indian Institute of Technology Delhi, India

Gadolinium oxide (Gd₂O₃) is expected to exhibit strong interactions with external magnetic fields due to the high
magnetic moment of Gd (7.94 μB). Applications range from a positive contrast agent in magnetic resonance imaging (MRI) to use as a cooling agent in magnetocaloric effect (MCE) based refrigerators. In this work, we report on the preparation of Gd₂O₃ nanospindles by a hydrothermal method, followed by measurement of its mass magnetization. Powdered Gd₂O₃ source (CAS: 12064-62-9, 99.9% trace metals basis, Sigma-Aldrich) was subjected to aqueous colloidal hydrothermal synthesis and subsequently annealed at 500°C to produce cubic phase (JCPDS: 882165) Gd₂O₃, inferred from powder X-ray diffraction (PXRD, Advance Bruker D8, Ni-filtered Cu Kα radiation (λ = 1.5418 Å)). The morphology of nano-spindles (length ~100 ± 10 nm) was studied by field-emission scanning electron microscopy (FESEM-FEI QUANTA 3D FEG). Raman spectra confirmed the cubic phase of Gd₂O₃ with a highly intense and characteristic peak at 361 cm⁻¹. A small quantity of the product (1.23 mg) was wrapped in Teflon tape and exposed to magnetic fields in the range [-2,2] kOe in an Alternating Gradient Magnetometer (Micromag 2900 PMC) at room temperature. Measurements of magnetic moment (emu), converted into mass magnetization (emu/g), exhibit a quasi-saturated hysteresis behavior at limits of magnetic field excitation. The saturation magnetization (Mₘ), retentivity (Mᵣ) and coercivity (Hᵥ) are found to be 540.809 ± 4.381 m emu/g, 23.348 ± 0.186 m emu/g, and 21.218 ± 1.024 Oe, respectively over multiple measurements. The absence of saturation at the applied field in the magnetic hysteresis (M-H) curve suggests a mix of paramagnetic (PM) and ferromagnetic (FM) phases at room temperature. We are performing further materials analysis and investigating this magnetization result at different temperatures to validate it, and to understand the precise mechanism, in light of known defect-induced magnetization in various materials, albeit at lower temperatures. Potential applications include possible low-cost solution-processable magnetic devices and sensors.

EL03.06.29
Enhanced Gilbert Damping in Sputter Deposited Topological Insulator/Ferromagnet Heterostructures
Nirjhar Bhattacharjee¹, Ivan Lisenkov², Alexandria Will-Cole¹, Jiawei Wang¹ and Nian Sun¹ ²; ¹Northeastern University, United States; ²Winchester Technologies, LLC, United States

Topological insulators (TI) have been known to possess topologically protected surface conducting states [1] and Rashba 2D electron gas (2DEG) due to band bending at interfaces [8]. A TI placed in contact with a ferromagnetic (FM) metal generates spin-orbit torques (SOT) on the magnetization in FM [2,3]. A signature of SOT in TI/FM bilayers is an increase in Gilbert damping in FM. SOT in TI/FM (ferromagnet) films have been reported previously with TI films epitaxially grown with molecular beam epitaxy [2, 3]. Here we report enhanced Gilbert damping in sputter deposited TI/FM, BiₓTe₁₋ₓ/CoFeB (BT/CFB) films (x = ~0.4). Samples of 20nm BT film were grown on a Si/SiO₂ substrate at 250C and at 30C followed by 20nm CFB deposition at 30C (room temperature) using RF and DC magnetron sputtering respectively. X-ray diffraction (XRD) measurements reveal a crystalline 250C BT film compared to an amorphous 30C BT film. Room temperature broadband ferromagnetic resonance (FMR) measurements were conducted for 250C and 30C heterostructures and a control sample where the TI was substituted with 3nm Al. A full width at half maximum (FWHM) resonance linewidth was extracted as a function of frequency to calculate Gilbert damping. The control and 30C samples show almost identical linewidth, but the 250C sample linewidth is much broader. The Gilbert damping coefficient, α, for 250C sample is α = 0.3, compared to α = 0.03 for 30C and α = 0.02 for control. The calculated spin-mixing conductance for 250C sample is g = 4e²/2 m-2 which is in an order of magnitude higher than reported value for CFB/Pt films [4]. Moreover, the presence the crystalline TI film adjacent to FM induces static effects on the magnetization. M-H loop measurements reveal emergence of out of plane magnetic anisotropy (OPMA) for the 250C sample at lower thicknesses (<5nm) of CFB films. This change in the magnetic anisotropy and spin pumping in the BT/CFB heterostructure is attributed to presence Rashba 2DEG because of strong spin-orbit coupling [5-8] at the interface, which is enhanced for the crystalline phase of BT. Further, spin-torque FMR studies on our samples is being carried out to characterize the effects on magnetization dynamics due to sputtered TI/FM interfaces.

References:
EL03.06.30
Substrate-Modulated Ferromagnetism of Two-Dimensional Fe$_3$GeTe$_2$  Luyao Song, Luman Zhang, Xinyu Huang, Lei Ye and Junbo Han; Huazhong University of Science and Technology, China

Ferromagnetism in two-dimensional (2D) Van der Waals materials promises to revolutionize and develop spintronic devices and has received increased attention due to the electrical stability and sensitive tunability of an external field. To achieve high performance in spintronic devices, the effect of device substrates on the ferromagnetism of 2D materials also plays a critical role in practical device design and fabrication but has not yet been examined. Here, we systematically demonstrated the substrate-modulated ferromagnetism of 2D Fe$_3$GeTe$_2$ based on different substrates. The out-of-plane ferromagnetism of Fe$_3$GeTe$_2$ thin films prepared on Al, SiO$_2$ and Au substrates was probed using Magnetooptical Kerr effect techniques. Based on the experimental data, Fe$_3$GeTe$_2$ thin films with the same thickness were modulated to show different $T_C$ on different substrates, with the highest $T_C$ on Au substrate, especially in a thin layer. The underlying reason was explained by the first-principle calculation and mean field approximation, revealing that the charge redistribution and lattice distortion play an important role on magnetic properties changes. Our work provides a practical way to modulate the magnetic properties of ferromagnetic materials permanently without applying any additional treatment processes, and a feasible theoretical method to study the fundamental physical properties of ferromagnetic materials.

SESSION EL03.07: Multiferroics III
Session Chair: Quanxi Jia
Wednesday Morning, December 4, 2019
Hynes, Level 1, Room 101

8:30 AM *EL03.07.01
Electrically Reversible Spin Texture in Ferroelectric Oxides  Evgeny Y. Tsymbal; University of Nebraska-Lincoln, United States

Spin-orbit coupling is known to be responsible for non-trivial spin configurations and a number of emergent physical phenomena. Ferroelectric materials are especially interesting in this regard due to broken space inversion symmetry, which enforces the emergence of the bulk Rashba and Dresselhaus spin-orbit coupling, and reversible spontaneous polarization, which allows for a non-volatile electrical control of the spin degrees of freedom. This talk addresses two classes of ferroelectric oxide materials exhibiting dissimilar spin textures due to different space-group symmetries. First, we consider a technologically relevant oxide material, HfO$_2$, which is known to be ferroelectric in a non-centrosymmetric orthorhombic phase. We show that HfO$_2$ exhibits Dresselhaus-type spin texture driven by spin-orbit coupling, and argue that this material can be used as a tunnel barrier to produce tunnelling anomalous and spin Hall effects that are reversible by ferroelectric polarization. Another example involves a class of materials capable to maintain a persistent spin texture. This property has been predicted to support an extraordinarily long spin lifetime of carriers promising for spintronics applications. We show that the persistent spin texture can be enforced by non-symmorphic space-group symmetry of the crystal, which makes it a robust intrinsic property of the bulk material. Using symmetry analyses and theoretical modelling based on density-functional theory, we demonstrate this property for a handful of oxide materials, which can be synthesized in laboratory. Among them BiInO$_3$, a wide band gap ferroelectric semiconductor, is the most promising candidate which sustains persistent spin texture around the conduction band minimum. The reversible spontaneous polarization of BiInO$_3$, allows for an electrical control of the spin polarization, which can be selectively induced by circular polarized optical pumping.

1. L. L. Tao, T. R. Paudel, A. A. Kovalev, and E. Y. Tsymbal, Reversible spin texture in ferroelectric HfO$_2$, 
2. M. Y. Zhuravlev, A. Alexandrov, L. L. Tao, and E. Y. Tsymbal, Tunneling anomalous Hall effect in a
3. L. L. Tao and E. Y. Tsymbal, Persistent spin texture enforced by symmetry, 
9:00 AM *EL03.07.02
Tunable Magnetotransport Properties of Epitaxial Nanocomposite Films Aiping Chen¹, Haiyan Wang², Judith L. MacManus-Driscoll¹ and Quanxi Jia⁴; ¹Los Alamos National Laboratory, United States; ²Purdue University, United States; ³University of Cambridge, United Kingdom; ⁴University at Buffalo, The State University of New York, United States

Over the past two decades, new discoveries and major advances have been made to enhance controlled synthesis of epitaxial ferromagnetic oxide films and to gain fundamental understanding of their physical properties. Tunable magnetotransport properties, in particular, have been achieved through interfacing ferromagnetic materials with binary oxides at the nanoscale by forming nanocomposite films, where both the ferromagnetic and binary oxides are of nanoscale dimensions. In this talk, we will overview our strategies in synthesis and characterization of epitaxial magnetic nanocomposite films. Using controlled synthesis, advanced probing, and theoretical modeling, we are able to understand the effect of interface strain on the magnetotransport properties of ferromagnetic materials such as Laₐ₀.₇Sr₀.₃MnO₃ films.

9:30 AM *EL03.07.03
Magnetoelectric Coupling by Giant Piezoelectric Tensor Design Chang-Beom Eom; University of Wisconsin--Madison, United States

Strain-coupled magnetoelectric (ME) phenomena in piezoelectric / ferromagnetic thin-film bilayers are a promising paradigm for sensors and information storage devices, where strain manipulates the magnetization of the ferromagnetic film. In-plane magnetization rotation with an electric field across the film thickness has been challenging due to the virtual elimination of in-plane piezoelectric strain by substrate clamping, and in two-terminal devices, the requirement of anisotropic in-plane strain. We have overcome both of these limitations with lithographically patterned devices with a piezoelectric membrane on a soft substrate platform, in which in-plane strain is freely generated, and a patterned edge constraint that transforms the nominally isotropic piezoelectric strain into the required uniaxial strain. We fabricated 500 nm thick, (001) oriented [Pb(Mg₁/₃Nb₂/₃)O₃]₀.₇-[PbTiO₃]₀.₃ (PMN-PT) unclamped piezoelectric membranes with ferromagnetic Ni overlayers. Guided by analytical and numerical continuum elastic calculations, we designed and fabricated two-terminal devices exhibiting Ni magnetization rotation in response to an electric field across the PMN-PT. Similar membrane heterostructures could be used to apply designed strain patterns to many other materials systems to control properties such as superconductivity, band topology, conductivity, and optical response.

This work has been done in collaboration with J. Irwin, S. Lindemann, W. Maeng, J. J. Wang, V. Vaithyanathan, J.M. Hu, L.Q. Chen, D.G. Schlom, C.B. Eom, M.S. Rzchowski.
This work was supported by the Army Research Office through grant W911NF-17-1-0462.

10:00 AM BREAK

10:30 AM *EL03.07.04
Towards Low-Voltage Multiferroic/Magnetoelectric Operation Lane W. Martin¹,²; ¹University of California, Berkeley, United States; ²Lawrence Berkeley National Laboratory, United States

Applications in advanced, beyond Moore’s law computing are driving researchers and industry alike to explore a broader set of materials than ever before. While industry has maintained, in some form, their ability to continually meet the demands of Moore’s law by increasing the number of transistors on chip, largely in part from efforts in scaling and size reduction of the transistors themselves and the associated circuit area, the same cannot be said for energy scaling. In the last fifteen years, scaling has deviated from Dennard’s trend which states that the power density of circuits stays roughly the same as transistors get smaller, assuming, concurrent voltage reductions are made. Herein lies the challenge – while we have reduced transistor and circuit size, voltages of operation have not been scaled at the same rate. As a result, power and energy dissipation now stands as one of the most pressing challenges for advanced nanoelectronics. This has motivated renewed attention to a wide variety of routes to reduce the voltage of operation of next-generation logic. Such approaches have thrust materials – including multiferroics and magnetoelectrics – back into the mix as candidates for beyond CMOS computing.

Despite considerable research on multiferroic and magnetoelectric materials in the last decade and advances in our
ability to synthesize, control, characterize, and fabricate these materials, the requirements of beyond Moore’s law computing are already pushing these materials to their limits. In this talk, we will explore recent efforts to reduce the operating voltages of multiferroic and magnetoelectric devices including exploring both new and old materials in ever decreasing sizes. In particular, we will explore efforts to push the size limits of these materials whereby reducing the thickness of films provides a direct pathway to reduced operation voltages. Special attention will be given to challenges in achieving ultra-thin-film operation in multiferroics such as BiFeO$_3$ and Bi$_{1-x}$La$_x$FeO$_3$ as well as in magnetoelectric composite structures based on piezoelectric/ferroelectric materials such as BaTiO$_3$ and (1-x)PbMg$_{1/3}$Nb$_{2/3}$O$_3$-(x)PbTiO$_3$ (PMN-PT). For example, while considerable work has been done in PMN-PT as bulk ceramics, single crystals, and thick films, essentially no work on ultra-thin films has been considered. We will explore the evolution of relaxor order and actuation potential as we reduce relaxor film thicknesses to the range of 5-100 nm. Studies suggest surprising enhancement of relaxor character with reducing thickness and the presence of a complex, thickness evolution to structure and properties. We will explore other approaches including orientation dependence and chemical routes to reduce polarization or manipulate structure in such a fashion that it reduces the costs of switching polarization. For example, in PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films, it has been shown that merely changing film orientation from (001)- to (111)-oriented structures can dramatically change coercive field scaling (thus avoiding classical Janovec-Kay-Dunn scaling trends) as a result of changes in materials symmetry which produce low-energy switching pathways. Finally, we will explore the effects of these approaches on the realization of low-voltage magnetoelectric coupling in heterostructures such as BiFeO$_3$-based spin valves and composite ferromagnet/piezoelectric stacks. To end, we will discuss where these ideas could lead us next and what metrics can be met using these materials and methods.

11:00 AM *EL03.07.05
Voltage Controlled Néel Vector Switching in High-$T_N$ Magnetoelectric Thin Films Christian Binek, Ather Mahmood, Will Echtenkamp, Junlei Wang, Takashi Komesu and Peter Dowben; University of Nebraska-Lincoln, United States

Voltage-controlled magnetization switching at interfaces or boundaries enables dissipationless control of remnant magnetic states. It paves the way towards ultra-low power and non-volatile spintronics. We exploit substitutional Boron doping of the magnetoelectric antiferromagnet Cr$_2$O$_3$ to fabricate voltage switchable all antiferromagnetic memory devices which operate between room temperature and 400K, i.e., significantly above the antiferromagnetic ordering temperature $T_N = 307$ K of pure Cr$_2$O$_3$. $T_N$-enhanced and anisotropy reduced magnetoelectric films are grown via pulsed laser deposition in the presence of borane background gases. Boundary magnetization associated with two degenerate orientations of the Néel vector serves as state variable which can be isothermally written and read out. Writing is achieved through voltage-controlled switching of the Néel vector. Read out takes place by sensing an anomalous Hall-like signal originating from an electric current driven through a lithographically patterned Pt Hall bar deposited on top of the B-doped Cr$_2$O$_3$ film. In device architectures based on voltage-controlled exchange bias where remnant magnetization of a ferromagnetic film serves as state variable, B-doping does not translate into improved performance. Although B-doping can increase the blocking temperature, exchange coupling is not accompanied by effective pinning and thus voltage-control of the ferromagnet. The detrimental effect of B-doping on perpendicular exchange bias is attributed to reduced magnetic anisotropy and canting of the interface magnetization relative to the surface normal. It takes place despite perseverance of antiferromagnetic order and magnetoelectric functionality above 307 K as evidenced by magnetometry and photoemission spectroscopy. In contrast to pure chromia, where order parameter switching is controlled by the competition between magnetoelectric and anisotropy energy, the switching mechanism in B-doped chromia seems to be additionally affected by a sizable electric field dependence of the magnetic anisotropy. Our results demonstrate that $T_N$-enhancement and anisotropy reduction through B-doping of Cr$_2$O$_3$ is successfully utilized in voltage-controlled spintronic devices with reduced complexity. Our Hall bar structures based on B-doped chromia show voltage-controlled switching up to 100 K above room temperature paving the way to CMOS compatible ultra-low power magnetoelectric MRAM and logic devices.

We acknowledge support by SRC and NSF through ECCS 1740136, MRSEC DMR-1420645, and NNF under Award NNCI: 1542182 and support by ARO through MURI W(11NF-16-1-0472.

11:30 AM EL03.07.06
SHG-Active Boundaries between Nonpolar Magnetic Domains in MnWO$_4$ Shingo Toyoda$^1$, Manfred Fiebig$^{1,2}$, Takahisa Arima$^{1,3}$, Yoshinori Tokura$^{1,3}$ and Naoki Ogawa$^{1,4}$; $^1$RIKEN CEMS, Japan; $^2$ETH Zürich, Switzerland;
Domain walls often show a novel functionality very different from that of bulk states. Despite their importance, the domain wall physics are not well understood compared to the bulk cases because of the lack of experimental techniques to investigate the confined walls. In the present study, we conducted a SHG imaging measurement which allows us to probe the domain walls in MnWO4. We found multiferroic domain walls in a non-multiferroic environment.

MnWO4 crystalizes in a centrosymmetric space-group $P2_1/c$, and shows successive magnetic phase transitions below the Néel temperature $T_N = 13.5$ K. In the AF2 phase, the magnetic order breaks the space-inversion symmetry and ferroelectric polarization appears along the $b$-axis [1], while the other phases have non-polar magnetic structures. Correspondingly, SHG is allowed only in the AF2 phase, while it is forbidden in the AF1 and AF3 phases. However, it was found that non-zero SHG signal exists even in the SHG-forbidden AF1 phase [2]. We revealed that the SHG signal in the AF1 phase comes from wall-like structures. Polarization anisotropy and spectroscopy measurements of the SHG signal suggest that the wall in the AF1 phase should have a magnetic structure similar to that of the multiferroic AF2 phase. The results indicate the existence of domain walls breaking space-inversion symmetry, although the bulk phase is centrosymmetric. We propose the emergence of multiferroic domain walls in a non-multiferroic environment.


11:45 AM EL03.07.07
A Dynamical Magnetic Field Accompanying the Motion of Ferroelectric Domain Walls Dominik M. Juraschek1,2, Quintin N. Meier1, Morgan Trassin2, Susan E. Trolier-McKinstry3, Christian Degen2 and Nicola Spaldin2; 1Harvard University, United States; 2ETH Zürich, Switzerland; 3The Pennsylvania State University, United States

The domain walls that separate different orientations of electric polarization in ferroelectric materials have long been of interest because their motion governs the process of ferroelectric switching in an electric field [1]. Recently, a range of unexpected behaviors have been discovered at domain walls that do not occur in the bulk of the domains, such as ferrielectricity, magnetoelectricity, and electrical conductivity or even superconductivity, suggesting additional interest in domain walls as functional entities in their own right [2].

At the same time, the magnetization caused by the usual motion of electric charges has been revisited over the last years in the context of time-varying ferroelectric polarizations. This newly described dynamical multiferroicity, associates a magnetization $\mathbf{M}$ of the form $\mathbf{M} \sim \mathbf{P} \times \partial_t \mathbf{P}$ with a ferroelectric polarization $\mathbf{P}$. A range of existing coupled electric-magnetic phenomena fall within the dynamical multiferroicity framework, and new behaviors, including a phonon Zeeman effect, exotic quantum criticality and phonon orbital magnetism have been proposed [3-5].

Here we establish the link between these two concepts -- dynamical multiferroicity and ferroelectric domain wall functionality -- by showing theoretically that the motion of ferroelectric domain walls can be accompanied by a dynamical magnetic field. We extend the formalism of dynamical multiferroicity to the case of domain wall motion and present numerical results for the prototypical ferroelectric barium titanate (BaTiO3), based on a combination of density functional theory calculations and phenomenological modeling. We propose two experimental setups that possibly allow the detection of the dynamical magnetic field using nitrogen-vacancy center magnetometry, and we show that the magnitude of the effect lies well above the present detection limit.

1:30 PM *EL03.08.01
**Delta-E Effect Magnetic Field Sensors** Benjamin Spetzler, Sebastian Zabel, Phillip Durdaut, Anne Kittmann, Cai Müller, Julius Schmalz, Gerhard Schmidt, Martina Gerken, Jeffrey McCord, Reinhard Knöchel, Michael Höft, Eckhard Quandt and Franz Faupel; Kiel University, Germany

Magnetic field sensors based on the delta-E effect utilize the resonance shift of a high frequency mechanical resonator in a magnetic field, due to the change in Young’s modulus of a magnetostrictive material. Delta-E effect sensors are not affected by 1/f amplifier noise and allow broadband magnetic field measurements at low frequencies down to DC with very high dynamic range. Moreover, they are robust against microphony effects and mechanical noise. Fully integrable magnetic field sensors were achieved via replacement of magnetic by electric excitation.

Since our first publication of this sensor concept in 2011 [B. Gojdka et al., Appl. Phys. Lett. 99, 223502 (2011); Nature 480, 155 (2011)], much progress has been made in understanding the complex interplay of magnetic, mechanical and electrical properties. This holds for different designs of cantilever sensors, but also for surface acoustic wave devices. Here we present a comprehensive magneto-electromechanical model that considers the interaction of magnetic, mechanical and electrical properties and show current experimental results. We discuss the delta-E effect in general and its application in diverse types of electrically excited sensors, including the most common types such as bending or bulk resonators, but also shear resonators and surface acoustic wave sensors. The model provides detailed understanding of the general limits of the sensitivity, which arise from using the delta-E effect as the sensing principle. Realistic detection limits are predicted in combination with a noise equivalent model. The simulations are validated with experimental data using different sensor designs and magnetic layers. We also discuss simultaneous operation of delta-E sensors in the delta-E mode and the direct magnetoelectric mode, e.g. for localization of the sensor.

2:00 PM *EL03.08.02
**Magnetoelectric MEMS Doubly-Clamped Resonators for Vector Magnetic Field Sensing** Margo Staruch, Steve Bennett, Jeff Baldwin, Konrad Bussmann and Peter Finkel; U.S. Naval Research Laboratory, United States

Magnetoelectric (ME) resonators are of significant interest for next generation magnetic field sensors, as the direct coupling of magnetostrictive and piezoelectric phases enables high magnetic field sensitivity with exceptionally low operational power requirements. In this work, we present silicon based ME thin film resonators with clamped-clamped boundary conditions, that are fully suspended to achieve a string mode resonance. The heterostructure is comprised of a magnetoelastic FeCo or FeCoV layer, which is coupled through strain to an AlN piezoelectric layer with high $\varepsilon_{31,fpiezoelectric}$ coefficients. A negative or positive shift in the resonant frequency was observed for fields applied parallel and perpendicular to the length of the beam, respectively, consistent with the magnetostriction measurements and the expected magnetoelastic strain developing in the beams due clamped-clamped boundary conditions. A linear behavior in the field dependent resonant frequency when the field is perpendicular to the length is most likely due to a well-defined hard axis in this direction resulting from high shape and stress-induced anisotropy energies. Together, these results suggest that through modification of the magnetic anisotropy, the frequency shift and angular dependence can be tuned, producing highly directional structures for magnetic field sensors. Finally, the sensor performance is evaluated and benchmarked against conventional magnetic field sensors.

2:30 PM BREAK

3:30 PM *EL03.08.03
**Phase-Field Modeling of Multiferroic Heterostructures** Jia Mian Hu$^{1,2}$, Jianjun Wang$^1$, Tian-Nan Yang$^1$ and Long-Qing Chen$^1$; $^1$The Pennsylvania State University, United States; $^2$University of Wisconsin–Madison, United States

Phase-field method has been applied to modeling both direct and converse magnetoelectric effects in multiferroic heterostructures including the coupled evolution of magnetic and ferroelectric domain under electric fields. This
presentation will discuss our recent applications of the phase-field method to understanding the strain-mediated voltage control of magnetic skyrmions in nanoscale multiferroic heterostructures. It is shown that a nanoscale skyrmion in a magnetic disk can be repeatedly created and deleted by strain imparted from the underlying piezoelectric layer. We analyzed the strain-mediated skyrmion switching dynamics based on both phase-field simulations and analytical theories. We will discuss the possibility of performing high-throughput phase-field simulations of magnetic switching of multiferroic heterostructures. In particular, using a combination finite-element calculations and phase-field simulations, we studied the 3D geometrical effects of Ni islands on the strain relaxation and magnetic domain structures and switching in Ni/PMN-PT nanoscale heterostructures under an external electric field. Finally, we will also discuss potential applications of a dynamical phase-field model to understanding the ultrafast dynamics of ferroic domains in multiferroics.

4:00 PM *EL03.08.04
Strain-Mediated Magnetoelectric Effect in Self-Assembled Epitaxial Nanocomposites  
Xiao Tang, Min Gao, Jiefang Li and Dwight Viehland; Virginia Tech, United States

Spinel magnetostrictive cobalt ferrite (CoFe$_2$O$_4$, CFO) can vertically integrate nanopillars embedded in a matrix of perovskite piezoelectric bismuth ferrite (BiFeO$_3$, BFO), self-assembling the ‘1-3’-type nanocomposites [1, 2]. These two phases exhibit a considerable magnetoelectric (ME) effect due to the coupling via strain at the interfaces [3]. The ME effect of CFO with either rhombohedral or tetragonal BFO has been studied [4, 5]. To further increase the ME coefficient, such ‘1-3’-type nanocomposites were epitaxially deposited on piezoelectric single crystal substrates (i.e. Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$-x%PbTiO$_3$, PMN-xPT). An applied electric field (E) of 3 kV/cm was able to induce a giant magnetization change (~93% for ΔM/M$_r$), equivalent to a converse ME coefficient of 1.3×10$^{-7}$ s/m [6]. Moreover, multiple distinguishable magnetization states were obtained, which were stable on removal of the E [6]. This multi-state ME nanocomposite thus has potential for neuromorphic-like computing and multilevel-cell memory devices.

From an energy-saving perspective, CuFe$_2$O$_4$ (CuFO) that shows low loss and high mechanical quality factor was used to replace the typical CFO in our ME nanocomposites [7]. The CuFO-BFO/PMN-PT nanocomposites exhibited notably slimmer M-H loops than CFO-BFO/PMN-PT ones, and a significantly larger ME coupling effect than pure CuFO/PMN-PT heterostructures [7, 8]. The findings demonstrate a trade-off between ME effects and energy losses that can be modified by material choices and nanocomposite topography.

Our investigations on CFO-BFO and CuFO-BFO shed light on the feasibility to approach non-volatility in nanocomposites, even though the individual phases/substrate had only volatile properties [8]. It simplifies materials selection for multi-state systems, averting difficulties with compositional non-uniformity and property repeatability in particular with regards to PMN-xPT crystal substrates.


4:30 PM *EL03.08.05
Anisotropic Spin-Orbit Torque Generation in Epitaxial SrIrO$_3$ by Symmetry Design  
Tianxiang Nan$^{1,2}$, Trevor Anderson$^1$, Jonathan Gibbons$^2$, Kyusung Hwang$^3$, Neil Campbell$^1$, Hua Zhou$^4$, Yongqi Dong$^4$, Gy Kim$^5$, Dingfu Shao$^6$, Tula Paudel$^7$, Neal Reynolds$^2$, Xinjun Wang$^4$, Nian Sun$^8$, Evgeny Y. Tsymbal$^6$, Siyoung Choi$^5$, Mark Rzchowski$^1$, Yong Baek Kim$^3$, Daniel C. Ralph$^2$ and Chang-Beom Eom$^1$; $^1$University of Wisconsin Madison, United States; $^2$Cornell University, United States; $^3$University of Toronto, Canada; $^4$Argonne National Laboratory, United States; $^5$POSTECH, Korea (the Republic of); $^6$University of Nebraska, United States; $^7$Northeastern University, United States

Spin-orbit coupling (SOC), the interaction between the electron spin and the orbital angular momentum, can unlock rich phenomena at interfaces, in particular interconverting spin and charge currents. Conventional heavy metals have
been extensively explored due to their strong SOC of conduction electrons. However, spin-orbit effects in classes of materials such as epitaxial 5d-electron transition metal complex oxides, which also host strong SOC, remain largely unreported. In addition to strong SOC, these complex oxides can also provide the additional tuning knob of epitaxy to control the electronic structure and the engineering of spin-to-charge conversion by crystalline symmetry. Here, we demonstrate room-temperature generation of spin-orbit torque on a ferromagnet with extremely high efficiency via the spin-Hall effect in epitaxial metastable perovskite SrIrO$_3$. We first predict a large intrinsic spin-Hall conductivity in orthorhombic bulk SrIrO$_3$ arising from the Berry curvature in the electronic band structure. By manipulating the intricate interplay between SOC and crystalline symmetry, we control the spin-Hall torque ratio by engineering the tilt of the corner-sharing oxygen octahedra in perovskite SrIrO$_3$ through epitaxial strain. This allows the presence of an anisotropic spin-Hall effect due to a characteristic structural anisotropy in SrIrO$_3$ with orthorhombic symmetry. Our experimental findings demonstrate the heteroepitaxial symmetry design approach to engineer spin-orbit effects. We therefore anticipate that these epitaxial 5d transition-metal oxide thin films can be an ideal building block for low-power spintronics.

SESSION EL03.09: Multiferroics IV
Session Chair: Jinxing Zhang
Thursday Morning, December 5, 2019
Hynes, Level 1, Room 101

8:30 AM *EL03.09.01
Theoretical Design of Low Dimensional Polar Materials Shuai Dong; Southeast University, China

Achieving novel physical properties, such as superconductivity, ferromagnetism, and ferroelectricity, in two-dimensional (2D) materials should enable numerous functionalities in nanoscale devices. In recent years, interests in high-performance 2D ferroelectric materials have also grown rapidly across multiple scientific and engineering disciplines. Here, two new 2D polar materials are predicted based on physical analysis and by using density functional theory calculations. The first one is a 2D type-II multiferroic magnetoelectric material (MXene Hf$_2$VC$_2$F$_2$) and and the second one is a noncollinear ferrielectricity materials (dioxydihalides $M$O$_2$X$_2$ family, where $M$= Mo and W; $X$= Cl and Br).

For multiferroic MXene Hf$_2$VC$_2$F$_2$ monolayer, its ferroelectricity originates directly from its magnetism [1]. The noncollinear 120° Y-type spin order generates a polarization perpendicular to the spin helical plane. Remarkably, the multiferroic transition is estimated to occur above room temperature.

For dioxydihalides $M$O$_2$X$_2$ monolayer, it is predicted to display noncollinear ferrielectricity, induced by competing ferroelectric and antiferroelectric soft modes [2]. More importantly, this intrinsic noncollinearity of dipoles generates unique physical properties, such as $Z_2 \times Z_2$ topological domains, atomic-scale dipole vortices/anti-vortices, and negative piezoelectricity.

Our studies will open the door to a new branch of 2D materials in the pursuit of intrinsically strong magnetoelectricity and noncollinear ferrielectricity.

References

9:00 AM *EL03.09.02
Strong Magnetoelectric Coupling by Tailoring Interfacial Chemistry and Physics in Correlated Oxides Jinxing Zhang; Beijing Normal University, China

Magnetoelectric effects, magnetic-field-mediated polarization and/or electric-field-controllable magnetism, have attracted enormous attentions owing to the growing demands of new-generation information technologies. However, large direct and/or converse magnetoelectric coupling in thin-film materials is challenging (Nat. Mater. 18, 203
(2019)), which inhibits the practical application in future high-density and high-throughput electronic/spintronic devices. Here, via artificially design of correlated oxides at atomic scale, large magnetoelectric response by controlling the interfacial chemistry and physics has been achieved, accompanying the strong interplay of spin, charge, orbital and lattice degrees of freedom. This atomic tailoring of the quantum order parameters in oxide interfaces provides an alternative pathway towards realizing strong and controllable magnetoelectric effects with thin-film integrations.

9:30 AM EL03.09.03
Search for Local Magneto-Electric Effects in Cr$_2$O$_3$
Martin H. Dehn$^{1,2}$, J. Kane Shenton$^3$, Donald J. Arseneau$^4$, Sarah Duniger$^4$, Bassam Hitti$^4$, Stefan Holenstein$^5$, Michael Fechner$^6$, Hubertus Luetkens$^7$, W Andrew MacFarlane$^1$, Ryan M. McFadden$^1$, Quintin N. Meier$^3$, Gerald D. Morris$^4$, Zaher Salman$^7$, Nicola Spaldin$^3$ and Robert F. Kiefl$^{1,2}$; $^1$University of British Columbia, Canada; $^2$Stewart Blusson Quantum Matter Institute, Canada; $^3$ETH Zürich, Switzerland; $^4$TRIUMF, Canada; $^5$Universität Zürich, Switzerland; $^6$Max Planck Institute for the Structure and Dynamics of Matter, Germany; $^7$Paul Scherrer Institut, Switzerland

The bulk properties of the prototypical linear magneto-electric (ME) antiferromagnet Cr$_2$O$_3$ have been extensively studied. Here, we report on a muon spin rotation (μSR) study using spin polarized muons to probe the local ME effect. This was motivated by the recent prediction that a point charge inside a linear ME creates a monopolar magnetic field distribution [1]. μSR is a unique and novel way to test such predictions since the muon may act both as a test charge and a sensitive probe of the induced local magnetic field.

Prerequisite for a search for such local or muon induced magnetoelectricity is a thorough understanding of the local electronic structure and magnetic interaction of the muon within the host material. We find that the muon, a light interstitial probe, occupies several distinct stopping sites in Cr$_2$O$_3$, and displays a rich dynamic behavior that we interpret in the context of local muon hopping, thermally activated site transitions and the formation of a charge-neutral muon-polaron complex.

Furthermore, when Cr$_2$O$_3$ is prepared in a single magnetic domain, a shift in the local magnetic field is observed in response to an applied electric field, with the sign of the shift depending both on the field direction and domain state. The origin of this apparent magneto-electric effect is discussed.


9:45 AM EL03.09.04
Concept of Artificial Magnetoelectric Materials via Geometrically Controlling Curvilinear Helimagnets
Oleksii Volkov$^1$, Ulrich Rößler$^2$, Jürgen Fassbender$^1$ and Denys Makarov$^1$; $^1$Helmholtz-Zentrum Dresden-Rossendorf e.V., Germany; $^2$Leibniz Institute for Solid State and Materials Research Dresden, Germany

Magnetoelectric materials are of the great interest due to their unique coupling of the magnetic and electrical order parameters. In these materials magnetic states can be manipulated via electric field and vice versa, offering exciting prospectsives for energy efficient memory, logic and sensor devices. However, a sizeable magnetoelectric coupling for technologically relevant applications is obtained for a limited set of single-phase bulk materials. Typically, this restriction can be removed by using two-phase materials, containing strain-coupled magnetoelectric heterostructures based on piezoelectric-magnetostrictive bilayers. Although the concept is promising, there is a clear limitation regarding the fact that strain-induced changes result in the modification of all intrinsic magnetic parameters, in particular anisotropic couplings. Ideally, it would be advantageous that electric field control of magnetic state is achieved without change of global intrinsic magnetic parameters.

We propose a novel type of artificial magnetoelectric material [1], which allows an electric field-induced deterministic switching between magnetic states without influencing intrinsic magnetic parameters. The proposal refers to geometrically curved helimagnets [2,3] embedded in a piezoelectric matrix or sandwiched between two piezoelectric layers. In contrast to typical strain-coupled magnetoelectric heterostructures, we exploit the geometric coupling between the piezoelectric matrix and curvilinear helimagnets. Namely, a small geometrical deformation causes a drastic modification of magnetic state of the helimagnet through a magnetic phase transition between a homogeneous magnetic state and a periodical one. Resulting transformations of the average magnetization from non-zero to zero value can be uniquely assigned to logical “1” and “0”. This paves the way towards the realization of novel magnetoelectric devices with geometrically tunable and deterministically switchable magnetic states.
We provide not only the general concept but also show analytical validation for a prototypical example of torsional nanospring helimagnets. Furthermore, we put forth a discussion on the feasibility of the experimental realization of the concept including the choice of materials and fabrication approaches.


10:00 AM BREAK

10:30 AM EL03.09.05
Contact-Free Measurement of Light-Induced Currents at Domain Walls in Multiferroic BiFeO₃
Burak Guzelturk¹, Antonio Mei², Lei Zhang³, Liang Z. Tan⁴, Anisha Gurcharn Singh¹, Darrell G. Schlom³, Lane W. Martin¹ and Aaron Lindenberg¹; ¹Stanford University, United States; ²Cornell University, United States; ³University of California, Berkeley, United States; ⁴Lawrence Berkeley National Laboratory, United States

Multiferroic BiFeO₃ (BFO) films with periodic stripe domains produce anomalously large open circuit voltages under visible light illumination with exciting promise in solar energy applications. However, the microscopic origin of this photovoltaic effect has not been understood yet. Here, we make contact-free measurements of light-induced currents in stripe domain BFO films with 71° domain walls using terahertz emission spectroscopy. With this approach, we avoid undesired modifications to the ferroelectric polarization due to the physical electrodes, hence allowing us to disentangle different photovoltaic responses intrinsic to the BFO films. Analyzing the radiated terahertz fields, we find that the current flows perpendicular to the domain walls. This observation strongly indicates the predominant role of the domain walls in the separation of photogenerated charges and enables quantitative estimates of the currents and built-in fields associated with the domain walls. Furthermore, samples with increasing domain wall density show enhanced terahertz emission providing additional evidence for domain wall-mediated charge separation. On the other hand, we find that bulk photovoltaic effects only play a minor role in the photovoltaic response of the stripe domain BFO films with a contribution smaller than 5%. This work enables new fundamental understanding of photoferroelectric responses and defines novel opportunities for ferroelectric-based optoelectronics and efficient bias-free terahertz emitters.

10:45 AM EL03.09.06
Magnetoelectric Switching Dynamics in BiFeO₃
Eric K. Parsonnet¹, Yen-Lin Huang¹, Bhagwati Prasad¹, Chia-Ching Lin², Tanay Gosavi², Dmitri Nikonov², Ian Young², Vishal Ravi¹, Jonathan Reichanadter¹, Akshay Pattabi¹, Lei Zhang¹, Jeffrey Bokor¹, Lane W. Martin¹ and Ramamoorthy Ramesh¹,¹; ¹University of California, Berkeley, United States; ²Intel Corporation, United States

With room temperature coupling between magnetic and electric degrees of freedom, BiFeO₃ (BFO) has attracted much attention as a leading candidate for magnetoelectric applications. These include a variety of spintronic applications such as a magnetoelectric spin orbit (MESO) logic device where there exist stringent requirements on switching speed. Although there does not exist a wealth of true time-dynamics studies of ferroelectrics, a previous study on Pb(Nb₀.₀⁴Zr₀.₂₈Ti₀.₆₈)₀₃ found ultrafast ferroelectric switching at ~220ps. Time-resolved BFO measurements have, to date, not been reported. There has been extensive work studying the equilibrium or quasi-static magnetoelectric coupling in BFO, but dynamics and fundamental limitations on switching have yet to be explored. Via pulsed ferroelectric (PUND) I-V measurements we provide novel data probing the limits of magnetoelectric switching speeds and study the effect of film thickness on dynamics. We probe the effects of chemical composition on magnetoelectric switching by studying two model systems, namely BFO and La-doped BFO. The data reveal low-nanosecond switching, much faster than previously reported in (La)BFO. Importantly, by exploring lateral scaling of device size, we demonstrate a pathway to the switching speeds required for spintronic applications. By employing giant magneto-resistance (GMR) and longitudinal magneto-optical Kerr effect (MOKE) studies, we are working towards direct observation of voltage control of magnetization on such timescales.

11:00 AM EL03.09.07
High-Throughput Phase-Field Simulations of Anisotropy and Voltage-Controlled Magnetization in Multiferroic Heterostructures
Jianjun Wang, Tian-Nan Yang, Jacob Zorn and Long-Qing Chen; The Pennsylvania State University, United States
Understanding magnetic domain structures and their responses to electric fields in multiferroic heterostructures is critical to the design of electric-field-driven spintronic devices. In this presentation, I will show high-throughput finite-element and phase-field simulations of piezoelectric strain anisotropy and its relaxation, magnetic domain structures and their responses to applied voltages as function of the in-plane dimensions and thickness of the magnetic Ni nanoslands grown on a Pb(Mg₁/₃Nb₂/₃)O₃-PbTiO₃ (PMN-PT) membrane. The piezoelectric strain anisotropy is found to increase with the in-plane aspect ratio, but it can be significantly relaxed, as large as >80%, in nanoslands of thickness larger than >15 nm. Magnetic domain diagrams are established to identify the domain structures for Ni nanoslands of different lengths of in-plane major and minor axis, as well as thickness. When a voltage is applied to the multiferroic heterostructure, the single-domain magnetic domain can be switched by the piezoelectric strain, whereas the vortex domain is not switched. However, for a multiferroic heterostructure with a thick nanosland wherein most of the piezoelectric strain is relaxed, the single-domain magnetic domain shows a weak response to the voltage and cannot be switched by the voltage.

I will also show how to use a phase-field approach to identifying the magnetic anisotropy, which is similar to experimental rotating magneto-optical Kerr effect method and anisotropic magnetoresistance measurement. By performing high-throughput phase-field simulations to obtain thousands of $M-H$ loops, hundreds of remanent magnetization and coercive field versus external magnetic-field direction polar diagrams can be established, which are used to further construct directional angle and coercive field of the easy axis versus strain anisotropies diagrams. Thermodynamic energy analysis are performed to understand the simulation results, which revealed that the strain anisotropy impacts the directional angle and the coercive field of the easy axis by modifying the valley and peak positions, as well as the barrier of the free energy profile. This presentation will contribute to a computational understanding of strain anisotropy and voltage-controlled magnetic properties in strain-mediated multiferroic heterostructures.

**References:**

**11:15 AM EL03.09.08**
**Template Free Fabrication and Characterization of Vertically Aligned BiFeO₃ Nanorods**

Swati Dhua and Somnath C. Roy; Indian Institute of Technology Madras, India

BiFeO₃ (Bismuth Ferrite or BFO) is a complex oxide that has been widely investigated for multiferroic properties as well as solar energy harvesting. In the recent times, various different nanostructures such as nanoparticles, thin films, nanowires and nanorods have been reported. In the case of 1D nanostructures such as nanorods and wires, vertical alignment from the underlying substrate holds special importance because of resulting ordered morphology and higher surface to volume ratio. Theoretically it is shown that the intrinsic stress generated due to the quantum confinement may result in shifting the ferroelectric and ferromagnetic transition temperature and also can induce giant magnetoelastic effect. Literature review suggests that, although different morphologies of 1D structures of BFO have been fabricated, highly aligned and vertically oriented nanorods have not been fabricated in template free conditions. Such structures hold special importance, particularly in solar energy and piezoelectric nanogenerator applications.

This work presents first successful fabrication of vertically aligned BiFeO₃ nanorods on FTO coated glass substrate using chemical bath technique followed by the deposition of Bismuth layer by DC sputtering. The significance lies in achieving such structures in template free condition that allows tailoring of the diameter and length and also the formation of heterostructures during the growth process. The crystallinity, microstructure, morphology and chemical composition have been confirmed by XRD, TEM, SEM and XPS. The multiferroic properties have been investigated by Piezoelectric Force Microscopy (PFM), P-E loop measurements and Vibrating sample magnetometry. The maximum obtained value of $d_{33}$ is 54 pm/V whereas a weak remnant magnetization of around 3 emu/cm³ is observed even at low temperature of 5 K. Finally, the optical and photocatalytic characteristics have been investigated by optical absorption and photo-electrochemical water splitting experiments. At 1 Sun illumination, a photocurrent density of around 55 μA/cm² (0.8 V vs Ag/AgCl) is observed which is found to be stable with time. The developments open up new avenues for BiFeO₃ where 1D nanostructures are desired.

**11:30 AM EL03.09.09**
**Control of Highly Anisotropic Ferroelastic Domains in LaCoO₃ Films and Ferromagnetism Using Strain**
Coupling of ferroelastic and ferromagnetic order parameters in materials offers a means to achieve novel multiferroic applications. We report the observation of one-dimensional ferroelastic domains in LaCoO$_3$ thin films that are intimately linked to magnetization. Unidirectional structural modulation is achieved by selective choice of substrate or growth plane, which produces broken in-plane rotational symmetry. Structural modification either through film growth or application of pressure is shown to affect the magnetism. Modification perturbs the crystal field energy, which leads to unexpected in-plane anisotropy of the orbital configuration and the magnetization.

Work funded by the U.S. Department of Energy, Basic Energy Sciences

SESSION EL03.10: Magnetoelectrics IV
Session Chair: Sarah Tolbert
Thursday Afternoon, December 5, 2019
Hynes, Level 1, Room 101

1:30 PM *EL03.10.01
Solution Processed Nanostructured Multiferroic Materials  Sarah Tolbert; University of California-Los Angeles, United States

In this talk, we examine multiple ways to control magnetism in solution processed nanostructured materials using an applied electrical bias. We begin with traditional multiferroic coupling, where electricity and magnetism are coupled through strain, and consider two systems. The first is a nanoporous magnetic or ferroelectric network produced using polymer templating of sol-gel oxides. The pores are then conformally filled with the opposite phase (either ferroelectric or magnetic) using atomic layer deposition to produce a three dimensional nanoscale composite. For these materials, we find the largest multiferroic response in materials with partly filled pores, emphasizing the role of residual porosity in controlling the elastic behavior and thus the multiferroic coupling of these composite materials. We next consider strain mediated switching in monolayer nanocrystal arrays. Here we show that nanocrystals can be controllably and reversibly switched from a superparamagnetic state, which has no time-averaged magnetic moment, to a ferromagnetic state using an applied bias. Finally, we explore a new type of multiferroic material, termed granular multiferroics, where exchange coupling between closely spaced magnetic nanocrystals can be modified by tuning the dielectric environment around the nanocrystals using either temperature or an applied electric field. In this work on nickel nanocrystals coupled to a soft ferroelectric, both temperature and field dependent changes in magnetism are observed in the vicinity of the ferroelectric Currie temperature, indicating that magnetism in nanocrystal arrays can indeed be tuned using dielectric changes.

2:00 PM *EL03.10.02
Voltage Control of Interfacial Magnetism in Multiferroic Based Spintronic Devices  Shishun Zhao, Qu Yang, Mengmeng Guan, Zhongqiang Hu, Ziyao Zhou and Ming Liu; Xi'an Jiaotong University, China

One of the central challenges in realizing magnetoelectric (ME) devices lies in finding a deterministic way to modulate magnetism in integrated circuits with a circuit-operation voltage. Ionic liquid (IL) gating on magnetic thin films with abundant electronic, chemical and magnetic interactions at the interface has become an emerging technology for controlling magnetism in a fast, compact and energy-efficient way. Compared with conventional strain effect dominated piezo/ferroelectric layer multiferroics, IL gating method has advantages like small gating voltage ($V_g<5$ V), easy-to-integration and compatibility with varied substrates such as Si, flexible substrates etc. In additional, unlike the oxide structures require a high temperature to overcome the oxidation energy barrier, the IL gating control process can be operated at room temperature, suitable for applications in room temperature environment. Here, we will summarize our recent progresses of IL gating control of magnetism in varied magnetic
heterostructures, as well as in different manners.[1-5] As IL gating process, proven to be a truly powerful and compatible gating method, enables giant ME tunability in different heterostructures and provides a tremendous potential in next generation of voltage-tunable spintronics/electronics.


2:30 PM EL03.10.03
Investigation of Diverse Magnetic Materials via Acoustically Driven Ferromagnetic Resonance Michael Page1, Piyush J. Shah2, Derek A. Bas1, Vladimir L. Safonov1, Maksym Popov3, Alexei Matyushov4, Anne Kittmann2, Viktor Schell5, Eckhard Quandt5, Ivan Lisenkov6, Gopalan Srinivasan7, Nian Sun4 and Michael E. McConney1; 1Air Force Research Laboratory, United States; 2Apex Microdevices, United States; 3Taras Shevchenko National University of Kyiv, Ukraine; 4Northeastern University, United States; 5Kiel University, Germany; 6Winchester Technologies, United States; 7Oakland University, United States

Recently, magnetoelastic coupling has been exploited to detect ferromagnetic resonance (FMR) using surface acoustic waves (SAWs)1, a technique known as ADFMR. GHz-frequency SAWs are produced and detected electrically using pairs of interdigital transducers (IDTs). A magnetic material is placed in the path of the SAWs, which can then interact with magnetic moments via magnetoelastic coupling. Absorption of the SAWs occurs at FMR, modulating the measured output. Landau-Lifshitz-Gilbert theory describes the interaction in terms of the external magnetic field with a characteristic four-lobe pattern, from which the magnetic anisotropy field, FMR resonance field, and magnetoelastic coupling coefficient can be inferred.

We study the effects of a variety of magnetic materials including Ni, FeCo, FeGaB, and FeCoSiB, to examine the dependence of ADFMR patterns on material parameters and geometries. We use a range of SAW frequencies from ~300 to 2000 MHz to explore spectral effects of the IDT design on transduction efficiency, and the frequency dependence of the resonance field. We also calculate the FMR linewidth and quality factor-figures of merit useful for determining the efficacy of future ADFMR devices.

2:45 PM EL03.10.04
Love Wave Magnetic Field Sensors Viktor Schell, Phillip Durdaut, Cai Müller, Anne Kittmann, Jeffrey McCord, Michael Höft and Eckhard Quandt; Kiel University, Germany

For the measurement of bio-magnetic signals there are high demands on the performance of the respectively utilized sensors. The requirements for these specific applications are a limit of detection (LOD) of significantly below 100 pT/Hz^{1/2}, a frequency bandwidth of 1 Hz to at least 20 Hz, better 100 Hz or above and a reduced size for achieving high spatial resolution or for the case of limited installation space. Further the device should be operable at room temperature and without magnetic shielding.

Promising candidates for fulfilling all these requirements are surface acoustic wave (SAW) magnetic field sensors, especially those using shear horizontal SAWs1. These so-called Love waves result from a piezoelectric substrate generating shear horizontal waves caged with a guiding layer with lower acoustic impedance confining the acoustic wave at the surface. As the sensitive element in these devices amorphous magnetostrictive thin films such as the alloy (Fe_{90}Co_{10})_{78}Si_{12}B_{10} seem to be particularly promising due to their high magnetostriction with simultaneously having a low magnetic anisotropy. Operating in a delay line configuration the magnetoelastically-induced change of shear modulus of the sensitive layer (ΔE/ΔG-effect) yields in a corresponding phase shift of the acoustic wave. While the application of amorphous magnetostrictive thin films in magnetoelectric cantilever composites was already studied extensively, the sensitivity and noise behavior in SAW sensors is not quite understood yet. However the quartz based Love wave devices with a working frequency of approximately 150 MHz show already very high sensitivities of up to 2000 °/mT and an equivalent LOD of 70 pT/Hz^{1/2} at 10 Hz and 30 pT/Hz^{1/2} at 100 Hz.

This work was funded by the German Research Foundation (DFG) through the Collaborative Research Centre CRC 1261 “Magnetoelectric Sensors – From Composite Materials to Biomagnetic Diagnostics”.

3:00 PM BREAK

3:30 PM EL03.10.05
**picoTesla Magnetoelectric Sensors with Low-Curvature Nano-Plate Resonators** Alexei Matyushov¹, James Zhou², Zhenyun Qian¹, Mohsen Zaeimbashi¹, Menghui Li¹, Cheng Tu¹, Huaihao Chen¹, Yingxue Guo², Matteo Rinaldi¹ and Nian Sun¹; ¹Northeastern University, United States; ²The University of Chicago, United States

Prior studies have shown the effectiveness of piezoelectric/magnetostrictive MEMS magnetometers featuring a nano plate resonator and using the ΔE effect for highly sensitive detection of DC magnetic fields. By monitoring changes in resonance frequency from applied magnetic fields, a sensitivity of a few Hz/nT has been achieved in unshielded lab environments. With dimensions of ≤ 200 μm across, and < 1 μm thick, these devices offer the advantages of small scale, including portability and low power consumption, as well as high spatial resolution in sensor arrays. However, a thorough understanding of magnetic properties and other performance aspects in these magnetometers has not been developed. In this study we report on the strong effects of resonator plate curvature on sensor performance. It was found that the total resonance frequency shift dropped off exponentially with increasing curvature by as much as two orders of magnitude. By fabricating a ΔE effect magnetometer with low curvature in the nano plate resonator, we achieved maximum magnetic field sensitivity of 4.98 Hz/nT. This is as much as two orders of magnitude higher frequency sensitivity than in other recently reported magnetometers, that also utilize the delta E effect, but which are composed of a cantilever structure and generally operate at lower frequencies.

3:45 PM EL03.10.06
**Cantilever Beam Magnetometer for Electric Field Induced Magnetization Measurements** Harinath Aireddy¹,²; ¹Alliance University, India; ²IIT Kharagpur, India

Optical double cantilever beam magnetometer was designed, fabricated and demonstrated its ability to measure magnetostriction (in-plane and out-of-plane), magnetization and magnetocrystalline anisotropy of ferromagnetic thin films as a function of the magnetic field. Notably, for the first time, here we demonstrate the well-established and simple cantilever beam technique for electric field modification of magnetization of ferromagnetic/ferroelectric heterostructures by considering the induced strains in ferromagnetic thin films through the converse piezoelectric effect in piezoelectric films. Moreover, this set-up also allows measuring the electromechanical properties such as transversal piezoelectric strain $(d_{31})$ and stress $(e_{31})$ coefficients of piezoelectric thin films. This magnetometer is simple in construction, inexpensive to manufacture, easy to operate along with noise subtraction provision and having sensitivity nearly 8 nm in the determination of cantilever beam deflection.

4:00 PM EL03.10.07
**Magnetoelectric Composite Sensor Based on Magnetostrictive Multilayers for Magnetic Frequency Conversion** Lars Thormählen, Matic Jovičević Klug, Sebastian Toxværd, Michael Höft, Eckhard Quandt, Jeffrey McCord and Dirk Meyners; Faculty of Engineering CAU Kiel, Germany

Magnetoelectric composites have been studied intensively in the recent past because of their preeminent magnetoelectric coupling, opening the path to highly sensitive magnetic field sensors operating at room temperature [1]. Moreover, this sensor approach yields the advantage to optimize the constituting phases independently. In the context of magnetic field sensing, the role of the magnetostrictive component is to respond to an external magnetic field by generating mechanical stress onto the piezoelectric phase. At least as important, irregular magnetization changes resulting from hysteretic effects have to be avoided in order to prevent significant noise contribution to the sensor output [2]. The multilayer approach increases the parameter space, which can be used to jointly attune the
magnetoelastic response towards high sensitivity and improved control of magnetization reversal [3].

The presented work focuses on thin film magnetostrictive phase composites, composed of (Fe90Co10)78Si12B10 multilayers. These layers are based on the stacking order unit Ta 5 / Cu 3 / MnIr 8 / FeCoSiB x [thickness in nm] with varying the FeCoSiB layer thickness x. The total thickness of the FeCoSiB layers is adjusted to 1 µm, 2 µm and 4 µm. The piezoelectric component is a 2 µm thick AlN layer. The constituents are grown on a Si substrate, one each side, by RF and pulsed DC sputter deposition respectively. Using UV lithography combined with dry and wet etching, magnetoelastic cantilever structures are fabricated with typical lateral dimensions of 2.3 mm x 25 mm.

Applying a multistep thermal treatment, parallel and antiparallel alignment of magnetizations in adjacent ferromagnetic layers is achieved in order to formulate a stable domain configuration in the magnetic layers [4].

The presentation reports on recent advances achieved by utilizing magnetostrictors that are exchange biased layer by layer. Applying magnetic frequency conversion yields minimum detectable magnetic fields as low as 50 pT/ Hz1/2 at 10 Hz [5], demonstrating the significantly improved performance of such macroscopic magnetoelastic field sensors.

Funding of the project work by the German Research Foundation through the CRC 1261 Magnetoelectric Sensors: From Composite Materials to Biomagnetic Diagnostics is gratefully acknowledged.


4:15 PM EL03.10.08
TiNiCu Thin-Film Shape Memory Alloy Substrates for Tunable Resonant Frequency Magnetoelectric Sensors Sabrina M. Curtis1,2, Duygu Dengiz1, Hanna Lewitz1, Lars Thommählen1, Justin Jetter1, Dirk Meyners1 and Eckhard Quandt1; 1Kiel University, Germany; 2University of Maryland, United States

Magnetic field sensors based on magnetoelectric composites can offer powerful diagnosis of biomagnetic signals originating in the brain and torso. Thin-film magnetoelectric (ME) composites comprised of FeCoSiB as the magnetostrictive layer and AlN as the piezoelectric layer have demonstrated sensors with a high sensitivity and low limit of detection at biomagnetic relevant frequencies. A magnetoelectric sensor will have its highest sensitivity when operated at its mechanical resonant frequency. Some medical operations, such as deep brain stimulation, would require a ME sensor with a tunable resonant frequency to locate the stimulated area of the brain during operation. This is a major limitation as most state-of-the-art ME sensors are mechanically designed to operate at one single resonant frequency. In this work, we show introducing a functionalized shape memory alloy (SMA) layer to the ME composite can offer a tunable ME sensor through a reversible gradual change in the Young’s modulus (E) of SMA material.

Here, AlN / FeCoSiB thin-film magnetoelectric composites are fabricated and characterized on functional TiNiCu SMA substrates. Through an induced temperature pulse, it is possible to gradually change the Young’s modulus of the SMA, thereby changing the mechanical resonant frequency of the magnetoelectric sensor [1]. Our analytical calculations show that the resonant frequency can be altered by 6% for a magnetoelectric sensor (2 µm AlN / 2 µm FeCoSiB / 25 µm TiNiCu / 100 µm Si) through a temperature induced reversible solid-to-solid phase transformation of the SMA from martensite (E = 41 GPa) to austenite (E = 83 GPa). For a 2.5 mm x 20 mm cantilever the resonant frequency can be gradually increased from 318 Hz to 340 Hz purely through this transformation. The difference in frequency between martensite and austenite phases becomes enhanced by increasing TiNiCu film thickness, or by eliminating the Si substrate.

Currently, MEMS compatible fabrication routes are being explored to build a full magnetoelectric sensor onto a TiNiCu substrate for experimentally verification. Characterization results on the effect of heat treatment and TiNiCu surface roughness on the growth and material performance of the piezoelectric layer (AlN) through piezoforce microscopy (PFM), X-ray diffraction (XRD), double beam laser interferometry (DBLI) and transmission electron
microscopy (TEM) will be presented.

Funding from the DFG is greatly acknowledged for this work


4:30 PM EL03.10.09
400MHz MEMS Antenna Based on Magnetoelastic Coupling Effect Huaihao Chen1, Xianfeng Liang1, Neville Sun1, Hwaider Lin2, Yuan Gao2 and Nian Sun1;2; 1Northeastern University, United States; 2Winchester Technology, LLC, United States

400MHz frequency band is the most commonly used band for Medical Implant Communications Service (MICS). However, most of recent antenna researches for this application are based on electromagnetic wave resonance, which lead to a comparable size to the wavelength [1, 2]. To solve this problem, a new antenna design based on the magnetoelastic coupling is introduced by our group [3], which is a thin-film bulk acoustic resonance (FBAR) antenna for 2.5GHz applications, based on the AlN resonator and magnetoelastic coupling. Since acoustic wave has smaller wavelength than electromagnetic wave, the antenna size can be easily scaled down by more than 100 times. However, for most AlN resonator designs, impedance matching is a problem because of the high electric impedance. Hence, a parallel antenna array structure is applied to reduce the impedance and increase the antenna gain [4]. In this work, nano-plate resonance (NPR) antenna arrays for 400MHz application are designed, fabricated and tested. This antenna is based on the magnetoelastic coupling between AlN thin film and FeGaB/SiO2 multilayer. The antenna array structure is shown in Fig. 1 (a) with 8um width and array numbers of 1, 4, 8 and 16. This strip structure resonates at in-plane mode, and this resonance is limited in width direction by the strip. The measured S-parameters are shown in Fig. 1 (b), with operating frequency of 371MHz, and 10dB-bandwidth of 3.875MHz. A radiation peak of S21 is observed clearly at the resonant frequency, and a peak antenna gain of -54.82dBi is achieved. This radiation peak is from the vibration and domain rotation of magnetic film. The measured S11 and calculated Z11 are shown in Fig. 2. For fewer array numbers, the impedance is higher, and the related return loss is also higher, so the radiation peak is cover by the baseline. For this reason, array structure with more than 16 strips is necessary for impedance matching and high antenna gain.

Reference

4:45 PM EL03.10.10
Electric Field Control of Magnetism in Double Perovskites Coupled with Bismuth Ferrite Vishal Ravi1, Bhagwati Prasad1, Yen-Lin Huang1, Jose Flores2, Fengyuan Yang2 and Ramamoorthy Ramesh1; 1University of California, Berkeley, United States; 2The Ohio State University, United States

Multiferroic materials offer exciting pathways to manipulate both magnetic and electronic properties simultaneously, which, in the case of bismuth ferrite, stem from the intrinsic linking of ferroelectric and antiferromagnetic degrees of freedom. By leveraging this fundamental coupling, we can modify and indeed switch the ferromagnetism of materials such as Co0.9Fe0.1 that sit adjacent to ferroelectric bismuth ferrite thin films, using only electric fields [1]. Using an oxide ferromagnet instead, such as La0.5Sr0.5MnO3, could potentially confer on these devices an improved fatigue life, as oxidation may be less critical [2].

This electric field control of magnetism through magnetic coupling opens up a vast array of applications, particularly in logic, data, and spintronics, where we may manipulate magnetic memories such as magnetic tunnel
junctions with the application of an electric field, instead of through more energy-intensive spin-transfer torque currents [3].

Double perovskites, such as Sr₂FeMoO₆ (SFMO) and Sr₂CrReO₆ (SCRO), are promising candidates for ferromagnets that may provide such coupling with bismuth ferrite. As half-metallic oxides with Curie points higher than room temperature, both materials exhibit spin-polarised currents and potential perpendicular magnetic anisotropy, which are desirable for magnetic tunnel junctions and other magnetoresistance-based devices [4][5]. Additionally, as these films are oxides rather than pure metals, they could provide an interface that is more robust against oxidation, leading to longer fatigue life.

We show the enhancement of these double perovskites’ coercive fields atop bismuth ferrite when compared to their isolated phases, which could uncover clues as to the strength of any magnetic coupling at the interface. We also explore magnetoelastic coupling by studying the effects of electric fields on the magnetisation of these double perovskites on bismuth ferrite, through giant magnetoresistance and anisotropic magnetoresistance measurements, in addition to correlated magnetic force microscopy and piezoresponse force microscopy images. These materials could lead to the next generation of low-power data storage and logic device technology.


mechanisms, a necessary step in ultimately optimizing system performance and efficiency. However, these can be strongly influenced by often experimentally inaccessible sub-surface effects, including thickness dependencies, microstructural or compositional heterogeneities, interfaces, and depending on the device design even simple geometric influences. Therefore, we recently introduced Tomographic-AFM for direct volumetric materials property mapping. 3-D resolved domain configurations and thickness dependent switching are specifically reported for monolithic La doped BiFeO$_3$, and a BiFeO$_3$/CoFeO$_3$ vertically aligned nanocomposite. In each case, ferroelectric domain nucleation and growth are further investigated as a function of thickness. Pure BiFeO$_3$ clearly obeys Kay-Dunn thickness scaling and a multistep switching process, and such multistep 180° switching is also observed for the La doped and nanocomposite films despite the substantially different local microstructure and even composition. Reconfigurations of domain walls upon electric field annealing furthermore lend insight into domain and domain wall stabilities.

**9:00 AM *EL03.11.02*

**Functionally Active Domain Walls in Ferroics and Multiferroics** *Marty Gregg*; Queen's Univ Belfast, United Kingdom

It is now well established that ferroelectric and multiferroic domain walls often have unique functional properties that are completely different from the domains that they surround: they can be semiconducting, metallic and even superconducting when the rest of the material is insulating; they can display magnetic order, which is absent elsewhere, and can possess aligned electrical dipoles when the matrix surrounding them is non-polar. In effect, ferroelectric and multiferroic domain walls represent a new class of nanoscale functional material. Crucially, they can be controllably shunted from point to point, created, or made to disappear; hence, a completely new paradigm of transient nanoscale devices may be possible, based on a “now-you-see-it, now-you-don’t” dynamic deployment of domain walls.

This talk will explore progress towards the realisation of these kinds of dreams and in particular show how injection, movement and removal of domain walls have enabled active control of nanoscale thermal conduction (in LaAlO$_3$ and LiNbO$_3$), the appearance of local negative capacitance (in Cu-Cl boracites), the existence of 1D mobile p-n junctions (in ErMnO$_3$ and Cu-Cl boracites) and the design of a new form of domain-wall memristor (in LiNbO$_3$).

**9:30 AM EL03.11.03**

**Design and Fabrication of ZnO-Based SMR Magnetoelectric Antennas for High-Gain Applications** *Xianfeng Liang*¹, Huaihao Chen¹, Neville Sun¹, Yuan Gao², Hwaider Lin² and Nian Sun¹; ¹Northeastern University, United States; ²Winchester Technologies, LLC, United States

Magnetoelectric (ME) antennas based on the suspended ME circular disk consisting of FeGaB/AlN thin-film have been demonstrated recently [1]. However, the FBAR devices are very fragile and delicate due to the releasing structure, although the complicated packaging process [2] is able to solve this problem. From the device point of view, the solid mounted resonator (SMR) with Bragg reflector has attracted much attention as a promising technology for the film bulk acoustic wave resonator (FBAR) devices [3]. Typically, the SMR devices are formed of a piezoelectric film, such as ZnO that is sandwiched between top and bottom metal electrodes, on top of a Bragg reflector. A resonance is created when a radio frequency (RF) signal is applied across the FBAR device. There are a variety of products such as filters [4], duplexer [4], and voltage controlled oscillators (VCOs) [5] based on SMR designs have been developed in past years.

In this work, we designed, fabricated and tested ZnO-based SMR ME antennas that operate at GHz with high gain performance. As shown in Fig. 1, the Bragg reflector consisting of three pairs of SiO$_2$/W layers was sputter deposited in one run with RF reactive magnetron sputtering for SiO$_2$ and DC sputtering for W. The piezoelectric ZnO layer was sputter deposited by RF reactive sputtering with Zn target and high-purity Oxygen gas. The XRD curves and rocking curves for ZnO films under different temperature were measured and exhibited in Fig. 2. In order to grow high quality ZnO films, it is vital to have sufficient ion bombardment during deposition. Therefore, high temperature of 450 degrees Celsius is preferred here with rocking curve FWHM of 2.25 degrees. After optimizing the performance of Bragg reflector and piezoelectric ZnO films, we fabricated and tested the SMR ME antennas. A gain enhancement of 12 dB was achieved in this novel design for robust ME antennas. Therefore, it is very promising in practical applications.
One of the key challenges to state-of-the-art antennas lies in their size miniaturization. Conventional antennas rely on an EM wave resonance and require a size of more than one tenth of the EM wavelength $\lambda_0$. In this work, a new miniature magnetoelectric (ME) antenna is presented utilizing the multilayer Bragg reflector structure of a solidly mounted resonator (SMR) to enhance small scale antenna gain up to -16 dBi. The antenna radiates using a magnetoelectric heterostructure consisting of AlN and FeGaB with resonator diameters of 500 um and 1000 um. Different ME resonator shapes and sizes are designed, fabricated and compared along with varying anchor widths and lengths to provide better impedance matching. The acoustic resonance in the heterostructure films operates with an out-of-plane mode of vibration so that the thickness of each layer was optimized to produce a resonant frequency at 1.5 and 2.45 GHz to allow for seamless on-chip integration with WiFi, Bluetooth and GPS devices. The SMR structure replaces the freestanding membrane structure \cite{1} with a Bragg acoustic reflector for concentrated energy confinement. The Bragg reflector was fabricated with a quarter wavelength mode configuration to create maximum particle displacement in the AlN and FeGaB layers. Three periods of alternating low and high acoustic impedance films, using silicon dioxide and tungsten respectively, were deposited on top of a silicon substrate to provide greater acoustic resonance within the ME heterostructure. Antenna gain measurements were performed in an anechoic chamber using a GSG probe and a reference horn antenna linked to a vector network analyzer. The robust features of the SMR has more advantages compared to its FBAR freestanding membrane counterpart allowing for low cost monolithic integration, high operating frequency, better thermal dissipation and structural stability that will be vital for small-scale antennas and other wireless applications.


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Composite multiferroics, composed of a magnetostrictive ferromagnet and a piezoelectric ferroelectric, have widely been targeted for beyond-CMOS logic due to their large coupling coefficients and high operating temperature\textsuperscript{1-3}. Magnetoelectric multiferroic systems potentially offer the lowest energy dissipation per bit operation in a scalable platform, yet significant materials challenges still exist in the field. For composite multiferroics, this requires finding
pathways to enhance piezomagnetic effects and coupling between layers, an effort that has seen relatively little work\(^4\). Here, we present a means to boost the magnetostriction of Fe\(_{1-x}\)Ga\(_x\) alloys and magnetoelectric coupling in a Fe\(_{1-x}\)Ga\(_x\)-(PMN-PT) composite multiferroic heterostructure through epitaxy.

In bulk, the magnetostriction coefficient of Fe\(_{1-x}\)Ga\(_x\) alloys versus Ga composition peaks near ~18% Ga occurring due to a phase change from the disordered A2 phase to an ordered BCC phase (D0\(_3\)), which reduces the magnetostriction coefficient\(^5\). A distinct advantage of thin film deposition is the potential to access metastable phases through epitaxy, allowing us to promote the chemically disordered BCC (A2) phase in our film at high (22%) Ga concentrations. We demonstrate that thin film epitaxy stabilizes a chemically disordered BCC Fe\(_{0.78}\)Ga\(_{0.22}\) alloy where the magnetostriction is enhanced by 200-300% relative to the bulk.

Transport-based magnetoelectric characterization shows 90 electrical switch of magnetic anisotropy and one of the largest converse magnetoelectric coefficients ever achieved at room temperature in a composite multiferroic\(^6\) and energy dissipation per operation scaling to 5.9 J cm\(^{-2}\), making our devices competitive with other state-of-the-art beyond CMOS technologies\(^6\). This hyperactive performance is achieved through epitaxial stabilization of a disordered, metastable phase of earth-abundant and rare-earth-free magnetostrictor, Fe\(_{0.78}\)Ga\(_{0.22}\). By epitaxially engineering our ferromagnetic layer to prevent the formation of deleterious intermetallic nanoregions, we provide a pathway to engineering new performance levels in rare-earth free magnetoelastic and magnetoelectric heterostructures.


**10:45 AM EL03.11.06**

**Room Temperature Lead Zirconium Palladium Titanate Multiferroic Nanoscale Films**

Karuna K. Mishra, Alvaro Instan, Mohan K. Bhattarai and Ram S. Katiyar; University of Puerto Rico, United States

Growth of single-phase magnetoelectric materials and their analysis of coupling mechanisms between ferroic order parameters (spin and polarization) is important from the point of view of next generation logic and memory devices. Herein, we report fabrication, dielectric, ferroelectric and magnetic measurement of a Pd-doped room-temperature magnetoelectric multiferroic Pb(Zr\(_{0.20}\)Ti\(_{0.80}\))\(_{0.70}\)Pd\(_{0.30}\)O\(_{3-\delta}\) (PZTPd) thin film. Highly oriented PZTPd thin films were deposited on (LaAlO\(_3\))\(_0.3\)((Sr\(_2\)AlTaO\(_6\))\(_0.7\)) substrates by following laser ablation processes in oxygen atmosphere using pulsed laser deposition technique. X-rays diffraction studies revealed that the film had tetragonal phase with c-axis orientation. The surface morphology studies using atomic force and scanning electron microscopic techniques suggest a smooth and homogeneous distribution of grains on the surface of the film with roughness \(\sim 1.8\) nm. Temperature dependent dielectric measurements were carried out in Pt/ PZTPd /LSMO metal-ferroelectric-metal capacitors that showed diffused behavior over a large range of temperatures at several frequencies, and exhibited a higher dielectric constant \(\sim 3000\) at 100 Hz at room temperature. The polarization hysteresis loops were obtained at room temperature, attributed to its ferroelectric behavior. Piezo force microscopy suggests a random polarization orientation in a grown film, whereas polarizations could be switched easily with a positive and negative electric bias. A well-saturated magnetization \(M-H\) loop with remanent magnetization of 1.6 emu/cm\(^3\) was observed at room temperature. The reason for magnetization in PZTPd thin film is found to be due to mixed oxidation states of Pd\(^{2+}\)/Pd\(^{4+}\) in the Pb(Zr\(_{0.20}\)Ti\(_{0.80}\))O\(_3\) matrix as complemented by x-rays photoelectron spectroscopic results. These findings suggest that our thin films are multiferroic (ferroelectric-ferromagnetic) at room temperature. The details will be presented in the meeting.

**11:00 AM EL03.11.07**

**Hydrogen-Driven Switching of Magnetic Anisotropy—Insights from First-Principles**

Konstantin Klyukin\(^1\), Geoffrey S. Beach\(^1\) and Bilge Yildiz\(^2\); \(^1\)Massachusetts Institute of Technology, United States; \(^2\)Department of Nuclear Science and Engineering, United States

Resistive and magnetic switching phenomena have recently attracted large interest for ultra-scaled non-volatile
memory and logic devices. The incorporation of hydrogen can significantly influence magnetic and electronic properties of functional materials allowing effective tuning magnetic anisotropy, magnetic moment and electroresistance. Despite extensive experimental investigations, very little is known about the phenomena on a molecular level and systematic investigations are needed to provide fundamental insights on the physical origin of phenomena. In this work, we consider a series of heterostructures (Co/Pd, MgO/Fe, etc) exhibiting perpendicular magnetic anisotropy (PMA) and employ density functional theory calculations (DFT) to determine the critical concentration of hydrogen needed for magnetic anisotropy switching. We show that anisotropy switching effect is mainly attributed to the electronic structure changes at the interface, while lattice expansion caused by hydrogen insertion plays a minor role. These results clarify the underlying mechanisms of magnetic anisotropy switching and help optimizing material combinations for hydrogen-based magneto-ionic devices.

11:15 AM EL03.11.08
First-Principles Prediction of Muon Stopping Sites in Magnetoelectric Cr$_2$O$_3$

Martin H. Dehn$^{1,2}$, Stefan Holenstein$^{3}$, J. Kane Shenton$^{4}$, Quintin N. Meier$^{4}$, Donald J. Arseneau$^{2}$, Sarah Dunsiger$^{3}$, Bassam Hitti$^{5}$, Hubertus Luetkens$^{3}$, W Andrew MacFarlane$^{2,1}$, Ryan M. McFadden$^{1}$, Gerald D. Morris$^{2}$, Zaher Salman$^{6}$, Nicola Spaldin$^{4}$, Michael Fechner$^{6,4}$ and Robert F. Kiefl$^{1,2}$; $^{1}$University of British Columbia, Canada; $^{2}$TRIUMF, Canada; $^{3}$Paul Scherrer Institut, Switzerland; $^{4}$ETH Zurich, Switzerland; $^{5}$Max Planck Institute for the Structure and Dynamics of Matter, Germany

Recent conceptual advances in our understanding of magnetoelectrics have led to renewed interest in materials such as Cr$_2$O$_3$. Muon spin rotation (µSR) is a promising technique for investigating recently predicted local magnetoelectric phenomena, acting as a probe of the local magnetic field at the muon stopping site(s). The ab initio prediction of muon stopping sites in materials is crucial to correctly interpreting µSR experiments. However, the quantum nature of the muon, together with its short lifetime (~2.2 µs), allow the muon to exhibit a rich range of dynamical phenomena that are challenging to capture using standard first-principles methods. Furthermore, the impact of the positively charged muon on the surrounding lattice can lead to significant changes to the muon behaviour and experienced local field.

Here we report on a µSR study of Cr$_2$O$_3$, focussing on the theoretical prediction of muon stopping sites and dynamics. We find that quantum corrections beyond the harmonic approximation are required to obtain accurate energy barriers between muon stopping sites. We also find strong evidence for a charge-neutral muon-polaron complex in Cr$_2$O$_3$, stabilised by a Jahn-Teller distortion. The latter finding has important implications for the charge state and behaviour of hydrogen defects in Cr$_2$O$_3$ and related materials.

**SYMPOSIUM EL04**

TUTORIAL: Introduction to Chalcogenide Discovery and Design
December 1 - December 1, 2019

* Invited Paper

TUTORIAL
Introduction to Chalcogenide Discovery and Design

Sunday Morning, December 1, 2019
Hynes, Level 2, Room 201
This tutorial will offer a brief introduction to theory and computations as well as to synthesis and characterization, in particular when applied to sulfides, selenides, tellurides, and multi-anionic systems. Oxide materials will also be included as it relates to chalcogenides more broadly. The focus of the symposium will be on understanding the distinctive nature of this group of materials in the context of materials discovery and design.

8:30 AM
**Density Functional Theory and Electronic Structure Calculations** Elif Ertekin, University of Illinois at Urbana-Champaign

We will discuss the application of first-principles density functional theory to the predicting bulk and defect properties of chalcogenides. This discussion will include a brief introduction to density functional theory, a practical discussion of how to carry out simulations, and an in-depth look at which properties can be reliably predicted, which properties require more scrutiny, and why. Our discussion will emphasize and distinguish between ground state and excited state, and equilibrium and non-equilibrium (i.e. response functions) properties of materials. Drawing from the fields of photovoltaics and thermoelectrics, several examples pertaining to chalcogenides will be described, including bulk properties and the prediction of phase stability, and simulations of point defects (formation energies, charge transition levels) and related properties such as dopability and carrier concentrations. This discussion is aimed at providing a basic understanding of the level of accuracy that is achievable or to be expected from density functional theory, as well as to serve as a guide to non-specialists what to look for when assessing results from electronic structure calculations.

9:15 AM
**Bulk Crystal Growth and Phase Diagrams for Metal Chalcogenides** Albert Davydov, National Institute of Standards and Technology

The tutorial focuses on single crystal growth of metal chalcogenide electronic materials, including layered van-der-Waals compounds, such as TMDC semiconductors and semimetals, Bi2(Se,Te)3 based topological materials, InSe and GeSe semiconductors, etc. The experimental methods will cover: a) vapor growth techniques including sublimation/crystallization and chemical vapor transport (CVT); and b) melt solidification that includes crystallization from near-stoichiometric compositions as well as from ‘self-flux’ or ‘foreign-element-flux’ solutions. Use of phase diagrams will be exemplified to guide choices for the crystal growth approaches: for example, why Bi2Se3, InSe, and GeSe can be grown both by CVT and Bridgman (i.e., direct melt solidification) methods, while TMDCs such as MoSe2 and WS2 can only be grown by CVT and not from the melt? The importance of often ignored ‘pressure variable’ when describing phase diagrams for metal-chalcogen systems will also be highlighted.

10:00 AM BREAK

10:30 AM
**High-Throughput Computations** Prashun Gorai, Colorado School of Mines and National Renewable Energy Laboratory

This talk will cover the recent developments in high-throughput (HT) computations that have led to a new paradigm in materials discovery and design. First, typical workflows for HT computations will be introduced followed by a discussion of software for HT workflows. Next, several examples of successful chalcogenide materials discovery, enabled by HT computations, will be discussed while also highlighting the challenges and downfalls of HT computations. Finally, materials databases that have resulted from these large-scale computational efforts will be briefly discussed. In closing, we will review the role of data informatics (e.g. data mining, machine learning) in the context of HT computations.

11:00 AM
**Thin Film Characterization** Akshay Singh, Massachusetts Institute of Technology
Now that we have prepared the bulk crystals and thin films of TMDs, how do we characterize the purity of the synthesized materials? Also, how do we qualify these materials for photonics and opto-electronic applications? In this part of the tutorial, we will discuss optical constants measurements using spectroscopic ellipsometry and fourier transform infrared spectroscopy (FTIR). We will discuss how performing cross-sectional transmission electron microscopy (TEM, to measure native oxides), atomic force microscopy (AFM, to measure roughness), and X-ray photoelectron spectroscopy (XPS, to measure composition profiles) techniques are important to uncover actual optical constants from thin films and bulk crystals. These techniques are also shown to help differentiate chalcogenides from undesirable oxide phases, and improve synthesis procedures.

11:30 AM
Tailor-Made Chalcogenide Colloids: Tuning Size, Composition and Structure of Nanomaterials Maksym Yarema, ETH Zürich

Colloidal chalcogenide nanocrystals are convenient building blocks of various solution-processed devices, such as displays, photovoltaics, thermoelectrics, and phase-change memory. Likewise, chalcogenide colloids are handy materials for the fundamental and use-inspired research, featuring size-dependent optical and electronic properties in addition to composition dependences and structure diversity. In this talk, we will summarize the state-of-the-art for the colloidal chalcogenide nanocrystals, outline challenges and future directions in the field. In particular, we will focus on multicomponent nanocrystals, for which composition-dependent effects are superimposed on size dependences. We will also discuss opportunities for chalcogenide colloids with metastable and amorphous structures.
lower temperatures due to facile diffusion and chemical reactions with and within the flux itself. The liquid fluxes are bona-fide solvents similar to conventional organic or aqueous solvents. These reactions can produce a wide range of materials, often metastable, from oxides to intermetallics, but typically the formation mechanisms are poorly understood. In this talk I will describe how we design, approach, perform, observe, understand, and engineer the formation of compounds from inorganic melts. I will focus on how novel chalcogenides can form using the fluxes but also design concepts such as the “dimensional reduction” and “panoramic synthesis”. For example, in systems such as K-Cu-S and K-Sn-S compounds that span metallic and insulating behavior can be isolated. Common structural motifs within these materials systems belie structural precursors in the melt that may be controlled by tuning reaction conditions and composition. Using complementary techniques of in-situ x-ray diffraction we can create time-dependent maps of reaction space and probe the mobile species present in melts. An important link in our chemistry is the concept of a ‘functional group,’ a fragment of a few atoms that behave predictably when combined with other functional groups or reagents. When well-defined building blocks are present and stable in the reaction, prospects for increased structural diversity and product control increase substantially. In such tunable and dynamic fluxes, synthesis can be directed towards new materials with an astonishing variety of properties ranging from nonlinear optics to energy conversion.

9:15 AM EL04.01.02
Cation Order and Band Gap Tuning across the Visible Spectrum Robert Makin III1, Krystal York1, Steven M. Durbin1, Nancy Senabulya2, Christina Jones2, Zihao Deng2, Logan Williams2, James Mathis2, Emmanouil Kioupakis2, Roy Clarke2 and Roger Reeves3; 1Western Michigan University, United States; 2University of Michigan, United States; 3University of Canterbury, New Zealand

Interest in alternative semiconductors to traditional indium- and gallium-containing compounds has prompted a large number of potential materials to be investigated recently, especially where earth-abundant, sustainably-sourced elements are available constituents. In the case of ternary heterovalent compounds such as those comprised of cations from columns II (e.g. Zn, Mg) and IV (e.g. Ge, Sn) along with an anion from column V (e.g. N, P), an interesting opportunity for band gap tuning arises from the ability to introduce a selective degree of ordering among the cation atoms [1,2]. Although somewhat analogous to what has been previously demonstrated in the case of the compound GaInP2, we see the opposite trend in these heterovalent materials: the band gap energy decreases with decreasing cation ordering. Using MgSnN2 and ZnSnN2 as a case study, we demonstrate an unprecedented degree of band gap tuning (a range of ~0.9 eV for ZnSnN2 and ~1.6 eV for MgSnN2) in each material as the order parameter is varied from its minimum value of zero to a maximum value of unity. Consequently, the two materials can be used to tune over the entire visible spectrum, from approximately 1.12 eV to 3.43 eV – without alloying. Instead, the order parameter is tuned by adjustment of process parameters describing the plasma-assisted molecular beam epitaxy growth technique, with better than 1% reproducibility. The order parameter is extracted from any of the following techniques: in-situ reflection high-energy electron diffraction (RHEED), x-ray diffraction, or Raman spectroscopy. We find that the value obtained from each technique agrees to within two decimal places. We demonstrate that the band gap variation with cation ordering can be understood in terms of an Ising model, which provides a numerical foundation for understanding variable ordering in terms of two endpoint states (fully ordered, and fully randomized). The major factor influencing the semiconductor band gap is in fact the motif distribution which correlates to the order parameter. The trend is replicated by hybrid density functional theory calculations implemented using the Vienna Ab initio Simulation Package (VASP); disordered structures were modeled using 2x2x2 special quasi-random supercells (SQS). We further demonstrate the viability of this approach by applying the model to published data for ZnGeN2, ZnSnP2, CuGaS2 and CuInS2, showing a reliable method for predicting the expected band gap energy as a continuous and quantitative function of cation ordering, and explaining the wide variation reported in the literature [3].

9:30 AM BREAK

10:00 AM *EL04.01.03
Coupling of Structure and Magnetism in Some $AB_4Q_8$ Lacunar Spinel Compounds
Emily Schueller, Julia Zuo, Stephen Wilson and Ram Seshadri; University of California, Santa Barbara, United States

The lacunar spinels $AB_4Q_8$ are compounds whose properties are dominated by tetrahedral clusters of $B$ atoms and are exemplified by compounds such as GaV$_4$Se$_8$. This compound is known to undergo a polar distortion to a ground state structure in the $R3m$ space group, and orders ferromagnetically with a relatively small magnetic moment. We develop an understanding into the relationship between crystal structure and magnetic order in this material, and the influence of electron correlations in establishing the observed ground state using first-principles density functional theory (DFT) electronic structure calculations. Because electrons are delocalized within V$_4$ clusters but are localized between them, the usual approaches to simulate electron correlations — such as the use of the Hubbard $U$ in DFT + $U$ schemes — do not adequately recreate the experimental ground state. Additionally, we find that magnetism and crystal structure are strongly coupled in this material, and only certain arrangements of magnetic moment within a V$_4$ cluster can stabilize the observed structural distortion. Once distorted, these compounds are capable of exhibiting skyrmionic ground states, and these are described in GaV$_4$Se$_8$ and some related compounds.

10:30 AM EL04.01.04
Designer Metal-Insulator Transition Compounds from Bayesian Optimization
Yiqun Wang, Akshay Iyer, Wei Chen and James Rondinelli; Northwestern University, United States

The chalcogenide lacunar spinel structures with composition AM$_4Q_8$ can host novel electronic responses, including metal-insulator transitions (MITs) for resistive random-access memory platforms and skyrmionic spin textures for novel spin-based logic. Indeed, many of the known compounds within the family are narrow-gap semiconductors that undergo structural, electrical, and magnetic phase transitions with external stimuli, e.g. pressure, electric pulse. Based on the current understanding of how local structure affects these functional responses, one may ask the naïve question of how to rationally select the chemistries for quaternary spinels to achieve improved performance and to what extent Vegard’s principle holds in ordered compositional variants. Here we utilize Bayesian optimization with Gaussian processes (BOGP) to identify quaternary lacunar spinels superior to their ternary counterparts. Our model successfully discovers most of the compounds on the Pareto front by exploring only less than 20% of the entire design space, leading to accelerated materials discovery via BOGP approach. We then perform density functional theory simulations to both validate the MITs in the predicated compounds and assess synthesizability, but also to expand our materials physics understanding. Our model presents an effective way for accelerated materials design and discovery in chemical composition space without using extra features (e.g. bond length, electronegativity). This method may be readily applied to other challenges in materials sciences and chemistry, especially where existing data is limited, and new data acquisition is costly.

10:45 AM EL04.01.05
Computational Prediction and Experimental Discovery of Semiconducting High-Entropy Chalcogenide Alloys
Zihao Deng, Alan Olvera, Joseph Casamento, Juan Lopez, Logan Williams, Ruiming Lu, Guangsha Shi, Pierre F. P. Poudeu and Emmanouil Kioupakis; University of Michigan, United States

High-entropy materials are formed by mixing typically five or more principal components into a single crystal structure, and show improved thermodynamic stability due to the large configurational disorder. This simple design principle has led to the discovery of a series of novel crystalline materials stabilized by the configurational entropy, from high-entropy metallic alloys, to entropy-stabilized oxides, carbides, and borides. While significant progress has been made to synthesize entropy-stabilized metals and ceramics for structural applications, little attention has been paid to the discovery of new semiconducting materials using the design principle of entropy stabilization.

Here, we present a new class of entropy-stabilized semiconducting alloys based on the IV-VI binary chalcogenides, namely Ge$_x$Sn$_{1-x}$Pb$_{1-z-y}$Sb$_z$Se$_{1-t}$Te$_{1-t}$ high-entropy chalcogenides (HECs). By utilizing high-throughput first-principles calculations, we investigate the thermodynamic stability of HECs over their entire composition space, and show that more than 50% of the investigated compositions are stable with respect to phase segregation to the competing binary ingredients at the experimental synthesis temperature. We further studied the enthalpic effect of the individual elements via machine learning with Gaussian Kernel-Ridge Regression on the high-throughput data. We show that
Sn and Se lower the enthalpy of mixing, while S is detrimental to the phase stability of HECs. We validate our theory prediction by synthesizing the equimolar GeSnPbSSeTe HEC using solid-state synthesis techniques. We find that the HEC crystalizes in a single-phase rocksalt structure upon fast quenching in liquid nitrogen, and shows a reversible phase transition in both DSC and temperature-dependent XRD, driven by the configurational entropy. In terms of their functional properties, equimolar HEC shows promising ambipolar dopability with Bi donors and Na acceptors, which opens up a wide range of possibilities for semiconducting electronic and energy applications. Our work demonstrates the potential of entropy stabilization in the discovery of novel multicomponent semiconductor alloys.

11:00 AM EL04.01.06
Designing Chalcogenide Interfaces as a Pathway to Topological Devices  Stephen D. Albright1,1, Ke Zou2, Frederick J. Walker1,1 and Charles H. Ahn1,1,1; 1Yale University, United States; 2University of British Columbia, Canada

Engineering interfaces of topological materials with other classes of functional materials, such as oxides, ferromagnets, or superconductors, serves as the basis for designing novel electronic devices based on topological materials. Topological crystalline insulators (TCIs), such as SnTe, are a particularly promising class of materials, possessing the same properties as conventional topological insulators and controllable by electric fields when integrated with oxide field effect devices. This work presents growth and characterization of SnTe films thin enough for incorporation with other functional materials. X-ray diffraction and atomic force microscopy confirm we achieve single-domain and continuous SnTe film growth on SrTiO3 substrates by integrating molecular beam epitaxy with net SnTe sublimation at raised substrate temperatures. By analyzing the hole carrier density, extracted from Hall measurements over a range of film thicknesses, we observe two-dimensional carriers confined to the SnTe/SrTiO3 interface. Magnetoconductance measurements confirm the observation of two-dimensional transport and furthermore reveal that conduction is consistent with topological states. The growth of ultrathin TCI films on an oxide substrate presented here provides a foundation for designing additional TCI interfaces and engineering novel topological devices.

11:15 AM *EL04.01.07
Synthesis of Compounds with Targeted Structures—Probing the Energy Landscape with Designed Precursors  David Johnson1 and Sven Rudin2; 1Univ of Oregon, United States; 2Los Alamos National Laboratory, United States

Unraveling structure-property relationships is often limited by the inability to test proposed relationship by synthesizing either isomaterials compounds or homologous series of compounds. Major limitations to discovering these "missing" compounds with targeted structures include the lack of synthetic routes to compounds that are metastable and the challenge of predicting the energy landscape around local free energy minima to assess potential metastability. Traditional solid-state reactions are typically diffusion limited, producing thermodynamic products as a result of high reaction temperatures and long reaction times. Fluid phase approaches are nucleation limited with high diffusion rates enabling much of the energy landscape to be explored, but limited means to control what crystallizes. We will discuss a third approach, based on controlling the composition of an amorphous intermediate on the nanoscale. Nucleation is typically the rate-limiting step, but slow diffusion rates limit the extent that the energy landscape is explored. Hence the nanoarchitecture of the precursor is preserved, enabling many new compounds to be synthesized that are intergrowths of two targeted constituents. The periodic structure of the precursor enables a variety of analytical approaches to be used to determine the reaction pathway, total and local compositions, and the structure of interlayer stabilized structures. In parallel, we have developed a theoretical approach to probe the energy landscape around proposed target compounds. We create islands of different known structures of a particular stoichiometry between slabs of the other constituent structure and allow the system to relax. One of three limiting situations typically occurs. The interlayer atoms may react with the known structure, rearrange into a disordered "island of disaster" or they can maintain the initial structure with surface and edge distortions. These last cases, where the structures are preserved, become potential synthetic targets. This approach lets islands with structures or compositions not known as bulk compounds to be tested for stability. Several examples will be presented showing that predicted structures could be synthetically prepared.

11:45 AM EL04.01.08
Control of Structural Polymorphism in MnTe  Yanbing Han1,2, Sebastian Siol1, Aaron Holder2, Bethany
Matthews⁴, Matthew Young¹, Janet Tate⁴, Stephan Lany¹, Qun Zhang² and Andriy Zakutayev¹; ¹National Renewable Energy Laboratory, United States; ²Fudan University, China; ³University of Colorado Boulder, United States; ⁴Oregon State University, United States

Chalcogenide semiconductors constitute an important class of electronic materials with a broad range of crystal structures and a plethora of useful properties. Independent control of chalcogenide composition and structure holds a promise to design these properties for practical applications. Recently, we demonstrated synthesis of low-density polymorphs of chalcogenide semiconductors by heterostructural alloying in the MnTe₁₋ₓSeₓ materials system [1]. The resulting “negative pressure” MnTe₀.₅Se₀.₅ alloy has noncentrosymmetric wurtzite structure and piezoelectric response that is not present in either of the MnSe or MnTe parent compounds.

This presentation will focus on two additional methods to synthesize metastable wurtzite structure of manganese telluride (MnTe), as a prototypical chalcogenide material with known polymorphism. The first approach is alloying MnTe with a small amount (10-20 %) of ZnTe, which drives the structural phase transition similar to that in yttria-stabilized zirconia (YSZ) [2,3]. The second approach is templated growth on MnTe on 5 nm thin ZnTe seed layers deposited on amorphous glass substrates.[3] Both methods lead to metastable wurtzite polymorph of MnTe with very different properties compared to the ground state nickeline structure, including 1 eV wider band gap and 1000–10 000 times lower electrical conductivity.

Overall, these results demonstrate new methods to synthesize metastable polymorphs of chalcogenide semiconductors, broadening the range of materials design methods for this class of compounds.

[4] Y. Han et al. under review
For the last 30 years, researchers in Southampton have been developing a novel family of chalcogenide glasses, driven initially by infrared optical applications. These materials, which include gallium and lanthanum sulphides and selenides, offer improved thermal and mechanical properties over commercially available chalcogenides. Today, the application space has shifted considerably and these same materials are increasingly being explored for electronic applications.

In this talk, we describe our work in this field, giving an overview of a glass fabrication and characterization before focusing on three specific devices under development; photonic crystals, flexible thermoelectric generators and electrochemical cells leading to new research in chalcogenide based solid-state batteries.

Three-dimensional complete photonic bandgap materials or photonic crystals block light propagation in all directions. The rod-connected diamond structure exhibits the largest photonic bandgap known to date and supports a complete bandgap for the lowest refractive index contrast ratio down to $\sim 1.9$. We have confirmed this threshold by measuring a complete photonic bandgap in the infrared region in Sn–S–O ($n \sim 1.9$) and Ge–Sb–S–O ($n \sim 2$) inverse rod-connected diamond structures. The structures were fabricated using a low-temperature chemical vapor deposition process via a single-inversion technique.

Flexible thermoelectric generators (TEGs) can provide uninterrupted, green energy from body-heat, overcoming bulky battery configurations that limit the wearable-technologies market today. High-throughput production of flexible TEGs is currently dominated by printing techniques, limiting material choices and performance. Here we report on the properties of roll to roll sputtered Bi2Te3 films are reported and we demonstrate the ability to tune the power factor by lowering run times, lending itself to a high-speed low-cost process. To further illustrate our route to high speed printing, we fabricate a thermoelectric device using Virtual Cathode Deposition, a novel high deposition rate PVD tool, for the first time. This Bi2Te3/Bi0.5Sb1.5Te3 TEG exhibits $S = 250 \ \mu V/K$ per pair and $P = 0.2 \ \text{nW}$ per pair for a $20 \ ^\circ C$ temperature difference.

Finally we have recently fabricated electrochemical metallization cells using a GaLaSO solid electrolyte focussing on endurance testing. Using ITO and silver electrodes, up to 4000 cycles were measured, (limited by the measurement equipment) with some deterioration in the on/off ratio seen after 1000 cycles and we are currently optimizing performance through doping with Se.

2:30 PM *EL04.02.03

**Dimensional Control of Light-Matter Interaction in Perovskite Chalcogenides**  
Jayakanth Ravichandran;  
University of Southern California, United States

Perovskite Chalcogenides are a new class of semiconductors, which have large chemical and structural tunability that translates to tunable band gap in the visible to infrared part of the electromagnetic spectrum. Besides this band gap tunability, they offer a unique opportunity to realize large density of states semiconductors with high carrier mobility. In this talk, I will discuss some of the experimental advances made both in my research group and in the research community on the theory, synthesis of these materials and understanding their optoelectronic properties.

Perovskite structure is composed of an octahedrally coordinated transition metal or main group element with anions such as oxygen, chalcogen or halogens. The octahedra is typically connected in the corners and the voids are filled by alkali, alkaline or rare earth elements. The valence and the size of the cations and anions can lead to different connectivity of these octahedra, which offers a knob to control both the chemical composition and the dimensionality of these materials. Moreover, the large number of elements in the periodic table can be accommodated in these extended perovskite and related structures, which allows us finer knobs to control the physical and chemical properties, in our case, we tailor light-matter interaction precisely over a broad energy range spanning the visible to infrared spectrum. We leverage this effect in early transition metal based perovskite chalcogenides and related phases to achieve properties such as highly anisotropic absorption and refraction ($\text{BaTiS}_3$, $\text{Sr}_{1+x}\text{TiS}_3$), unconventional band gap evolution ($\text{BaZrS}_3$ and $\text{Ba}_{n-1}\text{Zr}_n\text{S}_{3n+1}$ for $n \geq 1$). Finally, I will provide a general outlook for future studies on these exciting new class of materials.

References:
SESSION EL04.03: Phase-Change Functionality for Computing
Session Chairs: Paul Fons and Prashun Gorai
Monday Afternoon, December 2, 2019
Hynes, Level 1, Room 104

3:30 PM *EL04.03.01
In-Memory Computing—Accelerating AI Applications Evangelos S. Eleftheriou; IBM Research GmbH, Switzerland

In today’s computing systems based on the conventional von Neumann architecture, there are distinct memory and processing units. Performing computations results in a significant amount of data being moved back and forth between the physically separated memory and processing units. This costs time and energy and constitutes an inherent performance bottleneck. It is becoming increasingly clear that for AI application areas, we need to transition to computing architectures in which memory and logic coexist in some form. Brain-inspired neuromorphic computing and the fascinating new area of in-memory computing or computational memory are two key non-von Neumann approaches being researched. A critical requirement in these novel computing paradigms is a very-high-density, low-power, variable-state, programmable and non-volatile nanoscale memory device. There are many examples of such nanoscale memory devices in which the information is stored either as charge or as resistance. However, one particular example are phase-change-memory (PCM) devices, which are very well suited to address this need, owing to their multi-level storage capability and potential scalability.

In in-memory computing, the physics of the nanoscale memory devices, as well as the organization of such devices in cross-bar arrays, are exploited to perform certain computational tasks within the memory unit. For instance, crossbar arrays of PCM or other memristive devices can be used to store a matrix and perform analog matrix-vector multiplications at constant O(1) time complexity without intermediate movements of data. I will present how computational memories accelerate AI applications and will show small- and large-scale experimental demonstrations that perform high-level computational primitives, such as ultra-low-power inference engines, optimization solvers including compressed sensing and sparse coding, linear solvers and temporal correlation detection [1-3]. Moreover, the efficacy of this approach to efficiently address not only inferencing but also training of deep neural networks is discussed.

However, enhancing the performance of the devices is crucial for increasing the range of targeted applications and building the next-generation of computational memory-based systems. For example, PCM devices exhibit a limited dynamic range and the conductance response is highly nonlinear and stochastic. Moreover, additional technology-specific device behavior such as the conductance response asymmetry and temporal evolution of conductance values pose significant challenges for PCM. One approach to address some of these challenges is advances in synaptic-cell architectures. We will show how by using multiple PCM devices as a single synaptic unit we can improve the conductance change granularity, as well as the effects of nonlinearity, asymmetry, stochasticity and drift of PCM cells[4]. A second approach is the so-called projected PCM concept that aims to decouple the device read out from the electrical properties of the amorphous phase, thus significantly reducing the drift, noise and temperature-sensitivity [5-6]. We will also elucidate implementation and functionality of this class of devices.

The results show that this co-existence of computation and storage at the nanometer scale could be the enabler for new, ultra-dense, low-power, and massively parallel computing systems. Thus, by augmenting conventional computing systems, in-memory computing could help achieve orders of magnitude improvement in performance and efficiency.


4:00 PM EL04.03.02
Switching Effects in Ge-Te/Sb-Te Superlattices in the Presence of External Magnetic Fields Kirill V.
Interfacial phase-change memory (iPCM) based on chalcogenide superlattices have lower switching energy requirements than conventional phase-change memory [1]. The reason for this is believed to be associated with the minimization of thermal losses in the superlattice during the switching process [1-4]. Recently, it was reported that iPCM devices based upon Ge-Te/Sb-Te superlattices exhibit differences from GeSbTe-alloy phase-change memory devices, such as resistance dynamics at elevated temperatures [5]. Furthermore, bipolar switching [6] and the dependence of the switching properties of iPCM devices on the presence of an external magnetic field was found [7]. The latter suggests that the presence of an external magnetic field can affect the structure of Ge-Te/Sb-Te superlattices. In the current work, we used pre-magnetized TbFeCo bottom contacts in iPCM devices in order to explore the effects of magnetic fields applied to Ge-Te/Sb-Te superlattice films during their growth with regards to the switching properties of the fabricated iPCM devices.

The iPCM devices fabrication process have been reported in ref. [8, 9]. The bottom contact was formed by a 50 nm TbFeCo layer grown at room temperature. The contact was magnetized by applying an external magnetic field (1.5 T) after deposition at room temperature. Lower temperatures were used (150°C) for the superlattice growth in order to prevent demagnetization of the TbFeCo contacts. Thus, the Ge-Te/Sb-Te superlattices were grown in the presence of the external magnetic field induced by the bottom contact and this condition was maintained during device characterization: R-V, R-I, and I-V curves were obtained.

Under normal conditions, Ge-Te/Sb-Te superlattice structures used as an active (programmable) medium in iPCM devices do not contain elements sensitive to magnetic fields. However, according to recent reports [7], an iPCM device in the presence of an external magnetic field during the switching process at elevated temperatures, could lead to the localization of spin-polarized electrons, which would in turn result in a significant change in the resistance of the device. Therefore, a superlattice film grown in the presence of a magnetic field could exhibit enhanced magnetoresistance effects, especially when the switching process is performed at elevated temperature. In this work, it is shown that iPCM devices grown in the presence of a magnetic field have switching characteristics different from conventional iPCM devices. For example, bipolar switching was achieved in DC mode, similar to previously reported results [6]. But in the short pulse switching regime, it was found that the RESET process shows a lower switching voltage than it is required for the SET process, which is opposite to the typical iPCM switching behavior.

In conclusion, we achieved enhancement of magnetoresistance effects in Ge-Te/Sb-Te superlattices by use of a novel iPCM device structure with pre-magnetized bottom contacts.


4:15 PM EL04.03.03
Low Temperature Characterization of Resistance Drift in Amorphous Ge:Sb:Te3 Raihan Sayeed Khan, Helena Silva and Ali Gokirmak; University of Connecticut, United States

Phase change memory (PCM) is an emerging high speed, high density, scalable non-volatile memory that can be switched electrically between amorphous (high resistivity) and crystalline (low resistivity) phases of chalcogenides materials such as Ge:Sb:Te3 (GST) [1]. The resistance of GST drifts spontaneously after amorphization following a power law [2]. This behavior limits the utilization of intermediate states for multi-bit storage due to potential overlap of different resistance levels. Multiple processes may be contributing to resistance drift, including structural relaxation, crystallization and charge trapping. It is possible to get a better understanding of the relative contributions of these various phenomena by performing measurements at cryogenic temperatures.

In this work, we have electrically characterized resistance drift of melt-quenched amorphous Ge:Sb:Te3 (GST) line cells [3] in the 125K – 300 K temperature window with and without optical illumination using high resolution I-V
sweeps. Each device is amorphized using a 500 ns pulse and drift is monitored at the same temperature up to 10^4 seconds. We have found the drift coefficients to be approximately 0.1 in dark, with slightly decreasing trend with decreasing temperature. The experiments under light show a significant decrease in cell resistance and a distinctly different drift behavior from dark. Periodic switching of light shows upward resistance drift in dark and recovery under light with long time constants (> 10^2 s at 150K). The presence of resistance drift at cryogenic temperatures with similar drift coefficients as room temperature, as well as different behaviors with and without light, suggest that charge trapping is the dominant mechanism that contributes to resistance drift in amorphous GST.

References:

4:30 PM EL04.03.04
Solution Processed Copper Sulfide Based Resistive Switching Devices Prashant Kumar1, Murali Gedda1, Kalaivanan Loganathan1, Dipti Naphade1, Abhinav Sharma1, Hendrik Faber1, Emre Yengel1, Leonidas Tsetseris2, and Thomas Anthopoulos1,1 King Abdullah University of Science and Technology (KAUST), Saudi Arabia; 2National Technical University of Athens, Zografou Campus, Greece

Because of its fast operation speed, resistive random-access memory (RRAM) is widely anticipated to dominate future’s non-volatile memory (NVM) device technologies. However, the often high operating voltage window, the complex and hence expensive fabrication process are some of the major technological and economic obstacles for its commercialization. Here, we describe the development of solution processable copper sulfide materials and their application in high performance two-terminal NVM devices. We show that carefully controlled composition of copper sulfides (i.e. Cu2S, Cu2-xS and CuS) yields fast responsive memory device with remarkably low operating voltage window and highly reprogrammable operating characteristics. In particular, we demonstrate NVM devices with highly reprogrammable memory window of <300 mV, write/erase channel current ratio of >10^3, excellent data retention and superior memory endurance in excess of 1500 write/erase cycles. Finally, we demonstrate successful resistive switching in planar two-terminal sub-20 nm scale NVM devices. Using complementary suite of characterization techniques in combination with density functional theory calculations, we are able to elucidate the nanoscopic origin of the resistive switching mechanism.

SESSION EL04.04: Spotlight Talk: Phase-Change Materials
Session Chairs: Paul Fons and Prashun Gorai
Monday Afternoon, December 2, 2019
Hynes, Level 1, Room 104

4:45 PM EL04.04.01
Spotlight Talk—Growth of GeTe and Sb2Te3 Interlayer Structures for Interfacial Phase Change Devices via Molecular Beam Epitaxy Adrian Podpirka, David Shrekenhamer, Christine Zgrabik, Jonathan Pierce, Jarod C. Gagnon and Andrew Strikwerda; Johns Hopkins University Applied Physics Laboratory, United States

Phase change memories (PCMs) are based on the bad glass forming ability and metastability of the thermodynamic and kinetic transition in chalcogenide materials. This relies on the electrical and optical properties changing substantially when the atomic structure of the materials is altered. This transition, between a significant electrical resistance in the amorphous phase and a highly conductive state in the crystalline phase, has lent itself to numerous applications that include optical storage (i.e. blue ray and CDs) to electronic devices (i.e. Intel x-point technology). A novel subset of these materials uses the superlattice structure in order to greatly reduce the switching current and
total energy required, thereby overcoming the joule heating constraint common to conventional PCMs. These are known as interfacial phase change materials (iPCM). Though currently unsettled as to the origins of the mechanism, they have shown promise for use in microwave devices based on interlayer switching by reducing the thermal loads required. In this presentation, we investigate the growth of interfacial GeTe-Sb2Te3 structures via Molecular Beam Epitaxy (MBE) with differing orientations and various substrates (GaAs, Si, Al2O3) and report on the electro-optical properties associated with the morphological and structural changes in this material system. By varying the elemental flux and novel heating method, we are able to stabilize the superlattice structure in a 2D growth regime. The ability to grow via MBE on transparent substrates allows us to incorporate the iPCMs into next-generation electronic and optical devices that may benefit applications such as computing, sensing and communications.

4:50 PM EL04.04.02
Spotlight Talk—Electrothermal Modeling of Interfacial Phase Change Memory Md Tashfiq Bin Kashem, Jake Scoggin, Ali Gokirmak and Helena Silva; University of Connecticut, United States

Chalcogenide alloys are the most common phase change materials used in phase change memory (PCM), which has entered the market as a high-speed non-volatile memory [1,2]. One of the main challenges for PCM is the large power required to heat the active region above crystallization or melting temperature. Lower energy and higher speed operations have been demonstrated with thin film superlattice stacks of phase change materials known as interfacial phase change memory (iPCM) [3-6]. The mechanisms behind the improved performance of iPCM are still under investigation but recent work indicates similar crystallization and melt-quench operation of these devices [5].

In this work, we perform electrothermal finite element simulations of reset and set operations on iPCM structures consisting of alternately stacked Ge2Sb2Te5 (GST) and GeTe layers using COMSOL multiphysics [7-10]. Electrical pulses are applied for reset and set processes utilizing an internal circuit model where a transistor is used as an access device. Coupled electric current and heat transfer physics are employed to incorporate Joule heating and thermoelectric effects (Thomson heat within a single material and Peltier heat at material interfaces) with temperature dependent Seebeck coefficients, thermal conductivities, electrical resistivities, heat capacities and thermal boundary resistances (TBR) for each material / material pairs. Latent heat of fusion is included in the amorphous-crystalline and solid-liquid transitions [10], giving rise to heat release at the crystal-amorphous boundaries during crystal growth and heat absorption at the grain boundaries during amorphization. Grain boundaries and material interfaces have high energy sites, making them easier to melt, described as heterogeneous melting [10].

iPCM [5] structures utilize engineered interfaces formed between nanometer scale thin-film stacks, promoting amorphization through increased number of material interfaces and reduced thermal conduction due to TBR. Furthermore, the melting temperature, electrical conductivity and Seebeck coefficient of the different materials within an iPCM device differ. Hence, such layered structures may have the advantage of melting of only one of the alternating layers assisted by local heating or cooling due to Peltier effect at the interfaces. Our results on iPCM and conventional PCM structures of same dimensions and geometry (20 nm wide, 150 nm high pore-cells) show ~ 50% reduction in reset times and more consistent set times for iPCM cells due to lesser variations in grain sizes and location of boundaries.

Acknowledgment: This work is partially supported by the National Science Foundation under award DMR-1710468.

References:

SESSION EL04.05: Poster Session I: Chalcogenide Fundamentals and Materials for Photonics, Optoelectronics and Phase-Change Applications
Session Chairs: Steven Durbin and Rafael Jaramillo
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EL04.05.01
Chalcogenide Alloys Enable Reconfigurable All-Dielectric Metasurfaces Mikhail Y. Shalaginov1, Sensong An2, Tian Gu1, Yifei Zhang1, Claudia Goncalves1, Peter Su1, Clayton Fowler2, Vladimir Liberman3, Anuradha Agarwal1, Clara Baleine2, Kathleen Richardson3, Hualiang Zhang2 and Juejun Hu1; 1Massachusetts Institute of Technology, United States; 2University of Massachusetts Lowell, United States; 3University of Central Florida, United States; 4Lincoln Laboratory, MIT, United States; 5Lockheed Martin, United States

Material platform based on chalcogenide alloys, such as the recently emerged Ge-Sb-Se-Te, is uniquely poised for enabling new class of active meta-optical devices. Ge-Sb-Se-Te exhibits unique optical and structural properties, including high refractive index (3.3 - 4.7) in mid-infrared, low losses (k < 0.01), and the non-volatile phase-change ability with a significantly larger switchable thickness than the traditional Ge-Sb-Te alloys. Based on this material platform, we demonstrated all-dielectric phase-change metalens with a switchable focusing capability. This research finding opens up new avenues for further development of ultra-compact reconfigurable optical devices for thermal imaging and chemical sensing applications.

EL04.05.02
Cubic NaSbS2 as an Electrically Reconfigurable Semiconductor for Switchable Photovoltaic and Neuromorphic Devices Harikesh Padinhare Cholakkal, Abhijith Surendran, Biplab Ghosh, Rohit A. John, Arjun Moorthy, Natalia Yantara, Sudhanshu Shukla, Krishnamoorthy Thirumal, Subodh G. Mhaisalkar and Nripan Mathews; Nanyang Technological University, Singapore

In a bid to decouple the property-processing correlation which limits electronic materials' performance- we develop material systems that can be compositionally and electronically modulated by the application of electric fields. This requires the careful control of ionic insertion, transport and chemical transformation as well as a host materials system that is electronically fault tolerant and able to handle a wide composition variation. Highly connected and soft Ionic semiconductors such as halide perovskites serve as an archetype in this respect by allowing structural and compositional modulation without impeding the semiconducting property. This co-existence of ionic and electronic properties can be attributed to its defect tolerance – ie the ability of a semiconductor to retain its properties despite the presence of point defects. The presence of ns2 electrons, a high dielectric constant and the presence of the heavy element for strong spin orbit coupling effect are deemed the fundamental reasons for this effect. Based on these design rules, we evaluated Cubic NaSbS2 for similar properties utilising a combined experimental and theoretical approach.

First Principle Calculations indicate the presence of an antibonding valence band maximum eliminating deep traps at the Valence Band side. The cross gap hybridisation between Sb(p) and S(p) enable high dielectric constants and the p to p transitions enable high absorption coefficient in this material. The connected lattice with high ionic conductivity coupled with the above properties make it suitable for electronic and compositional reconfiguration by applied electric fields. We developed a novel solution processing strategy to form thin films of this class of compounds. The material possess a high absorption coefficient with an indirect band gap around 1.5 eV suitable for PV applications. In addition, it exhibits mixed electronic and ionic conductivity which can be modulated by the Na content and the ambient atmosphere. The material behaves as a superionic conductor on exposure to humidity enabling its application as humidity sensors and solid state electrolytes for thin film batteries. We also show for the first time, switchable photovoltaic effect in this Chalcogenide semiconductor by electrically re-configuring the material by ionic insertion. Furthermore, the Persistant photoconductivity of the material is utilised to demonstrate a reconfigurable photonic synapse with low energy consumption in an extremely simple architecture. Thus we report
a extremely versatile electrically reconfigurable Chalcogenide semiconductor with potential applications in Photovoltaics, battery, sensors and Neuromorphic devices.

**EL04.05.03**

**Resistance Switching in CdS by Donor-Level Switching** Han Yin and Rafael Jaramillo; Massachusetts Institute of Technology, United States

CdS exhibits large and persistent photoconductivity due to lattice relaxations associated with sulfur vacancies [1]. Sulfur vacancies are deep donors at equilibrium in the dark, but under photoexcitation they convert to shallow donors in a metastable state. This donor-level switching mechanism suggests a new way to control conductivity in electronic devices.

Here we demonstrate two-terminal electrical devices that exhibit donor-level switching. We fabricate and test vertical thin-film devices consisting of Ag/CdS/MoO₃/Au layer. MoO₃ is a hole-injection layer, due to its large electron affinity and nearly type-III alignment with CdS. We hypothesize that MoO₃ extracts electrons from the deep donor levels in CdS (possibly via the valence band), and thereby switches CdS into a highly-conductive state in a thin layer near the interface.

The hypothesis of electrically-stimulated donor-level switching ("photo"conductivity without photons) leads to several testable predictions, all of which are confirmed by device measurements. Our devices are in a high-conductivity state in equilibrium, and exhibit repeatable resistive switching with no electro-forming step. The active n-type layer is switched into a low-conductivity state by injecting electrons, and a high-conductivity state by injecting holes. These results support the hypothesis that the observed electrical switching behavior is due to donor-level switching, rather than mass transport (e.g. filament formation). We further support the donor-level switching hypothesis with numerical device simulations, pulsed electrical measurements, capacitance-voltage profiling, electron beam induced current (EBIC) measurements, X-ray absorption spectroscopy (XAS) mapping, and Raman microscopy. Spatially- and chemically-sensitive techniques suggest that no filaments are formed during switching.

Donor level switching represents a new mechanism for the design of electronic circuit elements such as variable resistors (e.g. for analog computing), ovonic switches, oscillators, and compliance limiters. We suggest that this mechanism is not unique to CdS, and can be found in any material with metastable charged defect states, including ZnO, CuInS₂, and AlGaAs. We end by discussing proposals to optimize defect level switching for particular applications by material selection and device design.


**EL04.05.04**

**Single-Shot Ultrafast Phase-Change Memory Materials** Desmond Loke¹, Jonathan Skelton², Tae-Hoon Lee³, Tow-Chong Chong¹ and Stephen Elliott³; ¹Singapore University of Technology and Design, Singapore; ²University of Bath, United Kingdom; ³University of Cambridge, United Kingdom

Although the combination of RAM chips and Flash memory have been leveraged widely in big data and artificial intelligence tasks, they usually fail to meet the commercial demands of either speed or scalability. Phase-change memory materials may overcome these limitations, yet the typical crystallization time is many times slower compared to the melting time, and as a result is insufficient for any real-world application. Here we demonstrate how the crystallization kinetics of a wide range of phase-change systems can be controlled by using a single-shot treatment via “initial crystallization” effects. Ultra-rapid and highly stable phase-change structures viz. conventional and sub-10 nm sized cells, stackable cells, and multilevel configurations have been demonstrated. Material measurements and thermal calculations also reveal the origin of the pretreatment-assisted increase in nucleation and growth time and the thermal diffusion in chalcogenide structures, respectively. This insight may accelerate the technological deployment of new types of phase-change memory.

**References**


EL04.05.05
Effect of the S-Shaped Negative Differential Conductance (SNDC) on the Switching of the GST- Based PCMs
Kazimierz J. Plucinski; Military University of Technology, Poland

In the switching of the Phase Change Memory based on the telluride chalcogenides, eg GST, the following two mechanisms can be recognized [1,2]:
- reversible switching mechanism between an electrical low conducting state and high conductive one, named as threshold switching or Ovonic Threshold Switching (OTS). This mechanism is associated with an S-Shaped Negative Differential Conductance (SNDC);
- thermally activated phase transition between high conductive crystalline and low conductive amorphous states – named as Ovionic Memory Switching (OMS).

OTS is a fundamental mechanism for PCM devices. Despite intensive research into the role of the OTS mechanism, the nature of the physical principle responsible for the conductance switching is still not fully understood [1,4]. One of the reasons for the lack of understanding of the OTS mechanism are deficiencies in the understanding of SNDC mechanism.

The critical analysis of the current state of knowledge in the field of SNDC, in particular the impact of SNDC-related effects on the OTS process will be presented based on the developed phase change algorithm.


EL04.05.06
Systematic Computational Study on Transition Metal-Based Ternary Tellurides for High-Endurance Phase Change Memory Applications
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Phase change random access memory (PCRAM) is a promising candidate for next-generation non-volatile memory applications, which rely on reversible electrical resistivity change in telluride-based phase change materials between the crystalline and amorphous phases. Ge-Sb-Te alloys have been the most studied phase change materials since they were discovered for rewritable optical disc applications in the 1990’s. Essentially, the same material has been used in conventional PCRAM applications, but it suffers from both thermal stability problems and a limited cycling due to the large changes in density (volume) occurring during the phase change processes. These were not serious issues for optical discs applications, but are for PCRAM. In this work, using an empirical relation linking the physical characteristics of phase change materials, we predict novel materials that are expected to exhibit small density changes upon the phase transition.

The optical properties of 18 different transition-metal-based ternary tellurides have been systematically examined by density functional theory simulations. On the basis of the aforementioned empirical law, which correlates density change with the optical contrast between the amorphous and crystalline phases of chalcogenides, the density changes occurring upon crystallization for hypothetical materials have been predicted. Cr₂Ge₂Te₆ was found theoretically to be one of the best materials for phase-change memory applications owing to its small density
change. This novel criterion will be useful in the screening of materials yet to be experimentally realized, and will help target promising materials for high-endurance phase-change memory applications [1].


EL04.05.07
Spotlight Talk—Growth of GeTe and Sb2Te3 Interlayer Structures for Interfacial Phase Change Devices via Molecular Beam Epitaxy
Adrian Podpirka, David Shrekenhamer, Christine Zgrabik, Jonathan Pierce, Jarod C. Gagnon and Andrew Strikwerda; Johns Hopkins University Applied Physics Laboratory, United States

Phase change memories (PCMs) are based on the bad glass forming ability and metastability of the thermodynamic and kinetic transition in chalcogenide materials. This relies on the electrical and optical properties changing substantially when the atomic structure of the materials is altered. This transition, between a significant electrical resistance in the amorphous phase and a highly conductive state in the crystalline phase, has lent itself to numerous applications that include optical storage (i.e. blue ray and CDs) to electronic devices (i.e. Intel x-point technology). A novel subset of these materials uses the superlattice structure in order to greatly reduce the switching current and total energy required, thereby overcoming the joule heating constraint common to conventional PCMs. These are known as interfacial phase change materials (iPCM). Though currently unsettled as to the origins of the mechanism, they have shown promise for use in microwave devices based on interlayer switching by reducing the thermal loads required. In this presentation, we investigate the growth of interfacial GeTe-Sb2Te3 structures via Molecular Beam Epitaxy (MBE) with differing orientations and various substrates (GaAs, Si, Al2O3) and report on the electro-optical properties associated with the morphological and structural changes in this material system. By varying the elemental flux and novel heating method, we are able to stabilize the superlattice structure in a 2D growth regime. The ability to grow via MBE on transparent substrates allows us to incorporate the iPCMs into next-generation electronic and optical devices that may benefit applications such as computing, sensing and communications.

EL04.05.08
Atomic Layer Deposition of GeSe Using GeIINMe2[(NiPr)2CNMe2] and Te(SiMe3)2 with NH3 Co-Reagent for Ovonic Threshold Switch
Manick Ha, Chanyoung Yoo, EuiSang Park, YoonKyeung Lee, Woohyun Kim, JeongWoo Jeon and Cheol Seong Hwang; Seoul National University, Korea (the Republic of)

Ovonic Threshold Switch (OTS) is a critical component for suppressing the sneak current in the cross-bar array (CBA) phase change random access memory (PcRAM), and GeSe is a feasible functional material of the OTS. The conventional method to grow GeSe OTS film is sputtering[1,2]. However, the sputtering is not suitable for the vertically integrated PcRAM (V-PcRAM), which must be the ultimate integration structure of the CBA-PcRAM. For this V-PcRAM fabrication, a growth method which guarantees the thickness and composition uniformities within the deep hole structure is necessary. Atomic layer deposition (ALD), therefore, must be the process of choice for such a purpose, and the authors’ group already reported high functionality of ALD-GeSe film as a feasible OTS material [3]. However, the previous work has a limitation of the growth process; the ALD-GeSe film must be grown at a low temperature of 70 oC due to the serious desorption of the precursors at higher temperatures. This might also hinder the achievement of the ultimate functionality of the same material.

In this work, therefore, the ALD process was improved to allow the growth of the ALD-GeSe films at much higher temperatures (up to 180 oC) by changing the Ge(II)-precursor from HGeCl3 to (Ge(iPrN)2CNMe2)NMe2 and co-injecting NH3 with the new Ge(II)-precursor. Under this condition, the (Ge(iPrN)2CNMe2)NMe2 was activated by accepting the lone pair electrons of NH3, which allowed the growth of the GeSe film at temperatures as high as 180 oC. The activated Ge(II)-precursor molecules feasibly reacted with the Se-precursor, (Si(CH3)3)2Se, resulting in the stoichiometric GeSe thin film deposition. The ALD process showed self-limiting growth behavior and produced highly uniform and stoichiometric GeSe films with the saturation growth rate around 39 ng*cm2*cy-1 at 70 oC substrate temperature (Figure 1). X-ray photoelectron spectroscopy analysis revealed that the composition ratio of Ge:Se was ~1:1 for all the ALD temperature from 70 to 180 oC. However, the N impurity level in the film varied depending on the substrate temperature; film grown at higher temperature contained lower N- impurity concentration (Figure 2 (a), (b)). This may cause discrepancies in the density and morphology of the deposited film. When the film was grown at 180oC, a high film density (4.23g*cm-3) and low N impurity content could be obtained. The presentation will also report the high electrical performance of the film as the OTS using an integrated cell structure of mushroom type, where the 10nm thick GeSe film was interposed between the planar-TiN top electrode and W-plug (diameter of 2um) bottom electrode.
Numerical Analysis of Mechanical Stress During Switching Operation in Phase-Change Memory
Hwanwook Lee and Yongwoo Kwon; Hongik University, Korea (the Republic of)

A chalcogenide material, Ge$_2$Sb$_2$Te$_5$ (GST), can undergo a fast nanosecond-transition between the amorphous and crystalline phases that have a resistivity difference of 1,000 times or more. This phase change can be controlled electrically and is used as phase change memory (PCM). However, amorphous and crystalline phases have a density difference of about 10% and cause a mechanical stress in the device due to the volume change during the switching operation. Repetitive switching operations between two phases lead to an open circuit failure, more specifically, the breakdown of the interface between GST and its contact electrode by the fatigue, which is called stuck reset. In this study, finite element analysis (FEA) was performed for several PCM cell architectures by combining electrothermal and solid mechanics models using COMSOL Multiphysics, a commercial FEA software. Simulation techniques and comparative study on the cell architectures will be presented.

TEM of GeSbTe Thin Films—Crystallization Dynamics, Void Formation and Elemental Segregation
Shalini Tripathi$^{1}$, Rongjung Wang$^{2}$, Paul Kotula$^{3}$, Gokhan Bakan$^{4}$, Helena Silva$^{1}$ and Barry Carter$^{3,1}$; $^{1}$University of Connecticut, United States; $^{2}$Applied Materials, Inc., United States; $^{3}$Sandia National Laboratories, United States; $^{4}$Atilim University, Turkey

Chalcogenide compounds show distinct properties in the amorphous and crystalline phases with orders of magnitude difference in electrical resistivity, making them prominent candidates for fast, non-volatile and high-density electronic memory devices. Adoption of this new technology has been hindered by the large power required to heat the active volume above crystallization or melting (for melt-quench amorphization), resistance drifts of the metastable phases, and void formation and elemental segregation during heating and cooling. We are using transmission electron microscopy (TEM) to study the changes that occur in these materials with the aim of relating microstructure findings to the physical and chemical properties.

GeSbTe (GST) thin films are deposited directly onto Protochips carriers by sputtering. The phase transformation is monitored in real time in the TEM using the Protochips heating holders. Materials characterization uses both a Tecnai F30 (operating at 200kV equipped with an EDS detector) and Titan ETEM (300kV Cs-image-corrected Titan) that can accept the same Protochips heating holders. The ETEM is equipped with a K3-IS direct electron detector camera allowing high-speed video recording (up to 1600 frames/s) of the structural changes in these materials upon heating and cooling. The aim is to observe the various phase transformations and other critical processes such as grain evolution, void formation and elemental segregation and study how these relate to the electronic behavior. High-resolution TEM images of GST films after heat treatment show coherent twin boundaries, which will be discussed together with the sensitivity of these films to the electron beam. Challenges associated with integrating results from different techniques will also be discussed.

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Spotlight Talk—Electrothermal Modeling of Interfacial Phase Change Memory
Md Tashfiq Bin Kashem, Jake Scoggin, Ali Gokirmak and Helena Silva; University of Connecticut, United States

Chalcogenide alloys are the most common phase change materials used in phase change memory (PCM), which has entered the market as a high-speed non-volatile memory [1,2]. One of the main challenges for PCM is the large power required to heat the active region above crystallization or melting temperature. Lower energy and higher speed operations have been demonstrated with thin film superlattice stacks of phase change materials known as interfacial phase change memory (iPCM) [3-6]. The mechanisms behind the improved performance of iPCM are
still under investigation but recent work indicates similar crystallization and melt-quench operation of these devices [5].

In this work, we perform electrothermal finite element simulations of reset and set operations on iPCM structures consisting of alternately stacked Ge$_2$Sb$_2$Te$_5$ (GST) and GeTe layers using COMSOL multiphysics [7-10]. Electrical pulses are applied for reset and set processes utilizing an internal circuit model where a transistor is used as an access device. Coupled electric current and heat transfer physics are employed to incorporate Joule heating and thermoelectric effects (Thomson heat within a single material and Peltier heat at material interfaces) with temperature dependent Seebeck coefficients, thermal conductivities, electrical resistivities, heat capacities and thermal boundary resistances (TBR) for each material / material pairs. Latent heat of fusion is included in the amorphous-crystalline and solid-liquid transitions [10], giving rise to heat release at the crystal-amorphous boundaries during crystal growth and heat absorption at the grain boundaries during amorphization. Grain boundaries and material interfaces have high energy sites, making them easier to melt, described as heterogeneous melting [10].

iPCM [5] structures utilize engineered interfaces formed between nanometer scale thin-film stacks, promoting amorphization through increased number of material interfaces and reduced thermal conduction due to TBR. Furthermore, the melting temperature, electrical conductivity and Seebeck coefficient of the different materials within an iPCM device differ. Hence, such layered structures may have the advantage of melting of only one of the alternating layers assisted by local heating or cooling due to Peltier effect at the interfaces. Our results on iPCM and conventional PCM structures of same dimensions and geometry (20 nm wide, 150 nm high pore-cells) show ~ 50% reduction in reset times and more consistent set times for iPCM cells due to lesser variations in grain sizes and location of boundaries.

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References:

EL04.05.12
Synthesis of Segregating Binary Alloy for Nanowire-Like Phase-Change Materials and Memory

Desmond Loke¹, Griffin Clausen², Jacqueline Ohmura², Tow-Chong Chong¹, Natasa Bajalovic¹ and Angela Belcher²;
¹Singapore University of Technology and Design, Singapore; ²Massachusetts Institute of Technology, United States

Non-volatile memories are pivotal components for emerging opto- and nanoelectronic applications such as smart displays and brain-inspired neuromorphic computing. Flash memories are currently the key player in the field, yet they fail to meet the commercial demands of scalability and speed. Phase-change materials (PCM), based on reversible switching between the crystalline state and amorphous state of a chalcogenide material, showing fast switching on 10 ns time scale, are promising alternatives explored by the industry. However, segregating-binary-alloy (SBA)-based PCM tends to show high consumption of energies and segregation of elemental components. Nanowire-like PCM has so far evolved as the most ideal candidate to achieve low-energy consumption PCM, however they are often synthesized by vapor-liquid-solid methods above 720 K, which would cause irreversible corruption of SBA-based PCMs. Here we leverage M13 bacteriophage as biological template to control the structure and assembly of SBA PCMs. We demonstrate a biologically templated, low temperature, wire-like PCM simply by leveraging the binding affinity of the negatively-charged amino acids on M13 bacteriophage surface to the precursor components of SBA-type germanium-tin-oxide systems. This study may open intriguing perspective for realizing
genetically-engineered PCM with tunable, reliable and fast switching characteristics.


**EL04.05.13**

**Plasma-Assisted Atomic Layer Deposition of GeSb Films Using Non-Halide Organo-Metallic Precursors for Phase-Change Electronic Devices**

Saidjafarzoda Ilhom, Adnan Mohammad, Deepa R. Shukla, Brian Willis, Helena Silva and Necmi Biyikli; University of Connecticut, United States

Germanium-antimony-telluride compound (GST) is one of the most widely known chalcogenide materials which has been heavily commercialized in phase-change memory (PCM) devices including the recently announced cross-bar memory architectures. Besides the ternary GST, binary versions (GeSb, SbTe, and GeTe) of this compound family show also interesting properties including phase transitions. Compared to more conventional deposition methods including rf-magnetron sputterin and pulsed laser deposition, atomic layer deposition (ALD) has recently attracted significant interest mainly due to its precision thickness control and ultimate conformal deposition capability, which becomes more and more critical as device sizes shrink down to single digit nanometers and device architectures become highly three-dimensional with increased complexity. Currently, most of the successful works towards the ALD growth of phase-change (PC) materials have been focusing on utilizing corrosive chemical compounds such as metal-halides and alkyl-silyls as the precursors and co-reactants. In this work we aim to produce highly uniform and void-free binary phase-change GeSb films using non-halide organo-metallic precursors at relatively low substrate temperatures. Towards this goal, GeSb films are grown on Si(100) and glass/quartz substrates via inductively-coupled plasma-enhanced atomic layer deposition using tetramethyl-germane ((CH₃)₄Ge) and tris(dimethylamino)-antimony ((CH₃)₂N)₃Sb as germanium (Ge) and antimony (Sb) precursors, respectively. Ar/H₂ plasma gas mixture was employed to remove the precursor ligands at each intermediate reaction steps. Growth experiments have been performed within 100 - 250 °C substrate temperature at 300 W rf-plasma power. *Ex-situ* materials characterizations are carried out to identify structural, chemical, optical and electrical properties of the grown GeSb films. Detailed temperature-dependent electrical characterization is performed to measure the phase-change transition properties of the ALD-grown GeSb layers.

**EL04.05.14**

**Direct Phase Transition of the Few Layer MoS₂ from 2H to 1T' State by Using 2D Electride: Ca₂N**

Krishna P Dhakal, Ganesh Ghimire, Kyungwha Chung, Sung W. Kim and Jeongyong Kim; Sungkyunkwan University, Korea (the Republic of)

The lattice engineering of the sulfide based transition metal dichalcogenide (TMDs) is difficult compared to selenide and telluride materials.1 Here, we report on the continuous phase transition of the few layers to bulk molybdenum disulfide (MoS₂) system by realizing the hetero-structures with the low work function (2.6 eV) two dimensional electrode (2D-Ca₂N) that contain highly mobile electrons, where the large work function differences (>2 eV) between them is the key of the degenerate electrons doping that is distributed over a distance of few tens of nanometer from the contact interface in contrast to the other surface limited (~1 nm) chemical functionalizations or ionic gating approaches.3 An electron doping density of ~10¹⁴ cm⁻² was estimated on the MoS₂ layers that performed exceptional thickness dependent lattice symmetry change from the 2H to 1T' phases until a few-layer (~10 nm) and then strong doping effect to the bulk samples resulting a giant band gap re-normalization by ~200 meV along with the softening of the commonly observed Raman modes by the Δω=10 cm⁻¹. As the MoS₂ thickness was decreased, well defined Raman peaks of 2H crystal were gradually disappearing along with the
emergence of other 1T' phase Raman modes, thus elucidating the symmetry change feature due to concentrated charge density in a thinner film. Additionally, a hetero-structure of the few-layer MoS2 demonstrated multiple in-plane anisotropic Raman modes, including those of metallic phases Raman modes along with the presence of the hugely shrunk (250 meV) optical gap and enhanced PL intensity than a pristine monolayer MoS2; a realization of the few-layer 2H-MoS2 crystal with distorted symmetry and direct band gap structure when placed on the top of the Ca2N. This is attributed to the long-range electron doping induced structural change across the K-Γ line, hence provided an opportunity to discover various kinds of 2D materials using a single 2D-dopant suitable for the future optoelectronic application.

KEYWORDS: MoS2, electride, doping, long range, phase-transition, direct band gap structure

References

EL04.05.15
Energy-Efficient Neuromorphic Computing through the Control of the Density, Location and Properties of Conducting Filaments in TiO2
Nicolas Emond and Bilge Yildiz; Massachusetts Institute of Technology, United States

Improvements in actual computing performance, which is based on von Neumann architecture, requires designing novel scalable, fast and energy-efficient technologies with both processing and storage capabilities. A typical example of systems with such capabilities is the human brain. Indeed, it has major advantages over supercomputers in terms of energy efficiency and adaptability due to its complex processing capability, made possible by the interconnection between \(10^{11}\) neurons and \(10^{15}\) synapses. The current "holy grail" of neuromorphic computing technology is thus to mimic brain performance for the development of superior computational systems. Among the proposed next generation device candidates to reproduce neuromorphic core architectures for pattern recognition and machine learning, redox-based resistive switching (RS) random access memories (RRAM) are particularly highly regarded due to their predicted high memory density, energy efficiency and speed. Within their metal–insulator–metal architecture, these devices store binary code information using the electric field-induced resistance change of the insulating oxide layer by conductive filament (CF) formation and rupture at chemical and structural defects. Despite such very attractive properties, a lack of control on the location and spacing of CFS formation, as well as on their properties, results in stochasticity and randomness of CFS formation in these devices, which in turns leads to detrimental variation in device performance and lack of reliability in training processes. Unfortunately, there is actually a lack of fundamental knowledge connecting these defects to their nucleation and evolution. Within this context, we initiated a study on the effect of strain on the microstructure, chemistry and RS properties of TiO2 thin films to resolve the thermodynamic and kinetic relations of heterogeneities to their intrinsic and local RS properties.

Epitaxial TiO2 films with varying thicknesses were pulsed laser deposited on Nb-SrTiO3 and Nb-TiO2 single-crystal substrates to investigate the effect of phase, strain, crystallinity and defects concentration on the nature of the CFS and the local RS properties of the films. The fabrication and characterization of TiO2-based two-terminal devices was also carried out to get information about their RS properties, mainly in terms of switching consistency and reproducibility. Such studies will not only allow gathering insights into defects location of formation but will further serve as a guideline while looking to introduce chemical disorder at specific locations into the TiO2 matrix. Such a selective doping along defects is expected to locally decrease the reduction enthalpy and provide preferential sites for CF formation. The objective here is to achieve proper control of CFS formation and properties to accordingly reduce the variability among RRAM devices and improve their switching symmetry.

EL04.05.16
Controlling Conductive Filaments in Resistive Switching Oxides by Controlled Chemical Disorder
Kevin J. May1, Yu Ren Zhou1, Vijay Naranyanan2, Takashi Ando2, Harry L. Tuller1 and Bilge Yildiz1;1 Massachusetts Institute of Technology, United States; 2IBM T.J. Watson Research Center, United States

There has been a growing interest in using specialized neuromorphic hardware to implement artificial neural networks for use in applications such as image and speech processing. These neuromorphic devices show promise
for meeting the significant parallel computing demands of such applications with higher speed and lower power consumption than software-based implementations. One approach to achieving this goal is through oxide thin film resistive switching devices arranged in a crossbar array configuration. Resistive switching can mimic several aspects of neural networks, such as short- and long-term plasticity, via the dynamics of switching between multiple analog conductance states—dominated by the creation, annihilation and movement of ionic species within the film (such as oxygen vacancies). These processes can be stochastic in nature and contribute significantly to device variability, both within and between individual devices.

This study focuses on reducing the variability of the set/reset voltages using model systems of HfO₂ grown on Nb: SrTiO₃ and Si/TiN substrates. We control the oxide microstructure via growth parameters and thermal treatment, to compare amorphous HfO₂ films with nanocrystalline columnar-grained films with both single (-111) texture and multiple orientations and selectively dope grain boundaries using thermal diffusion. By statistically comparing the electrical characteristics of at least 10 devices from each processing condition, film microstructure and dopants may be optimized for maximum resistive switching repeatability. Because the device requirements for practical resistive switching arrays are significant, controlling the variability of individual devices will likely be a consideration for every fabrication and processing step. This work provides a significant step towards understanding the mechanisms behind device variability and achieving devices that meet the strict requirements of neuromorphic computing.

EL04.05.17
Electrochemical Proton Intercalation Synapse for Analog Resistive Switching Xiahui Yao, Wenjie Lu, Nicolas Emond, Jesus A. del Alamo, Ju Li and Bilge Yildiz; Massachusetts Institute of Technology, United States

Analog resistive switching processor arrays are promising as in-memory computing hardware and to construct physical neural networks capable of implementing machine learning algorithms at higher operating speed and lower energy cost than conventional von-Neumann architectures. State-of-the-art analog resistive switches rely on the mechanism of either forming conductive filaments or inducing a phase change. These processes suffer from poor repeatability or high energy consumption, respectively. A fundamentally different mechanism is desired to address these challenges.

Herein we demonstrate proton intercalation induced resistive switching, that can be applied on a variety of layered or channeled materials including chalcogenides and metal oxides. A prototypical three-terminal resistive switching device was designed, with a channel of active material probed by two terminals (source and drain), a proton reservoir layer as gate terminal, and a proton conducting solid electrolyte separating the two. The electrical conductivity of the active material can be modulated by the precise control of proton intercalation, providing a highly reproducible resistive switching behavior. As the lightest cation, the shuffling of protons between the reservoir and the active material requires minimal energy.

A proof-of-concept device has been fabricated. 50 nm WO₃ was deposited by reactive sputtering as the active material, with a channel size of 100 μm x 500 μm. A 400 nm Nafion polymer electrolyte layer was deposited by spin coating. A 50 nm Pd electrode serving as both gate and solid proton reservoir was sputtered on top and later hydrogenated to palladium hydride. The energy consumption is only 3.5 fJ/μm² per state per potentiation and depression operation, comparable with state-of-the-art demonstrations. Extreme on/off ratio of more than 10⁷ in conductance was observed and more than 1000 distinct conductance states were demonstrated. Most important of all, a symmetric potentiation and depression behavior was achieved in a constant current pulse mode. Further, insight into the switching mechanism involving protons has been obtained through a combined examination of crystal and electronic structure using synchrotron X-ray absorption spectroscopy and in-situ X-ray diffraction. It is found that protons serve as donors to reduce the metal oxidation states in the active material and create gap states. The continuous filling of electrons into the empty d-orbital of W metal increase the charge carrier density and conductivity. Additionally, proton intercalation induced lattice distortion of the active material is found to result in higher crystal symmetry and better alignment of W-O₆ octahedrals. This also contributes to the enhanced conductivity after proton intercalation.

In summary, we successfully proved the feasibility of utilizing proton intercalation chemistry to induce the modulation of resistivity and prototyped an all-solid three-terminal analog resistive switch. The advantages of this switching mechanism, namely, low energy dissipation, good operating symmetry and multi-state capability, are demonstrated.
Lanthanide elements offer a versatile platform for the design of new magnetic and optical materials. The use of soft chalcogenide ligands introduces tunability of the crystal electric field of the lanthanide cations, which can result in new classes of materials with various potential applications. Exploratory crystal growth of these compounds is an important tool for creating new compounds, and the development of new synthetic routes is highly desirable to achieve the intentional synthesis of new chalcogenide materials.

One well-developed technique for obtaining crystals is flux crystal growth. Unlike solid state synthesis, which is usually performed at higher temperatures and which typically results in thermodynamic products, flux crystal growth enables access to kinetically stabilized phases by using fluxes with low melting points. Focusing on the synthesis of new magnetic materials, specifically those containing f-elements, we employed alkali iodide fluxes to obtain single crystals of new thiophosphate and thiosilicate compounds with incorporated lanthanide and uranium cations. A targeted synthesis of first two uranium(IV) thiosilicates was achieved by using CsI and CsI/NaI eutectic fluxes. We showed that different products can be achieved by using either SiS₂ or an equivalent mixture of Si and S. This highlights the complex reaction pathway that results in single crystals of Cs₂Na₄[U₂(SiS₄)₂(Si₂S₈)], in the case of SiS₂ starting material, or a polycrystalline product that was obtained when elemental sulfur and silicon were used. The use of alkali iodide fluxes has enabled us to synthesize over 20 new lanthanide thiophosphate compounds as high quality single crystals. The structures and physical properties of several of these phases will be discussed.

The charge transfer and spin coupling effects are explored at the interface of two-dimensional (2D) superconducting FeSe nanosheets and one-dimensional (1D) molecular photochromic potassium-7,7,8,8-tetracyanoquinodimethane (KTCNQ).[1] 2D superconducting FeSe layer is obtained in a large scale by liquid exfoliation and maintains the characteristics of its bulk counterpart.[2] Light-induced current density in 2D FeSe nanosheets device is enhanced by the electron doping from KTCNQ by the destabilized spin-Peierls phase[3] through their interface. The spin coupling at the interface of FeSe and KTCNQ shifts the dimerization transition temperature of KTCNQ from 389 K to 395 K. Our results suggest 2D exfoliated FeSe nanosheet as a versatile strongly correlated platform for the electron doping and inorganic-organic interface studies.

Chalcogenide perovskite-type materials have recently been investigated as alternative solar absorbers to the familiar oxide ferroelectric and halide perovskite families. In particular, Ba₃Zr₂S₇ (BZS) is a Ruddlesden-Popper chalcogenide, which was shown to exhibit a band gap of approximately 1.3 eV [1] that is ideally suited for solar absorption, and thermal stability up to at least 550 °C [2]. Knowledge of the thermal expansion of Ba₃Zr₂S₇ is also important during operation and fabrication of a photovoltaic device based on this material. Here we compute the temperature-dependent structural, lattice dynamical, and thermal expansion properties of Ba₃Zr₂S₇ using the self-consistent quasi-harmonic approximation [3] within the framework of density functional theory. We explain the mechanism of thermal expansion, report its effect on the band gap, and compare this behavior to other perovskite-structured oxides and chalcogenides materials.
N.Z.K. and J.M.R. were supported by U.S. Department of Energy (DOE) under Grant No. DE-SC0012375 and the National Science Foundation’s MRSEC program (DMR-1720319) at the Materials Research Center of Northwestern University, respectively. R.A.K. was also supported by the National Science Foundation’s MRSEC program (DMR-1720319) at the Materials Research Center of Northwestern University. A.B.A. was supported by AFOSR in the form of a PECASE (FA9550-17-1-0247).

**EL04.05.21**

Dielectric Response of Highly-Polarizable Complex Chalcogenide Semiconductors BaZrS3 and Ba3Zr2S7

Stephen Filippone1, Ignasi Fina2, Shanyuan Niu3, Boyang Zhao3, Jayakanth Ravichandran3, Dino Klotz1, Harry L. Tuller1 and Rafael Jaramillo1; 1Massachusetts Institute of Technology, United States; 2Universitat Autònoma de Barcelona, Spain; 3University of Southern California, United States

Complex oxides in perovskite and Ruddlesden-Popper crystal structures often have large, interesting, and useful dielectric response. Complex sulfides in similar structures may feature similarly large dielectric response while also featuring band gap in the visible and infrared, and likely have higher charge transport mobility than complex oxides. Complex chalcogenides may therefore be an uncommon class of highly-polarizable semiconductors.

We report measurements of the dielectric susceptibility of single crystal samples of BaZrS3 (BZS-113) and Ba3Zr2S7 (BZS-327). BZS-113 has a distorted-perovskite structure and a band gap of 1.8 eV. BZS-327 is a Ruddlesden-Popper variant and has a band gap of 1.3 eV. We use impedance spectroscopy to measure the complex dielectric response of single crystal and cold-pressed pellets over the frequency range 0.1 Hz – 1 MHz. We find that both phases are highly-polarizable, with room-temperature static dielectric constant (ε0) over 50 and dielectric loss tangent below 0.05. We also report temperature-dependent susceptibility and electrical resistivity and discuss the effects of incipient ferroelectricity, predicted for chemically-adjacent Sr-Ba-Zr-S compounds. The combination of strong and low-loss dielectric response and band gap in the VIS-NIR spectral range may be unique for inorganic semiconductors and is interesting for applications including photonics and solar energy conversion.

**EL04.05.22**

pi-Phase Tin and Germanium Monochalcogenide Semiconductors—An Emerging Materials System

Ran E. Abutbul1,2, Elad Segev1,2, Uri Argaman1, Guy Makov1,2 and Yuval Golan1,2; 1Ben-Gurion University of the Negev, Israel; 2Ilse Katz institute for Nanoscale Science & Technology, Israel

Cubic pi-phase monochalcogenides (MX, M = Sn, Ge; X = S, Se) are an emerging new class of materials that have recently been discovered. Here, their thermodynamic stability, progress in synthetic routes, properties, and prospective applications are reviewed. The thermodynamic stability is demonstrated through density functional theory total energy and phonon spectra calculations, which show that the pi-phase polytype is stable across the monochalcogenide family. To date, only pi-phase tin monochalcogenides have been observed experimentally while pi-phase Ge-monochalcogenides are predicted to be stable but are yet to be experimentally realized. Various synthetic preparation protocols of pi-SnS and pi-SnSe are described, focusing on surfactant-assisted nanoparticle synthesis and chemical deposition of thin films from aqueous-bath compositions. These techniques provide materials with different surface energies, which are likely to play a major role in stabilizing the pi-phase in nanoscale materials. The properties of this newly discovered family of semiconducting materials are discussed in comparison with their conventional orthorhombic polymorphs. These could benefit a number of photovoltaic and optoelectronic applications since, apart from being cubic, they also possess characteristic advantages, such as moderately low toxicity and natural abundance.
Sequential Structural and Antiferromagnetic Transitions in BaFe$_2$Se$_3$ under Pressure Yang Zhang; Southeast University, China

The discovery of superconductivity in the two-leg ladder compound BaFe$_2$S$_3$ has established the 123-type iron chalcogenides as a novel and interesting subgroup of the iron-based superconductor family. However, in this 123 series, BaFe$_2$Se$_3$ is an exceptional member, with a magnetic order and crystalline structure different from all others. Recently, an exciting experiment reported the emergence of superconductivity in BaFe$_2$Se$_3$ at high pressure [J. Ying et al., Phys. Rev. B 95, 241109(R) (2017)]. Here, our analysis unveils a variety of qualitative differences between BaFe$_2$S$_3$ and BaFe$_2$Se$_3$, including in the latter an unexpected chain of transitions with increasing pressure. First, by gradually reducing the tilting angle of iron ladders, the crystalline structure smoothly transforms from Pnma to Cmcm at $\sim$6 GPa. Second, the system becomes metallic at 10.4 GPa. Third, its unique ambient-pressure Block antiferromagnetic ground state is replaced by the more common stripe (so-called CX-type) antiferromagnetic order at $\sim$12 GPa, the same magnetic state as the 123-S ladder. This transition is found at a pressure very similar to the experimental superconducting transition. Finally, all magnetic moments vanish at 30 GPa. The information obtained in our calculations suggests different characteristics for superconductivity in BaFe$_2$Se$_3$ and BaFe$_2$S$_3$: in 123-S pairing occurs when magnetic moments vanish, while in 123-Se the transition region from Block- to CX-type magnetism appears to catalyze superconductivity.

EL04.05.24

An Ab Initio Study of Compressed Palladium Sulfide Isaías Rodríguez$^1$, David Hinojosa-Romero$^2$, Renela M. Valladares$^1$, Alexander Valladares$^1$ and Ariel A. Valladares$^2$; $^1$Faculty of Science, UNAM, Mexico; $^2$IIM-UNAM, Mexico

Recent experimental results indicate that palladium chalcogenides present interesting electronic behavior. In particular, superconductivity appears at 4.5 K in PdTe at ambient pressure. Similarly, PdS becomes a superconductor ($T_C = 1.8$ K) for pressures starting at 19.5 GPa [1]. As the pressure increases so does the $T_C$ reaching a value of 7 K at a pressure of 41.3 GPa. Recently we have predicted the superconducting transition temperature ($T_C$) of the Wyckoff phase of bismuth as 1.5 mK or below [2], and this was later experimentally corroborated. Afterwards we calculated $T_C$ for all bismuth solid phases under pressure and our results agree with experiment [3]. Here, we report an ab initio computational study of the effects of pressure on palladium sulfide (PdS), maintaining the original crystalline structure and compressing a 108-atom crystalline supercell computationally, as previously conducted for bismuth [4]. We calculate the electronic and vibrational density of states for the PdS system under pressure and relate them with its superconducting properties. We compare our results with the experimental ones reported in the literature.

REFERENCES:


EL04.05.25

Ab Initio Study of the BiS$_2$ Chalcogenide David Hinojosa-Romero$^1$, Isaías Rodriguez$^2$, Alexander Valladares$^2$, Renela M. Valladares$^2$ and Ariel A. Valladares$^1$; $^1$IIM-UNAM, Mexico; $^2$Faculty of Science, UNAM, Mexico

Bismuth, as a pure monatomic material, is a semimetal which possesses several interesting physical properties, not all of them well understood. The prediction of a critical superconducting temperature for its crystalline form at ambient pressure by our group [1] and its experimental verification several months later, have led us to ab-initio study bismuth in different conditions: amorphous [1], bi-layered [2], under-pressure phases [3] and mixed with copper [4]. In all of these systems, bismuth seems to contribute to their superconductive behavior and the modification of their critical temperature. Here we study the bismuth-sulphur chalcogenide which is known to contribute to superconductivity in the layered compound LaO$_{1-x}$F,BiS$_2$ which has a $T_C$ as high as 10.6 K. Using ab initio molecular dynamics and the undermelt-quench method, we generate layered and amorphous structures of the
BiS$_2$ system to study its electronic and vibrational properties and then relate them to possible superconducting properties. We shall report these results and study similarities and differences for the amorphous and layered structures and infer its relevance for superconductivity. We shall compare these results with those found for the bulk amorphous bismuth, the bi-layered, the under-pressure phases and mixed with copper, that we have recently calculated and reported.

REFERENCES:

EL04.05.26
Compositionally Modulated Telluride Heterostructure Nanowires Debadarshini Samantaray and Ravishanak Narayan; Indian Institute of Science Bangalore, India

Semiconductor nanostructures with modulated shape and size can be potential candidate for various applications in fields of nanoelectronics, photonics and thermoelectric. In this respect, Te (low band gap semimetal) and Te based nano structures have gained popularity due to their superior thermo-electric property. These properties get manifold when suitable material is incorporated into these systems; one e.g. could be having periodic arrangement of two different nanostructures (superlattice) (SL). But a general and simple scheme to obtain such superlattice 1-D heterostructure with clear and coherent interface is still challenging. In the current study, we have come up with a synthetic design to obtain telluride based compositionally modulated 1D- hetero-structure. Moreover, earlier theoretical studies suggest that SL nanowires can make huge impact on the thermo-electric conversion efficiency by minority carrier blocking.

Several gas phase reactions have resulted in vertical/ radial heterostructure. But we have come up with simple wet chemical synthesis method to obtain single crystalline SL nanowire. In this study, reactive dewetting phenomena has been exploited to obtain periodically arranged PbTe beads along the length of Te nanowire. Using this nanowire as template, the exposed part of the nanowire has been converted to either Ag$_2$Te or Cu$_2$Te to form PbTe-Ag$_2$Te or PbTe-Cu$_2$Te SL nw. TEM analysis shows, these nanowires are single crystalline in nature and having diameter of 60 nm and lengths in micron. Further characterization has been done using STEM-HAADF-EDAX and tomography to understand the morphology and composition. Thermal and electrical conductivity measurements have been carried out on these SL nanowires by Raman and two probe measurement respectively. Further, optical measurements in these system shows intricate nature, which can be attributed to quantum confinement in these SL structures.

EL04.05.27
Earth Abundant, Cation Mutated Delafossites Cu$_3$M$_2$SbO$_6$ Ethan Rubinstein and David O. Scanlon; University College London, United Kingdom

The electronic and optical properties of CuM$_3^{3+}$O$_2$ delafossites have been thoroughly investigated for numerous applications. A notable feature of these materials is a symmetry disallowed VBM to CBM transition often resulting in an optical band gap significantly larger than the smallest direct band gap [1]. CuGaO$_2$ has application potential as a hole transport layer for perovskite solar cells [2], and as part of hybrid electrodes for various photoelectrochemical cells [3][4]. CuInO$_2$ is known for its unusual bipolar dopability considering its wide optical band gap [1].

R. Nagarajan *et al.* successfully synthesized a set of 2+/5+ mixed B-site antimony based analogues [5] opening up a new materials space free of the relatively scarce and increasingly in demand gallium and indium. Of these analogues two earth abundant variants, Cu$_3$Mg$_2$SbO$_6$ and Cu$_3$Zn$_2$SbO$_6$, were found to have ordered crystal structures. In this study hybrid density functional theory with the HSE06 functional is used to predict the electronic structure, optical properties, and band alignments of the Mg and Zn variants. We compare and contrast these results with those of the
known Ga and In based delafossites, and speculate on their potential applications.


SESSION EL04.06: Layered Chalcogenides—Processing Advances
Session Chairs: Albert Davydov and Rafael Jaramillo
Tuesday Morning, December 3, 2019
Hynes, Level 1, Room 104

8:30 AM *EL04.06.01
Atomically Thin TMD Wafers for Technology in the 21st Century Jiwoong Park; University of Chicago, United States

Manufacturing of paper, which started two thousand years ago, simplified all aspects of information technology: generation, processing, communication, delivery and storage. Similarly powerful changes have been seen in the past century through the development of integrated circuits based on silicon. In this talk, I will discuss how we can realize these integrated circuits thin and free-standing, just like paper, using two-dimensional materials based on transition metal dichalcogenides and how they can impact the modern information technology.

In order to build these atomically thin circuits, we developed a series of chemistry-based approaches that are scalable and precise. They include wafer-scale synthesis of three atom thick semiconductors and heterojunctions (Nature, 2015; Science 2018), a wafer-scale patterning method for one-atom-thick lateral heterojunctions (Nature, 2012), and most recently, atomically thin films and devices that are vertically stacked to form more complicated circuitry (Nature, 2017). Once realized, these atomically thin circuits will be foldable and actuatable, which will further increase the device density and functionality.

9:00 AM EL04.06.02
Facile Synthesis of Non-Stoichiometric Modulated Copper Selenide (Cu2−xSe) Using Chemical Vapor Deposition for Electronic and Electrochemical Applications Konar Rajashree1, Gili Yaniv2, Eti Teblum1, Madina Telkhozhayeva1, Gilbert D. Nessim1 and Louisa Meshi2; 1Bar Ilan University, Israel; 2Ben-Gurion University of the Negev, Israel

Two-dimensional architectures are considered excellent candidates for electronics and electrochemical applications. Some of the most commonly researched 2D layered materials are: graphene, boron nitride, black phosphorous, and transition metal chalcogenides (TMCs). TMCs are promising high-performance materials for next-generation energy storage systems because of their high theoretical capacity, high energy density, and high voltage. Among them, copper-based chalcogenide nanocrystals and related alloys have been widely investigated due to their non-toxicity, low cost, and ability to achieve band-gap energies of 1.0–1.5 eV [1-2].

Copper selenide has attracted a lot of attention because of its abundant applications in photoelectric devices, medical treatments, gas sensors, and catalysis. Copper selenides exist as a variety of stoichiometric and nonstoichiometric phases such as CuSe, Cu₂Se₃, Cu₃Se₄, Cu₅Se₄, Cu₁.₈Se, Cu₂Se, Cu₅Se₄, and Cu₂₃-Se [4]. Among them, Cu₂−x-Se shows unique structures and properties. Cu₂−x-Se has Se atoms in a simple face-centered cubic (FCC) structure with the space group Fm-3m, but the superionic Cu ions are kinetically disordered throughout the structure, resulting in a quite high electrical conductivity. Thus, researchers concentrated their synthesis of Cu₂−x-Se with different sizes and shapes through various techniques.

Here, we report the synthesis of bulk 2D layered copper selenide using atmospheric pressure chemical vapor deposition (AP-CVD), with elemental selenium as a precursor. Using top-down approaches (drop casting, etc.), we deposited mono/few-layer flakes on substrates. The layered material was characterized using XRD, HRSEM, TEM, UV-VIS, and AFM to confirm its morphology and stoichiometry. We identified our material as a modulated
structure based on the FCC basic structure (Fm-3m), similar to reported in [5]. It should be noted that due to structural modulation, structure characterization was possible here through electron diffraction only which allowed to conclude modulation vector. AFM measurements demonstrated that the single flakes had a lateral size of approximately 3-6 μm. HRSEM images of the dropcasted material on Si/SiO2 wafer showed copper selenide flakes on top of each other and the presence of layers has also been confirmed by TEM. We will show that this material is a potential candidate for electronic and electrochemical applications.

References:

9:15 AM *EL04.06.03
Epitaxial Growth of Layered Metal Chalcogenides via Metalorganic Chemical Vapor Deposition Xiaotian Zhang, Mikhail Chubarov, Tanushree H. Choudhury, Anushka Bansal and Joan M. Redwing; The Pennsylvania State University, United States

2D metal chalcogenide semiconductors have received considerable attention due to their compelling properties and layered crystal structure. Much of this work has focused on transition metal dichalcogenides (TMDs, MX2 where M=Mo, W and X=S, Se, Te), but there is growing interest in group III (Ga, In) and group IV (Sn, Ge) chalcogenides to expand the suite of layered materials. Much of the research to date has been carried out using flakes exfoliated from bulk crystals but techniques for wafer-scale epitaxial growth of single crystal monolayer and few layers films are rapidly developing.

Our work has focused on the epitaxial growth of 2D layered chalcogenides using gas source chemical vapor deposition (CVD) also referred to as metalorganic CVD (MOCVD). The process is carried out in cold wall reactor geometries at moderate pressures (100-700 Torr) using hydrides (H2Se, H2S) as the chalcogen source in a H2 carrier gas. In the case of TMDs, a multi-step method involving modulation of the metal hexacarbonyl precursor source flow rate was developed to independently control nucleation and lateral growth of domains at elevated temperature (>700°C) which is beneficial to enhance the surface diffusivity of transition metal adatoms. Using this approach, uniform, coalesced monolayer and few-layer TMD films (MoS2, WS2, MoSe2 and WSe2) were obtained on 2” sapphire substrates at growth rates on the order of ~1 monolayer in 10-60 minutes. In-plane X-ray diffraction demonstrates that the films are epitaxially oriented with respect to the sapphire. Post-growth dark-field transmission electron microscopy carried out on monolayers transferred from the sapphire reveals that the films consist of highly ordered micron-sized single crystal regions bounded by low angle grain boundaries. Epitaxial growth of indium selenide was also investigated using trimethyl indium (TMIn) and H2Se in H2. In this case, lower growth temperatures (<500°C) and lower reactor pressures (100 Torr) were necessary to reduce the extent of gas phase pre-reaction of precursors and obtain a stoichiometric film. Under these conditions, epitaxial growth of beta-In2Se3 was demonstrated on c-plane sapphire and (111) Si substrates with both island growth and step-flow growth modes observed. Prospects for utilizing MOCVD for the growth of epitaxial 2D heterostructures will also be discussed.

9:45 AM EL04.06.04
Substrate Directed Synthesis of MoS2 Nanocrystals with Tunable Dimensionality and Optical Properties Tomojit Chowdhury1, Jungkil Kim1, Erick Sadler1, Chenyang Li1, Tim Mueller1, Todd Brintlinger1, Hong-Gyu Park1 and Thomas J. Kempa1, 1Johns Hopkins University, United States; 2U.S. Naval Research Laboratory, United States; 3Korea University, Korea (the Republic of)

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have demonstrated enormous potential in optoelectronic, catalytic, and device studies. Although “top-down” approaches can be used to define crystal morphologies and dimensions, the ability to tailor the physical properties of TMD crystals through explicit synthetic control is a major challenge. We introduce a gas-phase synthesis method that significantly transforms the structure and dimensionality of MoS2 crystals without lithography. Synthesis of MoS2 on Si (001) surfaces pre-treated with phosphine (PH3) furnishes high aspect ratio (~1:20) nanoribbons of crystalline 2H phase MoS2. The widths of the MoS2 nanoribbons can be systematically controlled in the range of 70 – 500 nm by varying the concentration of PH3 gas introduced during the Si (001) surface treatment step. Detailed kinetic studies along with adsorption energy
calculations indicate that the nature and concentration of the underlying Si–phosphide moieties are instrumental in transforming growth of MoS\textsubscript{2} from a conventional 2D triangular to quasi-1D morphology. Notably, the room temperature photoluminescence (PL) of 1D MoS\textsubscript{2} crystals exhibits an emission peak which is blue-shifted by 50 meV relative to that of 2D MoS\textsubscript{2} nanocrystals. Extensive structural, electronic, and optical characterization of these new materials was carried out through a combination of electron microscopies (ac-STEM, HAADF, EELS), scanning probe microscopies (AFM, NSOM), optical spectroscopies (confocal Raman, PL), and electrical transport measurements.

10:00 AM BREAK

10:30 AM *EL04.06.05
Growth of Chalcogenide Based Layered Materials by Molecular Beam Epitaxy Roman Engel-Herbert; The Pennsylvania State University, United States

Two dimensional layered materials offer remarkable properties that are not found in their three-dimensional counterpart. Given its simplicity mechanical exfoliation is conventionally applied to prepare these material systems in the monolayer limit. However, since the materials are not very robust, but rather mechanically soft and chemically reactive in ambient atmosphere – making them prone to a sizeable defect formation during the top-down preparation method – the utilization of a bottom-up approach is highly desirable to study the intrinsic properties in the monolayer limit. Molecular beam epitaxy (MBE) is an ideal method of choice; however the nucleation and growth of layered chalcogenide materials encompasses a specific set of challenges.

In this talk the growth kinetics specific to chalcogenide thin films is discussed and contrasted to the growth of other materials by MBE. Emphasis is placed on experiments to determine the temperature dependent sticking coefficient of the volatile chalcogenide element using a heated quartz crystal monitor to derive growth conditions to access self-regulated growth. Strategies to suppress the formation of twin domains during the layer nucleation stage and strategies to promote the growth of large single domains to achieve high quality monolayer and few layer materials are discussed using the specific examples of PtSe\textsubscript{2} on sapphire, Te on TiO\textsubscript{2} and FeSe on SrTiO\textsubscript{3}. Emphasis will be placed, how in-situ spectroscopic ellipsometry can be used as complimentary diagnostic tool to RHEED to optimize growth conditions and achieve high quality layered chalcogenide-based materials.

11:00 AM EL04.06.06
Growth and Characterization of Large-Area Ultrathin InSe Hadallia Bergeron, Linda M. Guiney, Megan E. Beck, David Lam, Chi Zhang, Silu Guo, Katherine Su, Vinayak Dravid and Mark C. Hersam; Northwestern University, United States

The lack of large-area synthesis methods for emerging 2D materials presents a significant challenge for nanoelectronic devices and systems. In particular, InSe is a semiconducting van der Waals (vdW) material that possesses exceptional band-gap tunability as a function of thickness in the ultrathin limit. Despite its desirable electronic properties, InSe is a relatively under-investigated 2D material, primarily due to the fact that high-quality samples have only been achieved via mechanical exfoliation as opposed to large-area ultrathin-film growth. While many of the extensively studied and synthesized vdW 2D material systems have relatively simple phase diagrams (e.g., MoS\textsubscript{2}), the complex phase diagram for InSe has hindered the development of large-area films, thus motivating more fundamental studies aimed at characterizing and understanding growth mechanisms.

Towards that end, we use diverse surface characterization techniques (e.g., X-ray photoelectron spectroscopy, Raman spectroscopy, atomic force microscopy, transmission electron microscopy, and selected area electron diffraction) and in operando X-ray diffraction to study the structural and compositional evolution of ultrathin InSe films grown by pulsed laser deposition with subsequent vacuum thermal annealing. By monitoring the post-deposition annealing temperatures, we rationally determine the synthesis conditions to realize ultrathin InSe films with high uniformity over large areas, controlled thickness, and no detectable impurities. Using this optimized method, ultrathin InSe films are patterned for the fabrication of top-gated field-effect transistors that demonstrate homogenous device behavior. Thus, our work provides a pathway to large-area ultrathin InSe films with high crystalline quality, thickness tunability, and generalizability to a wide range of substrates suitable for nanoelectronic applications.
Temperature-Controlled Phase Selection in Pulsed-Laser Deposited Gallium Sulfide Thin Films

Kazutaka Eriguchi1,2,3, Petra Specht1, Junqiao Wu1,2 and Oscar D. Dubon1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3SUMCO Corporation, Japan

Gallium sulfide is a III-VI semiconductor with multiple stable phases including (layered) hexagonal and monoclinic, GaS and Ga2S3, respectively. The layered GaS crystal structure is composed of Ga-Ga and Ga-S covalent bonds that extend in two dimensions while interlayer bonding occurs by van der Waals interaction. With a room-temperature band gap of 2.6 eV, GaS has been used for a variety of applications requiring ultrathin layers including transistors and photodetectors and is an attractive candidate for flexible electronics. On the other hand, Ga2S3 exists mainly in the monoclinic form with covalent bonds in three dimensions (i.e., not layered) and a reported band gap of ~3.0 eV.

Thin films of GaS and Ga2S3 have been grown by a variety of methods including chemical vapor deposition, chemical vapor transport, chemical bath deposition. Each method has advantages and challenges. Until now, pulsed-laser deposition (PLD) has been considerably less explored, yet possesses characteristics that are attractive for the synthesis of layered materials. Specifically, PLD is a physical vapor process that enables the “digital” deposition of target materials due to the use of a pulsed laser as an energy source for the evaporation of source materials.

We demonstrate the selective, pulsed-layer deposition of hexagonal GaS and monoclinic Ga2S3 epitaxial films on sapphire substrates from a single Ga2S3 target under high vacuum conditions. Growth with substrate temperatures between 400 °C and 550 °C results in the formation of GaS films, indicating non-stoichiometric transfer from target to film (i.e., loss of sulfur presumably due to its high vapor pressure). Surprisingly, the stoichiometric transfer occurs for substrate temperatures above 650 °C but with a lower growth rate under otherwise the same growth conditions as those used to grow GaS. In the temperature window between 550 °C and 650 °C, films displayed a mixture of phases which is consistent with a monotonic decrease in the Ga:S ratio in films from 1:1 to 2:3. By changing the substrate temperature in this narrow growth range, we are able to synthesize heterostructures of GaS and Ga2S3, thereby providing the unprecedented opportunities to realize heterojunctions from a single materials system in a single growth process and to investigate the heteroepitaxy of two-dimensional crystals on three-dimensional crystals and vice versa.

Materials synthesis and characterization were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, under contract DE-AC02-05CH11231 within the Electronic Materials Program (KC1201). K.E. acknowledges support from SUMCO Corp., Japan.

Intergration Challenges for Transition Metal Dichalcogenides

Peter Litwin, Keren Freedy, Maria Sales, David Olson, Samantha Jaszewski, Shelby Fields, Jon Ihlefeld, Patrick Hopkins and Stephen J. McDonnell; University of Virginia, United States

The last 15 years has seen a renewed interest in layer materials with a new focus on their potential in nanoelectronic applications. These materials have a long history of use as dry lubricants and have been previously studied for their photoelectrochemical and photovoltaic properties. While there have been prior reports on monolayer 2D materials including ‘a single carbon hexagonal layer’ and ‘single-layer MoS2’, it was the seminal work of Novoselov and Geim that triggered this remarkable interest in monolayer 2D for nanoelectronics and it was the demonstration of a monolayer MoS2 based transistor in 2011 that sparked an exponential rise in publications on MoS2 and the subsequent increased interest in the transition metal dichalcogenide (TMDC) family in general.

The focus of this presentation will be on various integration challenges for TMDCs. These include the synthesis of TMDC thin films, the formation of metal contacts on these films, the deposition of high-k dielectrics on the TMDCs, and the synthesis of TMDCs on novel substrates. The presentation will include a summary of our parametric studies of WSe2 molecular beam epitaxy graphite which demonstrates that substochiometric is difficult to completely avoid without the use of seeding layers. We demonstrate the seeding layers not only prevent the formation of substochiometric material, but also dramatically improve the reproducibility of our growths.

In our metal-TMDC interface studies we build on prior work showing interface reactions with Ti and MoS2, to...
demonstrate how thin oxide layers can be used to engineering the interface, preserving a sharp interface while having a minimal impact on the thermal properties of the structures. We find that similar results are observed for WSe$_2$, but that some reaction with TiO$_x$ and WSe$_2$ is observed.

In our prior work we demonstrated the importance of functionalizing TMDCs prior to atomic layer deposition (ALD) of metal oxides to ensure a uniform layer. However in the present work we extend these studies to consider the thermal stability of the HfO$_2$-MoS$_2$ and HfO$_2$-WSe$_2$.

Finally we will present a summary of our growths of TMDC on a range of substrates, with a particular focus on the interface chemistry formation between WSe$_2$ and Ferroelectric hafnium zirconium oxide.

SESSION EL04.07: Layered Chalcogenides—Solid State Fundamentals
Session Chairs: Thomas Kempa and Akshay Singh
Tuesday Afternoon, December 3, 2019
Hynes, Level 1, Room 104

1:30 PM EL04.07.01
Imaging Structure-Directed Phonon Dynamics in MoS$_2$ with Ultrafast Electron Microscopy Yichao Zhang and David J. Flannigan; University of Minnesota, United States

The large elastic strains that can be sustained by van der Waals bonded layered materials (e.g., TMDs) cause significant modification of the electronic band structure through modulation of bond distances and crystal symmetries. This manifests as measurable variations in the electronic and optical properties [1,2]. In addition to static (i.e., time-invariant) strain, ultrafast transient strains can be induced in such materials via femtosecond (fs) photoexcitation. For example, in-plane atomic motions and out-of-plane interlayer coupling in MoS$_2$ have been studied with ultrafast reciprocal-space electron and X-ray diffraction [3,4]. Similarly, bright-field imaging in ultrafast electron microscopy (UEM) has been used to study the nucleation, propagation, and relaxation of coherent elastic strain waves in a number of TMDs arising from the release of impulsive local strain mediated by defects [5-7].

Here, we report the direct imaging with UEM of photoexcited localized anisotropic coherent acoustic-phonon dynamics in single, freestanding, multilayer MoS$_2$ flakes. Combining picosecond temporal resolution and nanometer spatial resolution in bright-field imaging, we observe and quantify both the in-plane nucleation and propagation of acoustic phonons and an interlayer low-frequency breathing mode spatially isolated and localized within two regions of different layer number and along two distinct crystallographic zone axes. Transient structural information induced via fs photoexcitation was extracted by monitoring Bragg diffraction-contrast motion within discrete, nanoscale regions. Propagating and stationary coherent contrast motion occurring within differently-oriented crystal regions occurs via excitation of both intralayer and interlayer phonon modes. The distinct dynamics are resolved within a single field of view and along a single incident electron wavevector. Isolation of the strongly-scattering coherent dynamics reveal a response delay of a few ps for the intralayer mode, indicating a coupling to, and excitation of, the low-frequency interlayer breathing mode. Further, the sensitivity of the measurement is such that a rapid dephasing of the breathing mode relative to an adjacent nanoscale crystal region is observed, indicative of a difference of one to three MoS$_2$ layers and a lag in energy transmission between the crystal boundaries. These results provide new insights into the microscopic nature of intra and interlayer acoustic-phonon dynamics and mode coupling in MoS$_2$ and layered materials in general, especially with respect to the dramatic influence of nanoscale morphology on photoinduced strain [8].

[8] This material is based upon work supported by the National Science Foundation under Grant No. DMR-1654318. Partial support was provided by the Arnold and Mabel Beckman Foundation in the form of a Beckman Young Investigator Award.

1:45 PM EL04.07.02
Sub-Nanosecond Crystallization of Melt-Quenched MoS₂—An Ab Initio Molecular Dynamics Study
Paul Fons¹², Alexander V. Kolobov³¹, Yuta Saito¹, Yuji Sutou⁴ and Muneaki Hase⁵; ¹National Advanced Institute of Science and Technology, Japan; ²Japan Synchrotron Radiation Institute (SPring-8), Japan; ³Herzen State Pedagogical University, Russian Federation; ⁴Tohoku University, Japan; ⁵University of Tsukuba, Japan

MoS₂ is a two-dimensional transition metal dichalcogenide that has gathered much attention with the shift in the research community’s focus from metallic graphene to alternative two-dimensional materials with semiconducting properties. With the lifting of inversion symmetry, monolayer MoS₂ has a direct bandgap of 1.8 eV leading to strong light-matter interaction. In addition, the 2D character of the monolayer leads to reduced dielectric screening and the resulting enhancement in Coulomb interaction leading to large excitonic effects. The high melting point of MoS₂ of more than 1450 K, however, has led to challenges in the growth of thin films. In particular, the large vapor pressure of Sulphur in combination with the high growth temperatures required for film growth have been problematic underscoring the need for a non-conventional approach to growth. In this presentation, ab-initio molecular dynamics is used to show that crystalline MoS₂ can be grown from the amorphous phase on sub-nanosecond time scales with the van der Waals (vdW) gaps serving to strongly orient the resulting structure. The plane wave Vienna ab-initio simulation package (VASP) was used to first form a melt-quenched amorphous phase. The amorphous phase was then heated to just below the melting point and the dynamics of the system were studied. The formation of ABAB rings of Mo-S bonds was observed to precede the emergence of vdW gaps leading to the formation of well defined lattice planes. In the presentation, we will explore details of growth process and probe critical interactions that allow the formation of the crystalline phase on sub-nanosecond time scales using confined thin film amorphous opening up new avenues for large scale growth of 2D MoS₂.

2:00 PM EL04.07.03
Thermal Degradation of Monolayer MoS₂ on SrTiO₃ Supports
Wenshuo Xu¹₂ and Jamie Warner¹; ¹University of Oxford, United Kingdom; ²Beijing Institute of Technology, China

Monolayer MoS₂ is a wide-bandgap semiconductor suitable for use in high-temperature electronics. It is therefore important to understand its thermal stability. We report the results of a study on thermal degradation of MoS₂ monolayers supported on SrTiO₃ substrates in ultrahigh vacuum (UHV). Our studies were carried out on the (111), (110), and (001) terminations of SrTiO₃ substrates, but MoS₂ was found to degrade on all of these surfaces in a similar way. By scanning tunneling microscopy, we show that MoS₂ monolayer crystals maintain their structure up to 700 °C under UHV, at which point triangular etch trenches appear along the 〈2-1-10〉 lattice directions (i.e., sulfur-terminated edge directions) of the MoS₂ crystals. The trenches are due to the preferential loss of sulfur, allowing molybdenum to be oxidized by oxygen originating from the SrTiO₃ substrate. The intensity of the A-exciton photoluminescence (PL) peak and the E₂g¹ and A₁g Raman signals reduced significantly following treatment at this temperature. The crystals continue to degrade at higher annealing temperatures in UHV until they transform into MoO_x (x = 2–3) particles at 900 °C, and the optical properties characteristic of MoS₂ are lost entirely in PL and Raman spectra. The initial sulfur loss and the formation of MoO₃ are confirmed by X-ray photoelectron spectroscopy. The macroscopic triangular shapes of the MoS₂ crystals are retained until the residual particles evaporate at above 1000 °C. The optical properties of the 700 and 800 °C UHV-annealed samples can be partially recovered upon sulfur annealing. This work establishes a pathway of the thermal degradation of SrTiO₃-supported monolayer MoS₂ in vacuum from smooth MoS₂ crystals to crystals with sulfur vacancies (etch trenches), followed by MoO₃ and finally MoO₃ particles. We also demonstrate how sulfur annealing can be used to heal the defects.

2:15 PM BREAK
2:45 PM *EL04.08.01
Electronic and Photonic Properties of Emerging Low-Dimensional Chalcogenides Materials \textit{Han Wang};
University of Southern California, United States

In this talk, I will discuss our recent work in studying the electronic and photonic properties of emerging low-dimensional chalcogenides materials, and in developing them for novel semiconductor device applications. The first part of the talk will focus on discussing our recent research on the phonon-spin and phonon-electron coupling in chalcogenides ferromagnetic monolayer materials and its electronic device applications. In the second part of the talk, I will discuss our work on studying the unique optical properties of chalcogenides perovskite BaTiS$_3$ over a broad wavelength range from mid-IR to visible, and the new non-linear photonic device applications it can enable. I will conclude with remarks on promising future research directions of low-dimensional chalcogenides materials, and how these newly developed low dimensional materials may enable new functional electronic and photonic devices for sensing, communication, and computing applications.

3:15 PM EL04.08.02
2D Rules—Band Gap Engineering in Weakly Interacting van der Waals Heterostructures \textit{Francis H. Davies,}
Ned T. Taylor, Conor J. Price, Shane G. Davies and Steven P. Hepplestone; University of Exeter, United Kingdom

The band gap is of paramount importance to almost all of the electronic and optical properties of semiconducting materials. By controlling the size of the band gap and their electronic structure, we can control both the transport properties and the optical interactions of such materials. The ability to energetically control electrons in solid-state devices is pivotal in the fields of sensing, renewable energy [1], information processing and communications technology [2]. Here we present the rules of 2D band gap engineering in 2D heterostructures. Our insights offer the potential of engineering not just the band gap, but the electronic dispersion itself; making it far more versatile than strain engineering of band gaps.

The field of 2D semiconductors has been of growing research interest in recent years, but 2D heterostructures have only recently become experimentally viable [3]. We have performed a large scale first principles study of many transition metal dichalcogenides and other 2D semiconductors using density functional theory. These 2D layered heterostructures demonstrate weak inter-layer interactions. Due to this, the band structures of individual layers of a heterostructure have a high fidelity to their isolated counterparts. We show that a layered heterostructure will, therefore, have a dispersion which consists of an overlay of its components’ band structures with one key change due to interlayer interaction which we discuss at length. We determine that the electronic dispersions of 2D layered heterostructures can be tailored by layer composition, and demonstrate a wide range of potentially attainable tunable band structures.


3:30 PM EL04.08.03
Anisotropic Optical Properties of 2D Silicon Telluride \textit{Romakanta Bhattarai, Jiyang Chen, Thang B. Hoang,}
Jingbiao Cui and Xiao Shen; University of Memphis, United States

Silicon Telluride (Si$_2$Te$_3$) is layered semiconductor material with a unique crystal structure where Si atoms form dimers to fill the sites between the hexagonally close-packed Te atoms.\textsuperscript{1} Theoretical investigations showed that Si dimers can rotate between four possible orientations within the Si$_2$Te$_3$ layer, giving rise to a unique structural variability that could have potential new applications in electronic and optoelectronics devices.\textsuperscript{2} Recently, two-dimensional Si$_2$Te$_3$ multilayers, along with nanoplate and nanowires have been reported.\textsuperscript{3} Combining the reduced dielectric screening from low dimensionality and the structural variability from Si dimer rotation, the optical

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properties of 2D Si\(_2\)Te\(_3\) is particularly interesting. In this study, we report a combined computational and experimental investigation of the optical properties of 2D Si\(_2\)Te\(_3\). Using many body GW approximation and Bethe-Salpeter equation (BSE), we obtain the dielectric constants of bulk and monolayer of Si\(_2\)Te\(_3\). A strong optical anisotropy is discovered. The imaginary dielectric constant in the direction parallel to the Si-Si dimers is half of the value perpendicular to the dimer. We show this effect originates from the particular compositions of the wavefunctions in the valence and conduction bands. The optical measurement of the absorption spectra of 2D Si\(_2\)Te\(_3\) nanoplates shows modulation of the absorption coefficient under 90-degree rotation, confirming the computational results. We also found that the BSE calculations reduce GW quasiparticle band gap by 0.3 eV in bulk and 0.9 eV in the case of a monolayer, indicating a large excitonic effect in Si\(_2\)Te\(_3\). Furthermore, including the excitonic effect in bulk calculations significantly reduces the imaginary dielectric constant in the out-of-plane direction, indicating a strong effect of Coulombic interaction of the out-of-plane excitons in the case of Si\(_2\)Te\(_3\) multilayers. The results show rich features and tunability in the optical properties of 2D Si\(_2\)Te\(_3\).


ACKNOWLEDGMENTS
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3:45 PM EL04.08.04
A Physical MoS\(_2\) Sensor Simulation Using Scanned Gate Microscopy Steven G. Noyce, James Doherty and Aaron D. Franklin; Duke University, United States

The field of nanoelectronic chemical sensors faces a gap between theory and observation in applied sensor demonstrations. For example, theoretical predictions of the operating point at which maximal signal-to-noise ratio (SNR) will be obtained are at odds with trends of measured SNR versus gate voltage. This work seeks to bridge this gap for the case of molybdenum disulfide (MoS\(_2\)) chemical sensors by studying a MoS\(_2\) device that is influenced by a controlled local charge, which simulates an analyte. The extensive control available in this physical sensor simulation provides pathways to explore and resolve discrepancies between computational sensor simulations and demonstrated sensors. Realizing this level of control with sub-nanometer and pico-amp precision required the development of an advanced characterization system (a customized scanning gate microscopy setup), which was then utilized to test the response of MoS\(_2\) field-effect transistors (FETs) in a variety of configurations. Sensitivity of the device to a local charge was mapped across locations near the device surface, revealing localized sensitive “hot spots” within the 2D channel. Similar maps were taken across a range of operating points and charge-to-surface distances, allowing for the extraction of sensor metrics. For instance, the SNR was shown to peak in the transistor subthreshold regime, reaching over 4 times its value in the linear regime. The comparison of these controlled measurements with electrostatic and 2D current flow models leads to increased understanding of the behavior of MoS\(_2\) FETs in sensors, indicating directions for the optimization of future sensor design and operation.

4:00 PM *EL04.08.05
Controlling Light-Matter Interactions in Chalcogonede-Based Topological Semimetals—Novel Physics to Devices Ritesh Agarwal; University of Pennsylvania, United States

Can one control photoresponse in materials via patterning optical intensity distribution and polarization? In this talk, we explore this idea on a new class of topological material, Weyl semimetals (WSMs). WSMs are a family of gapless topological materials with broken inversion and/or time reversal symmetry in which the conduction and valence bands cross at single points in momentum space, which are called the Weyl nodes. The electronic bands are topologically nontrivial and display linear dispersion around the Weyl nodes, hosting unique quasiparticles called the Weyl fermions with interesting properties. The optical excitation properties of WSMs are only starting to be explored. We will introduce a new second order nonlinear optoelectronic probe, which we call spatially dispersive circular photogalvanic effect (s-CPGE) and demonstrate its sensitivity to detailed band features owing to its unique excitation mechanism. In WSMs such as MoTe2 and MoW1-xTe2 (x=0.3, 0.9) in the inversion symmetry broken...
For the total energy calculations using DFT, we use the Hubbard temperature for the configurations that yield a ferromagnetic ground state. We simulate their magnetic phase change using lattice Monte-Carlo simulations. Finally, we extract the Curie temperature of iron (Fe) doped WSe$_2$ as high as 307 K and manganese (Mn) doped WSe$_2$ as high as 232 K.

Clusters of dopant atoms in monolayer WSe$_2$ have attracted immense attention in the recent past for their possible use in future, energy-efficient, spintronic devices. A class of 2D-DMS candidates are transition-metal dichalcogenides (TMDs), substitutionally doped with magnetic-transition-metals (Cr, Fe, Mn, etc.). Especially promising are TMDs based on heavy elements like tungsten (W) and selenium (Se). Thanks to their strong spin-orbit interaction, they easily mediate magnetic interactions among the dopant transition-metal atoms.

In this work, we investigate magnetism in magnetically doped WSe$_2$ monolayers using Density Functional Theory (DFT). We investigate various doping concentrations and various configurations with different relative positions of the dopant atoms. Specifically, we investigate the effect of clustering of the dopant atoms on the magnetic properties of doped monolayer WSe$_2$. In our computational model, we first determine the magnetic ground state of the doped WSe$_2$ monolayers by comparing the total energies of various magnetic configurations calculated using DFT. Next, we simulate their magnetic phase change using lattice Monte-Carlo simulations. Finally, we extract the Curie temperature for the configurations that yield a ferromagnetic ground state.

For the total energy calculations using DFT, we use the Hubbard $U$ model within DFT+$U$ to take into account the enhanced electron-correlation energy of the dopant atoms. The electron-correlation energy in the $d$ orbitals of the magnetic-transition-metals significantly impacts the magnetic order of the material system. To correctly account for the electron-correlation energy of the dopant magnetic transition-metal atoms, we first calculate the Hubbard $U$ parameter for each configuration using the linear-response method. Next, we use the calculated Hubbard $U$ parameters for subsequent total energy calculations using DFT+$U$.

For structures with a ferromagnetic ground state, we quantify the magnetic order of doped WSe$_2$ with different doping configurations by calculating their Curie temperature using a two-step approach. In the first step, we build the classical Heisenberg Hamiltonian by obtaining the exchange interactions among the dopant transition-metal atoms. To account for the long-range interactions, we use a parameterized function to define the exchange interactions with asymptotic decaying exponential behavior. We optimize the parameters of the functional form representing the exchange interactions by least square fitting the Heisenberg Hamiltonian to the total energy difference between the magnetic and the non-magnetic configurations obtained from the DFT+$U$ calculations. In the next step, we simulate the magnetic phase change of the classical Heisenberg Hamiltonian using the lattice Monte-Carlo method to obtain the Curie temperature.

From our DFT+$U$ calculations, we additionally extract formation energies, showing that the clustering of the dopant atoms is energetically favorable in monolayer WSe$_2$. Further, we find that the magnetic order strongly depends on the type of dopant transition-metal atoms and their relative position in the monolayer WSe$_2$. The strong positional dependence of the dopant atoms on the magnetic order is the result of a trade-off between the minimization of the kinetic energy and the exchange energy. Finally, we conclude by calculating the Curie temperature for various doped structures with ferromagnetic ground states. We predict the optimum doping conditions necessary for obtaining a Curie temperature which exceeds room temperature in transition-metal doped monolayer WSe$_2$. Among our studied magnetic configurations, we find a Curie temperature of iron (Fe) doped WSe$_2$ as high as 307 K and manganese (Mn) doped WSe$_2$ as high as 232 K.
Electron-Phonon Interactions in Defective Germanium Selenide  
Tianlun Huang, Arielle Cohen, David K. Lewis and Sahar Sharifzadeh; Boston University, United States

We utilize first-principles density functional theory (DFT) and many-body perturbation theory (MBPT) to study the optoelectronic properties of monolayer germanium selenide (GeSe), emphasizing the role of point defects and electron-phonon interactions; two phenomena that will be present in and can dominate the properties of real materials. We systematically study a series of charged vacancies, their trap state energies, and their impact on optical absorption. Additionally, by approximating the role of electron-phonon interactions, we determine how the defect-induced trap states are modified by the presence of phonons at finite temperature. We determine that the excitonic properties of the material are significantly affected by the presence of defects and phonons, with implications for devices fabricated using this material system.
it is extremely important to understand the key features behind such subtle sources of structural defects. Distinguishing features related to the weakness of vdW forces, and hence relevant to most systems based on vdW epitaxy, and features specifically related to some particularities of the system under investigation.

Here, several x-ray diffraction tools are combined to investigate defects in bismuth telluride films grown by molecular beam epitaxy on BaF2 (111) substrates. Intrinsic topological surface states have already been observed in such films [1], making them good candidates for applications in spintronics or quantum computing. Compositional fluctuation, twinned domains, and bulk free carriers are among the main problems reported in these films [2]. Desorption of tellurium is the root of compositional fluctuation. But, from tellurium vacancies to bismuth rich phases there are a whole gamut of possible processes involved. Antisite occupation can follow the introduction of vacancies in the vdW gaps, promoting films full of point defects detrimental to lattice perfection. At some instant, lattice energy is minimized by turning point defects into bismuth bilayers (BLs). This is a critical instant in terms of free carriers since films with only point defects, only BLs, or coexisting point defects and BLs may have completely different behaviors. Twinned domains can be a simple consequence of low degree of lateral ordering in vdW epitaxy, or of any other source of lateral inhomogeneities still to be identified. Moreover, lattice misfit can be slightly different in bismuth rich films [3], giving the opportunity to study the actual impact of lattice misfit in vdW epitaxy.


EL04.09.03 Polariton Propagation and Exciton Phase Correlations in an Optical Microcavity with Embedded Topologically-Disconnected Transition Metal Dichalcogenide Microflakes Yamuna Paudel¹, Shaina Raklyar¹, Yuri Lvov², David W. Snoke³ and German V. Kolmakov⁴; ¹NYC College of Technology CUNY, United States; ²Rensselaer Polytechnic Institute, United States; ³University of Pittsburgh, United States

Due to strong light-matter interactions and exciton stability, transition-metal dichalcogenides (TMD) provide a platform for optoelectronic applications at room temperatures. By considering coupled dynamics of cavity photons and TMD excitons, we studied exciton-polariton propagation in an optical microcavity with an embedded TMD layer. Specifically, we considered the case where the TMD layer is non-uniform and consists of a set of separate, topologically disconnected microflakes. Via numerical simulations we demonstrated that polaritonic modes can propagate in the system if the TMD coverage is high enough. However, the polaritonic excitation spectrum is broadened compared to that in the case of an ideal homogenous embedded TMD layer. We also found that although the TMD flakes are disconnected, the phases of the excitonic wave functions in different flakes are strongly correlated. We attribute the latter to the exchange by cavity photons emitted and re-absorbed by the TMD excitons. Finally, we discuss the possibility to use the TMD polaritonic system in optoelectronic applications. This work was supported in part by the Department of Defense under grant No. W911NF1810433.

EL04.09.05 Resistless Patterning Techniques for Transition Metal Dichalcogenides Jian-An Ke, Kevin Bogaert and Silvija Gradečak; Massachusetts Institute of Technology, United States

Two-dimensional (2D) materials such as graphene and transition metal dichalcogenides (TMDs) exhibit many interesting properties that make them promising materials for novel electronic and optical applications. The application space could be further broadened by having the ability to combine these materials into more complex heterostructures. Conventional patterning methods rely on coating a polymer-based resist that is then exposed (by light or electron beam), developed, and selectively removed. Each of these steps adds to the process complexity, and in the case of 2D materials, potential materials damage. A resistless patterning technique is therefore desirable, due to fewer potentially damaging processing steps, which naturally improves yield and is more cost-efficient.

In this work, we demonstrate two distinct direct-write patterning methods for 2D TMD heterostructures grown by chemical vapor deposition (CVD). The first approach is based on laser-induced method for controlling the location
of MoS2 nucleation within patterned WS2. We investigate WS2 defect formation as a function of the laser power and wavelength and demonstrate the site selectivity of subsequent MoS2 growth. In an effort to push the patterning resolution, the second resistless technique uses electron beam to directly pattern MoS2 on Si/SiO2 substrates. By exposing the substrate by electron beam, we show that CVD-grown MoS2 preferentially nucleates at the exposed patterns. We will discuss the underlying mechanisms that govern both patterning methods, properties of the resulting TMD materials, resolution limits, as well as the application for more complex TMD heterostructures. These direct-write technique will simplify the process of heterostructure patterning and enable the routine fabrication of complex device architectures.

**Feasibility of Layer-Number Determination of Few to Monolayer MoS2 via Combined Simulation and Electron Diffraction Experiments**

Yichao Zhang and David J. Flannigan; University of Minnesota, United States

Properties of transition metal dichalcogenides (TMDs) are sensitively dependent upon a number of structural and morphological features within the few to monolayer limit. For example, the electronic and optical properties of MoS2 can be tuned via variation in single layer number and applied elastic strain [1,2]. Owing to this sensitive dependence at the single-layer level, development of methods for precisely and accurately determining local layer number is important for unambiguously determining the relationship between function and structure. Among other viable methods (e.g., Raman spectroscopy and atomic force microscopy), transmission electron microscopy (TEM) is an especially attractive platform for such measurements, as it enables combined comprehensive characterization and correlative in situ measurements of the electronic and structural properties, with atomic- to millimeter-scale spatial resolution. For layered materials, a practical approach in TEM for determining layer number involves analysis of relative Bragg-spot intensities in parallel-beam electron diffraction (PBED) patterns over a range of specimen tilt angles [3]. Such an approach has been explored via simulations for few and monolayer MoS2 [4], while experimental methods aided by prior knowledge of layer number have been applied [5]. Accordingly, systematic experimental measurements employing PBED in TEM on MoS2 specimens with initially unknown thicknesses, as directly compared to simulations, are needed to establish the practical feasibility, accuracy, and precision of such an approach.

Here, we combine PBED experiments in TEM with simulations to systematically study the robustness of the specimen tilt-angle approach for determination of layer number at the single-layer level in MoS2. Bragg-spot intensities as a function of tilt angle were simulated through calculation of the associated crystal shape function of the reciprocal-space rods and the structure factors, following Mkhoyan and co-workers [4]. Few and monolayer specimens were prepared using mechanical exfoliation, with subsequent mounting onto holey SIN TEM membranes. Bragg-spot intensities for the \{100\} and \{110\} families of planes were mapped over a wide range of tilt angles and for different tilt axes (with respect to a particular in-plane crystallographic direction). Overall, agreement between experiments and simulations were good for an MoS2 monolayer, indicating the method may be practically useful for identifying such specimens. However, deviations ranging from subtle to severe were observed with increasing layer number, indicating the approach becomes increasingly limited as sensitivity of Bragg-spot intensities and tilt angle to layer number decreases with increasing thickness. Potential sources of error and deviation from simulated results will be discussed [6].

[6] This material is based upon work supported partially by the National Science Foundation under Grant No. DMR-1654318 and partially by the National Science Foundation through the University of Minnesota MRSEC under Award Number DMR-1420013. Partial support was also provided by the Arnold and Mabel Beckman Foundation in the form of a Beckman Young Investigator Award
We demonstrate, for the first time, wafer-scale graphene/MoS$_2$ heterostructures prepared by chemical vapor deposition (CVD) and their application in vertical transistors and logic gates. A CVD-grown bulk MoS$_2$ layer is utilized as the vertical channel, whereas CVD-grown monolayer graphene is used as the tunable-work-function electrode. The short vertical channel of the transistor is formed by sandwiching bulk MoS$_2$ between the bottom indium tin oxide (ITO, drain electrode) and the top graphene (source electrode). The electron injection barriers at the graphene-MoS$_2$ junction and ITO-MoS$_2$ junction are modulated effectively through variation of the Schottky barrier height and its effective barrier width, respectively, because of the work-function tunability of the graphene electrode. The resulting vertical transistor with the CVD-grown MoS$_2$/graphene heterostructure exhibits excellent electrical performances, including a high current density exceeding 7 A/cm$^2$, a subthreshold swing of 410 mV/dec, and a high on-off current ratio exceeding 10$^3$. The large-area synthesis, transfer, and patterning processes of both semiconducting MoS$_2$ and metallic graphene facilitate construction of a wafer-scale array of transistors and logic gates such as NOT, NAND, and NOR.

**EL04.09.08**

**Spray-Deposited Molybdenum Disulfide Nano flakes Aiming Energy Storage Devices**

Maykel d. Klem, Gabriel Nogueira, Caroline Sousa and Neri Alves; São Paulo State University (UNESP), School of Technology and Sciences, Brazil

Among a variety of 2D graphene-like materials, molybdenum disulfide (MoS$_2$) has attracted much attention due to its remarkable physical, electrical and optical properties [1]. MoS$_2$ is a layered material member of the transition metal dichalcogenides family and presents a direct bandgap of 1.8 eV when in monolayer. Furthermore, MoS$_2$ can produce high specific area nanostructures and presents great electrochemical performance [2]. These are desirable features for application in energy storage devices. However, the mass production of large-area electrodes based on MoS$_2$ is a major problem. Here we present the synthesis and characterization of MoS$_2$ nano flakes deposited over stainless steel substrates by spray. We obtained the MoS$_2$ by hydrothermal synthesis, using thiourea and sodium molybdate dihydrate as precursors. The resulting black powder was collected by centrifugation and washed several times with water and ethanol. The obtained material was exfoliated in a solution of water and isopropanol (30%wt.) assisted by sonication. After 3 h of sonication, the dispersion was centrifuged at 5000 rpm over 1 h and the supernatant was collected. The film deposition was carried out by transferring the as-prepared dispersion (supernatant) to an airbrush coupled to a modified 3D printer base with in-line displacement. We produced a supercapacitor with the spray-deposited MoS$_2$, using the stainless-steel substrate as the current collector. We used a gel-like electrolyte based on Poly (vinyl alcohol) (PVA) and phosphoric acid (H$_3$PO$_4$). SEM images showed a flower-like structure for the MoS$_2$ black powder collected from the autoclave, which is broken into nanoflakes during the exfoliation process. XDR analyses showed that the sprayed films are highly crystalline, presenting the characteristics peaks of the hexagonal semiconducting microstructure (2H-MoS$_2$). Preliminary tests showed a specific capacitance of 18 F/g for the supercapacitor. The device also exhibited a good electrochemical behavior over cyclic voltammetry (C-V) measurements. In conclusion, here we demonstrated the production and characterization of spray-deposited films based on MoS$_2$ nanoflakes and its application as an energy storage device electrode.

**Acknowledgements**

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**References**


**EL04.09.09**

**Atomic and Electronic Structure of the Edges of Bulk and Monolayer Tin disulfide (SnS$_2$)**

Tao Yan, Pratap M. Rao and Aaron Deskins; Worcester Polytechnic Institute, United States

Because of its two-dimensional structure and semiconducting properties, tin disulfide (SnS$_2$) is of interest for applications in electrochemical catalysis and sensing, as an electron transport layer for photovoltaics, and as an active material in photodetectors and thin film transistors. While the atomic and electronic structure of the basal planes of bulk and monolayer SnS$_2$ are well known, the same is not known for the edges, which could have a major influence on the performance of SnS$_2$ in the aforementioned applications. This paper reports on density functional...
theory (DFT) simulations and experimental measurements of the atomic and electronic structure of the edges of bulk and monolayer SnS₂ under different chemical conditions. We found that, with increasing sulfur coverage, the band gap of SnS₂ edges becomes smaller and there’s a transition from indirect to direct bandgap of bulk SnS₂ edges and form indirect to direct to indirect bandgap of monolayer SnS₂ edges. These results thereby determined the influence of chemical synthesis conditions on the electronic structure of the edges.

EL04.09.10
2D Chalcogenide Perovskites—Atomic and Electronic Structures Chen Ming and Yi-Yang Sun; Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Perovskite materials are intrinsically two dimensional, as any termination along two parallel (100) surfaces with a finite thickness could produce a self-passivated slab, which is not too different from the widely studied transition-metal dichalcogenides. The stacking of such slabs gives rise to the so-called Ruddlesden-Popper phase. In this work, we perform a systematic study on the atomic and electronic structures of such slabs (or 2D chalcogenide perovskites) following a generalized Glazer’s notation used for bulk perovskites. The pattern of the octahedron distortion in thin slabs is found to be distinctly different from that in bulk, which in turn affects the electronic structures. The thermodynamic stability and the effect of strain (in the case of freestanding slabs) and substrate (in the case of epitaxial growth) are studied based on density functional theory calculations. Comparison with halide and oxide perovskites will also discussed in this talk.

EL04.09.11
Heterojunction of 2D-MoS₂ with p-Type MnO Quantum Dots for Improved Photoresponse Somak Mitra, Yusin Pak, Naresh Alaal, Bin Xin and Iman Roqan; King Abdullah University of Science and Technology, Saudi Arabia

Photodetection characteristics can be improved by optimized heterojunction architecture in photodetector device. A two-dimensional (2D) platform material can be used for stably transferring the photogenerated signals into circuitry with a quantum confined nanostructure material from which photonics aspects and enhanced absorption can be exploited. In this work, we will present a heterojunction device structure of 2D molybdenum disulfide (2D-MoS₂) and manganese oxide quantum dots (MQDs). Solution-processed P-type manganese oxide quantum dots (MQDs) with a mean diameter of 4.9 nm are synthesized by femtosecond laser ablation (FLA). MQDs were uniformly spray-coated onto the 2D-MoS₂ to fabricate the active layer. The p-n junction structure of n-type 2D-MoS₂ and p-type MQDs reveal a significantly enhancement in the photoresponse of the photodetector by 2-5 folds. At the same time the photoresponse in the ultraviolet region has been improved due to MQDs. The dark current of the photodetector device is reduced by heterojunction structure compared to bare 2D-MoS₂ photodetector. This work revealed that solution-processed quantum dots hybridized with 2D material can lead to different high-performance flexible and cost-effective optoelectronic, sensor devices for large scale.

EL04.09.12
Building an All-Sulfide TaS₂/Cu₂-II-Sn-S₄/CdS Solar Cell and Putting it on Silicon Andrea Crovetto, Rasmus Nielsen, Alireza Hajijfarassar, Ole Hansen, Brian J. Seger, I.B. Chorkendorff and Peter Vesborg; Technical University of Denmark, Denmark

A few transition metal dichalcogenides are high work-function metallic compounds and could therefore be effective hole contacts in a variety of (opto)electronic devices. Nevertheless, when considering - for example - the field of photovoltaics, it is difficult to find reports of conductive contacts that are not elemental metals or transparent conductive oxides. Here, we incorporate the metallic compound TaS₂ into the device structure of emerging photoabsorbers (Cu₂BaSnS₄ and Cu₂SrSnS₄) and fabricate all-sulfide solar cells. Compared to reference cells built with a standard elemental metallic contact (Mo), the all-sulfide solar cells are more efficient by about 10% relative. We will discuss some of the properties of the TaS₂ hole contact, its stability, and the possible reasons for the efficiency improvement.

For the growth of Cu₂BaSnS₄ and Cu₂SrSnS₄ we propose an oxide precursor route involving thermal conversion of sputtered oxide films (Cu₂BaSnO₄ and Cu₂SrSnO₄) in an H₂S atmosphere at the same temperature normally used for the more common non-oxide precursors. Interestingly, Cu₂BaSnS₄ and Cu₂SrSnS₄ crystallize in a trigonal structure where Cu, Ba(Sr), and Sn have distinct coordination environments. This major structural difference from the well-studied tetrahedrally-coordinated kesterite Cu₂ZnSnS₄ implies that substitutional defect formation is in general
unfavorable in Cu$_2$BaSnS$_4$ and Cu$_2$SrSnS$_4$. In fact, both compounds are found to have sharper absorption and emission edges than kesterite, and their room-temperature photoluminescence peak is well aligned to their band gap. Finally, there is a long-standing dream of depositing sulfide semiconductors as wide band-gap absorbers on silicon solar cells, in order to realize highly efficient double-junction (tandem) cells. Progress towards this ambitious goal has been hampered by the relatively low efficiency of sulfide absorbers, and by integration issues with the Si bottom cell due to the relatively high temperatures needed to grow and crystallize many sulfides. Here we attempt to address the second issue by incorporating a very thin TiN diffusion barrier between the two sub-cells, which helps preserve the silicon cell during a sulfurization process at 550°C. Efficiencies up to 3.3% for Cu$_2$ZnSnS$_4$/Si tandems have been reached so far when incorporating the TiN barrier layer.

EL04.09.13
Spontaneous Nanopattern Development Directed by Interfacial Light Absorption Anisotropy
Azhar I. Carim, Nicolas A. Batara, Anjali Premkumar, Madeline C. Meier, Kathryn R. Hamann, Harry A. Atwater and Nathan S. Lewis; California Institute of Technology, United States

Photoelectrodeposition of Se-Te alloys using unstructured illumination spontaneously generates nanopatterned films with significant long-range order. The feature sizes, periodicities, anisotropies, and orientations of the nanoscale pattern can be selected by manipulating the input optical excitation. Isotropic morphologies consisting of ordered arrays of nanopores were generated using unpolarized and circularly-polarized illumination whereas linearly-polarized light resulted in highly-anisotropic lamellar-like morphologies with the in-plane orientation of the patterns controlled by the direction of the light polarization. Elliptical polarization inputs effected additional morphological complexity. The pattern periodicity was encoded by the illumination spectral profile. A single periodicity in single spatial direction was only generated even with the use of broadband and multimodal spectral profiles and the periodicity was found to be sensitive to all investigated tuning of such profiles. Structures with nonequal periodicities in the two orthogonal in-plane directions could also be generated and both periodicities could be independently controlled. The deposition process was assessed computationally using a two-step iterative model wherein a finite-difference time domain method was first used to calculate the spatially-varying levels of light absorption in the growing structure. This instructed a Monte Carlo method in which deposition was simulated to occur preferentially near areas of high localized light absorption. These computational results matched the experimentally observed patterns indicating that pattern development was directed by evolution of interface to maximize anisotropic light collection.

EL04.09.14
Systematic Prediction of the Electronic and Magnetic Properties of Vacancy, Antisites and Defect-Complexes of Monolayer CrS$_2$, MoS$_2$ and WS$_2$
Emmanuel Igumbor, Guy M. Dongho-Nguimdo, Evans M. Benecha, Abdulrafiu Raji and Enrico B. Lombardi; University of South Africa, South Africa

Graphene is one of the first two-dimensional (2D) materials to be experimentally synthesized. Since then, 2D materials have attracted great attention because of their unique physical properties: ability to be used for future nano-electronic, optoelectronics and other industrial applications. However, graphene has a major deficiency due to its gapless band structure, which limits its use for applications in semiconductor devices. Recently, 2D transition metal dichalcogenides (TMDs) materials have attracted significant interest. Research has shown that novel electronic and photonic devices have been demonstrated using 2D TMDs. This discovery paved the way for intense scientific consideration of 2D mono layers CrS$_2$, MoS$_2$ and WS$_2$. Point defects are inevitable in in chemically grown 2D materials due to the imperfection of the growth process. Defects are inevitably introduced during the synthesis of TMDs by means of chemical vapor deposition. Point defects including sulphur vacancies, transition metal vacancy, antisites and defect-complexes as well as how they influence the electronic and optical properties of CrS$_2$, MoS$_2$ and WS$_2$ are not well known. In this report, we predicted the electronic, magnetic and structural properties of intrinsic point defects in CrS$_2$, MoS$_2$ and WS$_2$ that may be observed under certain conditions. Density functional theory calculations were performed to model the structural and electronic properties of defects in CrS$_2$, MoS$_2$ and WS$_2$. The ultrasoft psuedopotential was used to separate the valence electron from the core electrons and the generalized gradient approximation was used as the exchange correlation functional.

Whereas sulphur vacancy is predominant energetically favorable in the S-poor chemical condition, the transition metal (TM) vacancy is energetically more favorable in the S-rich chemical condition. While the antisites of the CrS$_2$
and WS$_2$ are energetically more favorable when a chalcogen atom is replace by a TM atom of the host, the antisites of the MoS$_2$ on the other hand, is energetically more favorable when a Mo is replaced by an S atom. The antisites show that they are sensitive to chemical rich environment. The S$_{TM}$ and TM$_S$ are desirable in the S-rich and TM-rich chemical limit conditions, respectively. While the V$_{CS}$, V$_{MoS}$ and V$_{WS}$ are stable complexes with respect to their binding energies, the V$_{TM}M_S$ and V$_{VS}M_T$ are more energetically favorable in the N configurations. Introduction of defects in CrS$_2$, MoS$_2$ and WS$_2$ modulated their wide band gaps. While sulphur vacancies in CrS$_2$, MoS$_2$, and WS$_2$ behave as $p$-type semiconductor, the Cr$_S$ on the other hand, behaves as an $n$-type semiconductor. Defect-complexes; $V_WW_S$, $V_SM_S$ and $V_CSS$ induced higher magnetic moment, relatively to other defects. The $V_WM_S$, $V_{MoMoS}$, $V_{Mo2}$ and $V_{W2}$ induced several occupied defect states in the band gap of their host, exhibiting metallic character and are highly spin polarized relative to other defects. The delocalized disorder antisites in CrS$_2$, MoS$_2$ and WS$_2$ are important centers of carriers, which may reduce the mobility of charge carriers. Furthermore, whereas all the defects in WS$_2$ enhance the spin orientation of the host, for the MoS$_2$, the complexes distorted its spin orientation and induced magnetic moment. The spin polarized induced defects could be useful for spintronics application.

EL03.06.21

Magnetic, Electrical and Magnetocaloric Properties of Fe$_{90}$Ta$_{10}$ Thin films

Surabhi Shaji$^1$, Nikhil R. Mucha$^1$, Prakash Giri$^2$, Manosi Roy$^1$, Christian Binek$^2$ and Dhananjay Kumar$^1$; $^1$North Carolina A&T State University, United States; $^2$University of Nebraska–Lincoln, United States

Fe$_{90}$Ta$_{10}$ (Fe-Ta) thin films, deposited using a pulsed laser deposition (PLD) method, have been found to exhibit characteristics of a soft ferromagnetic material with very low coercivities (1-10 mT) and saturation magnetization ~ $16 \times 10^5$ A/m. Our field dependent magnetization data (MH) at various temperatures (20 K - 250 K) were used for the indirect measurement of magnetocaloric effect (MCE) to determine the entropy change in the material. An MCE is reported for the first time in rare-earth free Fe$_{90}$Ta$_{10}$ (Fe-Ta) thin films. This material system in thin film has shown a crystallographic transition from regular body centered cubic (BCC) crystal structure to an iron rich hexagonal laves phase structure which is isomorphous with the structure type, MgZn$_2$ (C14). Applying the Maxwell relation to the MH curves at various temperatures, we have numerically calculated $\delta M/\delta T$ vs H the integration of which provides quantitative information about the isothermal entropy change. We have observed a positive MCE with maximum entropy change of 6.9 J/K-m$^3$ for the magnetic field changing from 0.05-0.5 T in Fe-Ta system. Although the maximum of the mass specific entropy change is rather small in comparison with existing magnetocaloric material, the entropy change saturates for moderate applied magnetic fields around 0.15 T. This is more than an order of magnitude lower than the magnetic fields generally used to realize a large MCE effect. Efforts have been made to improve the mass specific entropy change by optimizing the deposition parameters and by varying the levels and types of dopants in the FE host.

8:00 AM EL04.10.01

Metal-Insulator Transition in Quasi-One-Dimensional HfTe$_3$ in the Few-Chain Limit

Scott Meyer$^{1,2}$, Thang Pham$^3$, Sehoon Oh$^{1,2}$, Marvin Cohen$^{1,2}$ and Alex Zettl$^{1,2}$; $^1$University of California, Berkeley, United States; $^2$Lawrence Berkeley National Laboratory, United States; $^3$Massachusetts Institute of Technology, United States

Constraining the physical size of solids can dramatically influence their electrical, optical, magnetic, thermal, and mechanical properties. Intrinsically low-dimensional materials, including van der Waals (vdW) bonded quasi-two-dimensional compounds (exemplified by graphite, hexagonal boron nitride, and transition metal dichalcogenides (TMD)) and quasi-one-dimensional vdW compounds (exemplified by transition-metal trichalcogenides (TMT)), are particularly intriguing, in that the bulk state already presents weakened inter-plane or inter-chain bonding, which leads to strong structural, electronic, and phononic anisotropy. Constraining the dimensions of these 2-D vdW materials down to “atomic thinness” can result in various degrees of additional size quantization with profound consequences. Therefore, it is a reasonable expectation that the 1-D vdW TMT materials would exhibit additional
size quantization phenomena with novel and unexpected properties when isolated down to the few- and single-chain limit. Here we report the successful synthesis and structural characterization of HfTe$_3$ within the hollow cores of multiwall carbon nanotubes (MWCNT). The selectable inner diameter of the MWCNT constrains the transverse dimension of the encapsulated HfTe$_3$ crystal and thus, depending on the inner diameter of the nanotube, HfTe$_3$ specimens with many chains (~20), down to few chains (3 and 2), and even single isolated chains, are obtained. The MWCNT sheath simultaneously confines the chains, prevents oxidation in an air environment, and facilitates characterization via high resolution transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). Together with complementary density functional theory (DFT) calculations, we find a coordinated interchain spiraling for triple and double chain HfTe$_3$ specimens. Additionally, HfTe$_3$ shows a structural transition via a trigonal prismatic rocking distortion to a new, unreported crystal phase, concomitant with a metal-insulator transition, as the number of chains is decreased below four.

8:15 AM EL04.10.02
Extrinsic Doping of Antimony Selenide for Photovoltaics Laurie J. Phillips$^1$, Oliver Hutter$^1$, Theo Hobson$^1$, Christopher Savory$^{2,2}$, David O. Scanlon$^{2,2,3}$, Ken Durose$^1$ and Jonathan Major$^1$; $^1$University of Liverpool, United Kingdom; $^2$University College London, United Kingdom; $^3$Harwell Science and Innovation Campus, United Kingdom

Control of the doping in antimony selenide (Sb$_2$Se$_3$), both native and extrinsic, remains a key challenge for the material if it is to reach its full potential as a high-efficiency photovoltaic absorber. Carrier concentrations in Sb$_2$Se$_3$ are often low, with most reports of the material finding quasi-intrinsic or light p-type doping. Several studies have already shown the complicated defect chemistry of Sb$_2$Se$_3$, however, there is a paucity of studies into the deliberate doping of the material. In this study, we identify suitable doping strategies to achieve both n-type, and p-type material, first in single crystals and then apply this knowledge to create thin-film devices using a simple post-growth diffusion process. We investigate native defects and extrinsic doping in single-crystal Sb$_2$Se$_3$ through a combination of deep-level transient spectroscopy, density functional theory calculations, hot-probe, hall effect and secondary ion mass spectrometry techniques. We show that stoichiometric Sb$_2$Se$_3$ is an intrinsic semiconductor and identify tin and chlorine as effective extrinsic dopant species. We then discuss routes to achieve controlled doping profiles and high carrier concentrations in Sb$_2$Se$_3$ thin films. This study provides a greater understanding of doping in Sb$_2$Se$_3$, and offers a roadmap to high efficiency devices through extrinsic doping processes.

8:30 AM EL04.10.03
Dopability in Antimony Selenide—Suppressing Amphoteric Antisites Christopher Savory$^1$, Laurie J. Phillips$^2$, Jonathan Major$^2$ and David O. Scanlon$^1$; $^1$University College London, United Kingdom; $^2$University of Liverpool, United Kingdom

With the global demand for energy increasing year on year, diversification beyond current technologies and materials is crucial to meeting this demand by accessing more sustainable materials in a wider variety of device architectures and applications. In photovoltaics, while silicon is the dominant technology, its poor absorption puts upper bounds on device thinness, while established ‘thin-film’ materials such as CdTe allow strong absorption from nanometre-thin films and flexible devices but suffer from toxicity and low abundance of constituent elements. Antimony Selenide, on the other hand, is a highly promising candidate chalcogenide photovoltaic absorber, possessing a very high absorption coefficient, near-ideal band gap and relatively abundant constituents. Solar cells utilising it as the absorber layer are nearing 10% in efficiency, and the pseudo-1D nature of the material, with van der Waals interactions, has been highlighted as a potential reason for benign grain boundaries. Our recent theoretical work, however, has found that despite a high dielectric constant and a ns$^2$ ‘lone-pair’ cation configuration, both characteristics that have been associated with the concept of defect tolerance, Sb$_2$Se$_3$ possesses multiple low formation energy intrinsic defects with mid-gap transition levels that could severely hinder future improvements in open circuit voltage. In this study, we discuss these hybrid density functional theory calculations on the intrinsic defects of Sb$_2$Se$_3$ with focus on examining how the amphoteric behaviour of selenium allows for such low formation antisite defects, which may pin the Fermi level. Further, we examine the carrier capture behaviour of these defects and which defect levels may be responsible for the trap states seen in experimental DLTS measurements. Finally, we have also performed calculations on numerous extrinsic dopants to assess possible routes to doping in Sb$_2$Se$_3$, including passivation of deep intrinsic levels, and, in collaboration with colleagues at the University of Liverpool, potential contaminants that may affect current and future devices. Through these results, our study examines the specific effects at play within
Sb\textsubscript{2}Se\textsubscript{3} but also explores the consequences on the applicability of ‘defect tolerance’ within post-transition metal chalcogenide materials.


8:45 AM EL04.10.04
Adjusting Interfacial Chemistry and Electronic Properties of Photovoltaics Based on a Phase-Pure Sb\textsubscript{2}S\textsubscript{3} Light Absorber by Atomic Layer Deposition
Ignacio Minguez Bacho\textsuperscript{1}, Pascal Büttner\textsuperscript{1}, Craig Pointer\textsuperscript{2}, Florian Scheler\textsuperscript{1}, Dirk Dohler\textsuperscript{1}, Maïssa Barr\textsuperscript{1}, Dmitrii Pankin\textsuperscript{3}, Stefan Fliege\textsuperscript{4}, Ruriko Hatada\textsuperscript{4}, Alina Manshina\textsuperscript{3}, Elizabeth Young\textsuperscript{2} and Julien Bachmann\textsuperscript{1}; 1Friedrich-Alexander University Erlangen-Nürnberg, Germany; 2Lehigh University, United States; 3St. Petersburg State University, Russian Federation; 4Technische Universität Darmstadt, Germany

The combination of oxide and heavier chalcogenide layers in thin film photovoltaics suffers limitations associated with either oxygen incorporation into the chalcogenide layer or a chemical incompatibility which results in dewetting issues and defect states at the interface. Here, we establish atomic layer deposition (ALD) as a tool to achieve three goals in this field. Firstly, it allows one to obtain highly pure Sb\textsubscript{2}S\textsubscript{3} light absorber layer. Secondly, it provides high precision in the tuning of its thickness, demonstrated here between 30 and 160 nm. Thirdly, it is exploited to generate an ultra-thin adhesion layer of ZnS between 0.2 and 2.0 nm that simultaneously resolves dewetting and passivates defect states at the interface, thereby slowing down interfacial charge recombination. The materials stack is characterized by XPS, Raman, and SIMS, and its (photo-)physical properties are measured by UPS and transient absorption spectroscopy. The comparison of solar cells with and without oxide incorporation in Sb\textsubscript{2}S\textsubscript{3}, with an optimum ultra-thin ZnS interlayer below 1.0 nm, and with systematically varied Sb\textsubscript{2}S\textsubscript{3} thickness provides a complete picture of the physical processes at work in devices with optimized power conversion efficiency beyond 5.0 %.

9:00 AM EL04.10.05
Electrochemical and Photoelectrochemical Stability of Cu\textsubscript{2}BaSn(S,Se)\textsubscript{4} and Cu\textsubscript{2}BaSn(S,Se)\textsubscript{4} Based Photocathodes for Solar Water Splitting
Yihao Zhou, Betul Teymur, Edgard Ngaboyamahina, Charles Parker, David B. Mitzi and Jeffrey Glass; Duke University, United States

During the last decade, various chalcogenide materials (Cu(In,Ga)(S,Se)\textsubscript{2}, CuGa(S,Se)\textsubscript{2} and Cu\textsubscript{2}ZnSn(S,Se)\textsubscript{4}) have been studied as photocathodes for solar water splitting because of their high optical absorption, suitable band position and tunable bandgap. However, concerns including Zn-Cu antisite disordering and element scarcity/toxicity (In, Ga) remain as obstacles for their further performance improvements and practical applications. Most recently, Cu\textsubscript{2}BaSn(S,Se)\textsubscript{4} has attracted considerable attention as emerging chalcogenide materials with all earth-abundant elements and less tendency for antisite disordering compared to Cu\textsubscript{2}ZnSn(S,Se)\textsubscript{4} while maintaining the desirable electronic and optical properties for solar energy conversion applications. Previously, studies of Cu\textsubscript{2}BaSn(S,Se)\textsubscript{4} photocathodes focused on improvements of photocurrent density and onset potential. However, the stability of the Cu\textsubscript{2}BaSn(S,Se)\textsubscript{4} was not fully understood and stability beyond 10 hours (a concern for its practical application) was not yet demonstrated. The current study investigates the electrochemical and photoelectrochemical stability of bare Cu\textsubscript{2}BaSn(S,Se)\textsubscript{4} based photocathodes from both experimental and theoretical viewpoints. Additionally, long term stability of Cu\textsubscript{2}BaSn(S,Se)\textsubscript{4} with overlayers and catalyst was examined.

The stability of the bare Cu\textsubscript{2}BaSn(S,Se)\textsubscript{4} was found to significantly degraded at both positive and negative potentials but remains relatively stable in the middle potential range (e.g., 0 V/RHE to 0.4 V/RHE). Careful SEM, XPS, EDS and XRD measurements reveal different degradation mechanisms of Cu\textsubscript{2}BaSn(S,Se)\textsubscript{4} electrodes at different potentials. For positive potential, an electrochemically induced mechanical delamination was observed to cause the device performance to degrade. When a more negative potential was applied (e.g., -0.4 V/RHE,), photoelectrochemical corrosion was found to be responsible for the photocurrent decrease. Self-reduction and
oxidation potentials of Cu₂BaSn(S,Se)₄ was calculated thermodynamically and compared with the experimental results. Combining the theoretical and experimental results, the S/Se self-oxidation and Cu/Sn self-reduction were proposed to explain the degradation at positive and negative potentials respectively. Long term stability of Cu₂BaSn(S,Se)₄ photocathodes with TiO₂/CdS overlayers and Pt catalyst was tested for more than 100 hours continuously with AM 1.5G solar simulator at 0 V/RHE. It was found that more than 50% of the photocurrent was retained after 100 hours of testing. The decrease of photocurrent was attributed to Pt catalyst delamination and verified by EDS and SEM images. The present results elucidate the potential dependent stability and degradation mechanism of the Cu₂BaSn(S,Se)₄ system. Results of protected Cu₂BaSn(S,Se)₄ photocathodes highlight the possibility of practical Cu₂BaSn(S,Se)₄ solar water splitting devices with high efficiency (>10 mA/cm² at 0 V/RHE) low cost (solution-processed) and considerable stability (appropriate catalyst). The above results are also instructive for studying the stability of other existing chalcogenide materials and designing new chalcogenide materials with higher stability.

9:15 AM *EL04.10.06
Accelerated Discovery of Metal Oxides and Chalcogenides for Solar Energy Conversion Aron Walsh; Imperial College London, United Kingdom

The design criteria for sustainable thin-film photovoltaic devices includes the chemical (e.g. abundance, toxicity, stability, scalability) and physical (e.g. band gap, absorption, doping density, contact behaviour) properties of the underlying materials. Many non-conventional inorganic materials are currently being investigated including oxides (e.g. Cu₂O) and sulphides (e.g. SnS); however, none are close to reaching their theoretical potential as defined by the Shockley–Queisser limit [1].

I will discuss the latest advances in materials modelling [2] for the discovery of new materials for solar energy conversion. The role of predictive simulations can vary from high-throughput screening of candidate compounds, rigorous assessment of physical responses, to the optimisation of device architectures. Particular attention will be paid to what can learned from the high-performance of perovskite solar cells and the reduction of non-radiative electron-hole recombination that limits the performance of many new technologies. Examples will be taken from our exploration of kesterite (e.g. Cu₂ZnSnS₄), matlockite (PbFCl type), herzenbergite (SnS), and antimonselite (Sb₂Se₃) systems [3-5].

[1] "Emerging inorganic solar cell efficiency tables" J Phys Energy (2019); https://doi.org/10.1088/2515-7655/ab2338


[3] "Lone-pair effect on carrier capture in Cu₂ZnSnS₄ solar cells" J. Mat. Chem. A 7, 2686 (2019); https://doi.org/10.1039/C8TA10130B


9:45 AM EL04.10.07
First-Principles Simulations of Stability, Optical and Electronic Properties of Competing Phases in Chalcopyrite-Based Photoelectrodes Joel B. Varley¹, Abhishek Sharan², Fernando P. Sabino², Anderson Janotti², Tadashi Ogitsu¹ and Nicolas Gaillard³; ¹Lawrence Livermore National Laboratory, United States; ²University of Delaware, United States; ³University of Hawaii, United States

One promising approach to economical and sustainable fuel production is through photoelectrochemical (PEC) hydrogen production. However, the widescale deployment of existing state-of-the-art photoelectrodes has been hampered by issues with durability, efficiency and cost. Chalcopyrite-based tandem photoelectrodes are attractive candidates in that they offer a great flexibility in the choice of component materials necessary that drive the
reactions for different device designs, offering ways to reduce the cost and to improve the performance. The synthesis of low-band gap chalcopyrites like CuInSe2 and alloys with CuGaSe2 (CIGSe) are known to exhibit a variety of Cu-poor phases (ordered-vacancy compounds or OVCs) that can greatly influence the resulting properties of fabricated devices, while the existence and properties of these phases in wider-band gap chalcopyrite compounds and alloys remains largely unexplored. Using hybrid functional calculations, we discuss the stability, optical and electrical properties of OVCs in a number of other chalcopyrite chemistries beyond CIGSe. We discuss the influence of such phases on the resulting absorption and band offsets that would result upon their formation, which have implications in device design. We additionally discuss experimental fingerprints that could be used to identify the existence of such phases in synthesized material.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and funded by the HydroGen Consortium within the Department of Energy Office of Energy Efficiency & Renewable Energy (EERE) and Fuel Cell Technologies Office.

10:00 AM BREAK

SESSION EL04.11: Defects and Transport
Session Chairs: Yuval Golan and Janet Macdonald
Wednesday Morning, December 4, 2019
Hynes, Level 1, Room 104

10:30 AM EL04.11.01
Interfaces between PbSnSe and III-V Semiconductors Brian B. Haidet, Eamonn T. Hughes and Kunal Mukherjee; University of California Santa Barbara, United States

Group-IV chalcogenides are a fascinating material system with rare properties that arise from the nature of their bonding. The rocksalt alloys of PbSn1-xSe have important mid-infrared optoelectronic properties, with certain compositions host topologically non-trivial states. We explore the epitaxial integration of PbSnSe alloys with zincblende III-V materials for control over these unique electronic properties via hybrid interfaces to a mature materials platform. Here, we use PbSe as a model material to explore how IV-VI materials nucleate and grow on III-V materials. The thin films in our study are synthesized by molecular beam epitaxy from compound IV-VI sources. We show how to independently tune the substrate surface chemistry and lattice mismatch using buffer layers of (In,Ga)(As,Sb) alloys; finding that both influence the growth behavior of PbSe. Characterization of the (001) rocksalt/zincblende interface by electron microscopy reveals a unique arrangement of atoms that mediates dissimilarity in atomic identity, crystal structure, and valence.

With these tools in hand, we demonstrate routes to create atomically sharp and uniform interfaces between these material systems, paving the way to the measurement of the band alignment. The growth mode and lattice-mismatch also results in the generation of dislocations at the interface of PbSnSe and III-V materials that propagate into the film. We do not fully understand the properties of these dislocations, their relationship to interface preparation, and their impact on electronic properties. To this end, we present results from atom probe tomography and electron microscopy to provide a detailed microstructural description of these features. We see evidence for strong deviation in composition at these defects. Finally, dislocations are not always harmful and here we show that the glide of these dislocations can be used to our advantage to grade across composition in PbSnSe in (111) oriented films to explore the growth of metastable cubic SnSe-rich phases. These growth studies are now guiding our designs of hybrid heterostructures to understand and control the unique properties of IV-VI materials.

10:45 AM EL04.11.02
Electronic Structure and Defect Physics in Emerging Quasi-1D Antimony Chalcogenide Optoelectronic Materials Baiyu Zhang and Xiaofeng Qian; Texas A&M University, United States

Low dimensional chalcogenides become very attractive for electronic and optical applications, largely owing to their unique physical and chemical properties strongly augmented by low-dimensionality. The low dimensionality reduces dielectric screening and enhances Coulomb interaction, resulting in pronounced optoelectronic response and
forming quasiparticles such as excitons and polaritons. Here we present our first-principles theoretical study of quasi-1D antimony chalcogenides, an emerging class of optoelectronic materials possessing intermediate bonding between weak van der Waals and strong covalent interactions. We show that this unique quasi-1D structure mediates its dielectric screening environment, giving rise to highly anisotropic electronic and optical properties that are promising for low-cost photovoltaics and novel optoelectronics. We will further discuss the defect physics in antimony chalcogenides including both intrinsic and extrinsic point defects as well as their impact on relevant device performance. Our results provide valuable theoretical insights on the emerging antimony-chalcogenide based non-toxic and earth-abundant photovoltaics and open exciting avenues for optoelectronic applications of quasi-1D chalcogenides.

11:00 AM EL04.11.03
Investigating the Mechanisms Behind the Emergence of Magnetic Properties in Nominally Nonmagnetic Metal Chalcogenide Semiconducting Nanocrystals Alex Khammang and Robert W. Meulenberg; University of Maine, United States

Metal chalcogenide semiconducting nanocrystals (NCs), such as CdSe, possess striking size-dependent optical properties and have been shown to have applications as both optoelectronic (i.e. solar cells and laser emitting diodes) and biomedical devices (i.e. biological markers) [1]. These types of materials typically consist of an inorganic core, which dictates most of the physical properties, and an organic layer on the surface, which helps dictate chemical stability. While much work has been performed towards understanding the fundamental physics of the core NC, the surface science of these materials remains relatively unexplored. Although it is believed that the surface of NCs are primarily responsible for chemical stability, recent reports have suggested that the surface layer does much more, including affecting photoluminescence (PL) quantum yields and PL lifetimes [2]. Quite remarkably, the surface layer even has been shown to convert nominally non-magnetic materials, such as CdSe, into “magnetic NCs” [3]. This result is curious, as the bulk state of these materials exhibit diamagnetic properties. These exciting results suggest that is may be possible to pair these induced magnetic properties with the inherent PL properties of these materials without introducing chemical dopants. The multi-functionalization of CdSe and ZnO semiconducting magnets may lead to better biomedical applications such as targeted drug delivery, targeted organelle extraction, and magnetic hyperthermia treatments.

To gain further insight on how the surface layer affects the magnetic properties, our current work focuses on altering the NC surface chemistry by controllably varying the surface ligand concentrations and by systematically varying the types of ligands (i.e. headgroup) on the surface of spherical CdSe and ZnO NCs. Our work reveals that CdSe NCs exhibit weak paramagnetic (PM) properties in the presence of an external magnetic field as previously reported [3]. Sequential ligand removal does not yield a proportional response to the magnetic properties, but in general the PM properties are enhanced with fewer surface ligands attached. We hypothesize that after the removal of ligands the surface of the NC restructures by forming Se-Se bonds. DFT calculations suggest that removal of a full surface layer can result in a Se-Se triplet state that is energetically favorable compared to the singlet state and may be the source of magnetism in this system [4].

Similarly, ZnO NCs become paramagnetic or ferromagnetic at the nanoscale and it is generally accepted that the mechanism behind the magnetic phenomenon in ZnO results from interstitial point defects near the surface of the NC [4]. It has been shown that by variation of both the size and type of surface ligands, ZnO NCs can exhibit differences in the magnetic responses. Preliminary results suggest that ZnO NCs on the order of 30 nm exhibit PM behavior and while 4 nm ZnO NCs exhibit ferromagnetic behavior. The size dependencies are suggestive of surface defects, as the aspect ratio increases as NCs decrease in size. Very little is known about how the magnetic properties are affected when altering the surface ligand concentration and while surface reconstruction could be the source of the magnetism, reconstruction alone may not be the only source of magnetic properties.

1 N. Sahu, N. Brahme, and R. Sharma, Luminescence 31, 1400 (2016)
The search for new thermoelectric materials requires optimizing a set of interrelated, complex, and often conflicting material properties. Amongst the many desirable features needed to achieve good thermoelectric performance in semiconductors, two critical ones are low thermal conductivity and high carrier concentrations (dopability). This presentation will highlight recent combined computational and experimental efforts to tailor and understand thermal and electronic properties of a chemically-diverse set of telluride-based diamond-like semiconductors (DLS) within the Cu₂III₁IV₄Te₄ (III = Zn, Cd, Hg, IV = Si, Ge, Sn) material space and other related compounds. We use combined computational first-principles methods, synthesis, and characterization to comprehensively assess this space for thermoelectric performance. To address thermal properties, first-principles modeling together with thermal transport measurements together suggest that substantial site disorder arising from the prevalence of IIIB$_{\text{Cu}}$ and CuIIIB antisite defects gives rise to ultra-low thermal conductivities. The measured trend in the thermal conductivities corresponds well to the spectral mismatch of the Cu and group IIIB species in the phonon spectrum, suggesting the key role of these antisite defects in scattering thermal carriers. To address dopability, we use density functional theory to investigate the intrinsic defect chemistry of several telluride DLS including Cu₂HgGeTe₄ and the related ordered oxygen-vacancy compound Hg₂GeTe₄, and predict achievable carrier concentrations. Experimentally, carrier density control has been demonstrated within the Cu₂HgGeTe₄-Hg₂GeTe₄ solid solution. Our first-principles analysis shows that Cu₂HgGeTe₄ can range from degenerate p-type to highly n-type under different thermodynamic environments. In agreement with high-temperature x-ray diffraction and resonant spectroscopy experiments, the predominant defects in the quaternary are found to be antisite defects with Cu and Hg. On the other hand, as Hg₂GeTe₄ does not contain Cu-related antisites, native defects exhibit relatively high defect formation energies, and Hg₂GeTe₄ is predicted to have an equilibrium Fermi energy near mid-gap for all growth environments and a wide dopability window. To overcome the small intrinsic carrier concentrations in Hg₂GeTe₄, we use first-principles to screen and recommend a set of extrinsic dopants that can be used to tune the carrier type from p-type to n-type.


SESSION EL04.12: Quantum Dot Synthesis and Optoelectronics
Session Chairs: Vladan Stevanovic and Vanessa Wood
Wednesday Afternoon, December 4, 2019
Hynes, Level 1, Room 104

1:30 PM *EL04.12.01
Chalcogenide Nanocrystals as Optoelectronic Materials Dmitri V. Talapin; University of Chicago, United States

Development of nanostructured materials has introduced revolutionary approaches for materials processing and electronic structure engineering. These materials can offer the advantages of crystalline inorganic solids combined with inexpensive solution-based device fabrication. Along these lines, semiconductor quantum dots are explored as the functional elements for printable electronics, light emitting devices, photodetectors, solar cells and lasers. All these applications require efficient coupling between individual nanostructured components. The advances in the surface chemistry of semiconducting nanostructures are poised to enable advances in additive manufacturing of semiconducting and multifunctional materials. Specifically, I will discuss inorganic linkers that permit electronic coupling between the nanocrystals and composition-matched molecular semiconductor "solders" that convert nanocrystals in the high quality inorganic semiconductors. I will also introduce a general chemical approach for photoresist-free, direct optical lithography of functional inorganic nanomaterials (DOLFIN). Examples of patterned materials include metals, semiconductors, oxides, and magnetic and rare earth compositions. No organic impurities are present in the patterned layers, which helps achieve good electronic and optical properties. The conductivity, carrier mobility, dielectric, and luminescence properties of optically patterned layers are on par with the properties of state-of-the-art solution-processed materials. The ability to directly pattern all-inorganic layers using a light exposure dose comparable to that of organic photoresists opens up new opportunities for thin-film device manufacturing.

2:00 PM EL04.12.02
Composition-Dependent Properties of Multicomponent Chalcogenide Nanocrystals—Old Concept Enables New Opportunities Maksym Yarema, Olesya Yarema and Vanessa Wood; ETH Zurich, Switzerland

Colloidal chalcogenide nanocrystals comprise an important class of materials with a plethora of uses in photovoltaic, thermoelectric, catalytic, phase-change memory and other applications. Traditionally, the properties of such chalcogenide colloids are tuned by accurate control over their size, exploiting quantum confinement phenomena. Multicomponent chalcogenide nanocrystals provide an extra tuning knob: composition-dependent effects (i.e., tunable ratio between constituent cations) are superimposed on nanoscale size dependences. Synthesis of multicomponent nanocrystals, however, remains a synthetic challenge, due to side reactions and difference in reactivity of starting elemental precursors. In this talk, I will summarize our recent work, regarding ternary and quaternary chalcogenide nanomaterials. Taking example of I-III-VI group nanocrystals, I will highlight an amide-promoted synthetic approach that enables
independent control over nanocrystal size and composition. The method is based on addition of amide superbase, which accelerates the nucleation rate of nanocrystals and, ultimately, diminishes the reactivity difference between M\(^+\), M\(^{2+}\), and M\(^{3+}\) ions. We will demonstrate a generality of amide-promoted synthetic approach for various chalcogenide nanocrystals and discuss the limitations of the method.

In the following, we will focus on quaternary Cu-Zn-In-Se nanocrystals, for which we develop a predictive model for the synthesis in broad range of Indium-rich compositions. We will discuss an interplay between size and composition effects on structural and optical properties of Cu-Zn-In-Se nanocrystals. We will detect optimal ternary and quaternary compositions with enhanced luminescence efficiencies, which can be associated with structural ordering of cations and cationic vacancies. These results can provide better understanding of structure-property relationships for multicomponent nanocrystals and ultimately guide the development of multicomponent nanomaterials with optimized optical and electronic properties.

2:15 PM EL04.12.03  
**Polymer Guided Formation of Metal Chalcogenide Nanocrystal Networks**  
Paul D. McNaughter, Stephen Yeates and David J. Lewis; University of Manchester, United Kingdom

The ability to control the assembly of inorganic nanocrystals within polymer hosts is an important requirement for the use of metal chalcogenide nanocrystals in optical, energy capture and electrical devices. A popular route to the forming polymer-inorganic nanoparticle mixtures is to synthesis the particles and then mix with the polymer. This has disadvantage that when removing the solvents typically used that the conformational entropic penalty of the polymer existing at the nanoparticle surface and the enthalpic interactions between polymer and particle cause the particles to become immiscible with the polymer.

A route that has been explored to tip the balance to better mixtures of polymers and particles is to synthesise the particles within the undissolved polymer, *i.e. in situ*. The polymers of interest are solution processed in the same solution as the precursors for the desired metal chalcogenide.\(^1,2\) In particular, metal xanthates have proven to have the solubility in compatible processing solvents and also breakdown at relatively low temperatures, avoiding the decomposition of the polymer matrix. Our group has used this technique to form randomly ordered mixtures of polymer and lead chalcogenide nanocrystals where we reintroduced size control of the synthesised nanocrystals.\(^3–5\)

In this work we use electrospinning and electrospray techniques to form fibres containing highly aligned polymer chains and the required metal xanthate complexes. Upon heating the aligned polymers act as the environment the nanocrystals form within and direct the location of the resulting nanocrystals.


2:30 PM BREAK

3:30 PM *EL04.12.04  
**Synthesis of Unnatural Polytypes of the Copper Chalcogenides**  
Emil Hernández-Pagán\(^1\), Suresh Sarkar\(^2\), Alice Leach\(^3\), Christopher Sharp\(^3\), Evan Robinson\(^3\), Andrew LaCroix\(^4\), Yilun Zhao\(^3\) and Janet E. Macdonald\(^4\); \(^1\)The Pennsylvania State University, United States; \(^2\)The University of Chicago, United States; \(^3\)Vanderbilt University, United States; \(^4\)Lander University, United States

Geology has the advantages of extreme temperatures, pressures, and cooling rates to achieve a dizzying array of diverse crystalline phases of metal chalcogenides. As solution phase chemists, we alternatively have access to diverse organochalcogenide precursors and chemistries with distinctive reactivities both in rate and mechanism. These precursors provide new methods to control crystalline phase in colloidal nanocrystal synthesis. At times, solution phase chemistry is even more powerful than geology as new “unnatural” polytypes of binary and ternary
compounds not present in the geologic record can result. These new polytypes present an emerging class of materials with new optical, electronic, and chemical properties. Here we will present examples from our research along with a study of the mechanism of formation that will provide the basis for further discovery of new materials. CuInS₂ has a band gap of 1.5eV and is a potential replacement for CdSe and CdS semiconductors in optoelectronic applications. While the favored thermodynamic structure is chalcopyrite, in some nanocrystal syntheses, a metastable wurtzite-like polymorph forms. We will show how the chalcogenide precursor reactivity influences the preferential formation of one of two binary intermediates, either pseudo-hexagonal Cu₂S or othorhombic In₂S₃. These binaries provides the anionic substructure which dictates the final phase of the ternary product after a second step of partial cation exchange.

With this mechanistic understanding, the class of hexagonal ternary copper sulfides has been expanded to now included the synthesis of wurtzite-like CuFeS₂, another rare, unnatural polymorph, instead of chalcopyrite. In this case, Cu₂S nanocrystals are intentionally prepared and used as a reagent. However, the exchange process itself can be disruptive, and there is a ligand dependence of the retention of structure even in cation exchanges at moderate temperatures.

The syntheses of hexagonal ternary copper sulfides are facilitated by the facile synthesis of pseudo-hexagonal Cu₂S, which is the thermodynamic phase. Similar intentional two step syntheses to hexagonal ternary copper selenides is hampered because the thermodynamic phase of Cu₂Se is cubic. Indeed, the hexagonal phase is not known to the geologic record, and it was synthesized only once before through cation exchange from CdS nanocrystals. We will present the first known direct synthesis of hexagonal Cu₂Se: a product that is facilitated by a didodecylselenidenidenprecursor. Similar syntheses that use dodcecylselenol or include phosphine precursors produce the thermodynamic cubic phase. Details of the relationship between precursors used and phase selection is revealed by in situ ⁷⁷Se NMR of nanocrystal syntheses.

4:00 PM EL04.12.05
Effects of a Lead Chloride Shell on Lead Sulfide Quantum Dots Sarah Brittman¹, Adam Colbert¹, Todd Brintlinger¹, Paul D. Cunningham¹, Michael Stewart¹, William Heurer², Rhonda Stroud¹, Joseph Tischler¹ and Janice Boercker¹; ¹U.S. Naval Research Laboratory, United States; ²U.S. Naval Academy, United States

PbS quantum dots are already commercialized in short-wave infrared (SWIR) photodetectors and are under development for single-photon sources, photovoltaics, and light-emission applications. Nevertheless, key aspects of their fundamental physics such as their excitonic fine structure, exciton-phonon coupling, and exciton dynamics are still not well understood. Using a popular synthesis from the literature,¹ we find that these PbS nanocrystals are coated in a previously unnoticed shell that is measurable in transmission electron micrographs.² The shell contains lead and chlorine, beyond the monoatomic chlorine termination previously proposed. Identifying this shell and its influence on the nanocrystals’ excitonic structure is a crucial first step toward understanding the physics of PbS quantum dots.

Earlier work has correlated the diameters of PbS nanocrystals to their excitonic absorption; however, we observe that PbS quantum dots synthesized in saturated dispersions of PbCl₂ can deviate from the previous 1Sₓ-1Sᵧ energy vs. diameter curve by 0.8 nm. In addition, their surface differs chemically from that of PbS quantum dots produced via other syntheses, which affects their excitonic absorption spectrum.

This result has important implications for understanding the growth mechanism of this reaction, the linewidth of these quantum dots’ photoluminescence, and electronic transport within films of these nanocrystals. Such fundamental knowledge is critical to further our understanding of PbS quantum dots and their development into optoelectronic devices.


4:15 PM EL04.12.06
Delayed Luminescence and Memory Functionality in CdS/ZnS Ligand Capped QLEDs Christian Blauth¹,², Paul Mulvaney¹ and Tadahiko Hirai²; ¹University of Melbourne, Australia; ²CSIRO, Australia
Quantum dot light-emitting diodes (QLEDs) emitting at 410 nm were studied by time-resolved electroluminescence measurements. A novel transient device current overshoot after voltage turn-off was observed which is attributed to the accumulation and storage of charge carriers at the ligand-quantum dot interface. Short ligands produced short rise times and prevented current overshoots, whereas longer ligands caused a storage of charge carriers, a slower response and notable current overshoots. This overshoot can be attributed to the internal electric field between the injected, and stored and trapped electrons and holes upon switching-off of the external voltage. Thereby, trapped charges at the quantum dot/ligand interface recombine and produce an electroluminescence spike. Applying a dual step voltage pulse, prevents this overshoot, and instead a delayed luminescence is found. As the accumulated charge carriers are immobile and trapped in shallow states at the ligand/quantum dot interface, a reverse pulse was applied to fully deplete the emissive layer. With the transient overshoot disappearing after the device has been turned on and operated, a measure for degradation of QLEDs has been identified.

Upon using a 5nm thick Al interlayer under the hole transport layer, accumulated charge carriers can increase the conductance of the active layer during the forward voltage sweep. This introduces a memory window, a new device functionality, with ON/OFF states that can be reversed by applying a negative bias. The height of the memory window depends on the length of ligand passivating the chalcogenide quantum dot. During backward voltage sweeps, previously injected charge carriers recombine until the active layer is free of charge carriers and show a low conductance state. Voltage-capacitance measurements confirm the changes in charge carrier population within the active layer that depend on both the direction of the bias sweep as well as the ligands surrounding the quantum dots. A complete memory cycle with read, write, erase and re-read modes has been demonstrated.

4:30 PM *EL04.12.07
Beneficial Impurities in Surfactant Assisted Synthesis of Colloidal Nanoparticles Yuval Golan; Ben-Gurion University of the Negev, Israel

While surfactant assisted synthesis is the most common technique used for the preparation of colloidal nanoparticles, researchers in the field often encounter serious irreproducibility issues. In this talk, we will present several examples for the role of ‘beneficial impurities’ in nanoparticle syntheses.[1-5] Specifically, controlled amounts of alkylammonium-alkylcarbamate surfactants were shown to strongly affect alkylamine-assisted synthesis of anisotropic colloidal ZnS nanoparticles.[4,5] Furthermore, a new cubic semiconducting binary phase (denoted as the π-phase) has been discovered in recent years in the form of colloidal nanoparticles. The first π-phase materials to be discovered were tin mono-sulfide, π-SnS [6,7] followed by tin mono-selenide, π-SnSe [8], and density functional theory calculations predict additional π-phase compound semiconductors.[9] Increasing experimental and computational evidence points out that ‘beneficial impurities’ can be used for achieving phase control in the tin mono-chalcogenide system.

References
EL04.13.01
Maximum Efficiency of Kesterite Solar Cell Limited by Nonradiative Recombination Sunghyun Kim¹ and Aron Walsh¹,²; ¹Imperial College London, United Kingdom; ²Yonsei University, Korea (the Republic of)

The theoretical maximum efficiency of a solar cell such as Shockley-Queisser limit has mainly focused on the radiative recombination as the limiting factor. However, in practical solar cells, the nonradiative recombination is unavoidable due to the formation of native point defects and often the dominant recombination mechanism [1]. We will predict the theoretical maximum efficiency of kesterite solar cells (Cu₂Zn(Ge,Sn)(S,Se)₄), taking into account both radiative recombination and non-radiative carrier recombination mediated by the native point defects. We calculate the thermal equilibrium concentrations of native defects and their capture cross-sections. We find that the sulfur vacancy (VS), sulfur vacancy-donor complex and Sn antisites (SnZn) produce deep levels and large capture cross-sections resulting in the low open-circuit voltage and the low solar-to-electricity conversion efficiency [2, 3]. The predicted upper limit is compared to the current generation of best performing kesterite solar cells. We suggest that the codoping and alloying may improve the efficiency of kesterite solar cells.


EL04.13.02
Effects of Aluminium Doping on Kesterite Cu₂ZnSnS₄ Thin-Films Ahmet S. Nazligul, Mingqing Wang and Kwang-leong Choy; University College London Institute for Materials Discovery, United Kingdom

In recent years Cu-based chalcogenide Cu₂ZnSnS₄ (CZTS) has attracted a lot of attention as an earth-abundant alternative for CIGS solar cells. To date, the research in this field has been focused on solar cell applications. However, the efficiency of CZTS solar cells has not experienced a real improvement in the past five years. Therefore, research is beginning to explore new applications for this material such as sensors, water-splitting and charge-extraction layers. In this project, aluminium doping has been introduced to CZTS thin-films for the first time. CZTS films were deposited in atmospheric conditions via a low-cost and environmentally friendly solution-based method. The effects of up to 3 % Al doping in a range of different annealing temperatures from 350 °C to 550 °C without any sulfurization/selenization were examined. Our results show that Al has no significant effect for the samples heat-treated at 350 °C. On the other hand, we observed successful doping for the samples heat-treated above 450 °C. Our EDS, XRD and Raman results suggest that Al is replacing Sn sites in these samples. The Al doping caused a drop in resistivity while increasing the charge-carrier concentration, bandgap and grain sizes. The biggest reduction in resistivity was observed for 2% doped and heat-treated at 450 °C samples. In these samples the resistivity reduced from 13.34 Ω.cm to 0.42 Ω.cm while charge-carrier concentration increased from 7.85×10¹⁷ to 1.74×10²⁰ cm⁻³. Such improvement in charge-carrier concentration is promising for using Al-doped CZTS thin-films as hole transport layers in Perovskite solar cells, while an increase in the bandgap is advantageous for water-splitting applications.

EL04.13.03
Impact of Ag-Doping on Cu₂ZnSnS₄ (CZTS) Thin-Film Solar Cell Heydar Honarvar Nazari¹,² and Tara P. Dhakal¹,²; ¹Binghamton University, The State University of New York, United States; ²Center for Autonomous Solar Power (CASP), United States

CZTS-based solar cell is one of the most attractive p-type solar absorbers due to its low cost and earth-abundant elements. In addition, CZTS has a band gap of 1.5 eV and high absorption coefficient (10⁴ cm⁻¹) required to be a near ideal solar cell absorber. We report the impact of silver (Ag) doping on CZTS solar cell and how the dopant mitigated the defect density. We
deposited 10 to 20 nm thick Ag layer on top of the CZTS precursor before annealing in sulfur environment for crystallization of the Ag-doped CZTS (ACZTS) film. Ag-doping has shown to improve $V_{oc}$, but we observed it is important to control the Ag for optimal p-type conductivity. Although $V_{oc}$ improvement was achieved, Ag doping of CZTS increased series resistance due to more defects in the crystalline structure. Our recent study showed that by doping a small amount of Ag could improve $V_{oc}$ up to 0.65 (V), compared to bare CZTS which was 0.605 (V). It improved by 10% compared to the cell with no Ag ions. The formation Ag$_2$S which has a higher formation energy compared to other defects is expected, which in turn may have it lowered the number of Cu$_{Zn}$ antisite defects. Moreover, Ag ion has large atomic radius improving grain sizes of ACZTS and lowering GB effect. The highest efficiency based on Ag-doping of CZTS showed 6.4% in our lab compared to the CZTS cell with ~6% efficiency due to the gain in $V_{oc}$. Jsc also improved due to lowering Cu$_{Zn}$ antisite defects.

**EL04.13.04**

**High Performance CZTSSe Solar Cells by Using Cadmium-Free Non-Toxic Zn(O, S) Buffer Layers** Cheng-Ying Chen$^{1,2,3}$, Yun-Fu Chen$^{1,2}$, Wei-Hao Chen$^{1,2}$, Fang-Yu Fu$^{1,2}$, Narmatha Koothan$^4$, Yu-Hsuan Yu$^4$, Kuei-Hsien Chen$^2$ and Li-Chyong Chen$^{1,3}$; $^1$National Taiwan University, Taiwan; $^2$Institute of Atomic and Molecular Science, Academia Sinica, Taiwan; $^3$Center of Atomic Initiative for New Materials, National Taiwan University, Taiwan; $^4$Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

The future deployment of photovoltaics demands stable, abundant, non-toxic materials. Kesterite Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) has attracted attention due to its non-toxicity, low cost, earth-abundant elements and its band gap can be tuned easily. However, efficiency of CZTSSe (12.6%) is much lower than CIGS (22.9%), mainly due to a large $V_{oc}$ deficit. Several factors have been suggested for this $V_{oc}$ deficit, including large amount of defects, undesirably thick MoS$_2$ layer at the rear of the CZTSSe cell, coexistence of secondary phases and unfavorable band alignment at the CZTSSe/CdS heterojunction interface. The importance of the conduction band offset (CBO) at the absorber/buffer interface is well known. A cliff structure (CBO<0) can increase interface recombination, while a spike (CBO>0) results in blocking of the photocurrent and reduce fill factor. Commonly, it is assumed that a small cliff is present at the CZTSSe/CdS interface, which highlights the need to replace CdS with materials with a lower conduction band in order to avoid an unfavorable band alignment. Furthermore, this CdS-based solar cell is desirable to replace with a more environment-friendly highly effective n-type buffer layer.

In this work, we have demonstrated the non-toxic Zn(O,S) as an alternative buffer layer for CdS by chemical bath deposition (CBD) and atomic layer deposition (ALD). One is chemical bath deposition (CBD) that is simple and well prepared. The other is atomic layer deposition (ALD) that can deposit uniformity for atomic level as well as the conformal coverage over large-scale areas. The Zn (O, S) buffer layer band gap (3.5eV) is wider than CdS (2.4eV) which can achieve higher short-circuit current density (Jsc) due to the enhanced transmission of the wavelength region between 350 nm and 550 nm.

Finally, we obtained 5.4% efficiency of CZTSSe solar cell with open circuit voltage ($V_{oc}$) of 440 mV, short-circuit current density ($J_{sc}$) of 25 mA/cm$^2$, and fill factor (FF) of 50.2% by chemical bath deposition (CBD) ZnO. Subsequently, we got 9.77% (~ 10.75% in the cell effective area) efficiency with open circuit voltage ($V_{oc}$) of 460mV, short-circuit current density ($J_{sc}$) of 36.07 mA/cm$^2$, and fill factor (FF) of 58.06 % by atomic layer deposition (ALD) ZnO, which is the highest reported efficiency of CZTSSe with a Cd-free buffer layer. Apart from this, we successfully established the number of precursor cycles using the ALD process to control the O/S ratio and thickness. It helps us adjust the appropriate conduction band offset (CBO) to avoiding an unfavorable band. The morphology, elemental composition, and distribution of the absorber layers are being examined by X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF), scanning electron microscopy (SEM), Transmission electron microscope (TEM), and X-Ray Photoelectron spectroscopy (XPS).

**Reference:**


**EL04.13.05**

**Vapor-Phase Selenization of Powder-Fabricated Cu$_2$GeS$_3$ Thin Films** Hak-Young Ahn$^{1,2}$, Jong-Ku Park$^2$, Seung
Yong Lee2,3, Byeong-Kwon Ju1 and So-Hye Cho2,3; 1Korea University, Korea (the Republic of); 2Korea Institute of Science and Technology, Korea (the Republic of); 3Korea University of Science and Technology, Korea (the Republic of)

Selenization is a process of supplying selenium (Se) in gas phase typically at the elevated temperature. The process has been applied for the formation of chalcogenide thin films for electronic, optical and thermoelectric devices. However, the commonly used method for selenization has limitations such as using toxic gas H2Se gas, high temperature and high equipment cost due to the necessity of two zone furnace system. Therefore, a low-cost and facile method of selenization with a precise control of Se supply is needed.

Herein, we demonstrate one-step and one-zone selenization process of chalcogenide thin films by a new Se source which is a mixture of inert Al2O3 and Se. It was found that Al2O3 in the mixture plays a role as a controller of Se vaporization and therefore by adjusting ratios of Al2O3 vs. Se, we were able to control selenization vapor supply. And mechano-chemical synthesis of Cu2GeS3 particles and the transformation of a thin film of Cu2GeS3 to that of Cu2GeSe3 through selenization will be discussed. During our synthesis of Cu2GeSe3, only elemental Cu, Ge and S were used without any solvent and the thin film of Cu2GeS3 was fabricated by the solution phase, ink printing method followed by the annealing under Se environment. When the selenization method was used for Cu2GeS3 semiconductor thin film, we found resulting selenized thin film has better morphology and electrical properties than that selenized with Se powder alone. This alternative method consumes much less Se than previous methods so that it can be considered environmentally less toxic and has a benefit of low-cost and facile process. And also, this process can broaden applicability by easily controlling the band gap of various chalcogenide materials and thin films.

EL04.13.06
Cesium-Related Compound—An Emerging Chalcogenide Material and Its Influence on CIGS Thin-Film Solar Cells Ishwor Khatri, Tzu-Ying Lin, Mutsumi Sugiyama and Tokio Nakada; Tokyo University of Science, Japan

Current world record CIGS solar cells are achieved by post-deposition treatment (PDT) of heavy alkali metal fluorides (such as KF, RbF and CsF). These alkali-PDT processes are predicted to form alkali-containing compounds such as K-In-Se and Rb-In-Se. The structure and chemistry have intensively been investigated so far. However, the properties of Cs-containing compounds formed by CsF-PDT have not yet been widely discussed. We thus investigated the influence of CsF-PDT on the formation of Cs-related compounds, and its beneficial and detrimental effects on solar cell performance.

CIGS thin films were deposited using three-stage deposition process on Mo-coated SLG substrates. CsF-PDT was performed at a substrate temperature of 350 °C for 2 minutes. The CIGS solar cells were fabricated with MgF2(105nm)/Ni/Al (2-2.5μm)/ZnO: Al(300nm)/ZnO(100nm)/CBD-CdS/CIGS (2.5-3μm)/Mo (700nm)/SLG (1.8mm) structure. TEM and SAD analyses revealed that the Cs-related secondary compounds are present on the surface of CIGS thin film after CsF-PDT. XPS narrow scan spectra confirmed Cu depleted regions at the surface area with a few tens of nanometers, whereas SIMS and EDS-line scan showed that Cs was distributed throughout the CIGS absorber. We noticed that CsF-PDT modifies CIGS surface and formed Cs-related compounds such as Cs-In-Se or Cs-In-Ga-Se. These Cs-related compounds provide several beneficial electronic effects. Presence of Cs-related compounds at the surface of the CIGS thin film reduce interfacial recombination, thereby, improving open-circuit voltage and efficiency. Recombination mechanisms in the devices were characterized using temperature dependent current density-voltage measurements and time-resolved photoluminescence based on different Cu/(In+Ga) and Ga/(In+Ga) ratios. CsF-treated CIGS thin films with near-stoichiometric (Cu/(In+Ga)) yields higher efficiencies. Furthermore, we found the important role of Cs-related compounds in heat-light soaking (HLS) and heat-bias soaking (HBS).

EL04.13.07
A Study of Potential Induced Degradation (PID) and Recovery Mechanisms in CIGS Solar Cells Solhee Lee1, Soohyun Bae1, Se Jin Park1, Yoonmook Kang2, Hae-Seok Lee2 and Donghwan Kim1,2; 1Korea University, Korea (the Republic of); 2KU-KIST Green School, Korea (the Republic of)

CIGS solar cell is a high-efficiency cell with more than 22% efficiency, and can also be modularized in a large area. CIGS module efficiency is approaching the multicrystalline silicon module efficiency. For safety and supporting reasons, photovoltaic (PV) modules have to be grounded and PV modules are serially connected to generate high
voltage and power. When several hundreds of volts induced to modules, degradation is occurred. This is called potential induced degradation. The term ‘potential induced degradation (PID)’ was first introduced by S. Pingel and coworkers in 2010 [1]. Efficiency deterioration by PID phenomenon has been reported in large capacity photovoltaic systems. In c-Si solar cells, decrease in shunt resistance by Na+ ion immigration is known as the cause of PID. However, the mechanism during PID in CIGS solar cells is not known yet. For commercialization of CIGS thin film solar cells, PID study in CIGS solar cell is important. Since PID is known to be common in modules, in this research, an experimental structure was designed to replicate PID in cell level. As an experimental method, the cell was degraded with 600 V bias at 65 °C in darkness. Light I-V, dark I-V and external quantum efficiency (EQE) were performed to investigate the degree of degradation. To image the position of PID by electroluminescence (EL) and lock in thermography (LIT) measurements were also performed. We tried to extract the mechanism of PID in CIGS solar cells through the change of element or doping concentration. Furthermore, recovery was confirmed with no bias at room temperature in darkness.


**EL04.13.08**
**Potassium Treatments for Solution-Processed Cu(In,Ga)(S,Se)2 Solar Cells** Essam AlRuqobah and Rakesh Agrawal; Purdue University, United States

Cu(In,Ga)Se2 (CIGSe) has emerged as an attractive thin-film solar cell material owing to its high light absorption coefficient and tunable bandgap. In CIGSe processing and fabrication, the use of alkali treatments has been implemented extensively. Sodium treatment is considered a requirement for high efficiency CIGSe solar cell as it was found to improve the performance and growth of CIGSe absorber films. However, one of the more significant developments in recent years has been the discovery of the beneficial effects that potassium treatments have on CIGSe solar cells, particularly on the absorber surface. When applied, it was found that potassium induces copper and gallium depletion from the surface of CIGSe films. Moreover, a high-bandgap K-In-Se phase also forms on the surface of films subjected to potassium treatments. In practice, these two phenomena lead to an improved CIGSe device by mainly improving the quality of CIGSe/CdS p-n heterojunction.

Despite these significant beneficial effects, the use of potassium has been limited to expensive vacuum-based CIGSe processing. Here, we develop a route to apply potassium treatments to low-cost solution-processed CIGSe films grown from colloidal sulfide-based nanoparticle inks. By adding potassium through e-beam evaporation of KF prior to growth, we find that the grain growth of CIGSe is enhanced with potassium addition and that a larger-grained thicker coarsened film results compared to untreated selenized CIGSe film, similar to what is observed in sodium-treated films. We also observe via XPS that films treated with potassium show depletion of gallium from the surface, and that the amount of gallium depletion correlates with the amount of potassium added. Similar effects on film surface were also observed for films that have undergone potassium treatment through a soak in KCl solution prior to selenization. Furthermore, it was also observed through XPS that films treated with KF showed the presence of a different Se chemical state on the surface, which is attributed to a K-In-Se phase. Devices that were fabricated with potassium treatments were found to have enhanced optoelectronic performance which was mainly manifested in higher open-circuit voltage and higher fill factor, compared to films that are untreated or treated with sodium only.

In conclusion, we purpose a route to apply potassium treatments for solution-processed CIGSe devices. We also conduct a systematic study on the effects of potassium on CIGSe film growth, surface environment, and optoelectronic properties.

**EL04.13.09**
**Heavy-Metal-Free Quantum Dot Inks for Thin-Film Tandem Solar Cells** Filip Dinic, Larissa Levina, Edward H. Sargent and Oleksandr Voznyy; University of Toronto, Canada

Tandem solar cells are a promising route to increase the efficiency of solar cells. They require semiconductor materials with a bandgap wider than that of silicon, e.g. GaAs, GaInP, CuInGaSe. However, due to vacuum processing of these materials, their price remains an order of magnitude higher than that of silicon. We propose to utilize chalcogenide based colloidal quantum dot (CQD) inks to achieve scalable and low-cost solution processing of the state-of-the-art photovoltaic materials. Films are prepared by thermally annealing and sintering the QDs, resulting in bulk direct bandgap semiconductors, which have been demonstrated to be highly efficient light absorbing layers. The key challenges in this field revolve around improving CQD packing and further reducing the
defect densities. We will demonstrate that inorganic atomic ligands can eliminate the need for organic long chain ligands required for colloidal stability, and at the same time can be used as abundant passivating agents in the resulting films. We will demonstrate the proof-of-principle results based on lead-free chalcogenide based CQDs, primarily CdTe and CuInS.

**EL04.13.10**

**Controlling Magnetism in Boron-Doped Cadmium Sulfide with Light** Bilal Azhar and Rafael Jaramillo; Massachusetts Institute of Technology, United States

The large and persistent photoconductivity displayed by some semiconductors provides a way to control magnetism with light, through illumination-control of free carrier concentration and thereby magnetic interaction in dilute magnetic semiconductors. CdS is a wide band-gap semiconductor that displays large and persistent photoconductivity, and is predicted to become magnetic when doped with certain non-magnetic dopants including Boron [1]. In this work, we experimentally test the prediction of magnetic CdS:B, and the hypothesis that magnetism can be controlled by photoconductivity. We make CdS:B nanoparticulate powders by co-precipitation [2]. We use X-ray diffraction and plasma optical emission spectroscopy to quantify boron doping, and we characterize the effect of doping on electronic structure using optical spectroscopy. We use nuclear magnetic resonance (NMR) and magnetometry to confirm the presence of magnetic B, and to study the position of B in the CdS lattice. Finally, we report the effect of above- and below-band gap illumination on the magnetism of B sites and the magnetic order of CdS.


**EL04.13.11**

**Copper Chalcogenide Thin Films Proposed for UV-Inhibited, Nutrition-Conserving Solar Dehydration of Fruits** P. Karunakaran Nair, Angélica Lizbeth Espinosa Santana, Anabel López Ortiz and M. T. Santhamma Nair; Universidad Nacional Autonoma de Mexico, Mexico

Degenerate n-type semiconductors such as SnO\(_2\):F, In\(_2\)O\(_3\)::Sn or ZnO:Al, and of p-type, Cu\(_{2-x}\)S, Cu\(_{2-x}\)Se, Cu\(_{2-x}\)O of electrical conductivity superior to 10\(^3\) \(\Omega^{-1} \text{ cm}^{-1}\) and carrier concentrations of 20\(^{21}\) \(\text{cm}^{-3}\) make use of degeneracy of energy levels, the same way as metals do. They behave as conductors at wavelengths of electromagnetic radiation above 1500 nm, with high reflectance and low transmittance. In the case of thin films (150 – 200 nm) of copper chalcogenides, with optical bandgap of 1.3 to 2.5 eV, this leads to a bell-shaped transmittance curve, with near-zero transmittance at wavelengths below 500 nm and very low as well as wavelengths above 2000 nm. The overall optical transmittance of 25 – 30 % has a maximum at 550 – 650 nm, absorptance of 60 – 70 % and reflectance of 15 – 20 % for solar radiation. We deposited copper sulfide selenide thin films on the outer wall of on one side of cellular polycarbonate sheet by floating it on a chemical deposition solution of copper nitrate, thiourea, and sodium selenosulfate. This film, protected with food-safe adherent polyethylene sheet, is fixed at 2 cm from a layer of sliced fruit (strawberry) or fruit pulp (blackberry) placed under the sun. Due to the high solar absorptance of 60 %, the device acts as a 600 W/m\(^2\) heater and raises the temperature of the fruit layer to 60 \(^\circ\)C, which is optimum to conserve food value during drying and also to assure a viable drying rate. The cellular structure inhibits convectional heat loss to the ambient from the top (exposed) side of the sheet, without the copper chalcogenide coating. Further, the absence of UV radiation notably retains the antioxidant nutritional value of the product. This advantage is detected in free radical (DPPH) aided spectrophotometric characterization. The UV-inhibited drying also retains the appearance of the product. This approach is may be directly applicable in a rural setting, where a timely drying of fruit products during harvest reduces large-scale loss.

**EL04.13.12**

**Functional Antimony Sulfide Selenide Photovoltaic Prototype Modules via Chemical Deposition** Jesús Alberto González Iñiguez, José Diego Gonzaga Sánchez, Carolina Senaí Avendaño Peréz, Angélica Lizbeth Espinosa Santana, M. T. Santhamma Nair and P. Karunakaran Nair; Universidad Nacional Autonoma de Mexico, Mexico

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Can we build in “our” laboratory a functional photovoltaic prototype module, which is stable under the sun and is open to innovation to achieve technological viability? Yes. We present the prototype module, FTO/CdS/Sb₂SₓSe₃/C-Ag, which is stable, functional to light up 20 mW blue light emitting diode and open to innovation in any laboratory. It is build on commercial F-doped SnO₂ (FTO) substrate of 7.5 cm x 2.5 cm in area, with an 80 nm CdS thin film deposited in 1 h form a chemical bath at 80 °C. Subsequently four sequential depositions of Sb-S-Se are made on it in a total of 10 h at 80 °C from chemical bath containing potassium antimony tartrate, thioacetamide and sodium selenosulfate. This film is of 350 nm in thickness, and amorphous. The sun appears deep red when viewed through it. Seven graphite electrodes of 2 cm x 0.5 cm at a separation of 0.4 mm are placed on it by hand painting colloidal acrylic based graphite suspension. This structure now goes into an oven at 250 - 290 °C for 05 – 1 h, under a nitrogen flow. The Sb-S-Se film surrounding the cell is etched-off with NaOH solution, and the underlying CdS with dilute HCl. Using a SiC scribe the cells are isolated. The heating renders the graphite electrodes of sheet resistance 25 Ω and the underlying layer is transformed to a carbon-doped p-absorber. The Sb-S-Se film is crystallized, with the composition, Sb2S0.9Se2.1 with a bandgap of 1.42 eV, and electrical conductivity 10⁻⁵ Ω⁻¹ cm⁻¹ under light. An estimated light generated current density, 28 mA/cm² under the sun should be available in a solar cell. The prototype module is completed by applying colloidal silver paint on the graphite electrode and interconnecting it to the silver-paint electrode on the FTO base of the neighboring cell. A commercial acrylic lacquer encapsulates the module. The prototype is of Voc 3.1 V, Jsc 22 mA, maximum power 30 mW. Innovation is possible with modification/ replacement of the CdS window, compositional (bandgap) variation along the thickness and heat-processing of the absorber film, and in the application of back contact. We also present results on module produced by combining chemical deposition and thermal evaporation in the production of the absorber film, whereby bandgap is modified along the absorber thickness.

**Effects of Substrate Material and Substrate-Assisted Laser Patterning on Material Properties of CdSe Thin Films**

Hasan H. Gullu¹, Ozge Bayrakli Surucu², Makbule Terlemezoglu³,⁴, Cansu Emir² and Mehmet Parlak³,⁴

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II-VI semiconducting chalcogenides have become a great part of research interest due to their possibility to use in a wide range of device applications with their remarkable optoelectronic properties as ideal direct band gap, high absorption coefficient and photosensitive behavior in the visible region of spectrum. Based on these optical and electrical properties, these compounds have been investigated as an alternative material system in the fabrication of low cost optoelectronic devices and used as promising materials for the development of current technological devices. Among these compounds, cadmium selenide (CdSe) thin film has long been popular in the field of optoelectronics due to their high transparency in visible region, direct and wide band gap value, photoconductivity, high electron affinity and n-type semiconducting behavior. Although this type of films have potential applications in fabrication of light emitting diodes, thin film transistors, gas sensors, photodetectors and solar cells, in recent years, attention has been directed to alternative methods as variations in chemical constituents, doping, formation of ternary analogues, surface patterning in order to manipulate the material characteristics of thin films to improve the performance of the devices. In this study, CdSe thin films were deposited on a soda-lime bare glass and indium tin oxide (ITO) coated glass substrates using direct evaporation of high purity and stoichiometric CdSe powder at room temperature. Bare glass substrates were used in thin film characterization processes and ITO coated glass substrates was employed to create transparent conducting oxide layer for possible device applications. For the deposited CdSe thin films, energy dispersive X-ray (EDS) analysis showed an average atomic percentage of CdSe is near to stoichiometric composition of the source material as Cd:Se ratio (50:50). The X-ray diffraction profile of the samples was indexed according to JCPDS files and the characteristics diffraction peaks were observed in a good agreement with the literature without any formation of secondary phase in the structure. The surface imaging using scanning electron microscopy (SEM) and detailed surface morphology analysis by using atomic force microscope (AFM) showed that the deposited CdSe thin films are dense and compact in nature. From the optical transmission studies, films were found in direct optical transition characteristics and the band gap values of the samples were calculated using Tauc plots. In addition to the film analysis on different substrates, substrate-assisted laser patterning was investigated as an alternative technique to create functional structures for possible optoelectronic applications. The straight and continuous line patterns on bare and ITO coated glass substrates were optimized in terms of pulse repetition rate, laser power, pulse energy and the feeding speed of the nanosecond pulsed Nd:YAG laser system. Uniform periodic pattern without any damage to the glass substrates were achieved with a wavelength in the infrared region. It was observed from EDS spectrum of the films that the stoichiometric transfer of material from source.
powder to the deposited films on different substrates with different line patterns was achieved. In the case of surface morphology, the effects of laser patterning on characteristics of the CdSe thin films deposited on bare and coated glass substrates were investigated by SEM and AFM images. UV/Vis spectrophotometer was used to discuss the transmittance and reflectance characteristics of these patterned samples.

EL04.13.14
Synthesis, Characterization and Optical Properties of Copper Antimony Sulphide (CAS) Thin Films for Low Cost Photovoltaics Kimberly A. Weston and Richard A. Taylor; University of the West Indies, St Augustine, Trinidad and Tobago

An attractive class of semiconducting materials with non-toxic, low-cost and highly efficient characteristics have emerged as promising alternatives for applications in solar cell technologies. Novel materials or structures with properties that match the spectral distribution of the solar spectrum are therefore required to produce materials of high efficacy. One copper-based semiconductor metal chalcogenide, copper antimony sulphide (CAS) as thin films, is an excellent candidate for potential photovoltaic (PV) applications, since, in addition to the elements’ abundance, low toxicity and simple inexpensive processing protocols, bulk CAS has a strong absorption coefficient of $10^5$ cm$^{-1}$ and a band gap between 0.5 and 2.0 eV, matching well with the solar spectrum as well as excellent photostability. Interestingly, there are sparse reports of tuning the optoelectronic properties with metal dopants for the CAS material and few reports have been written for the synthesis of CAS thin films via the aerosol assisted chemical vapour deposition (AA-CVD) method. As-synthesized thin films of CAS microstructures have various morphologies and stoichiometries which are dependent on AA-CVD parameters of deposition temperature and time.

Homogeneous films of deposition temperatures 500, 550 and 600 °C, synthesised at 30 minutes and 1 hour are non-stoichiometric with mixed morphologies and particle sizes range from 0.3 to 1 µm. Consequently, the optical properties indicate that as-synthesized CAS thin films absorb near the end of the ultra-violet region but mainly in the visible portion of the spectrum. Indirect transitions occur between 0.89 to 3.40 eV. With detailed elucidation from powder X-ray diffraction, Raman spectroscopy, scanning electron microscopy, atomic force microscopy, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, steady-state and time-dependent electronic spectroscopy we have been optimizing AA-CVD protocols to effectively control the materials properties, and if achieved, this will provide possible enhancement of photocurrentivity and furthermore, PV efficiency of thin films.

EL04.13.15
Basic Improvements in Antimony Chalcogenide Thin Films to Build Efficient and Stable Solar Cells Fabiola De Bray Sánchez, Angélica Lizbeth Espinosa Santana, M. T. Santhamma Nair and P. Karunakaran Nair; Universidad Nacional Autonoma de Mexico, Mexico

Of orthorhombic crystalline structure, Sb$_2$S$_3$ and Sb$_2$Se$_3$ with optical bandgap ($E_g$) of 1.88 and 1.1 eV respectively can produce solar cell absorbers with $E_g$ of 1.3 – 1.6 eV, which can offer short circuit current density of 25 – 35 mA/cm$^2$. Antimony sulfide selenide thin film solar cells reported from our group has conversion efficiency ($\eta$) of 5 – 6 % [1]; and from other groups, it had touched 9 %. To be commercially viable, this value should move toward 20 %.

We present methodologies to improve material properties in antimony sulfide selenide thin films produced by thermal evaporation of chemical precipitate or commercial powders of the binary compounds and their mixtures. Chemical precipitates are produced in our laboratory from solution mixtures of potassium antimony tartrate, thiocacetamide and sodium selenosulfate. To improve the crystalline grain diameter, SbCl$_3$(melting point, 94 °C) is added to the evaporation source mixture. To prevent Sb$_2$S$_x$Se$_{3-x}$ film becoming n-type, Se powder is added to the mixture. The material produced this way has the mobility-lifetime product improved by an order of magnitude, to $10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$ superior to that in the other two chalcogenides and a higher p-type electrical conductivity in it due to the low activation energy for Sb-vacancy creation. The $E_g$ of the materials produced is 1.48 – 1.54 eV. All these modifications have led to the development of solar cells with 6.5 % efficiency at absorber thickness 350 – 400 nm and in cell area, 0.5 cm$^2$. In prototype modules of area 7 cm$^2$, it is 4.8%. These cells are encapsulated with commercial resin, for keeping them stable under the sun over many days of operation.

Efficient 1D-Sb₂Se₃ Based Solar Cells in Substrate Configuration
Pedro Vidal-Fuentes¹, Yudania Sánchez¹, Marcel Placidi¹, Victor Izquierdo-Roca¹, Alejandro Perez-Rodriguez¹² and Edgardo Saucedo¹; ¹IREC, Spain; ²Universitat de Barcelona, Spain

One of the most attracting applications for emerging chalcogenide electronic materials is the use of low-dimensional/quasi-covalent compounds as absorbers for direct solar energy conversion into electricity. In this sense, 1D-Sb₂(S,Se)₃ is becoming a relevant thin film chalcogenide semiconductor. In particular, 1D-Sb₂(S,Se)₃ has shown remarkable improvements in the last few years, demonstrating solar cells in superstrate configuration with power conversion efficiencies higher than 7%. In fact, and similarly to CdTe, most of the devices reported in the literature so far have been prepared using this configuration, whiles the substrate configuration option is being marginally used. Additionally Sb₂(S,Se)₃ has shown a high degree of flexibility thanks to the relatively low temperatures required for the synthesis and crystallization of this compound (300-400 °C), being fully compatible with polymeric, steel, ceramic and TCO/glass substrates. This versatility makes this compound very promising for ubiquitous applications such as building integrated photovoltaics, wearables, or autonomous IOT applications among others. Nevertheless, all these technological applications require the urgent development of efficient devices in substrate configuration.

In this work we present a systematic optimization of the synthesis of 1D-Sb₂Se₃ thin films onto conventional Glass/Mo back contact using standard substrate configuration. For the synthesis of 1D-Sb₂(S,Se)₃, an innovative sequential process based on reactive annealing under Se atmosphere of thermally evaporated Sb layers was developed. The study is centered in the analysis of the reactive thermal annealing conditions (temperature, time, pressure) on the compositional, structural and morphological properties of the 1D layers. By adjusting the annealing parameters, we obtain continuous layers with large and homogeneous grains, excellent crystalline quality, and 1D preferential orientation perpendicular to the substrate. We will show that the annealing temperature and Se quantity control in the layer, are the key parameters for controlling the morphology, as well as the structural, optical and electrical properties.

After a first optimization, we report a 1D-Sb₂(S,Se)₃/CdS heterojunction with a promising power conversion efficiency of 5.3% in substrate configuration, demonstrating a Voc of 403 mV (the highest reported value for this configuration to the best of our knowledge).

Additionally, this study is complemented with a wide range of fundamental characterization techniques including photoluminescence, Raman, SEM, XRF, XRD, and with a complete analysis of the impact of the absorber stoichiometry under different regimes (Se-rich, Se-poor, Sb-rich and Sb-poor conditions). All this will be correlated with the optoelectronic characterization (JV, IQE, CV) of the solar cells. Finally, the main urgent challenges to develop Sb₂Se₃ type solar cells in substrate configuration will be presented and discussed.

Tin Chalcogenide Thin Films—Essential Resource for Direct Conversion of Energy
Enue Barrios Salgado¹², Rohini Neendoor Mohan¹, Diana Eréndira Lara Llanderal¹, Fabiola De Bray Sánchez¹, M. T. Santhamma Nair¹ and P. Karunakaran Nair¹; ¹Universidad Nacional Autonoma de Mexico, Mexico; ²Universidad Autónoma de Nayarit, Mexico

Among SnS-CUB, SnS-ORT, SnSe-CUB and SnSe-ORT of cubic and orthorhombic crystalline structures, tin chalcogenides offer an interval of bandgap (Eg) of 1 – 1.74 eV of p-type conductivities owing to the relative abundance of Sn(II) vacancies in them, acting as acceptors. These convert to n-type semiconductors, SnS₂ or SnSe₂ of Eg 1.7 – 2.2 eV when heated at 350 – 420 °C in presence of sulfur or selenium vapor – in which donor centers created due to S – or Se vacancies dominate. We find that heating SnS-Se-CUB films at 350 °C leads to SnSe-ORT and when the heating is done in presence of Se, it forms n-type SnSe₂, both of conductivity 0.01 Ω⁻¹ cm⁻¹ allowing us to build thermoelectric couple with a Seebeck coefficient of 1 mV/K to explore further. In a solar cell structure of SnO₂:F/CdS/SnS-CUB:Ag/C-Ag, a conversion efficiency of 1.5% is achieved, opening up a path toward improving tin sulfide solar cells produced by chemical deposition via diffusion of Ag provided through ion-exchange reaction of SnS-CUB in a dilute AgNO₃ solution. An encouraging new result is that heating of SnS-CUB at 450 °C in presence of S-vapor produces phase-pure p-type Sn₂S₃ film with an Eg of 1 – 1.4 eV and a light generated current density for solar cells in excess of 30 mA/cm². Such conversion takes place via an intermediate formation of SnS₂ due the descending values of the enthalpy of formation of these materials: in kJ/mol, – 91 to – 99 (Sn₉-rock salt - cubic or ORT); – 131 (SnS₂); and – 230 (Sn₂S₃). With energy level diagram very close to that of SnS-ORT, and with an advantage of p-Sn₂S₃ to be phase-pure, free from detrimental n-SnS₂, here is an alternative tin chalcogenide for solar cells. A major attraction of Sn₂S₃ is that it may stabilize also an n-type semiconductor, as per theoretical
model. With a low lattice thermal conductivity, it is also poised to be a prospective thermoelectric element.

**EL04.13.18**

**Cl-Doped SnS Single Crystal and Its N-Type Conduction**

Issei Suzuki¹, Sakiko Kawanishi¹, Yuki Iguchi², Koichi Sato², Takahisa Omata¹ and Hiroshi Yanagi¹; ¹Tohoku University, Japan; ²University of Yamanashi, Japan

Tin monosulfide (SnS) is expected as a light-absorber material for next-generation solar cells due to its advantageous properties: the optimal band gap (~1.0 eV), high light absorption coefficient just above the band gap, and non-toxic and earth-abundant constitutional elements. Since Sn vacancies are easy to form in SnS due to their low formation enthalpy and introduce holes, SnS naturally exhibits p-type conduction and inversion of the carrier type to n-type by doping is quite difficult [1,2]. Nevertheless, n-type SnS was reported in very limited case, that is, heavily Pb-doped SnS (Sn₁₋ₓPbxS, x>0.15), which would, however, cancel the advantage of non-toxicity of SnS [3]. SnS-based solar cells fabricated so far accordingly employed hetero-junction structures, for instance, p-SnS/n-CdS or p-SnS/n-Zn(O,S) [4]. These devices involving the hetero-junction exhibited low conversion efficiencies of ~5% at highest because of unfavorable band offset and/or defect states at the hetero-junction interface suffering from interface recombination [5]. In order to improve the conversion efficiency of the SnS-based solar cells, n-type SnS which enables p/n homo-junction is therefore indispensable.

In this study, we grew single crystals of Cl-doped SnS (i.e., SnS₁₋ₓClₓ) using SnCl₂ as a flux, expecting that chlorine substituting sulfur of SnS would generate electrons. The mixture of Sn, S and SnCl₂ powders were sealed in the vacuum silica glass tube and heated at 520 °C for 24 h, and subsequently cooled down to 240 °C over a period of 36 h and then to room temperature over a period of 12 h. The remaining flux (SnCl₂) was washed away with ethanol and acetone.

Single crystals of SnS in the form of shining lamellate with a surface in perpendicular to the a-axis were obtained. Typical surface area and thickness of the crystals were from 10 to 20 mm² and from 28 to 39 μm, respectively. EPMA analysis indicated that Cl was homogeneously distributed in the single crystal with a concentration of 0.14 at% and segregation of Cl was not found.

Hall coefficient of the single crystal was negative, which indicates that the carrier type is successfully inverted to n-type by Cl doping. The Fermi level of the Cl-doped SnS single crystal determined by XPS was 0.1 eV below the conduction band minimum, whereas that of undoped p-type SnS is generally located at 0.2-0.3 eV above the valence band maximum [2,5], which clearly supports that Cl-doped one is n-type. Hall mobility of electrons of Cl-doped SnS single crystal measured in perpendicular to a-axis was 101 cm²V⁻¹s⁻¹, which is at the same order of magnitude as the Hall mobility of holes of undoped SnS single crystal (100-500 cm²V⁻¹s⁻¹ [6]).


**EL04.13.19**

The Influence of Deposition Temperature and Duration on VTD-SnS Absorber Layer

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Orthorhombic tin sulfide (SnS) has recently been emerged as a very promising absorber material for thin-film solar cells (TFSCs). It has an ideal optical band gap (~1.3 eV) and it comprises of relatively earth abundant constituents and non-toxicity. But till date, the highest efficiency obtained from the SnS-based solar cells is 4.36%, which is fairly low compared to its theoretical limit of ~32%. SnS is a non-cubic material unlike CIGS or CdTe, crystallizing in an orthorhombic structure (JCPDS No. 39-0354, a = 4.3291 Å, b = 11.1923 Å, c = 3.9838 Å). It easily leads to the formation of layered features. Therefore, controlling the morphology of the SnS absorber with dense and pinhole-free grains is crucial.

In this study, the influence of vapor transport deposition (VTD) conditions of tin sulfide (SnS), i.e., growth temperature and duration, on the formation of secondary phases, preferred orientation, and solar cell performance, was investigated. In the growth temperature effect experiment, the morphology is grew as plate form with increasing
temperature and the secondary phase was found at low temperature. Also, it was confirmed that the film thickness was increased linearly with duration and when the growth duration increases to 10 min, a dramatic improvement in the device performance is noted. Finally, fabricated SnS TFSCs (thin film solar cells) achieved near 4% efficiency ($V_{oc}$; 0.342 V, $J_{sc}$; 19.8 mA cm$^{-2}$, FF; 58.0%) at 600 °C growth temperature and 10 minutes duration. In addition, working stability under continuous illumination and damp-heat (85/85) conditions was investigated for the best cell in this study.

**EL04.13.20**

*Understanding the Band Gap of Germanium Selenide* Christopher Savory$^1$, Philip Murgatroyd$^2$, Tim D. Veal$^2$, Jonathan Alaria$^2$ and David O. Scanlon$^1$; $^1$University College London, United Kingdom; $^2$University of Liverpool, United Kingdom

Germanium selenide, GeSe, is a member of the IV-VI family of chalcogenide semiconductors, including the champion thermoelectric SnSe, and has itself been studied in the context of many electronic applications, including thermoelectrics, photocatalysis, phase-change memory and photovoltaics.$^{1,2}$ Despite an increasing amount of research interest in recent years, some questions still remain over its fundamental properties, particularly its bulk band gap, recorded values of which range from 1.06 eV to over 1.5 eV with uncertain characterisation as indirect or direct.$^{3,4}$ Theoretical values using standard Density Functional Theory (DFT) also demonstrate similar variation, although the monolayer is consistently a direct gap semiconductor.$^5$ Given the fundamental importance of the band gap to a material’s use within optoelectronic applications, clarification is necessary to establish the most optimal application for this material.

In this study, we use multiple levels of theory, from standard and hybrid DFT to quasiparticle self-consistent GW calculations in combination with Fourier-transform Infrared Spectroscopy (FTIR) measurements of single crystal and thin films of GeSe to characterise its band gap and provide further understanding into its suitability as a solar absorber. We also discuss how the balance between in-sheet covalent bonding and van der Waals interactions between layers affects the electronic properties of the material, including the influences that have previously lead to variations in recorded band gap. Finally, we examine its dynamical stability in comparison with Raman spectroscopy to examine the structural behaviour of the system, and how this can further influence the overall behaviour of GeSe. We believe these results will help influence future interest in GeSe as a solar absorber as well as further discussion surrounding the IV-VI family.


**EL04.13.21**

*Modern Solar Cells Based on the World’s Oldest Photovoltaic Material—Selenium and Selenium-Tellurium Alloys for Thin-Film Photovoltaic* Ido Hadar, Tze-Bin Song, Weijun Ke, Xiaobing Hu, Zhongzhen Luo, Vinayak Dravid and Mercouri G. Kanatzidis; Northwestern University, United States

The photovoltaic properties of selenium have been discovered over 140 years and were utilized at that time to produce the first solid-state ‘thin-film’ solar cell. This discovery boosted modern research and technologies based on semiconductors, and lead to the implementation of selenium in many functional devices. Upon the rise of competitive semiconductors and mainly silicon, the usage in selenium slowly declined. In recent years, the photovoltaic community gains new interest in this simple elemental semiconductor as a possible absorber for extremely low-cost and highly scalable solar cells. For this application, selenium shows few desirable properties such as high absorption coefficient, intrinsic environmental stability and fabrication at low-temperature (below 200°C).

In this research, we first study the main parameters that are required to optimize the quality and efficiency of selenium-based solar cells, using modern tools and approach. We indicate the importance of careful annealing of the selenium film, very close to its melting temperature to obtain high-quality films. As selenium has an anisotropic structure, composed of 1D chains, we study how the alignment of the crystals in the thin film changes the device.
properties. Finally, we indicate the importance of light illumination (and excitation) of the film during the fabrication process to enhance and improve the crystallization of the film.

Following these results, we study how the selenium bandgap (1.7 eV), can be tuned to the optimal value for photovoltaic absorber (1.2-1.4 eV), by alloying selenium with the isomorphic low bandgap semiconductor tellurium. We found that the addition of tellurium causes a strong non-linear shift of the alloy’s valence band minimum energy, leading to a non-linear decrease of the bandgap. This non-linear shift enables to reach the desired bandgap by alloying a fairly small amount of tellurium (~10%). Photovoltaic devices based on the selenium-tellurium alloy indeed show improved current density and spectral response as a result of the optimized bandgap. The overall efficiency of the selenium-tellurium devices is still lower than the pure selenium devices, due to lower voltage and fill-factor, but we indicate the main causes to the lower properties and suggest some improvements to the device structure which should improve the device efficiency.


**EL04.13.22**

**Electrical Properties of c-Se/Ga_2O_3 Avalanche Photodiodes** Keitada Mineo, Shigeyuki Imura, Kazunori Miyakawa, Masakazu Namba and Misao Kubota; NHK Science & Research Laboratories, Japan

The demand for high resolution and high-speed imaging devices has increased with the emergence of next-generation broadcasting systems such as full-featured 8K Super Hi-Vision with 33 million pixels and 120 Hz frame rate, which are respectively 16 and 4 times greater than those of current 2K Hi-Vision systems. However, with increasing number of pixels and frame rate, the sensitivity of the image sensor decreases. The sensitivity decreases because of a reduction in the amount of light received per pixel and per frame. To address this problem, we have been studying the stack-type complementary metal–oxide semiconductor (CMOS) image sensor overlaid with a poly-crystalline selenium (c-Se)/gallium oxide (Ga_2O_3) photodiode [1][2]. In this image sensor, high sensitivity can be realized by multiplying photogenerated charges using the avalanche phenomenon. c-Se has a high absorption coefficient in the entire visible light range compared to silicon (Si) that is mainly used to make conventional photodiodes. Therefore, incident light can be absorbed in a thinner film and charge multiplication can be induced using relatively low voltages compared to conventional Si photodiodes. Ga_2O_3 has a wide bandgap of 4.5 eV; the large energy barrier between the work function of indium tin oxide as an electrode and the valence band of Ga_2O_3 prevents hole injection from the electrode, thereby increasing the dark current. To further reduce the operating voltage required for avalanche phenomenon in the c-Se/Ga_2O_3 photodiode, we investigated the effects of doping impurities into Ga_2O_3 and c-Se. First, Sn-doped Ga_2O_3 was fabricated via RF sputtering using a mixed target of tin oxide (SnO_2) and Ga_2O_3. By increasing the concentration of Sn that served as a donor, the photocurrent increased at a low voltage because the increase in Ga_2O_3 carrier concentration achieved via Sn doping caused the depletion layer to mainly spread into c-Se. Then, tellurium (Te)-doped c-Se was prepared by annealing amorphous Se (a-Se) formed on a thin Te nucleation layer. By increasing the carrier concentration of c-Se via the diffusion of Te that served as an acceptor, the avalanche phenomenon could be observed at a low voltage because a high electric field was applied to c-Se. By adding impurities to both Ga_2O_3 and c-Se, an avalanche multiplication factor of 10 could be obtained at an operating voltage of 16 V, which is lower than the operating voltage of non-doped photodiodes (21 V). We believe that the c-Se/Ga_2O_3 avalanche photodiode will lead to the development of high-sensitivity image sensors.


**EL04.13.23**

**Amorphous Selenium Direct Conversion X-Ray Detector with 7.8-Micron Spatial Resolution** Chris Scott1, Yunzhe Li1, Celal Con1, Michael Farrier1 and Karim Karim1,2; 1KA Imaging, Canada; 2University of Waterloo, Canada

Imaging using x-ray radiation plays a significant role in advancing industry and fundamental research by utilizing the highly penetrating nature of x-rays to study the internal composition of materials. Image quality is fundamentally limited by the number image forming photons, which is governed by the detector quantum efficiency (QE). Conventional high spatial resolution scintillator-based indirect conversion detectors have poor QE due to thinning of the scintillator to minimize secondary optical scatter. This makes them non-ideal for emerging scientific imaging
tasks such as phase-contrast x-ray imaging (e.g. for visualizing low density composite materials).

We have developed a direct conversion detector by integrating amorphous selenium (a-Se) photoconductor material and a CMOS readout circuit with 7.8 µm pixel pitch. Unlike the optical scatter in scintillators, the spread of absorbed energy from x-ray interactions in the photoconductor does not significantly degrade spatial resolution as the a-Se thickness is increased. The detector was vertically integrated by CMOS post-processing using thermal evaporation. An a-Se layer of 118 µm and top biasing electrode were directly deposited. After packaging, wire-bonding was performed below the glass transition temperature of a-Se to prevent crystallization. Finally, a high-voltage connection was provided from the package to the surface of the electrode. A biasing voltage of 500 V was applied to the electrode, resulting in an internal electric field of 4.2 V/µm.

The detector was characterized at 60 kV with 2 mm Al filtration. Using the slanted-edge technique the pre-sampling MTF of the detector was measured. The line-spread function had a full width at half-maximum of 8.7 µm and in the spatial frequency domain the MTF decreased to 30% at Nyquist frequency, ≈64 cycles/mm, i.e. equivalent to 7.8 µm spatial resolution. The theoretical upper bound on the DQE at zero spatial frequency, DQE(0), is equal to the detector QE of 0.49. The measured DQE(0) was determined to be approximately 0.42, a decrease due to the presence of noise and additional pathways of signal loss.

To the best of our knowledge, this characterization demonstrates the highest spatial resolution direct conversion detector reported for the hard x-ray regime. In addition, our results suggest that a-Se photoconductors offer a high detection efficiency alternative to scintillator technology for high spatial resolution x-ray imaging tasks such as phase contrast x-ray imaging.

EL04.13.24
Two-Stage Melt Processing of Phase Pure Selenium for Printable Triple Mesoscopic Solar Cells Jiawen Wu1,2 and Hongwei Han1,2; 1Huazhong University of Science & Technology, China; 2Wuhan National Laboratory for Optoelectronics, China

Hexagonal selenium with a direct band gap has been developed for optoelectronic applications through the last 130 years. Most advances have been made using vacuum deposition or solution methods. Herein we demonstrate a simple two-stage melt processing (TSMP) method to incorporate selenium in printable triple mesoscopic solar cells under ambient conditions. While a simultaneously triggered polymerization and depolymerization between several types of Se chains happen during the melt processing, we successfully realize phase-pure hexagonal selenium inside the mesopores with high crystallinity. We found that the TSMP method has an obvious effect on the CB energy level, band gap and crystal phase of selenium by ultraviolet electron spectroscopy, ultraviolet-visible absorption spectroscopy and in situ X-ray diffraction. Compared with the single melting process, the power conversion efficiency of the printable mesoscopic device was increased eight times to 2% through TSMP. These findings provide a new strategy for the melting process to obtain a more efficient photovoltaic device.

EL04.13.25
Evolution of Physicochemical Properties as Function of Size and Design Principles of Transition-Metal Dichalcogenide Nanoflakes—Insights from Ab Initio Investigations Naidel A. Caturello1, Rafael Besse1, Augusto C.H. Da Silva1, Diego Guedes-Sobrinho1, Matheus P. Lima2 and Juarez L. F. Da Silva1; 1University of São Paulo, Brazil; 2Federal University of São Carlos, Brazil

Two-dimensional transition metal dichalcogenides (2D TMDs) have been brought into the limelight due to their unique optical, electronic, and mechanical properties, which enables them for a wide range of applications.[1,2] Defined by the chemical formula \( MQ_2 \), where \( M \) is a transition-metal and \( Q = S, Se, Te \), each monolayer of a 2D TMD is composed of a metallic plane sandwiched by two \( Q \) planes, where the coordination around the metal atoms can be trigonal prismatic, octahedral, and distorted octahedral (named 2H, 1T, and 1T' phases, respectively).[3] Despite the great technological and scientific interest drawn by those compounds, the atom-level understanding of how the physicochemical properties of 2D TMDs evolve with system size is still far from satisfactory. Thus, we report \textit{ab initio} density-functional theory investigations of 2D TMDs nanoflakes with diverse sizes and chemical compositions, namely (i) \( (MoSe_2)_n \), with \( n = 15, 63, 108, 130, 154, \) and \( 192,[4] \) (ii) \( (MoQ_2)_n \), \( Q = S, Se, Te \), with \( n = 1 – 16,[5] \) and (iii) \( (WQ_2)_n \), \( Q = S, Se, Te \), with \( n = 1 – 16, 36, 66, \) and \( 105.[6] \) We found that the 1T' phase has the lowest energy for small MoSe\(_2\) nanoflakes, and a size-induced 1T' → 2H phase transition occurs, which is mainly
due to the higher edge formation energy of the 2H phase. Furthermore, for the $n = 1 - 16$ size range for both Mo$Q_2$ and W$Q_2$ nanoflakes we observed a transition in energetic preference from structures elongated in one dimension with almost-equilateral trusses composed metallic lattices (1D), to 1T' nanoflakes. The mechanism of stabilization of the 1T' nanoflakes in relation to the 1D geometries results from a combination of two stabilization effects, namely the edge charge modulation in the edges of the structures, and the distortion of the octahedral geometry throughout the core of 1T' nanoflakes. Both 1D and 1T' maintain the same $Q$-terminated edge configurations, which stabilizes both morphologies in relation to 2H stoichiometric monolayer fragments. Since the edge charge effects are more intense in the order Te $<$ Se $<$ S, the cluster size in which 1D $\rightarrow$ 1T' occurs increases in the order $M_S^2 < M_{Se}^2 < M_{Te}^2$, $M = Mo, W$. Furthermore, for the W$Q_2$ nanoflakes we have established systematically that the most stable nanoflakes are composed of junctions between triangular building blocks. The geometric forms originated from those junctions are stabilized due to maximization of bonds formed within the core of the nanoflakes. Therefore, by extending the sizes of the nanoflakes we could extend our understanding to the interplay of nanoflake size and stability. As a whole, our investigations could establish that the mechanisms of stabilization of the group-6 TMDs nanoflakes can be summarized as follows: (a) conservation of the $Q$-terminated edge configuration; (b) geometry of the nanoflakes as junctions of triangular building blocks; (c) edge charge modulation effects in order to stabilize 1T' nanoflakes opposed to 1D stripes; and (d) octahedral distortions responsible for breaking the degeneracy of electronic levels. Therefore, we could establish the criteria for the proposition of stable $MQ_2$, $M = Mo, W$; $Q = S, Se, Te$ nanoflakes, and our findings can help to explain independently obtained experimental results.[6]


EL04.13.26
High Performance Ag:Se Nanoparticle Based Flexible Near-Infrared Photodetectors Won-Yong Lee, Seunghyun Ha, Hyunjae Lee and Jaewon Jang; Kyungpook National University, Korea (the Republic of)

Novel, low-voltage, high-detectivity, solution processed, flexible near-infrared (NIR) photodetectors for opto-electronic applications were realized and their opto-electronic properties were investigated for the first time. This was achieved by synthesizing Ag:Se nanoparticles (NPs) in aqueous solutions, and depositing highly crystalline Ag:Se thin films at 150 °C with re-distributed Ag:Se NPs in aqueous inks. The high conductivity and low trap concentration of the 150 °C annealed Ag:Se films result from the Ag formed inside the films and the improved film quality, respectively. These factors are both critical for the realization of high-performance flexible photodetectors. The fabricated device exhibited a high detectivity of $7.14 \times 10^9$ Jones (above $1 \times 10^9$) at room temperature, delivering low power consumption. This detectivity is superior to those of reported low bandgap semiconductor systems, although the device had undergone 0.38% compressive and tensile strains. Moreover, the performance of the device is better than that of MoS$_2$-based phototransistors, black arsenic phosphorus field-effect transistors (FETs) or commercial thermistor bolometers at room temperature (D* $\sim 10^8$ Jones) and exposed to mid-infrared (MIR) light.

EL04.13.27
Design and Synthesis of Novel Semiconductor Nanostructures for Photon Upconversion Tory Welsch, Jill Cleveland, Eric Chen, Christopher Milleville, Kyle Lennon, Jing Zhang, James Bork, Joshua Zide and Matthew Doty; University of Delaware, United States

Photon upconversion is a process by which two or more low-energy photons are absorbed and one higher-energy photon is emitted by a material. Materials that can achieve photon upconversion are desirable for many applications such as optoelectronic devices, drug delivery, and photovoltaics. A key advantage of using semiconductor nanoparticles for photon upconversion is their wide tunability in structure, which consequently affects their absorption and emission properties. We have synthesized colloidal quantum dot (QD) heterostructures for this purpose, in which two QDs with different bandgaps are separated by a wide-bandgap nanorod. While our
CdSe(Te)/CdS/CdSe core/rod/emitter structures demonstrate near-infrared (NIR)-to-visible photon upconversion, their upconversion efficiencies show significant room for improvement. The performance of these structures can be enhanced through a better understanding of their underlying properties and the effect of these properties on upconversion efficiency. While we can further our understanding through theoretical modeling, we must also consider the constraints of available synthesis techniques. Synthesis parameters such as ion precursors, organic ligands, and temperature, among others, can be tuned within well-studied procedures to create structures with the desired composition, structure, and resulting optical behavior. For example, introducing a bandgap gradient along the nanorod through doping has been found to funnel carriers to the emitter, increasing both quantum yield and upconversion efficiency. We have therefore studied an “inverted” emitter/rod/core structure which allows this gradient to form more naturally during synthesis. We have also found that charge carrier separation can be improved by controlling the position of the core along the rod and by optimizing the length of the rod. This has led us to explore spherical core/shell/shell structures with varying shell thicknesses and gradients and to explore other material compositions such as PbS to further tune absorption and emission wavelengths. We present these synthesis methods, the resulting structures, and their impact on upconversion performance as characterized by photoluminescence and power dependence measurements. We describe how further upconversion performance enhancement can be achieved through improved structural control, which will allow for future incorporation into various photonic device applications.

**EL04.13.28**
**Mid-IR Ag2Se-Based Colloidal Quantum Dot Photodetectors** Ayaskanta Sahu¹, Dong Kyun Ko², Shihab Hafiz², and Michael Scimeca¹; ¹New York University, United States; ²New Jersey Institute of Technology, United States

Mid-wavelength infrared (IR) photons have high penetration through airborne obscurants such as fog and mists, rendering mid-IR photodetectors ideal for use in long-distance thermal sensing and enhanced night vision applications. Colloidal quantum dot-based mid-IR photodetectors present a promising path toward fabricating sensors and imagers at significantly reduced cost compared to state-of-the-art epitaxial grown quantum-well IR detectors. Herein, we report on recently discovered silver chalcogenide quantum dots that exhibit distinct optical absorption in the mid-IR. These colloidal quantum dots demonstrate a narrow bandgap metastable tetragonal phase, not available in bulk, and contain excess electrons, allowing intraband optical transitions between the first and the second conduction energy levels. In this talk, I will present the synthesis, characterization, and photoconductive photodetector device characteristics of this relatively benign colloidal IR material, in contrast to highly toxic Hg-based competing mid-IR devices.

**EL04.13.29**
**Molecular Modeling of Two-Dimensional Quantum Dot Solids Formation Using the Simple Molecular Reactive Force Field** Isaiah Chen and Paulette Clancy; Johns Hopkins University, United States

Quantum dots composed of lead chalcogenides (PbX, X = S, Se, Te) have shown considerable promise for use in various applications ranging from photovoltaics to optoelectronics, including commercial implementations in displays and cell phones. However, there has been limited use with these nanoparticles in electronic devices due to the lack of coupling between multiple quantum dots. Consequently, there has been a significant amount of research focusing on the combination of self-assembly and directed attachment of colloidal quantum dots at fluid interfaces to form two-dimensional quantum dot superlattices. Currently, the mechanism for the formation of two-dimensional quantum dot superstructures is not fully understood and, not unrelatedly, materials that are produced experimentally contain defects that hinder the performance of the material. Various factors, such as inhomogeneous coupling, variation in quantum dot size and shape, and positional misalignment, create structural disorder that is detrimental to the overall charge transport in the chalcogenide material.

We are using ab initio Density Functional Theory (DFT) and Molecular Dynamics (MD) to study the atomic behavior behind the oriented attachment of multiple colloidal lead sulfide quantum dots. These methods serve as an important tool for elucidating the thermodynamic and kinetic factors that govern the interactions between the organic ligands bound to the surfaces of the quantum dots and the amine-based chemical trigger used to remove them from the surface and the epitaxial bridge formation between multiple colloidal quantum dots. We have studied reactions between the ligands and the chemical trigger in solution using the PBE functional in DFT.

While the DFT calculations provide an accurate picture of the interparticle interactions, we need to turn to a semi-
empirical approach that will allow us to access orders-of-magnitude-larger system sizes. To do so, and to accurately model a system with multiple lead sulfide quantum dots, we use the Simple Molecular Reactive Force Field (SMRFF), which we have developed to model the reactive processes that give rise to PbS bond formation. The SMRFF potential is drawn from a combination of simple potentials (Morse/Tersoff, Lennard-Jones, and Coulombic). The parameters for each individual potential are obtained using a training set with multiple 32-atom geometries. For each geometry, the energy of the system is calculated using DFT and the SMRFF parameters are optimized to match the energy as closely as possible. With this fully parameterized SMRFF potential, we are then able to provide the first reactive force field simulation of epitaxial bridge formation between multiple PbS quantum dots. The ability to watch this process allows us to understand how misalignment and processing conditions, such as thermal annealing, affect the nature of the bridges including defect formation.

**EL04.13.30**

**Electrochromism of Electrophoretic CdSe QD Films**

Yauhen Aniskevich\(^1\,^2\), Mikhail Artemyev\(^2\), Genady Ragoisha\(^2\) and Eugene Streltsov\(^1\); \(^1\)Belarusian State University, Belarus; \(^2\)Research Institute for Physical Chemical Problems of Belarusian State University, Belarus

Quantum dots (QDs) and QD films are actively studied due to their properties tunable by particle size, shape and composition. Electrochemical treatments can affect QD film properties, e.g. by surface modification or electrochemical doping. The electrochemical doping proceeds via electron transfer from an electrode substrate to quantum dot which fills energy level in conduction band. The latter causes changes in QD film absorbance and luminescence.

Here we report on electrochemistry and spectroelectrochemistry of CdSe QD films obtained by electrophoretic deposition on FTO from CdSe QD colloidal solution.

Cyclic voltammetry of CdSe QD films in deaerated 0.1 M TBAPF\(_6\) solution in acetonitrile has revealed particle size effects which were also dependent on electrode potential scan rate. A cathodic current shoulder develops in the negative scan below −1 V followed by monotounous current increase at more negative potentials. Current response after scan reversal depends on the QD particle size. For the smallest particles studied (2.8 nm), no considerable anodic current was observed, contrary to the case of bigger particles (6.3 nm) which caused a distinct anodic peak. The negative scan also produces changes in absorbance spectra of the QD films by filling electron energy levels in conduction band. As the potential is scanned negatively, absorbance of first exciton decreases almost to the background level. The variation of absorbance reveals electrostimulated changes in the whole film not restricted to the interface. The changes in optical properties were observable even with naked eye, while the electrode color was varying in the potential scan. Spectroelectrochemical data have revealed reversible character of the electrostimulated optical effects.

We also consider effects of oxidant in the electrolyte solution on electrochromic response.

Thus, our investigation has revealed the reversible electrochromic behavior of electrophoretically deposited oleate-capped CdSe QD films with the size-dependent electrochemical response of the films.

This work has been supported by Horizon 2020 research and innovation program under MSCA-RISE-2017 grant agreement No. 778357.

**EL04.13.31**

**Copper-Based Chalcogenide Nanostructures—Tunable Structural and Electronic Properties towards Enhanced Photoconductivity**

Richard A. Taylor, Shanna-Kay Spencer and Kimberly Weston; University of the West Indies, Trinidad and Tobago

In recent years, copper-based multinary chalcogenide semiconductors have emerged as promising non-toxic, low-cost and high efficiency alternatives for thin film solar cell applications. However, it is still difficult to prepare them in high quality and controllably tune their structural, electronic and optical properties. As such, our research has been focussed on developing facile and attractive routes to tune structure and optical properties of promising ternary chalcogenide solar absorber materials including un-doped and doped copper indium sulphide (CIS) and the emerging copper antimony sulphide (CAS) nanostructures, as examples. In particular, we have been able to effect time-dependent and dopant-dependent phase transformation of CIS and CAS nanoparticles via hot-injection colloidal chemistry using a unique combination of metal-organic precursors and capping agents over a range of temperatures. Un-doped CIS quantum dots of quasi-spherical morphology with fairly narrow size distribution (5.6 ± 1 nm) exhibit time-dependent phase transformation from wurtzite to chalcopyrite structures. However, wurtzite to
chalcopyrite phase transformation was also induced in silver-doped CIS with increasing Ag⁺ dopants and corresponding tuning of electronic absorption and emission properties across the visible to near-infrared spectral region influenced by In³⁺ and Ag⁺ interstitial and Cu⁺ vacancy defects. Also, as-synthesized (60 – 70 °C) CAS nanoparticles (2 – 20 nm) exhibit tunable morphology of spherical, hexagonal and plate-like structures with tunable indirect band gap between 3.39 and 3.54 eV, atypical for CAS. These findings suggest attractive routes to tuning structure and optical properties and effective means for possibly enhancing photoconductivity in these ternary chalcogenides. With detailed elucidation from powder X-ray diffraction, Raman spectroscopy, transmission electron microscopy, atomic force microscopy, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, steady-state and time-dependent electronic spectroscopy we have been able to propose mechanisms of phase transformation and the effect of stoichiometry (including intrinsic and extrinsic dopants) on structural and electronic properties in these materials for tunable photovoltaic effects.

EL04.13.32
Analysis of Self-Assembled Quantum Dot Superlattices for PV Applications Adam J. Moule¹, Xiaolei Chu¹, Hamed Heidari Mezerji¹, Alex Abelson², Caroline Qian², Davis G. Unruh¹, Chase M. Hansen¹, Gergely Zimanyi¹ and Matt Law²; ¹University of California, Davis, United States; ²University of California, Irvine, United States

Epitaxially-fused colloidal quantum dot (QD) superlattices promise to combine the unique photophysics of QDs with the efficient band transport of bulk-semiconductors. PbS and PbSe QD layers have demonstrated multiple exciton generation in response to photo excitation by high energy photons. We would like to extend the multi-exciton generation to thick arrays of QDs, which is possible if the structural order of the film is improved to reduce electronic traps. Here we focus on fabrication of extended superlattice films with multi-layers of QDs and examine how the fabrication method affects the local order. Specifically, we form ordered arrays of QDs at a liquid-liquid interface and then reduce the spacing between QDs using in-situ ligand exchange. The resulting films are characterized using high-resolution scanning transition electron tomography (STET). We are able to resolve the position of each QD in a sample encompassing 1000’s of QDs. In addition of the particle positions, we also resolve the presence (or lack of) of epitaxial connections between neighboring QDs and the thickness of the neck formed between neighboring QDs. This morphological information is used to generate an electronic model. Our model shows that the energetic disorder caused by heterogeneous epitaxial bridging between QDs in a single domains is about one order of magnitude less important than the presence of disorder at grain boundaries between superlattice domains. This presentation will explore the link between structural and electronic order in these complex 3D samples.

SYMPOSIUM EL05

Diamond and Diamond Heterojunctions—From Growth and Technology to Applications
December 2 - December 5, 2019

Symposium Organizers
Thomas Schuelke, Fraunhofer USA
Emmanuel Scorsone, CEA
Mariko Suzuki, Cornes Technologies Ltd
Satoshi Yamasaki, National Institute of Advanced Industrial Science and Technology

Symposium Support
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Applied Diamond Inc.
DiamFab
SESSION EL05.01: Diamond Devices/Technology
Session Chair: Emmanuel Scorsone
Monday Morning, December 2, 2019
Hynes, Level 1, Room 107

8:15 AM WELCOME

8:30 AM *EL05.01.01
GaN Nanowires on Diamond for NV-Center Control Martin Stutzmann, Martin Hetzl, Max Kraut, Theresa Hoffmann and Julia Winnerl; Technische Universität München, Germany

Diamond is an interesting substrate for the growth of GaN nanowires and other nanostructures such as nano-fins for a number of reasons. It is chemically and mechanically very stable, has a high thermal conductivity, a much larger electrochemical window than GaN, is optically transparent up to a photon energy of about 5.3 eV, and can be very effectively doped p-type by controlled substitutional boron incorporation, e. g. during CVD growth. Therefore, heteroepitaxial structures of AlGaN thin films on diamond substrates have been investigated with increasing emphasis since more than a decade, mainly for electronic and optoelectronic applications. In comparison, much less work has been devoted the growth of AlGaN nanowires on diamond, which is the main topic of the work described here.

We are interested in GaN nanowires on single crystalline diamond substrates for electrical and optical addressing and read-out of nitrogen-vacancy (NV) centers as the most sophisticated solid-state qubits available so far. The target of this work is to develop a technology for the integration of surface-near NV-centers in the intrinsic layer of p/i-diamond/n-GaN hetero-diodes with varying concentrations of implanted NV-centers were then fabricated and characterized with respect to their optical and electronic properties. In particular, it was observed that the efficiency of the optical read-out of the NV photoluminescence is increased by an order of magnitude for diamond covered with an optimized periodic GaN nanowire array compared to the bare diamond substrate. Fourier imaging of the NV photoluminescence allows the determination of the crystallographic orientation of single NV centers underneath a GaN nanowire. Furthermore, efficient electroluminescence of NV centers could be achieved by forward current injection. Finally, an outlook will be given to the future implementation of GaN nano-fins and -grids on different substrates including diamond.

9:00 AM *EL05.01.02
Diamond Electronic Devices for Power Electronics Etienne Gheeraert1,2; 1University of Grenoble-Alpes, France; 2University of Tsukuba, Japan

The key to the efficient transmission and conversion of low-carbon electrical energy is the improvement of power electronic devices. Diamond is considered to be the ultimate wide bandgap semiconductor material for applications
in high power electronics due to its exceptional thermal and electronic properties. Two recent developments - the emergence of commercially available electronic grade single crystals and a scientific breakthrough in creating a MOS channel in diamond technology, have now opened new opportunities for the fabrication and commercialisation of diamond power transistors. These will result in substantial improvements in the performance of power electronic systems by offering higher blocking voltages, improved efficiency and reliability, as well as reduced thermal requirements thus opening the door to more efficient green electronic systems.

In the literature, several diamond-based field-effect-transistors (FETs) have already revealed good on state performance and high blocking voltage capability (~2kV) in a wide range of operating temperatures. The possibility of generating an inversion regime in diamond metal-oxide-semiconductor FET (MOSFET), and the new Deep Depletion regime (D2MOSFET) specific to wide bandgap semiconductors pave the way for a new generation of power devices. The critical part of the transistor is the gate oxide, with electrical charge traps located within the oxide or at its interface with the semiconductor. These traps can screen the gate potential and shift the threshold voltage, making the devices unusable.

The current research carried out mainly in Japan and Europe will be presented, with the various device architectures explored, including MOSFET, MESFET, D2MOSFET and rectifiers. Results obtained in the framework of the first European research collaboration on diamond devices, aiming at fabricating the first HVDC diamond based converter will also be presented.

9:30 AM *EL05.01.03
Diamond Growth and Device Technology for Quantum Sensing Mutsuko Hatano; Tokyo Institute of Technology, Japan

Nitrogen-vacancy(NV) centers in diamond have superior physical properties at room temperature for quantum sensing of the magnetic field, electronic field, temperature, and pressure enabling scalable applications from atomic-scale to macroscopic range. We would like to introduce our recent progress on materials and devices.

- Homoepitaxial growth: Higher generation yield of selectively-aligned NV ensemble formed with precise depth control for scalable applications [1,2].
- Heteroepitaxial growth: Diamond film with aligned NV ensemble on Si (111) substrates via the 3C-SiC layer by original antenna-edge type microwave plasma CVD [3].
- Devices: Charge state control of NV centers by pn junctions [4]. As applications, we would like to introduce the bio-cell imaging with the magnetic marker[5], internal device sensing [6], and probe-type prototype system.

This study was supported in part by MEXT Q-LEAP and KAKENHI (17H01262 and 18H01472).


10:00 AM BREAK

SESSION EL05.02: Optical Devices
Session Chair: Martin Stutzmann
Monday Morning, December 2, 2019
Hynes, Level 1, Room 107

10:30 AM *EL05.02.01
Development of an Ultra-Sensitive Biosensor Based on Mid-Infrared Diamond Waveguide Spectroscopy
Mikael Karlsson¹², Pontus Forsberg¹, Lars Österlund¹², Fredrik Nikolajeff¹², Per Ola Andersson¹², Joakim Bergström¹, Julian Haas³ and Boris Mizaikoff⁴; ¹Uppsala University, Sweden; ²Molecular Fingerprint Sweden AB, Sweden; ³FOI Swedish Defence Research Agency, Sweden; ⁴Ulm University, Germany
In this presentation, our latest work in the development of an ultra-sensitive biosensor based on diamond waveguides will be highlighted. We have during the last years been working on the design and fabrication of mid-infrared (MIR) diamond waveguides. The diamond MIR waveguides together with a broadband tunable quantum cascade laser (QCL), emitting in the so called molecular fingerprint region, are the two key elements in our newly developed label free MIR biosensor. In our approach MIR light is coupled into microfabricated diamond waveguide structures, which are purposefully designed to sustain single or multimode standing waves. The associated evanescent waves that are created at the waveguide surface will extend into the surrounding media and interact with the analyte thus provide the sensing volume. In existing commercial technologies, attenuated total reflection IR (ATR-IR) spectroscopy, IR light from a thermal emitter is coupled through a millimeter sized diamond crystal, with up to 10 internal reflections in the diamond crystal. This is a powerful technology and is today used for i.e. quality control in medical and food industry, protein analysis, forensics, etc. However, the relatively low sensitivity of this technique hinders its use in many applications. Our biosensor achieves unsurpassed sensitivity due to the large number of standing waves nodes created in our waveguides which roughly can be translated to the number of internal reflections per length unit is maximized. Moreover, the use of a bright QCL laser as a light source further increases the sensitivity of our biosensor – therefore an ultra-sensitive sensor is realized. Finally, the diamond waveguide material facilitates further functionalization by means of organic chemistry thus extending the capabilities of traditional silicon or gold based biosensor technologies, and we demonstrate here one possible route to fabricate selective affinity layers for protein fishing on nanocrystalline diamond overlayers.

Several designs of diamond waveguides are discussed, ranging from thin film diamond slab waveguides, rib waveguides, to microfabricated free hanging diamond waveguides. Different dimensions of microfabricated polycrystalline diamond waveguides have successfully been fabricated with thicknesses ranging between 5 to 15 µm. Focused ion beam etching has been applied to study the effect of controlled surface roughness of the in- and out coupling area of the waveguides, and to establish limits of attainable throughput of the waveguides. The complete setup of the biosensor is presented.

To demonstrate the strength of using a bright QCL as a light source, we show how a multi-reflection diamond crystal (450 µm thick) can be used for non-invasive glucose monitoring in human saliva. Furthermore, we present measurements on different types of analytes at low concentrations using our waveguide designs to demonstrate the sensitivity of the sensor.

Currently, our main activity is on analyzing different forms of the protein alpha-synuclein, which is relevant in understanding the mechanism behind Parkinson’s disease. We have previously shown that ATR-IR spectroscopy can be used to analyze the secondary structure of different alpha-synuclein aggregates. Moreover, it is also possible to see the difference in the IR-spectra between the native state and the neurotoxic misfolded state of the protein. However, the ATR element is impractical to functionalize and the sensitivity of the ATR-IR spectroscopy is too low to be used on relevant samples from patients. In contrast, our diamond waveguide biosensor exhibits the desired key properties to analyze the secondary structure of alpha-synuclein at biologically relevant concentrations. Future work includes the functionalization of the diamond waveguide sensor surface to selectively adsorb alpha-synuclein from cerebrospinal fluid, with the ultimate goal to detect Parkinson’s disease at an early stage.

11:00 AM EL05.02.02
Alligator Photonic Crystal Cavities in Bulk Diamond Kevin C. Chen1, Sara Mouradian2, Eric Bersin1 and Dirk R. Englund3; 1Massachusetts Institute of Technology, United States; 2University of California, Berkeley, United States

Central to quantum information processing is the entanglement generation rate, which can be Purcell enhanced by coupling a quantum emitter to a cavity. One-dimensional hole-y photonic crystal cavities in diamond have already demonstrated >10,000 quality factors and small mode volumes [1], two necessary characteristics for achieving high cooperativity. However, color centers such as the nitrogen vacancy center typically exhibit severe spectral diffusion near surfaces, resulting in reduced coupling rate under the presence of holes. Inspired by Hood et. al.’s atomic platform [2], we propose using the alligator photonic crystal cavity that removes the airgaps and thus pushes the emitters farther away from surface charge states. Here, we report the simulation results and the characterization of alligator cavities in bulk diamond. Realization of this nanophotonic structure allows for a more noise-resilient cavity QED system essential for constructing a scalable quantum network.

Acknowledgements
K. C. Chen acknowledges funding support by the National Science Foundation Graduate Research Fellowship Program (GRFP) and the Army Research Laboratory Center for Distributed Quantum Information (CDQI).

References
The ability of pigeons to sense the magnetic field of the Earth has long been established through behavioral studies, however, the underlying biophysical mechanisms are yet to be determined. Magnetoreceptors in the beak\(^1\), retina\(^2\) and inner ear hairs\(^3\) have been proposed. Markers for neuronal activation have previously been used to link the vestibular brain-stem region to magnetic stimulation\(^4\). This activation is contingent on the lagena being intact, providing strong evidence that magnetoreceptors are present in inner ear hairs and support the ferrimagnetic particle receptor hypothesis for magnetoreception. These results warrant further investigation into iron containing cells within this part of the pigeon anatomy. The discovery of quasi-spherical structures in the cuticular plate of the inner ear hair of pigeons was subsequently made, with these structures being termed ‘cuticulosomes’\(^3\). These objects are of potential relevance to the problem of magnetoreception due to their position in the pigeon anatomy and because they contain ferritin granules. Cuticulosomes have been imaged using TEM and characterized using elemental analysis. Statistics surrounding the occurrence of these spherical structures having been developed through Prussian Blue staining experiments, however, we have limited information on their magnetic properties\(^3\).

Quantum magnetic microscopy techniques\(^5\)–\(^7\) provide an opportunity to remedy that situation. The nitrogen-vacancy centre in diamond has a sensitivity to magnetic fields which allows for the mapping of both fluctuating magnetic moments and of static magnetic fields from samples affixed to the surface of the diamond\(^8\). Here we apply diamond-based quantum magnetic microscopy to probe the fluctuating magnetic fields emanating from individual cuticulosomes. The magnetic images are correlated back to the anatomical location providing critical in-situ magnetic information. The stray magnetic field from the cuticulosomes was also mapped using our quantum imaging microscopes under the application of a bias magnetic field. The magnitude of the stray magnetic field increases with the size of the bias field applied with the dependency of the stray fields on the externally applied field providing additional insight into the magnetic properties of cuticulosomes.

The quantum imaging technique applied here provides new physical insights into the magnetic properties, i.e. magnetic susceptibility, of individual cuticulosomes. The information gleaned will aid in the effort to understand the functionality of cuticulosomes, and crucially, if they have any bearing on the ability of pigeons to sense magnetic fields.


11:30 AM *EL05.02.04
Lightweight and Compact Laser Processing Heads Based on Diamond Lenses Martin Traub\(^1\), Carlo Holly\(^2\), Mario Hesker\(^2\), Angelo Di Meo\(^3\), Dennis Arntz\(^4\), Jan Bremer\(^1\), Dieter Hoffmann\(^1\), Christoph E. Nebel\(^1\) and Reinhart Poprawe\(^5\); \(^1\)Fraunhofer Institute for Laser Technology ILT, Germany; \(^2\)TRUMPF Photonics, Inc., United States; \(^3\)RWTH Aachen University, Germany; \(^4\)EdgeWave GmbH, Germany; \(^5\)Fraunhofer Institute for Applied Solid State Physics IAF, Germany
For laser materials processing like cutting and welding, multi-kw continues wave fiber and disc lasers are used. State-of-the-art high power laser optics used for these applications are mainly based on fused silica as an optical material. High purity synthetic fused silica offers high transmission, but due to the limited thermal conductivity, significant radial thermal gradients occur inside the optical components caused by the residual absorption of the substrate’s and coating’s material. As the lenses have to be cooled at the outer non-irradiated section of the aperture, these gradients cannot be avoided by design. The inhomogeneous temperature distribution of the lenses causes three effects: firstly, the shape of the lens changes due to thermal expansion. Secondly, the index of refraction varies, and thirdly, mechanical tension is caused by inhomogeneous heating of the lens, and thereby stress birefringence can be observed. Therefore, first and higher order optical properties of optical systems for high-power lasers depend on the temperature, leading to focal shift and thermally induced aberrations commonly referred to as thermal lensing. In addition, high thermal loads of the optical coatings and the bulk material limit the minimum diameter of the optical setup.

Due to its outstanding optical, thermal and mechanical properties, monocrystalline synthetic diamond is a very promising material to overcome these limitations: the extremely high thermal conductivity which is approximately three orders of magnitude higher compared to fused silica results in a nearly uniform temperature profile and provide efficient cooling of the optical coatings on the diamond-air interfaces. In addition, the diamond’s high Young’s modulus and index of refraction allow for thinner lenses as the radius of curvature is nearly three times larger for a diamond lens compared to a fused silica lens of the same power, and the coating design also benefits from the high index of refraction.

In a cooperation of the three Fraunhofer Institutes ILT, IAF and IPT the complete process chain for setting up small and lightweight laser processing heads has been developed. This process chain includes optimized CVD based growth of synthetic diamond, grinding, centering as well as characterization of diamond lenses, optical design of all-diamond optical systems for materials processing, high performance optical thin film coatings for diamond lenses, and mechanical design as well as testing of laser processing heads. To characterize the diamond lenses, we have measured surface deviation, surface roughness, local birefringence and the intensity profile of a laser beam focused by diamond lenses designed and manufactured by the Fraunhofer consortium. The coating consists of a single layer of a low-absorption material.

We have realized two compact material processing heads based on diamond lenses. The first demonstrator is designed for thin metal sheet cutting. One of the main goals of the optical and mechanical design process was to minimize the laser processing head’s weight and size. Therefore, no conventional fiber mount and collimating optics was foreseen. Instead the optical fiber is directly connected to the laser processing head. The lens mount is made of copper and cooled by water. To adjust the nozzle’s outlet to the laser’s focal plane, the nozzle can be axially moved by a threaded cylinder. The realized laser processing head weights approx. 200 g. For the cutting experiments, a 1 kW single mode fiber laser was used, and the sheet metal was attached to a motorized x-y-table. The second demonstrator is used for laser material deposition and is based on a similar optical and mechanical design, but generates a larger laser spot. This demonstrator was also successfully tested in first material processing experiments.

SESSION EL05.03: Diamond Growth I
Session Chair: Matthias Muehle
Monday Afternoon, December 2, 2019
Hynes, Level 1, Room 107

1:30 PM *EL05.03.01

An inductively coupled toroidal plasma is used as an energy source alternative to microwave plasma for chemical vapor deposition (CVD) of diamond material. With up to 12 kW output power, the patented Plasmability platform leverages a powerful, scalable, and efficient 400 kHz RF power supply.

The Plasmability system has been designed specifically for the needs of diamond deposition: high flux atomic hydrogen (power density ~800 W/cm³) distributed uniformly as a line source. As currently manifested, the plasma
shape is ideal for the growth of single crystal diamonds in arrays up to 15mm wide by 35mm long. Plasma-to-sample distance is dynamically controlled during the entire growth process over a range of several millimeters, keeping the growing surfaces at all times at an optimum distance relative to the plasma.

Recent average growth rates of homoepitaxial single crystal diamond exceed 160 um/hr with optical grade clarity. Raman spectroscopy, XRD rocking curve, and birefringence of the material verify the growth of high-quality diamond. Leveraging the high growth rates available, Plasmability is pursuing large area single crystals (beyond 1 inch).

This work is carried out in part under support from Army Research Laboratory SBIR Contract W911QX-18-C-0017.

2:00 PM EL05.03.02
MPACVD Growth of 4-inch Diameter Diamond Films at 2.45GHz with High Uniformity (<5%) Alexandre Fiori1, Mariko Suzuki1 and Philippe Bergonzo2,3; 1Seki Diamond Systems, Cornes Technologies Ltd., Japan; 2Seki Diamond Systems, Cornes Technologies USA, United States; 3University College London, United Kingdom

Progresses in CVD allowed high quality diamond films to be deposited on large area for emerging applications. 4-inch diameter diamond films can be produced by large and low energy-efficiency hot-filament CVD and 915MHz plasma-assisted CVD systems. At the opposite, small chamber and energy-efficient 2.45GHz plasma-assisted CVD systems appear less attractive for large area deposition due to the shorter wavelength of the microwave source. De facto, three resonance modes of the 2.45GHz microwave cavity must be necessarily superposed in order to obtain a plasma large enough to cover a 4-inch area1. Recent encouraging simulations indicated that superposed resonance modes2 of a 2.45GHz microwave cavity could be stable in a clamshell-type MPACVD system. Simulations aside, stable microwave resonance modes must be experimentally identified in presence of plasma and feed gas mixture to perform CVD process. Indeed, the presence of plasma and gas mixture with non-uniform dielectric constants distribution in the microwave cavity modified the resonance modes from simulation results.

In this study, a 2.45GHz MPACVD has been employed to grow 4-inch diamond films on Silicon wafers. Effects of plasma conditions and substrate temperature on the deposition rate and thickness uniformity of diamond films have been studied. It suggested that substrate temperature distribution and diamond film quality are affected by gas convection and IR light emissions from the plasma. Furthermore, film thickness uniformity has been improved by a continuous plasma boundary layer on the diamond film. Preliminary results showed variations in diamond film thickness <1% and <5% for 3-inch and 4-inch areas respectively, with growth rates in the order of 0.8 µm/h using high quality process conditions (low methane, no nitrogen). Values above 3 µm/h are conceivable at high methane content or beyond with nitrogen addition.

References:
2 - J. Weng et al., Vacuum 147, pp 134-142 (2018)

2:15 PM EL05.03.04
Towards Large-Area mm-Thick Diamond Single Crystals with Optimized Optical Properties Ovidiu Brinza1, Alexandre Tallaire2,1, Riadh Issaoui1, Vianney Mille1, Fabien Benedic1 and Jocelyn Achard1; 1LSPM-CNRS, Laboratoire des Sciences des Procédés et des Matériaux, Université Paris 13, France; 2IRCP-CNRS, Institut de Recherche de Chimie Paris, Chimie ParisTech, Université Paris Sciences et Lettres, France

Thanks to its intrinsic outstanding optical and semi-conducting properties, diamond is one of the most promising candidates for a large number of high added-value applications[1]. Among them power electronics devices as well as quantum sensors based on nitrogen-vacancy or silicon-vacancy color centers offer great perspectives. However, the development of such applications is still hampered by the low availability of large and thick diamond single crystals with very well controlled of point and extended defect densities.

In the last twenty years, the microwave Plasma Assisted Chemical Vapour Deposition (PACVD) technology has witnessed important progresses allowing the control of crystal quality, purity and doping[2]. Nevertheless, synthesis of high quality single crystalline diamond layer still remains limited in size due to the very low availability of substrates with dimensions higher than typically 5x5 mm² at a reasonable cost [3]. Moreover, the ability of the process for growing diamond layers thicker than a few mm without any growth interruption is not yet clearly
demonstrated.

In this presentation we will focus on this particular topic where growth strategies for diamond single crystals fabrication by MWPACVD will be presented. The control of crystal morphology as a function of growth conditions will be discussed as well as the feasibility of fabrication of 4 mm thick large area (8X8 mm²) diamond substrates without growth interruption. Attention will be also paid to the control of doping level in order to provide diamond material suitable for power and quantum sensing related applications.

References

2:30 PM EL05.03.05
Single Crystal Diamond Plates Produced by the Mosaic Technique and the Subsequent Crystal Quality Improvement with Thick Layer Growth Ramon D. Diaz¹, Aaron Hardy², Paul Quayle¹, Jacob Leach³, Elias Garratt¹,² and Timothy A. Grotjohn¹,²; ¹Michigan State University, United States; ²Fraunhofer USA Center for Coatings and Diamond Technologies, United States; ³Kyma Technologies Inc., United States

The electrical, mechanical, and thermal properties of diamond make it a promising material for new generation electronic devices. To accelerate the continuing progress of this technology, researchers require access to high quality, large-area substrates. One approach to producing large area substrates is to use Microwave Plasma-Assisted Chemical Vapor Deposition to grow a continuous layer of single crystal diamond across an array of individual diamond plates in a process known as the mosaic technique. In this technique multiple individual diamond substrates are cut and polished to be lattice matched and then a continuous diamond layer is grown across all the individual substrates forming a larger single crystal piece. Our effort has been to minimize the misorientation of the neighboring substrate tiles, reducing stress in the overgrown layer, and demonstrating low misorientation (≤ 0.25°) across the mosaic crystal for the three orthogonal crystal directions. In this report, we especially focus on the capacity of the diamond lattice to accommodate and relieve the stress due to the remaining misorientation along selected crystal directions as the crystal growths thicker. High resolution x-ray diffraction is used to map the orientation of the grown layer across the surface. Subsequent growths allow us to chart the evolution of the misorientation as the layer thickness is increased. Results show how the overall reduction rate in relative misalignments are dependent on the initial interface configuration and top surface off-cut orientations. Mosaic samples composed of up to 4 tiles have been grown up to 11mm x 11mm using this technique.

This material is based upon work supported by the US Army Research Laboratory (ARL) under Contract No. W911QX-18-C-0005.

2:45 PM BREAK

SESSION EL05.04: FET Devices
Session Chair: Etienne Gheeraert
Monday Afternoon, December 2, 2019
Hynes, Level 1, Room 107

3:30 PM EL05.04.01
Diamond for High Power RF Electronic Devices Kevin G. Crawford, James D. Weil, Pankaj B. Shah, Mahesh R. Neupane, Dmitry A. Ruzmetov, A G. Birdwell and Tony Ivanov; U.S. Army Research Laboratory, United States

Interest in the diamond material system for electronic applications has rapidly increased in recent years, becoming a
With its ultrawide band-gap of 5.47 eV, extremely high thermal conductivity of > 20 Wcm⁻¹K⁻¹ and intrinsically high breakdown field of 10 MV/cm, diamond is a promising candidate in achieving next generation high-power electronic devices [1-4]. Progress in this area has been typically hindered by the lack of matured doping techniques and on-going development of novel fabrication strategies to overcome the challenges in working with diamond [5]. The U.S. Army Research Laboratory is investing in the development of surface transfer doped diamond field effect transistors for RF power applications [6-8]. Surface transfer doping offers an alternative to substitutional doping that alleviates the challenges of introducing impurity dopants into diamond’s tightly packed carbon lattice. Historically, spontaneous accumulation of volatile atmospheric adsorbents on the hydrogen terminated diamond surface when exposed to air has provided the necessary surface acceptor states for transfer doping [1, 9]. However, this method of transfer doping when exposed to ambient air is highly sensitive to environmental conditions such as temperature, humidity and molecular composition [9]. More recent results demonstrate enhanced surface transfer doping utilising high electron affinity transition metal oxides, such as MoO₃. By further encapsulating these materials with thick dielectric, we observe excellent long-term and thermal stability. This approach of encapsulated metal oxide has been incorporated into our diamond MESFET designs, improving output current density and stability of devices in both atmosphere and with elevated temperatures. Through a novel approach to gate lithography, gate-source spacing has been reduced to < 100 nm for a 400 nm gate length. Comparing a range of gate-source and gate-drain spacings showed improved peak output current and transconductance, while also significantly improving device breakdown. These results show great scope for improvement of diamond power devices through adoption of tailored design features, such as asymmetric gates, and incorporation of robust, encapsulated, transition metal oxides for superior doping.


3:45 PM EL05.04.02
Low Noise Diamond Delta-Channel FET Simulation Study Liping Hua¹, Wesley Spain¹, Matthias Muehle², John D. Albrecht¹, Timothy Grotjohn¹,² and Tom Zimmermann¹; ¹Michigan State University, United States; ²Fraunhofer USA, Inc, United States

The technological efforts to access geothermal energy or natural resources, such as fossil fuels, are steadily increasing and motivate the industry to drill much deeper wells. In order to drill wells efficiently, data monitoring from the downhole drilling process such as, pressure, temperature, inclination, and azimuth are all important to the drilling equipment’s condition. However, during the downhole drilling process, temperature variations, pressure amplitude fluctuations, and mechanical rig vibrations have the potential to cause high noise levels in the sensor circuits. That can significantly decrease the signal-to-noise ratio of the sensor circuits, which can ultimately result in a loss of the monitoring signal. To acquire data from a high noise environment, high-temperature stable low-noise sensor circuits are required. The base unit of those circuits is a durable low-noise field effect transistor (FET). Current commercially available Si-based sensor circuits can operate at a maximum temperature of 300 °C for wells just as deep as 12,000 ft. A great challenge of downhole drilling beyond 12,000 ft is the steadily increasing...
We have studied diamond solution gate FETs (diamond SGFETs) which can operate in solutions [2]. Diamond methods [1].

SGFETs are directly immersed in solutions and the drain current (a common source potential line was connecting the gate electrode with SGFET. In this work, we removed the common potential line to realize an electric wireless communication and investigated propagation distance in the seawater environment.

In this communication system, the gate electrode was applied with an input voltage from a gate electrode. We proposed the new electric seawater communication method utilizing the gate electrode as a transmitter and SGFET as a receiver [3]. However, the previous work was not considered entirely wireless because a common source potential line was connecting the gate electrode with SGFET. In this work, we removed the common potential line to realize an electric wireless communication and investigated propagation distance in the seawater environment.

In this communication system, the gate electrode was applied with an input voltage $V_G$ from 100kHz to 10MHz. SGFET was applied with an output voltage $V_{DD}$. A load resistance $R_D$ was connected to the drain electrode of SGFET. Then, the electric signals ($v_G$) were transmitted from the gate electrode to SGFET in NaCl 35g/L solutions which had the same concentration as seawater. Distance between the gate electrode and SGFET was gradually increased from 0.1m to 5m using a cylindrical tube (diameter=2cm). In each distance, the switching characteristics, $v_{DS}$ of SGFET, were measured.

The switching characteristics show that SGFET responds to $v_G$ at least 10MHz in each distance. The $v_{DS}$ of SGFET is observed with differential pulses responding to the $v_G$ potential change. We assume that differential pulses mainly occur due to series CR (high-pass filter) circuit with the electric double layer capacitance $C_{EDL}$ of a SGFET channel and the load resistance $R_D$. As a result, propagation distances of electric signals are at least 5m. In contrast, $I_{peak}$ of differential pulses decreases as the distance increases from 0.1m to 5m. This is because the solution resistance $R_{Sol}$ increases as the electric signals are transmitted in a longer path. $R_{Sol}$ is defined as $R_{Sol}=\rho l/A$ where $\rho$ is resistivity of solutions, $l$ is distance and $A$ is cross sectional area. In this case, $\rho=0.2\Omega m$, $A=\pi r^2$, then, the value of $R_{Sol}$ is calculated as $(0.2/\pi)\times 10^4\Omega$. However, $R_{Sol}$ might become much smaller in a large cross-sectional area such as seawater in open space. In conclusion, this method can be applied to wireless communication in seawater with the propagation distances of at least 5m.

In order to match the temperature requirements, the silicon-based circuits need to be replaced. Materials with wider bandgaps than silicon provide that distinctive advantage of high-temperature operation stability. The wider bandgaps offer higher operating temperatures before the thermally activated intrinsic carrier current causes latch-up in the sensor circuits. Diamond is chosen for its ultra-wide bandgap with 5.45 eV compared to silicon with a bandgap of just 1.1 eV. However, all doping impurities in diamond possess a high thermal activation energy. To engineer a diamond circuit able to operate over a wide temperature range between 0 °C and 600 °C, a diamond delta-channel FET concept is proposed. This concept is based on a sandwich structure that consists of a highly boron doped film in between of two intrinsic diamond layers. A full activation of the boron acceptors can be achieved by high doping concentrations of $10^{20}$ cm$^{-3}$. The total sheet charge concentration of the FET profile should not exceed $4\times10^{13}$ cm$^{-2}$ profile due to breakdown limitations, requiring a maximum thickness of the delta channel of only 4 nm. Because of an out-diffusion of free charge carriers into the intrinsic diamond material adjacent to the highly doped delta-channel, the charge carriers can reach higher hole mobilities within the delta-channel design. The high charge carrier density combined with the high speed of its charges lead to a high current drive, and correspondingly results in a high transconductance, which perfectly fits to a low-noise sensor circuit design.

In this work, a low noise diamond delta-channel FET is proposed for electronic circuits operating up to of 450 °C. This delta-channel FET structure is designed in TCAD Sentaurus, and simulation results of its performance will be presented. The noise performance versus temperature will also be reported on based on the simulations.

4:00 PM EL05.04.03
Short Distance Electric Seawater Wireless Communication Utilizing Diamond Solution Gate FET Kaito Tadenuma1, Yutaro Iyama1, Yu Hao Chang1, Yukihiro Shintani1 and Hiroshi Kawarada1,2; 1Waseda University, Japan; 2The Kagami Memorial Research Institute for Materials Science and Technology, Japan

Seawater wireless communication has been required for scuba diver’s communication, seawater drone control, development of seabed resources, etc. The conventional communication methods are acoustic wave, visible light wave and electromagnetic wave. On the other hand, electric seawater communication can take advantage of the high electrical conductivity of seawater. This is more suitable for short distance communication than the conventional methods [1].

We have studied diamond solution gate FETs (diamond SGFETs) which can operate in solutions [2]. Diamond SGFETs are directly immersed in solutions and the drain current ($I_{DS}$) is remotely controlled by electric signals ($V_{GS}$) from a gate electrode. We proposed the new electric seawater communication method utilizing the gate electrode as a transmitter and SGFET as a receiver [3]. However, the previous work was not considered entirely wireless because a common source potential line was connecting the gate electrode with SGFET. In this work, we removed the common potential line to realize an electric wireless communication and investigated propagation distance in the seawater environment.

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The H-terminated surface of diamond when exposed to NO2, O3 or just laboratory air forms a 2D hole conductive layer in the diamond surface with a surface resistance 1.5 k ohm sq⁻¹. Field effect transistors, FETs, made in this conductive layer have exhibited impressive currents, 1.3 A mm⁻¹ [1], and high operational frequencies, fT = 70 GHz [2]. However, this surface layer is not stable and FET performance degrades over time on the scale of hours to days [3]. Overcoating the diamond surface with Al2O3 generates a higher surface resistance, 5 k ohm but the diamond’s surface resistance is stable in time. However, FETs using Al2O3 degrade when electrically stressed [4]. This presentation describes using an atomic layer deposition technique, ALD, to deposit an oxide alloy of Al2O3 and SiO2 with resistances between 1.8 to 3.5 k ohm sq⁻¹, which is stable at room temperature in laboratory air for > ½ yr and to 600 °C in N2. FETs using this alloy exhibit no degradation when electrically stressed for >120 hr in laboratory air.

This 2D hole conductive layer is generated by a non-diamond absorbed or deposited layer that removes electrons for diamond’s valance band, generating mobile positive charges, holes, in the diamond. Compounds that have such electron gettering properties are called Lewis Acids. Oxide alloys of Al2O3 and SiO2 are industrially used as Lewis acid catalysis in the petroleum industry. Neither Al2O3 nor SiO2 alone exhibit significant acid properties. However, the surface of the oxide alloy contains a very deep electron acceptor with a Hammett acidity, H₀,max, of -11.99 [5] at a surface density of 1.6x10¹⁴ cm⁻² [6]. From the H₀,max value the acceptor trap is estimated to be 0.7 eV below the valence band of H-terminated diamond.

We found that ALD deposited Al2O3/SiO2 did not decrease the surface resistance over that of just Al2O3. However, two procedures were found to give lower resistances. One was to precoat the ALD system with SiO2 and then deposit ALD Al2O3 on the H-terminated diamond to the desired thickness. The other approach was to co-deposit SiO2 and Al2O3 using H₂O, Al(CH₃)₃, and (OC(CH₃)₃)SiOH, which resulted in a diamond surface resistance equivalent to that obtained with Al2O3 alone. However, by rapid thermal annealing to 600°C for 1 minute the lower resistance was obtained. Typical surface mobilities with both ALD procedures were from 50 to 70 cm² V⁻¹ s⁻¹ with carrier densities of 3x10¹³ to 6x10¹³ cm⁻². We speculate that carrier densities >10¹⁴ and lower surface resistances are possible with appropriate control of this alloy at the diamond surface.

References

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Two-dimensional hole gas (2DHG) diamond FETs have demonstrated excellent radio-frequency (RF) performances such as cutoff frequency ($f_T$) = 70 GHz [1], maximum oscillating frequency ($f_{\text{max}}$) = 120 GHz [2] and output power density ($P_{\text{out}}$) > 2.1 W/mm at 1 GHz [3, 4]. These achievements are results of miniaturizing gate length and access region using self-aligned-gate (SAG) process. However, diamond FETs fabricated by SAG process is low breakdown voltage (about ~20 V). So, the carrier velocity ($v$) calculated from $f_T = v/2 \pi L_G$ is low (< 0.6×10^7 cm/s) and RF voltage swing at large-signal operation is small. To solve these issues, diamond FETs need to be fabricated a high-voltage resistant structure. Recently, we have fabricated high voltage diamond FETs exceeding 1500V [5] with 200 nm atomic-layer-deposition (ALD)-Al$_2$O$_3$ film. The channel mobility of 2DHG diamond FETs are as low as around 100 cm$^2$/Vs, Above 0.4 MV/cm (40 V/μm), however, the hole velocity reaches the saturation velocity of 1.4×10^7 cm/s and the low mobility does not so much affect FET performance in the high electric field. In this study, ALD-Al$_2$O$_3$ 2DHG diamond MOSFETs with 100 [6] and 200 nm Al$_2$O$_3$ were fabricated on a II-a polycrystalline diamond substrate which has high crystallinity, (110) preferential orientation and grain size of approximately 300 μm. The dimension of devices at 200 nm thick Al$_2$O$_3$ diamond MOSFETs are as follows. The source-gate length ($L_{SG}$) and the gate length ($L_G$) were fixed 0.5 μm and 1 μm, respectively, while the $L_{GD}$ ranged from 1.5 to 4.5 μm.

As a result, the carrier velocity exceeded 1.0×10^7 cm/s at 100 nm thick Al$_2$O$_3$ diamond MOSFET and reached to 1.4×10^7 cm/s at 200 nm thick Al$_2$O$_3$ diamond MOSFET. The latter devices maximum drain current density was −740 mA/mm at $V_{GS} = −28$ V and $V_{DS} = −40$ V, the lowest on-resistance of 25 Ω mm and the transconductance of 13 mS/mm at $V_{DS} = −40$ V with 9 V $V_{GS}$ 16 V were obtained. Extrinsic $f_T$ was 22 GHz at $V_{GS} = 16$ V and $V_{DS} = −40$ V for $L_{GD} = 1.5$ μm. Hence, using $f_T = v/2 \pi L_G$, the carrier velocity achieved 1.4×10^7 cm/s by $f_T$ of 22 GHz at $L_G$ of 1 μm. It is the first diamond MOSFET operation at the saturation velocity and is comparable to GaN based HEMTs. RF large-signal performance was evaluated using load pull system at 1 GHz in class-A operation. At 100 nm thick Al$_2$O$_3$ diamond MOSFETs, the maximum $P_{\text{out}}$ of 3.8 W/mm was obtained at high $V_{DS} = 50$ V. It is the highest in diamond [6]. At 200 nm thick Al$_2$O$_3$ diamond MOSFET, the $P_{\text{out}}$ of 2.5 W/mm and maximum power gain of 8.0 dB were obtained at $V_{GS} = 16$ V and $V_{DS} = −70$ V for $L_{GD} = 4.5$ μm. The large-signal RF performance was evaluated at $V_{DS} = −70$ V for the first time in diamond.

potential approximation, they discussed about the importance of the different scattering modes to the mobility values. In this work, we will extend the previous work to the general of diamond/oxide interface (H- and O-terminated) and introduce a full description of the valence bands and hole scattering mechanisms (light holes, heavy holes, spin-orbit and sub-bands due to quantum confinement). The maximum expected mobility achievable in a diamond 2D hole gas will be discussed and compared to recent experimental results.

References

SESSION EL05.05: Diamond MOSFETS
Session Chair: Julien Pernot
Tuesday Morning, December 3, 2019
Hynes, Level 1, Room 107

8:30 AM *EL05.05.01
Recent Progress in Inversion Channel Diamond MOSFET Norio Tokuda1,2, Tsubasa Matsumoto1, Takao Inokuma1, Satoshi Yamasaki2,1, Hiromitsu Kato2, Toshiharu Makino2 and Christoph E. Nebel3,1; 1Kanazawa Univ, Japan; 2National Institute of Advanced Industrial Science and Technology, Japan; 3Fraunhofer Institute for Applied Solid State Physics, Germany

We demonstrated the first operation for an inversion channel MOSFET using diamond semiconductor [1]. Here, we precisely controlled the MOS interface using an atomic layer deposition of Al2O3 film on OH-terminated diamond (111) surface and pn-junctions using selective growth of heavily B doped on n-type diamond layer for the formation of source/drain. The field-effect mobility $\mu_{FE}$ of the p-channel diamond MOSFET was $8 \text{ cm}^2/\text{Vs}$ at the highest, which is much lower than the hole mobility of $6,300 \text{ cm}^2/\text{Vs}$ at RT [2]. Recently, we investigated the interface state density $D_{it}$ dependence of $\mu_{FE}$ in inversion channel diamond MOSFETs [3]. In this study, we will report the key techniques for the demonstration of the inversion channel diamond MOSFET and its recent progress.

Acknowledgements
This work was partially supported by Kanazawa University SAKIGAKE Project 2018 and JSPS KAKENHI Grant Numbers JP17H02786, 17H03248, 18KK0383, and 19K15042.

References

9:00 AM EL05.05.02
A Contact Resistance Comparison with Different Thickness of PEALD Al2O3 Passivated H-Diamond MOSFET with Al2O3 Dielectric Layers Yichen Yao, Harshad Surdi, Manpuneet Benipal, Franz A. Koeck and Robert J. Nemanich; Arizona State University, United States

A prior study from our group has achieved an ohmic contact with thin PEALD Al2O3 on top of a hydrogenated diamond surface establishing a sheet resistance ~16 kOhms/square. In this study, we extend the application of the PEALD interfacial layer as a protective passivation layer to avoid degradation of the hydrogen terminated conducting surface during during device fabrication process. from XPS characterization, the valence band offset confirms that the electrons from the valence band of diamond can be transferred to states of this very thin Al2O3
interfacial layer. As a first step to fabricating MOSFET devices, different PEALD Al2O3 thicknesses are used to establish the source and drain contact. We used pure Au as the contact metal, and Al / Au for the gate contact. A circular FET design was used to reduce the gate leakage current and a 4 nm thermal ALD Al2O3 layer was used for the gate dielectric. A threshold voltage of 0.8 V is shown in the device with a highest drain current of ~40 mA/mm. The gate length of these devices is 4 or 6 microns with an asymmetrical distance of LGS of 4 microns and LGD of 16 microns. The results show a decreasing trend of the contact resistance of the PEALD Al2O3 interfacial layer with reduction of the thickness of this tunneling layer. Our device results have indicated that the interfacial Al2O3 layer, may reduce the contact resistance for a H-diamond MOSFET.

This research is supported by the NSF through grant DMR-1710551 and a grant from MIT-Lincoln Laboratory.

9:15 AM EL05.05.03
(111) Vertical-Type 2DHG Diamond MOSFETs with Hexagonal Trench Structures Jun Nishimura¹, Masayuki Iwataki¹, Nobutaka Oi¹, Aoi Morishita¹, Atsushi Hiraiwa¹ and Hiroshi Kawarada¹;² ¹Waseda University, Japan; ²The Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, Japan

In power devices, vertical structure is suitable for low on-resistance and large current operation which are required for power electronics. We have ever reported (001) vertical-type diamond MOSFETs [1] using two-dimensional hole gas (2DHG) which is induced irrelevantly of their crystal orientation by C-H termination structure and high temperature atomic layer deposition (ALD)-Al2O3 [2]. In this paper, we fabricated vertical-type 2DHG diamond MOSFETs with hexagonal trench structures using the (111) diamond for the first time. The (111) diamond has advantages for high carrier density owing to their C-H dipole structure and low sheet resistance [3] compared to the (001) diamond. As the results, the maximum current density is 3 times higher than that of the previous works at the same drain voltage (VDS) [1]. And, the minimum specific on-resistance Ron of 9.2 mΩcm² was obtained the device with large hexagonal trench of 12 µm on a side. Fabrication process was as follows. First, the undoped and nitrogen-doped layer were epitaxially grown on the (111) p+ diamond substrate by microwave plasma chemical vapor deposition (MPCVD). The nitrogen-doped layer (~1×10¹⁹ cm⁻³) worked as a current blocking layer. Second, hexagonal trench structures were formed by inductive coupled plasma reactive ion etching. Length on each side of the trench (WT) was 10-20 µm, and depth (DT) was fixed at 3.0 µm. Third, 200 nm regrowth undoped layer was deposited by ALD method. The gate length was fixed to 6 µm, while 3 µm (half) of the gate overlapped with the source electrode. The drain current density (ID) normalized by gate width of 72 µm (6WT) at VDS of -20 V and -50 V are -250 mA/mm and -680 mA/mm, respectively. Those values are almost 3 times higher than those of vertical-type (001) diamond FETs at the same VDS [1]. The main reason is the conduction path of the former (001) vertical FET are composed of {001} surface only, but those of the present (111) vertical FETs are higher (111) surface and {110} or {211} side walls, where the sheet conductance is higher than that of {001}. The drain current on/off ratio is about 9 orders of magnitude at room temperature. For this result, the film thickness and concentration of the nitrogen-doped layer are sufficient. The maximum drain current density and lowest specific on-resistance normalized by device active area are -5400 A/cm² and 9.2 mΩcm² for VDS of -50 V and VGS of -20 V. The specific on-resistance is lowest ever reported for the (111) diamond FETs. These performances will be improved by the device structure miniaturization and drift layer resistance reduction. If the trench size shrinks to as small as 2 µm, the Ron will be below 1 mΩcm².


9:30 AM EL05.05.04
Diamond:H/Transition-Metal Oxides Transistors—From MOSFET to MESFET Moshe Tordjman¹,², Youngtack Lee¹,³, Alon Vardy¹, Rafi Kalish² and Jesus A. del Alamo¹;¹Massachusetts Institute of Technology, United States; ²Technion—Israel Institute of Technology, Israel; ³Inha University, Korea (the Democratic People's Republic of)

Surface transfer doping of hydrogen-terminated diamond (Diamond:H) leading to a two-dimensional hole gas (2DHG) represents a significant recent advance towards high-performance diamond transistors. Recently, Transition-Metal Oxides (TMO), such as MoO3, WO3, V2O5 and ReO3,¹⁴ have been shown to yield a far more efficient and stable surface transfer doping process. This is of great significance for future diamond electronics.
In this talk, we present recent progress in Diamond:H FETs by engineering the gate stack from a typical metal-oxides-semiconductor FET (MOSFET) towards a metal-semiconductor FET (MESFET). This is seen to yield a drastic improvement in key features such on/off ratio (8 orders of magnitudes), a very low subthreshold swing (67 mV/dec) and low gate leakage.

A comparative Diamond:H/Transition-Metal Oxide FET study will be also presented and will show how the different Transition-Metal Oxides properties influence FET performance. A proposed oxide approach is suggested and demonstrated that enhances hole drift mobility by a factor of two, while keeping a high value of carrier concentration.

Based on these findings, a path towards improvement of Diamond:H/TMO transistor performance and stability will be outlined.

References:

9:45 AM EL05.05.05
Normally off Hydrogen Terminated Diamond Field Effect Transistor (C-H MOSFET) Device with Deep Donor Doping Using Nitrogen Termination

Reem M. Alhasani, Mohammed M. Alhasani, Taichi Yabe and Hiroshi Kawarada; Waseda University, Japan

The p-type conduction of hydrogen terminated (C-H) diamond is attractive for developing high preference of high power or high frequency devices such as high-power field effect transistor (FET) [1]. In this work, the interface charge effect with nitrogen doping on C-H diamond FET is investigated. So far, we have reproduced the FETs characteristic of C-H diamond FET by 2-dimensional (2D) acceptor model [2] or 2D negative charge sheet model [1] confirmed 2D hole gas (HG) close to surface. However, these acceptors or negatively charged sites are scattering centers for carrier (holes) transport near the C-H surface. The device exhibits good DC operation and achieved both normally off and normally on characteristics depending on nitrogen concentration [3]. Before that the normally off mode achieved with oxygen termination in diamond full or partially close to C-H diamond FET. Partially SiO2 in C-H diamond also exhibited normally off operation achieved with -3eV threshold voltage and maximum current density IDMAX=-44mA/mm[4].

In this work, the normally off (enhancement mode) C-H diamond Al gate overlapped field effect transistor (FET) with donor investigated. We simulated nitrogen doping (donor model) in concentration of 3e16 cm-2 corresponding to near surface positive charge of 5e11 cm-2. All the device parameters are similar to the former simulation [1] where source and drain contact resistance is very low because of very low Schottky barrier height (SBH) [5]. As gate is negatively biased, an upward bending of valence band is observed. It indicates that there is a hole accumulation layer (2DHG) under valence band maximum at the diamond side. The MOSFET capacitor characteristic shows the fixed fermi level position as a function of capacitance voltage at 1.7eV from the conduction band due to nitrogen as donor. The maximum current density of the Al2O3/C-H diamond device is ~70 mA/mm at the gate voltage of -26V with-voltage step of 4V between +26V~-26V. Also, we observed the gate threshold voltage Vth= -3V with negative gate bias normally off operation. The reason is that no intersection between valence band and fermi level caused by the positive charge cancelling the negative charge at Al2O3/C-H diamond interface. So, the negative charge effect at the interface becomes very weak leading to normally off.

Reference:
1) H. Kawarada et al.; Scientific Reports. 7, 42368/1-8, (2017)
4) T. Yabe, H. Kawarada et al. MRS Fall Meeting (2018)

10:00 AM BREAK
10:30 AM EL05.06.01
Electrochemiluminescence at Boron Doped Diamond Electrodes—A Powerful Tool for Analytical Applications Emmanuel Scorsone and Matthieu Hamel; CEA, France

Electrochemiluminescence (ECL) is a phenomenon in which photons are emitted during electrochemical reactions. It already proved to be a very promising analytical tool for sensing applications where both high sensitivity and selectivity are needed. Indeed, it merges the advantages of chemiluminescent analysis with the absence of background optical signal, with wide possibilities for reaction control using diverse electrochemical protocols. ECL can be observed in organic solvents where both oxidized and reduced forms of luminescent species are produced, e.g. by sweeping electrode potential between anodic and cathodic. Excitation energy is then obtained from recombination of oxidized and/or reduced species. As an example, superoxide ions may be involved through electrochemical reduction of dissolved oxygen. In aqueous environments, simultaneous oxidation and reduction of luminescent species is difficult to achieve due to electrochemical splitting of water, implying the use of a co-reactant. In this case luminescent species are oxidized at the electrode together with the co-reactant, which gives a strong reducing agent after some chemical transformations. In this context, Boron Doped Diamond electrodes offer numerous advantages that have been little explored for ECL analytical applications. They display high electrochemical stability together with resilience to fouling, and good optical transparency. Furthermore, in aqueous media electro-generated hydroxyl radicals play important roles in ECL, implying that a co-reactant family can be expanded by taking advantage of the strong oxidation ability of electrogenerated hydroxyl radicals at boron doped diamond electrodes. The potential of diamond electrodes for ECL analytical applications will be discussed and illustrated through a comparative study using different electrode materials. An example of application for foodstuff analysis will be presented.

10:45 AM EL05.06.02
Full Diamond Implant for Neural Prosthesis Lionel Rousseau1, Emmanuel Scorsone2, Gaelle Lissorgues1, Blaise Yvert3 and Serge Picaud4; 1ESIEE Paris, ESYCOM, UPEM, France; 2LIST/LCD, France; 3BrainTech Laboratory U1205 Inserm, France; 4Institut de la Vision, UMR 7210, France

Some properties of diamond are very interesting for the development of implantable medical devices. Especially they offer a way to achieve stable implants. This is due to the chemical stability of the material, along with its high density, which prevents any chemical species to penetrate into the bulk of any diamond layer. Furthermore diamond can be doped with boron to achieve outstanding electrode materials for the stimulation of biological tissues. A major issue associated with chronic implant for neuronal interfacing is that structure is not hermetic. This is due to the fact that metal tracks are generally embedded in polymer layer to isolate them from the tissues. But following long term implantation, the polymers are likely to swell and water molecule will migrate inside the polymer thus modifying its dielectric properties. To address this issue, we propose to develop a full diamond implant by combining intrinsic material and BDD electrodes. By assembling the same material both for stimulation electrodes and passivation layer we are aiming to prevent current leakage at the interface.

To validate this new structure we developed strips that combine boron doped and intrinsic diamond materials. These structures are placed on an accelerated aging set up for several days. The BDD electrodes are stimulated by biphasic pulses in Phosphate Bovine Solution (PBS) and the stability of the electrodes in these conditions is monitored by electrochemical impedance recording. Strips with conventional materials have also been fabricated (organic or inorganic materials) to compare their behavior in the same experimental conditions with our diamond based structures. The preliminary trials demonstrate that diamond structures are stable at least over 45 days.

Furthermore, in order to achieve a cortical implant, it is necessary to fabricate soft implantable devices. It is well
known that diamond is the hardest material with a high Young modulus close to 1000 GPa. To demonstrate the feasibility of a soft full diamond implant structure, a novel implant containing metal track in contact with BDD electrodes and encapsulated in thin intrinsic diamond was fabricated. Here intrinsic diamond is locally open above the BDD electrodes to allow interfacing with neurons. The mechanical properties (flexibility, etc.) of such an implant are currently being investigated and in-vitro and in-vivo testing are being prepared.

11:00 AM EL05.06.03
Enabling Efficient, Economical Grid-Scale Energy Storage through Diamond  
Alex Bates, Mahendra Sunkara, Sam Park and William Paxton; University of Louisville, United States

Redox flow batteries (RFBs) are considered by many to be the most logical approach to addressing grid-scale energy needs. A RFB operates via an exchange of energy through the simultaneous electrochemical reduction and oxidation of redox couples in half-cells. A redox couple consists of an oxidizing species and its corresponding reducing species. The fundamental RFB consists of two electrolytes (containing the redox couples), two electrodes, and an ion-exchange membrane. The electrolytes are stored in external tanks and are cycled through the electrochemical cell via pumps or gravity. As the electrolytes flow, redox species are brought to the electrode surface where they either give or receive an electron from an external circuit. During this process the cell is either charged or discharged and the converted species flow back to the storage tanks.

RFB technology offers several advantages over current state of the art energy storage technologies including: 1) Scalability – capacities ranging from 1kW to 100+MW with minimal design changes; 2) High efficiencies – expected round-trip efficiency of ~85%; and 3) Separation of power and energy – capacity can be increased by simply increasing the volume of stored electrolyte. Implementation of RFBs have been hindered by availability of redox couples. Vanadium is the most predominant redox couple as it possesses multiple oxidation states, allowing it to be used in both sides of the battery (Positive electrode: V^{5+} ↔ V^{4+}; Negative Electrode: V^{2+} ↔ V^{3+}). While other redox couples are such as Fe, Cr, and Br are frequently reported, there are very few that are compatible with the graphite electrodes used in the standard RFB configuration. Recent results have demonstrated boron-doped diamond (BDD) to be an exceptional alternative to the standard graphite electrode by enabling a wide range of redox couples that are more cost effective, environmentally friendly, and sustainable while also offering improved efficiencies and energy densities than current state-of-the-art.

Diamond has proven itself to be a superior material for a variety of applications and its utility in electrochemistry has become increasingly apparent over the past decade. In addition to diamond’s ability to resist fouling and corrosion in extreme environments, it’s most critical advantage for flow batteries is it’s extremely high overpotential for both hydrogen and oxygen evolution (-1V to 2.5V, respectively). This large window enables the use redox couples that would occur in either the hydrogen or oxygen evolution reaction regime with common electrodes such as graphite or platinum. Despite these advantages, it has not been until now that BDD has been considered for use in RFB technology and has led to the identification of several additional relevant redox couples that were previously out of reach. This research represents a monumental advancement of redox flow battery technology and could be the solution to grid-scale energy challenges.

11:15 AM EL05.06.04
Boron-Doped Diamond Superconducting Quantum Interference Devices Operating above Liquid Helium Temperature  
Aoi Morishita¹, Taisuke Kageura¹,², Ikuto Tsuyuzaki¹, Shotaro Amano¹, Minoru Tachiki², Shuichi Ooi², Shunichi Arisawa², Yoshihiko Takano⁰ and Hiroshi Kawarada¹,⁴, ¹Waseda University, Japan; ²National Institute for Materials Science, Japan; ³Kagami Memorial Laboratory for Materials Science and Technology, Japan

Superconducting quantum interference devices (SQUIDs) are widely used as high-sensitive magnetometers in several fields. However, there is still a problem with material robustness in advanced SQUID applications such as scanning SQUID microscope. Superconducting boron-doped diamond is one of the materials that can solve the above problems due to its excellent robustness and characteristics. Recently, we have demonstrated a first single crystalline diamond SQUID [1], whose Josephson junctions (JJs) were formed by step-edge structure. However, it was operated at 2.6 K because the structure included (001) sector superconducting transition temperature $T_c$ of 4.0 K [2]. Operating temperature of SQUID is significant for constructing a complex SQUID system with a simple cooling system. Thus, in this work, we have demonstrated diamond SQUIDs operating above liquid helium temperature 4.2 K using only (111) growth layer with $T_c=10$ K [3].

JJJs were fabricated by epitaxial growth on shallow trench as below: The boron-doped diamond layer was epitaxially grown across the 30 nm deep trench, which was formed via focused ion beam method. The weak link was formed in
the boundary of discontinuous (111) sector on the trench. The effective loop area ($A_{\text{eff}}$) was 68\times68 \mu m^2 and strip width was 36 \mu m. It showed two-step superconducting transition at 10.5 K and 8.0 K. The $I$-$V$ characteristics from 1.6 K to 10 K showed clear DC Josephson effect. There was no hysteresis above 4.0 K. The critical current $I_c$ was 0.42 mA and the $J_{\text{c}}R_{\text{n}}$ product was 0.21 mV at 4.2 K, where $R_{\text{n}}$ is the normal resistance. In the magnetic field dependence of voltage, SQUID oscillation was observed up to 10 K. The oscillation interval ($B_{\text{ext}}$) was 0.52 \mu T. This value agreed with calculated $B_{\text{ext}}$ obtained by $\Phi_0/A_{\text{eff}}$ where $\Phi_0$ is flux quantum. We also fabricated another sized SQUID, which had smaller $A_{\text{eff}}$ (=21\times56.5 \mu m^2) and narrower strip width (=15 \mu m) than the former. It operated up to 8.0 K. For this sample, $B_{\text{ext}}$ was 1.70 \mu T, which agreed with calculated $B_{\text{ext}}$. Therefore, the operations of SQUIDs were demonstrated up to 10 K for former larger sample, and 8.0 K for latter smaller sample. These operating temperatures are dramatically higher than those of SQUIDs of both step-edge structure [1] and nanocrystalline diamond [4]. For the larger sample, $V_{\text{p-p}}$ was 2.0 \mu V and magnetic field sensitivity $V_{\text{p-p}}/B_{\text{ext}}$ was 3.8 \mu V/\mu T at 8.0 K. For the smaller sample, $V_{\text{p-p}}$ and $V_{\text{p-p}}/B_{\text{ext}}$ were 4.0 \mu V and 2.4 \mu V/\mu T, respectively at 8.0 K. These values are higher than that of diamond SQUID with step-edge structure, 1.6 \mu V/\mu T.

In conclusion, we have demonstrated two different sized diamond SQUIDs composed of only (111) boron-doped growth layer operating above liquid helium temperature.


11:30 AM EL05.06.05
Development of Single Crystal CVD Diamond Based Microdosimeters for Particle Therapy Izabella A. Zahradnik1, Michal T. Pomorski1, Philippe Barberet2, Zeljko Pastuovic3, Jeremy Davis4, Ludovic De Marzi5, Wataru Kada6, Guillaume Boissonnat1, Alexandre Dabat-Blondeau1, Samuel Salvador2, Laurent Leretier7, Yolanda Prezado8, James Vohradsky4, Dominique Tromson1, Samuel Saada1 and Anatoly Rosenfeld4; 1CEA Saclay, France; 2CNRS, UMR5797, CENBG, France; 3ANSTO, Australia; 4CMRP, University of Wollongong, Australia; 5Institut Curie, Centre de Protonthérapie d'Orsay, France; 6Gunma University, Faculty of Science and Technology, Japan; 7LPC Caen, France; 8CNRS/NARA, France

Particle therapy is an innovative mode of radiotherapy (RT) for cancer treatment. The determination of the relative biological effectiveness (RBE) of the clinical particle beams deployed in such RT is of great importance for both the estimation of the therapeutics effects in tumour and the right input parameters for the treatment planning system with the aim of sparing the healthy tissue around the tumour. The physical microdosimetric parameters, such as lineal energy, are used as input parameters for the MK (microdosimetric kinetic) model to calculate the RBE of a given ion beam (protons and $^{12}$C ions). However, there is a lack of practical experimental tools to characterize this quantity, which is a challenging task. In this context, diamond detectors have shown dosimetric advantages, such as outstanding spatial resolution, good sensitivity to high beam intensities, small energy dependence, radiation hardness and tissue equivalence. For more than ten years, CEA-LIST has been developing diamond-based dosimeters for RT applications. Currently, based on scCVD diamond membranes, new prototypes of microdosimeters for particle therapy are being developed at the CEA Diamond Sensors Laboratory (LCD).

Materials and Methods: Two novel diamond-based dosimeter prototypes have been developed based on a super-thin self-standing scCVD diamond membranes obtained by deep Ar/O$_2$ plasma etching process. The processing of the first prototype, DIAµDOS p+ consists additionally of a p+-i junction which was created by a CVD growth of thin boron-doped scCVD layer on top of an intrinsic 4 \mu m thick diamond membrane. Multiple microdosimetric sensitive volumes ($\mu$SVs) were formed on the membrane surface using projection photolithography, followed by local plasma etching of the p+ diamond layer. The characteristic behaviour of the micro p+-i junction was determined by a 1.8 V built-in potential which resulted in full depletion of the device at 0V-bias$^2$. In the processing of the second prototype, DIAµDOS-guard-ring, only single crystal CVD diamond membrane was involved. A thin layer of Al for electrical contacts has been deposited on both sides of the membrane. On the front side, using laser photolithography, $\mu$SVs in different sizes have been shaped. These $\mu$SVs are interconnected by thin bridges and surrounded by an isolating guard ring in a distance of 2 - 10 \mu m from the active region. Applying different bias to the back electrode of the device and collecting the signal at the $\mu$SV’s electrode, a full CCE for different particles can be achieved. Results: The characterization of the diamond microdosimeters has been made possible by particles microbeams at IBIC facilities in Australia, France and Croatia. The active $\mu$SVs of the microdosimeter were irradiated using a raster scanning method and the charge transport properties of the device determined with sub-micron precision by measuring the charge collection efficiency, radiation hardness, $\mu$SVs 3D spatial definition and
the pulse-height spectra. By combining all measurements a large range of experimental measured lineal energy was explored. Using MC radiation transport and TCAD simulations, the obtained measurements with the diamond microdosimeter were compared with theoretically predicted results. The radiation response, as well as the design of the sensors, were optimized. The final prototype of the diamond-based device was integrated with universal sponsors carrier and a suitable multi-channel electronics. The performance of the diamond device was evaluated using clinical particle beams at Ion Therapy Centers in France and Japan. Finally, the response of the diamond microdosimeter in conjunction with MKM was used for RBE determination and demonstrates the great potential of diamond microdosimeter and its ability to measure microdosimetric quantities in clinical ion beams. \(^1\)M. Pomorski et al., Appl. Phys. Lett. 103, 112106, 2013, \(^2\)I. A. Zahradnik et al., Phys. Status Solidi A, 1800383, 2018.

**11:45 AM EL05.06.06**

**Performance of 4.5-μm PIN Diamond Diodes as Thermal Neutron Detectors** Jesse Brown\(^1\), Jason Holmes\(^1\), Franz A. Koeck\(^1\), Holly Johnson\(^1\), Manpuneet Benipal\(^1\), Kevin Herminghuysen\(^2\), Praneeth Kandlakunta\(^2\), Andrew Kauffman\(^2\), Susan White\(^2\), Anna Zaniewski\(^1\), Ricardo Alarcon\(^1\), Raymond Cao\(^2\), Stephen Goodnick\(^1\) and Robert J. Nemanich\(^1\); \(^1\)Arizona State University, United States; \(^2\)Ohio State University, United States

The properties of diamond that contribute to its value in radiation detection include large bandgap, high electron and hole mobilities, high breakdown field, and high displacement damage threshold. These properties combine to enable radiation hard, low background, and efficient particle detectors. Research at Arizona State University has developed and demonstrated diamond p-i-n particle detectors based on epitaxial growth of n-type, phosphorus doped diamond, p-type, boron doped diamond, and high purity undoped (intrinsic) diamond. The detector i-layer thickness has been adjusted to match the penetration depth of designated alpha particles, which minimizes background due to gamma radiation and high energy particles. Moreover, the detectors operate in pulse mode with a bias of only a few volts. The unique properties of the p-i-n diode led to the development of a new method to mitigate the effects due to the accumulation of trapped charge in the diamond. Recognizing these advantages led us to propose the development of an efficient thermal neutron detector through the integration of a boron nitride neutron absorption layer and an optimized diamond p-i-n detector. Like diamond, boron nitride is a hard, high temperature material that is expected to survive in extreme environments. A number of BN/diamond pin neutron detectors have been fabricated at Arizona State University and tested at the Ohio State University Nuclear Reactor Laboratory. The tests include pulse counting measurements at a thermal neutron beamline with a flux of \(4\times10^6\) n/cm\(^2\)/s, and irradiation of the detectors in the core of the reactor for a fluence of \(10^{15}\) n/cm\(^2\). The thermal beam results show performance as expected with no significant background above threshold and with a reasonable expectation of pulse counting capability at fluxes up to \(10^{10}\) n/cm\(^2\)/s. The irradiation results indicate the onset of a new capability in advanced sensor instrumentation based on diamond diodes.

**SESSION EL05.07/MQ01.03: Joint Session: Quantum Effects**

**1:30 PM *EL05.07.01/MQ01.03.01***

**The Tin Vacancy Center in Diamond—An Interesting New Qubit Candidate?** Christoph Becher; Saarland University, Germany

Quantum bits based on solid-state spins are promising and potentially scalable systems for the implementation of quantum technologies ranging from quantum information processing to quantum-enhanced sensing and metrology. Ideally, they combine individually addressable spins with very long coherence times, optical emission spectra with narrow homogeneous and inhomogeneous broadenings and bright single-photon emission. In this respect, impurity-vacancy color centers in diamond based on group-IV elements (SiV, GeV, SnV, PbV) have emerged as interesting systems promising to combine all desired favorable properties.

Both the SiV and the GeV center feature superior spectral properties, i.e. at liquid helium temperatures (4K), they exhibit a narrow zero phonon line (ZPL) with a four-line fine structure and close to lifetime-limited linewidths [1,2].
Furthermore, both allow for fast all-optical addressing and control of their spin states [3,4]. However, at temperatures around 4K both color centers exhibit spin coherence times ($T_2^*$) of only a few tens of nanoseconds due to phonon-induced decoherence processes [3,4] and the SiV reaches millisecond spin coherence times only at millikelvin temperatures and in pure samples [3,5]. A potential resort are vacancy defects with a heavier group-IV impurity atom, such as SnV and PbV centers, featuring a larger ground state splitting and thus less susceptibility to phonon-induced decoherence.

Here, we report on spectroscopy of SnV centers [6,7,8] where we find two charge states, i.e. SnV(-) and SnV(0), which both show promising optical properties. The SnV(-) features a ground and excited state splitting considerably larger (850 GHz and 3000 GHz, respectively) as compared to the SiV center, potentially enabling long spin coherence times even at liquid He temperatures. This defect is a bright single photon emitter, showing a narrow inhomogeneous distribution of zero phonon lines in a high-temperature annealed sample [6] and truly lifetime-limited transition linewidths down to 20 MHz. Furthermore, we determine the charge transition from the negative to the neutral charge state as a function of the excitation wavelength and find it to coincide well with theoretical predictions [9]. For the SnV(0) center we find emission lines that again agree well with theoretical calculations [10]. The neutral charge state is particularly interesting due to its potentially long electron spin coherence times.

References

2:00 PM EL05.07.02/MQ01.03.02
Development of Scalable Technology for NV-Magnetometry and Photonics on Single Crystalline Diamond
Christian Giese¹, Patricia Quellmalz¹, Helge Gehring², Wolfram Pernice² and Christoph E. Nebel¹; ¹Fraunhofer IAF, Germany; ²University Muenster, Germany

The unique properties of the negatively charged nitrogen vacancy color center (NV⁻) in single crystalline diamond have been explored for developing new types of devices for photonics and scanning probe magnetometers with high sensitivity and spatial resolution over more than a decade. This growing field is in need of thin, free-standing ultra-clean diamond devices with complex geometries. The fabrication of such structures in large numbers will be the topic of this presentation.

Free-standing diamond devices as photonic crystals or NV-scanning-probe heads are typically manufactured from diamond membranes of below 30µm thickness. The latter are expensive and available only in small numbers which makes a scaling of the production very challenging. In addition to this, the homogeneity in thickness below micron level is crucial for many applications and remains practically unachievable via polishing on large surfaces.

An alternative method based on so-called faraday-cage-angled-etch (FCAE) pioneered at the group of prof. Loncar at Harvard university is based on the capability to create free-standing diamond devices via dry chemical underetching. We have employed FCAE to create mechanical and optical components and will report on the characteristics of the devices investigated via SEM as well as optical and mechanical metrology.

References

2:15 PM EL05.07.03/MQ01.03.03
Rapid, High-Resolution Magnetic Microscopy of Single Magnetic Microbeads
Julia M. McCoey, Robert W. de Gille, Babak Nasr, Jean-Philippe Tetienne, Liam T. Hall, David A. Simpson and Lloyd Hollenberg; University of
Melbourne, Australia

Magnetic microparticles are used in a variety of research applications including cell sorting\(^1\), targeted drug delivery\(^2\) and optical force traction microscopy\(^3\). The magnetic properties of such particles can be customized for specific applications with the uniformity of individual magnetic microparticles having a significant bearing on their function. Prior to the study discussed here, most magnetic characterization techniques have quantified the magnetic properties from large bead ensembles\(^4\). As such, there is a significant demand for magnetic imaging techniques to evaluate and visualize the magnetic fields from single beads. New insights into the magnetic uniformity, anisotropy, and alignment of magnetic domains can be found through measurements of the magnetic properties of single beads. Here, magnetic microscopy based on the nitrogen-vacancy centre in diamond is applied to image and characterize individual magnetic beads with varying magnetic and structural properties: ferromagnetic and superparamagnetic/paramagnetic, shell (coated with magnetic material), and solid (magnetic material dispersed in matrix). The magnetic microscopy described here probes both the fluctuating moments of the beads studied as well as their static magnetic moments. The single-bead magnetic images identify irregularities in the magnetic profiles from individual bead populations. Magnetic simulations account for the varying magnetic profiles and allow to infer the magnetization of individual beads\(^5\). Additionally, this work shows that the imaging technique can be adapted to achieve illumination-free tracking of magnetic beads, opening the possibility of tracking cell movements and mechanics in photosensitive contexts.


2:30 PM *EL05.07.03/MQ01.03.03

**Quantum Sensing of Atomically Thin Magnets** Patrick Maletinsky; Basel University, Switzerland

The recent discovery of long-range magnetic order in atomically thin “van der Waals” (vdW) crystals has attracted significant attention due to their fundamental and technological interest, including predictions of exotic magnetic phases and unique opportunities to control magnetism at the atomic scale. I will present recent experiments, where we employ a single-spin-based quantum sensing technology for quantitative, nanoscale probing of atomically thin vdW magnets. Specifically, I will describe experiments, where we employ a diamond-based, scanning probe quantum sensor to address magnetism in the prototypical vdW magnet CrI\(_3\), down to the level of atomic monolayers. Our approach enabled nanoscale imaging of magnetic domains, quantitative determination of CrI\(_3\)’s layer-dependent magnetization, and revealed a delicate interplay between magnetic and crystalline order in CrI\(_3\). Next to addressing fundamental open questions in the nanomagnetism of atomically thin CrI\(_3\), our results yield attractive perspectives for future probing of dynamical properties of two-dimensional spin systems using single spin quantum sensors. Amongst other things, these could yield experimental evidence for the still elusive quantum spin liquid, which is believed to occur in monolayers of certain vdW compounds.

3:00 PM BREAK

3:30 PM *EL05.07.05/MQ01.03.05

**Imaging the Domain Pattern of In-Plane Layered Antiferromagnets using Diamond Magnetometry** Martin S. Wornle, Pol Welter and Christian Degen; ETH Zurich, Switzerland

Antiferromagnetic materials are promising candidates for new memory devices with fast electrical writing and readout capabilities. Imaging the magnetic state of antiferromagnets on the sub-micrometer scale, however, is challenging because these materials do not exhibit a macroscopic magnetization.
In this talk, we will discuss the application of scanning diamond magnetometry for investigating the microscopic domain structure of in-plane layered antiferromagnets, like tetragonal CuMnAs. After introducing the basics of the technique, we will discuss models and concepts for analyzing the magnetic stray field emanating from the antiferromagnetic domains. We will further show that current pulses lead to changes in the domain pattern and analyze these changes as a function of the current amplitude and direction.

4:00 PM EL05.07.06/MQ01.03.06
Metrology Driven Development of Point Defect Synthesis and Localization Nazar Delegan¹, Samuel J. Whiteley²,¹, Edward Bielejec¹, David D. Awschalom²,¹ and Joseph F. Heremans¹,²; ¹Argonne National Laboratory, United States; ²The University of Chicago, United States

The negative nitrogen-vacancy (NV⁻) defect in diamond has quantum spin properties observable from cryogenic temperatures to ~1000 K. Parallel to this, SiC based divacancy (VV) complexes photoluminesce in the telecom infrared range, extending their technological applicability. Both of these spin-based quantum sensors are known to be responsive to changes in local strain, electric, magnetic, and thermal fields. Building on this foundation, we discuss recent advances of defect 3D localization in the context of improving and controlling their spatial resolution and crystalline environment. This progress is fueled by nanoimplantation and nanoscale strain-sensitive X-ray imaging techniques. The insights provided serve to better understand the defect’s lattice surroundings, guide future synthesis efforts, improve the creation efficiency, and advance the goal maintaining coherence times of the spin states.

4:15 PM EL05.07.07/MQ01.03.07
First Principles Discovery and Understanding of Color Centers in Diamond for Quantum Information Science Isaac Harris¹,², Christopher J. Ciccarino², Johannes Flick², Dirk R. Englund¹ and Prineha Narang²; ¹Massachusetts Institute of Technology, United States; ²Harvard University, United States

Defect centers in diamond are promising candidates for applications such as quantum sensing, networking and computation. Previous work has experimentally identified several defects such as the NV⁻ and group IV related defects. However none of these color centers have shown the ideal combination of optical transitions, coherence times, and ease of fabrication and integration, motivating an ab initio search of new color centers in diamond. Towards this goal, we present first principles calculations of a new class of emitters, the group III-vacancies, which are theoretically shown to have a promising ground state structure for quantum applications, a noise insensitive optical transition, and are thermodynamically favored in intrinsic diamond. The ground state fine structure, as well as the excited electronic structure will be discussed in this talk. Further, we will show the electron-phonon coupling parameter calculations to determine the Jahn-Teller distortion, as well as the phonon sideband of the optical emission. Finally, we will discuss how the ab initio results compare with experimental quantities such as the ground state spin structure and optical emission properties.

4:30 PM *EL05.07.08/MQ01.03.08
Understanding and Mitigating Quantum Decoherence of Nitrogen-Vacancy Center Spins for High-Spatial Resolution Quantum Sensing Ania Bleszynski Jayich¹ and Dolev Bluvstein²; ¹University of California, Santa Barbara, United States; ²Harvard University, United States

The nitrogen vacancy (NV) center defect in diamond is emerging as a powerful quantum-enabled technology, in particular in the realm of sensing and imaging with ultra-high spatial resolution. The performance of these solid-state quantum sensors is highly dependent on their quantum coherence and charge-state stability, which are sensitive to their local environment. Surfaces are an important part of the defect's environment, in particular when targeting high spatial resolution sensing, which necessitates close proximity between the sensor and target. To identify and mitigate the deleterious environmental effects, I discuss several materials-based and quantum-control approaches. Specifically, I discuss the formation of highly-coherent NV centers via a gentle, bottom-up method of nitrogen delta-doping during chemical vapor deposition growth of diamond thin films followed by low energy (~ 150 keV) electron irradiation. I present measurements of the density and coherence properties of the NV centers formed in this way as a function of growth and irradiation parameters [1]. In the second part of the talk, I discuss the spin and charge state properties of shallow NV centers, and introduce techniques to mitigate decoherence due to paramagnetic surface spins [2] as well as charge state instabilities near surfaces [3]. These approaches to improved sensors will ultimately enable truly nanoscale spatial resolution imaging of magnetic, electric, and thermal fields in a
variety of condensed matter and biological systems.


SESSION EL05.08: Poster Session
Session Chairs: Timothy Grotjohn, Paul May and Robert Nemanich
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EL05.08.01
Structural Characterization of Phosphorus- and Nitrogen- Co-Doped Nano-Crystalline Diamond Grown by MW PE CVD
Fernando Lloret1,2, Sanakaran Kamatchi Jothiramalingam1,2, Marina Gutierrez3, Paulius Pobedinskask1,2 and Ken Haenen1,2; 1Hasselt University, Belgium; 2IMEC vzw, Belgium; 3Univ de Cadiz, Spain

Diamond is a very interesting material for many applications due to its excellent properties. The advantage of nanocrystalline diamond (NCD) facing single crystal diamond is the possibility to cover large areas. However, the granular nature of NCD leads to properties based on the interplay between grains and grain boundaries.[1] Grain boundaries are then fundamental in NCD layers. In this direction, the addition of nitrogen during the growth process has been reported to affect to the grain size. Appropriate N2 contents can increase the sp² bonding structure in NCD films, promote the smoothness of diamond surface, and efficiently raise the conductivity of electrons, thus making the films possessing n-type conducting property.[2] However, these properties are associated to a modification of the microstructure of the diamond films which, in turn, altered the electrical properties of the films. An alternative for n-type doping is the use of phosphorus atoms. Substitutional phosphorus incorporation in NCD films with a concentration of about 10¹⁹ cm⁻³ has been already reported.[3]

In this work, NCD layers co-doped with nitrogen and phosphorous are studied. With the aim to obtain the advantages of both dopants, i.e. good conductivity and smoothness surface, a 200 nm thickness N-P co-doped NCD layer has been grown by microwave plasma enhanced chemical vapor deposition (MW PE CVD) over 100-oriented Si substrates. The phosphorous content as well as the methane concentration were kept constant while N2 was varied from 0.2% to 2% for each sample. Optical emission spectroscopy was carried during the depositions revealing the main species in the plasma for the different gas mixtures. Scanning electron microscopy (SEM) observations show an increase of the surface roughness for samples growth at low N2 ratio. This is confirmed by transmission electron microscopy (TEM). TEM micrographs show a drastic change in the film morphology with the N2 increasing. Grain size is reduced with the increasing of the N2 during growth. Scanning mode TEM (STEM) - electron energy loss spectroscopy (EELS) shows the increase of the sp²-sp³ ratio with the N2 addition. Phosphorus incorporation in the layers is also revealed.


EL05.08.02
High Power, High-Frequency Diamond RF Schottky Barrier Diodes Cristian J. Herrera-Rodriguez1, Xenofon Konstantinou1, Aaron Hardy2, Timothy A. Grotjohn1,2, John D. Albrecht1,2, John Papapolymerou1 and Michael Becker2; 1Michigan State University, United States; 2Fraunhofer USA CCD, United States

CVD diamond is one of the most promising semiconductor materials for RF applications due to its exceptional mechanical, electronic, and thermal properties, such as wide bandgap, high breakdown electric field, high mobility, and high thermal conductivity. Therefore, CVD diamond constitutes a material ideal for high-power, high-frequency, and fast switching applications. The Schottky potential barrier at a metal-semiconductor interface is good for fast switching and it has a low voltage drop in the forward biased regime of a Schottky Barrier Diode (SBD). SBDs are fast because the dynamic response of the switching operation is dominated by the extraction and injection of the majority carrier into the depletion region of the Schottky/diamond junction, with no minority carrier recombination being involved. This study fabricated and tested diamond SBDs for high frequency, high power applications.

Schottky Barrier Diodes were fabricated on layered lightly/highly boron doped (p-/p+ respectively) epilayers on High-Pressure, High-Temperature (HPHT) diamond substrates. High-quality diamond epitaxial layers were grown at MSU by Microwave Plasma-Assisted Chemical Vapor Deposition (MPACVD) using 2.45 GHz microwave resonant cavity systems. The large-signal SBD impedances were obtained using Active Load/Source-Pull (L/S-P) by injecting 20 dBm at 10 GHz to the diode with -4 V applied, giving a value of $\text{out} = 40.2 - j169.3 \Omega$ and $\text{in} = 57.74 - j293.8 \Omega$. After conjugately matching the diode input and output, an output power of $\sim 32 \text{dBm} = 1.58 \text{W}$ was attained for an injected power of $\sim 34 \text{dBm}$, giving an RF power density of W/mm**2 and a loss of approximately 2 dB. The SBD s-parameters were measured. In order to extract the loss due to impedance mismatch during the s-parameters measurement, impedance matching at 10 GHz was performed using the Advanced Design System (ADS) software using stub input/output matching networks. A loss of $\sim 1.75 \text{dB}$ was obtained in the post-matching simulations. It should be underscored that the small-signal SBD impedances extracted from the s-parameters vary from the large-signal impedances obtained via Active L/S-P. This is expected since the SBD dynamic resistance changes with RF power.

EL05.08.03
Generation and Removal of sp² Carbon on Diamond and Nanodiamond Surfaces Kerry Whittlesea1, Simon Astley1, Joseph Durk1, Simon Cooil1, Benjamen Reed1, Tom Wang2, Rachel Cross1 and Andrew Evans1; 1Aberystwyth University, United Kingdom; 2Element Six, United Kingdom

The ability to modify and functionalise the surface of nanodiamonds make them suitable and useful for a vast variety of applications from drug delivery to nanocomposites1,2, however, the detonation synthesis of nanodiamonds produces shells of graphitic carbon around the bulk diamond-like core3. The graphitic shell is desired in applications such as drug delivery and biological composites as it enhances surface reactivity4. However, in the majority of applications, this shell is considered an impurity as it prohibits the properties of the nanodiamond surface, which can be terminated and treated in ways which are beneficial.

Whilst sp² carbon surface layers can be generated at high temperatures in ultra-high vacuum, the surface layers of sp³ carbon on diamond and nanodiamond are removed by annealing in either air or oxygen atmospheres5 at ambient pressures. Previous studies have reported that the temperature at which sp³ carbon at the bulk diamond surface is converted to sp² carbon can be significantly reduced in the presence of a metal catalyst6. The conversion at the bulk diamond-metal interface can be controlled to form single or multi-layer graphene as diamond can provide the source of carbon and is an ideal lattice-match substrate for the growth of graphene7.

A similar process of heating in the presence of a metal catalyst was applied to nanodiamonds where a reduction in the conversion temperature between sp³ carbon to disordered sp² carbon was observed. Using surface sensitive photoelectron-based techniques, the removal and generation of sp³ carbon on diamond and nanodiamond surfaces has been studied for a selection of substrate materials and surface preparation.

References
EL05.08.04
Nonlinear Optical Response from Diamonds—The Effect of NV Centers
Mari Motojima1, Yuta Kainuma2, Toshu An2, Hidemi Shigekawa2 and Muneaki Hase1; 1University of Tsukuba, Japan; 2Japan Advanced Institute of Science and Technology, Japan

The optical and magneto properties of the negatively charged nitrogen-vacancy (NV) center in diamond has been extensively investigated because of its application to quantum sensing, such as magnetic and electric fields and to quantum information technologies. In most cases, near-infrared luminescence upon the excitation by green laser can be controlled by the irradiation by microwave, which tunes the optical transition path between the excited and ground states. To extend the optical property of diamond over the current generation of linear optical regime, one requires ultrashort laser pulses, which enables one to induce nonlinear optical effect, such as the nonlinear refraction and nonlinear absorption. Almeida et al. recently reported on nonlinear optical spectra in high-purity diamond using femtosecond laser pulses with photon energy from 0.83 to 4.77 eV and measured coefficients for the nonlinear refraction and nonlinear absorption [1]. Because of the absence of defect-related bands below the band-gap (Eg = 5.5 eV), the two nonlinear optical effects were enhanced for E = Eg/2. Although there are several investigations on nonlinear optical effects in diamond and nano-diamonds [2,3], the effects of the NV center on the nonlinear optical phenomena have not yet been examined. This issue is, however, important to further study new functionality of diamond photonics to advance nonlinear quantum sensing. Here we explore the NV center induced nonlinear optical effects in pure diamond, specifically optical Kerr effect and two-photon absorption in transparent region using 800 nm light, at which NV related bands will be sensitive. It is found that both the nonlinear optical effects enhanced by the introduction of NV centers.


EL05.08.05
The Effect of Methane Concentration on the Properties of Lightly Boron-Doped Single Crystal Diamond Layers
Rozita Rouzbahani1,2, Fernando Lloret1,2, Danny E. Vanpoucke1,2, Sanakaran Kamatchi Jothiramalingam1,2, Daniel Araujo3 and Ken Haenen1,2; 1Institute for Materials Research (IMO), Hasselt University, Belgium; 2IMOMEC, IMEC vzw, Belgium; 3Dpto. Ciencia de los Materiales, Universidad de Cadiz, Spain

The fabrication of high power diamond electronic devices requires an improvement of the crystalline quality of the doped layers. This is one of the limiting factors of the structural and electrical properties of chemical vapor deposited (CVD) layers. Although recent advances in CVD synthesis have enabled the growth of free-standing, single crystal, intrinsic, and boron doped diamond, defects—such as dislocations—remains an important point of attention. Several research groups1,2 have reported on the significant influence of the [B]/[C] ratio in the plasma feedgas on the electrical properties of B-doped single crystal diamond (SCD) films. In this study, the impact of the methane concentration on the crystalline quality and electrical properties of lightly B-doped SCD layers is investigated. The samples were grown in a homemade CVD reactor on 3X3 mm2 Ib (100)-oriented high pressure high temperature (HPHT) substrates. Growth was performed in a conventional [CH4]/[H2] plasma (1%, 2%, and 3%) with residual trimethylboron as the boron source, used for all of the samples. The p layers were characterized by Hall effect in a wide temperature range, Fourier transformed infrared (FTIR) spectroscopy, X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), optical microscopy, and transmission...
electron microscopy (TEM). The TEM study of the sample grown at 1% methane concentration showed a high-quality $p$-SCD film without any observed dislocations in a thickness of 1 μm. In the XAS measurements of the sample grown at 3% methane, small absorption peaks occurred around 282 eV to 285 eV in the C K-edge region which are assigned as acceptor levels in semiconducting B-doped diamonds. These peaks were not observed in the samples grown at lower methane concentrations (1% and 2%). XPS measurements indicated that the intensity of the B 1s peak is increased by increasing the methane concentration which showed a higher B-doping level. In FTIR spectroscopy, the 2800 cm$^{-1}$ peak has been used by research groups to estimate the vacant acceptor concentrations in the range of $10^{16}$ to $10^{18}$ cm$^{-3}$. The boron concentrations estimated by FTIR were compared to the result of the Hall effect which confirmed the same [CH$_4$/H$_2$] dependence as observed by X-ray spectroscopy, with a sample grown at 3% methane showing a higher boron incorporation than those grown at 1% and 2% methane concentrations in the plasma feedgas. These results were corroborated by first principle density functional theory (DFT) calculations. The formation of more growth centres, due to higher methane concentrations, are found not to significantly change the adsorption energy of the boron impurity at nearby sites. Instead, these growth centres are shown to dramatically increase the formation of missing H defects, which are premium boron incorporation sites, thus indirectly increasing the boron concentration.

References:

EL05.08.06
Mesoscale Crystallographic Structure Analysis and Boundary Condition Influence on Lateral Grown Single Crystal Diamond by Microwave Plasma Assisted Chemical Vapor Deposition Shengyuan Bai, Ramon D. Diaz and Elias Garratt; Michigan State University, United States

For decades, diamond has shown superior properties that make it desirable for novel electronic materials. However, fabricating large size high quality single crystal diamond wafers faces multiple challenges. Lateral outgrowth of CVD diamond with designated pocket holders makes it highly possible for large size diamond wafers to be realized. A mixed analysis of crystallographic structure of laterally grown CVD diamond and influence of pocket holder boundary condition is key to understanding how to eventually fabricate large size high quality single crystal diamond wafers by microwave plasma assisted chemical vapor deposition (MPACVD).

In this work, single crystal diamonds were grown laterally on High Pressure High Temperature (HPHT) substrates with designated pocket holders by Microwave Plasma Assisted Chemical Vapor Deposition (MPACVD) and characterized by a micro X-ray diffraction (μ-XRD) mapping technique with a 300 μm beam size to show the evolution of diamond crystal structure information during growth and provide feedback on growth strategies. By understanding how crystal structure evolves during growth we can understand the mechanisms linking processing conditions the structure and properties of grown material.

A series of CVD diamond is grown on standard HPHT (3.5mm x 3.5 mm) with various thicknesses (600 μm – 1400 μm) using designated sample holders. High-resolution x-ray rocking curve (HRXRC) and full width at half max (FWHM) μ-mapping of the (400) diamond peaks illustrate the evolution of crystallographic changing after each processing. Relatively low values for misorientation (typically within 0.05°+/−0.003°) and FWHM (typically around 0.025°+/−0.003°) for CVD diamond are compared after a series of growth. Evolution mapping of growth and regrowth suggest an upper limit in FWHM exists for a single CVD growth, which is promising for CVD diamond to have a high quality single crystal sample. Thus, a large size single crystal CVD diamond with uniform crystal orientation (low bending in the crystal structure) and low mosaicity (small FWHM) can be achieved.

Moreover, preliminary results demonstrate single crystal CVD diamond prefers to grow laterally in an exponentially decay way towards the pocket boundary, and smooth single crystal diamond (SCD) edges are formed after growth. The growth trajectory of the diamond profile satisfies an exponential decay relationship as it gets closer to the pocket boundary, which suggests a moderate plasma density region makes the main factor for a diamond sample to grow as a single crystal. Based on the growth rate according to specific diamond crystal orientation, lateral
outgrowth using series of designated pocket holders shows the effective diamond area can be enlarged from the 3.5mm x 3.5mm standard HPHT to around 5mm x 5mm CVD diamond in a single run. Regrowth on CVD plate using iteration method with wider iteration holders is promising for SCD samples to keep growing even larger.

EL05.08.07
Hydrogen-Terminated Diamond Field-Effect Transistor with Double Dielectric Layers of HfSiO4/Al2O3
Yanfeng Wang, Xiaohui Chang, Wei Wang and Hong-Xing Wang; Institute of Wide Band Gap Semiconductors, School of Electronics and Information Engineering, Xi’an Jiaotong University, China

Diamond film collects all the outstanding properties of mechanics, electronics, heat, and optics etc. together making it have potential applications in the fields of wide range optical transparent window material, super-hard coating tolls, especially, in the field of high power electron devices which can work with high frequency and in high temperature environment. Recently, researchers have extensively investigated hydrogen-terminated diamond (H-diamond) field effect transistors (FETs). H-diamond surface can form a p-type conduction layer with a sheet hole density and hole mobility of 10^{13} cm^{-2} and 50-150 cm^{2}V^{-1}s^{-1}, respectively. However, this conduction layer is thermally and chemically unstable and vulnerable to the ambient environment such as oxidation of diamond surface or higher annealing even in vacuum. All these would cause the missing of p-type conduction layer and the degradation of FET performance. This problem could be solved by fabricating dielectric layers on diamond surface to maintain the p-type conduction channel, which also acts as a insulators. Various dielectric layers have been used such as SiO2, Al2O3, HfO2, Ta2O5, and ZrO2 on H-diamond surface. However, there are few reports on using dielectric of HfSiO4, which has excellent thermal stability, adequate band gaps (from 15 to 25 depending on hafnium content).

In this work, investigation of H-diamond FETs with ALD-Al2O3/ SD-HfSiO4 dielectric layers have been carried out. Firstly, gold electrodes were patterned on H-diamond by electron beam evaporation technique. Secondly, UV-ozone was used to insulate p-type conduction channels between source and drain electrodes. The length of channels were 20μm. Then, 4nm ALD-Al2O3/ 30nm SD-HfSiO4 dielectric layers were fabricated on p-type conduction channels by ALD and SD technique. Finally, electrical properties of this diamond FETs were investigated. The detail will be presented in the conference.

SESSION EL05.09: Diamond Processes/Technology
Session Chair: Ken Haenen
Wednesday Morning, December 4, 2019
Hynes, Level 1, Room 107

8:15 AM EL05.09.01
Fabrication and Characterization of Modified Boron-Doped Diamond Electrodes for Peroxynitrite Detection and Quantification
Eman Darwish1,2, Mai Rashwan1,3, Jinyi Wang1, Sayed Moalla2, Zeinab Answer3, Haitham Kalil4 and Heidi Martin1; 1Case Western Reserve Univ, United States; 2Port Said University, Egypt; 3Suez Canal University, Egypt; 4Cleveland State University, United States

Endogenous and exogenous, reactive oxygen species (ROS) have a significant, damaging effect on cell metabolism, including in neural systems. Peroxynitrite (PON) has emerged as a secondary ROS that is linked with oxidation and/or nitration of biomolecules, and is the product of the diffusion-limited reaction of superoxide and nitric oxide radicals. Its short lifespan and fast reactivity increase the challenge of measuring its concentration under physiologic conditions. Several methods exist for peroxynitrite detection in aqueous environments, yet the problem of real-time quantification remains. In this paper, the electrochemical behavior of peroxynitrite has been studied using boron-doped diamond (BDD) microelectrodes. For more than a decade, diamond-based sensors have been successfully applied to electrochemical detection of various analytes in biological and environmental systems, due to its wide potential window, and stable, low background current. In addition, the diamond has more predictable surface to fine-tune for optimized detection of peroxynitrite. In this research study, the direct, real-time electrochemical oxidation of peroxynitrite on BDD electrodes was investigated. A wide range of physicochemical characterizations was conducted to demonstrate the catalytic
oxidation of PON on surface-modified diamond microelectrodes. Initial attempts were made to determine whether PON is generated during simulated, neural stimulation pulses, in a nitric oxide containing environment. Developing BDD microsensors that can monitor the electrochemical signature of peroxynitrite will be an important step forward towards improving the safety of electrical stimulation of cells as well as general monitoring of PON levels as an indicator of tissue deterioration and age-associated diseases.

8:30 AM EL05.09.02
Thermal Optimization of Metal/Nanocrystalline Diamond Junctions via Diffusion Barriers Henry Aller1, Zhitao Guo1, Karl Hobart2, Tatyana I. Feygelson2, Alan J. McGeoughy1, Andrew Gellman1 and Jonathan A. Malen1; 1Carnegie Mellon University, United States; 2U.S. Naval Research Laboratory, United States

Overheating cripples the efficiency of electrical devices. Diamond heat sinks can facilitate heat dissipation and directly lower operating temperatures. The advent of nanocrystalline diamond (NCD) deposition techniques provide the ability to work with diamond on nanometer length scales, which cannot be done with traditional machining. Thermal optimization of metal/NCD junctions, used to adhere NCD to the device, is required to maximize the efficiency of the heat sink.

We examine thermal transport across Au/contact/NCD junctions, for the contacts Cr, Ni, and Ti. For each contact, the thermal boundary conductance (TBC) is measured using frequency domain thermoreflectance for contact thicknesses between 0 and 10 nm. Cr and Ti are predicted to chemically react with NCD to form enthalpically favorable carbides. Grown carbides add thermal resistance, lowering the TBC of the Au/contact/NCD junction. During deposition of the contact, NCD grain boundaries may act as low-resistance highways for carbon diffusion, promoting carbide growth. Thus, fine-grained materials like NCD may be at risk of forming low TBC junctions with metals, hindering the ability of future NCD heat sinks. To mitigate reactions, we deposited 0 to 10 nm thick Ni diffusion barriers between Cr or Ti and the NCD. The measured TBC of the Au/(Ti or Cr)/Ni/NCD junctions is used to quantify the improvement from reaction mitigation.

8:45 AM EL05.09.03
Synthesis and Characterisation of Tin Monoxide—A Potential Ultra-Low Work Function Multilayer for Terminating Diamond Surfaces Sami Ullah, Mattia Cattelan, Gary Wan and Neil Fox; University of Bristol, United Kingdom

Diamond electrodes terminated with surface layers can impart significant changes to the electronic properties of a diamond interface and we have previously reported on studies of the tunability of surface work function by substituting hydrogen with oxygen under controlled conditions 1. Engineering a functionalised diamond surface that is stable and reproducible is of technological importance to future diamond electronic devices such as Schottky junctions and electron-emitting electrodes for field emission, thermionic energy converters, secondary electron multipliers.

Tin monoxide has been considered as potential material for battery anodes, coating, gas sensing, catalysis, etc. The application area of SnO extends over photovoltaics, displays, information storage, etc. as it has a large optical bandgap of 4.12 eV, high transparency (~90%) non-toxic and abundant 2. SnO has been found to form a layered structure in a crystallographic direction of [001] with a monolayer thickness of 0.48 nm. Sn 5s form a lone pair of electrons which point towards the interlayer spacing and result in dipole-dipole interaction leading to a Van der Waals gap of 2.52 A between the layers. Various groups have demonstrated the growth of SnO mono and multiple layers by various methods but many of these result in an upper SnO2 layer that forms as soon as the sample is taken into the oxygen environment as SnO is metastable and hence rapidly converts into SnO2.

We have produced mono and multiple layer SnO on conductive, p-type single-crystal diamond under ultra-high vacuum (UHV) conditions by e-beam evaporation and characterised in-situ by Spot Profile Analysis Low-Energy electron diffraction (SPA-LEED)and Energy Filtered Photo Emission Electron Microscopy (EF-PEEM) and X-ray Photoemission Spectroscopy (XPS). We quantify the change in work function between mono and few-layer SnO and its effect upon the barrier height of a p-type diamond Schottky junction.

References
2. Pei, Y., Liu, W., Shi, J., Chen, Z. & Wang, G. Fabrication and Characterization of p-Type SnO Thin Film with
High c-Axis Preferred Orientation.

9:00 AM EL05.09.04
High Pressure and High Temperature Treatment for Ion Implanted Diamonds Rei Fukuta, Yohei Murakami, Fumitaro Ishikawa, Masafumi Matsushita, Toru Shinmei, Hiroaki Ohfuji and Tetsuo Irifune; Ehime University, Japan

High pressure and high temperature (HPHT) technique is a process enabling diamond synthesis and the control of diamond properties. The HPHT-processed diamonds show characteristic properties which cannot be achievable by the other technique. E. g., there is a report for optical emissions from Sn-vacancy (Sn-V) center in HPHT-treated diamond reported by Iwasaki et al.[PRL 119, 253601, 2017.], which shows the prospect for its application to a light source of quantum emitters. Nanoscale structural design trying to obtain new functions of existing materials is a key issue for the realization of future devices and applications. To explore the functions of diamond, HPHT technique would have potential to activate its unknown properties as in the case of impurity activations of the above reports. We consequently investigate the effect of HPHT treatment on P and Sn implanted diamond on its surface.

For the investigations, we employed commercially available single crystalline diamond (001) substrate synthesized by chemical vapor deposition. We introduced P and Sn by ion implantation at $1 \times 10^{20}\text{cm}^{-3}$ uniformly from the surface to the depth 300 nm and 50 nm, respectively. Subsequently, we applied HPHT treatment at 15 GPa and 2300°C for 20 min. The treatment is expected to induce recrystallization and heal the damage of the diamond surface. The sample surface after HPHT treatment showed square holes aligned to specific crystal orientation, suggesting crystallographic rearrangement of constituent elements. Secondary ion mass spectrometry showed the profiles of P and Sn after HPHT with the density similar to the ion implantation. We also observed atmospheric impurities, H, O, and N in the diamond. The amount of those elements varies by the conditions of ion implantation and HPHT treatment. Hence, the proper ion implantation and HPHT treatment can preserve the implanted elements in the host matrix and suppress the contaminations of atmospheric elements. The Sn-doped sample showed sharp photoluminescence emission at 1.999eV and 2.003eV at low temperatures after HPHT as reported by Iwasaki. These results show great potential of HPHT as a material engineering tool for diamond.

9:15 AM EL05.09.05
Lateral Boron Doped Diamond Nanowires—Fabrication and Function Alex C. Pakpour-Tabrizi; University College London, United Kingdom

Electronically active low dimensional structures have been made in a variety of material systems. Nanowires in particular are of interest in fields as varied as quantum computing, sensing and power electronics to name but a few. By utilising a mix of additive and subtractive processing a novel lateral diamond nanowire is fabricated and characterised. The substrate and foundation for this nanowire is a highly boron doped diamond epilayer, grown on high purity insulating single crystal diamond. The dopants are confined spatially in a 1-2nm region, this delta function like distribution can be shown to have similar electronic properties to a bulk doped. The $\delta$-doped epi-layer is then patterned and etched to leave wires with dimensions on the order 10-20nm and arbitrary controllable lengths. In this talk we will discuss the transport mechanisms and phenomena observed, as well as showing a novel field effect transistor utilising a number of these wires to achieve high current handling and demonstrate the scalability of this unique technology.

9:30 AM EL05.09.06
A New View of X-Ray Radiation Damage in Diamond Leora E. Dresselhaus-Cooper1, Suzanne Ali1, Sean Breckling2, Philip K. Cook3, Jon Eggert4, Eric Galtier4, Lisseth Gavilan-Marin5, Arnulfo Gonzalez5, Marylesa Howard2, Kento Katagiri6, Hyunjung Kim7, Sangsoo Kim8, Sunam Kim8, Sungwon Kim8, Sungwook Kim7, Stephan Kuschel4, Jae Ja Lee4, Chuanlong Lin9, R. Stewart McWilliams10, Daewoong Nam8, Norimasa Ozaki6, Ricardo Pablo Pedro11, Henning Poulsen12, Alison Saunders1, Frank Schoofs13, Toshimori Sekine6, Hugh Simons12, Bihan Wang8, Wenge Yang9 and Can Yildirim14; 1Lawrence Livermore National Laboratory, United States; 2Nevada National Security Site, United States; 3BOKU, Austria; 4SLAC National Accelerator Laboratory, United States; 5NASA Ames, United States; 6Osaka University, Japan; 7Sogang University, Korea (the Republic of); 8Pohang Accelerator Laboratory, Korea (the Republic of); 9HPSTAR, China; 10University of Edinburgh, United Kingdom; 11Massachusetts Institute of Technology, United States; 12Technical University of Denmark, Denmark; 13U.K. Atomic Energy Authority, United Kingdom; 14CEA, France
Single crystals of diamond have high mechanical strength and are very resilient to high-intensity X-ray radiation. Diamonds are thus irreplaceable in applications across X-ray optics and high-pressure physics, serving as windows, monochromators, and anvils in high pressure cells. The physics underlying diamond’s unusual properties stems from its strong $sp^3$ covalent bonds and simple symmetry. As diamonds eventually damage under ultra-high intensity X-ray radiation, the tetrahedrally bound $sp^3$ carbon atoms are known to graphitize to trigonal bipyramidal $sp^2$ hybridized carbon atoms. This change in local symmetry mechanically destabilizes the material by adding low-energy pathways along which the crystal may deform. Studies of the mechanism by which high-energy X-rays graphitize diamond and the resulting changes to the mechanical properties have been limited. Few characterization techniques can measure the lattice defects and microstructure of a crystal deep beneath its surface—especially as the material responds to external stimuli.

We use ultrafast dark-field X-ray microscopy to directly image changes to the phase, strain and lattice tilt with ultra-high sensitivity as diamond responds to the high intensity X-ray radiation at an X-ray free electron laser. With these results, we demonstrate how minor changes to the microstructure of diamond from the incident radiation cascade into large-scale deformations. This work demonstrates how this novel high-sensitivity technique can give us a new view of the link between radiation and mechanical damage in diamond, informing applications across X-ray science, high-pressure science and astrophysics.

This work was performed in part under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

9:45 AM EL05.09.07
Experimental and Modelled I-V Characteristics of Boron-Doped Diamond at High Electric Fields Including Self-Heating Effect Andrew Taylor1, Nicolas Lambert1,2, Pavel Hubík1, Jiri Bulir1, Joris More-Chevalier1, Hasan Karaca1, Clément Fleury1,2, Jan Voves2, Zbyněk Soban2, Dionyz Pogany3 and Vincent Mortet1,5; 1Institute of Physics of the Czech Academy of Sciences, Czechia; 2Czech Technical University, Czechia; 3Technische Universität Wien, Germany; 4Silicon Austria Labs, Austria; 5Czech Technical University in Prague, Czechia

Diamond is a wide band gap semiconductor with high thermal conductivity, carrier mobility and breakdown field, which make it particularly suitable for the fabrication of high power electronic devices. However, the development of diamond devices is limited by the high ionization energy of its dopants, which leads to only a small fraction of them being ionized at room temperature. When stressed by a high electric field, a current multiplication has been observed in boron-doped diamond (BDD) attributed to Impurity Impact Ionization (III) and the ionization of the neutral acceptors1. In this work, we analyse the current multiplication in BDD including the combined effects of Self-Heating (S-H) and III. Epitaxial BDD layers with different acceptor concentrations in $3.1 \times 10^{18} - 6.1 \times 10^{19}$ cm$^{-3}$ range have been grown in an AX5010 microwave plasma enhanced chemical vapour deposition system. Quasi-static current-voltage (IV) characteristics were measured using a Transmission-Line Pulse setup2 with 100 ns pulse duration on concentric titanium/gold ring-disk electrodes structures patterned by standard lithography and wet etching methods. S-H was analysed using Transient Interferometric Mapping (TIM)3 of the thermal energy distribution between electrodes in ns time scale. The experimental IV characteristics were modelled by taking into account S-H effect and III using finite element method. The simulated IV characteristic, in particular the negative differential resistance (NDR) region appearing due to S-H effect, is in good agreement with the experimental data. This work was financially supported by the project 17-05259 S of Czech Science Foundation and the SGS Student Grant “Electric Discharges II: experimental research, modeling and applications” ID: SGS19/167/OHK3/3T/13.


10:00 AM BREAK
SESSION EL05.10: Doping
Session Chair: Satoshi Yamasaki
Wednesday Morning, December 4, 2019
Hynes, Level 1, Room 107

10:30 AM *EL05.10.01
Engineering and Transport Properties of Diamond Bipolar Devices Aboulaye Traore1,2, Toshiharu Makino1,2, Hitoshi Umezawa2, Hiromitsu Kato3, Masahiko Ogura2, Yukako Kato2, Daitsuke Takeuchi2 and Satoshi Yamasaki2; 1University of Tsukuba, Japan; 2National Institute of Advanced Industrial Science and Technology, Japan

Semiconducting diamond is touted for its outstanding intrinsic and thermal properties that promise tremendous devices performances advantages for power control and conversion applications. Over the last few decades, basic works in diamond growth and doping have allowed the extension of known devices technologies to diamond as well as the development of new devices concepts. However, to achieve high performance diamond devices that can outperform the existing and emerging technologies, much remains to be understood in many areas such as the diamond devices physics, the effects of defects (intrinsic and extrinsic) on diamond devices transport properties, the diamond surface passivation, and the diamond devices design (edges termination issues).

This presentation will be focused on the electrical transport in diamond bipolar devices such as diamond p-i-n diode. Bipolar diamond devices are very promising and attractive devices because of the conductivity modulation phenomenon that allows to counterbalance the effects of high ionization energies of dopants in diamond (0.58 eV and 0.38 eV for Phosphorus donor and Boron acceptor respectively).

In our work, diamond p-i-n diodes have been used to study carrier recombination mechanisms, charge carrier dynamics, and impact ionization in diamond. Our pioneering works on the electrical characterization of the diamond p-i-n diode in dynamic and the optimization of diamond p-i-n devices design to suppress the electric field crowding at devices edges for an accurate measurements of impact ionization coefficients by electron beam induced current method (EBIC), will be introduced and discussed.

11:00 AM EL05.10.02
Tunable Barrier for High Temperature Diamond PIN Diodes Mohamadali Malakoutian1, Harshad Surdi2, Franz A. Koeck2, Manpuneet Benipal3, Srabanti Chowdhury1, Stephen Goodnick2 and Robert J. Nemanich2; 1University of California, Davis, United States; 2Arizona State University, United States; 3Advent Diamond, United States

The wide bandgap, high carrier mobilities, high breakdown field and highest thermal conductivity identify diamond as the ideal power semiconductor material. A particular advantage of diamond over all other semiconductors is operation in high temperature, high radiation and extreme environments. Diamond PIN diodes or PIN-Schottky diodes will be crucial components in power conversion and control systems that can operate in extreme environments. In this study the transport characteristics of high purity diamond PIN and PIN-Schottky diodes are measured and simulated for temperatures ranging from room temperature to 500°C. While the forward current density increases due to dopant activation and thermionic emission, the reverse current increases by many orders of magnitude consistent with thermionic emission theory. The diode forward/reverse rectification ratio consequently decreases by many orders of magnitude. Attempts to engineer the barrier using different metals (with different work functions) show very limited success. This study presents an alternative approach where the diode barrier is engineered by increasing the phosphorus doping in the n-type layer. Experimental results and simulations establish that the barrier can be varied from about 1 eV to greater than 3 eV which restores the high temperature (500°C) rectification ratio to nearly 10^4. The simulations also consider the forward current properties and they establish how the specific diode characteristics can be tuned for operation at elevated temperature up to and exceeding 500°C. This tunable approach appears may provide an advantage for diamond diodes (over other power semiconductors) for high temperature operation.

Research supported by NASA through the HOTTech program, and the NSF through grant IIP–1747133. Authors acknowledge the support of the ASU NanoFab supported by NSF grant NNCI – 1542160.

11:15 AM EL05.10.03
Observation of Metallicity in n-Type Doped Diamond Thin Films Dhruba Das and Mamidanna Ramachandra Rao; IIT Madras, India
Electronic properties of doped-diamond are of great technological interest due to the possibility of diamond-based electronic devices for high power electronics and for the fabrication of QUBITs. With a bandgap of 5.5 eV at room temperature (RT), diamond is an electrical insulator however when it comes to substitutional incorporation of impurities in its lattice via doping, it becomes extremely selective unlike Si and Ge and its conductivity has been seen to change drastically with doping. Doping of diamond lattice by boron to make it p-type has been the most successful so far by incorporating boron atoms in the gaseous phase during the growth process and this has shown enhanced electrical conduction making it metallic and even superconducting [1,2] signaling an insulator-to-metal transition (IMT) at low temperatures provided the dopant concentration is above a critical value ~10^{21} cm^{-3}. Nitrogen and phosphorus are the famous candidates for the n-type doping in diamond which contributes an extra electron in the system. Nitrogen doping has not yet brought much success in terms of electrical conductivity during the past one decade as it fails to form a shallow donor level with its donor level at Ec − 1.7 eV because of dramatic localization of the donor electron on a neighboring carbon atom with a subsequent formation of a lone-pair on the nitrogen atom. Phosphorus, on the other hand, being a large impurity does not relax in an analogous fashion unlike nitrogen, and thus leads to a substantially shallower donor level at Ec − 0.6 eV, which is still rather deep for room-temperature ionization.

Over the last two decades, much work has been done on making diamond n-type with increased conductivity but so far, the highest achieved conductivity is 143 (Ω-cm)^{-1} [3,4] in nitrogen doped (20% N2) ultrananocrystalline diamond (UNCD). For the first time, we report the formation of n-type diamond by nitrogen doping in ultrananocrystalline diamond deposited on silicon substrate with resistivities similar to copper (ρ_{copper} ~ 1.68 x 10^8 Ω-m at 20 °C) with metallicity being observed throughout the temperature regime for few doping concentrations. Developing nitrogen doped UNCD thin films was carried out by depositing an ultrananocrystalline diamond thin film on Si in hot filament chemical vapor deposition reactor followed by ion implantation by N⁺ ions with different energy and fluences and subsequent annealing to make the vacancies and dopants mobile so that substitutional doping can be ensured inside the lattice. These implanted films were characterized by Raman spectroscopy for their UNCD nature before and after annealing post-implantation.

References:

11:30 AM EL05.10.04
Boron Doping Quantification in Single Crystal Diamond by Solid Solution Strengthening Fernando Lloret₁², David Eon³, Etienne Bustarret¹ and Daniel Araujo⁴, ¹Hasselt University, Belgium; ²imec vzw, Belgium; ³Univ. Grenoble Alpes, CNRS, France; ⁴ Universidad de Cadiz, Spain

The metallic behavior of highly boron doped diamond (BDD) is an asset for the development of the future diamond-based electronic technology. However, boron concentration quantification still remains expensive and, in some cases, difficult. Secondary ion mass spectroscopy (SIMS) is the most accurate technique but requires special care when steep profiles are involved [3]. It is also a very expensive tool. Alternatively, boron doping can also be quite precisely evaluated by cathodoluminescence (CL). This technique collects the photons generated by the interaction of the incident electrons with the electrons of the sample. The consecutive radiative recombination signal depends on the electronic properties of the sample. In particular, at low temperature, excitons bound to boron impurities have specific spectral signatures that make it possible to determine the boron levels. However, one of the main restrictions to the use of this technique is the presence of dislocations. The strain generated around the dislocation bend the valence and conduction bands trapping all the carriers. Their mobility is then strongly reduced and electrons and holes recombine mostly through non-radiative channels, while a relatively weak broad band (A-band) may result from the remaining radiative carrier recombination at the dislocation. In regions where the density of defects is high enough to close all radiative channels, the evaluation of the doping levels by CL is no more possible. In this case, the quantification of boron becomes a challenge. We propose here to use the interaction between boron atoms and dislocations specific to these regions in order to estimate the doping level by transmission electron microscopy. Substitutional boron incorporation within BDD can be seen as allowing elements into the crystalline lattice forming a solid solution. The non-uniformity generated by boron atoms makes plastic deformation more difficult by impeding dislocation motion, thus creating an increase in the yield stress of the material also called strengthening.
Upon lateral growth, dislocations are pushed forward, along a specific course \(^2\). Their trajectory varies when they pass through a doped layer because of the solid solution strengthening. An increase in the dislocation length is observed, necessary to accommodate locally the additional tension generated by the boron impurities in the doped layer. In this work, boron doped/undoped superlattices have been laterally overgrown over patterned substrates. Two 001-oriented HPHT substrates were etched away by inductively coupled plasma reactive ion etching (ICP-RIE) leaving a pattern array of 5 µm diameter and 1µm height disks. Over these substrates, p\(^+\)/p bilayers were grown with different [B]/[C] ratios for each sample. The presence of dislocations was ensured by the roughness substrate surface after etching. The dislocation length was measured by high resolution TEM for both samples. Boron content was then estimated by the above proposed method, and compared to that reported in the literature for similar growth conditions.


**Ab Initio Study of Boron, Boron-Hydrogen and Vacancy Complexes in Diamond and Their Effect on the Electronic Structure of Diamond**

Nandan Tandon\(^1\), John D. Albrecht\(^1,2\) and Timothy A. Grotjohn\(^1,2\); \(^1\)Michigan State University, United States; \(^2\)Fraunhofer USA Center for Coatings and Diamond Technologies, United States

Diamond has been identified as an attractive material for high power devices because of its physical and electronic properties. In comparison to other wide-bandgap semiconductors diamond exhibits high carrier mobilities and thermal conductivity. The electronic properties of diamond are defined by the dopants that are present during growth or introduced in diamond to achieve p- and n-type conductivity by ion implantation of boron or phosphorous respectively. This process of introducing dopants also creates defects such as vacancies and interstitials along with the presence of dopant atoms. Among the implanted dopants, the number of activated dopants is found to be only a few percent. Thus, it is interesting to study the geometry of dopants and other factors which result in such low levels of active dopants.

In this work we have used first principles density functional theory based calculations within the supercell approximation to identify the structure and electronic properties of complexes formed from carbon vacancy, boron, boron-hydrogen and interstitials in diamond. Total energy calculations were performed to identify ground state structures for various defects and formation energies were used to predict the probability of presence of that defect. Ionization energies for different defects are evaluated using the marker method. Formation energy of substitutional boron is found to be lower in presence of hydrogen. As seen by others, we also find that a single vacancy relaxes into a tetragonal distorted structure of the nearest carbon atoms from the original tetrahedral structure. This structure is lower by 0.22 eV compared to the original tetrahedral structure. Activation energy of vacancy diffusion is found to be 2.8 eV using the nudged elastic band method. Spin-polarized calculation of single vacancy shows that there is small magnetic moment on all 4 carbon atoms surrounding the vacancy and the total energy of such a calculation is lower than a paramagnetic calculation. Other results which include spin-polarized calculations on diamond will also be shown.
Nitrogen vacancy (NV) center in diamond is expected as a magnetic sensor with high sensitivity at room temperature and single NV center succeeded in detecting $^1$H spins out of the substrate [1]. For improvement of magnetic sensitivity, both shallow and aligned NV ensemble is required since the magnetic sensitivity is inversely proportional to the root of number of NV centers contributing to the measurement [2, 3]. Delta-doping of N was tried by diamond growth on N-terminated (001) diamond and estimated 2D concentration of NV centers was $1 \times 10^{11}$ cm$^{-2}$ [4]. This method can control the depth of NV ensemble precisely unlike ion implantation or N-doped layer which are popular methods to fabricate NV ensemble. However, NV centers in (001) delta doped layer would be not aligned because possibility of each four sites adjacent to N becoming a vacancy are equivalent. In the case of (111) delta doping layer, NV centers will be aligned because a top site is more preferable to become a vacancy than other three equivalent sites. Recently, we established the method to fabricate N-terminated diamond with high coverage causing no damage on the surface [5, 6]. We partially succeeded to make aligned two-dimensional NV ensemble from N-terminated (111) diamond with half mono layer coverage embedded by high purity (111) diamond film. N-terminated (111) surface was fabricated by nitrogen radical exposure method [5, 6]. After that, thin layer (thickness is about 10 nm) of high purity (111) diamond film was epitaxially grown on the N-terminated surface using microwave plasma enhanced chemical vapor deposition method. We confirmed that N density in the high purity diamond film was below $1 \times 10^{16}$ cm$^{-3}$ by secondary ion mass spectroscopy (SIMS). We also confirmed the formation of NV ensemble with 2D concentration of about $1 \times 10^{11}$ cm$^{-2}$ using the confocal PL-intensity mapping. Optically detected magnetic resonance (ODMR) with static magnetic field applied along the [111] axis was used to determine whether the NV ensemble was highly aligned or not [7]. The ODMR spectrum of the NV ensemble had only two dips, which might be derived from the NV center whose orientations were aligned along the [111] axis. In conclusion, NV ensemble was fabricated by diamond growth on N-terminated (111) diamond and was aligned along the [111] axis.


Acknowledgements
We thank Dr. Liam P. McGuinness and Prof. Fedor Jelezko for their help in building CFM setup.

1:45 PM EL.05.11.02
Optical Emission Properties of Ion-Implanted Nanodiamonds and Their Applications Sini Nanadath Shibu1, Dzianis Saladukha1, Tomasz J. Ochalski2, Haitao Ye2 and Chengming Li3; 1Cork Institute of Technology, Ireland; 2University of Leicester, United Kingdom; 3University of Science and Technology Beijing, China

The recent development of novel super-resolution imaging techniques coincides with the efforts to synthesize optically bright and stable biomarkers. It is known that the electrical resistivity of nanodiamonds is quite high with a bandgap of 5.5 eV and at room temperature they are dielectrics. Fluorescent nanodiamonds (FNDs) can be produced using a variety of methods with a wide range of sizes ranging from several nanometers to tens of micrometer, which defines their penetration and adhesion properties. Nano-diamonds (NDs) synthesized by microwave plasma chemical vapor deposition (MPCVD) techniques are an interesting class of diamond materials that can be used for a plethora of applications.

There has been low usage of FNDs as a biomarker due to their weak quantum efficiency compared to all other biomarkers, nanoparticle, and fluorescent dyes. Thus, the main challenge is to enhance the emission intensity from the FNDs. The NDs are subjected to nitrogen ion-implantation at an implantation energy 20keV with various implantation fluences. Implantation depth concentration and crystalline distortion level profiles have been calculated using Low Energy Approximation. The NV defects fabricated through implantation are optically active color centers which will enhance the photoluminescence properties by energy transitions between the defect states and carbon states. Here we report the comparison between the unimplanted and nitrogen ion-implanted diamond nanoparticles on the basis of photoluminescence and Raman spectroscopies. In addition, we will be investigating the concentration

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of nitrogen atoms and crystal disorder influence on the optical emission dynamics of diamond nanoparticles. The present study will provide guidance for the future synthesis of fluorescent nano-diamond markers for biosensing and bioimaging applications in multidisciplinary fields. For example, we can use the differently doped nanodiamond fluorophores mixed with milk powders as biomarkers to identify the various milk constituents.

2:00 PM EL05.11.03
Growth Mechanism of SiV Centre Rich Diamond Multiply Twinned Particles and Their Applicapility in µ-Light-Emitting Diodes
Jürgen Weippert1, Taro Yoshikawa1, Christoph Schreyvogel1, Lutz Kirste1, Michael Kunzer1, Andreas Graff2, Volker Cimalla1 and Vadim Lebedev1; 1Fraunhofer Institute for Applied Solid State Physics (IAF), Germany; 2Fraunhofer Institute for Microstructure of Materials and Systems (IMWS), Germany

The inclusion of Silicon Vacancy (SiV) centers into synthetic diamond has already proven to be a valuable tool for the production of optoelectronic devices such as p-i-n diodes, photonic crystals or single-photon emitters[1]. In our recently published work we have shown the preparation of synthetic diamond multiply twinned particles (MTPs) in icosahehedron shape[2]. Here we present the expansion of this work regarding MTPs having the shape of both completed dodecahedrons and icosahehedrons which were grown by plasma-assisted CVD on Si(111) surfaces. This process ensures the reliable inclusion of SiV centers thus eliminating the necessity of any post-CVD implantation methods. Also, the resulting lms provide a sufficient conductivity for further applications.

The growth mechanism was found to consist of several differentiable steps: first, octahedral, single crystalline particles grow up to edge lengths around ca. 300 nm. At this stage, the formation of penetration twin structures sets on, resulting in the controlled growth of particles with dodecahedral and later icosahedral symmetries. The SiV centers form predominantly by redeposition of sputtered Si atoms at the initial growth stages and by bulk diffusion along grain boundaries for thicker films.

Their characteristic photoluminescence emission at 738 nm was found to have a FWHM in the range 3-4 nm. Closed MTP layers were used to fabricate diodes and µ-LEDs based on vertical diamond/Ti Schottky contacts by sputtering 500 μm thick Ti electrodes atop the grown films. Already with this simple approach a long-time photostability with constant spectral features could be achieved.

References:

2:15 PM EL05.11.04
Effects of Annealing on Defect Concentrations and Structures in Irradiated Single-Crystal Diamond
Erik Vyhmeister-Cancel1 and Elias Garratt1,2; 1Michigan State University, United States; 2Fraunhofer Center for Coatings and Diamond Technologies, United States

Single-Crystal diamond is a promising material of interest for next-generation radiation sensors in extreme conditions, such as the LHC or FRIB. A major property of interest is the resistance of diamond to radiation damage.

Radiation damage in diamond is confined almost exclusively to the creation of point-like defects. Due to its radiation hardness, the lattice is not amorphized as in Silicon, with interstitial-vacancy pairs being the primary damage caused. At temperatures above 100C, carbon interstitials become mobile and can recombine with lattice vacancies, healing the lattice. At temperatures >400C, vacancies mobilize, further

Defect structures are studied by the use of Raman and Photoluminescence (PL) spectroscopy, expanding on previous work that used X-Ray diffraction (XRD). XRD imaging comparing irradiated to non-irradiated regions of diamond show no clear connection between diffraction profile and radiation damage. Radiation damage at doses of 10^15 neq/cm² does not appear to cause amorphization, but instead a distribution of point defects. Point defects in diamond are optically active, accessible with PL, and Raman can measure structural irregularities that create additional vibrational modes.

This study presents spatially resolved imaging of point defects, correlating residual damage directly to the intensity of incident radiation. The effects of different annealing procedures on the types of defects (GR1, NV0) present in the
diamond are investigated. Additionally, concentrations and the spatial correlations between different types of defects are studied.

Radiation damage causes decreases in detector efficacy and charge collection efficiency. Removing these point defects by annealing increases the overall lifespan of the detector, reducing operational costs. This research evaluates and determines the optimal annealing procedure for single-crystal diamond damaged by GeV heavy ions, and possible applications to other radiation damage.

2:30 PM BREAK

SESSION EL05.12: Nanodiamond
Session Chair: Anke Krueger
Wednesday Afternoon, December 4, 2019
Hynes, Level 1, Room 107

3:30 PM EL05.12.01
A Spectroscopic Surface Study of Amine-Terminated Nanodiamonds Kerry Whittlesea, Simon Astley, Anita Brady-Boyde, Joseph Durk, Zheshen Li, Tom Wang, Rachel Cross and Andrew Evans; 1Aberystwyth University, United Kingdom; 2Centre for Storage Ring Facilities (ISA), Denmark; 3Element Six, United Kingdom

Nanodiamonds are a promising nanomaterial being considered for an increasing number of applications as they possess many of the exceptional bulk diamond properties, such as hardness and non-toxicity, at sub-micron length scale, making them more bio-compatible1. The termination, functionalisation or modification of the nanodiamond surface is an important factor when considering its potential applications; for example, functionalising the nanodiamond to attach specific bio-molecules2. This is due to its high surface to bulk ratio and surface reactivity. There is further interest in nanodiamonds as fluorescent biomarkers due to the well-explored defect in diamond known as the nitrogen-vacancy (NV-) centre. Incorporation of the NV- centre, which is sensitive to external magnetic fields and can be detected optically3, is very successful in bulk diamond and in larger nanodiamonds4, but is still challenging for smaller nanodiamonds.

There is an interest in amine-terminated nanodiamonds as it would allow a variety of functional molecules, such as DNA, antibodies, and polymer building blocks, to be more easily and straightforwardly bonded to the nanodiamond2. Understanding the surface chemistry and properties is important in order to optimise the attachment of different molecules to the nanodiamonds and deliverance into the body.

In this study, the surface of amine-terminated nanodiamonds has been measured and characterised using a variety of spectroscopic techniques. Surface-sensitive photoelectron spectroscopy techniques (XPS, UPS, and NEXAFS) under ultra-high vacuum and in near ambient pressures (NAP-XPS) have been used to anneal and measure the surface of the nanodiamonds. Fourier Transform Infrared Spectroscopy (FTIR), a non-destructive widely used technique used to identify organic materials, was used to provide more detail on the chemical structure of the nanodiamond. The FTIR spectra were recorded at the AU-IR beamline at ASTRID2, Denmark, where the synchrotron radiation based FTIR provides enhanced spatial resolution as a result of increased brightness.

This paper presents a detailed spectroscopic study of amine-terminated nanodiamonds with the aim of better understanding the surface for potential biophysics applications.

References


3:45 PM EL05.12.02

Near Ambient Modification of Nanodiamond Substrates for Applications in Drug Delivery Simon Astley¹, Di Hu¹, Kerry Whittlesea¹, Tom Wang², Rachel Cross¹ and Andrew Evans¹; ¹Aberystwyth University, United Kingdom; ²Element Six, United Kingdom

Fluorouracil (5FU) is a highly asymmetrical, polar molecule commonly used in a range of cancer drug treatments including bowel, breast and skin cancer. Previous studies show that 5FU suffers a catalytic degradation on silver substrates, but is inert on graphene [1,2]. Nanodiamonds are enabling the exploitation of diamond’s unique properties at ever decreasing length scales in applications such as quantum optics, biosensors and drug delivery [3,4]. With their high surface: bulk atomic ratio, the surface termination of nanodiamonds is a crucial design parameter in all of these applications; for example in controlling their attachment to specific bio-molecules or aggregation in specific biological sites based on their zeta potentials [5]. The Nitrogen-Vacancy (NV-) centre, which can be commonly found in nanodiamonds, allows for in-situ biosensing.

To investigate changes in the surface termination of nanodiamonds exposed to gases and liquids at high temperature, in-situ photoelectron spectroscopy has been applied under ultra-high vacuum and at near-ambient pressures using laboratory and synchrotron radiation excitation. This has been done to monitor changes in chemical composition and electronic properties of the nanodiamonds and to observe, in real time, the evolution of oxygen species to discover the optimal treatment controls for obtaining specific bonding types for attaching individual drug molecules.

Using these modified surfaces, 5FU has been attached to various diamond and nanodiamond surfaces. The adsorption was found to be strongly dependent on the surface termination, where the ratio of 5FU to the diamond surface can be controlled, and this effect can be seen for all sizes of nanodiamonds.


4:00 PM EL05.12.03

Fabrication of Nanodiamond and Q-Carbon by Ultrafast Quenching of Carbon Structures for Electron Field Emission Devices Ariful Haque and Jagdish Narayan; North Carolina State University, United States

In this study, we report on the direct conversion of sp² rich carbon nanotube (CNT) and amorphous carbon structures into nanostructured diamond and Q-carbon by nanosecond pulsed laser annealing for electron field emission (FE) applications. Upon irradiating the CNTs with nanosecond pulsed laser at a suitable energy density, the tips and bends of the CNTs are melted in a highly undercooled state (due to the geometry constraint of the temperature distribution and 1D heat flow) to form the ideal platform for efficient FE devices. The highly undercooled state of carbon is a metastable phase and the nucleation of nanodiamonds occurs from this state. The whole process (rapid melting, solidification, and growth) takes place in less than 200-250 ns. The characteristic Raman peak at 1332 cm⁻¹ downshifts to 1324 cm⁻¹ for diamond nanostructures due to the phonon confinement effect. The high-resolution electron-energy-loss spectroscopy of the laser irradiated CNTs shows a characteristic peak at 292 eV for σ⁺ for sp³ bonding of diamond. The diamond crystal structure and the local crystalline perfection and orientation at the laser...
irradiated regions are confirmed by electron-back-scatter-diffraction in high-resolution scanning electron microscopy. The laser irradiated CNT structures with nanodiamond seeds were used to grow large diamond crystals in hot-wire chemical vapor deposition. Furthermore, nanosecond pulsed laser annealing technique was used to convert the amorphous carbon film (grown by pulsed laser deposition) into large area quenched carbon (Q-carbon) film for field emission applications. The Q-carbon field emitter shows excellent field emission properties, such as a low turn-on electric field of ~2.40 V/μm, the high emission current density of ~32 A/cm² and a critical field of ~2.45 V/μm for transition from a linear region to the saturation region in the F-N plot. Moreover, the Q-carbon field emitters illustrate enhanced field emission properties and good field emission stability throughout the temperature range from room temperature to 500K. Overall, this work shows that the pulsed laser annealing technique can be used efficiently for the controlled fabrication of nanodiamond and Q-carbon based high-performance field emitters on different substrates for versatile applications.

4:15 PM EL05.12.04
Nanodiamonds as Raman Probe to Assure Blood Quality Sofia Navarro-Espinoza, Karla Santacruz-Gómez, Mónica Acosta-Elias, Erika Silva-Campa, Jose A. Sarabia-Sainz, Alexel J. Burgara-Estrella, Aracely Angulo-Molina, Beatriz Castaneda, Diego Soto-Puebla and Martin R. Pedroza-Montero; Universidad de Sonora, Mexico

Storage of blood, even in blood bank conditions, generates the deoxygenation of red blood cells (RBC) and morphological changes that alter the erythrocyte membrane, changing its normal shape and functional reliability. These disturbing phenomena impair the capacity of RBC to transport oxygen and diminish the quality of blood. In this work, we investigate how the RBC changes evolve in time (from 0 to 18 days) with a combined scanning laser technique based on AFM-Raman to evaluate roughness, osmotic fragility, and oxygenation characteristics. To enhance the Raman signal and distinguish the oxygen markers, we added nanodiamonds (ND). The ND showed an additional feature; they helped to reoxygenate the blood and interrupted the generation of reactive oxygen species (ROS). The analysis of the deoxygenation process revealed that morphological alterations do not generate biochemical changes in the hemoglobin Raman fingerprint, even though RBC became more fragile and prone to breakage. This effect is noteworthy because after a transfusion RBC have to pass through tiny capillary vessels, where good elastic properties of RBC are needed. The results also indicate that blood has to be used within the first five days after collection to reduce storage lesions and assure quality.

4:30 PM EL05.12.05
Thermometry of Intracellular Structures with Nanodiamonds Martín R. Pedroza-Montero¹, Francisco A. Pedroza-Montero¹, Karla Santacruz-Gómez¹, Mónica Acosta-Elias¹, Erika Silva-Campa¹, Jose A. Sarabia-Sainz¹, Alexel J. Burgara-Estrella¹, Aracely Angulo-Molina¹, Beatriz Castaneda¹, Sofia Navarro-Espinoza¹ and Diego Soto-Puebla¹; ¹Universidad de Sonora, Mexico; ²universidad de Sonora, Mexico

Nanodiamonds (ND) have a significant impact on medicine and biology because of their biocompatibility properties and unaltered performance in physiologic environments. Furthermore, their low toxicity allows working very close to cells, even at the intracellular level. The metabolic processes related to the life of the cell generates or consumes thermal energy. The disturbance of those vital processes by pathologies and stressing factors induce changes in the cell temperature, while reparation or programmed death are triggered. The measurement of temperature improve the knowledge of biologic events, and it is a useful resource for monitoring treatment or therapy; it also provides information of particular interest in the study of the pathology of cancer. A nanothermometer based on ND is an excellent option because it possesses magnetic, electric, and optical properties that exhibit a dependence on temperature in the biologic range centered around 37.5°C. In this work, we present experimental insights and data from the emission spectra of fluorescent nanodiamonds (FNDs), and we followed its behavior as the temperature changes through a phenomenological model. For a more realistic approach, we used FNDs with different N-V centers concentrations in solution. We fit the fluorescence curves to remove background and other spurious luminescent processes associated mostly with impurities or contamination. We also performed calculations based on changes of intensity, semi-width, and position shifts related to the Zero-Phonon Lines of N-V centers to obtain thermometric scales with low errors and precision around 0.01°C. Also, we incubated FND HeLa cells and evaluated the time stability of the fluorescent signal at RT. The results allow establishing FND as thermal probes for reading temperature both in situ and in real time, based in their luminescence signal with the use of simple instrumentation.

4:45 PM EL05.12.06
Nanodiamonds for Improving Lubrication of Titanium Surfaces in Simulated Body Fluid Asghar Shirani¹.
Hip implants are often made from titanium or titanium-based alloys. However, wear during the operation inside the human body is a key source of implant failure and adverse health effects. We propose new insight on the lubrication of titanium components. Addition of small amounts (less than 0.2 wt.%) of nanodiamonds (NDs) to simulated body fluid promotes a substantial improvement in friction (3 times reduction) and wear (up to 2 orders of magnitude wear reduction) behavior of the titanium surfaces. Interestingly, the amount of NDs needed for improvement of friction and wear characteristics is critically dependent on the applied loads. With higher contact loads, larger concentrations of NDs are needed for better friction and wear reduction. Analysis of the wear track formed during sliding indicates the formation of a carbon-rich tribolayer which improves tribological properties of the contacting surfaces. Our results suggest that the carbon layer is formed from the nanodiamonds embedding in the top layer of titanium.

8:30 AM *EL05.13.01
Simulation of Diamond Surface Chemistry—Reactivity and Properties Karin Larsson; Uppsala University, Sweden

The diamond material possesses very attractive properties, such as superior electronic properties (including high carrier mobility), large electrochemical potential window, and a controllable surface termination. Boron-doped diamond surfaces, with attached Pt nanoparticles as the catalytic surface, are nowadays working as a new class of electrode materials. The boron-doped diamond electrode is a semiconducting material with very promising properties like i) a wider potential window in aqueous solution, ii) low background current, and iii) corrosion stability in aggressive environments. The phenomena of diamond surface termination have experimentally been observed to significantly influence the broad-band infrared reflectivity and conductivity. H-terminated diamond surfaces have been found to be hydrophobic, and to show unique p-type surface electronic conductivity. On the other hand, oxygen-terminated diamond surfaces generally show hydrophilic properties, but no electronic conductivity.

The surface reactivity of diamond is expected to affect both chemical processes at the surface and properties related to the surface electronic structure. Examples of factors with the capability to influence the surface reactivity are i) type of plane, ii) surface termination, and iii) doping. Theoretical modeling based predominantly on Density Functional Theory (DFT) has during the last decade proven to become highly valuable in the explanation and prediction of experimental results. The simulation and theoretical analysis of especially surface reactivities has been shown to aid important information.

At this presentation, the combined effect of surface termination and doping on the electronic properties of diamond surfaces, will be especially highlighted. In addition, the effect by a water adlayer will also be considered. All results are based on high-level calculations using DFT calculations.

9:00 AM EL05.13.02
Diamond Surface Band Bending Estimation by ARXPS Gonzalo Alba¹, Rodrigo Alcántara¹, Pilar Villar¹, Jesús Cañas², Juliette Letellier², Gauthier Chicot², David Eon², Daniel Araujo³ and Julien Pernot²; ¹University of Cádiz, Spain; ²Université Grenoble Alpes, Institut Néel, France

Diamond surface XPS contributions is still having a big controversy in the literature and most of the measurements are based on surface normal photoelectron emission. In this sense, angle-resolved XPS experiments allow to obtain different sensitivity depth by varying the electron take-off angle, what is useful to clarify surface contributions, although it is rarely found in diamond.
Recently, a downward band bending in the very near surface has been reported by using this technique. However, the common interpretation of a band bending in X-ray photoelectron spectroscopy, based on peak energy shifts referenced to a known fixed energy level, can be wrong in some cases. Besides XPS peak shifts could exist due to band bending, the correct estimation in the case of a large band bending with a short width near the surface must be done considering the band bending region as a new XPS peak. The shape of this peak depends on the band bending characteristics and XPS experimental parameters.

In this work, an approximation to the shape of a surface band bending is described theoretically and applied to the deconvolution of ARXPS spectra of H-terminated and O-terminated diamond surfaces. A downward and an upward surface band bending are found, respectively.

REFERENCES:

9:15 AM EL05.13.03
Ab Initio Study—Ni Catalytic Effect on Diamond (111) Surface Jeongwoo Yang¹, Jong Hwan Park¹, Jin Woo Park², Byung Deok Yu² and Nong Moon Hwang¹; ¹Seoul National Univ, Korea (the Republic of); ²University of Seoul, Korea (the Republic of)

Although catalytic metals play an essential role in the production of industrial high temperature and high pressure (HTHP) diamonds, their role has not been clearly understood. This study provides a microscopic interpretation on the role of the Ni catalytic metal through density functional theory (DFT) calculations. In addition to the metal solvent-catalytic effect, it has been found that Ni removes the strong π-bond (Pandey chain) on the diamond (111) surface, which is an obstacle to diamond growth. When Ni atoms were attached to the diamond (111) surface, the diamond bulk-like surface was more stable than the Pandey chain surface structure, indicating that de-reconstruction could occur by Ni. The results of projected density of state (PDOS), charge distribution, and Bader charge analysis show directly that the surface C-C π-bond is weakened by the charge redistribution caused by covalent bonding of Ni and C. Also, the nudged elastic band (NEB) calculation shows that the Ni surfactant-mediated growth is kinetically possible. Therefore, applying these results to other elements will provide a better understanding of the role of catalytic metals in diamond growth.

9:30 AM EL05.13.04
Fluorination of Diamond Materials for the Control of Surface Properties Anke Krueger; Universität Würzburg, Germany

For many applications the surface chemistry of diamond is a key factor for the control of properties such as the wetting behavior, the electron affinity of the surface[1] or the control of charge states of lattice defects[2]. By attaching either electron withdrawing or donating surface groups the charge state e.g. of shallow NV centers can controlled.

Additionally, surface termination also plays a role in the density of states and the band structure of the diamond material. Therefore, the homogeneous and stable surface functionalization with electrically active atoms or groups is a key step in the fabrication of diamond based devices for e.g. photocatalytic or quantum applications. Here we report on the fluorine termination of diamond surfaces using different wet-chemical fluorination methods. These treatments lead to highly functionalized materials with different surface species. Characterization using e.g. solid-state NMR techniques, XPS and IR methods have been used to characterize the fluorinated materials qualitatively and quantitatively.

This research has received funding from the European Union’s Horizon 2020 Program (Grant Agreement no. 665085, DIACAT, www.diacat.eu) and Deutsche Forschungsgemeinschaft under grant KR3316/6-2.

References
9:45 AM EL05.13.05
Real-Time Oxidation and Reduction of Diamond Surfaces at Near Ambient Pressure Simon Astley, Di Hu, Johnathan Ash, Joseph Durk, Kerry Whittlesea, Simon Cooil, Rachel Cross and Andrew Evans; Aberystwyth University, United Kingdom

The effects of the diamond surface can influence its use in electronic, optical and quantum applications and it is particularly important for nanodiamonds, due to their large surface to bulk ratio. The usual preparation methods for single crystal diamond involve mechanical polishing and etching with the aim of producing flat, defect-free O-terminated or H-terminated surfaces. Nanodiamonds are prepared using similar etching procedures. The surface structure and the terminating species influence properties such as wettability, electron emission and adsorption and the control of surface properties requires precise control of the preparation methods. Here we compare the oxidation and reduction of single crystal diamond and nanodiamonds using acid etching, in-vacuo plasma exposure and annealing in near ambient pressure oxygen and hydrogen. The surface sensitive methods of ultraviolet and x-ray photoelectron spectroscopy (PES) using laboratory and synchrotron sources were used to monitor changes in the physical, chemical and electronic structure during surface oxidation and reduction. Near-Edge X-ray Absorption Spectroscopy (NEXAFS) was applied to determine the unoccupied density of states and the orientation of surface bonding and this synchrotron method is particularly sensitive to non-diamond carbon species at the surface. In-vacuo annealing removes and modifies the surface oxygen as revealed by real-time monitoring of the O1s and C1s core level spectra from room temperature to 1000 C. The PES results are compared with DFT calculations that suggest that ether (C-O-C) groups are the preferred bonding arrangement with alcohol (C-OH) groups preferentially desorbed during the annealing process. Changes in composition were further correlated with changes in electrical conductivity and work function. DFT was also applied to model the desorption of oxygen species at specific temperatures and showed a deformation in the surface/sub-surface structure in situations where only some types of oxygen groups are present. Oxidation and reduction of diamond and nanodiamond surfaces at higher gas pressures were studied using near ambient pressure PES to reveal surfaces of comparable and, in some cases, superior quality to those produced by in-vacuo annealing and plasma exposure. At 1 mbar of O2gas, non-diamond carbon species were removed and an additional oxygen species was observed that was not present on the vacuum-prepared samples, but was predicted by the DFT calculations.

10:00 AM BREAK

SESSION EL05.14: Quantum Effects III
Session Chair: Christoph Becher
Thursday Morning, December 5, 2019
Hynes, Level 1, Room 107

10:30 AM *EL05.14.01
Diamond Nanophotonics with Group IV Defects Igor Aharonovich; University of Technology-Sydney, Australia

Diamond color centers are attractive candidates for integrated quantum photonics circuitry. Over last decade, much focus has been put to study the NV center in diamond. However, its broad emission and low proportion of zero phonon line photons, makes it challenging to scale up and efficient collection of coherent photons. In this talk I will describe our recent efforts into studying a new class of defects, associated with group IV elements such as Si and Ge. These defects exhibit narrow band emission and form a symmetric complex with two vacancies, therefore less susceptible to strain. In my talk I will focus on two aspects: First, I will describe the progress of fabricating nanoscale diamond membranes, that we utilize for electrical excitation and for device fabrication. An example of a rink resonator and a microdisk cavity is shown in figure 1. Second, I will describe emerging experiments involving anti stokes excitation of single quantum emitters, that provide a new avenue for optical sensing with unprecedented sensitivity. I will summarize with an outlook into new potentially interesting color centers.

11:00 AM EL05.14.02
Identifying the Structure of the SnV⁻ Defect in Diamond—Experimental Evidence of the Split-Vacancy Configuration

Ulrich Wahl¹,², Joao Guilherme Correia², Renan Villareal¹, Emilie Bourgeois³,⁴, Milos Nesladek³,⁴, Andre R. Vantomme¹ and Lino M.C. Pereira¹; ¹KU Leuven, Belgium; ²Instituto Superior Técnico, Portugal; ³imec, Belgium; ⁴Institute for Materials Research, Belgium

Point defects in diamond are being intensively investigated, both for their applications in processing and communication of quantum information, as well as for metrology. So far, the negatively charged nitrogen-vacancy center (NV⁻) has been the most studied defect [1]. Thanks to its efficient optical spin polarization and spin-state dependent fluorescence, it is being exploited, for example, in the context of high-sensitivity magnetometers [2]. More recently, owing to their superior optical properties, the group-IV-vacancy centers (SiV⁻ [3, 4], GeV⁻ [5] and SnV⁻ [6]) have emerged as the leading type of point defects for quantum computing and networking applications. Whereas it is generally accepted that the N atom in the NV⁻ center occupies a substitutional C site, the group-IV atoms in group-IV-vacancy centers are expected to occupy bond-centered sites, in a split-vacancy configuration. In this configuration, rather than being accompanied by a neighboring vacancy, the group-IV atom is located at the center of two neighboring lattice positions, while the vacancy is “split” over the two lattice sites. However, experimentally, these structural configurations had so far been only indirectly determined.

In this contribution, we present a detailed, direct characterization of the structure of the SnV⁻ defect. To this end, we relied on the electron emission channeling technique to determine the lattice site of implanted radioactive ¹²¹Sn ions in diamond with very high precision (experiments performed at the ISOLDE facility at CERN, Geneva). The anisotropic patterns of the charged β⁻ particles emitted during the decay of the radioactive isotopes are characteristic of the lattice site of the emitting Sn atoms. From fitting the experimental data to theoretically calculated patterns [7] using a two-dimensional fit procedure [8], the Sn lattice location can be accurately determined. Using a combination of electron emission channeling from ¹²¹Sn and photoluminescence measurements, we have unambiguously identified the SnV⁻ defect in the split-vacancy configuration, with the Sn atom located exactly at the bond-center position (with a precision better than 0.04 Å). While in the as-implanted state the PL spectrum from the sample was dominated by radiation damage-induced features, following annealing at 915°C for 1 hour the signature of the SnV⁻ center (in the form of a strong 621 nm line) was clearly visible. Establishing a detailed understanding of the SnV⁻ structure is particularly important, since the superior properties of the group-IV-vacancy centers are to a large extent a consequence of the inversion symmetry of the split-vacancy configuration.

lab-grown diamonds. Microwave assisted plasma vapour deposition reactors have been widely used to elaborate carbon-based materials in particular diamond. The performance of the process is strongly influenced by the interaction between microwave and the plasma which in fact depends on the precursor gas composition, pressure and operating conditions. Growing diamond for jewellery implies growing rough diamond of 4 to 6 mm in thickness and managing the colour of the diamond after they are cut. Many attempts with different gas composition have been achieved around the world leading to different colours of diamonds as well as different growth rates. We propose here an overview of the different processes used to grow these thick diamonds. Also we propose to show how the local conditions at the plasma / surface interface may strongly change as a function of the conditions in the case of the most simple gas composition, i.e. a mixture of hydrogen and methane. A self-consistent model has been constructed incorporating the stiff methane-hydrogen chemistry. We will discuss some of the results obtained using this self-consistent model and their comparison with the experiments.

SESSION EL05.16: Diamond for Electronic Devices  
Session Chair: Gauthier Chicot  
Thursday Afternoon, December 5, 2019  
Hynes, Level 1, Room 107

1:30 PM EL05.16.01  
Temperature Reduction of AlGaN/GaN MIS HEMTs Using Overgrown Polycrystalline Diamond Films  
Junya Yaita1,2, Kotani Junji1,2, Atsushi Yamada1,2, Shiro Ozaki1,2, Yoichi Kamada1,2, Toshihiro Ohki1,2, Yuichi Minoura1,2, Yusuke Kumazaki1,2, Naoya Okamoto1,2, Kozo Makiyama1,2 and Norikazu Nakamura1,2; 1Fujitsu Limited, Japan; 2Fujitsu Laboratories Ltd., Japan

GaN-based high electron mobility transistors (GaN HEMTs) have been expected for high output power density applications such as radars and long distance wireless communication. Although the GaN has superior electric characteristics, a low thermal conductivity of GaN limits the output power density. In order to improve thermal dissipation, the GaN HEMTs on high-thermal-conductivity diamond has been reported. In addition to the backside of GaN HEMTs, diamond on GaN is expected to improve thermal dissipation. However, there were few reports on the deposition of diamond layer on GaN HEMT and the heat-spreading effect by diamond deposition has not been investigated in detail. In this study, we carried out growth of diamond on GaN HEMTs and investigated the heat-spreading effect by Raman thermography.

Polycrystalline diamond films were directly grown by hot-filament chemical vapor deposition (HF-CVD) on AlGaN/GaN MIS HEMTs. The HEMT devices with SiNx insulator showed low gate leakage current of <10^-2 A/mm even though the diamond growth was carried out under high temperature. In addition, the HEMTs with overgrown polycrystalline diamond films showed higher transconductance of 154 mS/mm than that of non-diamond grown HEMTs of 134 mS/mm. In order to evaluate effect of surface diamond heat-spreader, we performed Raman thermography and clearly observed the temperature reduction of around 10 degrees even under relatively low power operation of ~5 W/mm. This temperature reduction inhibits the degradation of electron mobility caused by increased optical phonon scattering, resulting in increase in transconductance as we experimentally observed. Therefore, direct growth of diamond by HF-CVD on AlGaN/GaN MIS HEMTs enables to temperature reduction and improve its performance.

[Acknowledgements]: This work was partially supported by Innovative Science and Technology Initiative for Security, ATLA, Japan.

1:45 PM EL05.16.02  
Seeding and Growth of Diamond on GaN and AlN  
Paul W. May, Edmund Smith, Afaq Piracha and Robson Mackenzie; Bristol University, United Kingdom

With improvements to epitaxial growth and device fabrication, GaN device performance is now limited by near-junction heat removal1. A possible solution to this problem is to deposit a layer of diamond onto the GaN to act as a heat spreader2. Diamond has excellent thermal conductivity, making it well-suited for use as a heat spreader. However, its use in GaN devices is hindered by the significant differences in thermal expansion and lattice constants.
between diamond and GaN\textsuperscript{3,4,5}.

Work has been centred on developing a low temperature diamond CVD process to overcome the significant lattice mismatch and thermal expansion differences between the diamond and GaN layers, which has previously resulted in delamination. A novel seeding process involving 2-step seeding with micro- and nano-diamond particles has also been developed to increase thermal conductivity across the diamond-GaN interface. The deposited layers have been non-destructively examined utilising X-Ray Tomography (XRT), allowing an assessment of the quality of the interface in the middle of the wafer without inducing any stresses and potential delamination onto the substrate. With the optimisation of growth procedures, diamond layers 50 µm thick can now be reliably grown directly onto GaN substrates with no barrier layer, however the interface remains too mechanically weak for most device applications.

To improve adhesion, diamond films were also grown on GaN substrates with barrier layers of either 200 nm of AlN or 20 nm of Al metal. The Al layer is thin enough that we believe it completely converts to aluminium carbide during the CVD process. We shall present results from these growth studies and evaluate the thermal and mechanical performance of these barrier layers, as well as report on progress towards developing a large-area CVD reactor suitable for 6”-diameter GaN wafers.

References

2:00 PM EL05.16.03
The Impact of Plasma Temperature on the Stress and Quality Factor of Over-Grown Polycrystalline Diamond on GaN
Mohamadali Malakoutian\textsuperscript{1}, Matthew A. Laurent\textsuperscript{1} and Srabanti Chowdhury\textsuperscript{2}; \textsuperscript{1}University of California, Davis, United States; \textsuperscript{2}Stanford University, United States

Gallium Nitride (GaN) as a wide bandgap material, is an attractive choice for high-power and high-frequency semiconductor devices. However, self-heating effect limits GaN-based high electron mobility transistor (HEMT) capabilities due the lack of effective heat spreading through the device [1]. Polycrystalline (PC) diamond, owing to its high thermal conductivity (10-2000 W/m.K), can be used as a capping layer for spreading the heat [2]. For effective cooling, diamond must be grown as close as possible to the source of heat, which is the channel in a HEMT. In this abstract we describe our approach of growing PC diamond on GaN layer to allow maximum heat transfer from the GaN channel to the diamond layer. Achieving a high-quality diamond-GaN interface is necessary to accomplish effective heat transfer. As hydrogen plasma is one of the main species in diamond growth using microwave plasma chemical vapor deposition system, it damages the GaN and changes the properties of the 2-dimensional electron gas (2DEG). A 20 nm Si\textsubscript{3}N\textsubscript{4} has been used as a protection layer on top of the N-polar GaN on sapphire wafer, which also reduces delamination of the diamond by making a SiC interlayer. As the coefficient of thermal expansion (CTE) for diamond (~1.1 µm/m.K) and GaN/sapphire (~4.1/5.3 µm/m.K) are different, the possibility of diamond delamination due to large residual stress is high. In another aspect, to reach the thermal properties of bulk diamond, it is vital to increase the quality of the grown layer. In this work, we have used Raman spectroscopy and scanning electron microscopy (SEM) to investigate the effect of growth plasma temperature (600-850 C, with 50 C steps) on both the stress and quality factor of PC diamond.

The grain size of the diamond layer increases from 113 nm at 600 C to 419 nm at 850 C and the thickness changes from 130 to 696 nm when the temperature changes from 600 to 850 C. We have observed a higher growth rate in vertical axis than lateral axis, which is due to the high nanoparticle seeding density (>10\textsuperscript{12} cm\textsuperscript{-2}) and growth using hydrogen plasma. The quality factor can be determined by \textit{sp}\textsuperscript{3}/\textit{sp}\textsuperscript{2} carbon bonding ratio of their Raman peaks. Diamond quality factor shows a parabolic behavior and increases with temperature (90.10% at 600 C to 98.57% at 850 C), as the thickness and grain size of the film increase.

The residual stress (thermal and intrinsic) of the diamond film plays a critical role in the delamination of diamond from the substrate. Thermal stress is caused by the difference in the CTE between diamond and substrate during the cooling cycle and intrinsic stress is due to the incorporation of impurities and defect formation. The residual stress in the diamond film can be calculated using the shift in the \textit{sp}\textsuperscript{3} diamond Raman peak from 1332 cm\textsuperscript{-1} [3]. The diamond
Layer stress shows a compressive nature and increases with temperature by a parabolic behavior (-4.2 GPa at 600 °C to -6.3 GPa at 850 °C). Increase in the thickness and grain size is the main reason for larger compressive stress. In this study, up to 850 °C we observed no delamination of the diamond film from the substrate. However, the absolute value of the stress is high, which can be explained by the large compressive stress in sapphire during the cooling process.

Increasing thickness and grain size of diamond results in a higher quality factor (close to bulk diamond), while increases the compressive stress and the possibility of delamination. So, in order to prevent delamination and have a high-quality diamond on GaN/sapphire, it is needed to decrease the compressive stress by relaxing PC diamond layer. The relaxation of diamond layer can be done by adding a thin ultra-nano-crystalline-diamond (UNCD) layer during the growth.

![Image](image-url)


This research is supported through the SRC JUMP program.

**2:15 PM EL05.16.04**

**Design of Efficient Schottky Diodes for Medium-Voltage AC/DC Power Converters**

Xiaoxue Wang¹, Wesley Spain¹, Matthias Muehle², John D. Albrecht¹,², Timothy Grotjohn¹,² and Tom Zimmermann¹; ¹Michigan State University, United States; ²Fraunhofer USA, Inc., Center for Coatings and Diamond Technologies, United States

With the development of long-distance transmission, offshore transmission and renewable energy technology, AC and DC systems have become the popular trend for future power systems. The AC/DC converter is the key part to make it happen. In modern power systems, converter modules like half-bridge structures and full-bridge structures of paralleled insulated-gate bipolar transistor (IGBT) and Schottky barrier diodes are common in the industry. However, the current of a single Schottky barrier diode at the same voltage level lacks greatly behind the IGBT performance. Thus, multiple Schottky barrier diodes may need to be paralleled with IGBTs in order to match the current performance of the IGBTs operating at the same voltage level. Furthermore, due to inherent small variances in the manufacturing process of the Schottky barrier diodes, devices will slightly differ from each other and current asymmetries and an imbalanced voltage distribution potentially occurs in the power modules, leading to higher harmonic waves and severe power losses. Therefore, there are urgent needs of improved Schottky barrier diodes for efficient AC/DC converters in the market.

Diamond is considered as an ultimate semiconductor for high power applications due to its high charge carrier mobility and saturation velocity and excellent thermal conductivity. The extremely high breakdown field up to $10^7$ V/cm is very promising for medium and high voltage rectifiers and converters. To address the highly visible diode performance shortcomings, we designed and investigated a high-power vertical diamond Schottky barrier diode. The newly designed high-power diodes possess a current drive higher than 50 A at a forward bias of 10 kV in the temperature range between room temperature (300 K), optimal diode operation temperature (450 K) and the temperature at full carrier activation of the boron acceptors (800 K). However, the diode performance will be affected by several parasitic elements originated by the choice of the used materials and the device design, which can lead to an electrical field concentrating edge effect. In order to decrease the electric field within the high-power diode and to improve its performance, this work investigates edge effect termination strategies by introducing passivation layer structures, n⁺-guard rings, and floating n⁺-islands. Several high-power diode designs were in-silico tested at different temperatures (300 K, 450 K and 800 K). According to the TCAD simulations, the on-resistance of the power-diode at 450 K is the lowest and a high current density of ~2500 A/cm² can be achieved at 10 kV for the basic diamond Schottky diode design. This performance is also investigated versus variations in the expected electric field breakdown strength of diamond. The implementation of passivation layer structures, guard rings, and floating islands is studied for performance improvements. The here developed design shall be technologically realized and implemented in a highly efficient AC/DC power converter, later on.

**2:30 PM EL05.16.05**

**Experimental and Theoretical Study of Impact of Methane Concentration on Boron-Doped Single Crystal Diamond Films for Schottky Barrier Diodes**

Rozita Rouzbahani¹,², Fernando Lloret¹,², Danny E. Vanpoucke¹,²,
Paulius Pobedinskas\textsuperscript{1,2}, Shannon S. Nicley\textsuperscript{1,2,3}, Daniel Araujo\textsuperscript{4} and Ken Haenen\textsuperscript{1,2}; \textsuperscript{1}Institute for Materials Research (IMO), Hasselt University, Belgium; \textsuperscript{2}IMOMEC, imec vzw, Belgium; \textsuperscript{3}Department of Materials, University of Oxford, United Kingdom; \textsuperscript{4}Dpto. Ciencia de los Materiales, Universidad de Cadiz, Spain

Despite recent advances in the synthesis of chemical vapor deposition (CVD) single crystal diamond (SCD), the device performance of applications based on diamond still remains far below the theoretical capacities.\textsuperscript{1} This is mostly associated with the presence of dislocations which leads to an increase of the leakage current and a reduction of the boron concentration in the heavily B-doped layer.\textsuperscript{2} Therefore, the optimization of the growth conditions of B-doped layers has a crucial role in the improvement of diamond based electronic applications such as Schottky barrier diodes. We have grown a series of B-doped SCD films which were characterized to identify the optimal conditions. The B-doped SCD films were grown by microwave plasma enhanced CVD in a home-built reactor on 3 X 3 mm\textsuperscript{2} Ib (100)-oriented high pressure high temperature (HPHT) substrates. Two sets of samples, B-doped and un-doped, were grown with different amount of methane concentration (0.5%-3%) in the plasma. For heavily B-doped SCD depositions, trimethylboron (TMB) was used as the boron source with a constant 997 ppm \text{[B]/[C]} ratio. For un-doped samples, the residual TMB in the chamber was used. The grown layers were characterized by Hall effect in a wide temperature range, Fourier transformed infrared (FTIR) spectroscopy, Raman spectroscopy, X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), optical microscopy, and transmission electron microscopy (TEM). By means of TEM, the high quality of the $p^{++}$ and $p$ layers was shown, except for the sample grown with 0.5% methane concentration, on which defect features similar to etch-pits were observed and confirmed by AFM. This sample also showed a very low boron incorporation into the $p^{++}$ layer due to the plasma gas chemistry which seems to create etch-pits, as seen in the morphology. FTIR\textsuperscript{3}, Raman spectroscopy\textsuperscript{4}, and Hall effect measurements indicate a higher B-doping level when the methane concentration is increased in both heavily and lightly B-doped SCD films. The electrical conductivity and mobility of the $p^{++}$ samples grown at 1%, 2%, and 3% methane concentration had almost no temperature dependence due to the metallic-like conduction properties in these heavily B-doped films. A careful investigation of the XPS spectra of lightly B-doped SCD layers at various methane concentrations indicated that the intensity of B 1s peak became stronger by increasing the methane concentration. The C K-edge XAS spectra of these layers were recorded in surface sensitive total electron yield (TEY) mode under different incident angle, which demonstrated that the diamond lattice structure can be distorted by increasing the methane concentration resulting in a higher B-doping level. The increase of the B-doping level with increasing methane was corroborated by first principle density functional theory (DFT) calculations. These showed that the presence of CH\textsubscript{2} sites has no significant impact on the binding energy of an adsorbed B atom. However, the presence of CH\textsubscript{2} sites increase the chance of H-defect site formation, providing additional B binding sites. The effect of using various methane concentrations in heavily B-doped SCD layers were further studied in their influence on the performance of Schottky barrier diodes.

References:

2:45 PM CLOSING REMARKS AND STUDENT AWARDS

SYMPOSIUM EN01

Challenges in Battery Technologies for Next–Generation Electric Vehicles and Grid Storage Applications
December 2 - December 5, 2019

Symposium Organizers
Maria Forsyth, Deakin University
Xiaolin Li, Pacific Northwest National Laboratory
Cengiz Ozkan, University of California, Riverside

Final Program 1/13/2020 323
8:00 AM *EN01.01.01

**Design Strategies for Anchoring Sulfur in Metal-Sulfur Batteries** Aninda J. Bhattacharyya; Indian Institute of Science, India

Over the last decade, there has been a paradigm shift towards usage of earth abundant and cost effective materials in rechargeable batteries. A prominent example in this context, is sulfur. Sulfur delivers a high theoretical capacity of 1672 mAh g⁻¹, nearly one order higher compared to the best known intercalation cathodes (IOCs) used in Li/Na-ion batteries. The high theoretical capacity originates from the possibility of higher than one exchangeable Li-ion per S-atom (theoretically two exchangeable Li-ions per S-atom) as compared to only one Li-ion/formula unit of IOC. Additionally, S is cheap, highly abundant and non-toxic in nature. Despite these advantages, the chemical reactions determining the mechanism and quantum of electrical energy storage in a liquid electrolyte based Li-S battery pose several challenges. The main challenge is due to the various intermediate polysulfides formed during the reversible conversion of elemental S₈ to metal-sulfide. Bulk of the work related to metal-S rechargeable battery revolves around materials design strategies of a suitable carbon/(non-carbon)-host matrix targeted towards the entrapment of S and prevention of leaching out of polysulfides into the electrolyte. However, this limits the extent of S-loading and depending on the host may simultaneously increase the un-utilizable mass of S in the electrode. The presentation will discuss some of our important recent results in the context of M-S (M: Li, Na, Mg) highlighting the critical role of materials design and in operando monitoring studies for the development of highly stable metal-S bateries. The talk will discuss at length various ways for efficient anchoring of sulfur and the polysulfides at the S-cathode for various rechargeable metal-S batteries. Strategies will include (a) design of novel S-scaffolds based on molecular systems such as covalent organic frameworks (COFs), conducting carbon-based scaffolds, (b) additives and (c) interlayers based on non-carbonaceous nanoparticles. Our studies reveal several interesting fundamental insights related to the mechanism of storage which eventually have strong bearing on the metal-sulfur battery performance.

8:30 AM EN01.01.02

**Formation of Magnesium Dendrites in Magnesium-Based Batteries and Design of Metallic Magnesium Anodes** Rachel D. Davidson; Texas A&M University, United States

We have recently demonstrated the first definitive examples of dendrite formation in magnesium batteries and will additionally detail our progress towards design of metallic anodes which mitigate such growths. The utilization of metallic anodes holds promise for unlocking high gravimetric and volumetric energy densities for rechargeable batteries, however, lithium metal has a high propensity for dendrite formation, the plating of lithium as anisotropic fractal structures that can bridge across liquid and solid electrolytes to the cathode, thereby short circuiting the cell. Such catastrophic failure represents a major roadblock to this seemingly simple approach to achieving improved storage capacities. Magnesium-based batteries are considered a possible alternative, given the high earth-abundance of magnesium and the potential for higher volumetric energy density offered by its divalent charge. A promising advantage of switching to Mg-based batteries derives from the many reports which claim that Mg is inherently non-dendrite forming. Initial reports noted that Mg could be plated as relatively smooth deposits under charging conditions that resulted in dendritic growth for lithium. Since these reports, there has been substantial progress in development of cathodes and electrolytes, however, there has been little to no further vetting of the notion of
metallic magnesium anodes. Through combining video microscopy studies of symmetric Mg-Mg cells with detailed 3D tomographic characterization of thin film morphologies and mesoscale modeling we demonstrate some of the first definitive examples of dendritic growth on magnesium anodes and elucidate mechanisms of formation. We have additionally designed metallic magnesium nanowire and nanotube arrays which have the potential for yielding low-volume expansion, lower current density anode materials. Our work opens the door for development of anode designs that mitigate dendrite growth, which will be crucial for further progression of Mg-based battery technology.

8:45 AM EN01.01.03
A Scalable Dry-Powder Manufacturing Technology of Lithium-Ion Batteries from Commercial Product to Further Designs Yangtao Liu¹, Jin Liu¹, Brandon Ludwig², Yan Wang¹ and Heng Pan²; ¹Worcester Polytechnic Institute, United States; ²Missouri University of Science and Technology, United States

An advanced power-based spraying technology was developed by us to fabricate electrodes for the lithium-ion batteries to replace the conventional slurry cast method. The additive manufacturing technology is a low cost, highly efficient way to avoid toxic NMP solvent from electrode fabrication. The removal of solvents shortened the production time from days to seconds, analyzed to reduce 20% of production cost, and enabled a more precise control of electrode microstructure during manufacturing. With the continuous processing system, the technology has a good potential to be scaled up and commercialized. Beyond the current commercial materials, we can also demonstrate this technology with a wide range of compatibility on producing electrodes, including different types of cathodes (LCO, LMO, NCM), anodes (MCMB), advanced architecture designs (Ultra-low binder recipe (<1%), high-energy thick electrodes (>280um), hierarchical micro-structured). In addition, the flexible arrangement strategy of spraying guns promoted the development of hierarchical designs to be practically available to the lithium-ion market.

9:00 AM EN01.01.04
Learning Only Buys You So Much—Practical Limits on Battery Price Reduction I-Yun Hsieh, Menghsuan Sam Pan, Yet-Ming Chiang and William H. Green; Massachusetts Institute of Technology, United States

Wide deployment of electric vehicles (EVs) would greatly facilitate global de-carbonization, but achieving the emission targets depends on future battery prices. Conventional learning curves for manufacturing costs, used in many battery projections, unrealistically predict battery prices will fall below $100/kWh by 2030, pushing EVs to be economically competitive with internal combustion engine vehicles (ICEVs) in the absence of incentives. However, in reality, essential materials costs set practical lower bounds on battery prices. Our 2-stage learning curve model projects the active material costs and NMC-based Lithium-ion battery pack price with mineral and material costs as the respective price floors. The learning rates are found to be 3.5% for chemical synthesis and 16.5±4.5% for battery production. The improved model predicts nickel-manganese-cobalt (NMC) battery prices will fall only to about $124/kWh by 2030 – much cheaper than today, but still too expensive to truly compete with ICEVs, due primarily to the high prices of cobalt, nickel, and lithium. Our results suggest that stabilizing raw materials prices and/or stimulating R&D activities on alternative battery chemistries will be important to achieve environmentally sustainable EV-based ground transportation at an attractive price.

9:15 AM EN01.01.05
Investigation of Megahertz Frequency Modulation Effects on Charge and Discharge Behavior of Lithium-Ion Batteries Bohua Wen, Ping-Chun Tsai and Yet-Ming Chiang; Massachusetts Institute of Technology, United States

Over the past several years, reports have emerged of ultrafast charging algorithms for lithium ion batteries [1,2] that in at least one instance [3] is attributed to megahertz frequency modulation of charging/discharging currents. Such algorithms are claimed to dramatically improve active material utilization as well as cycle life, but no mechanisms have been proposed in published work, nor, to our knowledge, have mechanistic studies have been conducted. In this work, we use a recently developed technique [4] in which single electrode particles having capacities of a few nAh can be interrogated with electrodynamic measurements (EIS, GITT, polarization-depolarization) while varying the state-of-charge. This capability allows clean separation of interfacial vs bulk transport limitations at the individual particle level, without complicating factors from typical composite electrode microstructures. To this capability, we have added AC pulse charging and discharging at ultra-low currents (down to picoA) with high-frequency waveforms (up to ~ MHz).
With this capability, we aim to answer a number of questions such as: Are these effects real? Are they significant?
And, what are possible mechanisms by which ion transport kinetics in a lithium ion battery are responsive to megahertz frequency excitation?

This work was supported as part of the NorthEast Center for Chemical Energy Storage (NECCES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DESC0012583.

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1. https://techcrunch.com/2015/05/05/nucleus-scientific-launches-to-revolutionize-batteries/

9:30 AM EN01.01.06
Enhancing the Viability of Grid Scale Sodium Systems (Na-ion and RT Na-S) through Fundamental In Situ Optical and UV-vis Investigation Rachel Carter1, Danniel Reed2, Ryan H. DeBlock3, Megan Sassin1, Corey T. Love1 and Partha Mukherjee4; 1U.S. Naval Research Laboratory, United States; 2Purdue University, United States; 3University of California, Los Angeles, United States

Replacing lithium ions with sodium ones in energy-storage systems is highly attractive due to the ~1300× enhancement in material abundance. However, the 25% larger volume of sodium ions prevents a drop-in substitution. For example, the typical graphite-based anode used in Li-ion systems are not amenable to reversible Na-ion intercalation and cathodes designed for Li-S cannot accommodate the larger volume expansion. Herein, we employ a specially designed in-situ electrochemical cell developed at the Naval Research Laboratory1 to probe the optical characteristics of electrodes under charge-discharge operation, yielding key information on electrochemical mechanisms.

For Sodium-ion anodes, disordered “hard carbon” anodes show more promise than graphitic carbons for Na-ion cells, but their charge-storage mechanisms are more complex, involving surface association, bulk cation-insertion reactions, and micropore-based deposition. Using the in-situ cell, we examine the sodiation of carbon nanofoam papers (CNFPs), which were recently reported for their high-capacity and high-rate charge-storage properties in nonaqueous Na-ion electrolytes.2 Imaging the CNFP during galvanostatic “discharge” (reduction in half-cell configuration vs. Na metal) reveals distinct color changes from grey to black to bronze to blue, caused by carrier concentration variation with increasing Na-ion association/insertion at the carbon electrode. We correlate these optical changes with variations in the complex discharge profile of the CNFP, which arises from multiple defect- and porosity-enable Na+-storage mechanisms that are supported by this electrode. This fundamental understanding will enable optimization of defect concentration and porosity of this anode material for the realization of this system. Alternatively, the RT Na-S system that boasts higher energy than Li-ion, in addition to high material abundance, is stalled by material challenges at the metal anode and conversion cathode. The soluble nature of discharge products and their interaction with the metal limit energy and cyclability.3 However, using the in-situ cell, careful mapping of discharge mechanisms is achieved in conjunction with anode observation. The discharge products (Na2Sn, 8<n<1) and relative quantities are determined, due to their distinct colors, with UV-vis spectroscopy. Since these behaviors prove strongly dependent on electrolyte solvent, the study is valuable to selection of optimal composition for anode stability and cathode performance.


9:45 AM EN01.01.07
Ultrahigh Speed Charging of LiCoO2 Cathode Thin Film with Dielectric Materials Shintaro Yasui1, Sou Yasuhara1, Takashi Teranishi2, Yumi Yoshikawa2 and Mitsuru Itoh1; 1Tokyo Institute of Technology, Japan; 2Okayama University, Japan
Li ion battery is one of suitable energy storage in our life, such as mobile electronic devices and electric vehicles. For delightful and convenient existence, high speed charging and long battery life are very important. Actually, charging time of smart phone is too long, which is about 5 hours to fully charge when the battery is empty. In this case, 0.2C is used for charging current, otherwise battery capacity is reduced “like broken” under higher C-rate (higher speed charging). This is because SEI layer, which is decomposed materials of electrolyte, LiF, organic solvent etc., is deposited on active cathode and anode materials. In this paper, we have achieved to obtain the ultrahigh speed charging and very tough cycling properties in LiCoO2 cathode thin film battery decorated with dielectric BaTiO3.[1] The important point is the blocking of creating SEI on cathode surface. In details, we have investigated interface reaction between cathode and electrolyte using epitaxial thin film battery. We have tried to insert artificial SEI of high dielectric constant materials, BaTiO3, on the cathode LiCoO2 epitaxial thin film. The high rate performance and cyclability are enhanced by existence of triple phase interface, cathode LiCoO2 – electrolyte LiPF6 (EC:DEC)– dot BaTiO3. The key point of this effect is that high dielectric constant material is better. We will discuss an effect of decolated dot materials. [1] S. Yasuhara, S. Yasui et al., Nano Lett. 19 (2019)1688.

10:00 AM BREAK

10:30 AM *EN01.01.08
Understanding the Factors Impacting Battery Failure Propagation and Its Mitigation Joshua Lamb and Loraine Torres-Castro; Sandia National Laboratories, United States

Developing battery systems resilient to thermal runaway propagation is of great concern when designing resilience into large battery systems. This is particularly difficult when working with pouch format cells as the format exists primarily to drive increased energy density within systems, which itself makes failure propagation more likely to occur. Our work here focuses on module to module propagation and potential tools that might be used to mitigate this failure. We have constructed 3S3P configuration batteries with various mitigation strategies used to prevent module to module propagation. This has included conductive, insulating and advanced materials and is coupled with analysis of the heat transfer across these barriers to better understand the underlying mechanisms that can better improve propagation resistance in systems constructed with pouch format cells. We have used both mechanical and thermal initiation techniques to explore the different behaviors that might occur when the character of the initial failure changes as well. This includes the failure propagation from a single cell failure initiation as well as the failure of an entire 1S3P module within the pack. Finally, we look at the differing roles that both changes to energy density of the pack as well as changes to the heat transfer between cells might play in mitigating thermal runaway propagation.

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11:00 AM EN01.01.09
Safety Assessment of Solid-State Lithium Batteries Alvaro Masias1,2, Mihir Upadhye2 and Jeff Sakamoto2; 1Ford Motor Company, United States; 2University of Michigan, United States

Continuous improvements in lithium-based battery technology has facilitated the recent growth of personal electronics and the increasing introduction of electrified vehicles. Lithium-ion technology has evolved steadily since its introduction in 1991 with ever increasing specific energy. However, it is likely that more advancements in battery performance characteristics are necessary to enable the widespread adoption of electrified vehicles.

One of the leading candidates for next generation battery technology is the solid state (SS) battery, where a liquid electrolyte and polyolefin thin film separator are replaced by an ionically conducting solid. While SS battery technology replaces the flammable electrolyte of lithium-based technology with a non-flammable ceramic, glass or polymer, the addition of highly reactive lithium metal and potentially brittle separator materials may introduce different safety challenges. In this context, a safety assessment of lithium metal SS batteries is performed against existing international battery safety test standards and regulations, with an emphasis placed on water exposure and vibration.
Catholyte Formulation of Flow Li/O₂ Batteries

Francesca Soavi¹, Irene Ruggeri¹, Federico Poli¹, Catia Arbizzani¹, Stefania Rapino¹, Francesca De Giorgio¹,² and Alessandro Brillonità,² ¹University of Bologna, Italy; ²Battery srl, Italy

Lithium/O₂ (air) batteries are promising exceptionally high specific energy, that can be theoretically 2-3 times higher than today Li-ion batteries.

Low cycling efficiency, low cycle life and slow discharge kinetics are still considered the main issues to be addressed for the development of high performance Li/O₂ batteries. The discharge product, lithium peroxide (Li₂O₂) which is formed on the cathode surface is an insulator that affects battery capacity and causes high overpotential during recharge and, thus, low recharge efficiency.

This process can be controlled by tailoring the electrolyte environment. Glyme-based solvent-in-salt (SIS) electrolytes have been recently proposed for Li-O₂ batteries. In SIS glyme-Li⁺ complexes are formed. They improve the electrochemical stability of the electrolyte and stabilize superoxide ion with a positive effect on cathode passivation.

An additional strategy for improving Li/O₂ battery performance is the use of a flowable catholyte ink. It is an organic dispersion of carbon particles which also acts as oxygen carrier, therefore improving Li/O₂ battery rate response. In this catholyte, ORR takes place on the solid phase of the carbon particles. Consequently, cathode surface passivation is limited, the battery cell death is delayed and the Li/O₂ battery energy increased. Such approach enabled areal capacity of 180 mAh cm⁻², energy of 500 mWh cm⁻² and current of 4 mA cm⁻². Here, we discuss about three strategies to improve semi-solid Li/O₂ battery cycling performance. Specifically, we report on i) a scanning electrochemical microscopy (SECM) investigation carried out to investigate the Li₂O₂ formation mechanism in salt-in-solvent and SIS electrolytes based on TEGDME and LiTFSI and in ionic liquids, ii) a semi-empirical modeling study that enables to predict the best cell design that improves the power gain of the flow Li/O₂ battery and iii) the study of the carbon composition of the semisolid catholyte that permits to achieve the exceptional high specific energy of 1 kWh kg⁻¹.

Acknowledgments

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References


Determining the Mechanisms by Which Dissolved Transition Metals Cause SEI Failure in Advanced Li-Ion Batteries

Oliver Harris¹, Kevin Leung², Yue Qi³ and Maureen Tang¹; ¹Drexel University, United States; ²Sandia National Laboratories, United States; ³Michigan State University, United States

One of the most serious lifetime problems for established Li-ion and emerging “Beyond-Li” batteries is electrolyte...
degradation from unwanted side reactions. For many high-voltage and high-energy cathode materials, transition metal dissolution is known to accelerate capacity fade leading to unacceptably short battery lifetimes. Metals like Mn, Ni, and Co deposit at the anode and disrupt the formation and performance of the solid-electrolyte interphase (SEI), a vital battery interface responsible for protecting the electrolyte from the highly reductive anode. This results in continual Li loss and uncontrolled SEI growth. Understanding the role of each metal in undermining the passivation of the SEI is necessary to mitigate this degradation and enable commercialization of high-voltage Li-ion cathodes.

In this work, we interrogate the effects of transition metals on the SEI via in-situ electrochemical characterization. We apply generator-collector measurements and other electroanalytical techniques in order to probe mechanisms of transition metal incorporation into the SEI and their effect on through-film electron transport. By using convection to control electrode cross-talk, we observe the presence of metal contaminants from an upstream cathode at the downstream anode. Electrochemically interrogating the SEI with functionalized ferrocene mediators and interpreting voltammetry with continuum-scale models shows that incorporation of dissolved transition metals increases both the density and the activity of active sites within the SEI [2]. In a separate set of experiments, we compare Mn, Ni, and Co contaminants to explain the particularly detrimental effects of Mn [3-4]. We develop microkinetic models for an electron-tunneling mechanism and an electrocatalytic cycling pathway. Density functional theory is used to predict material parameters such as bandgap doping and redox potentials. Comparison of theory and experiment suggests that kinetic parameters dominate over thermodynamic redox potentials and point to the importance of the metal’s local coordination environment within the SEI.


11:45 AM EN01.01.12
Lithium Titanate Hydrates with Superior Power Rate and Ultralong Cycle Life for Lithium-Ion Batteries
Shitong Wang¹, Zilong Tang², Jun Lu³ and Ju Li¹; ¹Massachusetts Institute of Technology, United States; ²Tsinghua University, China; ³Argonne National Laboratory, United States

Ti-based materials (e.g. Li₄Ti₅O₁₂ and TiO₂) have received considerable attention owing to their outstanding high-rate capacity and cycling stability, as well as their improved safety standards over graphite. Here we show there exist a series of lithium titanate hydrates with similar performance compared to most outstanding Ti-based electrodes (including the materials after modification) reported at present. That is, water promotes structural diversity (e.g. 2D layered) and nanostructuring of compounds, but does not necessarily degrade electrochemical cycling stability or performance in aprotic electrolytes. As new members in the Li-H-Ti-O material system, lithium titanate hydrates not only greatly expand the research scope of the Li-Ti-O and H-Ti-O material system, but also propose a new method for electrode materials modification. More significantly, they provide greater inspiration and guidance to other hydrated transition-metal compound systems in energy storage applications.

References:
Due to the large demand of electric vehicles and grid energy storage systems, many ongoing researches are focusing on the improvement of energy density, capacity, cycling stability and rate performance of Li-ion batteries. Lithium, Manganese-rich layered oxide cathode (LMR-NMC) is one of the promising cathode materials for the near future owing capacities of over 250 mAh g⁻¹ and energy density of over 1000 Wh kg⁻¹ between voltage range 2.0 – 4.8 V. Though, two main challenges still remain before these materials can be fully applied commercially; capacity fading and voltage fading. Here, we focus on the structure, properties and electrochemical performance of co-dope LMR-NMC, Na₆Li₁ₓMnₓNi₀.₅₄Co₀.₃₃O₂₋₀.₃Fₓ, synthesized via hydroxide co-precipitation followed by solid-state reaction. Initially, LMR-NMC with single dopant ratio was examined and best performance of each dopant was then selected in order to maximize the capability of co-dope material. Comparison among pristine, Na dope, F dope and co-dope samples were intensively analyzed. Regarding to the electrochemical studies, CD has the best performance in term of capacity (97%) and voltage retention (91%) after 100 cycles at 0.2 C with initial discharge capacity of 260 mAh g⁻¹ at 0.1 C. Based on this discovery, higher voltage and capacity retention LMR-NMC material are obtained allowing us to heighten the possibility of using LMR-NMC commercially in next-generation batteries.

1:45 PM EN01.02.02
Atomic-Scale Mechanisms of Enhanced Electrochemical Properties of Mo-Doped Co-Free Layered Cathodes for Lithium-Ion Batteries Linze Li¹, Jianguo Yu², Devendrasinh Darbar³, Ethan C. Selt⁴, Jagjit Nanda⁵ and Chongmin N. Wang⁶; ¹Pacific Northwest National Laboratory, United States; ²Idaho National Laboratory, United States; ³Oak Ridge National Laboratory, United States

Cobalt-free layered oxides with high specific capacity and low cost have emerged as promising candidates that can be used as next-generation cathodes for lithium ion batteries. Practical implementation of these materials, however, have been hindered by their low rate capability, structural instability, and fast capacity decay. Recent studies show the introduction of a small amount of cation dopants can strongly improve the electrochemical performance of layered cathodes. But the underlying mechanisms remain illusive due to the lack of information at atomic scale. Here, with a combination of atomic-resolution STEM imaging and first principle calculations, we reveal the microscopic origin of enhanced electrochemical properties of LiNi₀.₅Mn₀.₅O₂ doped with ~1 at % Mo. Our observations provide direct atomic-scale evidence that the small amount of Mo dopants distributed uniformly in the host lattice can significantly hinder the Li/Ni cation mixing. And such structural changes can strongly suppress the detrimental phase transformations not only at the surfaces but also at the grain boundaries within the bulk of the cathode materials, leading to an enhanced capacity and cycling properties. These results provide useful insights into the fundamental understanding of doping effects on the structural stabilities of layered cathodes.

2:00 PM EN01.02.03
The Origin of Al Dopant Enhanced Cycling Stability in NCA Cathodes Lianfeng Zou¹, Jianyu Li², Zhenyu Liu³, Guofeng Wang³, Manthiram Arumugam² and Chongmin N. Wang¹; ¹Pacific Northwest National Laboratory, United States; ²The University of Texas at Austin, United States; ³University of Pittsburgh, United States

For the majority of cathodes in Li ion batteries, cationic doping offers an effective means to enhance electrochemical performance, in which the alien dopants are generally considered to operate via modifying bulk properties. In contact to the liquid electrolyte, the electrode surfaces often act as primary sites that suffer from structural and compositional degradation, however, the doping effects on the modification of electrode electrolyte interface (EEI) properties remain vague. By combining atomic level imaging, spectroscopic analysis and DFT simulation, we demonstrate that the dopant extends its effective domain from bulk to surface via dynamic evolution, which significantly improve the cathode/anode-electrolyte interface stability. Using Ni-rich cathode as a model system, we show that, during the materials synthesis stage, the trace amount of Al dopants migrate and accumulate beyond the surfaces and lead to the epitaxial growth of scattered Al₂O₃ nano-islands; upon cycling, the Al provides an additional physical barrier for slowing down the electrochemical degradation. The buffer zone developed by dopant evolution mitigates the electrode-electrolyte interactions and alleviates the performance decay during the battery operation.

2:15 PM EN01.02.04
Improving Electrochemical Performance of Lithium-Sulfur Batteries Using Flexible Fibrous Cathode Additives Avinash Raulo and Bhanu Nandan; Indian Institute of Technology Delhi, India

Lithium-Sulfur batteries (LSB) are considered as high-potential candidate for next generation electrical energy
storage technology due to the low cost and naturally abundant sulfur-based cathode, that endows the battery with a high theoretical energy density of 2600 Wh kg⁻¹ and specific capacity of 1675 mAh g⁻¹. However, rapid capacity fading due to the formation of soluble lithium polysulfide (LiPS) intermediates, electrically insulating property of sulfur and LiPS pose great challenges for the realization of long lasting LSBs for commercial applications. Present study dealt with the fabrication of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate-sulfur@polyacrylonitrile electrospun nanofibers, which can be potentially used as flexible additives in the cathode of lithium-sulfur batteries. The unique architecture of thus fabricated nanofibers not only trap the intermediate LiPS and suppress their dissolution into liquid electrolyte but also provide rapid charge transfer pathway to improve the reaction kinetics. As a result, LSB with nanofiber incorporated cathode shows better cycle life and improved rate performance compared to the bare sulfur cathode owing to the adsorption effect of the nanofibers.

2:30 PM *EN01.02.05
Anion Redox Materials—A Comprehensive Study Combining Computation and Experiments Shirley Meng; University of California, San Diego, United States

Intercalation compounds based on transition metal cation redox has been studied over a few decades, while their potential based on oxygen anion redox has been under heated debate recently. The richness of anionic redox chemistry in the solid state inspires the materials community to explore new systems for next generation electric energy storage. At the same time, advanced computational and experimental tools to quantify the anionic redox activities are under development to study the underlying science that triggers a reversible and stable anionic redox activity. Possible approaches are outlined to further improve electrochemical performance of anion redox, realizing its full potential. In this talk, we will showcase the new computational methodology that enables the stabilization of oxidized lattice oxygen ions and follow up by demonstrating experimental evidence that is the true signal of oxidized lattice oxygen ions.

3:00 PM BREAK

3:30 PM EN01.02.06
Largely Improved Battery Performance Using Micro-Sized Silicon Skeleton Caged by Polypyrrole as Anode Junjie Niu; University of Wisconsin-Milwaukee, United States

The emerging demands in large energy storage for portable electronic devices and transportations are attracting more interest in developing next-generation lithium-ion batteries (LIBs) with a series of new electrode materials, thus to achieve a 3-5 times higher capacity to meet a strategic perspective energy-density of 500 Wh/kg or higher. Silicon, with a theoretical capacity up to 4000 mAh/g, is considered as one of the promising anodes to achieve this goal. The industry R&D in Si-led anodes is widespread, and the release of commercial products for portable electronics seems imminent, although simultaneous achievement of high capacity and sufficient calendar life for automotive applications remains to be demonstrated due to a 360% volume expansion of silicon (Liu, Nano Lett 2011). The significant volume expansion makes the silicon not suitable for large amount loadings in actual batteries (Szczech, Energy Environ Sci 2011). The current ratio of silicon in graphite anode is typically less than 10%, which largely limits the overall energy density. Certain amounts of strategies have been tried to overcome this challenge by constructing various nano-structured configurations. Due to the light-weight, simple synthesis and low cost, recently scientists start to pay attention in applying polymeric materials in LIBs (Chao, Adv Mater 2014).

In this presentation, I will introduce a largely improved battery performance using micro-sized silicon skeleton caged by polypyrrole polymer as anode, which was synthesized via a facile wet-chemical strategy (Lv et al. 2019, under review). The industry available, micro-sized AlSi alloy was used as precursor, which ensures a scalable production with low cost. The hollow skeleton configuration provides sufficient spaces to accommodate the drastic volume expansion/shrinkage upon charging/discharging while the minimum amount of conductive polymer serves as a protective layer and fast channel for Li⁺/e⁻ transport. The battery with the micro-silicon cage as anode displays an excellent capacity retention upon long cycling at high charge/discharge rates and high material loadings. A specific capacity as high as 1660 mAh/g (~5X times graphite) with a high Coulombic efficiency of ~99.8% and 99.4% were achieved after 500 cycles with 3 mg/cm² loading and 400 cycles with 4.4 mg/cm², respectively. At higher 1.0 C, the capacity close to 1150 mAh/g was remained after 500 cycles with such high loading. The areal capacity of as high as 6.4 mAh/cm² with 4.4 mg/cm² loading was obtained, which suffices a high battery energy density in powering large devices such as electric vehicles (EVs).
Tailoring Electrode-Electrolyte Interfaces in Lithium-Ion Batteries Using Molecularly Engineered Functional Polymers Laisuo Su, Jamie Weaver, Mitchell Groenenboom and B. Reeja Jayan; 1Carnegie Mellon University, United States; 2National Institute of Standards and Technology, United States

The performance and stability of lithium ion batteries (LIBs) depend on charge transfer processes and reactions at electrode-electrolyte interfaces (EEI), making interfaces design a key issue. Here we engineer this interface using conformal, functional polymer nanolayers via a novel vapor-based deposition technique. We demonstrate that poly(3,4-ethylenedioxythiophene) (PEDOT) nanolayer doubles the capacities of LiCoO2 at high rates and extends its 4.5 V cycling life by 160%. The improved rate performance is enabled by high diffusion coefficient of Li⁺ in PEDOT measured from neutron depth profiling. Such behavior is further understood by density functional theory (DFT) calculation. The extended cycling stability comes from strong interactions between PEDOT and Co atoms, as suggested from X-ray photoelectron spectroscopy and DFT calculation. Additionally, in-situ synchrotron X-ray diffraction reveals that PEDOT uniformizes current distribution and improves LiCoO2 structural stability during cycling tests. This work adds understanding and provides guidelines for designing the EEI for advanced LIBs.

The North American Solution to Climate Change and the Role of Battery Storage Christine Hallquist; Cross Border Power, United States

Christine Hallquist, was CEO of a Vermont utility that was recognized for its leadership in transitioning to a 96% carbon-free electric supply by 2018. Christine spent 10 years as a member of a strategic advisory team to the National Rural Electric Association, which provided electricity to 56% of America’s land mass. The advisory group oversaw research projects with the Department of Energy, the National Laboratories, and industry. Christine was vice-chair of the advisory group and scheduled to move to chair when she left to become the democratic candidate for governor of Vermont in 2018. Her role in addressing climate change began in 2005 when the Vermont governor asked her to join an advisory group that traveled to Quebec to hear the report of the Intergovernmental Panel on Climate Change. She has now formed a Canadian Company, Cross Border Power, whose mission is to solve climate change and produce grid-scale storage as part of that mission.

In order to understand the challenge ahead it is important to understand our current energy mix. According to the US Energy Information Administration, 81% of energy consumed in the US comes from fossil fuels. The per-capita daily use of electricity in 2018 was 11.6 kWh with 63% of the electricity generated from fossil fuels. In order to solve climate change, North America will need to transition its energy supply to 100% carbon-free sources of electricity 100% of the time. If we assume no improvement in efficiencies, this means the per capita use of electricity would rise to 61 kWh. That said, we can expect significant improvements in efficiency through transitioning to cold climate and geothermal heat pumps as well as electric transportation. We will increase the amount of electricity generated while transitioning. This will result in significant demand for additional wind and solar on the electric grid.

The electric grid was designed for rotating generators. The collective rotation of the interconnected generators provided system-wide inertia, which resulted in electrical stability. Eliminating those rotating generators and replacing them with wind and solar generation will require a tremendous amount of battery storage to inject the lost inertia and balance the supply with the load. While battery technology has been improving, from a cost and performance standpoint we have a long way to go.

The electric grid in Northern Vermont is already facing electrical stability problems from a large deployment of wind and solar. This area has become an ideal test case for studying impact and solutions. Presently, with all generation operating at peak output, the system is over capacity by at least 1/3, which means the wind projects are required to shut down due to grid stability issues, thus wasting the generation. These same stability issues are
showing up all around the world, including California, Texas, Spain and Germany.

Christine’s presentation will address what is needed to solve the problems on the northern Vermont electric grid as well as what it will take to accomplish the North American Solution to Climate change. She will discuss the economics, physics and engineering challenges as well as the enabling policy changes that will can help accelerate the implementation. Included in her presentation will be the role of battery storage, the present state of storage and what developments are needed in order to fully decarbonize our energy portfolio.

4:30 PM EN01.02.09
A Novel Route for the Large-Scale and Low-Cost Fabrication of Silicon-Graphite Composites for Lithium-Ion Batteries Joseph Schwan¹, Giorgio Nava¹, Matthew G. Boebinger², Matthew T. McDowell² and Lorenzo Mangolini¹; ¹University of California, Riverside, United States; ²Georgia Institute of Technology, United States

Over the last decade the research community engaged in significant efforts to develop silicon-based anodes and boost the energy density of lithium-ion batteries. This goal is considered instrumental for the development of more efficient electric vehicles and stationary storage systems. While, from a material engineering standpoint, silicon-carbon nanocomposites have been demonstrated as one of the most promising strategies to produce electrodes with long-cycle life, overcoming the problem of silicon swelling upon lithiation, synthesis methods suitable for the low-cost industrial-scale manufacturing of these delicate and carefully engineered structures have still to be demonstrated. In this contribution, we present two innovative production systems purposely designed to be simple, cost-effective and suitable for future large-volume material production.

The first innovation is a method to produce silicon nanoparticles -NPs- with (i) high-purity (oxygen content <3%) and (ii) tailored nanoscale size. The system comprises a non-thermal radiofrequency plasma reactor serially connected to a tubular furnace. The plasma discharge quickly converts a silicon containing gas into silicon NPs and ensures a high precursor utilization (over 90%). The aerosol is then seeded into the furnace where the NPs are sintered into larger structures at high-temperature. The final particle size can be precisely adjusted between 5 nm and 60 nm (size distribution within 10% of the average value) by simply changing the temperature of this second thermal stage (800-1000°C).

The second innovation is chemical vapor deposition -CVD- method that allows growing highly graphitized and conformal layers of carbon directly onto the surface of silicon NPs. The NPs are introduced into a hot-wall furnace with an alumina combustion boat and are wrapped with a conformal coating of amorphous carbon resulting from the dissociation of acetylene -C₂H₂- at 650 °C. After removing C₂H₂, the furnace is ramped up to 1000°C in Argon -Ar- yielding a controlled graphitization of the carbon-shell with no detectable presence of silicon carbide.

The combination of the two aforementioned approaches achieves the production of a battery grade silicon-carbon nanomaterials with tunable properties (i.e. size, graphitic carbon content and carbon shell thickness). The as-produced composites demonstrate outstanding electrochemical performance as “drop-in” additives in graphite-dominant anodes. The addition of small amount of the Si-based active material (10% in wt) enables the fabrication of electrodes with a gravimetric capacity of around 600 mAh g⁻¹, first cycle CE of 90% and capacity retention of 81% over 100 cycles. The optimized composite material is used to fabricate a prototype 60 mm x 40 mm high-energy density pouch cell and its performance are compared to the one of a state-of-the-art commercial graphite-based battery.

4:45 PM EN01.02.10
Stable Cycling with High Energy and Power Densities of Silicon-Graphene Anode Electrode for Li-Ion Battery Doyoung Kim¹,², Yongguang Luo², Hee Min Hwang¹,², Simgeon Oh¹,² and Hyoyoung Lee¹,²,²; ¹Center for Integrated Nanostructure Physics, Korea (the Republic of); ²Sungkyunkwan University, Korea (the Republic of)

As the era of electric vehicles arrives, it is necessary to develop li ion battery with high energy and power densities. Energy and power density, which are directly related to the performance of an electric vehicles and required by all electric devices. The commercial graphite anode li ion battery has limited gravimetric capacity of ~370 mAh g⁻¹, low charge rate and low retention stability due to the sluggish intercalation reactions during charging. Silicon are emerging as next-generation anode materials to solve these problems. Silicon has a high theoretical capacity (~4,200 mAh g⁻¹), which is ten times higher than commercial graphite anode materials. However it has a significant problem of stability due to the high expansion ratio (~ 400 %) and solid electrolyte interface that accompany the
charging reaction. Silicon is classified as an alloy material that participates in direct bonding with li ions. Because of this, more than a certain amount of li ions are involved in the bonding with silicon, which causes expansion and pulverization at the same time. This is a typical retention stability degradation problem for silicon-based anode electrodes.

To avoid a degradation of a silicon anode for a lithium ion battery, we report new 2D multi-layered rGO/Si electrode prepared by a direct growth of Si into porous rGO film on current collector. The direct Si deposition method on the porous rGO film can intercalate Si layer into the rGO film by replacing oxygen related groups of GO with Si nanoparticles through \textit{in-situ} thermal reduction of GO film. The thickness of rGO/Si thin-layered film can be controlled from a sub-nanometer to micrometer thickness Si electrode. Its rGO layers tightly hold Si layers and also were acted as a pre-volume against an expansion of Si layer with Li charging, leading to give a highly stable li ion battery. The 2D thin-layered film provided a short pathway for Li ion transport insertion and desertion process due to a nanometer thickness of Si and graphene. In addition, the 2D film gave a high conductivity even without binder and/or conductive agents, providing a high initial capacity of 2,978 mAh g$^{-1}$ at 0.5C and a high reversible capacity at 0.5C (~ 1,791 mAh g$^{-1}$ at 500 cycles).

**SESSION EN01.03: Poster Session**

**Session Chairs**: Xiaolin Li and Cengiz Ozkan  
Monday Afternoon, December 2, 2019  
8:00 PM - 10:00 PM  
Hynes, Level 1, Hall B

**EN01.03.01**  
**Optimization of Synthesis and Characterization of Ni-Rich LiNi$_{2-y}$Mn$_{0.5-y}$Co$_{0.5-y}$O$_2$ via Co-Precipitation Method in a Continuous Stir Tank Reactor**  
Anshika Goel, Natasha Chernova, Hui Zhou, M. Stanley Whittingham and Fredrick Omenya; Binghamton University, United States

In the past few years the lithium-ion batteries (LIBs) industry has expanded from consumer electronics to automotive industry. Lithium nickel manganese cobalt layered or NMC are state of the art cathode materials that have replaced the original lithium cobalt oxide cathode due to their promising high energy density. In NMC, Ni provides high capacity to the cathode material, while Co and Mn provide structure stability and safety over cycling. To further increase the energy density, current research is focused on nickel-rich oxides. The structure, morphology, and electrochemical performance of these oxides are highly dependent on the method of synthesis. Even slightest variations in the synthesis conditions can result in widely divergent characteristics when used as cathode material. The presentation will discuss various reaction condition optimization for synthesis of NMCs like pH control, concentration of chelating and precipitating reagents and how does it affect the morphology and other properties of the material like tap density, electrochemistry and magnetic properties. In this work we have used Powdered X-ray Diffraction (PXRD), UV-Vis Spectroscopy, magnetic properties, Scanning Electron Microscopy (SEM) and tapped density to discuss various changes in physical and chemical properties of material with respect to reaction condition.

Acknowledgement.  
This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy, through the Advanced Battery Materials Research Program (Battery500 Consortium).

**EN01.03.02**  
**TEM Failure Analysis of Electrochemically Delithiated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ Spinel**  
Xiang-Yun Song; Lawrence Berkeley National Lab, United States

LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode material which has a higher working voltage (4.8 v) and larger specific capacity (148 mAh/g) has been studied by high resolution transmission electron microscopy (TEM). The purpose of this work was focused on the battery failure mechanism through TEM observations and analysis of microstructural properties of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel material, meanwhile the samples before and after electrochemical cycling was compared. XRD and SEM/EDS were further used to evaluate the battery failure mechanism.
Comparing with fresh LiNi_{0.5}Mn_{1.5}O_{4} particles before cycling, many LiNi_{0.5}Mn_{1.5}O_{4} particles after cycling, which also called original single crystal grains, display a tendency of nano-polycrystalline. This kind of polycrystalline properties can be mainly represented by three major microstructural features in cycled LiNi_{0.5}Mn_{1.5}O_{4} spinel material. First, many electron diffraction patterns that show FFT (Fast Fourier Transform) patterns got from TEM image area do not exhibit a regular single crystal diffraction pattern, but more complex patterns. 2nd, lattice defects appeared in LiNi_{0.5}Mn_{1.5}O_{4} particles, which are proved by lattice images and FFT patterns. And last major difference after cycling is that some smaller nano particles precipitated on the particle surface.

In order to compare and analyze LiNi_{0.5}Mn_{1.5}O_{4} spinel material more efficiency, a detailed lattice structural model of spinel corresponding to the TEM lattice image and its FFT pattern is presented.

**EN01.03.03**

*Unveiling Lithium Storage in Oxygen-Vacancy-Controlled MoO_{3-x} without Any Binders or Conductive Materials*

Sooeun Shin, Jaesang Yoon, Hochul Nam, Eunsoo Kim, Won-Sub Yoon and Hyungjung Shin; Sungkyunkwan University (SKKU), Korea (the Republic of)

High capacity and cycling stability are two important key points in developing lithium-ion batteries. One of potential candidates as an anode material is MoO_{3} is due to facile Li^{+} hosting in layered structure and thus resulting high theoretical capacity. Here, we present oxygen-vacancy-controlled MoO_{3-x}, where oxygen vacancies act as shallow donors and result improved electrical conductivity of the active materials. Without the use of additional binders and conductive materials, we were able to examine the Li-storage mechanism directly on MoO_{3-x}. We clearly demonstrate Li-storage capacity based on reversible formation/disruption of SEI films as an extra with the conjunction of Li ion intercalation as well as electrochemical reactions in the layered structures and surprisingly not resulting from the previously known conversion reactions in MoO_{3-x}. By conjugating the surface of MoO_{3-x} with Cu_{2}O via annealing process, we investigate the role of Cu_{2}O. According to our experimental results obtained by electrochemical analysis, *ex-situ* transmission electron microscopy and *ex-situ* X-ray absorption spectroscopy Cu_{2}O act as an effective catalyst for the formation of SEI films and reversible reaction of MoO_{3-x} with Li^{+} ions. As a result, Cu_{2}O@MoO_{3-x} exhibits a charge capacity of 1,100 mAh/g from the second cycle and maintains high reversible capacity, while MoO_{3-x} exhibits a charge capacity of 900 mAh/g and fades to 590 mAh/g for 100 cycles at 1 A/g. Cu_{2}O@MoO_{3-x} shows capacity of ~ 390 mAh/g at 10 A/g up to 1,000 charge/discharge cycles.

**EN01.03.05**

*Mitigation of Microscale Reaction Heterogeneity by Crystallinity Tuning for Ni-Rich Cathode in a Li-Ion Cell*

Hyungyeon Cha and Jaephil Cho; UNIST, Korea (the Republic of)

To date, nickel-rich cathode materials have been greatly developed by modification of surface and bulk morphology, structural design, and concentration gradients. However, the intrinsic problems originated from the morphological characteristics have not been completely prevented. The anisotropic expansion of each primary particles give rise to the morphological collapse upon the long-term cycling, resulting in a reaction inhomogeneity of the secondary particles.

Interestingly, we have investigated such reaction inhomogeneity induce the serious state-of-charge (SOC) heterogeneity in the thick electrode. We carried out 3-electrode full-cell test with an additional lithium metal electrode to track the LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{2} (NCM) cathode and graphite anode potential. These results show the cathode and anode potential steadily rise during the cycling at the high temperature of 45 °C. Noticeably, the cut-off potential was upraised from the 4.38 V to 4.47 V after 200 cycles, indicating that the additional lithium ions could be extracted from the cathode structure. We confirmed the potential was different according to the position in the thick electrode and the high potential distribution was concentrated on the surface particles from the Raman spectroscopy analysis using the cross-sectioned electrode. The Raman spectroscopy is a powerful and novel analysis tool for observing the degradation of metal oxide cathode materials in a microscale. The overutilization of the cathode particle in the surface accompanies severe morphological collapse with nickel dissolution, threatening the integrity of the graphite particles. In this regard, we suggest tuning the crystallinity of the NCM particles from the polycrystallinity to single grain. We intensively investigated the degradation mechanism of the single grain LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} and conventional NCM under the high temperature.
Understanding the Multivalent Charge-Storage Mechanism of Na$_3$V$_2$(PO$_4$)$_3$ for Aqueous Zinc-Ion Batteries

Jesse S. Ko$^1$, Partha P. Paul$^1$, Natalie Seitzman$^2$, Ryan H. DeBlock$^3$, Bruce S. Dunn$^3$ and Johanna N. Weker$^1$;

$^1$SLAC National Accelerator Laboratory, United States; $^2$Colorado School of Mines, United States; $^3$University of California, Los Angeles, United States

Research on “beyond lithium-ion” technology remains to be an ongoing challenge in identifying materials capable of reversibly storing multivalent ions, such as Mg$^{2+}$, Ca$^{2+}$, and Zn$^{2+}$. For prospective Zn$^{2+}$-based positive electrode materials, questions regarding the accommodation of Zn$^{2+}$ remains largely unanswered. In the present study, we explore the charge-storage mechanism of a V-based Na$^+$ superionic conductor (NASICON) framework, Na$_3$V$_2$(PO$_4$)$_3$ (NVP), by X-ray synchrotron characterization to unravel potential-dependent structure-property relationships. We ascribe the reversible electrochemical behavior of NVP cycled in a Zn$^{2+}$-based electrolyte to a two-stage intercalation process involving both Na$^+$ and Zn$^{2+}$. The initial charging profile at C/20 indicates Na$^+$ extraction from Na$_3$V$_2$(PO$_4$)$_3$ to NaV$_2$(PO$_4$)$_3$, observed by a single plateau in the galvanostatic charge/discharge profile, while subsequent discharge results in two plateaus corresponding to Na$^+$, then Zn$^{2+}$ insertion. Operando X-ray diffraction of the zinc-ion cells were collected to examine the changes associated with the first charge/discharge cycle, which showed reversible behavior based on shifts in X-ray reflections. To examine distinct changes linked with Na$^+$ and Zn$^{2+}$ two-stage intercalation process, electrodes were prepared ex situ for Rietveld refinement to understand variations in the crystal structure parameters. Furthermore, changes in V oxidation state, V-O coordination, and the presence of Zn$^{2+}$ was studied by X-ray absorption spectroscopy. The results of this work present a thorough investigation of the multivalent charge-storage mechanism for a well-established NASICON framework, and may provide further insight into other related structures.

Honeycomb Layered Cathode Frameworks for Rechargeable Potassium-Ion Battery

Titus Masese$^1$, Kazuki Yoshii$^1$, Minami Kato$^1$, Satoshi Uchida$^1$, Zhen-Dong Huang$^2$, Keigo Kubota$^3$ and Hiroshi Senoh$^1$; $^1$National Institute of Advanced Industrial Science and Technology (AIST), Japan; $^2$Nanjing University of Posts & Telecommunications, China; $^3$AIST-Kyoto University Chemical Energy Materials Open Innovation Laboratory (ChEM-OIL), Japan

Potassium-ion battery (PIB) has recently attracted great attention, as a low-cost alternative to lithium-ion technology. PIB can be a high-voltage contender considering the significantly negative potential of the K$^+/K$ redox couple, which is close to or even lower than Li depending on the solvent [1]. Nonetheless, the large ionic radius of potassium coupled with significant strain accompanying potassium extraction / insertion, the number of potassium-based compounds (particularly, cathode materials) has greatly been undercut. In this work, we will highlight the electrochemical performance of honeycomb-based layered frameworks as potential cathode frameworks for rechargeable potassium-ion batteries [2].

References:

Carbon Nitride Phosphorus as an Effective Lithium Polysulfide Adsorbent for Lithium–Sulfur Batteries

Vandung Do$^{1,2}$ and Won Il Cho$^2$; $^1$Korea University of Science and Technology, Korea (the Republic of); $^2$Korea Institute of Science and Technology, Korea (the Republic of)

Lithium–sulfur (Li–S) batteries are attracting substantial attention because of their high-energy densities and potential applications in portable electronics. However, an intrinsic property of Li–S systems, that is, the solubility of lithium polysulfide (LiPS), hinders the commercialization of Li–S batteries. Herein, a new material, that is, carbon nitride phosphorus (CNP), is designed and synthesized as a superior LiPS adsorbent to overcome the issues of Li–S batteries. Both the experimental results and the density functional theory (DFT) calculations confirm that CNP possesses the highest binding energy with LiPS at a P concentration of ~22% (CNP22). The DFT calculations explain the simultaneous existence of Li–N bonding and P–S coordination in the sulfur cathode when CNP22 interacts with LiPS. By introducing CNP22 into the Li–S systems, a sufficient charging capacity at a low cutoff
voltage of 2.45 V, is effectively implemented, to minimize the side reactions, and therefore, to prolong the cycling life of Li–S systems. After 700 cycles, a Li–S cell with CNP22 gives a high discharge capacity of 850 mAh g\(^{-1}\) and cycling stability with a decay rate of 0.041\% cycle\(^{-1}\). A 4-stack pouch cell with a high-S-load of 6.1 mg cm\(^{-2}\), which shows a capacity of 699 mAh g\(^{-1}\) and CA of 93\% after 74 cycles at 0.2 C. This is primarily ascribed to strong interactions between LiPS and CNP22, as well as a high S reutilization during cycling. The incorporation of CNP22 can achieve high performance in Li–S batteries without concerns regarding the LiPS shuttling phenomenon. The advantages of the Li–S cells with CNP22 are obvious, and therefore, CNP22 is a suitable material for constructing reliable Li–S batteries.

**EN01.03.09**

**Ultrastable and Fast Battery with an Organic Cathode and Liquid Potassium-Sodium Anode**

Roman Kapaev\(^1,2\), Keith J. Stevenson\(^1\) and Pavel Troshin\(^1,2\); 1Skolkovo Institute of Science and Technology, Russian Federation; 2Institute of Problems of Chemical Physics, Russian Federation

Alkali metal-ion batteries using metal anodes (Li, Na, K) are attractive because of their high specific capacities and low voltages. However, these anodes suffer from the dendrite growth issue, which causes short-circuiting of the cells and might lead to their ignition and even explosion. Recently, it has been proposed to use dendrite-free anodes based on potassium-sodium alloys (PSAs), which are liquids at temperatures down to −12.6 °C. However, there are no reports where asymmetric cells with PSA-based anodes show stable operation for >1000 charge-discharge cycles. This is likely due to the relative instability of the cathodes that have been utilized in these cells.

Here we developed a cell with the PSA-based anode and an organic polymer cathode, which is a derivative of hexaazatripenylene. The selected cathode material ensures excellent stability over >10000 cycles at 10 A g\(^{-1}\) (>70 C rate, specific capacity 135 mA h g\(^{-1}\)) with 88\% capacity retention after 10000 cycles. In addition, the organic cathode demonstrates exceptionally fast redox kinetics, showing the discharge capacity of 60 mA h g\(^{-1}\) at 50 A g\(^{-1}\) (>800 C rate), which is ~30\% of the capacity reached at a relatively low current density of 0.2 A g\(^{-1}\).

**EN01.03.10**

**Advanced Cathodes for Intermediate-Temperature Na Batteries**

Xiaowen Zhan, Xiaochuan Lu, Jeff Bonnett, Nathan Canfield, Hee-Jung Chang, Jonathan Sepulveda, Vincent Sprenkle and Guosheng Li; Pacific Northwest National Laboratory, United States

The challenges associated with integrating renewable resources, such as the intermittent solar and wind power, have placed substantial demands on the development of energy storage systems. Sodium-based battery technologies that are economical (because Na is abundant) and have long cycle life are gaining importance especially for stationary energy storage applications. Intermediate-temperature Na batteries have demonstrated several advantages over their conventional high-temperature counterparts, including superior battery safety, lower operating temperature and manufacturing cost, potentially longer cycle life, and easier assembly. However, there is still a lack of cost-effective cathode materials with high energy density and rate capability suitable for large-scale applications. In this work, we will introduce some of our recent findings on advanced conversion-type cathodes for intermediate-temperature Na batteries with the emphasis on new cathode reaction mechanisms.

**EN01.03.11**

**X-Ray Imaging Analysis in All-Solid-State Secondary Battery Using Silver Ion**

Koji Kandori\(^1\), Hisao Yamashige\(^2\), Noritoshi Furuta\(^3\), Takamasa Nonaka\(^4\) and Yuki Orihashi\(^1\); 1Ritsumeikan University, Japan; 2Toyota Motor Corporation, Japan; 3SOKEN, Inc., Japan; 4Toyota Central R&D Labs., Inc., Japan

All-solid-state rechargeable batteries are expected to be used widely as post lithium-ion batteries. Recently, the ionic conductivity of the solid electrolyte has been dramatically improved to the similar order as organic electrolytes. However, to improve the performance of all-solid-state rechargeable batteries at the cell level, it is important to not only enhance the ionic conductivity of the solid electrolyte but also to understand the diffusion behavior of carrier ions in composite electrodes. Ion diffusion in composite electrodes is complicated during charging and discharging in all-solid-state rechargeable batteries. In the case of a liquid electrolyte using an organic solvent, the transport number is lower than 1.0[1], and it is known that ion concentration distribution is caused in the electrolyte[2, 3]. On the other hand, in principle, no ion concentration distribution occurs in the solid electrolyte since in the solid electrolyte, the transport number of carrier ions is approximately one. Therefore, it is considered that ion diffusion phenomena in solid electrolytes are different from liquid systems. Although ion diffusion in composite electrodes of
bulk-type all-solid-state batteries proceeds through active materials and solid electrolytes, its diffusion path is very complicated, and its analysis is a challenge. Therefore, few observation examples of the dynamic behavior of carrier ions during the operation of the batteries have been reported. Another factor is that lithium ion, which is a general carrier ion, is a light element and it is difficult to detect the ions directly. In this research, as a model case of the all-solid-state rechargeable battery, the diffusion behavior in the composite electrode was directly observed by high energy synchrotron X-ray using the all solid secondary battery cell which uses silver ion as a carrier. Silver ion conductors have the advantage that solid electrolytes exhibiting high conductivity at room temperature have already been reported[4]. Also, silver ions are sensitive to X-ray. By using X-ray transmission imaging method with synchrotron X-ray with high transmittance, spatial resolution, and temporal resolution, the silver ion concentration distribution in the electrode during charging and discharging in the model battery was directly observed[5]. From the obtained results, the apparent diffusion coefficient in the composite electrode was calculated.

A silver-ion conductor, Ag₆I₄WO₄, was prepared as a solid electrolyte for all-solid-state silver battery. To observe the ion concentration distribution in the bulk-type all-solid-state rechargeable battery, an Ag | Ag₆I₄WO₄ | TiTe₂ cell was fabricated. Synchrotron X-ray radiography measurements were performed in SPring-8 (Hyogo, Japan). X-rays were irradiated during discharge with a constant potential at 72 mV, and transmission intensity was measured with a two-dimensional detector to obtain an image.

The apparent diffusion coefficient in the composite electrode was estimated from this imaging measurements. This result suggests that ion diffusion in the composite electrode governs the performance. Thus, it has been suggested that ion diffusion in the composite electrode is important at a scale of hundreds of microns of the actual electrode thickness.

References

EN01.03.12
Advanced Lithium/Oxygen Flow Batteries—Challenges and Opportunities
Francesca De Giorgio¹, Alessandro Brilloni²,¹, Federico Poli²,¹ and Francesca Soavi²,¹; ¹Startup BETTERY, Italy; ²University of Bologna, Italy

Advanced, next-generation lithium batteries play a key role in the market penetration of electrochemical energy storage systems that will boost the progress of sustainable alternative sources of energy and transport. The emerging flow lithium batteries (FLBs) are attracting great interest thanks to the combination in a unique solution of the high specific energy of lithium batteries and the design flexibility of redox flow batteries that, in turn, allow to decouple energy and power.

Different kinds of FLBs have been proposed, such as batteries featuring semi-solid anolytes and/or catholytes with Li-ion intercalation powders, such as LiFePO₄ or Li₄Ti₅O₁₂, dispersed in organic electrolyte, and Li/S, Na-ion and Li/O₂ flow batteries. However, advancements in materials, cell design and concepts are still mandatory to achieve the leap forward in next battery generation.

BETTERY is an Italian Innovative Startup that aims to bring into market a radically new battery concept, i.e. NEw Semi-Solid flow lithium OXygen battery (NESSOX) that combines the high energy density of Li/O₂ batteries with the flexible and scalable architecture of redox flow batteries. NESSOX, featuring a lithium metal anode and a semi-solid, flowable catholyte, displays the highest practical specific energy and energy density ever reported, up to 500 mWh cm⁻², allowing to extend the drive range of electric vehicles to consumer acceptable values. The flowable nature also permits a breakthrough in the battery field thanks to the fast recharge by “catholyte refueling”. The main technology challenges faced by BETTERY to bring NESSOX into market are here presented and discussed.

Acknowledgements
The Authors would like to thank for financial support H2020 SME Instrument Phase 1, EIT Raw Materials Battery Challenge 2019, Climate-KIC Startup Accelerator Italy 2018, Stage 1 and Stage 2, The Gaetano Marzotto ‘Company Idea’ Prize (2018), PNI Cube 2017.
EN01.03.13
Fabrication of Iron(II) Oxide Embedded Hole-Rich Carbon Shells for Efficient Electrocatalysis in Rechargeable Zn-Air Battery
Dong Eun Kim, Seung Youn Lee, Muhyeon Kim and Chang Keun Kim; Chung-Ang University, Korea (the Republic of)

Hole-rich carbon shells containing Iron(II) oxide (Fe$_2$O$_3$@NHC) were fabricated and exploited as electrocatalysts for rechargeable Zn-air battery. Fe$_2$O$_3$ particles were firstly synthesized by a hydrothermal reaction of Iron(III) nitrate, followed by wrapping glucose on the particles. The resulting glucose-coated Fe$_2$O$_3$ particles were annealed with urea to incorporate nitrogen on the carbon sp$^2$ structure, and then etched by hydrogen peroxide to form hole-rich structure. The formation of Fe$_2$O$_3$@NHC was confirmed by some analysis including HR-TEM, XPS, Raman and BET. The Fe$_2$O$_3$@NHC exhibited high specific surface area and high electrochemical surface area (ECSA) due to its hole-rich structure and incorporated N species. The electrocatalytic activity of the Fe$_2$O$_3$@NHC was confirmed by rotating ring disk electrode (RRDE). The Fe$_2$O$_3$@NHC exhibited outstanding oxygen reduction and evolution reaction activities in alkaline condition, which were comparable to noble-metal based catalysts. When the Fe$_2$O$_3$@NHC was used as a catalyst for the cathode of Zn-air battery, the battery showed outstanding energy density and good charge-discharge cycle stability. Therefore, the excellent catalytic activity and stability of Fe$_2$O$_3$@NPCs make them promising catalysts for rechargeable Zn-air battery.

EN01.03.14
Capacity Degradation Due to LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ Phase Transition at Cathode Composite Using Li$_6$PS$_5$Cl Solid Electrolyte in All-Solid-State Batteries
Hyeon-Ji Shin$^{1,2}$, Jiwon Jeong$^{1,3}$, Kyung Yoon Chung$^{1,2}$ and Hun-Gi Jung$^{1,2}$; $^1$Korea Institute of Science and Technology, Korea (the Republic of); $^2$Korea University of Science and Technology, Korea (the Republic of); $^3$Korea University, Korea (the Republic of)

Commercialized lithium ion batteries (LIB) have applied on electric vehicle running over 300 miles, but there is still a hazard of flammability due to liquid based electrolyte. Therefore, many researchers have been trying to ensure safety issues of flammable accident from liquid electrolyte. Solid electrolyte (SE), especially sulfide based SE, is expected that ionic conductivity in all-solid-state batteries (ASSBs) could catch up with liquid electrolyte level in LIB. Among the various sulfide-based SE, Li$_6$PS$_5$Cl (LPSCl) have been considered as promising SE because of its low cost, relatively stable with conventional cathode, and high ionic conductivity (1.3x10$^{−3}$ S cm$^{−1}$) at room temperature[1].

Average capacity have 140 mAh g$^{−1}$ using LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (NCM523) active material as cathode and LPSCl as SE. However, the electrochemical performance of pellet-type cell consisting of NCM523 composite cathode/LPSCl/Indium foil shows that the capacity is rapidly decreased after 20 cycles, and the capacity retention falls down below 50% within 50 cycles. Janek’s group reported a side reaction of carbon-containing cathode composite which accelerates the oxidation of sulfide-based SE on cathode surface[2].

In this study, interestingly, we figured out that declined lifetime of cell is originated from not only side reaction in which an electrolyte is decomposed at interface between NCM523 active material and LPSCl but also cathode deterioration due to NCM523 phase transition. In particular, TEM analysis revealed that the Ni/Li cation mixing resulting in phase transition from layered R(−)3m phase to the spinel phase Fd(−)3m, and this result could be supported by confirming the change of Ni oxidation states analyzed by XANES. From above analysis, the similar mechanism as LIB has been observed to cause cathode deterioration, and we will discuss further more in detail which system is occurred the deterioration more quickly and what the reason is.

Reference
EN01.03.15
A Thermal Management Approach for Safety Operation of Electric Vehicles or Hybrid Electric Vehicles
Application Jeemut Bahan Sangiri, Chandan Chakraborty and Sudipto Ghosh; Indian Institute of Technology Kharagpur, India

Li-ion batteries (LIBs) are one of the promising energy storage devices with diverse applications in portable devices, Electric Vehicles (EVs), Hybrid Electric Vehicles (HEVs) due to their impressive energy density and cycle life. However, the issues like abnormal temperature inside the LIBs leads to thermal runaway, material degradation, capacity fading and hence the performance deteriorates. In this work we have incorporated finite element method (FEM) based technique to couple thermal and electrochemical model in the battery electrode for safety and reliability. The FEM model explains about the quantification of heat generation inside the battery pack by integrating convection forced air cooling with the battery pack to maintain the temperature of the battery pack within the safety limits. Consequently, this model is tested with a real-time system for the superior battery health and performance.

EN01.03.16
Mn0.9Co0.1O2 Spinel Coatings for the Stabilization of Nickel-Rich NMC Cathodes for Li-Ion Batteries
Luqman Azhari and Yan Wang; Worcester Polytechnic Institute, United States

NMC811 (Ni0.8Mn0.1Co0.1O2) is a cathode material of significant commercial interest for next generation lithium ion batteries due to its higher capacity and lower cost compared to current LiCoO2 cathodes (200mAh/g vs 140mAh/g). However, in the highly charged state (V > 4.3V vs Li/Li+), side reactions between high valence nickel and electrolyte jeopardize prolonged usage and stability. In this work, we address these issues by utilizing an industrially viable coprecipitation process to apply a chemically stable Mn0.9Co0.1O2 spinel coating to protect the NMC material. After forming the metal hydroxide precursor, dilute solutions of manganese and cobalt sulfate are added in order to encourage coating formation while preventing supersaturation and the subsequent precipitation of separate crystals. The thin Mn0.9Co0.1O2 spinel coating formed post-sintering is observed to improve capacity retention during electrochemical cycling at an upper voltage cutoff of 4.5V and at elevated temperatures of 55°C. In addition, electrochemical performance at high charge/discharge rates surpasses that of MnO2-coated NMC811. The results suggest a method for an industrially viable process to synthesize and stabilize Ni-rich cathodes for improved lithium-ion batteries.

EN01.03.18
Tungsten Oxide Coated Graphite Anode Material for Enhancement of High Rate Capability Lithium-Ion Battery
Dong Jae Chung1, Dae Sik Kim2, Hyun Jong Kim1, Hyun Dong Yoo1 and Hansu Kim1; 1Hanyang University, Korea (the Republic of); 2Korea Electronics Technology Institute, Korea (the Republic of)

As demands for electric vehicles (EV) and mobile electronics are increased, energy storage device becomes important. Lithium ion Battery (LIB), currently one of the most promising solution to EV, has critical issue in terms of fast charging problem. Graphite material, currently used as anode materials for LIB, has prominent limitation in term of high rate capability. To overcome this limitation, many materials have been researched for alternative of commercialized graphite material. Herein, we prepared tungsten oxide coated graphite by facile sol-gel reaction. the prepared tungsten oxide coated graphite showed enhanced the high rate capability of LIB. Without any reversible capacity fading, the tungsten oxide coated graphite anode electrode showed an outstanding rate capability of 90.28 % of the capacity retention at a rate of 5C (1800 mA g\(^{-1}\)) compare to that tested at a rate of 0.2C (72 mA g\(^{-1}\)). In further characterization, microstructure and electrochemical performance of the tungsten oxide coated graphite will be discussed in more detail.

EN01.03.19
A Novel Approach to Synthesize Micrometer-Sized Porous Silicon with Internally and Externally Interweaved CNT as a High Performance Anode for Lithium-Ion Batteries
Donglin He, Tianying Wang, Ping Li and Xuanhui Qu; University of Science and Technology Beijing, China

Silica fume is an industrial by-product or solid waste of the manufacture of silicon metal and ferrosilicon alloys,
which is collected from the smoke dust of electric arc furnaces. When the smelting temperature reaches 1700 °C or more in the electric furnace, bits of silicon reacts with oxygen in the air to form silicon monoxide, which can be further oxidized to silica. After cooling, silica fume is obtained by collecting the fine spherical particles via a dust collector. Recently, silica fume has been widely used as the admixtures to product concrete and cement. However, exploring high value-added utilization from silica fume is still expected for silicon smelters.

In this work, we synthesized a novel structural microspheres consisting of cross-linked CNT, porous Si/SiOx nanoparticles, CNT, and carbon coating (CNT/SFDP-Si/SiOx@C microspheres) by combining an inverse water-in-oil microemulsion approach with magnesiothermic reduction, in which silica fume, an inexpensive industrial by-product, is used as the porous Si precursor. The CNT/SFDP-Si/SiOx@C microspheres features a unique secondary structure, providing multiple significant advantages for solving the problems associated with Si. (I) the nanosized primary particle size prevents fracture; (II) the internal luxuriant voids offer enough space for the expansion of Si; (III) the internally and externally wired CNT construct a long distance electrically conductive networks and a electrical fast track to reinforce electron transport and acts as a structure protector to keep stability of the secondary microspheres without been destroyed; (IV) carbon exhaustively coats the outerface of the microspheres and inner nanosized Si particles, reducing SEI formation and retains the internal void space for silicon expansion; and (V) the space-efficient packing inside the secondary particles the micron-sized secondary microspheres possess low surface area and high tap density.

Thus, the CNT/SFDP-Si/SiOx@C microspheres displays stable capacities of 576.2 mAh g−1 at 2 C over 1000 cycles. The excellent electrochemical performance of CNT/SFDP-Si/SiOx@C microspheres manifests its supremacy as widespread anode material for both LIBs.

EN01.03.22
Cobalt-Free Quaternary Amorphous Alloy Cathodes for Lithium-Ion Battery Tiange Yuan and Oleksandr Voznyy; University of Toronto, Canada

Currently, lithium cobalt oxide cathodes have been extensively used in personal electronic devices due to their light weight and high energy density. However, the high cost of cobalt due to its decreasing available resource limits its application in electric vehicles manufactures. We synthesized quaternary cobalt-free amorphous alloys through a high-throughput robotic synthesis system with machine learning. The amorphous materials promise high structural flexibility for tuning and a less-energy-intensive production. The sol-gel synthesis enabled us to obtain multicomponent homogeneous amorphous alloys. The properties of materials were easily tuned by adjusting procurers’ ratio, temperature, reaction time. The combination of high-throughput synthesis with machine learning helped us to avoid the guess-and-check method and fastened the research. Theoretical modelings revealed the working mechanism of amorphous materials. We obtained quaternary amorphous cathode with unprecedented performance while avoiding undesirable toxic or expensive components.

EN01.04.01
Deeply Rechargeable Zinc Anodes in Alkaline Electrolyte Nian Liu; Georgia Institute of Technology, United States

Zinc metal anode possesses 3 times the volumetric capacity of Li metal anode, is compatible with non-flammable aqueous electrolyte, and remains on the same side of separator when discharged to ZnO in alkaline electrolyte. Indeed, primary zinc-air batteries have long been used for electronic devices requiring extremely high energy density (e.g. hearing aid). However, rechargeable zinc-air batteries have not been successful, preventing their entrance into larger markets such as electric vehicles, data center UPS, and indoor machinery. In this presentation, I will show my lab’s recent efforts towards making deeply (100% depth of discharge) rechargeable zinc-based
batteries, via nanostructured material design. This presentation is based on the following six recent publications from my lab:
2. Graphene oxide-modified zinc anode for rechargeable aqueous batteries. *Chemical Engineering Science* 2019, 194, 142-147. (Cover article)

8:45 AM *EN01.04.02
Lithium Metal Plating Stability against Solid Electrolytes—Understanding and Experimental Validation Paul S. Albertus; University of Maryland, United States

Enabling the stable cycling of Li metal at rates and other metrics of practical significance is a key route to substantially increase the energy content of Li-based batteries beyond present Li-ion technology. Therefore, a careful analysis of lithium plating stability across a range of conditions and materials platforms is essential to understand and quantify the processes that lead to lithium growth through a separator and subsequent cell shorting. This talk will provide an overview of the current state of understanding of lithium plating stability, with a focus on both modeling and experimental methodologies. Emphasis will be placed on solid electrolyte systems, along with current gaps in knowledge and experimental validation of plating stability hypotheses. A number of practical issues and perspectives gained from the time the author served as a Program Director at ARPA-E working in the area of lithium metal batteries will also be included.

9:15 AM EN01.04.03
In Situ Characterization of Heterogeneity in Parasitic Li Plating During Extreme Fast Charging in Lithium-Ion Batteries Partha P. Paul1, Vivek Thampy1, Chuntian Cao1, Hans-Georg Steinrueck1, Andrew Jansen2, Venkat Srinivasan2, Ira Bloom1, Tanvir Tanim3, Michael F. Toney1 and Johanna N. Weker1; 1Stanford Synchrotron Radiation Lightsource, United States; 2Argonne National Laboratory, United States; 3Idaho National Laboratory, United States

With the increasing demand for electric vehicles, there is an urgent need for Li-ion batteries (LIBs) with extreme fast charging (XFC) capabilities. A major challenge in such batteries is retention of battery capacity over cycling under XFC conditions when recharging times are comparable to traditional refueling times. Current literature states parasitic Li plating on the anode is the major factor contributing to decreasing battery capacity and therefore shortened battery life [1]. However, the techniques used for understanding Li plating under in situ conditions has primarily involved characterization of Li by averaging over entire specially built cells [2].

While this approach provides a good starting point, the plating process is expected to be heterogeneous across the cell. Therefore, we use X-ray diffraction to:
1. Study the spatial heterogeneity in Li plating across a full pouch cell at various length scales.
2. Correlate the total amount of plated Li to the capacity loss of the cell during cycling.

The non-destructive nature of X-ray based techniques enables characterization of the Li plating across multiple length scales on the same cell. Towards this, single layer pouch cells (4cm x 6cm) with a porous graphite anode, NMC (LiNi0.5Mn1.5Co2O4) cathode and an EC:MC electrolyte were charged at different rates within the XFC regime and characterized using high energy x-rays.

At the mm-scale, powder diffraction was used to study the spatial heterogeneities and correlations between various species at the cell level. The analysis showed that the intensity of plated Li was directly correlated to the intensity of Li-graphite staged phases (LiC), even after discharging. These Li-rich regions in the cell also corresponded directly to depleted anode
(reduced graphite intensities), irrespective of the charging rate and regime. Additionally, the regions showing high Li intensity were analyzed for the orientation spread of plated Li. At the end of 450 cycles, the plated Li shows a random polycrystal orientation, without any direct evidence of a preferential texture, as suggested by some earlier studies [3]. Finally, the persistence of Li plating with increased number of XFC cycles as well as the effect of the cycling rate were examined in detail at the cell level. At the microscale, microdiffraction was used to study regions with significant Li plating, as found from the mm-scale scans. Such microscale analysis yields the size of plated Li crystallites as well as the local orientation/texture of plated Li, as a function of the charging rate and capacity fade.

The understanding gained from this study provides foundational knowledge of the conditions that promote and those that minimize parasitic Li plating. Based on this knowledge, parameters such as the XFC charging rate, charging protocol, electrolyte composition and anode architecture can be optimized, such that parasitic plating is minimized. This optimization will in turn help to guide the rational design of the next generation of XFC capable LIBs with a consistent performance.


9:30 AM EN01.04.04
Quantifying Inactive Lithium in Lithium Metal Batteries Chengcheng Fang1, Jinxing Li1, Minghao Zhang1, Yihui Zhang1, Fan Yang2, Min-Han Lee1, Mei Cai3, Jing Gu2, Kang Xu4 and Shirley Meng1; 1University of California, San Diego, United States; 2San Diego State University, United States; 3General Motors Research and Development Center, United States; 4U.S. Army Research Laboratory, United States

Inactive lithium (Li) formation is the immediate cause of capacity loss and catastrophic failure of Li metal batteries (LMBs). Differentiating and quantifying the Li⁺ in solid electrolyte interphase (SEI) components and the unreacted metallic Li, which together comprise the inactive Li, is the key to understanding the mechanisms leading to capacity decay. However, this has not yet been successful due to the lack of effective diagnosis tools that can accurately differentiate Li⁺ in SEI and the unreacted metallic Li. Here, by establishing a new analytical method, Titration Gas Chromatography (TGC), we accurately quantify the contribution from unreacted metallic Li to the total amount of inactive Li. We identify the unreacted metallic Li, rather than the (electro)chemically formed Li⁺ in SEI, as the dominating cause for the inactive Li and capacity loss in LMBs, clearing the long-term misconception in the field that the low CE is caused by the continuous repairing of SEI fracture. Using cryogenic electron microscopies to further reveal the micro- and nanostructure of inactive Li, we identified two ways for deposited metallic Li to lose electronic connections with the bulk electrode, thus becoming electrochemically inactive. Coupling the quantification of the global content of inactive Li to observations of its local atomic structure, we reveal the formation mechanism of inactive Li in different types of electrolytes, and determine the true underlying cause of low CE in Li metal deposition and stripping. We ultimately propose strategies for highly efficient Li deposition and stripping to enable Li metal anode for next generation high energy batteries.

9:45 AM EN01.04.05
Visualization of Ion Transport in Liquid and Polymer Electrolyte for Lithium Metal Batteries Yuan Yang and Qian Cheng; Columbia University, United States

Visualization of ion transport in electrolyte provides fundamental understandings of electrolyte dynamics and electrolyte-electrode interaction, shedding light on material designs to enhance device performance, such as batteries and fuel cells. However, this task is extremely challenging for existing techniques, since it is difficult to capture the low ionic concentration (<1 M) and the fast dynamics (1-10 s) of the electrolyte. Here we show that an emerging Stimulated Raman Scattering (SRS) microscopy offers the required spatial (sub-micrometer optical resolution), temporal (faster than 1 s per frame) and chemical (around mM) sensitivities to address this challenge.

The SRS microscopy has been used to study ion depletion and lithium dendrite growth in both liquid and polymer electrolyte, and distinct behaviors are observed. In liquid electrolyte, we observe a three-stage lithium deposition
process, each corresponding to no-depletion, partial-depletion and full-depletion regime of Li⁺, respectively. A positive feedback mechanism between the inhomogeneous growth of lithium and the local ionic concentration or flux. In polymer electrolyte, we clearly see phase separation due to ion depletion and observe the accompanying transport of plasticizer inside, which was not observed in the past. These new understanding also leads to new strategies to suppress lithium dendrites. This study shows that SRS microscopy is a powerful technique for imaging ion transport and will open various applications in materials and energy fields.

References:

10:00 AM BREAK

10:30 AM *EN01.04.06
Challenge of High Energy Batteries for Electric Vehicles Application Mei Cai, Shuru Chen and Fang Dai; General Motors, United States

Highly emerged electric vehicle (EV) market evokes the demands on advanced batteries with high energy density. Li-metal batteries, including Li-NMC and Li-S, have been recognized as promising candidates beyond conventional Li-ion for next generation EV application. However, besides the energy density, automotive industry has other critical requirements on specific parameters. In this talk we will first present the requirements for future electrical vehicle application and the impact of high energy density Li-metal batteries on automotive industry. Some recent development on Li-NMC and Li-S batteries will be reviewed. The concerns and challenges of using Li metal as anode in batteries will be discussed. Moreover, we will also compare the difference of Li-NMC and Li-S in the EV applications and their specific challenges. Lastly, we will introduce some strategies on how to solve these challenges from both materials and cell levels, and also show some of our recent progress on Li-metal batteries.

11:00 AM EN01.04.07
Enhancing Electrode/Electrolyte Interfacial Stability in Solid State Lithium Batteries by Surface Coating Yuan Yang, Qian Cheng and Aijun Li; Columbia University, United States

Interfacial stability is critical to the performance of solid-state batteries. Various promising solid electrolytes are unstable with either cathode or anode, such as sulfide electrolyte / LATP / LAGP with lithium metal, and polyethylene oxide (PEO) electrolyte with 4 V layered oxides. Such incompatibility limits the performance and commercialization of solid state batteries. In this talk I will present recent studies on improving interfacial stability of LATP/Li and 4 V cathode/PEO interface. At the LATP/lithium interface, a nanoscale boron nitride coating blocks electron transfer and can significantly enhance the stability between LATP and lithium. Long cycle life of 500 cycles is achieved in LiFePO4/LATP/BN(PEO)/Li cells. On the other side, we also enhance the stability between 4 V cathode and PEO electrolyte by surface modification. Long cycle life of 400 cycles is achieved, much better than previous reports.

References:
Qian Cheng, Aijun Li, Yuan Yang et al., Stabilizing Solid Electrolyte-Anode Interface in Li-Metal Batteries by Boron Nitride-Based Nanocomposite Coating, Joule 2019.

11:15 AM EN01.04.08
Conduction Mechanism and Electrochemical Stability of Closo-Borate Electrolytes for All-Solid-State Batteries Léo Duchêne, Ryo Asakura, Ruben-Simon Kühnel, Arndt Remhof and Corsin Battaglia; Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The conduction mechanism and electrochemical stability of closo-borates, a particularly promising class of solid-state electrolytes for all-solid-state batteries [1,2], is investigated. We find from electrochemical impedance spectroscopy that the temperature dependent conductivity is characterized by three distinct regimes of conductivity. In the lowest temperature regime, conductivity remains low before a glass-like transition identified by X-ray diffraction and calorimetry causes a faster increase of cation conductivity through site disordering. Correlated ion diffusion evidenced by nuclear magnetic resonance originates from the coupling of the cation and anion motion due to short-range ion-ion interactions combined with background energy fluctuations, which we can associate through quasi-elastic neutron scattering experiment to fast librations of the anions. In the third regime, the thermal energy
increases above the background energy fluctuations resulting in non-correlated ion diffusion. I will further discuss recent progress in the fabrication of all-solid-state batteries based on closo-borate electrolytes and strategies to increase the electrochemical stability to enable a 4 V all-solid-state battery class bringing closo-borate-based all-solid-state batteries to a technology readiness level comparable to that of sulfide-based all-solid-state batteries.


11:30 AM EN01.04.09
**Bridging Length Scales via Advanced Analysis Techniques for All-Solid-State Energy Storage Systems**

Nikhilendra Singh\(^1\), Timothy S. Arthur\(^2\), James Horwath\(^2\), Eric A. Stach\(^2\), Marm Dixit\(^3\) and Kelsey B. Hatzell\(^3\);\(^*\)
\(^{1}\)Toyota Research Institute of North America, United States; \(^{2}\)University of Pennsylvania, United States; \(^{3}\)Vanderbilt University, United States

Advances in hybrid and electric technologies combined with a demand for green initiatives have motivated recent diversification in energy storage research for automotive electrification. To meet customer expectations for hybrid and electric vehicles, furthering the capability of existing battery systems remains critical. As such, new battery systems with higher energy density, power density and cycle life than the state-of-art Lithium (Li)-ion battery are needed. Post Li-ion battery systems, especially those focused on the utilization of Li metal have recently come to the forefront of research. The ability to directly utilize Li metal anodes in rechargeable batteries presents itself as an ideal, albeit challenging, situation. Li metal anodes could provide a maximum possible theoretical specific capacity (3860 mAh/g) in comparison to commercially used anodes (e.g. graphite – 380 mAh/g). Hence, significant efforts in recent literature have targeted the development of robust systems, capable of use with Li metal. One such system is Li-sulfur which has attracted attention due to its high theoretical capacity (1673 mAh/g) and potential low cost. However, this system is hindered by polysulfide dissolution and electrolyte decomposition at the Li metal anode. Among the various strategies which have been employed to overcome such hurdles, the use of solid-state electrolytes (inclusive of polymers, gels and conducting ceramics) stands out, as the implementation of solid-state electrolytes can also serve as a mechanical barrier towards Li dendrite formation. However, these electrolytes exhibit relatively lower ionic conductivities and display poor interfacial stability towards Li metal anodes. While advances in solid-state electrolyte materials continue to improve their ionic conductivities, little is known about the interfacial interactions between sulfide-based solid-state electrolytes and Li metal which can greatly affect their electrochemical performance. Hence, studies into understanding the relationship properties between Li metal and these solid-state electrolytes is essential towards realizing a sulfide-based all-solid-state Li battery.

Here, we present the electrochemical properties of various sulfide-based solid-state electrolytes in contact with Li metal. Further, we present tandem analytical ex-situ and in-situ studies via transmission electron microcopy and X-ray tomography to reveal the interfacial interactions between Li metal and solid-state electrolytes, the deposition and dissolution properties of Li metal from these electrolytes, and the effects of the deposition and dissolution properties on the bulk electrolyte structure. The presented studies allow for comparisons of Li deposition and dissolution properties below and above the critical current densities for each solid-state electrolyte material and stand to help clarify both interfacial and morphological evolution mechanisms during Li cycling from them.

11:45 AM EN01.04.10
**Nanostructured Ionic Liquids in Lithium Metal Batteries**

Lan Zhang\(^1\), Haiyan Bian\(^1\) and Suojiang Zhang\(^1\);\(^*\)
\(^{1}\)Institute of Process Engineering, CAS, China; \(^{2}\)University of Chinese Academy of Science, China

With wide liquid range, negligible vapor pressure, strong designability, high thermal and electrochemical stability, ionic liquids (ILs) are almost the ideal candidate for safe electrolyte in lithium ion or lithium metal batteries. While for one thing, most ILs are highly viscos, which may possibly reduce the electrolyte conductivity; and for the other, ILs are composed of large cations and ions, complicated interaction with lithium salt usually lead to reduced Li ion transference number (t\(_{\text{i,li}}\)). As a result, in spite of all the fascinating characteristics, most IL electrolytes still show limited conductivity and t\(_{\text{i,li}}\), which hinder them far from application.\(^{1-3}\)

Combining the concept of ionic liquid and nanostructured materials, nanostructured ionic liquids (NIL) is a new type of matter that possess the properties of both IL and nano materials. By tethering IL structure onto nano particles
such as SiO$_2$, Al$_2$O$_3$, we prepared several NILs and use them in lithium sulfur flow battery\cite{4},

electrospun nano fiberous separator\cite{5}, as well as electrolyte additive, we found that the NILs could increase the $t_{Li^+}$ by anchoring the cation, and its strong interaction with anion could further regulate the transport of anions, on which enhanced electrochemical performance could be obtained.


**SESSION EN01.05: Li Metal Battery II**
Session Chairs: Mei Cai and Xiaolin Li
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Independence East

1:30 PM *EN01.05.01
Design of Single-Ion Polymeric Nanoparticles for Solid-State Lithium Metal Battery Applications **Luca Porcarelli**\textsuperscript{1,2}, Haijin Zhu\textsuperscript{1}, Roberto H. Aguirresarobe\textsuperscript{2}, Nicolas Goujon\textsuperscript{2,1}, Jose R. Leiza\textsuperscript{2}, Maria Forsyth\textsuperscript{1,2} and David Mecerreyes\textsuperscript{2}; \textsuperscript{1}Deakin University, Australia; \textsuperscript{2}University of the Basque Country, Spain

While inorganic nanoparticles have received great attention for solid-state lithium metal battery applications, rather less interest has been paid to all-polymeric nanoparticles despite the availability of easily up–scalable polymerization techniques for the synthesis of nanoparticles with functionalized surfaces. In this work, we report composite electrolytes based on all-polymeric methacrylic sulfonamide nanoparticles designed to provide transference numbers close to unity. Mixing the particles with conventional electrolytes, such as poly(ethylene oxide) or propylene carbonate, we obtained mechanically robust nanocomposite electrolytes with storage moduli values as high as 10\textsuperscript{6} Pa and ionic conductivity values up to 10\textsuperscript{-4} S cm\textsuperscript{-1}. The comparison of lithium dynamics and mechanical properties suggest decoupling of these two antagonistic properties in our nanocomposite electrolytes. Pulsed–field gradient NMR showed that the mobility of lithium–ions exceeded by several orders of magnitude the mobility of the sulfonamide anions tethered to the particle surface. Finally, the electrochemical performance of symmetrical lithium cells are presented, showing promising results. Our findings suggest that all-polymer nanoparticles could represent a paradigm shift for solid-state lithium metal battery applications.

2:00 PM EN01.05.02
Polymer in Quasi-Ionic Liquid Electrolytes for High-Voltage Lithium Metal Batteries **Haiping Wu**\textsuperscript{1}, Linchao Zhang\textsuperscript{1,2}, Xia Cao\textsuperscript{1}, Quyan Li\textsuperscript{1}, Michael S. Ding\textsuperscript{3}, Kang Xu\textsuperscript{1}, Jiguang Zhang\textsuperscript{1} and Wu Xu\textsuperscript{1}; \textsuperscript{1}Pacific Northwest National Laboratory, United States; \textsuperscript{2}Institute of Solid State Physics, China; \textsuperscript{3}U.S. Army Research Laboratory, United States

All-solid-state lithium (Li) metal batteries (LMBs) are considered good candidates for the next generation power sources because of their excellent safety compared to the liquid electrolyte-based batteries. However, the poor interfaces between the inorganic solid electrolyte and the two electrodes (cathode and anode) make the practical applications of all-solid-state inorganic batteries very challenging. Polymer electrolytes are more promising in processability due to their flexible characteristics. Polyethylene oxide (PEO) is the most widely studied polymer in Li metal polymer batteries (LMPBs). Nevertheless, the performance of conventional LMPBs remain limited by the poor room-temperature ionic conductivity of the PEO-based electrolytes. Conversely, the low oxidative resistivity of ethylene oxide (EO) segments (< 4 V vs. Li/Li\textsuperscript{+}) of PEO restricts the utilization of 4 V class cathode materials in LMPBs, resulting in a low energy density of the batteries. Therefore, developing high voltage all-solid-state LMPBs is of high significance. In this work, polymer-in-salt electrolytes (PISEs) were developed by mixing PEO and lithium bis(fluorosulfonyl)imide (LiFSI) at high Li\textsuperscript{+}/[EO] ratios. The optimal PISE exhibited a high oxidation voltage (4.38 V vs. Li/Li\textsuperscript{+} on Al) and moderate conductivity (0.07 and 0.27 mS cm\textsuperscript{-1} at 60 and 80 °C, respectively).
The all-solid-state Li|PISE|LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 cells were evaluated with a high cut-off voltage up to 4.4 V. Additional details will be reported during the 2019 Fall Materials Research Society (MRS) Meeting & Exhibit and ensuing presentation.

Acknowledgement

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, the Advanced Battery Materials Research (BMR) Program of the U.S. Department of Energy (DOE) under contract no. DE-AC02-05CH11231.

2:15 PM EN01.05.03
Dispersion Quantification of an Ion-Conducting Polymer in Electrodes for Solid-State Batteries Adriana A. Rojas, Tatiana Loureiro, Lucienne Buannic, Brian Chiou, David Laughman and Wesley Hoffert; A123 Systems, United States

With an increase in demand for high energy dense storage devices for electric vehicles or intermittent energy sources, comes an increase for the need for efficient processing of materials that lead to safe and optimal-performing batteries. Safety can be enhanced with the incorporation of solid-state materials whereby an ion-conducting polymer matrix is established through the mixing and coating process of an electrode. These ion-conducting pathways are heavily dependent on the starting material sizes, the composition of the electrode, as well as the type of mixing profiles that are implemented. The efficacy of these ion-conducting pathways are quantified systematically from SEM images using existing computer packages in order to understand the best set of conditions that can lead to high-performing electrodes for safe solid-state lithium ion batteries.

2:30 PM *EN01.05.04
Single-Ion Conducting Polymer Electrolytes for Safer High-Energy Lithium Batteries Dominik Steinle¹², Huu-Dat Nguyen³, Zhen Chen¹², Alexander Mayer⁴, Elie Paillard⁵, Stefano Passerini¹², Cristina Iojoiu³ and Dominic Bresser¹²; ¹Helmholtz Institute Ulm (HIU), Germany; ²Karlsruhe Institute of Technology, Germany; ³University Grenoble Alpes / CNRS, France; ⁴Forschungszentrum Juelsch, Germany

Polymer electrolytes are considered to play a decisive role for the realization of safer rechargeable batteries and may, additionally, allow for the employment of lithium metal anodes, thus, paving the way for significantly higher energy densities.¹² Beside mechanical strength, especially three characteristics appear to be of paramount importance: (i) Single-ion conduction to prevent the reversed cell polarization, negatively affecting the long-term cycling stability, (ii) suitable ionic conductivities at ambient temperature, and (iii) a homogeneous lithium deposition upon charge to avoid the dendritic metal deposition.¹² While (i) has successfully been addressed already in literature, commonly by covalently tethering the anionic function to the macromolecular backbone,¹³ (ii) appears to be intrinsically limited by its dependency on the segmental relaxation of the polymer.¹⁴ Remarkably, the key to overcome the conductivity limitation and simultaneously address also (iii) may rely on introducing structure into polymer electrolytes.⁵⁶
Starting from a brief review, covering early and very recent work, selected strategies for this general approach will be highlighted. A particular focus will be set on fundamental insights into the charge transport mechanism and how this translates into enhanced electrochemical properties as well as selected results for high-energy lithium batteries comprising Ni-rich Li[Ni_{1-x-y}Mn_xCo_y]O_2 cathodes – a cathode material that had commonly been considered incompatible with any polymer electrolyte due to its challenging interface chemistry.

References
3:00 PM BREAK

3:30 PM *EN01.05.05
High Capacity LiS-Batteries—New Materials, Concepts and Mechanisms Aleksander Matic, Marco Agostini, Shizhao Xiong, Matthew Sadd and Carmen Cavallo; Chalmers Univ of Technology, Sweden

To reach a step change in energy density of rechargeable batteries new chemistries need to be considered as the current state-of-the-art, the Li-ion battery, is approaching its theoretical limit. Among potential chemistries for next generation batteries the LiS-battery has for some time been highlighted as one of the most promising. The interest stems from the high specific capacity of the reaction between Li and S and a theoretical energy density of a LiS-cell up to five times higher than current Li-ion technology. In addition, sustainability is more and more at focus in battery technology and being based on abundant materials LiS-technology has also the potential radically improve this aspect.

Despite the very promising characteristics LiS-technology has so far not been realized in large scale applications due to problems involving low utilization of active material, low practical energy density, slow kinetics resulting in poor rate capability, and capacity fading. Most of the problems are directly related to the conversion reaction between Li and S where polysulfide intermediates (Li2Sx), which are soluble in many of the common battery electrolytes used, are produced. Whereas the solubility of polysulfides can be a problem in terms of loss of active material and side reactions if they migrate out of the cathode, it is also a prerequisite in order to have high active material utilization and fast kinetics. Thus, the key is to manage polysulfide dissolution, rather than preventing it, to prevent side reactions on the anode (most commonly Li-metal) and to maximize the fraction of active material in the cell, i.e. minimizing the amount of electrolyte as well as inactive components such as binders and conducting agents. New materials concepts are needed both for the electrode and the electrolyte in order to achieve this. Recently there has been considerable progress with the development of nanostructured and functionalized carbon structures on the cathode side as well as functional separators and new electrolytes.

In this contribution we present new materials concepts based on the use of self-supporting carbon structures and the use of catholytes, where a part of, or all, active material is dissolved in the electrolyte [1-3]. Carbon nanofiber membranes and self-standing graphene-based aerogels can be used directly as electrodes, without further processing or the addition of conducting agent, binders or metal current collector, thus maximizing the amount of active material in the cell [2-3]. The performance of these materials will directly depend on their nanostructure (surface areas, pore size and pore distribution) and on presence of functional groups being able to interact with the dissolved polysulfides. With a catholyte, on the other hand, we can both increase the amount of active material in the cell as well as help forming a stable interphase on the Li-anode [4]. We show that by these routes high practical energy density, high sulfur utilization, and stable cycling can be obtained in cells with high sulfur loading and very low amount of electrolyte. We also present result from operando experiments (Raman spectroscopy and x-ray imaging) where we directly follow the processes taking place during discharge and charge, as well as from complementary ex-situ techniques, in order to understand the reaction mechanism in these systems.

References

4:00 PM EN01.05.06
Dendrite Suppression for Metal Anodes Using Liquid Crystalline Electrolytes Zeeshan Ahmad, Zijian Hong and Venkatasubramanian Viswanathan; Carnegie Mellon University, United States

There is an increasing need for high energy density batteries for achieving complete electrification of transportation. Batteries based on metal anodes like lithium can achieve energy densities much higher than the current state of the
art. However, these batteries have been plagued by an unstable and uncontrollable growth of dendrites during electrodeposition leading to short circuit and loss of Coulombic efficiency. Here, we present a new approach using liquid crystalline electrolytes to suppress the growth of dendrites during electrodeposition in metal anode-based batteries. Liquid crystalline electrolytes provide fast ionic transport together with high cation transference number, wide temperature window, non-flammability and low-cost bulk manufacturing [1, 2]. However, the dendrite suppressing nature of liquid electrolytes due to their orientational order has not been explored. A nematic liquid crystalline electrolyte with a perturbed director field due to interface with lithium metal is associated with bulk distortion and anchoring free energy. This changes the free energy of lithium ions in the electrolyte leading to a change in the equilibrium overpotential and thereby the kinetics of metal electrodeposition when used in a metal anode-based battery. We employ a phase-field model to simulate the electrodeposition of lithium in the presence of a standard and liquid crystalline electrolyte. On comparison of metal surface growth metrics with a standard electrolyte, we find considerable suppression of dendrite growth using a liquid crystalline electrolyte. Finally, we propose some design guidelines for the properties of the liquid crystalline molecules/polymers in order to achieve dendrite suppression for practical applications in batteries.


4:15 PM EN01.05.07
Electrolytes for Lithium-Sulfur Batteries Rebecca Glaser1, Feixiang Wu1, Billy Johnson1, Jud Ready1, Mohan Sanghadasa2 and Gleb Yushin1; 1Georgia Institute of Technology, United States; 2U.S. Army Combat Capabilities Development Command, United States

As the world faces a growing need to electrify and reduce carbon emissions, batteries offer much needed energy storage for electric cars, mobile devices, and the grid. For transportation and mobile devices, lightweight batteries are key, while non-toxicity is important for low environmental impact. The lithium-sulfur (Li-S) battery combines low weight, non-toxicity, low cost, and high capacity. With one of the highest theoretical capacities (1166 mAh/g) of any conversion-type cathode, the pursuit of low cost, long-lasting Li-S batteries is a global research focus. However, it is difficult to achieve the promised high theoretical capacity because of polysulfide dissolution in to the electrolyte and reaction at the Li anode surface, depleting the active material in the cathode. Current electrolytes are not effective enough at managing the polysulfide dissolution and have the negative side effects of high viscosity and high cost. In this study, we evaluate several new electrolytes with advantageous physical properties. We compare conventional sulfur cathodes to high-loading cathodes to look at the impact of wetting on performance. The impact of salt combinations and ratios on conductivity, viscosity, electrochemical performance, and SEI composition will be discussed in this talk.

4:30 PM EN01.05.08
Surface Chemistry and Electrocatalysis in Metal Phosphide-Stabilized Li-S Batteries Yiren Zhong1, Yuxiang Yang1, Lichang Yin2, Peng He1 and Hailiang Wang1; 1Yale University, United States; 2Institute of Metal Research, Chinese Academy of Sciences, China

Abstract: Lithium-sulfur batteries promise high energy density, but their poor cycling stability has been limiting their practical applications. The unstable performance is tightly associated with the insulating nature of sulfur and the dissolution and diffusion of the lithium polysulfide (LPS) intermediates with the subsequent parasitic reactions and low S utilization. These problems will be further aggravated in the cells with a high loading cathode at a lean-electrolyte condition, which, however, is critical for realizing the projected high energy of Li-S batteries in practice. Herein, to solve these issues, we introduce a new class of LPS trapping materials, conductive metal phosphides to the Li-S batteries. Using cobalt phosphide (CoP) as an example, we first explore the surface chemistry and demonstrate that the surface oxidation layer, naturally generated under ambient environment, plays a key role in absorbing the LPS species and promoting their conversion kinetics, thus the performance of lithium sulfur batteries is stabilized. The CoP containing electrode with ultrahigh sulfur loading of 7 mg cm−2 could deliver a striking areal capacity of ~5.6 mAh cm−2 that is stable over 200 cycles. In another effort, we further verify that this distinct electrocatalytic and LPS binding effect could be applied to the lean electrolyte condition. The sulfur electrodes containing molybdenum phosphate (MoP) show the great decrease in the overpotentials for the charging and...
discharging reactions, giving rise to improvements in capacity, rate performance, and cycling stability.\textsuperscript{2} As a result, high-performance sulfur electrodes, that are steadily cyclable at a high areal capacity of 5.0 mAh cm\textsuperscript{-2} with a challenging electrolyte/sulfur (E/S) ratio of 4mL E mg\textsuperscript{-1}S, are successfully realized.


\textbf{4:45 PM EN01.05.09}
\textbf{Dual-Functioning Superoxide Carrier for Stable and Efficient Lithium-Oxygen Batteries} Youngjoon Bae, Hyeokjun Park, Youngmin Ko and Kisuk Kang; Seoul National University, Korea (the Republic of)

Low round-trip efficiency and poor cycle stability remain as major challenges of lithium oxygen (Li-O\textsubscript{2}) batteries. These issues are primarily triggered by or correlated with the radical species that are produced during the operation of Li-O\textsubscript{2} cell, which significantly deteriorate the electrolytes and air-electrodes. Regulating the reactivity of radical species in an electrochemical cell would thus open up opportunities to mitigate such side reactions. Here, we introduce a dual functional superoxide carrier that is capable of quenching the reactive radical species produced in Li-O\textsubscript{2} cell into stable intermediate complexes both in discharge and charge processes. It leads to a significant suppression of side reactions with a remarkably improved oxygen efficiency. In addition, it is found that the superoxide carrier is also capable of scavenging the superoxides from the surface of discharge products upon charging, thus substantially lowering the charging overpotential. The combined radical mediation and the scavenging of superoxides enables the cycle stability of a practical Li-O\textsubscript{2} cell employing the superoxide carrier over 200 cycles with 1,000 mAh/g specific capacity. Our findings indicate the importance of controlling the reactivity of radical species and suggest a new pathway to the stable and efficient Li-O\textsubscript{2} batteries.

\textbf{SESSION EN01.06: Sodium-Ion Battery}
\textbf{8:45 AM EN01.06.02}
\textbf{Storage for DAYS—Materials and Technologies for Long-Duration Energy Storage} Scott Litzelman\textsuperscript{1}, Max Tuttman\textsuperscript{1}, Vivien Lecoustre\textsuperscript{2}, Sean Vail\textsuperscript{2} and Gokul Vishwanathan\textsuperscript{2}; \textsuperscript{1}Advanced Research Projects Agency-Energy, United States; \textsuperscript{2}Booz Allen Hamilton, United States

Several grid energy services such as frequency regulation, demand charge management, and distribution upgrade deferral can be satisfied using energy storage systems with durations typically between 30 minutes and four hours. To enable deep penetration of renewable generators while maintaining grid reliability, however, long-duration energy storage (LDES) systems will be needed. To be cost-competitive, LDES systems require a unique optimization of various attributes—different than conventional lithium-ion battery systems--such as capital cost for energy, capital cost for power, and round-trip efficiency.

This presentation will introduce novel LDES technologies that are being funded by the Department of Energy, Advanced Research Projects Agency-Energy (ARPA-E) Duration Addition to electricitY Storage (DAYS) program that can cost-effectively provide 10 to 100 hours of power to the electric grid. The DAYS projects span a range of concepts, including electrochemical systems with low-cost active materials, pumped thermal storage via inexpensive storage media such as sand and concrete, thermophotovoltaics, and geo-mechanical storage. Key technical challenges and opportunities will be discussed. Although broad adoption of LDES for commercial applications will require policy changes, this presentation will also highlight potential early applications that can enable commercial scaling of these technologies.

\textbf{9:00 AM EN01.06.03}
Energy storage devices allow us to use energy in a flexible, high efficient and eco-benign way, which has profoundly shaped our everyday life. The most successful energy storage device is lithium-ion battery (LIB), which has dominated the portable electronic devices and are now penetrating deep into vehicle markets[1]. However, the limited reserves of lithium[2] and cobalt in the earth crust cannot fulfill the huge demand gap of electrochemical energy storage, and the fast expansion of LIB industry has already led to accelerated cost rising[3]. Therefore, worldwide research programs strategically encourage the development of energy storage devices beyond LIB, among of which, sodium ion battery (SIB) is a very attractive one.

Electrochemically charging induced phase transition is a common and thermodynamically-driven phenomenon for variety of cathode materials, which couples with chemical and mechanical effects leading to performance degradation. Phase transition is particularly complex for layered sodium transition metal oxides and its related detrimental effects remain elusive. Doping electrochemically inactive elements is proven to be an effective approach to suppress the phase transition and Na-vacancy ordering to achieve improved electrochemical performance. Herein, we take P2-type Na2/3Ni1/3Mn2/3O2 (P2-NNM) as an example to scrutiny the detrimental consequences upon high voltage cycling. We find that repeated P2-O2 phase transition breaks down cathode primary grains by generating high density of intragranular cracks, which is qualitatively proved to be the main cause of performance decay. Intriguingly, the nucleation and growth of intragranular crack is through loss of atoms rather than cleavage, resembling the stress corrosion cracking mechanism which preferentially nucleates at P2/O2 phase boundary. Moreover, we find the P2-structured cathode is not sensitive to surface degradation, which explains the superior performance of P2-NNM cathode when cycling at low voltage.[4] we also investigate Mg-doped P2-structured Na0.67Ni0.33-xMn0.67MgxO2, and find doping electrochemically inactive elements is an effective method to suppress grain cracking, leading to improved cyclability[5].


For modern society, energy storage and distribution are critical, with sodium ion batteries (SIB) potentially filling a critical role as a low-cost technology from earth abundant resources well-positioned to augment - or where suitable replace - lithium ion batteries (LIBs).[1] Thus, SIBs have gained prominence due to strong interest from both research and industry.

Here we explore current state-of-the-art Na-ion batteries in terms of both electrodes. Hard carbon-based materials are currently preferred for their low cost and operating voltage (and hence high energy density). Meanwhile, the most promising cathodes include sodium manganese-rich layered oxides (with the formula NaM1-yMyO2; y ≤ 0.33, M is one or more transition metals, e.g. Ni, Ti, Fe, etc.), due to their potentially attractive physical, electrochemical, and commercial properties.[2] However, these suffer from Jahn–Teller distortion, which may cause loss of capacity and multiple step plateaux. Nevertheless, doping and substitution have been employed to stabilize the structure and/or increase the average Mn oxidation state – resulting in many new materials with improved performances.[3–5] Critically, it has been shown that even small quantities can affect a significant improvement without sacrificing the advantages of these systems.

Given that many of these first-generation technologies are approaching commercialisation, as highlighted in our prototyping and commercialisation section, it is important to consider which future areas of research will best unlock the potential of SIBs.

Improving the power density and rate capability of Na-ion systems has led to interest in nascent Na-ion hybrid capacitors (a coupled supercapacitor- and faradic-type electrode). We will discuss the topic, including remaining challenges (e.g. initial pre-metalation, safety and cost) and the promising development of low-cost hard carbon and
high-performance intermetallic electrodes.[6,7]

High energy density, by contrast, is being targeted through advances in Na-air and Na-Sulfur (NaS) systems. Recent work has highlighted the great versatility offered by graphene-based aerogels as air-cathodes, thanks to their low density, high electronic conductivity, and adjustable porosity.[8] From this work, we will examine the specific role of this porosity on both cell capacity and efficiency - which has led to the development of a high-performance cathode, and represents a foundation for future Na-O2 cathode design.

The challenges and advances in ambient-temperature sodium-sulfur (Na-S) batteries will also be presented. This system is a safe alternative to commercialized high-temperature Na-S batteries (working at 300-350 °C), offering high theoretical energy density and low cost. Different optimization approaches, such as applying fluorine-containing electrolyte solvents with redox mediator additives or gel polymer electrolytes, will be highlighted.[9,10]

Meanwhile, safety and cyclability (key factors for any energy storage system) are being addressed by the ongoing development of all solid-state systems, and advances in this area will be discussed briefly.

Through this presentation, we hope to highlight the benefits of sodium-based energy storage systems, provide context for the current state-of-art, and provide insights into the future pathways for development.


9:45 AM EN01.06.05
First Principle Study of the Role of Lattice Dynamics on Ionic Conductivity of Solid-State Sodium Superionic Conductors Hamidreza Seyf, Vilas G. Pol and Partha Mukherjee; Purdue University, United States

All-solid-state batteries have the potential to be safe and more energy dense than traditional rechargeable batteries. This emergent energy-storage technology, however, is still critically limited by the (electro)chemical issues at the solid electrolyte/electrode interface and low ionic conductivity of the solid electrolyte. To accelerate the discovery of new superionic conductors is essential to establish meaningful relations between ionic transport and simple materials descriptors. Recent experimental studies on lithium fast-ion conductor suggested that there exists a correlation between lattice dynamics and ionic transport. It has been shown that in lithium-based fast ion conductor, the lattice softness correlates with low activation energies. Although, such findings highlight new strategies in controlling lattice dynamics to discover new lithium-ion conductors with enhanced conductivity, the universality of such lattice dynamics-based descriptors to understand and potentially control the ionic mobility of other ion conductors such as sodium is not clear. In this work, using an extensive ab initio molecular dynamics simulation based on density functional theory, we examine the applicability of the existing descriptors to a number of NASICON-like (sodium superionic conductors) and demonstrate the links between lattice dynamics and ionic transport in these structures. Finally, the correlation between lattice softness and pre-exponential factor of Na diffusivity, activation energy, and hopping attempt frequency will be obtained.

10:00 AM BREAK

10:30 AM EN01.06.06
Pillared Structure Design of MXene with Controlled Interlayer Spacing for High Performance Lithium/Sodium-Ion Storage Jianmin Luo1, Wenkui Zhang2, Xinyong Tao2 and Weyyang Li3; 1Dartmouth College, United States; 2Zhejiang University of Technology, China

Two-dimensional transition metal carbide materials (termed MXenes) have attracted great research interest for
electrochemical energy storage applications. Herein, with inspiration from the unique structure of pillared interlayered clays, our group demonstrated the fabrication of a series of pillar-structured MXene (Sn⁴⁺/S atoms pillared MXene) via a facile liquid-phase alkali metal ion/cationic surfactant pre-pillaring and Sn⁴⁺/S atoms pillaring methods. The interlayer spacing of Ti₃C₂MXene can be precisely controlled to be between 1 and 2.71 nm according to the size of the intercalated pre-pillaring agent (alkali metal ion, cationic surfactants). Because of the pillar effect, the obtained Sn⁴⁺ pillared MXene delivers a remarkable stable capacity of 765 mAh g⁻¹ at 0.1 A g⁻¹ for lithium-ion storage, and the obtained S atoms pillared MXene delivers an improved Na-ion capacity of 550 mAh g⁻¹ at 0.1 A g⁻¹ (=120 mAh g⁻¹ at 15 A g⁻¹, the best MXene-based Na⁺-storage rate performance reported so far), and excellent cycling stability over 5000 cycles at 10 A g⁻¹. We believe this pillared structure design of MXene will provide insight in synthesizing MXene-based nanostructures for high-performance energy storage devices.

10:45 AM *EN01.06.07
Anionic and Cationic Substitution to Control the Properties of Vanadium Fluorophosphates for Na-Ion Batteries Laurence Croguennec¹,²,³, Jacob Olchowka¹,²,³, Hoang Bao Long Nguyen¹,³,⁴, Thibault Broux¹,²,³, Paula Sanz Camacho¹, Carlos E. Alarcon Suesca¹,²,³, Dany Carlier-Larregaray¹,²,³ and Christian Masquelier⁴,²,³; ¹CNRS, University Bordeaux, France; ²RS2E, Réseau Français sur le Stockage Electrochimique de l’Energie, France; ³ALISTORE-ERI European Research Institute, France; ⁴Université de Picardie Jules Verne, France

Optimized carbon-coated Na₃V₂(PO₄)₂F₃ showed exceptional rate and electrochemical cycling capabilities, more than 4000 times at 1 C rate, as demonstrated by performance of the first hard carbon//Na₃V₂(PO₄)₂F₃ 18650 prototypes of 75 Wh kg⁻¹ prepared by our partner CEA.¹ These attractive results, among others, participate to a renewed interest in the field of Na-ion batteries considering vanadium fluorophosphates at the positive electrode. The optimization of their electrochemical performance requires the control of the carbon coating,¹ and the careful tuning of the oxygen and thus vanadyl-type defects’ concentration through a deep understanding and control of the reaction synthesis. Indeed, the competition between the ionic V³⁺=F bond and the covalent V⁴⁺=O bond has a major effect on the structure of the pristine materials, and then on the phase diagram and redox mechanisms involved upon their cycling in batteries.²,³ The influence of the anionic and cationic substitution will be illustrated for series of phases Na₃V₂ₓMₓ(PO₄)₂F₃₋ₓOₓ (M= transition metal) combining mainly Synchrotron X-ray diffraction and spectroscopic studies.²,³

Acknowledgements:
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11:15 AM EN01.06.08
Directional Flow-Aided Sonochemistry Yields Graphene with Tunable Defects to Provide Fundamental Insight on Sodium Metal Plating Behavior David Mitlin; University of Texas at Austin, United States

We report a directional flow-aided sonochemistry (FAS) exfoliation technique that allows for unparalleled control of graphene structural order and chemical uniformity. Depending on the orientation of the shockwave relative to the flow aligned graphite flakes, the resultant bilayer and trilayer graphene is nearly defect free (at-edge sonication graphene "AES-G") or is highly defective (in-plane sonication graphene "IPS-G"). AES-G has a Raman G/D band intensity ratio of 14.3 and an XPS derived O content of 1.3 at.%, while IPS-G has I_G/D of 1.6 and 6.2 at.% O. AES-G and IPS-G are then employed to understand the role of carbon support structure and chemistry in Na metal plating/striping for sodium metal battery (SMB) anodes. The presence graphene defects and oxygen groups is highly deleterious: In a standard carbonate solution (1M NaClO₄, 1:1 EC:DEC, 5vol.%FEC), AES-G gives stable
cycling at 2 mA/cm² with 100% CE (within instrument accuracy), and an area capacity of 1 mAh/cm². Meanwhile IPS-G performs on-par with the baseline Cu support in terms of poor CE, severe mossy metal dendrites, and periodic electrical shorts. We argue that SEI stability is the key for stable cycling, with defects IPS-G being catalytic towards SEI formation. For IPS-G, the SEI layer also shows F-rich "hot spots" due to accelerated decomposition of FEC additive in localized regions.

11:30 AM EN01.06.09
Highly Performing P/C Composite Anodes for Na-Ion Batteries Eliana Quartarone¹, Emanuele Vigo¹, Tobias Eisemann², Cristina Tealdi¹ and Stefano Passerini²; ¹Univ of Pavia, Italy; ²KIT, Germany

In the last years, black phosphorous has emerged as one of the most studied materials proposed as anode for rechargeable energy storage devices due to the high gravimetric and volumetric energy density, low cost and high availability. The 2D nature of this system makes it particularly intriguing and is the most studied and investigated form among the P allotropes. Two major drawbacks of the use of phosphorus as anode are under investigation. The first is the huge volumetric change due to the reaction P à R₃P (with R = Li, Na, K) that is of the order of 300-500% moving from Li to K. This colossal volume variation is consequence, of the poor cyclability of these electrodes. To overcome this problem, the strategy to develop P/C composites, has been recently explored. The other one is the optimal preparation of BP and relative composite. Black phosphorus is typically prepared by high-energy ball milling starting from the commercially available red phosphorous. However, several combinations of parameters (mainly speed rotation, filling factor, and duration) must be considered to have reproducible syntheses.

Here, we present some recent results on the optimization approach of Black Phosphorus as anode for advanced batteries. Particular attention is devoted to address the role of Carbon on the electrode electrochemical performance.

11:45 AM EN01.06.10
Sodium Induced Structural Changes of Carbon Coated TiO₂ Anatase Nanoparticles—High-Performance Materials for Na-Ion Batteries Giorgia Greco¹, Katherine A. Mazzio¹, Xinwei Dou² and Stefano Passerini²; ¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany; ²Karlsruhe Institute of Technology, Germany

The most promising candidate to replace lithium-ion batteries (LIB) are the Sodium ones (NIB). This is not only due to sodium abundance but also because of the main principles and cell structure, are very similar to LIB ones. Due to these benefits, SIBs are expected for use in applications related to large-scale energy storage systems and other applications not requiring top-performance.¹,²

The relevant issue that affect the large scale application of those battery systems is the anode material. Graphite and silicon, largely used in LIB, doesn’t show great performances in NIB.³,⁴ Hard carbon looks very promising because of capacity, the abundance and cost⁵, but suffer of instability in particular at long term.

In this work we propose a carbon-coated TiO₂ that looks very promising in term of capability, abundance, low-cost, and most importantly, shows high stability during cycling.⁶

In this work we show a comprehensive structural characterization study that combine XRD and XANES and EXAFS techniques in order to have a complete electronical and structural overview of the modifications induced by sodiation and desodiation. This work also demonstrates for the first time a coherent explanation of the structural changes observed, where an electrochemical induced short-range ordering is revealed upon cycling.


SESSION EN01.07: Zn Ion Battery
Session Chairs: Debra Rolison and Chunsheng Wang
Wednesday Afternoon, December 4, 2019
Sheraton, 2nd Floor, Independence East

1:30 PM *EN01.07.01
(More) Uniformly Reacting Electrodes Simplify Cell Engineering—The Case for Architectural Design Debra R. Rolison¹, Brandon J. Hopkins¹, Jesse S. Ko¹, Megan Sassin¹, Christopher Chervin¹, Joseph Parker¹, Jeffrey W. Long¹, Samuel W. Kimmel²⁻¹ and Christopher P. Rhodes²; ¹U.S. Naval Research Laboratory, United States; ²Texas State University, United States

Electrochemists understand that one electrode reacting in a more uniform manner allows more uniform reactivity at the countering electrode — unless that opposing electrode suffers from poor electrode kinetics or poor conductivity. This reactivity/conductivity mismatch under stress, such as deep depths of discharge or hundreds-to-thousands of charge–discharge cycles, is all too common between the positive and negative electrodes in batteries. Bringing an architectural perspective to the multifunctionality of energy-storing electrodes ensures wiring the critical per second reactions (electron transport, ion transport, and molecular transport) throughout the volume of the re-designed electrode, which concomitantly distributes the reacting surfaces in 3D, parcels out the imposed global current density to those surfaces rather than to a cross-sectional area, thereby lowering the local current density [1]. This concept will be explored with three case studies. The first two are enabled by zinc sponge anodes, which retain a metallic core that persists in 3D for direct wiring to the current collector even to >90% utilization of the metal [2,3]. When Zn sponges are cycled in alkaline electrolytes versus highly conductive silver oxide cathodes, high cycle life is obtained, even without relying on the cell engineering of additives and separator design typically required to thwart silver colloids spalling off during cycling [3]. When Zn sponges are cycled at high rate and to deep DOD in alkaline electrolytes versus harvested nickel hydroxide cathodes with the far lower conductivity and slower heterogeneous redox rates characteristic of NiOOH, 100% theoretical coulombic efficiency fades after 50+ cycles that can be immediately reversed by replacing the nickel electrode. We are thus currently redesigning the nickel cathode to develop better wiring to match the high performance of the monolithic zinc architecture. In the third case, we demonstrate that in neutral aqueous electrolytes of zinc sulfate and sodium sulfate, the discharge reaction at MnO$_x$ powder-composite cathodes can be transformed to hybrid capacitor+battery performance by using cathodes comprising nanoscale MnO$_x$–painted carbon nanofoam paper [4].


2:00 PM EN01.07.02
Reformulating Zinc-Sponge Battery Electrodes for Large-Format Applications Brandon J. Hopkins, Megan Sassin, Christopher Chervin, Joseph Parker, Jeffrey W. Long and Debra R. Rolison; U.S. Naval Research Laboratory, United States

Rechargeable zinc (Zn) batteries are safe, sustainable, and energy-dense alternatives to Li-ion batteries. Recent advances, such as monolithic Zn-sponge electrodes, have enabled long cycle lives by suppressing the formation of short-circuiting dendrites even after deep levels of discharge and charge. A substantial barrier to their widespread use has been the difficulty of manufacturing large-format electrodes for high-power applications. Here, we describe the development of scalable, multi-scale manufacturing methods to increase the mass production of zinc sponge electrodes, demonstrated through the fabrication and evaluation of electrodes in large-format cells. The potential of these electrodes for large-format zinc batteries is assessed through ex-situ and in-situ electrochemical characterization.
adoption in large-format applications has been their insufficient mechanical integrity when scaled beyond 1 cm². While most approaches to fortify these electrodes involve adding supportive inactive materials, we enhance electrode strength by tuning the zinc architecture via electrode-emulsion and heat-treatment modifications that also increase energy density and obviate lengthy processing steps. This reformulation achieves an electrode tensile strength that maps to large-format electrode sizes while maintaining a rechargeable capacity and retaining high energy density when paired with a nickel electrode. This advance in scalability provides an opportunity for applications that require large electrodes such as batteries for grid-storage, personal electronics, and electric vehicles.

2:15 PM EN01.07.03
The Dynamic Behavior of the Discharge Product in Zinc-Alkaline Batteries
Brendan E. Hawkins, Damon Turney, Ankur Jadhav, Gautam Yadav, Robert Messinger and Sanjoy Banerjee; The City College of New York, United States

Rechargeable zinc-alkaline batteries are attractive candidates for stationary energy storage applications because of their high energy density, low cost, inherent safety, and environmental friendliness. However, widespread commercialization of these batteries has been prevented, in part, by the low cyclability of the zinc metal electrode. One reason for the limited cyclability is the accumulation of discharge product in the electrode resulting in passivation and loss of active material. In historical literature, various types of discharge species have been identified, and the discharge product has been treated as an inert species that simply occupies space and blocks ion transport to the active material. In this work, we demonstrate that the discharge product, zinc oxide, undergoes dynamic chemical changes as a function of electrode potential, which affect properties such as the color, composition, and conductivity of the electrode. The dynamic properties of the zinc discharge product must be considered when developing new architecture and additives for rechargeable zinc electrodes.

In this study, we used a combination of in operando and ex situ techniques to investigate the chemical structure of the discharge product in zinc-alkaline electrodes. Namely, in operando Raman spectroscopy was used to demonstrate that the vibrational modes of the discharge product change as a function of voltage, indicating a change in the composition or structure of the discharge product. Simultaneous optical microscopy revealed an accompanying color change in the discharge product as a function of voltage. Subsequently, quantitative ex situ solid-state ¹H and ⁷Li magic-angle spinning (MAS) NMR spectroscopy were used to observe local environments and dynamics of cations in the crystal structure of the discharge product. Our observations suggest that the zinc oxide discharge product in zinc-alkaline batteries is electrochemically active, and that the properties of the material have a dependence on electrode voltage. This talk will summarize the effects of voltage on the discharge product and demonstrate the importance of considering the dynamic behavior of the discharge product when developing future rechargeable zinc electrodes.

2:30 PM BREAK

3:30 PM *EN01.07.04
Recent Advances in Rechargeable Zinc Manganese Dioxide Batteries for Grid Applications
Sanjoy Banerjee; City College of New York, United States

Zinc (Zn) anodes and manganese dioxide (MnO₂) cathodes are the electroactive components of alkaline cells which have dominated the market for single discharge disposable batteries for decades. They have high energy density, low cost, and outstanding safety and environmental characteristics. Transforming this non-rechargeable technology into a rechargeable system has the potential to provide very low-cost, safe and environmentally benign solutions for grid-scale energy storage. However, poor charge-discharge reversibility, especially of the MnO₂ cathode at high depths of discharge (DOD), has limited application of this otherwise very attractive technology.

Recent breakthroughs in obtaining excellent rechargeability of high DOD Zn anodes and MnO₂ cathodes achieved at the City University of New York Energy Institute (CUNY-EI) in partnership with Urban Electric Power, Inc. (UEP) will be reviewed. These developments, which received the 2019 ACS/EPA Green Chemistry Challenge Award, are now being commercialized to realize cell costs in the $40/kWh range. In this talk, the challenges in developing and manufacturing products based on such breakthroughs, e.g., into grid-scale rechargeable Zn/MnO₂ batteries for energy storage, will be discussed.

4:00 PM EN01.07.05
High Energy Density Zn-Ni Aqueous Semi-Solid Flow Battery for Grid Scale Energy Storage Thaneer Malai M. Narayanan1, Yun Guang Zhu1, Michal Tulodziecki1, Hernan Sanchez2, Quinn Horn2, Gareth McKinley1 and Yang Shao-Horn1; 1Massachusetts Institute of Technology, United States; 2Exponent, Inc, United States

Grid scale energy storage requires high energy density, low-cost and safe systems. Semi-solid flow battery is attractive to achieve these objectives as its energy density not limited by the active species solubility, and also enables usage of wide range of cheap and safe solid active material and aqueous electrolyte. In this study, we have designed high energy density suspensions for Zn-Ni alkaline semi-solid flow battery. Firstly, stability of the suspension was ensured by suspending the solid particles in polymer and 7 M KOH electrolyte matrix. Then, effect of conductive additive concentration on the electrochemical performance of the suspension was studied in a static cell. By selecting suitable concentration of conductive additive (14 w% of carbon black), we were able to achieve high energy density semi-solid battery (134 Wh/L catholyte, ~3 times of VRFB). Rheological study of these suspensions showed they have yield stress about ~200 Pa. As they don’t require high flow rate and narrow channels as VRFB, we found that the pumping loss in the flow channels for these suspensions is negligible (<1% w.r.t. energy output). Finally, scalability of this Zn-Ni semi-solid flow battery is tested in a 3-D printed flow cell.

4:15 PM *EN01.07.06
Water-in-Salt Electrolyte Li-Ion Batteries Chunsheng Wang; University of Maryland, United States

Water-in-salt electrolytes have considerably expanded the electrochemical window of the electrolytes to 3 to 4 volts, making it possible to couple many high capacity anodes and high-voltage cathodes for Li-ion, Na-ion and Zn batteries. Since the water is strongly bonded to the salts, the low water activity in electrolytes allows the cell to be open to the air and operate in a wide temperature range. The high oxidation stability window also enables a halogen conversion–intercalation chemistry in graphite that produces composite electrodes with a capacity of 243 milliampere-hours per gram (for the total weight of the electrode) at an average potential of 4.2 volts versus Li/Li+.

4:45 PM EN01.07.07
Materials and Performance of Metal Hydride/Air Battery for Stationary Energy Storage System Masatsugu Morimitsu; Doshisha University, Japan

A metal hydride/air battery (HAB) is an aqueous secondary battery consisting of a hydrogen storage alloy electrode, an air electrode, and an alkaline solution, of which the discharge reaction is water generation and the charge one is water decomposition. This unique system brings out the potential of air batteries which are no limitation on discharge capacity of the positive electrode unnecessary to storage the active mass, resulting in higher power density and energy density than the other types of secondary batteries. It is of importance that the discharge product is water, not solid, so that the plugging of the air electrode during discharge by solid products like lithium oxide in lithium/air batteries never occurs. The materials of HAB are further important in viewpoint of safety, because they are all non-flammable and are easily handled in air. Therefore, HAB is one of the promising candidates for next generation energy storage devices, which need that high performance and high safety should be compatible. Our project on the HAB development has been financially supported by Japan Science and Technology Agency (JST) from 2012 under the collaboration of two universities and three companies, in which the air electrode with bi-functional oxygen catalyst, the negative electrode using high capacity density of hydrogen storage alloy, and the cell design and configuration have been developed and modified. This paper presents the materials and performance of HAB including the preparation, characteristics, and activities of novel oxygen catalysts and the cell performance on energy density over 900 Wh/L and cycling behaviors of 500 cycles or more. A future plain for the application of HAB to stationary energy storage systems, which has been just started under Low Carbon Technology Research and Development Program by Ministry of the Environment (MOE), Japan, will be also indicated.
Large-scale energy storage is of significance to the integration of renewable energy into electric grid. Despite the dominance of pumped hydroelectricity in the market of grid energy storage, it is limited by the suitable site selection and footprint impact. Rechargeable batteries show increasing interests in the large-scale energy storage; however, the challenging requirement of low-cost materials with long cycle and calendar life restricts most battery chemistries for use in the grid storage. Recently we introduced a concept of manganese-hydrogen battery with Mn$^{2+}$/MnO$_2$ redox cathode paired with H$^+/H_2$ gas anode, which has a long life of 10,000 cycles and with potential for grid energy storage. We later expand this concept by replacing Mn$^{2+}$/MnO$_2$ redox with a nickel-based cathode, which enables $\sim 10\times$ higher areal capacity loading, reaching $\sim 35$ mAh cm$^{-2}$. We also replace high-cost Pt catalyst on the anode with a low-cost, bifunctional nickel molybdenum cobalt alloy, which could effectively catalyze hydrogen evolution and oxidation reactions in alkaline electrolyte. Such a nickel-hydrogen battery exhibits an energy density of $\sim 140$ Wh kg$^{-1}$ and estimated energy cost of $\sim$83 per kilowatt-hour and excellent rechargeability with negligible capacity decay over 1,500 cycles. The excellent stability and the low cost of the rechargeable hydrogen batteries demonstrate attractive characteristics for large-scale energy storage.

Synthetic cost and long-term stability remain two of the most challenging barriers for the development of aqueous organic redox flow batteries for grid scale energy storage. In this work, we present a new method for synthesizing water-soluble anthraquinones from inexpensive starting materials. Two anthraquinones have been synthesized by the method at the time this abstract is being submitted. Both of them show remarkable chemical stability of both oxidized and reduced forms: no chemical decomposition at high temperature for two weeks. When paired with a Ferro/ferrycyanide posolyte, a full cell of 1 V is achieved, exhibiting a capacity fade rate of around 0.02% per day, which is among the most stable redox-active molecules reported. One of these species has a solubility of 1 M, corresponding to 53.2 Ah/L, at pH 12. This method may be extended to the synthesis of other redox-active aromatics.

The redox-flow battery has gained increased attention as an alternative to Li-ion batteries for grid-scale energy storage. While a number of flow battery chemistries have been developed and are undergoing commercialization, none satisfy the full set of requirements necessary for wide-scale deployment. For instance, the vanadium redox flow battery has impressive performance metrics, but is prone to fluctuating costs which are currently prohibitively high. Redox-active organics have recently emerged as promising alternatives to existing flow battery chemistries. These systems offer a level of tunability not available with transition-metal-based systems. A number of redox-active core structures have been reported and for each core structure selective functionalization can modulate the solubility, ionic charge, redox-potential, and a number of other properties, providing nearly endless possibilities for molecular design. Presented will be our recent work on phenazine-based anolytes, which yield cell voltages of over 1 V when coupled with ferrocyanide and can achieve solubilities up to 1.8 M. The effect of various molecular design approaches on solubility, redox potential, and stability will be discussed.
After years of silence, redox-active organic compounds are re-emerging in the energy storage community bringing with them interesting opportunities such as design flexibility and lightweight. Moreover, thanks to the use of abundant chemical elements, organic chemistry provides great opportunities for discovering innovative electrode materials, which could be prepared (i) from renewable resources (biomass) and (ii) via eco-efficient processes, making the concept of greener and sustainable batteries possible [1]. They can also integrate a wide variety of electrochemical device architectures operating both in aqueous or non-aqueous electrolytes. Interestingly, the past decade has seen significant progress in the design of new organic compounds and today a myriad of promising electroactive organic materials have been investigated [2]. In addition, very promising data are now also reported in redox flow cell configuration [3]. Some of them exhibit attractive electrochemical behaviors such as long-term cycling stability and high-rate capability. In addition, they offer different electrochemical activities including the common reversible cation uptake/release as well as access to anion-inserting process bringing to us another playground in designing organic electrochemical storage systems including the development, in principle, of molecular ion batteries [4]. However, several improvements are needed to further promote organic electrode materials especially in terms of energy density values and only few studies have been reported in the literature regarding the assembly of full organic cells.

This contribution aims at reporting recent electrochemical data obtained with crystallized organic materials [5] and explaining how it is possible to tune the electrochemical activity of redox-active organic moieties depending on the molecular assembly and its electrostatic environment. We hope that such findings can pave the way for designing novel chemistries for rechargeable batteries.

References:

9:45 AM BREAK

10:15 AM *EN01.08.05
The Development of Diels Alder Poly(Phenylene) Membranes for Electrochemical Applications  
Cy Fujimoto; Sandia National Laboratories, United States

With significant growth in the clean energy sector (wind and solar), the search for an energy storage medium which is safe, durable and economical is at an all-time high and a variety of electrochemical systems are being evaluated; multiple flow batteries chemistries and electrochemical hydrogen production (electrolysis). The efficiencies, lifetimes and costs of these electrochemical systems are tied to the membrane separator; however, commercially available membranes do not meet all the requirements. At Sandia National Laboratories, we have been developing both anion and cation exchange Diels Alder poly(phenylene) membranes as electrochemical separators. Since these materials are hydrocarbons they are excellent low-cost alternatives to perfluorinated materials, and since the polymer backbone consists of only aromatic benzene units it offers high chemical and thermal stability. For example, as most electrochemical systems operate in either an acid or alkaline environment to enhance the electrolyte conductivity and widen the operation voltage window, the membrane separator needs to be inert in these conditions. However, it has been found that hydrocarbon polymers that contain heteroatoms in the polymer backbone are attacked in alkaline environment (polymer degradation), while all aromatic DAPP is stable in alkaline environments, even at high temperatures. This presentation will discuss the development and synthesis of various cation and anion exchange materials employing the DAPP backbone, and its performance in a variety of electrochemical applications.

10:45 AM EN01.08.06
Charge and Mass Transfer Enhanced Electrode for High-Performance Aqueous Flow Batteries  
Hongli Zhu; Northeastern University, United States

The scalability for an efficient process to fabricate electrodes with enhanced charge and mass transfer is still a
challenge for flow batteries. For the first time, this work introduces a scalable and effective surface modification method of graphite felt (GF) electrode based on the controlled electrochemical exfoliation to enhance the mass and charge transfer of the electrode. Exfoliation of the GF was conducted in ammonium sulfate ((NH₄)₂SO₄) aqueous solution by breaking the weak van der Waals forces between the graphitic layers. This reaction occurred through anion intercalation and subsequent gas evolutions, causing expansion of the graphite layers at room temperature for 1 min. Consequently, the exfoliation incorporated sufficient oxygen functional groups that increase the active surface area, resulting in enhanced reaction kinetics at the electrode-electrolyte interface and improved hydrophilicity enabling better electrolyte accessibility. The Brunauer-Emmett-Teller (BET) results verified that the specific surface area of E-GF is 1.19 m² g⁻¹, which is two times larger than that of the pristine graphite felt (0.55 m² g⁻¹). Further, spin-polarized density functional theory was also employed to reveal the role of introduced oxygen functional groups in accelerating the vanadium redox reaction. Benefitting from the sufficient oxygen groups and superior wettability, the as-prepared exfoliated GF (E-GF) shows brilliant electrocatalytic activity with minimized overpotential, higher volumetric capacity, and improved energy efficiency. Finally, the RFB assembled with the E-GF electrode delivered voltage and energy efficiencies of ~ 90 and 86 % at the current density of 100 mA cm⁻², respectively. Remarkably, compared to the traditional GF treatment method, the elimination of the high-temperature, energy consuming, and longtime treatment processes make this approach much more energy and time efficient, scalable, and affordable.

11:00 AM EN01.08.07
A Special TEM Li-Ion Battery Sample Preparation and Application on Investigation of the SEI Layer Nano Structural Property in Lithium Rechargeable Battery Xiang-Yun Song; Lawrence Berkeley National Lab, United States

Due to complex component and sensitive to the air and water of the lithium rechargeable battery, how to prepare a practical useful TEM (transmission electron microscopy) specimen from Li-ion cell has been critical to the TEM application in new generation batteries. We have developed an efficient way to prepare a TEM specimen from lithium ion cells that prevents electrode material contamination and chemical reaction from water or air and damage from mechanical stress.

By using our special technique for TEM specimen preparation the nano structural properties of SEI (solid-electrolyte-interphase) layer in Li(NiMnCo)O₂/graphite cell have been investigated. The MnF₂ nano-crystalline tetragonal structure in SEI layer was found and identified by HRTEM and EELS (electron energy loss spectrum). Furthermore, the morphology of MnF₂ nano-grains, its nucleation, distribution and SEI layer thickness were studied.

By using our special technique for TEM specimen preparation LiNi₀.₅Mn₁.₅O₄ cathode material has also been studied on the battery failure mechanism, which will be reported in other project.

11:15 AM EN01.08.08
Energy Dense Materials for Redox Flow Battery Applications James A. Suttil, Sharmila Samaroo, Neal McDaniel and Chris LaFrancois; Phillips 66, United States

Redox flow batteries (RFBs) offer a number of advantages over current stationary energy storage technologies, such as the decoupling of power & energy and inherently safer designs. However, the energy density of commercially deployed RFB electrolytes is relatively low when contrasted with competing technologies, for example Li-ion battery installations. A significant amount of research has attempted to increase the energy density of the electrolyte by 1) employing non-aqueous electrolytes to improve voltage separation between redox events, 2) increasing the number of electrons transferred between half-cells by employing electroactive species with multiple redox couples, 3) increasing the concentration of the electrolyte by preparing highly soluble or liquid state redox active molecules, or 4) a combination of the previous three modifications. This talk will highlight Phillips 66 investigation of single component iron-based ionic liquids that may satisfy all roles of an energy dense RFB electrolyte: namely the solvent, supporting electrolyte, and redox active species. This presentation will cover the preparation, characterization, and electrochemical testing of the aforementioned energy dense materials.

11:30 AM *EN01.08.09
Ionic Liquid Electrolytes for New Energy Storage Technologies—Towards High Rate and High Efficiency Cycling Robert Kerr, Kalani Periyapperuma, Thushan Pathirana, Mojtaba Eftekharinia, Maria Forsyth and Patrick

Final Program 1/13/2020 360
Howlett; Deakin University, Australia

The device performance characteristics of electrochemical energy storage (EES) technologies makes them suited to a broad range of applications spanning portable electronics and vehicle propulsion all the way to small-scale grid stabilization and remote power backup. With lithium-ion batteries (LIBs) currently the dominant chemistry in the market across all applications, there are now many opportunities to displace LIBs with new and emerging EES technologies that may be better suited to the particular device requirements or operating environment. The choice of electrolyte is one variable that can significantly alter the performance characteristics and desired operating environment of a given technology. Ionic liquids are an intriguing candidate to displace traditional electrolyte solvents owing to a number of favorable physicochemical and electrochemical properties, including thermal and electrochemical stability.

Recent work from within the group into the incorporation of ionic liquid electrolytes (ILEs) into three distinct battery types, namely lithium metal-based, sodium metal-based, and lithium anode redox flow, will be presented here. Investigations into the fundamental electrolyte properties, cycled electrode surface characterisations and device performance aspects have revealed a number of features which make ILEs a surprisingly attractive commercial prospect. The highlights of these features are the ability of ILEs to support high rate Li deposition (20 mA/cm²) through control of the Li nucleation process, and the ability to cycle Li metal with an average Coulombic efficiency of 99.0% over the first 100 cycles in a Cu|LFP configuration using a physical substrate modification approach. An understanding into these behaviors has been developed by considering the transport mechanisms in these electrolytes and the composition of the electrode surface deposits.

In an effort to bring ILEs into an industrially-relevant focus, device prototyping has been conducted at Deakin University’s Battery Technology Research and Innovation Hub (BatTRI-Hub). Here, we have demonstrated the capability of ILEs to enable high energy density pouch cell cycling in prototype devices capable of achieving a specific energy of 400 Wh/kg. Separator design has been identified as a primary factor which limits the cell cycle life and operational temperature range. Some of the key prototyping results will be presented and the implications for commercial application discussed.

SYMPOSIUM EN02

Materials for High-Energy and Safe Electrochemical Energy Storage
December 2 - December 6, 2019

Symposium Organizers
Miaofang Chi, Oak Ridge National Laboratory
Serena Corr, University of Sheffield
Feng Wang, Brookhaven National Laboratory
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* Invited Paper
SESSION EN02.01: Advances in Anodes I
Session Chair: Miaofang Chi
Monday Morning, December 2, 2019
Sheraton, 2nd Floor, Grand Ballroom

8:00 AM *EN02.01.01
Stabilization of Li Anode for High-Energy-Density Li-Metal Batteries Donghai Wang: The Pennsylvania State University, United States

Li metal and Li-alloy based anode materials are the most promising anodes for next-generation Li batteries. The poor interfacial stability (unstable solid-electrolyte interphase (SEI)) in the battery and microstructural failure of Li metal into mossy or dendritic Li during its plating/stripping have been two primary issues hindering their practical application. In this talk, first, I will present a strategy to reinforce the SEI with desired properties including good tolerance to the Li-based material volume change and efficient surface passivation against electrolyte penetration. The strategy works via introducing multiple functional components bonded to the Li-based material surface into the SEI. The SEI reinforced shows much better stability than the SEI reinforced by electrolyte additive strategy, which is the current state-of-art and commercially used solution to SEI stability issue. Second, I will present an approach of structured host for Li metal to promoting uniform Li plating/stripping at high deposition capacity and current density. This approach uses a polymeric sponge with high zeta potential to promote electrokinetic effects so as to alter Li-ion transport properties and reduce concentration polarization for Li plating/striping. High efficiency cycling of Li metal was achieved and demonstrated in Li metal battery cells at low N/P ratio and high deposition capacity and current densities.

8:30 AM EN02.01.02
Design Principles for Self-Forming Interfaces Enabling Stable Lithium-Metal Anodes Linsen Li1,2, Yingying Zhu2, Vikram Pande3, Venkatasubramanian Viswanathan2 and Yet-Ming Chiang1; 1Massachusetts Institute of Technology, United States; 2Shanghai Jiao Tong University, China; 3Carnegie Mellon University, United States

The path toward Li-ion batteries with higher energy-densities will likely involve use of thin lithium metal (Li) anode (<50 mm thickness), whose cyclability today remains limited by dendrite formation and low Coulombic efficiency (CE). Previous studies have shown that the solid-electrolyte-interface (SEI) of the Li metal plays a crucial role in Li electrodeposition and stripping behavior. However, design rules for optimal SEIs on Li metal are not well established. Here, using integrated experimental and modeling studies on a series of structurally-similar SEI-modifying model compounds, we reveal the relationship between SEI compositions, Li deposition morphology and CE, and identify two key descriptors (ionicity and compactness) for high-performance SEIs. Using this understanding, we design a highly ionic and compact SEI that shows excellent cycling performance in high specific energy LiCoO2 or NCA-Li full cells (1.3 Ah pouch cells, > 300 Wh/kg) at practical current densities. Our results provide guidance for rational design of the SEI to further improve Li metal anodes.

8:45 AM EN02.01.03
In Situ Magnetic Resonance Spectroscopy and Imaging of Li-Plating onto and Diffusion within Anodes of Li-Ion Batteries Sergey Krachkovskiy1, Kevin J. Sanders1, Andres Ramirez Aguilera2, Bruce Balcom2 and Gillian R. Goward1; 1McMaster University, Canada; 2University of New Brunswick, Canada

Li-ion batteries are nowadays considered as the main source of energy for an electric vehicle (EV) application; however, the significantly longer “refueling” time compared to standard internal combustion engine vehicles is a substantial disadvantage from the perspective of the end-user. It is speculated that increasing the charging rate by a factor of three should significantly reduce the gap between EVs and conventional automobiles, promoting further penetration of EVs on the mass market. However, a significant drawback of very rapid charging is lithium plating on the negative electrode, which arises if the current exceeds the intercalation rate at which lithium diffuses into the negative electrode. In this case, a film of metallic Li will deposit on the surface, which subsequently reacts with electrolyte, leading to an increase of the cell internal resistance, a lower capacity, and potential short-circuiting in extreme cases.

Here we report an application of the parallel-plate RF probe to monitor in situ deposition of Li metal on a graphite anode during charging of a single layer prismatic cell, assembled with electrodes extracted from a commercial
battery. We have demonstrated that part of the plated lithium was able to intercalate into the graphite after the
current was turned off. Moreover, the signal of deposited Li metal consists of two resonances corresponding to (1) a
“Li film” on the surface of the electrode, and (2) to dendrites orthogonal to electrodes’ planes. Our data demonstrate
that the Li metal intercalation into the graphite is primarily happening from the former type of deposited metal,
while the lithium stored in dendrites can partially dissolve into the electrolyte during the consecutive discharge of
the cell. Importantly, we were able to quantify the amount of reversibly and irreversibly deposited lithium. Finally, a
coexistence of three stages of intercalated into graphite Li (2L, 2 and 1) is demonstrated during a fast charge cycle,
suggesting a non-uniform lithiation of the electrode in that case.

   (2018).
   (2003).

9:00 AM EN02.01.04
Li, Si and LiSiOy Thin Films as Model Systems for Silicon Anodes in Li-Ion Batteries
Yun Xu1, Jaclyn Coyle2, Kevin N. Wood1, Eric Sivonxay3, Glenn Teeter1, Conrad Stold1, Sang-Don Han1, Kristin A. Persson3, Anthony
Burrell1 and Andriy Zakutayev4; 1National Renewable Energy Laboratory, United States; 2University of Colorado
Boulder, United States; 3Lawrence Berkeley National Laboratory, United States

Silicon is one of the most promising materials for high energy density anodes in next generation Li-ion batteries.
However, the long-term performance of Si anodes is currently limited due to large volumetric expansion and
contraction upon lithiation and delithiation, as well as continuous solid electrolyte interface (SEI) formation.
Understanding of this SEI is difficult due to its buried nature, rough sample morphology, as well as convolution of
chemical and electrochemical formation processes. Another important aspect of the SEI formation that needs better
understanding is the presence of native oxide SiOx at the Si surfaces exposed to ambient atmosphere.
Here, we report on our recent studies of lithium silicide (LixSi) and lithium silicate (LixSiOy) thin films, as model
systems to study SEI formation on Si anode with SiOx native oxide in Li-ion batteries. The LixSi and LixSiOy thin
films were deposited by combination of sputtering and thermal evaporation, on both Si and Cu foil substrates. The
resulting samples were studies by a combination of electrochemical (charge-discharge profiles, impedance
spectroscopy, etc), spectroscopic (x-ray photoemission spectroscopy XPS, Fourier-Transform Infrared Spectroscopy
FTIR) techniques, with high accuracy enabled by flat homogeneous character of the thin film model samples.
The results of our studies indicate that the SEI can be formed simply by chemical reduction of electrolyte on lithium
silicide surfaces, without any electrochemical driving force [1]. They also suggest that it may be possible to increase
the lifetime of the next-generation Li-ion batteries using prelithiated Si anodes. On the other hand, it is determined
that LixSiOy is not beneficial in stabilizing the Si anode surface during battery operation, due to large electronic
conductivity, and despite its ductile mechanical properties [2]. These results also suggest future directions for design
of artificial SEI layer coatings on Si anode surfaces.

9:15 AM EN02.01.05
Lithium-Ion Conductivity of Epitaxial Li4Ti5O12 vs State of Charge
Francesco Pagani and Corsin Battaglia; Empa—Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Using an epitaxial thin-film model system deposited by physical vapor deposition, we study the lithium-ion
conductivity of Li4Ti5O12, a common anode material for Li-ion batteries, in the absence of grain boundaries [1].
Epitaxy, phase purity, and composition across the film thickness are verified employing out-of-plane and in-plane
X-ray diffraction, transmission electron microscopy, time-of-flight mass spectrometry, and elastic recoil detection
analysis. We find that epitaxial Li4Ti5O12 grown on a single-crystal MgO(111) surface behaves like an ideal ionic
conductor that is well described by a parallel RC equivalent circuit, with an ionic conductivity of 2.5 × 10–5 S/cm at
230 °C and an activation energy of 0.79 eV in the measured temperature range of 205 to 350 °C [1]. To study
lithium-ion conductivity as a function of state of charge, epitaxial Li4Ti5O12 was also grown on an epitaxial Pt(111)
surface functioning as current collector [2]. Epitaxial Li4Ti5O12 was subsequently cycled galvanostatically in half-
cell configuration vs lithium metal in 1m LiPF6 in EC:DMC organic electrolyte. We find that epitaxial Li4Ti5O12
shows stable cycling at least up to 50 C. We also study lithium-ion conductivity and lithium-ion diffusion as function of state of charge by impedance spectroscopy and galvanostatic intermittent titration technique and interpret our results in the theoretical framework developed for phase-transformation materials [3].

References:
2. F. Pagani et al, in preparation

9:30 AM EN02.01.06
Pristine or Highly Defective? Understanding the Role of Graphene Structure for Stable Lithium-Metal Plating David Mitlin; University of Texas at Austin, United States

Abstract: We are the first to examine the role of graphene host structure/chemistry in plating-stripping in lithium metal anodes employed for lithium metal batteries (LMBs). Structural and chemical defects are bad since highly defective graphene promotes unstable solid electrolyte interphase (SEI) growth. This consumes the FEC additive in the carbonate electrolyte and is correlated with rapid decay in CE and formation of filament-like Li dendrites. A unique flow-aided sonication exfoliation method is employed to synthesize "defect-free" graphene (df-G), allowing for a direct performance comparison with conventional reduced graphene oxide (r-GO). At cycle 1, the r-GO is better electrochemically wetted by Li than df-G, indicating that initially it is more lithiophilic. With cycling, the nucleation overpotential with r-GO becomes higher than with df-G, indicating less facile plating reactions. The df-G yields state-of-the-art electrochemical performance; stable plating at 0.5 - 4 mA/cm², areal capacity up to 2 mAh/cm², cycle 1 CE at 98% and cycle 100 CE at 94%. With df-G the post cycled metal surface is relatively smooth and dendrite-free. Conversely, r-GO templates have CE rapidly degrade from the onset, with extensive dendrites after cycling. Extensive SEI growth and associated FEC depletion with r-GO are further confirmed by electrochemical impedance analysis and surface science methods (XPS). We therefore propose the following design rule for next-generation supports for LMBs: An ideal architecture will promote copious heterogenous nucleation of the plating metal, shielding it from the electrolyte. In addition, it is essential that the host is itself non-catalytic towards SEI formation.

9:45 AM BREAK

SESSION EN02.02: Advances in Cathodes I
Session Chair: David Scanlon
Monday Morning, December 2, 2019
Sheraton, 2nd Floor, Grand Ballroom

10:15 AM *EN02.02.01
High Capacity Cathodes Invoking Oxygen Redox Chemistry Peter Bruce; University of Oxford, United Kingdom

The lithium-rich transition metal oxides, e.g. Li[Li0.2Ni0.2Mn0.6]O2 can store charge on the oxide as well as the transition metal ions (oxygen redox). However, oxygen redox in these systems is almost always accompanied by substantial structural change and voltage hysteresis, limiting their application. Understanding the relationship between the oxidation of O²⁻ ions and the deleterious changes that are triggered by such oxidation is essential if we are to develop strategies for their mitigation and therefore unlock the high capacity of O-redox materials. Recent work on the relationship will be discussed.

10:45 AM EN02.02.02
Anomalous Segregation in Lithium-Rich Layered Oxide Uncovers New Theoretical Design Rule for Stable
Cathode in Lithium-Ion Battery

Here we report the TEM, X-ray, and first-principle investigation of a promising high-capacity lithium-rich 3d-4d (Mn-Ru) transition-metal layered compound. The incorporation of 4d transition metals here offers an uncharted phase space for mechanistic exploration as compared to the well documented 3d transition metal (TM) oxides. Using state-of-the-art electron and X-ray based techniques, we find surprisingly, after cycling, ruthenium segregates out as metallic nanoclusters on the reconstructed surface. Our calculations show that the unexpected ruthenium metal segregation is due to its thermodynamic insolubility in the oxygen deprived surface. This insolubility can disrupt the reconstructed surface, which explains the formation of a porous structure in this material. The revealed mechanism allows us to provide predictive guidance for the future design of lithium-rich as well as stoichiometric layered cathode materials.

This research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, and the Scientific Data and Computing Center, a component of the Computational Science Initiative, at Brookhaven National Laboratory under Contract No. DE-SC0012704. Dr. Enyuan Hu, Dr. Seongmin Bak, and Dr. Xiaojing Yang were supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Vehicle Technology Office of the U.S. Department of Energy through the Advanced Battery Materials Research (BMR) Program, including Battery500 Consortium under Contract DE-SC0012704. Work done by R.Z. is partially supported by the U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (EERE) under the Award Number: DE-EE0008444. This research used resources 8-ID, 23-ID-2, and 28-ID-2 of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. This research used resources of beamline 8.0.1 of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231. We acknowledge the technical support from beamline scientists Dr. Jianming Bai and Dr. Eric Dooryhee at the XPD beamline of NSLSII.

11:00 AM EN02.02.03

Mitigating Oxygen-Redox-Related Side Reactions in Disordered Rocksalt Li-Excess Cathode Materials for Li-Ion Batteries

There is an imperative need for resource-friendly and high-energy-density cathode materials for Li-ion batteries to satisfy the rapidly increasing need for electrical energy storage. To replace the Ni and Co, which are limited resources and are associated with safety problems in current Li-ion batteries, high-capacity cathodes made of earth-abundant and safer metals have been intensively sought after by battery scientists [1]. In this regard, disordered-rocksalt lithium transition metal oxides (Li-TM oxides) have received much attention as the cathode materials for abundant and safer metals have been intensively sought after by battery scientists [1]. In this regard, disordered-rocksalt lithium transition metal oxides (Li-TM oxides) have received much attention. To operate the disordered rocksalt cathodes, so-called ‘Li-excess’ (i.e., TM-deficient) composition (x>1.0 in Li$_x$TM$_{1-x}$O$_2$, e.g., Li$_{1.2}$TM$_{0.8}$O$_2$) is required, because otherwise, Li diffusion in the materials is very slow [2]. Meanwhile, the decreased TM-content due to ‘Li-excess’ often results in a limited amount of extractible electrons from TM-redox in the materials, for which a large number of electrons from oxygen (O-redox) are often additionally needed upon cycling [7]. Unfortunately, excessive O-redox activity triggers various O-redox-related side reactions, including (i) oxygen loss followed by metal densification and (ii) bulk crystal structure changes, all of which degrade the cycling performance of the disordered rocksalt cathodes [4,6]. Therefore, strategies to bypass the O-redox-related side reactions while maintaining the integrity of the disordered-rocksalt Li-excess framework should be highly important for the improvement of the disordered-rocksalt cathode materials.

In this talk, based on recent studies of fluorinated disordered-rocksalt compounds such as Li$_{1.15}$Ni$_{0.45}$Ti$_{0.3}$Mo$_{0.1}$O$_{1.85}$F$_{0.15}$, Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F, and Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F, I will discuss rational strategies to mitigate the O-redox-related side reactions in the disordered rocksalt cathodes [3,6]. In particular, I will show how the introduction of high valent cations (e.g., Nb$^{5+}$, Ti$^{4+}$, Mo$^{6+}$) and fluorine (F-) anion to the metal- and anion-sites,
respectively, can lead to Mn$^{2+}$/Mn$^{4+}$-redox-based disordered-rocksalt cathodes with ultrahigh capacity and a low cost [3].


11:15 AM EN02.02.04 Automated Computational Search of Anion Redox Li-Ion Battery Composition Space Daniel W. Davies¹, Alexander Squires², Keith Butler¹, David O. Scanlon⁴, Aron Walsh¹ and Benjamin J. Morgan²; ¹Imperial College London, United Kingdom; ²University of Bath, United Kingdom; ³STFC, United Kingdom; ⁴University College London, United Kingdom

The recent discovery of anionic redox chemistry in Li-ion batteries has already had promising implications for improving their capacity via increased electrochemical activity. Higher performance materials are now required to make this technology a reality and new strategies for designing compounds that exhibit this phenomenon are needed. Anionic redox activity requires a balance between the quantities $U$ (d-d coulomb repulsion) and $\Delta$ (charge transfer), which in turn are sensitive to the d-metals present in the crystal structure.[1] We present a computational study in which d-metals are systematically substituted into a range of prototypical cathode crystal structures using materials informatics tools that we have previously applied in the context of solar energy materials.[2,3]

The resulting 250 compounds are subject to an automated density functional theory (DFT) screening workflow, using the open-source python package Atomate. Our workflow facilitates the assessment the thermodynamic stability of the new phases, as well as relating electronic energy levels calculated accurately using hybrid DFT to the key heuristics $U$ and $\Delta$, in order to identify the most promising candidates. Data-driven discovery tools powered by supervised machine learning algorithms, which require large, high quality datasets,[4] are then applied to the calculation results in order to suggest new candidate compounds.

microscopy (cryo-TEM) to observe the morphology and surface chemistry of nanoscale electrochemically deposited lithium at atomistic scale. We have also demonstrated cryogenic focused ion beam (cryo-FIB) to characterize three dimensional and bulk morphology of electrochemically deposited lithium. This work depicts not only the importance of cryo-FIB for preparing sensitive battery materials, but also elucidate the impact of electrolyte and additive selection in the density and morphology of plated lithium, which directly impacts long term cycling performance. We further extend cryo-FIB to process and analyze TEM lamella of lithium metal and lithium metal solid-state batteries. The cryogenic imaging techniques can enable a new paradigm for studying beam sensitive materials and electrochemically activated compounds.

2:00 PM EN02.03.02
Ion Transport In Polyester and Polycarbonate Solid Electrolytes Jonas Mindemark; Uppsala University, Sweden

The traditional host material of choice for Li+-conducting solid polymer electrolytes (SPEs) has long been poly(ethylene oxide) (PEO) and with this material most of what we today know about ion transport in SPEs has been revealed. While PEO is an excellent material for solvating Li+ ions, the chelating ability of the oxyethylene repeating units in this material also result in excessive coordination strength, limiting the ability of the cation to shed its coordination shell and transfer between coordination sites. This ultimately restricts cation transport in this material and manifests as notably low cation transference numbers in PEO-based electrolytes. Hence, substantial interest has recently been raised in alternative host materials that show improvements in, e.g., cation transference number and room temperature ionic conductivity. While materials such as polyesters and polycarbonates eliminate the strong coordination of oxyethylene repeating units, other interesting effects become relevant.

This presentation will account for our recent efforts into understanding ion transport in polyesters, polycarbonates, and copolymers thereof, using a combination of molecular dynamics simulations, NMR spectroscopy, IR spectroscopy, and electrochemical measurements. This has revealed important effects of preferential coordination, competing plasticization and steric hindrance of side chains, and correlation of cation transference number with the ion coordination strength. Of particular interest is also the differences observed when comparing Li+ and Na+ conduction in these materials.

References
Z. Xue, D. He, X Xie, J. Mater. Chem. A 2015, 3, 19218–19253

2:15 PM EN02.03.03
High-Voltage All-Solid-State Batteries Based on Ceramic-Sulfide Electrolytes William Fitzhugh and Xin Li; Harvard University, United States

The ceramic-sulfide family of solid-electrolytes are amongst the most promising directions for achieving all-solid-state lithium ion batteries. While the ceramic-sulfides are celebrated for remarkably high ionic conductivity, even exceeding conventional liquid-electrolytes, they remain a narrow electrochemical stability window of approximately 1.7-2.1 volts vs lithium metal based on standard thermodynamic prediction. These electrochemical stability windows further narrow upon forming interfaces with many active materials. This talk will cover new approaches for enabling a largely expanded metastability window for both bulk ceramic-sulfides and interphases with common electrodes. 5V cells based on layered Li-Co-O and spinel Li-Mn-Ni-O will be presented that make use of these metastable widening techniques ceramic-sulfide voltages.

The underlying stabilization methods will be discussed from a detailed theoretical perspective. Ceramic-sulfides are known to undergo significant volume expansion during electrochemical decay. This volume expansion has been shown to be a viable means of substantial voltage widening for lithium ion battery cells [1,2]. The discussed theoretical framework will be used to evaluate experimental evidence of voltage-widening in both of the representative ceramic-sulfides Li10GeP2S12 and Li10SiP2S12.

Discussion on the interphases between ceramic-sulfides and common electrode materials will focus on our recent high-throughput computational work[3], in which over nearly 70,000 materials were evaluated for interfacial
chemical and electrochemical stabilities with Li10SiP2S12. This work cataloged over 2,000 coating materials that were determined to form stable interfaces with Li10SiP2S12 in the cathode voltage range (2-4V). These coating materials, combined with widened bulk electrochemical stability, suggest the path forward for all-solid-state lithium ion batteries based on ceramic-sulfide electrolytes.


2:30 PM *EN02.03.04
Lithionics—On the Design of Lithium Oxide Films for Solid-State Batteries and Novel Neuromorphic Computing Functions Jennifer L. Rupp; Massachusetts Institute of Technology, United States

Next generation of energy storage may largely benefit from fast Li+ ceramic electrolyte conductors to allow for safe and efficient batteries. With recent discoveries in thin film processing solid-state lithium ion conductors, such as Li-garnets and LIPON or LiSICON-based solids, have been recently considered as candidate materials not only for next-generation solid-state batteries but also for gas sensors measuring environmental CO2 and memristors owing to the fast ionic transport in the solid-state electrolyte.

In the first part of this talk, we review and underline the advantages of various Li solid-state conductor materials and reflect on opportunities of thin film processing, being a requirement to define precisely the lithium stoichiometries and related electronic state changes for transition metal ions, miniaturize the device, and reach high energy/information densities for energy storage, computation, and sensing.

In the second part, we focus on thin film processing and controlling Lithium stoichiometries to reach fast conductive phases for Li garnets and Li titanates as solid state battery, and memristive neuromorphic computing units. Insights on structure-phase-transport interaction and implications on performances will be exemplified for energy storage aiming high energy densities, and modulations of synaptic artificial weights through lithium induced metal-to-insulator transitions in lithium titanate memristors.

References
A low ride on processing temperature for fast lithium conduction in garnet solid-state battery films
A Simple and Fast Electrochemical CO2 Sensor based on Li7La3Zr2O12 for Environmental Monitoring
Glass-Type Polyamorphism in Li-Garnet Thin Film Solid State Battery Conductors
Accelerated Ionic Motion in Amorphous Memristor Oxides for Non-Volatile Memories and Neuromorphic Computing
Lithium Titanate Anode Thin Films for Li-Ion Solid State Battery based on Garnets
Designing Strained Interface Heterostructures for Memristive Devices
Interface-Engineered All-Solid-State Li-Ion Batteries Based on Garnet-Type Fast Li+ Conductors

3:00 PM BREAK
SESSION EN02.04: Dendrites I
Session Chair: Feng Wang
Monday Afternoon, December 2, 2019
Sheraton, 2nd Floor, Grand Ballroom

3:30 PM *EN02.04.01
The Electronic Reasons for Li Dendrite Growth in Solid Electrolytes Yue Qi1, Hong Kang Tian1, Zhe Liu2, Yanzhou Ji1 and Long-Qing Chen2; 1Michigan State University, United States; 2The Pennsylvania State University, United States

The experimental observation of Li dendrite growth inside mechanically hard solid electrolytes (SEs) raised an important question; can hard solid electrolytes mechanically stop Li-dendrite growth? Here we report a multiscale model coupling Density Functional Theory (DFT) calculations with the phase-field method to address the question. In particular, we investigate the roles of internal defects, such as pores and crack surfaces, inside a number of solid electrolytes including cubic Li7La3Zr2O12 (c-LLZO), β-Li3PS4, Li1.17Al0.17Ti1.83 (PO4)3 (LATP), and Li2PO2N. It is shown that LLZO surfaces have a much smaller band gap than the corresponding bulk and thus could trap significant excess electrons, while the other three systems do not exhibit significant differences in the surface and bulk band gaps. A fully coupled phase-field model was then developed to further examine the impact of excess surface electrons on the Li dendrite growth morphology in polycrystalline LLZO. This model successfully explained the experimentally observed dendrite intergranular growth and revealed that the trapped electrons may produce isolated Li-metal nucleation, leading to a sudden increase of Li-dendrite penetration depth. Finally, we compared the basic material properties and found that the Li ranked dendrite resistance in these SEs, based on the surface electronic properties instead of mechanical properties, is consistent with a broad range of experimental observations. Therefore, surface band gaps can be used as new descriptors to screen SEs with high Li dendrite resistance.

4:00 PM EN02.04.02
Advanced Safety Sensor for Lithium-Metal Battery via Bifunctional Auxiliary Electrode Orapa Tamwattana1, Sehwan Moon1, Hyekjun Park1, Gabin Yoon1, Won Mo Seong1, Myeong Hwan Lee1, KyuYoung Park1, Nonglak Meethong2 and Kisuk Kang1; 1Seoul National University, Korea (the Republic of); 2Khon Kaen University, Thailand

The demand for rechargeable batteries with higher energy density than lithium-ion batteries that are commercially available has been ever increasing 1, 2. Elemental lithium metal has thus come into the spotlight again as one of the most promising negative electrode materials owing to its exceptionally high theoretical capacity (3860 mAh g⁻¹) and the lowest negative electrochemical potential (-3.040 V vs. a standard hydrogen electrode) 3, 4. Moreover, its stable utilization is pivotal in the success of the next-generation electrochemical systems. Nevertheless, the commercialization of rechargeable lithium metal electrode has been retarded due to the catastrophic safety issue arising from lithium dendrite formation. Even with a small irregularity in lithium metal deposition during the initial stage of charge, further selective and self-amplifying lithium deposition follows due to the presence of favorable deposition sites 5, 6. The needle-like lithium dendrite can penetrate the polymer separator and possibly contact the opposite electrode, and such contact would result in a huge current flow through the internal circuit, triggering joule heating thermal runaway.

Unfortunately, it has been revealed that dendrite formation cannot be completely inhibited and some reported successes are only valid at low current densities and with low utilization levels of lithium metal. Batteries operating under extreme conditions might still be exposed to the potential risk of dendrite growth and internal short-circuit. Therefore, not only protective techniques for lithium metal but also sensing technologies to detect dendritic growth in advance are needed.

Herein, we introduce a lithium rechargeable battery system with a bifunctional auxiliary electrode that can detect the potential signs of an internal short-circuit and simultaneously prevent cell failure by inhibiting further dendritic growth of lithium metal. Based on this working principle, we provide guidelines for bifunctional auxiliary electrode design and demonstrate that it can act as both a safety sensor and a lithium scavenger. Finally, we show that our in-house designed cell, using a flexible and self-standing auxiliary electrode, can effectively alert the danger of a short circuit in real-time without additional dendrite growth. We expect that this finding will open up unexplored opportunities utilizing various auxiliary electrode chemistry for safe rechargeable lithium metal batteries.

Reference

**4:15 PM EN02.04.03**

**A New Li Metal Electrode by Ironing Controllable Lithium Into Lithiotropic Carbon Fiber Fabric (LiCFF)**

Junjie Niu; University of Wisconsin--Milwaukee, United States

The Department of Energy (DoE) announced the energy density target of >500 Wh/Kg for next-generation lithium-ion batteries in the incoming 3-5 years, to meet the rapidly growing market in electrical vehicles (EVs) and portable electronic devices. Li metal is considered as the most promising candidate as anode (Xu, *Energy Environ Sci* 2014). However, the dendrite forming, low Coulombic efficiency, and unstable solid electrolyte interphase (SEI) pose big challenges in applying Li metal in batteries (Chandrashekar, *Nat Mater* 2012). Here we present a novel, single-side Li-infused carbon fiber fabric (LiCFF) with a controllable, minimized Li loading, which shows a highly reversible plating/striping with an extremely low overpotential of less than 30 mV (Li foil: >1.0 V over 50 cycles) upon >3000 cycles (6000 and 2000 hours) at 1 and 3 mA/cm² in symmetric cells, respectively (*Xi Chen et al., ACS Appl Mater Interfaces, 2019, in print*). With a high areal capacity up to 10 mAh/cm² and a high current density of 10 mA/cm², the cell still shows a minimum overpotential of 150-175 mV after 250 cycles (500 hours). Full cell batteries using the LiCFF as ‘all-in-one’ anode without additional slurry-making process and nickel-manganese-cobalt oxide (NMC) as cathode exhibit an improved capacity retention when compared with Li foil: 32% at 0.5 C and 119% at 1.0 C capacity improved after 100 cycles. In parallel, the mossy/dendritic Li on the LiCFF was largely suppressed, which was confirmed using in-situ observations of Li plating/striping in a capillary cell. The excellent electronic conductivity of the carbon fabric leads to small contact/transfer resistances of 3.4/3.8 Ω (Li foil: 4.1/44.4 Ω), enabling a drastically lowered energy barrier for Li nucleation/growth. Thus a uniform current distribution results in forming a homogeneous Li layer instead of forming dendrite. The current LiCFF as anode with controllable Li (n/p ratio), improved cycling stability, mitigated dendrite formation, and flexibility displays promising applications in versatile Li-metal batteries such as Li-NMC and Li-S.

**Keywords:** Li metal; Carbon fiber fabric; Low overpotential; Dendrite; Lithium ion batteries

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**SESSION EN02.05: Advances in Cathodes II**

**Tuesday Morning, December 3, 2019**

**Sheraton, 2nd Floor, Grand Ballroom**

**8:00 AM *EN02.05.01***

**Reversible Oxygen-Redox Chemistry for Large-Capacity Sodium-Ion Battery Cathodes**

Masashi Okubo; The University of Tokyo, Japan

Increasing the energy density of sodium-ion batteries is of paramount importance toward achieving a sustainable society. The present limitation of the energy density is owing to the small capacity of cathode materials, in which the (de)intercalation of sodium ions is charge-compensated by transition-metal redox reactions. Although additional oxygen-redox reactions of oxide cathodes have been recognized as an effective way to overcome this capacity limit, the electronic structure during oxygen-redox reactions are yet to be fully understood. In this work, we employed combined analyses of synchrotron X-ray diffraction, soft X-ray absorption spectroscopy, and DFT calculations to demonstrate how reversible oxygen-redox reactions occurs in transition-metal oxides. As an oxygen-redox compound, we studied Na₂RuO₃ and Na₂Mn₃O₇, which exhibit highly reversible oxygen-redox reactions. Detailed analyses revealed that, while nonbonding oxygen 2p orbital plays a central role to trigger oxygen oxidation, hole generated on oxygen 2p orbital is stabilized by interaction with metal d orbitals. Furthermore, we found a self-ordering phenomenon of stacking faults upon desodiation from an oxygen-redox
layered oxide Na$_2$RuO$_3$, realizing much better reversibility of the electrode reaction. The cooperatively ordered vacancy in lithium-/sodium-rich layered transition-metal oxides is shown to play an essential role, not only in generating the electro-active nonbonding 2p orbital of neighboring oxygen but also in stabilizing the phase transformation for highly reversible oxygen-redox reactions.

Ref.
facile approach to faceted high-nickel content (doped) cathodes and we will finally discuss the potential scalability of this approach.

9:00 AM EN02.05.04
Towards Co-Free Ultra-High Ni Positive Electrode Materials for Li-Ion Batteries—Understanding the Role of Dopants Marc M. Cormier¹, Hongyang Li¹, Ning Zhang¹,², Aaron Liu¹, Julie Inglis³, Jing Li⁴ and Jeff Dahn¹; ¹Dalhousie University, Canada; ²Northeastern University, China; ³McMaster University, Canada; ⁴Tesla, United States

Increasing lithium-ion battery energy density and reducing cost without compromising lifetime or safety is an important goal for EV applications. While Co has been a critical constituent of Li-ion battery positive electrode materials such as NCA and NMC, instability of Co pricing and concerns about long-term availability motivate the reduction of Co content in these materials. This work pairs first-principles density functional theory (DFT) computations with experimental measurements to gain fundamental insight into how individual dopants influence the structural and electrochemical properties of LiNi₁₋ₓMₓO₂ (y=0, 0.05; M=Al, Mg, Mn, Co) and makes comparison with NCA materials. Trends in capacity reduction as a function of dopant valence and concentration can be explained using simple oxidation state analysis, which is shown to hold on the atomic scale from DFT computations. Similarly, computations over various Li configurations at high states of charge demonstrate preferred structural arrangements for Al and Mg, which helps understand the effective suppression of phase transitions otherwise observed in LiNiO₂ and LiNi₀.₉₅Co₀.₀₅O₂ using dQ/dV analysis and in-situ XRD. Oxygen binding energy computations as a function of dopant type and Li content paired with TGA and ARC measurements further reveal the mechanism through which small dopant concentrations help reduce the reactivity of ultra-high Ni materials with electrolyte at elevated temperature, potentially leading to safer Li-ion cells.

9:15 AM *EN02.05.05
Advanced In Situ X-Ray Diffraction in Revealing the Structural Changes of High Voltage Cathode under the Effect of Different Electrolytes Mei Cai and Meinan He; General Motors, United States

Fluorinated electrolyte is a promising candidate to replace the regular carbonate-based electrolyte because of its impressive anodic stability, conductivity as well as thermo-stability. Yet, most of the fluorinated electrolyte studies focused on the interfacial reaction and electrochemical performance. Although it is equally critical in understanding the interaction between different electrolyte systems and the bulk cathode structure to improve the energy density of the whole cell, the research regarding this topic is limited. In this work, bulk electrode analysis via in-situ XRD technique was carried out to unveil the high Nickel cathode structural changes by using different electrolytes and the results indicate the use of fluorinated electrolyte can mitigate the electrolyte decomposition. Most importantly, it can also assist the preservation of the crystal structure of high Nickel cathode by inhibiting the loss of active Li ion and transition metal during cycling. All results converge to the conclusion that the use of fluorinated electrolyte can not only stabilize the interface but also conserve the bulk structure. Owing to its impressive anodic stability, conductivity as well as thermo-stability, fluorinated electrolyte is a promising candidate over the conventional regular carbonate-based electrolyte for next generation functional electrolyte. Currently, most of the fluorinated electrolyte studies have been focused merely on the interfacial reaction and electrochemical performance. Although it is equally critical in understanding the interaction between different electrolyte systems and the bulk cathode structure to improve the energy density of the whole cell, the research regarding this topic is still lacking. In this work, bulk electrode analysis via in-situ XRD technique was carried out to unveil the high Nickel cathode structural changes in different electrolyte systems and the results indicated the use of fluorinated electrolyte can mitigate the electrolyte decomposition. More importantly, it can also assist the preservation of the crystal structure of high Nickel cathode by inhibiting the loss of active Li ion and transition metal during cycling. All results converge to the conclusion that the use of fluorinated electrolyte can not only stabilize the interface but also conserve the integrity of the bulk crystal structure.

9:45 AM BREAK
Understanding and Optimization of Solid Electrolytes and Li-S Solid-State Batteries

Wolfgang Zeier
University of Giessen, Germany

The advent of solid-state batteries has spawned a recent increase in interest in lithium conducting solid electrolytes, especially in the lithium thiophosphates. While current lithium electrolytes provide fast-ionic conduction to fundamentally study solid-state batteries, their ionic conductivities are not sufficient for thick electrode configurations, which will really allow high energy densities to be achieved.\(^1\)

In this presentation, we show how an understanding of the structure-transport properties of the lithium argyrodites Li\(_6\)PS\(_5\)X can help tailor the ionic conductivity. We show that an anion site-disorder between S\(^2-\)and X\(^-\)is beneficial\(^2\)and that an induction of the site disorder in Li\(_6\)PS\(_5\)I leads to a significant improvement of the conductivity.\(^3\)Having achieved the fastest lithium argyrodite so far with \(\gamma = 18\) mS/cm, solid-state batteries with thick electrode configurations (150 – 350 \(\mu\)m) can be built. Due to the optimized solid electrolyte, the solid-state battery can be cycled even at 1C with no capacity fade over 150 cycles. This work shows that optimizing solid electrolytes helps to achieve stable cycling at high rates in solid-state batteries with thick electrodes.

Further, we will show how the stability of thiophosphate electrolytes can be measured and that the operation window affects cell performance. Lastly, we show how volume changes, induced by electrochemical (de-)intercalation, affect the performance in solid state batteries providing an understanding of the underlying mechanocchemical influences in Li-S solid-state batteries.\(^4\)\(^-\)\(^6\)


High Energy Batteries with Si- and Li-Metal Anodes—Nanomaterials and Interfacial Design

Yi Cui
Stanford University, United States

The demand from portable electronics and electric vehicles call for high energy batteries beyond the current lithium ion batteries. Here I will present our recent progress on materials and interfacial design to enable much high energy density batteries, which include 1) High capacity Si anodes with success together commercialization; 2) Li metal anodes: host and interface design to over the lithium metal dendrite formation and interfacial instability; 3) Our pioneering development of cryogenic electron microscopy for understanding the battery materials and solid-electrolyte interphase down to atomic scale resolution.
EN02.07.01
The Multiscale and Multi-Modality In Situ and Ex Situ Microscopy and Spectroscopy Diagnosis on the Fading Mechanism of Rechargeable Batteries Chongmin N. Wang; Pacific Northwest National Laboratory, United States

In situ diagnosis appears to be one of the essential methods for gaining insights as how an electrode material failure, therefore feeding back for designing and creating new materials with enhanced battery performances. In this presentation, I will highlight recent progress on ex-situ, in-situ and operando S/TEM for probing into the structural and chemical evolution of energy storage materials. Both ex-situ and in-situ high resolution imaging enables direct observation of structural evolution, phase transformation and their correlation with mass, charge and electron transport, providing insights as how active materials failure during the cyclic charging and discharging of a battery. In particular, I will broadly cover the frontier of the current understanding of the fading mechanism of layer structured cathode and Li dendrite growth and interaction with separators. Subsequently, I will discuss some recent breakthrough experiments and observations for correlating the structural and chemical evolution with the electrochemical properties of both layered cathode and Li metal. In perspective, my presentation will target to stimulate this field of research to re-check what has been understood and what need to be done to tackle the technical challenges facing the application of the layer structured cathode and Li metal anode.

EN02.07.02
Observation of Electrode Reactions in Fluoride Shuttle Battery by Atomic Force Microscopy Taketoshi Minato1, Hiroaki Konishi1, Asuman Celik Kucuk1, Hiroshi Onishi2, Zempachi Ogumi1 and Takeshi Abe1; 1Kyoto Univ, Japan; 2Kobe University, Japan

The applications of rechargeable battery are growing in various field for the efficient energy systems [1]. To expand the application of the rechargeable battery, the developments of innovative rechargeable batteries which overcome the performances of current batteries are required. Fluoride shuttle batteries (FSBs) which is based on the shuttle of fluoride ions in electrolyte and fluorination/defluorination reactions on electrodes [2, 3] contains higher theoretical energy densities than current rechargeable batteries. We have developed organic electrolyte and electrodes from metal fluorides for FSBs [2, 4-10]. However, the reaction mechanisms on the electrode in FSB are not understood. For the further developments of FSB, the analysis of the reaction at the interface between electrode and electrolyte were performed by using atomic force microscopy (AFM) [1, 11-13]. In the presentation, we will show the investigation on the effects of electrolyte composition on the reaction mechanisms.

This research was supported by the Research and Development Initiative for Scientific Innovation of New Generation Batteries (RISING) and Research and Development Initiative for Scientific Innovation of New Generation Batteries 2 (RISING2) projects of the New Energy and Industrial Technology Development Organization (NEDO), Japan.

Lithium-sulfur (Li-S) batteries are a beyond Li-ion battery technology that provides large theoretical capacity (1672 mAh/g) while also being earth-abundant and low cost. In this study, we investigate the behavior of lithium polysulfides (LiPS; Li2Sx, x = 4, 6, 8) and lithium salt (LiTFSI; Li bis(trifluoromethane)sulfonimide) in model electrolyte solutions using small angle X-ray scattering (SAXS). A concentration series of polysulfides (ranging from 100 to 1500 mM depending on the solution) in solvents relevant to Li-S battery electrolytes (DOL:DME, acetonitrile) with a range of polysulfide solvation were selected after an initial screening of common solvents. Some aggregation of LiPS was observed at high concentrations (> 1000 mM based on the mass of sulfur) in both solvents, but DOL:DME-based solutions exhibited aggregation even at low concentrations. Fitting the data with a unified model yielded two distinct populations in the DOL:DME solutions – one with a radius of gyration (Rg) of about 5 Å and one with a Rg of about 12 Å. In the 1 M LiTFSI in DOL:DME solutions, the SAXS data showed a peak at all polysulfide concentrations, indicating quasi-periodic nanostructuring in the solution that is induced by the presence of the LiTFSI salt. This nanostructuring is also present in the 1 M LiTFSI in acetonitrile solutions, confirming that the effect originates from the LiTFSI salt. We will compare experimental results with those from molecular dynamics calculations. These results add molecular level insight into Li-S electrolytes and a better understanding of electrolyte-salt interactions.

The rapid growth in popularity of battery devices has brought energy storage and conversion to the spotlight of materials research. Bringing together researchers from a variety of disciplines spanning science and engineering, it is now a common goal to build batteries that are safe, long-lasting, and powerful enough to serve today’s most demanding applications. In order to meet these goals, a methodical development approach is needed, including material synthesis, processing, characterization, and design iteration.

In recent years, X-ray analysis has become a popular choice for electrochemical device characterization, including X-ray microscopy (XRM), X-ray fluorescence (XRF), and X-ray absorption spectroscopy (XAS). Owing to the high penetrating power of X-rays and non-destructive nature of X-ray interactions with matter, these techniques provide unique insight into electrochemical devices such as batteries, fuel cells, and catalysts. XRM employs the technique of computed tomography (X-ray CT or XCT), yielding 3D models of a material’s microstructure, while XRF provides elemental identification and XAS reveals chemical states. Combining these three techniques together results in a powerful characterization approach that compliments conventional electrochemical measurements and other analysis methods, while delivering new information about the material under study. However, while the use of XRM, XRF, and XAS for electrochemical device characterization continues to rise, the techniques are traditionally limited to synchrotron facilities only, which has limited the reach of these techniques for widespread use.

In our work, we have developed a suite of laboratory X-ray instrumentation, designed with battery, fuel cell, and catalyst research in mind. Our laboratory nano-XRM is capable of providing spatial resolutions down to 40 nm, creating a high-resolution model of material microstructures for time-evolved (4D) characterization and computational simulation incorporating fine features within the specimen. In tandem with this, our laboratory micro-XRF system provides sub-parts-per-million (sub-ppm) elemental detection sensitivities with < 10 um spatial resolutions, and pairs elemental identification with optical and x-ray radiographic imaging for spatially-resolved spectroscopic analysis. The most recent addition to this set of tools is the laboratory X-ray absorption spectrometer, which provides sub-eV energy resolution in a matter of minutes and yields oxidation state, coordination number, and bond length information non-destructively and without extensive specimen preparation. These three systems carry...
with them performance characteristics that begin to mirror those of synchrotron.

2:45 PM EN02.07.05
Direct Observation of Solution-Phase Discharge in Lithium Oxygen Batteries by Liquid Phase Transmission Electron Microscopy
Hyeokjun Park1,2,3, Donghoon Lee1,3, Jungwon Park1,3 and Kisuk Kang1,2,3; 1Seoul National University, Korea (the Republic of); 2Research Institute of Advanced Materials, Korea (the Republic of); 3Institute for Basic Science, Korea (the Republic of)

Non-aqueous lithium oxygen(air) battery has been considered as a promising next-generation energy storage system because of its highest theoretical energy density among all the battery chemistries which have been introduced so far. However, there are many hurdles in practical demonstration of the high energy density of lithium oxygen battery.1 One typical and serious problem is that premature passivation of insulating Li2O2 inevitably occurs on the surface of the cathode. Using redox mediators such as 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ), coenzyme Q10 (CoQ10), and Vitamin K2, that change the reaction pathway of producing Li2O2 from surface of electrode to bulk liquid phase is now suggested as a key solution to circumvent such passivation problems.2-4 However, such engineering is somewhat empirical with limited mechanistic understanding since most of previous experimental analyses for studying working principles of lithium oxygen battery are based on ex situ experiments. In this work, we implement a liquid TEM holder to capture real time status of the lithium oxygen battery while discharging with a typical redox mediator of DBBQ, which is one of recent emerging electron microscopy techniques for examinations of liquid samples.5,6 We successfully obtain a real time TEM movie presenting growth of Li2O2 on the solution phase and analyze the growth rate, morphology transformation of Li2O2. Interestingly, growth of Li2O2 in electrolyte solution during discharge involves distinct two-step pathway. Our findings can provide the answer for the unsolved question regarding the redox mediation mechanism, growth kinetics of discharge products, and morphology evolution of Li2O2 in lithium oxygen batteries.

References

3:00 PM BREAK

SESSION EN02.08: Electrolytes, Additive and Interfaces I
Session Chair: Zhengping Zhou
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Grand Ballroom

3:30 PM *EN02.08.01
Nonaqueous Liquid Electrolyte Based on Lithium bis(fluorosulfonyl)imide (LiFSI) for Lithium-Ion Batteries with Improved Calendar Life
Liyuan Sun1, Kate Digan1, Connor Tomshack1, Mengqing Xu2 and Derek C. Johnson1; 1A123 Systems, Inc, United States; 2Wanxiang A123 Systems Asia Co., Ltd, China

Lithium hexafluorophosphate (LiPF6) is adopted almost exclusively as the conducting salt of the electrolyte in current commercial lithium-ion (Li-ion) batteries because of the high ionic conductivity, good electrochemical stability and lower cost. However, thermal instability of LiPF6, which could lead to the generation of detrimental byproduct hydrogen fluoride (HF) through LiPF6 hydrolysis, raises challenges for LiPF6 based electrolytes to function well at elevated temperatures (>55°C) and in presence of inevitable moisture or alcohol impurities. Lithium bis(fluorosulfonyl)imide (LiFSI), with higher ionic conductivity and thermal stability, could be a promising alternative to LiPF6 since it bypasses the hydrolysis of PF6− that generates HF. However, a major technical challenge for LiFSI to be employed as a primary conducting salt is aluminum current collector corrosion generally seen from
around 4.2 (vs. Li/Li⁺) which is within the operating voltage of Li-ion batteries with lithium nickel manganese cobalt oxide (NMC) cathode. Lithium iron phosphate (LiFePO₄)/graphite Li-ion batteries have an operating voltage between 2.0 and 3.6 V (vs. Li/Li⁺), and therefore, could utilize LiFSI as the primary conducting salt without running into the aluminum corrosion issue.

The intent of this study was to evaluate a series of LiFSI based electrolytes in the LiFePO₄/graphite chemistry. It was found that the calendar life of LiFePO₄/graphite Li-ion batteries was significantly improved in high temperature storage when LiPF₆ was completely or partially substituted by LiFSI. Batteries using LiFSI based electrolytes also demonstrated improved power performance largely due to the superior ionic conductivity of these electrolytes. It was further confirmed that aluminum corrosion is not occurring within the operating voltage of LiFePO₄/graphite Li-ion batteries with LiFSI based electrolytes. This study reveals a promising path forward to produce LiFePO₄/graphite Li-ion batteries with much improved performance so as to meet OEM’s stringent requirements for next-generation Li-ion batteries.

BIAN Based Anode Binder/Additive for Improved Performance of Li-Ion Secondary Batteries Noriyoshi Matsumi, Sai Gourang Patnaik and Raman Vedarajan; Japan Advanced Institute of Science and Technology, Japan

Bisiminoacenaphthene (BIAN) has been an important ligand structure for a variety of metal complex and widely employed as a ligand for olefin polymerization catalysts. However, in spite of their unique electrochemistry, it has not been widely utilized for energy devices. In the present work, firstly BIAN based novel conjugated polymer was prepared by Sonogashira-coupling polymerization and the obtained polymer (P-BIAN)¹ was employed as anode binder in Li/EC:DEC/C type anodic half cells. Second, novel additive material bearing BIAN structure (BIANODA) was synthesized by condensation of acenaphthequinone with 2 eq. of dianiline compound, which was used as additive to improve the characteristics of MNC cathode material (LiMn₁/₃Ni₁/₃Co₁/₃O₂)². Electrochemistry of these materials along with characteristics of fabricated Li ion battery cells under these design protocol will be presented in detail.

The structures of P-BIAN and BIANODA were supported by NMR, IR spectra etc. Mn of P-BIAN was found to be 40000 when measured by gel permeation chromatography (THF as an eluent, PST standards). The BIAN based polymer, P-BIAN shows lower LUMO level in comparison with ethylene carbonate (EC). This means reductive doping of P-BIAN takes place prior to reductive decomposition of EC at anode surface, which will restrict thick SEI formation at anode. When cyclic voltammetry measurements were carried out for coin cell with P-BIAN, peak due to reductive decomposition of EC was not observed, unlike the case of PVDF. Further, after charge-discharge cycles, coin cell with P-BIAN exhibited much smaller internal resistance when compared with PVDF. This indicates that reductive doping of P-BIAN and restriction of SEI decomposition had synergistically decreased internal resistance of battery cells. As a result, coin cell with P-BIAN showed 1.5 times higher discharging capacity in comparison with coin cell with PVDF.

On the other hand, BIANODA has higher HOMO level than that of EC, which enables oxidative polymerization of BIANODA prior to oxidative decomposition of EC. This will restrict thick SEI formation at MNC cathode surface. Use of Schiff base can trap HF generated during the cycling, and strong binding property of BIAN can stabilize MNC cathode for long term use. Consequently, BIANODA additive had enhanced the discharging performance of MNC/EC:DC/Li cathodic half cells.


Designer Electrolyte Additives for High Energy Density Si Anode Based Li-Ion Battery Gebrekidan Gebresilassie G. Eshetu¹,², Felix Aupperle¹ and Egbert Figgemeier¹,³;¹Electrochemical Energy Conversion and Storage Systems Group, Institute for Power Electronics and Electrical Drives (ISEA), RWTH Aachen University, Germany; ²Department of Chemistry, College of Natural and Computational Sciences, Mekelle University, Ethiopia; ³Helmholtz Institute Münster, IEK-12, Forschungszentrum Jülich GmbH, Aachen/Münster, Germany

Silicon (Si) and its derivatives (Si/C composite, SiOₓ) have garnered enormous attention as anode materials for next-generation high-capacity lithium-ion batteries (LIBs). However, despite the prodigious beneficial features of pure Si, its large-scale commercialization is still hindered due to the existence of numerous inevitable defies such as colossal...
volume change during (de-)alloying, inherent low electric conductivity, low Coulombic efficiency, unstable/dynamic solid electrolyte interphase (SEI), electrode swelling, electrolyte drying etc. Among proposed mitigating strategies, the use of a fraction dose of molecular additives is hailed as the most effective, economic and scalable approach to realize Si and its derivative anode based LIBs. Additives can modify the nature and chemical composition of the SEI layer, which in turn dictates the obtainable capacity, rate capability, Coulombic/energy efficiency, thermal reactivity etc. of the battery system. Thus, we report a systematic and comparative investigation of various electrolyte additives, namely tetraethoxysilane (TEOS), (2-Cyanoethyl)triethoxysilane (TEOSCN), vinylene carbonate (VC), fluoroethylene carbonate (FEC), and a blend of TEOSCN, VC and FEC (i.e. VC/FEC/TEOSCN) using electrochemical analysis, X-ray photoelectron spectroscopy (XPS), Density Functional Theory (DFT) calculation and differential scanning calorimetry (DSC). The ternary mixture (FEC/VC/TEOSCN) results in a thinner SEI layer consisting of high shear modulus SEI-building species (mainly LiF). It also provides much improved thermal stability amid all tested additives, evidencing its potentiality to boost high capacity and safer Si anode-based LIBs. Pouch cells fabricated using Si anode, NMC cathode and LiPF6/EC-DEC electrolyte doped with TEOSCN-based additives demonstrated excellent electrochemical cycling performance for over 400 cycles with nearly 100% Coulombic efficiency. The improvement could be explained due to the fact that –C≡N group can undergo a polymerization reaction by decreasing the bond order from triple (C≡N) to double (C=N) and single (C-N) bonds, thus forming a chemically stable and highly ionically conductive material and also possibly Li3N as precipitates on Si surface. Moreover, strong nucleophiles formed by the reduction of the C≡N could attack FEC and/or LiPF6 stripping of –F to form LiF, as evidenced from XPS analysis.

Thus, nitrile-functionalized silanes are highly promising electrolyte additives to boost the electrochemical performance and safety-induced risks of Si anode-based LIBs, emanating from the formation of a robust SEI layer.

We believe that this study gives a valuable understanding and provides new insights on the use of electrolyte additives for highly-energy density and reversible Si and Si-derivative anodes in Li-ion batteries.

4:30 PM EN02.08.04
From Atomistic Understanding of Correlation and Transport to Design of Next-Generation Ionic Liquid-Based Electrolytes Nicola Molinar1, Jonathan Mailoa2 and Boris Kozinsky1,2; 1Harvard University, United States; 2Robert Bosch LLC, United States

Electrolytes control battery recharge time and efficiency, anode/cathode stability, and ultimately safety, consequently electrolyte optimization is crucial for the design of modern energy storage device. Electrolytes containing ionic liquids (ILs) are often regarded as attractive candidates to replace the currently-adopted organic solvents thanks to their superior chemical stability, however, poor transport properties are hindering their applicability. Given the ionic nature, these systems possess high degrees of ion-Ion correlation, therefore posing a non-trivial yet crucial and interesting challenge to understanding their transport properties.

Here we present molecular dynamics analysis of transport properties in IL-based electrolytes. First, the strong ionic interactions result in significant correlations and deviations from ideal solution behavior. By adopting rigorous concentrated multicomponent solution theory, we show that when accounting for intra- and inter-species correlation, beyond the commonly used uncorrelated Nernst-Einstein-based approach, an anomalously low and even negative Li transference number emerges. Second, we computationally confirm the recently measured negative Li transference number in Li-containing IL-based electrolytes, and extend this surprising result to a vast range of different chemistries, suggesting a universal behavior of this class of electrolytes. Additionally, we characterize the atomistic nature of the anion-cation clusters, formulate a way to compute the effective lithium charge, and show that lithium-containing clusters carry a negative charge in a remarkably wide range of compositions and concentrations. Third, we leverage our microscopic understanding to suggest and test modifications to increase the cation transference number. Our results have significant implications for the adoption of ionic liquid-based electrolytes as they provide a recipe for optimizing transport properties in next-generation highly correlated electrolytes.
EN02.09.01
An All-Solid Lithium-Ion Battery for Active Implantable Medical Devices with High Safety and Performance Stability Lukas Duwe, Arijit Bose and Mike Molinski; University of Rhode Island, United States

An all-solid lithium-ion battery (ASLIB) consisting of a polyethylene oxide (PEO)-based polymer electrolyte with a lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt, lithium titanate (LTO)-based anode and lithium iron phosphate (LFP)-based cathode has been fabricated. The solid polymer electrolyte has an ionic conductivity of ~10^{-4} S/cm at 40 °C. The electrolyte is prepared using a solvent free hot-pressing method. The electrodes consist of the active materials (LTO or LFP), carbon black, small amounts of PEO, LiTFSI, and a PVDF binder. A coin cell is assembled using these electrodes and electrolyte. The cell shows stable electrochemical performance over 20 charge/discharge cycles.

EN02.09.02
Scanning Electrochemical Microscopy of Two-Dimensional Titanium Carbide (Ti3C2Tx) MXene—Effects of Interlayer Spacing, Flake Size and Electrochemical Environment Sanju Gupta and Wyatt Ringo; Western Kentucky University, United States

Two-dimensional (2D) layered materials are increasingly studied in effort to discover new compounds and the fascinating properties engineered by their sheet-like structure. Graphene, atomic layer of carbon, is the most researched among 2D materials, albeit limited to just carbon in its composition. Recently, a new emergent family of 2D transition metal carbides and carbonitrides – so called “MXene” – are synthesized that may have wide-ranging applications, including energy storage, polymer nanocomposite fillers, water purification, transparent optical conductive coatings and electronic devices. Nevertheless, before the best application is identified, the fundamental chemical physics of these materials must be understood and therefore synthesis-structure-property relationships must be established. To our expanding interests in this emerging class of materials, we investigate the structure and properties of layered transition metal carbides (Ti3C2Tx) MXenes phases for renewable energy prepared by collaborator. We employed electron microscopy, optical absorption spectroscopy, Raman spectroscopy and advanced electrochemistry including SECM to determine surface morphology, nanoscale structure, lattice vibrational properties and surface sensitive electrochemical properties and physicochemical processes at solid/liquid interface.

EN02.09.03
Prospect of Thermal Shock Induced Healing of Lithium Dendrite Zijian Hong and Venkatasubramanian Viswanathan; Carnegie Mellon University, United States

Dendritic growth plagues the development of rechargeable lithium metal anodes. Recently, it has been reported that self-heating of the cell provides a mitigation strategy for suppressing dendrites. In order to study this phenomenon, we extend our recently developed nonlinear phase-field model to incorporate an energy balance equation allowing a full thermally coupled electrodeposition model using the open-source software package MOOSE. In this work, we consider the interplay between ionic transport and electrochemical reaction rate as a function of temperature and explore the possibility of using thermal shock induced dendrite suppression. We discover that, depending on the electrochemical reaction barrier and ionic diffusion barrier, self-heating could accelerate (larger reaction barrier) or decelerate (larger diffusion barrier) dendrite formation. Given that the electrolyte constituents can be used to tune both barriers, this study could provide an important avenue to exploit the self-heating effect favorably through electrolyte engineering.

EN02.09.04
Design of Graphene-Based Composites with Bio-Inspired Structures for Energy Storage Shenmin Zhu, Chengling Zhu and Yao Li; Shanghai Jiao Tong Univ, China

With the increasing demand for lithium-ion batteries in electronics and vehicles, great efforts have been drawn on promoting both the energy and power densities. The electrochemical properties of electrode materials directly affect
the performance of lithium-ion batteries, and therefore it is the primary issue to develop and optimize new-type electrode materials. The performance of high-capacity anode materials can be improved by constructing nanostructures and combining with carbon materials of high conductivity. How to develop effective and practical methods for the design and synthesis of anode materials for lithium-ion batteries is challenging.

Bionic design has been playing an important role in the invention of new tools. In recent years, a variety of bionic-designed anode materials with hierarchical structures have been developed, but they all share some defects: on the one hand, in most cases only the biological macro appearances were selected to emulate, while the microstructures of plants and animals were neglected; on the other hand, the bionic-designed composites are all based on amorphous carbon, which cannot satisfy the design requirements of anode materials with high rate performance, and therefore other materials with higher conductivity (e.g. graphene) are to be introduced in high-performance anode materials. Herein, this research focuses on bioinspired designing and constructing nanostructured graphene-based anode materials of high performance. By modifying the shape and chemical properties of graphene and controlling the bionic structures of the composites, a series of metal oxide/graphene composite anode materials with high capacity, high rate performance, are prepared and the mechanism is investigated.

References:

EN02.09.05
Fine-Tuning Electron Correlation in Ternary Vanadium Oxides Justin L. Andrews and Sarbajit Banerjee; Texas A&M University, United States

The use of correlated materials in applications that aim to harness electronic phase transitions or mitigate charge-localization altogether requires synthetic techniques wherein electron migration barriers can be modulated with some meaningful degree of tunability. Vanadium oxides represent an attractive model system owing to the relative narrowness of V 3d-derived bands. V₂O₅ can further intercalate metals (M⁺⁺) spanning the periodic table that trigger rearrangement of the V₂O₅₅ lattice giving rise to a structurally diverse family of mixed-valence compounds (MₓV₂O₅). The extent of electron correlation can be chemically tuned by careful selection of the intercalated metal ion (M) which introduces new electronic states, by stoichiometric control of the mixed oxidation state of the vanadium oxide framework (x), and by low-temperature topochemical modification of the vanadium oxide framework. The utility of this approach is demonstrated by its application to three materials design challenges. First, modulation of the thermally-driven metal-insulator transition in β'-CuₐV₂O₅ is achieved through precise control of Cu stoichiometry. Diffusion of copper between two distinct crystallographic sites is shown to modulate the thermal energy threshold for the melting of a self-trapped polaronic state on the vanadium-oxygen lattice as observed in the broadening of hybridized Cu 3d/O 2p states near the upper edge of the valence band. Notably, precise control is a critical requisite for designing materials for brain-inspired computing applications. In a second example, the copper atoms are topochemically leached from the β/β'-CuₓV₂O₅ compound to stabilize a metastable ζ-V₂O₅ phase with a unique quasi-1D structure. The broader dispersion of d-bands stemming from the lower symmetry crystal structure mitigates self-trapping of polarons relative to the thermodynamically-stable a-V₂O₅ phase, thereby increasing its Mg-ion storage capacity (from 50 to 92 mAhg⁻¹). Finally, the empty ζ-V₂O₅ phase is topochemically intercalated with Sn²⁺ to form a metastable β-SnₓV₂O₅ phase. As a result, hybridized Sn 5s/V 3d/O 2p states are introduced at energetic positions close near the valence band of photoabsorbing quantum dots. By tuning this overlap in β-SnₓV₂O₅/CdX heterostructures, we have achieved sub-picosecond hole transfer from quantum dot to vanadium oxide and demonstrated highly efficient hydrogen evolution.
EN02.09.06
Development of Thick LiCoO₂ Electrodes for High Energy Density Li Solid-State Thin-Film Batteries—A Raman Study Christophe Secouard, Arnaud Bazin, Séverine Poncet, Sami Oukasi and Hélène Porthault; Univ. Grenoble Alpes, France

The emerging market of autonomous microsystems such as Internet of Things and (implantable) medical devices has drawn attention to the need for new energy storage devices. Key features for such power sources are integration in the component architecture, footprint, and performance. Amongst several technical solutions, thin film solid-state lithium batteries (TFBs) appear to be a promising candidate to fulfill these requirements.

We present here the recent advances in our group regarding the development of excellent performance, highly-integrable TFBs. The fabrication process flow was carried out in a clean room environment using the TINY platform. The LiCoO₂/LiPON based TFBs are deposited on 8” silicon wafers in a pilot-line scale environment and subsequently patterned using specifically developed, microelectronics-compatible, photolithography processes. Using micromanufacturing techniques, the 0.75 mm substrate is thinned down to 50 µm and the dies are then laser-diced. The 5.3 mm² TFBs demonstrated discharge capacity above 600 µAh/cm² under C/5 galvanostatic cycling condition in the 4.2-3.0 V potential range. The average capacity loss over 30 cycles is around 0.1 %/cycle at 1 C current density in the stabilized regime.

Despite these state-of-the-art performances, when comparing the same electrode in liquid cell configuration, we notice capacity losses for the TFB and irreversible losses between first charge and first discharge, whichever the configuration. In the present work we use the TFB as an electrode-oriented system model to investigate on the possible phenomena which could account for these losses. We propose to examine the LiCoO₂ electrode and its interface with the electrolyte in various configurations and state-of-charge by means of 2D, cross-sectional Raman spectroscopy mappings. In the TFB configuration, the LiCoO₂ layer is well and homogeneously crystallized at open-circuit voltage (out of fabrication). The Raman mapping image after the first charge (4.2V) indicates that the Li extraction is uniform throughout the whole cathode thickness and no specific interfacial phenomenon is evidenced. Performing the same measurement after the first charge and first discharge reveals a fairly uncomplete restitiation with poor crystalline quality in the partially restitiated areas, which could account for the first-cycle irreversibility.

EN02.09.07
Flexible Pseudocapacitor with Higher Lifetime and Power Density, Based on Vanadium Nitride Nanoflower Himadri Raha, Debabrata Pradhan and Prasanta Guha; Indian Institute of Technology Kharagpur, India

With the recent trend of rampant development of modern portable electronic devices, their power requirement is changing rapidly, and so it is indispensable to redefine their energy storage systems from all the aspects of science and technology. The new age energy storage devices should store an ample amount of electronic charge even with fast charge transfer rate. The device should have a long lifetime and safe to use. Battery-capacitor hybrid system somehow solves the primary objective, i.e. energy and power density. However, it can not be a perfect choice because of the probable energy loss at the bridging circuit. Also, safety, flexibility and lifetime issues associated with conventional batteries make the hybrid system inferior compared to its electrochemical counterpart; i.e. supercapacitor, which could be a better choice. EDLCs are the fastest and long lasting supercapacitor, but they have poor energy density as compared to pseudocapacitor.

The redox reaction dominated pseudocapacitors suffer from poor lifetime, charge transfer rate and self-discharge through the high ESR. To improve energy density, and lifetime, we prepare flower like V₂N dominated V₂N@V₂C nanocomposite, to be used as a pseudocapacitative electrode material with extremely low ESR. The CV nature of this material confirms that the charge storing is not dominated by redox reaction and the trends of low ESR (about 6 Ω) and higher coloumbic efficiency also supports the finding. Three electrode measurement shows 31.38 mFcm⁻² specific capacitance at 1 mAcem⁻² current density. The less redox dependency and lower ESR improves its capacitance retention rate and coloumbic efficiency by 98% and 95.86% even after 3 thousand charge-discharge cycles. Although the use of lithium based electrolyte may improve energy density but the use of KOH as the electrolyte, makes the device highly safe as compared to lithium based energy storage device. A flexible supercapacitor prototype was fabricated using PVA-KOH gel electrolyte, and that too is performing well in terms of stability, ESR and coloumbic efficiency.

EN02.09.08
All-Solid-State Dendrite-Free Na Metal Battery Enabled by an Ultrathin Interfacial Layer Edward Matios, Huan Wang and Weiyang Li; Dartmouth College, United States
The commercialization of Na metal anode is largely hindered by several long-lasting challenges, namely metallic Na dendrite growth and unstable SEI formation. Meanwhile, these challenges can be effectively resolved by employing non-flammable solid Na conductor as an electrolyte. Solid electrolytes not only can eliminate severe safety concerns, they can also enhance electrochemical stability and prolong cycling life. However, solid ceramic electrolyte NASICON is subjected to high electrolyte/electrode interfacial resistance, leading to poor interface conductivity that results in non-uniform Na ion flux. The pairing of pristine NASICON with high-capacity metallic Na anode gives rise to large NASICON/Na interfacial resistance and poor interface conductivity that result in non-uniform Na ion flux across the interface. Specifically, Na tends to plate preferentially along the grain boundaries of NASICON where the Na ion flux is locally intensified, leading to detrimental dendrite-like nucleation on Na anode over repeated charge/discharge cycles. Theoretically, a homogeneous and stable interlayer with superior Na anode compatibility and ion conductivity can facilitate uniform Na ion flux across the interface, therefore effectively decrease the interfacial resistance and suppress unregulated dendrite-like Na formation during cycling.

In this work, we proposed the direct coating of an ultrathin graphene layer on NASICON by CVD. The Raman spectrum surface-modified NASICON reveals the three characteristic graphene peaks of D band, G band and a relatively weak and broad 2D band. The thickness of graphene-like layer coating on NASICON was estimated by both XPS depth profiling and TEM to be around 4 nm. This interlayer acts as a uniform and conductive network for Na ion transport. As a result, the surface-modified NASICON significantly decreased the interfacial resistance by more than 10-fold (524 Ω cm² to 46 Ω cm²), improved Na plating/stripping stability (at 1 mA/cm² current density with a 1 mAh/cm² capacity) with much smaller voltage overpotential and enabled uniform Na plating with minimized uncontrolled dendrite formation after 1000 cycles. This Na metal cycling with surface-modified NASICON is, to the best of our knowledge, the best performing all-solid-state Na symmetric cells reported. Moreover, SEM images revealed Na electrodes cycled with surface-modified NASICON remained smooth on the surface, while Na electrodes cycled with pristine NASICON exhibited dendrite morphology.

To evaluate the electrochemical performance of surface-modified NASICON as a solid ceramic electrolyte, solid-state batteries were assembled with Na3V2(PO4)3 (NVP) as cathode and bare metallic Na as anode. At 1C current density, NVP/Na battery delivered a high reversible initial capacity of 108 mAh/g with 85% capacity retention (~92 mAh/g) after 300 cycles at nearly 100% Coulombic efficiency. In contrast, the control experiment of NVP/Na with pristine NASICON showcased inferior performance with rapid capacity decay and very unstable voltage profiles.

Subsequently, this surface-modified NASICON was incorporated into an optimized PEO based solid polymer electrolyte, and the synergetic effects of the modified ceramic and optimized polymer electrolytes lead to great improvement in both interfacial wettability and ionic conductivity, leading to great reduction in Na cycling overpotential, facilitating uniform Na plating, and enabling superior Na-S and Na/NVP batteries. Overall, these works can provide valuable insights for all-solid-state dendrite-free battery development.


EN02.09.09

Tuning the Structural Properties of MnOx in MnOx/reduced Graphene Oxide Composites for High-Performance Electrochemical Capacitors Seogi Byun, Jungjoon Yoo and Hyunuk Kim; Korea Institute of Energy Research, Korea (the Republic of)

To overcome the low electrical conductivity, manganese oxide (MnOx) is coupled with reduced graphene oxide (rGO), and it can be significantly overcome through the hybridization. Moreover, the oxidation state and structural properties of MnOx are precisely adjusted to further enhance the electrochemical performance for practical electrochemical energy storages. In this work, MnOx/rGO hybrid films possess different crystallinity and oxidation states compared with bare Mn oxides and they are produced by a simple strategy with combining a solution based synthesis and post-thermal annealing process. The oxidation state and crystallinity (degree of hydrous states) of MnOx in the composite film is easily controlled by tuning annealing conditions such as temperature and atmosphere.
The resulting MnOx/rGO film not only has a high mechanical flexibility, but also the hybrid film based electrochemical capacitors shows remarkably enhanced electrochemical performances such as high specific capacitances and prolonged cycle-life after 10k cycles. Our work indicates that well-adjusted material properties of MnOx (crystallinity and oxidation states) are highly correlated with its energy storage ability. From the hybridization with rGO, our optimized MnOx/rGO hybrid film is potentially utilized as a promising electrode material for high performance flexible energy storage devices, and our proposed strategy can give a new insight for the fabrication of other transition-metal oxides/rGO based composites for flexible and wearable energy storage applications.

EN02.09.10
Enhanced Performance of Phosphate-Based Polyanionic Cathodes Using Water-in-(Bi)Salt Aqueous Electrolyte for Secondary Batteries—Two Case Studies Lalit Sharma1, Kosuke Nakamoto2, Shigeto Okada2 and Prabeer Barpanda1; 1Indian Institute of Science Bangalore, India; 2Kyushu University, Japan

Use of flammable organic electrolytes in secondary batteries possesses a safety threat and also it add to the cost of the battery in terms of battery fabrication. This force us to revisit the possible application of aqueous electrolytes where not only the toxicity is reduced but rate kinetics are also enhanced as there is a two-fold increase in the ionic conductivity. However, the limited working voltage window range to avoid water splitting makes it difficult to test all electrode materials in aqueous media especially high voltage materials. Hence, it is important to look for efficient and stable electrode materials compatible with aqueous electrolytes. Herein, we present two such case studies using earth-abundant Fe-based compounds. In the first case, performance of Na2FePO4F in aqueous electrolytes is demonstrated. The half-cell delivered a discharge capacity of 85 mAh g⁻¹ at 1 mA cm⁻² current density using a three electrode setup with excellent rate kinetics. A full cell assembled using NaTi2(PO4)3 anode delivered a reversible capacity of 85 mAh g⁻¹ at a voltage of 0.8 V battery (Sharma et al, ChemElectroChem, 2018, 6, 444-449). The second work is based on LiFePO4OH anode for aqueous lithium-ion batteries. In organic electrolytes, it delivered a stable discharge capacity of 140 mAh g⁻¹ at 2.6 V vs. Li⁺/Li. However, the half-cell configuration in aqueous electrolyte delivered a discharge capacity of 153 mAh g⁻¹ with very good rate kinetics. Interestingly, it was found to be working in the anodic range for aqueous batteries (Sharma et al, J. Power Sources, 2019, 429, 17-21). A full cell assembled with LiFePO4 cathode delivered discharge capacity of 120 mAh g⁻¹ at 0.8 V. The structural characterization along with electrochemical studies will be presented for both case cases.

EN02.09.11
Rechargeable Aluminium Organic Batteries Dong-Joo Yoo and Jang Wook Choi; Seoul National University, Korea (the Republic of)

While interest in rechargeable batteries has increased due to widespread usage of all-electric vehicles and drones, the locality and cost competitiveness of lithium and transition metal sources are prompting researchers to find alternative battery chemistry that can replace conventional lithium ion batteries (LIBs). As one of the most abundant elements in the Earth’s crust, aluminium has been of interest because it is a widely used commodity material in global commerce and has one of the highest theoretical capacities (8,056 mAh cm⁻³) on account of its multiple charge storage with trivalent ions. However, despite these advantages, research on aluminium ion batteries (AIBs) has not progressed significantly due to the limited electrolytes different from conventional non-aqueous and aqueous electrolytes. In addition, it is highly challenging to design cathode materials for AIBs, because trivalent aluminium ions (Al³⁺) normally have a very low ionic conductivity in most oxide or sulfide-based materials. Herein, we demonstrate a triangular macrocycle as a potential cathode material for AIBs, in which three redox-active organic units of phenanthrenequinone (PQ) are covalently linked. The PQ unit was firstly revealed to react with AlCl₂⁺ complex ions, and the formation of layered stacks of the triangular macrocycles allowed them to alleviate the strain induced during the insertion and extraction of the complex ions, showing high stability over thousands of cycles. Also, the use of cationic complex ions of AlCl₂⁺ increased the energy density of the whole cell by utilizing less chloride from electrolytes than that of anionic complex ions of AlCl₄⁻. These results constitute significant advances in the design of rechargeable aluminium batteries and provide a good starting point for the development of affordable large-scale energy storage devices.

EN02.09.12
An Investigation of Novel Solid State Electrolytes for Sodium Batteries Based on New Organic Ionic Plastic Crystals Karolina Biernacka; Deakin University, Australia
Sodium based batteries are emerging as a viable beyond Li-ion battery technology for future energy storage. Sodium has certain advantages such as greater abundance than lithium, great intrinsic safety and potentially a relatively high energy density. Currently, much research is focussed on the electrode materials (hard carbon anodes and new cathodes) however the electrolyte component is an important enabler of the technology. Ionic liquids and organic ionic plastic crystals (OIPCs) have been shown to be good electrolyte candidates for Na batteries, enabling Na metal anodes.

Organic ionic plastic crystals (OIPCs) are a unique class of solid state electrolyte material that are increasingly drawing attention due to their negligible volatility and increased safety in contrast to electrolytes based on organic, flammable solvents that are typically used in electrochemical cells. Moreover, many OIPCs are characterized by high thermal and electrochemical stability that makes them a perfect candidate for many electrochemical device applications. Tailoring the materials properties can be achieved by pairing various anions and cations. In order to enable use of OIPCs in sodium batteries a source of Na⁺ (as a second component) needs to be added to the neat plastic crystal. Addition of “dopants” to OIPCs may also result in enhanced mobility of ions in the electrolyte material by increasing the number and size of defects.

In this work we focus on a new OIPC - hexamethylguanidinium bis(fluorosulfonyl)imide (HMG FSI) - and the effect of doping with sodium salt (NaFSI). All electrolytes and neat OIPC were evaluated in terms of thermal properties, ionic conductivities, ion diffusion and electrochemical stabilities. HMG FSI displays excellent properties such high conductivity and a wide electrochemical stability window that makes it a promising material as a starting point for new solid state electrolytes. All compositions of OIPC with NaFSI resulted in solid-state electrolytes, and a phase diagram is proposed.

**EN02.09.13**

**Ionic Liquid-Based Gel Polymer Electrolyte Containing Zwitterion Additive for Lithium-Oxygen Batteries**

Hyun-Sik Woo¹, Hyebeen Son¹, Ji-Yun Min¹, Junki Rhee², Ho-Taek Lee² and Dong-Won Kim¹; ¹Hanyang University, Korea (the Republic of); ²Hyundai Motor Company, Korea (the Republic of)

The organic liquid electrolyte for lithium-oxygen battery has been mainly used because of its high ionic conductivity and wide electrochemical stability window. Despite these great electrochemical properties, the electrolyte depletion under semi-open system operation and electrolyte decomposition by highly reactive oxygen radical have been major obstacles to successful development of lithium-oxygen battery. The use of gel polymer electrolyte can effectively encapsulate organic solvent in the cell, suppress the electrolyte decomposition by superoxide anion radicals and provide stable interfacial characteristics with lithium electrode. These unique characteristics make gel polymer electrolyte a desirable electrolyte system for enhancing the cycling performance of the lithium-oxygen batteries. In this work, poly(methyl methacrylate) (PMMA)-based gel polymer electrolyte with non-volatile ionic liquid was synthesized. A chemical cross-linking reaction has been induced in the presence of divinylbenzene as a cross-linking agent by free radical reaction to obtain the three-dimensional cross-linked polymer network. As the non-volatile electrolyte, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide was added in order to improve the ionic conductivity of the gel polymer electrolyte. In addition, a zwitterion was synthesized and added as a functional additive to increase both dissociation of lithium salt and transport properties of Li⁺ ions as well as enhance the interfacial stability toward the lithium electrode. Our results demonstrate that the cycling stability of a lithium-oxygen cell assembled with gel polymer electrolyte could be remarkably improved by employing zwitterion additive due to its beneficial effects in the gel polymer electrolyte.

**EN02.09.15**

**Controlled Prelithiation Method of Silicon Monoxide by Lithium Naphthalenide for High-Capacity Lithium-Ion Batteries**

Daisuke Ito; Murata Manufacturing Co., Ltd., Japan

Recently, Lithium-ion batteries are widely utilized for a variety of applications, such as consumer electronics and electrical vehicles. Silicon monoxide (SiOx) is one of the most promising candidates for next generation anodes because of the high capacity and excellent cyclability. One of the remained issues for SiOx is the poor first-cycle Coulombic efficiency, in the range of 50-70%. In order to improve the first-cycle Coulombic efficiency, several prelithiation methods have been reported. Here we propose a facile prelithiation method by using a catalytic reaction between SiOx and lithium metal with naphthalene in ether solutions. The reaction continues until the electrochemical potential of SiOx equals to that of lithium naphthalenide. The catalytic reaction with naphthalene offers the practical implementation of highly scalable prelithiation for active materials in lithium-ion batteries. We demonstrate electrochemical performance of the prelithiated SiOx as well as the mechanism of the prelithiation
Li-metal batteries (LMBs) with composite polymer electrolytes (CPEs) have attracted considerable attention compared with conventional Li-ion batteries. However, the uncontrolled Li deposition and the flammability of CPEs are still pressing issues. Here, a non-flammable CPE is fabricated by composing of a flame-retardant trimethyl phosphate as the solvent, a poly(vinylidene) matrix, Li$_6$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ fillers, and a LiClO$_4$ salt. The CPE exhibits unique characteristics including non-flammability, high ionic conductivity, flexibility, and good thermal stability. More importantly, a fluoroethylene carbonate (FEC) additive is used on the surface of Li metal to facilitate the formation of a LiF-rich solid electrolyte interphase layer. The FEC-coated Li|CPE|LiPFeO$_4$ battery exhibits excellent cycling stability (at room temperature) with a discharge capacity of 152 mAh g$^{-1}$ and nearly 100% Coulombic efficiency over 500 cycles at 0.2 C. The non-flammable CPE has a high rate capability of 109 mAh g$^{-1}$ at 4 C. To potentially improve the energy density of the LMB, the LiPFeO$_4$ cathode is replaced with a high-voltage material LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. The obtained Li|CPE|LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cell exhibits a discharge capacity of 109 mAh g$^{-1}$ after 100 cycles at 0.2 C. Consequently, the strategy offers guidelines for the future development of safe batteries with high energy density.

Mixed ionic-electronic conductors (MIECs), which simultaneously conduct Li ions and electrons, can play a pivotal role when employed in the electrodes of solid-state batteries to achieve high energy and power densities. Both conductive agent and solid electrolyte can be substituted with MIEC catholyte in order to overcome the limitation of the conventional composite cathode such as lithium depletion on the electrolyte surface and CO$_2$ formation during the sintering. Furthermore, it is simpler to build a continuous conduction network between MIEC catholyte and the active material than conventional composite cathode which needs uniformly distributed network of two separate pathways for electrons (carbon) and Li ions (solid electrolyte).

In this study, we proposed new MIECs having perovskite structure. For the systematic materials design, the percolation for the macroscopic lithium conduction has been analyzed, moreover, oxygen vacancy formation and lithium diffusion barrier energies have been calculated with a density functional theory (DFT) and nudged elastic band (NEB) to estimate the electronic and lithium ion conductivities. In perovskites, high oxygen vacancy concentration can lead to high electronic conductivity owing to a large amount of carriers. Specifically, we have explored Li$_x$La$_y$MO$_{1.6}$ compositions with varying 3d transition metals and Li/La/vacancy configuration. With this strategy, we could achieve high lithium ion ($8.8 \times 10^{-5}$ S/cm) and high electronic ($2.0 \times 10^{-3}$ S/cm) conductivity together in the designed MIEC perovskite.

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The search for next-generation solid-state superionic conductors has attracted significant attention. Among Na superionic conductors, Na$_{11}$Sn$_2$PS$_{12}$ has been reported to have a room temperature ionic conductivity of 1.4 mS/cm.
In this study, we employ density functional theory to study the stability of Na$_{11}$Sn$_2$PS$_{12}$ and further explore the substitution of Sn with Ge. Our results indicate that Na$_{11}$Ge$_2$PS$_{12}$ is more stable than Na$_{11}$Sn$_2$PS$_{12}$. Furthermore, substituting Sn with Ge increases the band gap, improves the room temperature ionic conductivity by a factor of 2, and lowers the activation energy of Na hopping. Statistical analysis suggests that Na$_{11}$Ge$_2$PS$_{12}$ has a faster diffusion along the $ab$-plane compared to the $c$-axis. The Na diffusion in Na$_{11}$Ge$_2$PS$_{12}$ appears to occur with two different mechanisms depending on temperature: 1) an ion hopping process at lower temperatures ($<800$ K); 2) a fluid-like distribution of Na ions at higher temperatures ($>1000$ K). The computations suggest that Na$_{11}$Ge$_2$PS$_{12}$ is a promising candidate as a solid Na electrolyte due to its high room temperature ionic conductivity and phase stability. In light of these simulation results, we expect to stimulate further experimental studies on Na$_{11}$Ge$_2$PS$_{12}$.

Orthogonal Binder and Solvent Selection for Protective Double-Layered Sulfur Electrodes in Lithium-Sulfur Batteries

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The lithium-sulfur (Li-S) battery has been considered one of the promising post-lithium-ion battery systems due to its high gravimetric energy density and environmentally benignity. However, there remain unresolved issues such as the insulating nature of active material and an irreversible loss of polysulfide anions during cycling. In this study, conceived from multi-layer spin coating process in the film technology, a novel double-layered electrode structure comprised of a bottom sulfur cathode and an upper protecting layer (PrL) was developed by using orthogonal pairs of solvent and binder. While two different pairs of the binder and solvent, PVDF-NMP and PE-chloroform, were attentively selected based on Hansen solubility parameters (HSPs) to avoid intermixing between the sulfur cathode and PrL during the electrode fabrication process. Two distinctive carbon materials, mesoporous carbon sheet (MCS) and carbon paper (CP), were adopted as respective conductive media for each layer. This rationally designed electrode showed superior electrochemical performances in cycle life and rate capability. We believe our strategy is one of the key findings to the practical application of Li-S battery.

Solution Processed NiO Nanoparticles towards High-Energy and High-Power Density Inkjet-Printed Supercapacitors

Pavlos Giannakou, Mateus Masteghin, Robert Slade, Steven J. Hinder and Maxim Shkunov; University of Surrey, United Kingdom

The push towards self-powered electronics through energy harvesting, calls for the development of high-performance supercapacitors that can enable sustained, autonomous operation of electronic devices for applications such as wearable electronics, biomedical implants and internet-of-things. Low cost supercapacitors with high energy density can potentially work as stand-alone and maintenance-free power sources when combined with energy harvesters. Therefore, great efforts have been devoted to extend the energy density of these storage systems by using pseudocapacitive transition-metal oxides, which store energy by fast surface redox reactions, enhancing the storage ability of the system, while keeping the energy/cost ratio low. The limited electronic conductivity of most pseudocapacitive oxides leads to high electrode resistance and, consequently, lower power densities. As a result, pseudocapacitive devices with high energy density and high-rate handling ability remain a major challenge. Considering the pressing need for high-power and high-energy density storage devices through low-cost fabrication strategies, our work focuses on the fabrication and integration of high performance, fully solution processed, co-planar NiO micro-supercapacitors through inkjet printing. In this study, the phenomenon of electrical conductivity enhancement of NiO when the material is processed at the nanoscale, was exploited through a developed nanoparticle-based, inkjet-printable ink that was used to produce highly porous NiO electrodes that demonstrated up to 14 orders of magnitude higher electrical conductivity compared to single crystal NiO. The enhanced conductivity of the electrodes was reflected in the ultra-high charge/discharge rate handling ability of up to 50,000 mV s$^{-1}$ and the low relaxation time constant of just 30 ms of the devices, which is among the lowest achieved for any supercapacitors. A surfactant-based saturated magnesium perchlorate aqueous gel electrolyte with extended operating voltage window was developed to enable the operation of the devices up to 1.5 V. The devices showed remarkable areal and volumetric specific capacitances of up to 155 mF cm$^{-2}$ and 705 F cm$^{-3}$ at 5 mV s$^{-1}$ respectively, surpassing the best micro-supercapacitors known. The superior energy and power density of the devices bridges the gap between lithium-ion batteries and electrolytic capacitors, opening new exciting opportunities in the field of electrochemical energy storage and harvesting.
Effective Electrochemical Charge Storage in the High-Lithium Compound Li₈ZrO₆ Andreas Stein¹, Nam Tran¹, Brian Spindler¹, William Smyrl¹, Donald Truhlar¹ and Shuping Huang²,¹; ¹Univ of Minnesota, United States; ²Fuzhou University, China

Li₈ZrO₆, because of its high lithium content, has been considered as a CO₂ absorber, a blanket material for fusion reactors, and as a solid electrolyte for high temperature applications. In this presentation we examine the synthesis, structure, and electrochemical properties of Li₈ZrO₆/carbon nanocomposites as potential cathode materials for lithium-ion batteries with high specific capacity. These nanocomposites were synthesized by the reaction between zirconyl chloride and lithium benzoate as the source of both lithium and conductive carbon. Li₈ZrO₆ is a pseudolamellar compound with high lithium content and containing zirconium as a relatively abundant, low cost transition metal. Although Li₈ZrO₆ is intrinsically a poor conductor its intimate contact with in-situ produced carbon and its small grain size enabled by mechanical delamination allow for reversible electrochemical delithiation. Quantum mechanical calculations suggest that removal of 2 Li/formula unit is topotactic with only 1–2% volume change, but removal of more Li involves a distortion with possible loss of oxygen, although this may be kinetically prevented. In fact, coin half-cells containing Li₈ZrO₆/C as the cathode and Li-metal as the anode exhibited a capacity of 221 mAh/g (which corresponds to extracting 2 Li per formula unit) over at least 140 cycles. By applying a higher capacity limit, a discharge capacity of 331 mAh/g (which corresponds to extracting 3 Li per formula unit) was maintained over 15–20 cycles. Ex-situ and operando X-ray diffraction (XRD) studies of galvanostatically cycled cells showed that at these levels of charge, delithiation follows a reversible path with only small distortions around Zr atoms. During this process, crystalline grain sizes decrease continuously, shortening diffusion lengths within grains but increasing the number of grain boundaries and electrode/electrolyte interfaces. Given that Zr is already in its highest oxidation state in Li₈ZrO₆, charge storage appears to involve partial oxidation of oxygen atoms and production of small-polaron holes, as supported by XRD, X-ray photoelectron spectroscopy, and pair-distribution function studies and predicted by quantum mechanical calculations. At higher depths of charge, delithiation results in amorphization of the active electrode material. The charge storage mechanism in Li₈ZrO₆ is unusual among lithium-ion battery electrode materials and involves a combination of mechanisms that resemble intercalation and conversion reactions, as well as some capacitive storage at higher charge rates. With further refinement, Li₈ZrO₆/C based materials open up opportunities to develop new cathode materials for lithium-ion batteries that may improve on currently existing capacity barriers.

Quasi-Solid State Sodium-Ion Capacitor Based on Ionogel Separator Chunxian Xing and Haitao Zhang; Chinese Academy of Sciences, China

Development of sodium-ion based energy storage devices is becoming more popular on account that the excessive consumption of lithium resources, which will be expected more in the electrical vehicle and grid scale energy storage fields. However, the design and construction of safer sodium ion based devices are still hindered owing to lack of high performance electrodes materials and high ionic conductive solid state separators.

Here, we will report a new type of quasi-solid sodium ion capacitor with high safety and enhanced high-energy density by using flake-shaped MoS₂ nanohybrids and sodium-ion ionogel electrolyte. The optimized quasi-solid state sodium ion capacitor could deliver a high energy density up to 115 W h kg⁻¹ at 70 °C, and excellent durability up to 8000 cycles. The relationship between microstructure and performances was systemically evaluated. Energy storage mechanisms were also exploited by using electrochemical analysis and molecular simulation methods in order to disclose the temperature effects. Our study suggests that high performance capacitors with enhanced energy density and cyclability can be achieved by carefully programmed nanoarchitectures and optimized ionic liquid gel separators.

Reversible Cationic and Anionic Redox in Antifluorite-type Li₆CoO₄ Cathode Materials Hiroaki Kobayashi¹, Takashi Tsukasaki², Yoshiyuki Ogasawara², Mitsuhiro Hibino², Tetsuichi Kudo², Noritaka Mizuno², Itaru Honma¹ and Kazuya Yamaguchi²; ¹Tohoku University, Japan; ²The University of Tokyo, Japan

With the increase in the usage demands of lithium-ion batteries (LIBs) as power sources, it is imperative to further
improve the LIB performance. In particular, cathode materials in LIBs must exhibit a high energy density, long lifetime, and safety. For enhancement of energy densities in LIBs, use of reactions not involving redox of heavy transition metal ions is effective. Recently, using redox reactions of oxide ions in cathode materials has attracted much attention. In cathode materials referred to so-called Li-rich oxides, such as layered-rock-salt which a part of transition metal is substituted by lithium and cation-disordered-rock-salt which transition metal and lithium are located randomly in the same cation sites, an additional high capacity has been reported via the utilization of charge compensation by oxygen in addition to the transition-metal redox.

Antifluorite-type Li$_5$FeO$_4$, Li$_6$CoO$_4$, and Li$_6$MnO$_4$ have potentials as high-capacity cathode materials due to the rich lithium content which can be intercalated/deintercalated. Cathode performances of these materials were first reported in 1999 (S. Narukawa et al., Solid State Ionics 1999, 122, 59.), and very recently observation of oxygen redox in Li$_5$FeO$_4$ was confirmed (C. Zhan et al., Nat. Energy 2017, 2, 963.). However, the amount of reversible capacity with antifluorite-type materials were attributable to only redox of transition metals (Fe$^{3+}$/Fe$^{4+}$ in Li$_5$FeO$_4$ with 173 mAh g$^{-1}$ or Co$^{2+}$/Co$^{4+}$ in Li$_6$CoO$_4$ with 326 mAh g$^{-1}$).

Here we demonstrate reversible oxygen redox in antifluorite-type materials using mechanochemically treated Li$_6$CoO$_4$. After ball-mill treatment, tetragonal Li$_6$CoO$_4$ changed to cubic antifluorite phase. Since no decomposition of Li$_6$CoO$_4$ into CoO and Li$_2$O was observed, the cubic phase was attributed to cation-disordered Li$_6$CoO$_4$. This material exhibited charging capacity of 489 mAh g$^{-1}$ without O$_2$ gas evolution reaction and reversible capacity of 400 mAh g$^{-1}$, indicating more than 2 electrons were transferred reversibly. Co K-edge and O K-edge XANES spectra revealed that both redox of Co$^{3+}$/Co$^{4+}$ and O$^{2-}$/O$^{2+}$ proceeded during charge/discharge. According to XRD patterns, reversible transformation between cubic antifluorite phase and cubic rock-salt phase was observed. Since pristine Li$_6$CoO$_4$ was tetragonal, reversible reaction between tetragonal antifluorite and cubic rock-salt hardly proceed. The large reversible capacity with mechanochemically treated Li$_6$CoO$_4$ was probably derived from both downsizing effect of particles and transformation from tetragonal phase to cubic phase by cation-disordering.

EN02.09.24
Investigating on Lithium Plating/Stripping (P/S) Behavior for High Performance Li Metal Anode Quan Li$^{1}$, Hong y. Pan$^{1}$, Tian C. Yi$^{2}$, Bao g. Quan$^{1}$, Xue l. Wang$^{3}$, Howard Wang$^{3}$, Xi Qian Yu$^{1}$ and Hong Li$^{1}$; $^{1}$Chinese Academy of Sciences, China; $^{2}$Institute of High Energy Physics, Chinese Academy of Sciences, China; $^{3}$University of Maryland, United States

Lithium metal anodes have been considered as the ultimate choice for anode electrodes for rechargeable batteries because of the high theoretical specific capacity (3860 mAh/g), the lowest electrode potential (3.040 V versus standard hydrogen electrode) and low density (0.534 g/cm$^3$). The safety problem caused by the uncontrollable lithium dendrite and the poor cycling performance has limited the application of lithium second batteries several decades. Here the lithium plating/stripping (P/S) behavior are investigated respectively with non-aqueous electrolyte and solid-state electrolyte by combining interfacial modification and ordered three-dimensional structure methods. Lithium plating/stripping (P/S) behavior is regulated by both the interfacial conductivity and distribution of electric field induced by the structure. It was demonstrated that homogenous surface electronic conductivity and ordered three-dimensional structure could be beneficial to significantly improve lithium plating-stripping behavior and reach a high performance lithium metal anode.

EN02.09.25
Micro/nano-Structure VO$_2$/Carbon Nanofibers Interlayer as a Host of Polysulfides Immobilization and Conversion for High-Performance Lithium–Sulfur Batteries Zhihao Yu, TrungHieu Le, Tianji Gao, Ying Yang, Zheng-Hong Huang and FeiYu Kang; Tsinghua University, China

Lithium-sulfur batteries become one of the most promising batteries due to the high theoretical specific energy density. However, practical applications are currently hindered by a few obstacles, such as poor cycle performance notoriously caused by the shuttle effect of lithium polysulfides. Herein, we design a micro/nano-structure VO$_2$/carbon nanofibers composite via a hierarchical control method. And we utilize this self-supporting membrane as the interlayer in lithium-sulfur batteries. The VO$_2$ microsheets with a porous structure introduce an immobilization process of polysulfides, controlling the deposition of Li$_2$S$_3$ or Li$_2$S on the designed interlayer. An arranged relocation of sulfur species is induced during cycling, resulting in a shortened electron passage and an improved utilization of active material. The exposing VO$_2$ nanoparticles on carbon nanofibers provide a large amount of active sites for polysulfide conversion, which can effectively improve the redox kinetics. With a sulfur loading of 2.4mg cm$^{-2}$ and a sulfur content of 80% at the whole electrode level, the cell with micro/nano-structure
MoS$_2$ is a promising 2D material which could serve as anode for fabricating lithium ion batteries with high energy and power densities.\textsuperscript{1,2} Crystallinity (ordered layer structure) and defects (mainly edge and planar defects) in MoS$_2$ are shown to have significant role in deciding the electrochemical performance.\textsuperscript{3} In an effort to disentangle and understand the role of individual contributions on the electrochemical properties, we have synthesized planar and edge defect-rich MoS$_2$ (MoS$_2$-D) nanosheets and defect-suppressed ordered layers of MoS$_2$ (MoS$_2$-C) nanosheets from a wet chemically synthesized precursor. MoS$_2$-D are obtained upon annealing at 500 °C and MoS$_2$-C nanosheets are obtained upon annealing at 900 °C for 1 h. For MoS$_2$-D anodes, the crystallite size is small (∼3 nm) with an average 5 layers of S-Mo-S stack within a nanosheet. The nanosheets are mostly curled, resulting in large number of dislocations, edge and planar defect regions. MoS$_2$-C nanosheets have larger crystallite size (∼10 nm) with an average of 15 S-Mo-S layers. These crystalline nanosheets are mostly flat with less defects and the defects are mostly from the edge terminations and surface regions. Lithiation and delithiation characteristics, effective charge storage capability, rate capability and cycling stability are analyzed in the intercalation regime (1 to 3 V vs Li/Li$^+$). During initial lithiation, MoS$_2$-D nanosheets exhibit large Li intake ($x$=1.9) and show an initial lithiation capacity of 319 mAh/g ($\sim$Li$_{1.8}$MoS$_2$). The MoS$_2$-C nanosheets in contrast show smaller intake of Li ($x$=1.22) and has a capacity of 204 mAh/g ($\sim$Li$_{1.2}$MoS$_2$). The excess lithium intake is attributed to the interaction of lithium ions with planar and edge defect sites in MoS$_2$ nanosheets. The first reversible capacities are found to be 166 mAh/g ($x$=0.99) and 138 mAh/g ($x$=0.82) for MoS$_2$-D and MoS$_2$-C nanosheets, respectively, suggesting that a large fraction of initial Li intake for MoS$_2$-D nanosheets is electrochemically irreversible. At 10C current rate, the MoS$_2$-D and MoS$_2$-C nanosheets show reversible capacity of 37 mAh/g and 67 mAh/g, respectively. This indicates that the rate capability of well crystalline nanosheets is better. Interestingly, when tested for cycling stability at 10C-rate for 1000 cycles, at the end of 1000 cycles a ∼30% increase in capacity is noted for MoS$_2$-D anodes. Contrastingly, MoS$_2$-C nanosheets show capacity fading, with final capacity ∼80% of initial capacity. The decrease in capacity of MoS$_2$-C is due to the increasingly defiant Li diffusion upon continuous cycling. The gain in capacity in MoS$_2$-D nanosheets is attributed to the excess lithium retained at defects during the first lithiation. These excess lithium at defect sites shuttle around, reducing the diffusion lengths for lithium ions, thus effectively activating the electrode over repeated cycling. These results indicate that crystallinity and defects play complementary role in deciding the electrochemical properties of 2D MoS$_2$ in the intercalation regime. Thus, defect-rich nanosheets, MoS$_2$-D, exhibit large capacity at low current
rates and better cycling stability. Defect-suppressed nanosheets, MoS$_2$-C, on the other hand have better rate capability at high current rates and reasonable cycling stability.

References:

**EN02.09.28**
Efficiency and Quality Issues in the Production of Black Phosphorus by Mechanochemical Synthesis *Piercarlo Mustarelli*$^1$, Chiara Ferrara*$^1$, Pietro Galinetto*$^2$, Cristina Tealdi*$^2$, Eliana Quartarone*$^2$ and Stefano Passerini*$^3$; $^1$University of Milano-Bicocca, Italy; $^2$University of Pavia, Italy; $^3$Helmholtz Institute Ulm, Germany

Elemental phosphorous is emerging as one of the most intriguing anode materials for Li, Na, and K rechargeable batteries due to its specific capacity of 2596 mAhg$^{-1}$. (1) At the same time, the performances obtained from different tests are far from the theoretical values (~600-1000 mAhg$^{-1}$). Moreover, no clear indications about the phosphorous form most suitable for electrochemical applications is emerged until now. Elemental phosphorous exists as different allotropes, including white phosphorous, WP, red phosphorous, RP, and black phosphorous, BP. Orthorhombic BP, the most stable polymorph, presents a 2D structure, making it particularly intriguing as anode material. The preparation of ortho-BP is thus a central issue in development of anodes based on elemental P. Among the variety of complex synthesis approaches, high energy ball milling, HEBM, starting from the commercially available RP appears to be the most convenient. Even if HEBM is one of the most diffuse preparation method and several experimental procedures have been proposed, no systematic exploration of the synthesis parameters has been tackled to date.

In this work, starting from the mathematical model of energy transfer during the ball milling process, we investigate the effects on RP $\rightarrow$ BP conversion of three experimental parameters, the rotation speed, the milling time, and the weight ratio between the spheres and the milled material (BtPw ratio). The efficiency of the conversion process was verified by solid-state NMR, Raman spectroscopy, and X-ray diffraction. Whereas the first two parameters have a minor importance, the BtPw ratio plays a primary role in the RP $\rightarrow$ BP conversion. Yields approaching 100% can be obtained also with short milling times (15 min) and adequate rotation speed (e.g., 500 r.p.m.), provided that the BtPw ratio $>40:1$ is used. These results confirm the energy sustainability of the mechanochemical synthesis approach. (2)


**EN02.09.29**
$^{17}$O NMR and Electrochemical Characterization of Super-Concentrated Solutions as Electrolytes for Lithium Metal Batteries *Piercarlo Mustarelli*$^1$, Irene Ruggeri*$^2$, Andrea La Monaca*$^2$, Francesca De Giorgio*$^2$, Francesca Soavi*$^2$, Catia Arbizzani*$^2$, Vittorio Berbenni*$^3$ and Chiara Ferrara*$^4$; $^1$University of Milano-Bicocca, Italy; $^2$University of Pavia, Italy; $^3$University of Bologna, Italy; $^4$University of Pavia, Italy

The combination of electrochemical techniques with bulk and advanced spectroscopic ones is a powerful tool to investigate the processes occurring in the novel electrochemical energy storage systems based on lithium metal anode. NMR exploits the magnetic properties of atoms nuclei to find out information on the chemical environment in molecules and solids, as well as on its changes over time. The combination of $^7$Li and $^{17}$O (at natural abundance) nuclear magnetic resonance (NMR) [1] and electrochemical characterization is here proposed as an effective approach to investigate the Li$^+$ solvation structures and properties of electrolytes featuring tetraethylene glycol dimethyl ether and lithium-bis(trifluoromethane sulfonyle) imide. The NMR results, also supported by physicochemical characterizations such as thermal gravimetric analyses, differential scanning calorimetry, specific
conductivity and viscosity, provide information about the association of Li\(^+\) ions with anion and solvent molecules, so allowing a deeper knowledge on the relationships among structure and functional properties of super-concentrated solutions. The increase of the electrolyte concentration is, indeed, a multi-effective strategy to improve the performance of high energy batteries featuring Li metal anode [2, 3].


**EN02.09.30**

A Safe Quasi-Solid Electrolyte Based on a Nanoporous Ceramic Membrane for High-Energy, Lithium-Metal Batteries

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The use of lithium metal as the anode for Lithium Metal Batteries (LMB) requires having solid or quasi-solid electrolytes able to block dendrites formation during cell cycling. Here we reported on a hybrid electrolyte membrane based on nanostructured yttria-stabilized-zirconia, sintered by means of High Pressure-Field Assisted Sintering Technique (HP-FAST) in order to retain proper nano-porosity, and activated with a standard LiPF\(_6\)-EC-DMC solution. By a thorough physico-chemical and functional characterization, we demonstrated that the liquid is effectively nano-confined in the ceramic membrane, and the resulting quasi-solid electrolyte is non-flammable. A remarkable conductivity value of 0.91 mS cm\(^{-1}\) was observed at room temperature, with activation energy of 0.2 eV, and cation transference number, \(t^+ =0.55\), substantially higher than that of the pure liquid electrolyte. The hybrid electrolyte showed electrochemical stability up to 6 V vs. Li\(^+\)/Li, and excellent resistance to dendrite formation for more than 350 cycles in a Li/electrolyte/Li symmetrical cell. A full cell Li/electrolyte/LiMn\(_2\)O\(_4\) showed more than 90 mAh g\(^{-1}\) at 2C for more than 120 cycles. These very promising results indicated that nano-porous ceramic hybrid electrolytes may be conveniently used in LMB.

**EN02.09.31**

Kinetic Study of Redox Mediators for the Realization of High-Power Lithium–Oxygen Batteries

Youngmin Ko, Hyeokjun Park and Kisuk Kang; Seoul National University, Korea (the Republic of)

The use of redox mediator (RM) effectively reduces the high polarizations of lithium-oxygen batteries by mediating the electrochemical formation and decomposition of the discharge products. As the electrochemical reactions are mediated by RMs, the power capability of the system would be critically dependent on the intrinsic kinetic properties of RM in mediating the reaction. Herein, we performed comparative kinetic study for several reported oxygen evolution reaction RMs by probing RM-assisted charging process with respect to the rate of chemical decomposition of discharge product and the diffusivity of RM in the controlled lithium-oxygen cells. It is found that the overall kinetics of RMs have a positive correlation with the redox potential of RMs, and, multi-redox RMs can display distinct properties depending on its oxidation states. Among RMs investigated, DMPZ\(^{2+}\) (5,10-dihydro-5,10-dimethylphenazine) exhibit the highest reaction rate of lithium peroxide decomposition, while the mass diffusion rate is the highest for TEMPO\(^+\) (2,2,6,6-tetramethyl-1-piperidiny). Additionally, the choice of electrolyte is shown to greatly affect the rate capability of RM-assisted charge, and thus be carefully considered. This study suggests the importance of understanding the kinetics of RMs and provides guidelines for achieving an optimized RM/electrolyte combination to realize high-power lithium–oxygen batteries.

**EN02.09.32**

Perovskite Sr\(_{x}\) (Bi\(_{1-x}\)Na\(_{0.97-x}\)Li\(_{0.03}\))\(_{0.5}\)TiO\(_3\) Ceramics with Polar Nano Regions for High Power Energy Storage

Jiyue Wu and Haixue Yan; Queen Mary, University of London, United Kingdom

Dielectric capacitors are very attractive for high power energy storage. However, the low energy density of these capacitors, which is mainly limited by the dielectric materials, is still the bottleneck for their applications. In this work, lead-free single-phase perovskite Sr\(_{x}\) (Bi\(_{1-x}\)Na\(_{0.97-x}\)Li\(_{0.03}\))\(_{0.5}\)TiO\(_3\) \((x=0.30\) and \(0.38)\) bulk ceramics, prepared using solid-state reaction method, were carefully studied for the dielectric capacitor application. Polar nano regions...
(PNRs) were created in this material using co-substitution at A-site to enable relaxor behavior with low remnant polarization \( (P_{r}) \) and high maximum polarization \( (P_{\text{max}}) \). Moreover, \( P_{\text{max}} \) was further increased due to the electric field induced reversible phase transitions in nano regions. Comprehensive structural and electrical studies were performed to confirm the PNRs and reversible phase transitions. And finally, a high energy density (1.70 J/cm\(^3\)) with an excellent efficiency (87.2\%) was achieved using the contribution of field-induced rotations of PNRs and PNR-related reversible transitions in this material, making it among the best performing lead-free dielectric ceramic bulk material for high energy storage.

EN02.09.33

**Asymmetric Supercapacitors Based on 3D Graphene-Wrapped V_{2}O_{5} Nanospheres and Fe_{3}O_{4}@3D Graphene Electrodes with High Power and Energy Densities**

Nageh K. Allam; American University in Cairo, Egypt

Asymmetric supercapacitor (ASC) devices are emerging as effective high-performance energy storage systems. We report on the synthesis of novel and green electrode materials and their use to construct high-performance ASCs. The assembled ASCs are based on 3D porous graphene-wrapped V2O5 nanospheres as the positive electrode and Fe3O4@graphene as the negative electrode. The optimal ratio of the V2O5 nanospheres intercalated graphene sheets in the composite electrodes were identified. Compared to all positive electrode formulations, the V2O5@3DGr (33\%) hybrid electrode achieved the highest specific capacitance (612.5 F g\(^{-1}\)) at a current density of 1.0 A g\(^{-1}\). Based on the excellent electrochemical behavior of the fabricated electrodes, the assembled asymmetric supercapacitor devices of V2O5@3DGr//Fe3O4@3DGr exhibited a maximum energy density of 54.9 Wh kg\(^{-1}\) with a power density of 898 W kg\(^{-1}\) with an extended voltage of 1.8 V in 1.0M Na2SO4 aqueous electrolyte. Furthermore, the ASC device demonstrated excellent cycling stability with 89.6\% capacitance retention over 10,000 cycles. The outstanding electrochemical performance of the fabricated electrodes can be attributed to the synergic effect between graphene sheets and metal oxides (V2O5, Fe3O4) sandwich network structures. Interestingly, the proposed asymmetric electrode materials provide a promising strategy for integrating low-cost transition metal, green electrolyte, high energy, and power densities of supercapacitor devices and that can bridge the gap with commercial batteries.

EN02.09.34

**Improving the Cycling Performance and Reducing DCIR of NMC Cathode Materials by Dry Surface Doping**

Kitae Kim, Yang Shi, Yingjie Xing, Andrew Millonig, Bryan Kim and Derek C. Johnson; A123 Systems, United States

Lithium nickel manganese cobalt oxide (NMC) has become the most promising cathode material for next generation lithium-ion batteries due to high specific capacity and low cost. However, the fast capacity decay and DCIR growth during cycling still limit its practical application. Bulking doping approach can increase the cycling performance, while the specific capacity is sacrificed due to the electrochemically inactivity of dopants. The surface of cathode materials is exposed to the electrolyte and therefore more vulnerable to the lattice volume change and phase change, which greatly contributes to the capacity degradation. Therefore, restricting the doping to cathode surface may minimize the sacrifice in capacity while stabilizing the structures. In this work a unique dry process has been developed to achieve surface doping. This dry process eliminates the contact between the cathode materials with water or organic solvent and the possible damage of the cathode surface. In addition, this process eliminates the multi-step drying process to remove the solvent and the necessity of waste management. The dry surface doping technique significantly improves the cycling performance and reduces the DCIR increase during cycling. Meanwhile the crack formation and growth in cathode materials during cycling is suppressed. The result suggests great promise of using the cost-efficient process to improve the cycling performance and reducing DCIR of NMC cathode materials.

EN02.09.35

**Wide Temperature Range Ion Transport and Tunable Mechanical Properties of Molecular Ionic Composite Electrolytes**

Joshua Bostwick¹, Curt Zanelotti², Ciprian Iacob³,⁴, Andrew Korovich², Louis Madsen² and Ralph Colby³; ¹The Pennsylvania State University, United States; ²Virginia Tech, United States; ³National Research and Development Institute for Cryogenic and Isotopic Technologies, Romania; ⁴Institute of Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Germany
Polymer electrolytes show promise as alternatives to energy storage and electrochemical devices but have been limited due to their inverse correlation between ionic conductivity and shear modulus. Recently, we have discovered a new class of electrolyte material, termed a molecular ionic composite (MIC), through the combination of poly(2,2')-disulfonyl-4,4' benzidine terephalamide (PBDT), a rigid-rod (aspect ratio ~ 1000) sulfonated polyelectrolyte, and ionic liquids (ILs). MICs are thermally stable materials with simultaneous high conductivity and high modulus. However, the mechanisms underlying this fortuitous combination of properties remain unknown. In this study, we use rheology, dielectric spectroscopy and NMR diffusometry to measure the temperature dependences over a wide temperature range (-90°C to 200°C) of the linear viscoelastic response, ionic conductivity, dielectric constant, and ion diffusion coefficients in a series of non-crystalline MICs of varying PBDT concentration with the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm BF₄). We show that as the PBDT concentration in the MICs increases, the shear modulus increases into the MPa range while maintaining ionic conductivity within a factor of two of the neat IL. Additionally, by comparing the ionic conductivity with ionic diffusion, we show that increasing PBDT concentration in the MICs leads to more ions contributing to the conductivity.

References:

**EN02.09.36 Creation of Fine Spaces by Electrospinning and Application to Electrode Materials of Energy Devices**

Kyoichi Oshida, Nozomi Kobayashi, Kozo Ohsawa, Yoshihiro Takizawa, Tomoyuki Itaya, Masahiko Murata and Shogo Sato; Nagano College, Japan

This study aims to create controlled fine space by electrospinning, and to develop the electrode materials for high-performance energy devices.

With the popularization of mobile devices, household appliances, hybrid vehicles, electric vehicles, and the like, the use of power storage devices is expanding, and further performance improvements are required. Its performance is dependent on the capacity of the electrode. Particulate graphite has been used for the anode materials of currently widely used lithium-ion rechargeable batteries (LIBs), but the battery characteristics close to the theoretical capacity (372 mAh/g) have been realized previously. Therefore, the study of new anode materials is essential to achieve further high performance of storage devices. There is silicon (Si) with a theoretical capacity of 4200 mAh/g as an anode material to replace graphite, but there are many challenges for practical applications, such as the destruction of Si structures due to the large volume expansion rate (300-400%) upon the intercalation of Li ions. In this study, a novel electrode material was developed by compositing Si with carbon nanofibers derived from polyacrylonitrile (PAN).

The nanofibers have a large surface area because of thin nanofibers in complex entanglement with each other by electrospinning. The bulk density of nonwoven fabrics composed of nanofibers is small, and about more than 90 vol.% of them are occupied by space. We tried to absorb the expansion of Si by the space of nanofibers.

Solutions of solvents N,N-dimethylformamide (DMF) mixed with PAN, and Si particles were used for electrospinning. The ratio of PAN to Si particles is 2:1 by weight. Nanospaces are created by the binding of heteromorphic molecules in which different substances are combined at the molecular size level. The voltage from 20 to 30 kV was applied between the nozzle and the collector for electrospinning. Ultrasonic vibration was also applied to the needle tip, which is the nozzle of electrospinning, to forcibly mix the materials during spinning. The texture and structure of the nanofibers were observed and analyzed by SEM and transmission electron microscopy (TEM) combined with image processing.
In order to stabilize the nanofibers produced by electrospinning, they were heat-treated at 280°C in the air. Carbon nanofibers (CNFs) were made from them by heat-treatment at 700 to 1000°C in the nitrogen atmosphere. The prepared sample and polyimide (PI) and N-methyl-2-pyrrolidone (NMP) were kneaded, coated on a copper foil, and fired to prepare an electrode material.

Nano spaces were created in the CNFs and Si particles were able to be contained in the CNFs. Not only large Si particles but also small Si particles were found to contain CNT. In the second cycle of the charge/discharge experiment of LIB electrode made from the materials, a discharge capacity at 500mAh/g was obtained, which was 1.3 times the theoretical capacity using graphite. Although the decrease in capacity from the second cycle to the fifth cycle was small, the capacity decreased to the same level as the theoretical capacity of graphite near 15 cycles. The capacity at the first cycle charge reached 900 mAh/g, resulting in large irreversible capacity. It is considered that electrode breakage occurs, such as Si particles on the CNF surface exfoliate from the fiber due to the volume change. It may be because the energy was used to form organic film (called a solid electrolyte interface (SEI)) on the electrode surface. In order to put the LIB using the present anode material into practical use, it is necessary to suppress the irreversible capacity at the first cycle.

Mixing and electrospinning PAN with Si particles and the like to fabricate functional porous carbon materials with micropore and mesopore connected multidimensional structure leads to the development of next generation energy devices.

EN02.09.37
The Co-Rich Cathode with Controlled Surface Reactivity for Long-Term Lithium-Based Batteries Moonsu Yoon and Jaephil Cho; Ulsan national institute of science and technology, Korea (the Republic of)

The application of lithium-ion batteries (LIBs) has extended from portable devices to smart grid and energy storage system, resulting in the advancement of energy infrastructure in our society today. Yet further improvement, especially in volumetric density, is still required. Among various types of layered cathode materials (LiNi_{1-x-y}Co_{x}Mn_{y}O_{2}) for LIBs, conventional LiCoO₂ (LCO) still holds the record for practical volumetric energy density (2500 Wh L⁻¹ when charged to 4.30 V vs. Li⁺/Li) due to its high compressed electrode density (4.0-4.2 g/cc). For LCO cathode, charging above 4.3 V is a viable method to increase the energy density of LIBs. However, at the voltage limit exceeding ~4.35 V, it is plagued with a rapid capacity fading issue coupled with structural and surface deformations.

Herein, we have demonstrated surface-stabilized LiCo₀.⁹₅Ni₀.₀₅O₂ (denoted as S-LCNO) with superior cycle stability at high charge voltage of 4.45 V under practical conditions (loading density ~15 mg cm⁻², electrode density ~4.0 g cm⁻³ with both coin-type half-cell and pouch-type full-cell testing). Interestingly, the doped-Ni with oxidation state gradient (from 3+ to 2+) in S-LCNO only modestly changed the bulk chemistry, yet significantly modified the surface properties, such as decreasing surface reactivity to electrolyte decomposition in the close-to-surface region. Using spatially-resolved electron energy loss spectroscopy (EELS), we have found that the doped-Ni in Co-rich cathode, which redox potential (Ni²⁺/³⁺ and Ni³⁺/⁴⁺:e⁻ band) located above Co³⁺/⁴⁺:t²g band with respect to the O²⁻:2p band, is likely to mitigate the hole transfer to the O site at charged state, a crucial factor determining the degree of surface reactivity. Indeed, by measuring the leakage current during a floating test, we further observed that S-LCNO stably sustained a mild surface reactivity upon cycling, compared to commercial LCO. As a result, the interfacial degradations, such as surface structure transformation and side reactions from catastrophic EC dissociation, were effectively suppressed. This study would suggest the potential feasibility of facile doping strategy to enhance the surface stability with a comprehensive understanding of the kinetic origin of capacity decay in Co-rich cathode.

EN02.09.38
Designing Energy Storage Material and Layer Fabrication Procedures for the Thin- and Thick- Film Batteries Suman Pokhrel¹,², Michael Gockeln³ and Lutz Mädler¹,²; ¹University of Bremen, Germany; ²Leibniz Institute for Materials Engineering IWT, Germany; ³Fraunhofer Institute for Manufacturing Technology and Advanced Materials - IFAM, Germany

The advancement of the flexible electronic system is crucial for the development of electronic products including mobile, computers and many other related products. A major requirement to such electronics is the implementation of physically flexible high-performance energy storage system. The rechargeable thin films solid-state Li-ion batteries are key to power-drive such modern devices due to their properties such as high energy/power density
and/or high efficiency and long cycle life. Though these batteries are very attractive and promising both in terms of storage capacity and performance, the large scale production of the particle is quite expensive. A new innovative production, process optimization, and automation engineering of the large-scale battery production are important for economic viability. The current industrial Li-ion battery production route carries three major steps including (1) slurry-based electrode preparation (2) cell assembly (3) formation and aging. The recent electrode manufacturing procedure is a very complex and labor-intensive process warranting a new fabrication procedure to fulfill the market demand.

In the present work, the electrode fabrication was carried out following (1) traditional electrode manufacturing procedure with the phase pure Li$_4$Ti$_5$O$_{12}$ powder produced using high throughput screening of the precursor-solvent combinations$^1$ (2) material transfer from the collecting unit to the electrode substrate via role-to-lamination techniques (3) in-situ double flame direct deposition technique for C coating.$^2$ During the production process, the C aerosol stream from one individual flame was mixed with the stream of LTO active material to deposit either on the substrate or the collecting unit. While the in-situ direct deposition technique avoids the use of any solvent or binder for electrode preparation, the lamination technique allows studying the influence of lamination pressures on the electrochemical performance. All the powders/layers were characterized using advanced physiochemical techniques such as XRD, BET, and TEM imaging. The overall performance from role-to-role lamination technique for layer transfer showed enhanced specific discharge capacities compared to reference electrodes prepared using traditional electrode manufacturing procedure. The discharge capacity of 146.5mAh/g for 450 cycles at 1C with the charge retention of 85%, reveal high rate and efficient charge reversibility. This work clearly shows (1) a paradigm shift from labor-intensive electrode fabrication process to directly aerosol deposition (2) possibility of electrode deposition on a flexible/nonflexible polyimide substrate. To test this hypothesis, Li$_4$Ti$_5$O$_{12}$ electrodes were covered with a solid electrolyte and tested against lithium metal electrodes. The battery performance both at flat and physically bent conditions showed feasibility and uniqueness of the electrode fabrication procedure opening a new research opportunities for manufacturing flexible miniaturized thin film batteries.$^3$

References
3. M. Gockeln, J. Glenneberg, M. Busse, S. Pokhrel, L. Mädler, R. Kun, Flame aerosol deposited Li$_4$Ti$_5$O$_{12}$ layers for flexible, thin film all-solid-state Li-ion batteries, Nano Energy, 2018, 49, 564-573

EN02.09.39
The Effect of Lithium Surface Chemistry and Topography on Solid Electrolyte Interphase Composition and Dendrite Nucleation Melissa Meyerson$^1$, Jonathan Sheavly$^1$, Andrei Dolocan$^1$, Monroe Griffin$^1$, Anish Pandit$^1$, Rodrigo Rodriguez$^1$, Ryan Stephens$^2$, David Vanden Bout$^1$, Adam Heller$^1$ and Charles B. Mullins$^1$; $^1$University of Texas at Austin, United States; $^2$Shell International Exploration and Production Inc., United States

Lithium metal is an ideal replacement for graphite anodes in lithium batteries due to its 10 fold higher capacity; however, it suffers from safety and efficiency problems that have so far prevented it from being commercialized. In particular, the tendency of Li metal to form dendritic structures presents a major safety hazard as dendrites can lead to short circuit, thermal runaway, and battery fires. However, the causes of dendrite nucleation are numerous and complex. In order to disentangle these causes we studied the factors affecting dendrite nucleation using an array of analytical techniques, allowing us to examine the surface chemistry and topography with simultaneous ultra-high spatial resolution and chemical selectivity. From this, we developed a 3D picture of the chemical make-up of the native Li surface, the corresponding topography, and the subsequent solid electrolyte interphase (SEI) with better than 200 nm resolution. We find that, contrary to the general understanding, it is the initial surface chemistry rather than the topography that is the dominant factor leading to dendrite nucleation in this system. Specifically, the untreated native Li surface contains inhomogeneously distributed organic material which promotes the formation of LiF-rich SEI in those regions after exposure to electrolyte. These localized LiF-rich regions become preferential locations for dendrite nucleation, leading to inhomogeneous Li deposition on the surface. This has significant implications for battery research as it elucidates a mechanism for inhomogeneous SEI formation, something that is widely accepted, but not well understood. It also highlights the importance of lithium surface preparation prior to cell assembly, which is implicit in much of the literature, but not directly addressed. By homogenizing the native Li
Surface, we were able to homogenize the SEI and therefore, the Li deposition, leading to smaller dendrites and longer cycle life.

**EN02.09.40**  
Phase Transformations in the WO₃-Based Anode for Lithium-Ion Batteries  
Raman Bekarevich¹, Yurii Pihosh², Kei Nishikawa¹, Yoshinori Tanaka¹, Yoshitaka Matsushita¹, Takanobu Hiroto¹, Takahisa Ohno¹ and Kazutaka Mitsuishi¹; ¹National Institute for Materials Science, Japan; ²The University of Tokyo, Japan

Rechargeable lithium-ion batteries (LIBs) became an important part of human life because of unmatchable combination of their properties. In our days graphite is one of the most widespread anode materials, but, its small reversible capacity of 372 mAh g⁻¹ significantly reduces the energy density of LIBs. [1] Thus, an alternative anode material with higher reversible capacity, safety, and low cost needs to be found. Transition metal oxides with relatively high capacity and cycle stability are potential candidates to replace conventional graphite anodes. Tungsten oxide (WO₃) with a theoretical capacity of 693 mAh g⁻¹ stands out against other transition metal oxides due to combination of low cost and very large volumetric capacity of 5274 mAh cm⁻³. [2,3] However WO₃ struggles from the large volume changes upon lithiation / delithiation leading to disintegration of the electrode and fast capacity fade at high charging rates. [4] To address this issue we used a glancing angle deposition technique [5] to create array of vertically aligned WO₃ nanorods (NRs) directly onto current collector. Such anode configuration enables directional electronic/ionic transportation, leading to high electron collection efficiency. [6] Controlled geometry of NRs also enables us to minimize effect of volumetric expansion on the mechanical stability of electrode. [1] As a result, coin cells with WO₃ nanorodes as anode exhibited stable cycle performance up to 3C rates, without disintegration of the electrode. To clarify the lithiation mechanism upon cycling we studied the phase transformations in the active material during the first two cycles. Ex-situ X-Ray diffraction analysis, scanning and transmission analytical electron microscopy in combination with the first principles calculations suggested that conversion reaction plays a very important role in the formation of solid electrolyte interphase (SEI) and further transformation of initial WO₃ material into lithium tungstate. Formation of lithium tungstate at the very first lithiation may cause a large specific capacity drop after the first cycle, previously reported [7] for WO₃-based anodes. More experimental results will be presented and discussed during the conference.

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**EN02.09.41**  
Robust Pitch on Si-Based Anode Materials for Suppressing Undesirable Volume Expansion in Advanced Lithium-Ion Batteries  
Minseong Ko¹², Yoonkook Son¹, Kwonhoo Kim¹ and Seong-Hyeon Choi³; ¹Pukyong National University, Korea (the Republic of); ²LIV ENERGY, Korea (the Republic of); ³Chosun University, Korea (the Republic of); ⁴Ulsan National Institute of Science and Technology, Korea (the Republic of)

The huge volume change of high-capacity active materials has hindered their practical application for Li-ion batteries. Although various kinds of surface coating materials were applied to address this issue so far, the suitable coating sources satisfying both low cost and high mechanical strength have not still confirmed. Here, a cheap carbonaceous material, pitch, as a qualified coating source for Si anodes is thoroughly investigated. Specifically, from in situ lithiation and indentation tests, we discovered that pitch-coated Si nanoparticles could withstand both internal and external force without any mechanical failure. Through various physicochemical analysis, we elucidated the distinctive structural properties after its carbonization can support the outstanding mechanical strength. By applying pitch coating on the Si-nanolayer-embedded graphite (SG), pitch was homogeneously distributed on the SG, and it improved the electrochemical performance. Furthermore, in both half- and full-cell tests, pitch-coated SG exhibited higher capacity retention and cycling Coulombic efficiencies than acetylene- and sucrose-coated SG by
effectively mitigating the volume change and suppressing the continuous formation for solid electrolyte interphase. For more details, pitch-coated silicon nanolayer–embedded graphite (SG) exhibits superior capacity retention (81.9%) compared to that of acetylene-coated SG (66%) over 200 cycles in a full-cell by effectively mitigating volume expansion (< 50%), even under industrial electrode density conditions (1.6 g cc\(^{-1}\)). Thus, this work presents new possibilities for the development of high capacity anodes for industrial implementation.

EN02.09.42
Controllable Electrochemical Formation of Lithium Fluoride Coatings for Fluoride-Containing Lithium-Ion Cathodes

Haining Gao, Mingfu He and Betar M. Gallant; Massachusetts Institute of Technology, United States

Fluorine modification of lithium-ion (Li-ion) battery cathodes exhibits promising advantages compared to today's materials, including improved electrode stability, higher discharge/charge voltages, and higher energy density. However, practical applications of fluorinated cathodes are still limited by their synthesis methods. These rely currently on chemical reactions with F-containing reactants (e.g., NH\(_4\)HF\(_2\) or NH\(_4\)F), or solid-state reactions via high-energy ball milling. These methods require highly toxic or corrosive chemicals or consume a significant amount of energy. Here, we demonstrate a non-toxic, energy-efficient, electrochemical method to achieve lithium fluoride (LiF) coatings on electrode materials by reduction of a fluorinated gas: sulfur hexafluoride (SF\(_6\)). By discharging the Li-SF\(_6\) cell, a uniform LiF coating can be formed on the substrate materials (oxides or carbon). The discharge potential of the cell (~2.3 V) is fully within the stability window of the electrolyte, and thus, guarantees the formation of a "clean" LiF coating without contribution from contaminants, such as electrolyte reduction products. By tuning the discharge conditions, the morphology of the LiF coating can be precisely controlled. Additionally, the LiF coating formed in this approach is conformal, nano-scale and in intimate contact with the substrate, making it suitable for applications in battery materials. To demonstrate the practical feasibility of this method, we first applied LiF coating on various transition metal monoxides (MO, M = Mn, Ni) as model substrates for studying the LiF-splitting reaction and resulting phases formed upon cycling. The LiF-coated MO exhibited high reversible capacities (~200 mAh/g) when used as Li-ion cathodes, which can be attributed to successful LiF splitting and F-incorporation. In addition to the electrochemical performance, the morphology of LiF coating, the structural change of LiF-coated MnO during the activation (first charge) process, and the redox reaction mechanism will be discussed. This work develops an electrochemical "soft" synthesis approach for fluorinated cathodes, which is more practical and controllable than most of the currently investigated methods.

EN02.09.43
Advanced Alloying Anode for Magnesium-Air Battery

Shanghai Wei, Fanglei Tong, Xize Chen and Mark Taylor; University of Auckland, New Zealand

Mg-Air batteries have been receiving much attention in the recent years. Due to their high theoretical energy density and relatively low cost, they can be used as promising electrochemical energy storage and conversion devices. The theoretical voltage of the Mg–air battery is 3.1 V and the specific energy density is 6.8 kWhkg\(^{-1}\). However, Mg-air batteries are facing a number of challenges, including high self-corrosion properties and low discharge performance. In the present research, new magnesium alloys have been designed for improving the discharging performance. Microstructure and phase composition of alloys before discharge and after battery testing have been characterised by OM, XRD, SEM, TEM and STEM techniques. The electrochemical properties of these Mg alloys have been analyzed using a three-electrode electrochemical workstation.

EN02.09.44
Vanadium Pentoxide Thin Films and Quasi-Fractal Cathodes for Lithium-Ion Batteries

Judit Lisoni\(^1,2\), Joseba Orive Gómez de Segura\(^1,2\), José Tapia\(^1,2\), Fernando Guzmán\(^4\), Eduardo Cisternas\(^1,5\), Pedro Álvarez\(^1,6\) and Samuel Hevia\(^1,6\); \(^1\)Chilean Ministry of Economy, Development and Tourism, Chile; \(^2\)Universidad Austral de Chile, Chile; \(^3\)Universidad de Chile, Chile; \(^4\)Universidad Católica del Norte, Chile; \(^5\)Universidad de la Frontera, Chile; \(^6\)Universidad Católica de Chile, Chile

Vanadium pentoxide, V\(_2\)O\(_5\), is an interesting cathode material as the extraction/intercalation of Li is feasible without the need of carbon additives. Its theoretical capacity ranges from 294 to 437 mAh/g for two and three Li-ions, respectively. Its drawbacks are well known. It is accepted that nanostructuring the material enhances the battery performance, but it has not been yet explored how the geometry of the cathode can contribute to this matter. In this work, we investigate the electrochemical performance of V\(_2\)O\(_5\) thin films (2D systems) and those with a quasi-fractal
V2O5 was obtained from the thermal oxidation of vanadium layers. The qualification of the oxidation process was done using P-doped Si(100) substrates. The vanadium films were 25-200 nm thick. The oxidation annealing were carried out in air for 1 h at 350-600 °C; the time condition assures that the metal film is fully oxidized. The thickness conversion factor between the metal and the oxide was ~1.3. The quasi-fractal patterning was fabricated via lift-off of the metal layer using cracked white-egg templates ~300 nm thick, following the methodology of B. Han et al [DOI:10.1038/ncomms6674]. In the quasi-fractal systems, the effective area covering the substrate ranged from 10% to 60%. The oxidation procedure is then transferred to stainless steel substrates that are the cathode collector in Swagelok LiB cells. This oxide procedure formation avoids chemical impurities typically found upon wet chemical synthesis, rendering the obtained V2O5 as a simple model system to understand the influence of the cathode microstructure on the battery performance.

The oxidation temperature plays an important role in the crystallinity and morphology of the V2O5 and thus the electrochemical performance. At 500 and 600 °C, we produce single phase V2O5, with an orthorhombic crystalline structure. The 2D oxide films are polycrystalline while the quasi-fractal layers are strongly (010) textured. This is in turn reflected in the topography of the grains, formed by terraces with plateaus: the oxide films consist of rounded grains of a few hundreds of nm’s in diameter while the quasi fractal pattern is formed by elongated rhomboid shapes with lengths as large as 3.5 µm. The cyclability of the films was evaluated in the potential window of 2.0-4.0 V where V2O5 could intercalate 2 mol of Li. We found that the optimum capacity is observed for 50 nm vanadium films oxidized at 500 °C, producing excellent rate capability of 180 mAh/g at 2C and 120 mAh/g at 20C. The quasi-fractal patterns are currently being evaluated.

Our Density Functional Theory modelling of the Li insertion into bulk V2O5 allowed to reproduce the unit cell parameters and obtaining the voltage profile for Li-intercalation, which shows a good agreement with potential difference measured experimentally.

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**EN02.09.45**

**Rational Design and Sustainable Synthesis of Nanofibrous 3D Architecture for High-Energy, Fast and Safe Lithium Storage**

Shijie Wang1, Rutao Wang1,2, Ye Bian1, Dongdong Jin1, Yabin Zhang1 and Li Zhang1; 1The Chinese University of Hong Kong, China; 2Shandong University, China

Lithium-ion capacitors (LICs) are regarded as the promising energy storage devices owing to their balanced energy and power characteristics compared to both batteries and supercapacitors. To effectively couple the charge storage kinetics of the battery-typed anodes and capacitive cathodes, it is essential to employ high-capacity and high-rate anode materials. Moreover, as one aspect of the sustainable synthesis, the use of heavy metal and critical elements should be avoided. Currently, the mainstream anode material—graphite—suffers from sluggish charge transfer kinetics and potential safety issues due to the unfavorably low Li⁺ intercalation potential (0.01 V vs. Li/Li⁺). To overcome these adverse effects, intercalative Li4Ti5O12 (LTO) with outstanding rate capability and higher insertion potential is used. Nevertheless, the low capacity (175 mAh g⁻¹) and excessively high (1.55 V vs. Li/Li⁺) insertion potential renders it also unsuitable for high-energy LICs. In view of such dilemma between high-energy and safety, and further inspired by the discovery of novel polyanionic material Li2TiSiO5 (LTSO) [Liu et al, Energy Environ. Sci., 2017, 1456-1464], we rationally design a conductive 3D structure consisting of uniformly distributed and aggregation-free LTSO nanoparticles into nanofibrous carbon skeleton [Wang et al, Nano Energy, 2019, 173-181]. The synthetic procedures mainly involve facile and sustainable electrospinning process, followed by a morphology-preserved thermal transformation to convert organic Li, Ti, Si salts in-situ to LTSO and polymer nanofibers to carbon. It should be noticed that such strategy adopts biocompatible polymer precursors and get rid of heavy metal and critical elements. As-fabricated LTSO/C electrodes exhibit high-capacity (241.9 mAh g⁻¹ at 0.2 A g⁻¹), higher than 217.2 mAh g⁻¹ of graphite and 158 mAh g⁻¹ of LTO), superior rate capability (50% retention from 0.1 to 10 A g⁻¹, significantly higher than graphite and similar to LTO), and suitable Li⁺ insertion potential (0.1-1 V vs. Li/Li⁺ to balance between high full-cell voltage and safety). Subsequent kinetic analysis suggests that the high-rate performance probably derives from the pseudocapacitive mechanism, which is highly related to the unique 3D nanoarchitecture based on dispersive LTSO nanoparticles and interconnected conductive carbon framework. As a device level demonstration, the LICs employing LTSO/C anodes with high working potential of 4.2 V are fabricated, which exhibit a high energy density of 105.8 Wh kg⁻¹ and high power density of 28500 W kg⁻¹, effectively bridging the gap between lithium-ion batteries and supercapacitors. We believe that this work may be an essential reference for the rational design and sustainable synthesis of the desired LIC anodes for high-energy, fast, and safe energy storage.
Acknowledgement: This work was supported by General Research Fund (GRF) from the Research Grants Council (RGC) of Hong Kong (No.: 14203715 and 14218516). Shijie Wang is currently supported by Hong Kong Ph.D. Fellowship Scheme (HKPFS).

High Cyclability Conversion-Type MoS2/Nanoporous Carbon Anode for Lithium-Ion Batteries Xiao Feng Lim, Viet Thong Le, Jong Hak Lee, Chorng Haur Sow and Barbaros Oezyilmaz; National University of Singapore, Singapore

The current lithium-ion battery technology relies on intercalation-type materials which are highly stable but are limited in storage capacity [1]. Conversion-type materials are a way to greatly increase the energy density of a lithium-ion battery [2]. Molybdenum disulfide (MoS2) is one material that can act as both an intercalation- and conversion-type (via lithium sulfide) anode by controlling the voltage window of cycling [3]. However, it is plagued by problems of pulverization due to the large volume expansion during lithiation [4], poor electrical conductivity [5], and electrolyte dissolution [6], leading to poor cyclability [7]. In this work, we first synthesize MoS2 via a solvothermal route with nanoporous carbon, for strong electrical contact and mechanical support. We further improve the contact between MoS2 and the nanoporous carbon via a thermal treatment. The electrochemical performance shows a long cycling life (800 cycles), due to the structural stability of the nanoporous carbon matrix that minimizes the pulverization and loss of active material via polysulfide shuttling. The improved electrical contact and mechanical support also allowed for high utilization of the active materials. An exceptionally high capacity is achieved due to the lithium sulfide from the conversion of MoS2 and a capacitive contribution from the nanoporous carbon. In addition, an increasing electrochemical activation during cycling results in a significant capacity increment. Detailed material characterization such as scanning electron microscopy (SEM) will also be used to elucidate the origin of the high cyclability.

References:

Understanding the Sodium Battery Testing of Pure Phase SnSb Electrodeposited From an Ethaline Solution Jeffrey Ma and Amy L. Prieto; Colorado State University, United States

Current research on improving state of the art anode technology for Lithium-ion rechargeable batteries is focused heavily on the development of silicon and graphite/silicon composite anodes. However, for beyond lithium-ion research, such as sodium-ion batteries, both silicon and graphite perform poorly. Due to this, anodes that are tin-, phosphorous-, and antimony- based are at the forefront of potential sodium-ion anodes. Of these materials, SnSb has been shown to be a promising material, with a mixture of stable cycling and high energy density.

We have developed the electrodeposition of pure phase, crystalline SnSb from an ethaline solution at room temperature. Electrodeposition is an interesting process as it allows for the study of the anode material’s intrinsic properties without the presence of carbon and binders that are typically used in the slurry-based production of anodes. We will present the sodium battery cycling studies of the electrodeposited SnSb and compare them to Sn-
rich containing SnSb electrodes described in other previously reported electrodeposition processes. The incorporation of Sn is detrimental to the lifetime of battery material, which is a main motivation for the production of pure phased SnSb. We will present and discuss a suite of electrochemical characterization data used to understand the performance of the phase pure material.

EN02.09.48
Li-S Battery: A Promising Energy Storage Technology Sarish Rehman1, Tom Tranter2, Guobin Wen1, Michael Pope1 and Jeff Gostick1; 1University of Waterloo, Canada; 2University College London, United Kingdom

Lithium Sulfur batteries (LSBs) are of great scientific and commercial interest with potentially five times the energy density of current Li-ion technologies and lower cost. However, the technology suffers problems that have so far prevented their commercialization and wide scale adoption. These include poor cycle-life, limited sulfur utilization, and severe self-discharge during rest and charge. Compounding the problem is the rather complex, multistep reaction pathway that involves reduction from elemental sulfur to form shorter chain species of polysulfides and lithium-polysulfides (LiPS), which can be soluble or insoluble in the electrolyte. So far, modeling has helped to illustrate the processes and species that can be formed inside the cell at various states of charge. However, much more effort is needed to verify these results and supply the models with better data, as many parameters are assumed or fitted. The self-discharge phenomena is the focus of the present study which aims to validate a numerical model with experimental data over long periods of cycling and rest. We shed light on the nature of the LSB’s reversible and irreversible losses and predict their evolution over time.

References

EN02.09.49
A Porous N-Doped Carbon 3D Nanoweb-Li2S Cathode Material for High-Performance Lithium-Sulfur Battery Yoongon Kim, Hyunsu Han, Jaejin Bae, Yekyu Kim, Hyunwoo Ahn and Won Bae Kim; Pohang University of Science and Technology (POSTECH), Korea (the Republic of)

Novel honeycomb-like N-doped carbon three-dimensional (3D) nanowebs (HCNs) have been synthesized through a facile aqueous solution route for use as cathode materials in lithium sulfur batteries. The Li2S@HCN cathode delivers a high discharge capacity of 815 mAh g⁻¹ after 65 cycles at 0.1 C, along with a superior rate capacity of 568 mAh g⁻¹ even at 2 C. The outstanding electrochemical rate performance is ascribed to their unique 3D honeycomb-like nanoweb structure, consisting of nanowires derived from polypyrrole. These properties greatly enhance the electrochemical reaction kinetics by providing continuous electron pathway and hollow channels for electrolyte transport. Nitrogen doping in the carbon nanowebs also considerably improves the chemisorption properties by tuning the affinity between sulfur and oxygen functional groups on the carbon framework. The simple synthesis strategy and resulting unique electrode structure provide a new aspect of nanostructure research for high performance lithium sulfur batteries.

SESSION EN02.10: Beyond Li-Ion II
Session Chair: Serena Corr
Wednesday Morning, December 4, 2019
Sheraton, 2nd Floor, Grand Ballroom

8:00 AM *EN02.10.01
The Search for Solid-State Divalent Ion Conductors Andrew J. Martinolich and Kimberly A. See; California Institute of Technology, United States

Multi-electron redox processes are attractive charge storage mechanisms for next-generation, high energy density
batteries. Multi-electron redox can be achieved via >1 electron redox per transition metal in conventional intercalation-type materials or through conversion mechanisms using divalent cations. Electrodeposition of divalent cations, for example, yield smooth metal deposits compared to Li metal deposited at the same current densities suggesting that divalent metal batteries could be a viable next-generation chemistry. Many challenges remain for divalent-based chemistries, however, including developing and understanding materials that support solid-state divalent ion conductivity. Divalent ion conductivity is an essential fundamental process employed by intercalation electrodes, solid-state electrolytes, and solid-state interfacial layers. To begin understanding the fundamental mechanisms of divalent ion conductivity, we aim to probe divalent ion conductivity in electronically insulating solid-sate host matrices. We will discuss our first attempt at this with a case-study on ZnP2S3. ZnP2S3 supports Zn2+ conductivity with unexpectedly low activation energies (~350 meV) thanks to the flexible [P2S6]4- polyanion that we suggest distorts into the van der Waals gap at the transition state.

8:30 AM EN02.10.02
Synthesis, Characterization and Investigation of Non-Arrhenius Behavior in Anti-Perovskite Ion Conductors
Fei Wang, Ping-Chun Tsai, Yiliang Li, Lisheng Gao and Yet-Ming Chiang; Massachusetts Institute of Technology, United States

Amongst known families of solid electrolytes of potential interest for solid-state batteries, the anti-perovskites (A3BX) are of interest for the high ionic conductivities observed in certain compositions, and, like perovskites, the compositional flexibility provided by the possibility for ion substitution onto multiple lattice sites. For example, variations in the relative size of ions A, B and X result in changes in the Goldschmidt tolerance factor, or extent of disorder, that are accompanied by changes in the distribution of lithium migration energies. [1]

In surveying transport in this family of ion conductors, we observed a trend wherein numerous compositions show upwards curvature on an Arrhenius plot, indicating a non-constant activation energy. This is unusual as most solids exhibiting non-Arrhenius behavior exhibit a negative deviation. We have synthesized a wide range of Li and Na antiperovskites, and have confirmed non-Arrhenius conductivity with a positive deviation in compositions such as Na3OBr0.6I0.4. This talk will discuss compositional trends related to this behavior, and our attempts to understand the structural origin(s) of this behavior through temperature-dependent X-ray and neutron scattering, calorimetry, and other methods. Implications for the design of solid electrolytes for solid state batteries will be discussed.

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8:45 AM EN02.10.03
High Performance Aqueous Zinc-Ion Batteries Mediated by Hydrated Intercalation Jaeho Shin and Jang Wook Choi; Seoul National University, Korea (the Republic of)

While a recent fervor for the commercialization of electric vehicle applications has steered the battery industry’s efforts toward high energy density batteries, another significant path for research and development lies with grid-scale energy storage systems (ESSs). ESSs are pivotal in that they can be used to stabilize the power grid through frequency regulation operations. Ideally, power supply should match demand in order to maximize efficiency. However, this is hardly the case in reality because fluctuations in both supply and demand occur due to various reasons. For example, the sporadic nature of renewable energy sources such as wind often results in oscillations in power supply, while certain times during the day demand high levels of power. This mismatch is balanced through the use of ESSs. In order to accommodate such real-time changes, however, ESSs must be highly responsive to perturbations. In other words, high charge/discharge rate capability is critical for such responsiveness, where ESSs can store extra power and discharge when needed in a short period of time. Furthermore, as ESSs are composed of multiple battery modules, a fire may have devastating consequences on its surroundings and/or human lives. Thus, batteries that target ESS applications must meet two crucial requirements: high power density and safety.

In this respect, aqueous zinc ion batteries (AZIBs) are being tapped as potential candidates for ESS applications. AZIBs are promising systems for ESSs in several ways. First, the use of aqueous electrolytes significantly lowers
the risk of fire hazards. Second, the inherently high ionic conductivity of water creates an environment amicable for high rate battery operation. Third, zinc (Zn) is known for its stability in water, rendering its metallic form employable as an anode. Finally, the bivalence of the Zn²⁺ ion opens up possibilities for high capacity. Unfortunately, the use of water as the primary electrolyte solvent ironically entails a critical disadvantage: water splitting. This consists of hydrogen/oxygen evolution reactions at their respective electrodes, the potentials of which sum up to 1.23 V as determined by thermodynamics. Evidently, it is within this narrow voltage window the AZIB must operate. Beyond these boundaries, the irreversible HER/OER steps not only deplete the electrolyte, but also may degrade the electrodes.

In this sense, recent research efforts in AZIBs have primarily focused on discovering new cathode materials suitable for aqueous applications. With Zn generally established as the anode, the cathode becomes the key performance factor. The ideal cathode for AZIBs must meet the following conditions; i) a redox potential within the voltage window, ii) good intercalation kinetics, iii) well-defined ion diffusion channels, and iv) structural stability. Having taken such conditions into account, we have discovered that a mixed-valence vanadium oxide, V₆O₁₃, exhibits promising electrochemical traits such as 93% capacity retention after 2,000 cycles and high rate capabilities of up to 24.0 A g⁻¹. These results were correlated with synchrotron in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) experiments to reveal a single phase reaction pathway and reversible redox of vanadium upon Zn (de)intercalation. Interestingly, water plays a crucial role in this process, whereby Zn intercalation is significantly enhanced by means of hydrated intercalation. This intriguing phenomenon was probed via experiments and density functional theory calculations, which highlight the importance of the desolvation energy penalty at the electrode/electrolyte interface as well as the structural implications of co-intercalated water. These results show that V₆O₁₃ is not only a promising candidate for AZIB cathodes, but the reaction mechanisms responsible for such performance could also be extended to future investigations to pave the way for AZIBs.

9:00 AM EN02.10.04
A Chemically and Electrochemically Bifunctional Mobile Catalyst for Anti-Aging Li-O₂ Batteries Jonghak Kim, Chihyun Hwang, Gwan Yeong Jung, Sang Kyu Kwak and Hyun-kon Song; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Aprotic lithium-oxygen batteries (LOBs) have much higher energy density compared to today’s lithium ion batteries. However, highly reactive superoxide, the discharge intermediate of LOBs, triggers side reactions to deteriorate LOB performances. Also, high overpotential is required to oxidize the discharge product Li₂O₂ during charge due to the non-conductive nature of Li₂O₂. Herein, we present 4-carboxy-TEMPO as a bifunctional mobile catalyst soluble in LOB electrolytes for improving LOB performances. The roles of 4-carboxy-TEMPO is two-fold: (1) the chemo-catalyst to catalyze superoxide disproportionation reaction for suppressing the superoxide-triggered side reactions; and (2) the redox mediator to oxidize the discharge product Li₂O₂ in a kinetically effective way for reducing the overpotential during charge. As expected, the use of the mobile catalyst in LOB cells resulted in the 4-fold increase in cycle life from 50 cycles to 200 cycles, significantly reducing the overpotential during charge. Also, the discharge capacity increased 4-fold.

9:15 AM EN02.10.05
A Water-Miscible Quinone Flow Battery with High Volumetric Capacity and Energy Density Shijian Jin, Yan Jing, Michael J. Aziz and Roy Gordon; Harvard University, United States

A water-miscible anthraquinone with polyethylene glycol (PEG)-based solubilizing groups is introduced as the redox-active molecule in a negative electrolyte (negolyte) for aqueous redox flow batteries, exhibiting the highest volumetric capacity among aqueous organic negolytes. We synthesized and screened a series of PEG-substituted anthraquinones (PEGAQs) and carefully studied one of its isomers, namely 1,8-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione (AQ-1,8-3E-OH), which has high electrochemical reversibility and is completely miscible in water of any pH. A negolyte containing 1.5 M AQ-1,8-3E-OH, when paired with a ferrocyanide-based positive electrolyte across an inexpensive, non-fluorinated permselective polymer membrane at pH 7, exhibits an open-circuit potential of 1.0 V, a volumetric capacity of 80.4 Ah/L, and an energy density of 25.2 Wh/L.

9:30 AM OPEN DISCUSSION
10:15 AM EN02.11.01
Ultrathin, Flexible, Solid Polymer Composite Electrolyte Enabled with Aligned Nanoporous Host for Lithium Batteries Jiayu Wan, Jin Xie and Yi Cui; Stanford University, United States

The urgent need for safer batteries is leading research to all-solid-state lithium-based cells. To achieve energy density comparable to liquid electrolyte-based cells, ultrathin and lightweight solid electrolytes with high ionic conductivity are desired. However, solid electrolytes with comparable thicknesses to commercial polymer electrolyte separators (~10 μm) used in liquid electrolytes remain challenging to make because of the increased risk of short-circuiting the battery. Here, we report on a polymer–polymer solid-state electrolyte design, demonstrated with an 8.6-μm-thick nanoporous polyimide (PI) film filled with polyethylene oxide/lithium bis(trifluoromethanesulfonyl)imide (PEO/LiTFSI) that can be used as a safe solid polymer electrolyte. The PI film is nonflammable and mechanically strong, preventing batteries from short-circuiting even after more than 1,000 h of cycling, and the vertical channels enhance the ionic conductivity (2.3 ×10^−4 S/cm at 30 °C) of the infused polymer electrolyte. All-solid-state lithium-ion batteries fabricated with PI/PEO/LiTFSI solid electrolyte show good cycling performance (200 cycles at C/2 rate) at 60 °C and withstand abuse tests such as bending, cutting and nail penetration.

10:30 AM EN02.11.02
Revealing the Discrepancy in Capacity Ratio of Graphite to Si Strategical Material Design for Rapid-Charging Lithium-Ion Batteries Kihong Ahn1, Sujong Chae2, Seungkyu Park1 and Jaephil Cho1; 1Ulsan National Institute of Science and Technology, Korea (the Republic of); 2Pacific Northwest National Laboratory, United States

As devices requiring lithium-ion batteries become more diverse and more numerous, not only the energy density but also the customer's demand for power density are increasing. With reported in several papers, the charge rate of a lithium ion battery depends heavily on anode due to the kinetic and thermodynamic reasons such as electrochemical reaction in the vicinity of the interface between the active material and the electrolyte, the low diffusivity and conductivity of lithium ions into inner active materials(Graphite,Si). However, because charging performance (charging rate capability) of Lithium ion batteries decreases drastically with increasing charging rate. In fact, Most researches focused on numerical improvements in charging rate capability, but there was given less consideration for analytic explanation of how the improvement was originated from some reason. Conceptually, in this study, We has been demonstrated that the charging rate capability is improved by designing of the anode active material (SIN@1GnB) and qualitative and quantitatively tried to elucidate how this improvement corresponds with the physicochemical and electrochemical results. As with the step above, we have endeavored to compare the capacity composition on the individual lithiated components which are Graphite and Si or SiN (each capacity contribution of Graphite parts /Si part) of the promising the Si nanolayer embedded Graphite by deconvoluting the lithiated peaks and integrating the peak area through the differential capacity analysis. As a result, at 5C C-rate, there was a remarkable reversal in the Graphite to Silicon capacity ratio which it was 6 to 4, at 5C charged whereas the ratio was 3 to 7 in case of formation C-rate (0.2C) The reversal in this ratio was originated from the drastic reduction in the capacity of the graphite, which was due to the fact that for the same reasons as overpotential(so-called staging kinetics) related to the high resistance and low electronic/ionic conductivity of lithiated Si in itself the anode capacity is more favorable to exhibited by the Stage 2,2L, 3, 4) than the Stage 1 of graphite and. We have strategically designed the SiN@1GnB (SiN nanolayer coated Graphene lumps growth on MCMB).This architecture greatly increases electron / ion migration near the surface by graphene lump ,through the SiN nanolayer, and further accelerates migration of lithium ions toward graphite by the formed Li-Si-N ternary phase. In verification of the materials design strategies by the same method as above, we have demonstrated that there was not reversal of Graphite to Si-N ratio, which was 55 to 45. A differential capacity (dQ/dV) analysis
results also showed that the exhibited capacity by stage 1 and 2 was higher than that of Si, which facilitated the capacity utilization of graphite. Furthermore, by introducing the concept of “effective thickness expansion ratio” and comparing it according to the charging rate, graphite shows a rapid irreversible expansion (~20%) which means the lithium plating at 3C while SiN@IGnB shows the (~7%) negative value of the effective thickness expansion ratio, which means that there was less susceptible to lithium plating on the harsh condition of anode.

10:45 AM EN02.11.03
Stabilizing Silicon Anodes by In Situ Formation of Ternary Phases Binghong Han1, Chen Liao2, Fulya Dogan2, Stephen E. Trask2, Saul H. Lapidus2, Jack Vaughney2 and Baris Key2; 1Exponent, United States; 2Argonne National Laboratory, United States

Replacing the traditional graphite anodes by Si electrodes can greatly improve the energy density of lithium-ion batteries. However, the large volume expansion and the formation of highly reactive Li-Si binary phases during battery operations can cause continuous lithium and electrolyte consumptions as well as the fast decay of Si anodes. In this work, by adding a second metal cation (M) into the electrolyte, we stabilize the Si anodes during the lithiation process through in situ formation of Li-M-Si ternary phases. Firstly, using solid-state nuclear magnetic resonance spectroscopy, we show that the doping of M can dramatically suppress the chemical reactions between the Li-M-Si model compound and common electrolyte solvents. Guided by this discovery, new mixed-salt electrolytes with M cations were prepared and tested with graphite-free Si electrodes, which demonstrated higher capacity, better cyclability, and higher efficiencies in both half-cell and full-cell tests. Post-electrochemistry characterizations demonstrate that adding M salts leads to the co-insertion of M cations along with Li into Si during the lithiation, which stabilized the lithiated silicon anodes by forming more stable Li-M-Si ternaries. The new electrolytes fundamentally change the traditional Li-Si binary chemistry formed during operations while minimally affecting silicon electrochemical profiles and theoretical capacities. This study provides a new and simple approach to stabilize silicon anodes, which can enable the commercial application of Si as the next-generation anodes in lithium-ion batteries.

11:00 AM EN02.11.04
3D Tortuous Li Anode Design for High Current (30 mA/cm2) and High Capacity (30 mAh/cm2) Li Stripping/Plating Kun Fu; University of Delaware, United States

Lithium metal batteries are promising due to its high energy density and low density. But lithium dendrite caused by the lithium vertical deposition at high current density and energy density could penetrate the separator and the direct contact between lithium anode and cathode causes short circuit of cell, which impede its utilization. To address this challenge, we design a 3D Li metal anode composite with high surface energy artificial framework, which realizes the faster and uniform lithium ions transfer at high current density and a large amount of lithium deposition horizontally inside the artificial framework at high capacity without any lithium dendrite growth. The dendrite-free electrode has long cycle term of over 120 h at high current density of 30 mA/cm2 and capacity of 30 mAh/cm2. This work provides new ways to address the lithium dendrite issue and get longer lifespan at high current and energy density toward the next generation of Li metal batteries.

11:15 AM EN02.11.05
New Electrolyte for Lithium-Metal Batteries with High-Voltage NMC811 Cathode Xia Cao, Xiaodi Ren, Hongkyung Lee, Chaojiang Niu, Jun Liu, Jie Xiao, Wu Xu and Ji-Guang Zhang; Pacific Northwest National Laboratory, United States

Rechargeable lithium (Li) metal batteries (LMBs) with intercalation cathodes have been revived as promising battery chemistry in recent years due to their superior theoretical energy-densities comparing to the state-of-the-art Li-ion batteries. However, there is still significant barriers to be overcome before large scale commercialization of LMBs because of their limited cycle life and potential safety concerns. Li pulverization during cycling is one of the most critical barriers for safe operation of LMBs. Here we report a new approach to prevent Li pulverization in high-energy LMBs with a Ni-rich LiNi0.8Mn0.1Co0.1O2 (NMC811) cathode during long-term cycling by a highly stable SEI layer enabled by a novel electrolyte. A homogeneous solid electrolyte interphase layer on Li anode is generated in this electrolyte, which is rich in inorganic species and robust against cycling. It successfully minimizes Li loss and pulverization. Furthermore, this electrolyte also enabled the formation of a good cathode electrolyte interphase on the NMC811 cathode, which effectively stabilizes the NMC811 structure. Therefore, very high Li
Coulombic efficiency and great stability has been demonstrated in Li||NMC811 cells adopting this electrolyte. The details of the electrolyte together with post-mortem analysis on Li||NMC811 cells using this electrolyte will be discussed at the presentation.

SESSION EN02.12: Advances in Anodes II
Session Chairs: Miaofang Chi and Xueliang Sun
Wednesday Afternoon, December 4, 2019
Sheraton, 2nd Floor, Grand Ballroom

1:30 PM OPEN DISCUSSION

2:00 PM EN02.12.02
Exploring the Elastic Anisotropy of Lithium-Metal Using In Situ Nanoindentation James E. Darnbrough, David Armstrong and Mauro Pasta; University of Oxford, United Kingdom

Solid state batteries with Lithium metal anodes have huge potential as the next high energy-density cells. However, the development of solid state batteries has been hindered by new failure modes not seen in liquid and semi-solid electrolyte systems. A greater understanding of the physical properties of the component parts and the mechanical interaction between them during cycling is required for real battery applications. In order to investigate this we have developed a methodology to test the microstructural and mechanical properties of air sensitive battery-specific materials.

This new approach focuses on in-situ observation of plastic deformation with reference to crystallographic orientation. To demonstrate this we use the example of Li metal, which has previously been shown to have anisotropy in elastic and yield properties. Large single crystal tests and Density Functional Theory (DFT) modelling of the crystal structure have shown the anisotropy but the role of the microstructure and texture has yet to be explored for materials used in Li metal batteries.

In-situ nanoindentation and Electron Backscatter Diffraction (EBSD) allows for testing the mechanical properties of Li metal in specific crystallographic directions. The physical response to load measures elastic modulus, hardness and creep behaviour of the material. Observing the real time development of sink-in around indents is indicative of the dislocation activity caused by the highly localised stress in soft materials.

2:15 PM EN02.12.03
Strategies for the Stabilization of Metal Anodes for Li and Na Metal Batteries Yang Zhao and Xueliang A. Sun; Western University, Canada

Li-metal batteries (LMBs) and Na-metal batteries (NMBs) are considered as the promising candidates to replace the conventional Li-ion batteries (LIBs) due to their high theoretical energy density. For LMBs and NMBs, Li metal and Na metal are the ultimate choices to achieve their high energy density due to the high specific capacity, low electrochemical potential and lightweight [1]. However, as alkali metals, both Li and Na metal anodes suffer from serious challenges including 1) Li/Na dendrite formations and short circuits; 2) Low Coulombic efficiency (CE) and poor cycling performance; and 3) Infinite volume changes. This presentation mainly focuses on the design of multiple strategies for the stabilization of Li and Na metal anode for LMBs and NMBs.

Solid electrolyte interphase (SEI) layer is one of the key factors for the Li and Na deposition behaviors [2]. We developed different approaches to fabricate artificial SEI with significantly improved electrochemical performances. Firstly, we have demonstrated different ultra-thin protective layers for Li and Na metal anodes by advanced atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques, including Al₂O₃, alucone, and polyurea, et al [3]. More recently, we designed a natural SEI-inspired dual-protective layer for Li metal anode with precisely controlled thicknesses, compositions and mechanical properties [4]. Secondly, we developed the in-situ solution-based methods to fabricate the Li₃PS₄ and Na₃PS₄ as protective layers for both Li and Na metal anodes with significantly enhanced performances and reduced dendrite growth [5].

To address another challenge of volume change, 3D conductive interlayers and hosts have been designed for Li and Na metal anodes. Carbon paper (CP) and modified CP with carbon nanotubes have been used as host/interlayer with excellent electrochemical performance under high current density and high capacity [6].

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In conclusion, we developed the different approaches, including protective layers fabricated by ALD/MLD and solution methods, interlayers, and 3D skeleton design, for Li and Na metal anodes with enhanced electrochemical performances and reduced dendrite growth. Meanwhile, the ideas have been also applied to solve the practical issues for testing Li and Na metal batteries.


**2:30 PM BREAK**

**SESSION EN02.13: Electrolytes, Additives and Interfaces II**  
Session Chair: Hao Bin Wu  
Wednesday Afternoon, December 4, 2019  
Sheraton, 2nd Floor, Grand Ballroom

**3:30 PM *EN02.13.01**  
**All-Solid-State Batteries—From Interface to Electrodes**  
Xueliang A. Sun, Changhong Wang, Yang Zhao, Xiaona Li and Jianwen Liang; University of Western Ontario, Canada

The state-of-the-art rechargeable Lithium-ion batteries (LIBs) use liquid electrolytes and are the major choice for current EVs and portable electronic applications. However, these LIBs still suffer from many issues related to safety, lifespan and energy density. Accordingly, solid-state lithium batteries (SSLBs) have recently emerged as a promising alternative energy storage device due to their ability to overcome the intrinsic disadvantages of liquid-electrolyte LIBs and possess a greater volumetric energy density due to the use of solid-state electrolytes (SSEs). However, the interfacial issues between SSEs and electrodes (both cathode and anode) have a significant impact on the stability and lifetime of SSLBs [1-2]. The origin of these interfacial phenomena is the unstable contact and chemical reactions between electrodes and electrolytes to form an interlayer with extremely low electronic and/or ionic conductivities, which restricts the performance of the SSLBs. An artificial, uniform and ultrathin interfacial layer is critical to address these challenges [2]. Atomic layer deposition (ALD) and molecular layer deposition (MLD) are unique coating techniques that can realize excellent coverage and conformal deposition with precisely controllable at the nanoscale level due to its self-limiting nature, which are ideal for addressing the challenges of interface in SSLBs [2].

Our work apply ALD/MLD to rationally design novel coatings to address the interfacial challenges in SSLBs. The goal is to prevent capacity degradation of SSLBs caused by high interfacial resistance and chemical/electrochemical reactions between electrodes and electrolytes (e.g. sulfide-based). We will demonstrate to (i) stabilize the interface between cathode electrodes and electrolytes and prevent the formation of intrinsically high resistance layers, (ii) suppress elemental inter-diffusion during the operation of SSLBs, (iii) fabricate facile ionic transportation channels to facilitate ion exchange between different components of SSLBs, and (iv) buffer volume changes during cycling of SSLBs.

**References:**  
Lithium ion batteries have become the dominant form of energy storage used in consumer electronics and, recently, electric vehicles. However, high costs have prevented widespread deployment of lithium ion batteries for applications other than portable electronics, and the safety issues associated with liquid organic electrolytes remain to be addressed. In order to enable the greater utilization of electric vehicles, allow for grid scale energy storage, and meet the demands of new electronic applications, new materials for high energy density batteries must be developed. High capacity electrode materials like lithium metal have the potential to facilitate these technologies, but lithium metal electrodes are presently limited by significant side reactions, poor quality deposition, and the potential to form hazardous dendrites. Therefore, it is important to develop a clear understanding of the surface reactivity and growth behavior of the lithium metal at the interface with the electrolyte in order to enable stable long-term cycling.

The products that form as a result of electrolyte decomposition reactions at the electrode interface are known to be extremely important in determining the final cell performance. Specifically, fluorinated salts and solvent additives have been shown to enable stable cycling of Li metal anodes. This improvement is ascribed to the formation of LiF in the solid electrolyte interphase (SEI), yet the understanding of how LiF and other SEI compounds are formed and how they affect battery cycling is not complete. In this presentation, in situ spectroelectrochemical techniques including infrared spectroscopy (FTIR), differential electrochemical mass spectrometry (DEMS), and electrochemical quartz crystal microbalance (EQCM), are used to clearly identify components of the Li metal SEI. An understanding of SEI formation with respect to electrochemical potential and time will be discussed. With this understanding we provide new insights into the formation and chemical nature of SEI components that promote stable cycling of lithium metal electrodes.

Structural Properties of Nanoconfined Ionic Liquids at Metallic Interfaces for Supercapacitor Application
Antoine Laine1, Jean Comtet2, Antoine Niguès1, Lyderic Bocquet1 and Alessandro Siria1; 1ENS Paris, France; 2École Polytechnique Fédérale de Lausanne, Switzerland

Room Temperature Ionic Liquids (RTILs) are emerging materials for application in energy storage because of their wide physical stability, and large electrochemical window enabling the use of high voltage difference when used as electrolyte in capacitors. From a mechanical point of view, due to their solvent-free nature, the behaviour of RTILs strongly deviates from classical liquid description. The confinement of RTILs down to the nanoscale gives rise to exotic interfacial features resulting from the strong fluid-surface electrostatic interactions, thus highly dependent on the electronic nature of the surfaces. Then the exotic interfacial structural properties of RTILs confined with insulating surfaces have been extensively studied, but still need to be explored for metallic surfaces which are relevant for supercapacitors purposes. Furthermore, with the development of electrodes made of nanoporous materials in order to enhance the capacitance of RTILs based systems, it gets important to take into account the properties of RTILs under strong confinement.

Here, we use a tuning-fork based dynamic Surface Force Tribometer to experimentaly probe the mechanical properties of RTILs confined between extended gold surfaces. Our model sphere-plane geometry enables to probe
the mechanical properties of RTILs confined in a 'slit' for which the size is controlled with nanometric resolution. For strong confinement, 'slit' size under some tens of nanometers, the RTILs undergo a dramatic confinement induced phase transition from a liquid to a solid state. Thus the overall ionic dynamics within this solid interfacial phase may be reduced as the ionic mobility sinks from the liquid to the solid state. By further measuring the mechanical properties of the nanoconfined RTILs, the system exhibits a glassy nature and eventually a shear induced fluidization. Eventually, exploring the mechanical properties of nanoconfined RTILs may enable to provide insights into the dynamics of such solvent-free electrolytes to be used in capacitive applications.

4:30 PM EN02.13.04
The Effects of Electric Field Distribution on the Interface Stability in Solid Electrolytes Rishav Choudhury, Michael Wang and Jeff Sakamoto; University of Michigan, United States

Ceramic solid-state electrolytes could potentially enable Li metal anodes, leading to safer and more energy dense Li-ion batteries. However, it has been hypothesized that electric field amplification at electrode edges can destabilize the interface and lead to short-circuiting under extended cycling. In this study, symmetric Li/ Li6.5La3Zr1.5Ta0.5O12 (LLZO) cells were assembled with Li electrodes of varying geometries to observe the effects on Li electrodeposition. Modeling of the electric field distribution at the electrode/electrolyte interface showed that areas of high electric field were localized at sharp corners but uniformly distributed along regions of low, gradual curvature. To verify this, cells with varying electrode geometries were cycled under galvanostatic conditions until failure and spatial distribution of the degradation was analyzed using optical and electron microscopy. Critical current density was also measured to determine how electric field amplification caused by geometric effects impacts the cell performance. According to the models, isolated regions of high current density/curvature were shown to act as preferred sites for Li filament nucleation. This was experimentally confirmed by localized electrochemical impedance spectroscopy measurements. Non-uniform electric field distributions at the Li/LLZO interface could play a major role in determining cycling capabilities and failure modes of solid-state batteries. This may also have important implications for the manufacturing of Li-ion battery electrodes with geometry being a key consideration for increasing longevity.

4:45 PM EN02.13.05
Role of Solvent-Anion Charge Transfer in Oxidative Degradation of Battery Electrolytes Eric R. Fadel1,2,3, Francesco Faglioni4, Geory Samsonidze2, Nicola Molinari1,2, Boris Merinov5, William A. Goddard5, Jeffrey C. Grossman3, Jonathan Mailoa2 and Boris Kozinsky1,2; 1Harvard University, United States; 2Robert Bosch LLC, United States; 3Massachusetts Institute of Technology, United States; 4University of Modena and Reggio Emilia, Italy; 5California Institute of Technology, United States

Electrochemical stability windows of electrolytes largely determine the limitations of operating regimes of lithium-ion batteries, but the degradation mechanisms are difficult to characterize and poorly understood. Using computational quantum chemistry to investigate the oxidative decomposition that govern voltage stability of multi-component organic electrolytes, we find that electrolyte decomposition is a process involving the solvent and the salt anion and requires explicit treatment of their coupling. We find that the ionization potential of the solvent-anion system is often lower than that of the isolated solvent or the anion. This mutual weakening effect is explained by the formation of the anion-solvent charge-transfer complex, which we study for 16 anion-solvent combinations. This understanding of the oxidation mechanism allows to formulate a simple predictive model that explains experimentally observed trends in the onset voltages of degradation of electrolytes near the cathode. This model opens opportunities for rapid rational design of stable electrolytes for high-energy batteries.
Negative Redox Potential Shift in Fire-Retardant Electrolytes and Consequences for High-Energy Hybrid Batteries
Bruno Ernould, Gabriella Barozzino-Consiglio, Louis Sieuw, Jean-François Gohy and Alexandru Vlad;
Univ Catholique-Louvain, Belgium

Fire-retardant electrolyte formulations have attracted vivid attention recently given the surprising properties observed, with also the potential to solve the grand challenges of alkali-ion batteries: safety, use of metallic anodes and elevated anodic stability. Whereas these chemistries are still extensively studied and correlations are drawn to explain the enhanced electrochemical stability, one essential property - the redox potential - remains poorly characterized.

In this contribution we will report how the strong solvation (or coordination) of lithium cations by organic phosphates, the widely used flame-retardant constituents, induces a negative redox potential shift by as much as half of a volt (-0.5 V). Through a series of complementary 2- and 3-electrode measurements, with different reference electrode chemistries, we demonstrate that the redox potential shift is characteristic of mainly Li-cation (de)solvation processes whereas the redox potential shift of other, non Li-cation (de)solvation processes is negligible. Solvent coordination ratio, cation valence number as well as self-diffusion coefficients are determined via complementary NMR/DOSY methods and correlated with the electrochemical measurements. We will in particular highlight how these processes can impact the developments on high-energy hybrid battery concepts such as higher voltage dual-carbon (dual-ion) or organic batteries as well as the apparent enhancement of the anodic stability. These findings may also trigger the re-evaluation of the electrochemical stability mechanisms of the non-conventional battery electrolyte formulations towards a more realistic picture.


EN02.14.02
Electrochemical Properties of LiNi0.9Co0.1O2 Cathode Material Prepared by Co-Precipitation Using Citric Acid
Jong Dae Lee and Hyun Woo Park; Chungbuk National Univ, Korea (the Republic of)

Ni-rich materials were used as cathode materials for lithium-ion batteries in electric vehicles (EV), plug-in hybrid vehicles (PHEV) and energy storage systems (ESS) due to their high energy density and rate characteristics. Ni-rich cathode materials were prepared by co-precipitation using ammonia. However, ammonia is highly toxic and corrosive, which is considered hazardous when exposed to humans. To resolve the above problems, it is necessary to replace ammonia with an eco-friendly chelating agent. Another problem with Ni-rich materials were related to LiOH/Li2CO3 impurities formed on the surface of cathode material upon exposure to air. The LiOH/Li2CO3 impurities reacts with the LiPF6 electrolyte to form HF, which directly dissolves the transition metal ions of the cathode material, resulting in gas evolution and phase transition from layered to spinel.

In this study, spherical Ni0.9Co0.1(OH)2 precursors were prepared by co-precipitation using citric acid as a chelating agent. The cathode material was prepared by mixing precursor and LiOH H2O and sintering at 680, 700, 720 and 740 °C. The excessive Li on the surface of the synthesized material was removed by washing and the electrochemical performance was investigated. Also, in order to improve the crystallinity of the prepared cathode materials, it was recalcined at 700 °C to investigate its electrochemical characteristics. The particle size distribution, particle shape and crystal structure of the cathode materials were analyzed by SEM and XRD. The prepared precursor had spherical shape and average particle size of Dv(50)=6 µm. The electrochemical performance of the coin cell using a cathode material fabricated by co-precipitation method using citric acid as a chelating agent in LiPF6 (EC:DEC=1:1 vol%) electrolyte was evaluated by the initial charge/discharge, cycle stability, rate capability, and electrochemical impedance spectroscopy (EIS). The initial charge/discharge efficiency of LiNi0.9Co0.1O2 cathode materials prepared by recalcination was decreased, but the cycle capacity (187 mAh/g) and stability (85%) were improved and showed excellent rate capability.

EN02.14.03
Electrochemical Performance of Li2MnO3 / LiMn2O4 Composite Electrode Material for Lithium-Ion Battery
Riki Kataoka, Noboru Taguchi, Toshikatsu Kojima, Nobuhiko Takeichi and Tetsu Kiyobayashi; National Institute of Advanced Industrial Science and Technology, Japan

Li2MnO3, a layered lithium-rich manganese oxide, is one of the potential high-capacity positive electrode materials among the Li containing transition metal oxide materials but its low electrical conductivity restricts its electrochemical activity. We recently found that Li–Mn cation disordering of the Li2MnO3 resulting in the formation of a NaCl-type structure improves electrochemical activity of the Li2MnO3, i.e., a high initial discharge capacity of...
320 mA h g⁻¹. However, its cycling performance is still poor probably due to structural instability, especially, oxygen emission during charging. In this study, we found that the structural stability of NaCl-type Li₂MnO₃ was significantly improved by forming a composite with spinel-type Li₂MnO₄ by mechanical milling. The initial discharge capacity of the composite of Li₂MnO₃ and Li₂MnO₄ in molar ratio of 1:2, was 379 mA h g⁻¹ (more than 1100 Wh kg⁻¹ per active material) which is much higher than those of precursor NaCl-type Li₂MnO₃ (320 mAhg⁻¹) and spinel-type LiMn₂O₄ (298 mAhg⁻¹). This capacity corresponds to about 1.4 and 1.5 mol eq. Li ion insertion, i.e., the obtained electrochemical capacity of the sample cannot be explained by the redox reaction of Mn³⁺/⁴⁺.

The 50th discharge capacity of the composite electrode showed more than 70% of the initial one, while less than 50% for NaCl-type Li₂MnO₃ electrode.

The LiMn₂O₄ component in the composite enhanced the structural stability of NaCl-type Li₂MnO₃, resulting in a restricted oxygen emission from the Li₂MnO₃ domain during charging confirmed by ex-situ XRD analysis and GC-MS. Such a structural stability leads to a better cycling stability and effective utilization of the oxygen redox reaction compared to pure NaCl-type Li₂MnO₃ resulting in the higher reversible capacity.

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**EN02.14.04**

**Is Wurtzite-Type LiI Stable at Room Temperature?**

Yudai Omori, Reona Miyazaki and Takehiko Hihara; Nagoya Institute of Technology, Japan

It is widely known that the crystal structures of the most of alkali halides are the rock-salt type. For alkali borohydrides (MBH₄), the rock-salt structures are also stable at room temperature. Because of the high affinity between halide and BH₄⁻ ions, alkali borohydrides form the solid solution with alkali halides for the whole compositional range (for example, NaI-NaBH₄ systems [1]). However, only lithium borohydride is the exceptional; the crystal structure of LiBH₄ is wurtzite [2]. Furthermore, the solid solution of LiI-LiBH₄ is not the rock-salt type but high temperature phase (H.T. phase) of LiI (wurtzite) is stabilized at room temperature, which is clear difference from the other MBH₄-MI systems [3].

At the present stage, the solubility limit of LiBH₄-LiI systems is under controversial. The solubility limit of LiI into LiBH₄ was reported to be 33 mol% when the samples was synthesized by sintering at 543 K [3]. On the other hand, 50 mol% of LiI could dissolve in H.T. phase of LiBH₄ by mechanical milling [4]. Although, the rock salt structure is the stable phase of LiI at room temperature, it was reported that hexagonal phase of LiI was observed at the temperature below 273 K [5], which is the same structure with H.T. phase of LiBH₄. Thus, it is expected that the solubility limit highly depends on the fabrication procedure and/or temperature. The purpose of this research is investigating the solubility limit of LiI-LiBH₄ systems fabricated by low temperature milling.

All of the samples were fabricated in Ar filled glove box. LiI-LiBH₄ systems were fabricated by ball-milling at low temperature. LiBH₄ and LiI were purchased from Aldrich Co. Mechanical milling was carried out by using chrome steel pot (45ml) and 10 pieces of balls (10 mm in diameter). First, the given molar ratio of LiI and LiBH₄ were mixed in the mortar and encapsulated in the air-tight milling pot. Subsequently, the samples were kept at 213 K for one hour. Then, mechanical milling was performed at 400 rpm for 5 minutes. After milling, samples were cooled at 213 K again. Above cooling and milling cycles were repeated for 60 times, which resulted in the total milling time of 5 hours. The crystal structures of the samples were characterized by XRD measurement. The measurement was conducted at room temperature. The Li⁺ ion conductivities were measured by AC impedance method with Li electrodes. For the conductivity measurement, the powder samples were pelletized at ca. 150 MPa for 30 seconds. The thickness and diameter of the pellets were ca. 2 mm and 10 mm, respectively.

From XRD measurements, it was indicated that 2LiI·LiBH₄ (LiI : 67 mol%) is single phase of the hexagonal structure. Because LiI concentration is larger than 50 mol%, it can be said that LiBH₄ is not the host lattice but BH₄⁻ ions were introduced to the hexagonal modification of LiI. More specifically, this result indicates that wurtzite-type LiI was stabilized at room temperature. Further increase of the LiI concentration yielded to the two phase mixture of hexagonal (LiBH₄-LiI system) and rock-salt (unreacted LiI) structures. It should be noted that relative peak intensity of rock-salt LiI was reduced when LiI-LiBH₄ systems were fabricated by low temperature ball milling. Therefore, it is suggested that low temperature milling is the effective method for the stabilization of the hexagonal phase of LiI at room temperature.

References

High Reversible Energy Density in Mn-Rich Electrode Materials by Enabling Cation/Anion Redox Reaction

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Since the commercialization of Li-ion battery (LIB) in 1990s, it has been an essential energy storage technology for powering advanced portable electronics and now has been becoming a key enabler for transforming our society into sustainable energy paradigm by deploying electric vehicles and grid-scale applications for renewable energy sources. To realize this transformation, tremendous efforts have gone to develop high capacity electrode materials with low cost and high abundant raw materials. From now on, almost all Li-ion cathode materials are composed of only few transition metals such as Ni and Co, which are electroactive in layered cathode materials such as LiCoO$_2$ and Li(Ni, Mn, Co)O$_2$, causing constraints on their resources and availability. To replace Ni or Co with cheap and abundant Mn, developing Mn-rich electrode materials with high energy density will be very attractive. Recent study reports that Mn-rich electrode materials with disordered-rocksalt structure can achieve higher energy density than conventional layered materials by using Mn$^{2+}$/Mn$^{4+}$ double redox that was enabled by a fluorination process and high valent dopants. However, they still suffer from sluggish Li diffusion caused by fully cation-disordered structure and can be still lack of practical implementation.

In a departure from previous approaches, we take a strategy of enhancing reversible oxygen redox reaction for increasing energy density in Mn-rich materials by controlling of the atoms solubility. The resulting Mn-rich material can achieve the highest energy density, ~1100 Wh/kg among reported Mn-rich materials and deliver superior rate capability, up to 10C rate (3A/g). Interestingly, the superior rate capability with very high discharge capacity in the resulting material indicates that the Co-free Mn-rich material can be kinetically comparable to other only TM redox materials, contrary to previous observation in Mn-based materials. We believe that the findings in this study can unlock the potential of Mn-rich electrode materials and will provide new avenues for the design of electrode materials that have high energy density and that can be practically implemented for high performance Li-ion batteries.

First-Principles Modelling of Li$^+$, Na$^+$ and Mg$^{2+}$ Mobility in Bronzes and Other Complex Oxides

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High Li$^+$ mobility in electrode materials is required for high power Li-ion battery applications, enabling rapid charging and discharging rates. However, many conventional Li-ion electrode materials display slow ionic diffusion rates, leading to low capacity at high (dis)charging rate in bulk particles. Understanding and realising high ionic mobility in solids is also crucial for emerging sodium-ion and magnesium battery technologies, due to the larger size and high charge density of Na$^+$ and Mg$^{2+}$ respectively. For instance, mobility of Mg$^{2+}$ in many oxides is extremely poor, and achieving reversible Mg$^{2+}$ intercalation in oxide cathodes with both high capacity and high voltage at room temperature represents a major challenge in Mg battery development.

Transition metal oxides built from corner-sharing octahedra and the tetragonal/hexagonal tungsten bronze structure, but with empty interstitial sites reminiscent of ReO$_3$, have emerged as exceptional high-power Li-ion intercalation electrodes. Some materials in this family exhibit excellent capacity retention at high rates, which can be achieved in bulk particles without nanosizing. [1]

The corner-sharing framework of ReO$_3$ undergoes correlated distortions and rotations upon Li$^+$ intercalation, which stabilise the Li$^+$ ions and limit their mobility. [2] In contrast, bronzes that allow high-rate intercalation comprise some degree of edge-sharing among polyhedra in the $ab$ crystallographic plane. These provide structural rigidity, limiting framework distortions, and leading to ions occupying ‘frustrated’ intercalation sites. [1,3] Mobility of ions is enhanced when moving between frustrated sites, due to a smoothing of the potential energy surface. [4]

Here we present results of hybrid-exchange DFT calculations on a range of materials with bronze-type structures, including ReO$_3$, T-Nb$_2$O$_5$, V$_2$O$_5$, V$_6$Nb$_9$O$_{35}$, and Mo$_{2.5+y}$VO$_{12+y}$. [5] These materials display a range of structural features and connectivity including differently sized channels, $c$-axis separation, and elemental composition. We compare the behaviour of Li$^+$, Na$^+$ and Mg$^{2+}$ ions, thus exploring the effects of both varying ionic size and charge on intercalation and mobility.
Our calculations reveal that the smaller Li and Mg ions adopt frustrated coordination sites in some of the frameworks, whilst Na ions typically occupy stable sites with high coordination number due to their larger size. Low energy migration pathways exist between some sites for Li$^+$ and Mg$^{2+}$, indicating bronzes can be used to achieve high mobility for these ions. We also identify high energy regions in certain structures through which ions are unlikely to move, and thus represent bottleneck for ionic mobility under ambient temperature conditions. We can therefore begin to establish design principles for achieving high ionic mobility in bronzes for Li-ion battery materials and intercalation chemistries employing other charge-carrying ions.

Compositional Tuning of Solution-Processable Sulfide Solid Electrolytes for All-Solid-State Lithium-Ion Batteries

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The application of high-energy lithium-ion batteries (LIBs) has been expanded from mobile electronics to electric vehicles (EVs) and energy storage systems (ESSs). However, accidents of the explosion of LIBs not only for small-scale ones but also large-scale ones such as EVs happened frequently in recent years. Accordingly, the safety issue of conventional LIBs, originating from the use of organic liquid electrolytes, has emerged as a serious concern. In this regard, all-solid-state batteries (ASSBs) are one of the most promising next-generation battery systems. Especially, ASSBs employing sulfide solid electrolytes show outstanding performance, compared with those fabricated using oxide or polymer solid electrolytes. Sulfide solid electrolytes have a critical advantage of deformable property besides the high ionic conductivity, enabling intimate contacts with active materials by the simple cold pressing process. Furthermore, several sulfide solid electrolytes such as Li3PS4Cl and Li1-Li2SnS4 are reported to be fully dissolved in solvents without side reactions and to be recovered by eliminating solvents and the subsequent heat-treatment, i.e., solution-processable, which allows to directly coat solid electrolytes onto active materials or to infiltrate conventional LIB composite electrodes with solid electrolytes. Thus, the solution process of solid electrolytes could be an effective protocol to realize the scalable production of ASSBs with high energy density. Unfortunately, only a few candidates of solution-processable sulfide solid electrolytes (e.g., (LiI-)Li4SnS4, Li6PS5X (X = Cl, Br, I), (NaI-)Na3SbS4, Na4-xSn1-xSbxS4) have been reported so far. Moreover, the decrease of ionic conductivity after the solution process by approx. an order of magnitude is common.

In this presentation, compositional tuning of arylgrodite sulfide SEs via the solution process and its resulting electrochemical performances for ASSBs are presented.

Electrochemical Characteristics of Nb-Sb Compounds for Li-Ion Battery Anodes

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The accelerating development of portable electronic devices and electric vehicles increases the demand for better secondary batteries. Rechargeable Li-ion battery (LIB) is a representative secondary battery system, displaying a large energy density and high power. On the other hand, because conventional graphite anodes have a small theoretical capacity and slow rate-capability, the development of Li-alloy-based anodes is required for the realization of high-performance LIBs. Therefore, various Li-alloyable materials have been pursued for increasing the anode capacity. Among the Li-alloyable materials, many studies have focused on Sb-based systems because of its high gravimetric (Li3Sb: 660 mAh g⁻¹) and volumetric capacities (~4370 mAh cm⁻³). Although Sb-based systems have a higher energy density, they suffer from poor cycling behavior because a large volume change occurs during discharge/charge. Therefore, many studies have focused on Sb-based intermetallics and their nanostructured composites to alleviate or minimize the volume change that occurs during cycling.

In this study, to enhance the electrochemical behavior of the Sb, the intermetallic Nb5Sb4 compound was synthesized by a simple solid-state method and tested its electrochemical properties for use as LIB electrodes. The reaction mechanism of intermetallic Nb5Sb4 compound was examined during Li insertion/extraction using various ex-situ analytical tools, such as X-ray diffraction (XRD) and Nb K-edge extended X-ray absorption fine structure (EXAFS) and differential capacity (dQ/dV) plot. Additionally, the intermetallic Nb5Sb4 compound was tested as high performance Sb-based anodes for Li-ion battery.

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Enhanced Sn-Based Alloy Anodes in High Performance with Metal Carbides Matrix for LIBs

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As the development of electric vehicles and portable electronic devices accelerates, the needs for improved secondary batteries have risen considerably. A rechargeable Li-ion batteries (LIBs) are a representative energy storage system due to its high operating voltage and energy density. However, commercial graphite anodes in LIBs
show relatively good electrochemical performance, it has a low theoretical capacity and slow rate capability. Among the representative Li-alloy-materials (Si, Ge, Sn, P, and Sb), which exhibit higher theoretical capacities than commercial graphite anodes, the Sn-based anodes are considered as alternative anode materials due to higher conductivity and volumetric capacity than that of the other anode materials.

To design an easily manufactured, large energy density, highly reversible, and fast rate-capable Li-ion battery (LIB) anodes, Fe-Sn intermetallic compounds were synthesized, and their potential as anode materials for LIBs were investigated, including ex situ X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS) analyses at the Fe K-edge, along with a differential capacity plots (DCPs). Among the Fe-Sn intermetallic compounds, FeSn2 was selected on the basis of the electrochemical performances. To improve the electrochemical performance of FeSn2, it was modified using various transition metal carbides of TiC, WC, and SiC, which acted as a buffer matrix against the volume expansion during cycling. Furthermore, carbon black was used to manufacture FeSn2/TiC/C nanocomposite for stable cycling. The easily manufactured FeSn2/TiC/C nanocomposite for the Sn-based Li-ion battery anodes showed large energy density (first reversible capacity of 572 mAh g⁻¹), high reversibility (first coulombic efficiency of 74.3%), long cycling behavior (95% capacity retention after 200 cycles), and fast rate capability (approximately 458 mAh g⁻¹ at 3C rate).

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EN02.14.12
3-V Cu-Al Rechargeable Battery in Aprotic Electrolyte—A Battery with Only Metal Foils Huimin Wang¹ and Denis Y. W. Yu¹,²; ¹School of Energy and Environment, City University of Hong Kong, China; ²Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, China

To meet increasing demands for energy storage, many recent battery researches are devoted to new electrode chemistries and reaction mechanisms that promise substantial increase in energy density. Traditional positive electrode materials for lithium-ion batteries such as LiCoO₂ and LiFePO₄ rely on the redox reaction of the transition metal within the structure for charge-discharge. Though, the capacity is low because of their small charge-to-mass ratio. To break away from conventional thinking, here, we turn inexpensive Cu and Al foils, the common current collectors, into active materials as positive and negative electrodes, respectively, that undergo electrochemical reactions and charge transfer to store energy. The electrochemical reactions at the electrodes are given by

Cathode: Cu (s) ↔ Cu⁺ + e⁻
Anode: Al (s) + e⁻ + Li⁺ ↔ AlLi (s)

Here, we are successful in constructing a 3 V Cu-Al full cell the battery by coupling a Cu foil as the positive electrode with an Al foil as the negative electrode in LiTFSI-based aprotic electrolyte. During cycling, the charge transfer on the Cu electrode is achieved by stripping and deposition of Cu/Cu⁺, while that on the Al electrode is carried out by the alloying and dealloying reactions between Li and Al. TFSI⁻ anions migrate through the anion exchange membrane to balance the charge. Stable cycle performance is possible with the use of a highly concentrated electrolyte - a 3 V cell exhibits excellent cycle stability for more than 200 cycles in 6M LiTFSI DMC electrolyte.

Raman spectroscopy, electrochemical impedance spectroscopy (EIS), field emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS) were conducted on the Cu-Al cells and electrodes to further understand the reasons for the improved performance in the highly concentrated electrolyte. We found that the highly concentrated electrolyte suppresses Cu cross-over with the formation of large solvation structure, which also promotes smooth and non-dendritic Cu-metal plating, enhancing the long-term stability of the cell. XPS measurements show that an SEI derived from TFSI⁻ effectively passivates the surface of the Al electrode during initial cycling, leading to excellent capacity retention. Besides AEM, other common membranes, for example polypropylene, are also being examined as alternatives. More investigations on the interactions between the membrane and the solvation structure of electrolyte are underway.

Our findings demonstrate a novel 3 V battery that can be easily fabricated by putting two common metal foils (Cu and Al) together without any active material coating. Our Cu-Al battery can give a volumetric energy density of the range of 79-156 Wh L⁻¹, comparable to that of state-of-the-art all-vanadium redox flow batteries, and has potential to be used for future grid storage applications.
The Influence of Anode/Cathode Capacity Ratio on Cycle Life and Potential Variations of Lithium-Ion Capacitors

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Lithium-ion capacitors (LICs) incorporate the fundamental features of intercalation battery materials and double-layer capacitor materials, to bring together the desirable combination of high energy and power densities, long cycle life and materials stability. But, the presence of battery materials in anode also contribute towards LIC’s long-term capacity fade, based on its extent of utilization. This work studies the importance of anode to cathode capacity ratio, and its influence on the electrodes potential variation and capacity decay behaviors. In a LIC system based on activated carbon (AC) and hard carbon (HC), we show that increasing the HC:AC capacity ratio from 1.1 to 3, boosts the capacity retention of the LIC by 10% after 2,000 cycles at 1C rate, and by 28% after 20,000 cycles at 60C rate. During the intermittent EIS and 3-electrode galvanostatic tests at 0.25C rate, lower anode over-potential is observed for LIC with larger anode to cathode capacity ratio. Pointing towards a reduced charge transfer and Warburg diffusion resistances, based on the potential at which the anode was operating. We show that for LICs with different anode to cathode capacity ratios, the difference in cell impedances originates from the difference in anode potential or degree of lithiation, and anode inter-planar distance expansions and contractions. The 1C and 60C rates long term tests, and intermittent EIS and 3-electrode tests at 0.25C rate were all in agreement that LIC with larger HC:AC capacity ratio had a better electrochemical performance.

Copper Doped NCM622 Cathode Material with Increased Capacity

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As the most expensive and important part of Li-ion batteries (LIB) is the cathode, developing high performance cathode material is vital for large-scale application of next generation LIB. NCM cathode materials have been used commercially due to its high energy density. For example, LiNi₀.₆Mn₀.₂Co₀.₂O₂, a kind of Ni-rich NCM cathode, has higher capacity, which have emerged as an ideal cathode material for LIB. However, its capacity is not high enough to reach the theoretical capacity, so the capacity of NCM622 still needs to be improved. Element doping is an efficient way to improve the electrochemical properties of cathode materials, and several mono- and multi-valent doping cations have been used to dope NMC622. Here, Cu-doped NCM622 cathode (CuNCM) was prepared by a coprecipitation process. The cyclic voltammetry profile showed the obvious wider peak than the virgin NCM. From XRD results, the strongest peak shifted to higher angle and the lattice parameter is smaller in the refinement. The specific capacity of CuNCM is 186 mAhg⁻¹ and 180.5 mAhg⁻¹ in first cycle at 0.1C and 0.33C between 3 to 4.3 V, which is 14 mAhg⁻¹ higher and 17 mAhg⁻¹ than the virgin NCM respectively.

Novel Silane-Based Matrices for Silica-Mediated Electrolyte-Binder Coatings in All-Solid-State Hybrid Ceramic Electrolytes for Lithium-Metal Batteries

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In the context of Lithium Batteries (LB), Lithium Metal Batteries (LMBs), are considered a promising technology for meeting increased capacity and power demands, both for intermittent, renewable energy sources, and Electric Vehicles (EVs). With LMBs come particular challenges and obstacles, among which dendrite growth has been a significant concern for the LB research community. Fruits of research efforts have included exploring general strategies for preventing/stopping dendrites. This has been traditionally attempted with solid electrolytes that are either strong enough to halt dendrite advancement (high modulus materials), or prevent excessive concentration gradients (single-ion conductors).

In the latter category the highest Li⁺ conductivities are often found in inorganic materials such as ceramics, glasses or glass-ceramics. Conductivities are usually 1-2 orders of magnitude below traditional liquid electrolytes, though some systems have comparable conductivities. With the choice of a hard, inflexible electrolyte comes the challenge of impedance contributions from the electrode-electrolyte interface, as well as instability against the anode and even cathode.

A possible solution to the larger issue of ceramic electrolytes’ brittleness and fragility is to use them in a pulverized form, and combine with an appropriate binder. Binders generally are softer and able to conformally adhere to the
electrodes, solving the electrode-electrolyte interface, and grain boundary problems.

While this should be a straightforward solution, binders and ceramics tend to have dissimilar properties, such that there is lack of intimate contact, thus shifting the interfacial problem to the ceramic-binder interface. If unaddressed, ionic conduction happens preferentially in the organic binder, which almost inevitably has inferior ionic conductivity, and the ironically supposed compatibilizing component becomes the rate-limiting step. It is within this smaller context that this work takes place, seeking to develop a suitable electrolyte-binder interface.

Currently, a silica (SiO$_2$) mediated electrolyte-binder coating is being developed for a commercial, proprietary lithium ion conducting glass-ceramic (LICGTM) electrolyte, functionalized with opportune moieties. A silylated SiO$_2$ layer includes Li-solvating poly(ethylene oxide) (PEO) chains, as well as 2 different immobilized, pendant anion groups. The plan is to explore these moieties' effects on maintaining suitable conductivity values and minimizing concentration gradients at the interface, as well as avoiding dual ion conduction, as would be the case for LiX-based systems.

The formation of the silylated coating is achieved by a modified sol-gel method, starting with hydrolyzable silicon alkoxides (also known as silanes), with at least one group being non-hydrolyzable, and incorporating one of the above mentioned moieties.

In the case of silanes with PEO, these are referred to as monopodal (one silane group on one end of PEO) or dipodal (one silane group on both ends) PEG-silanes, while silanes with pendant anions (PA) are referred to as PA-silanes. Combinations of different silanes in different feed ratios have been explored, along with the incorporation of LiTFSI as a lithium source in select compositions. The alkoxides employed are either commercially available, or synthesized.

In this initial work, the bulk properties of these coatings have been explored. These have included thermal characterization by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), as well as electrochemical characterization by temperature-dependent conductivity through electrochemical impedance spectroscopy (EIS). Ongoing work has included bulk EIS characterization LICGTM wafers with different thicknesses of SiO$_2$.

EN02.14.16

Magnetic Resonance Characterization and Transport Studies of Sodium-Ion Based Electrolytes for Electrochemical Energy Storage

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In this work, Nuclear Magnetic Resonance (NMR) Diffusometry was used to investigate the transport properties of sodium electrolytes for two different materials systems. Variable-Temperature PFG NMR was performed on samples of NaPF$_6$ salt dissolved in glycol dimethoxy ethers (glymes), a novel electrolyte for use in Electric Double-Layer Capacitors (EDLCs), as well as NaPF$_6$ in mixtures of Ethyl Carbonate (EC), Propylene Carbonate (PC), Diethyl Carbonate (DEC), and Fluoroethylene Carbonate (FEC), at various concentrations. Self-diffusion Measurements for $^1$H, $^{19}$F, and $^{23}$Na were taken from 0-60°C, and ionic conductivities were calculated from the Nernst-Einstein relation:

$$\sigma_{\text{NMR}} = \frac{F^2[C]}{RT} \times (D_{\text{cation}} + D_{\text{anion}})$$

Where is the ionic conductivity, F is Faraday’s constant, R is the ideal gas constant, T is the temperature in Kelvin, C is the molar concentration, and $D_{\text{cation}}$ and $D_{\text{anion}}$ are the self-diffusion coefficients for the cation and anion, respectively. The results indicate significant ion pairing effects which increase with both increasing temperature and decreasing glyme molecular mass. We have also investigated ionic liquid-based Na electrolytes, and these results will be discussed in the context of practical use for Na-ion electrolytes for commercial energy storage.

EN02.14.17

In Situ Formation of Functional Material for Impeding Diffusion of Lithium Polysulfides and Mechanism Study for Enhancing the Performance of Lithium-Sulfur Battery

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Li-ion battery (LIB) has promoted the growth of global market such as portable electronic devices, personal mobilities, unmanned aerial vehicles and long-range electric vehicles. Over two decades of dedicated researches and developments, the energy density of LIB has increased about 2 times since its commercial release. However, it has been mostly achieved by the improvement in battery manufacturing technologies, and only little change has been made in active materials and their chemistry, reaching their own theoretical limitations. In this regard, exploring next-generation energy storage materials that satisfies high energy density and low cost is essential. Extensive studies on next-generation energy storage materials have narrowed down some candidate materials and sulfur has shown the most promising results among them. Its advantages such as its high theoretical capacity, natural abundance, non-toxicity and low cost render sulfur an attractive choice. However, lithium-sulfur battery suffers from rapid capacity fading and shuttling phenomena caused by reaction intermediates called lithium polysulfides (Li$_2$S$_x$, 4 $\leq x \leq$ 8). Low electronic conductivity of sulfur and reaction products also compels introduction of large amount of conducting carbon, lowering practical energy density of lithium-sulfur battery. Many efforts for encapsulating sulfur using polar conductive matrices (doped carbon, conducting polymers) have been made to alleviate these problems, however, most of the approaches are proven to be effective only for few hundreds of cycles. Instead of exploring bulky heavy materials for lithium-sulfur battery, we propose highly reactive electrolyte additive, which can immediately react with lithium polysulfides to form thin solid layer and results in effective blocking of migration of lithium polysulfides to anode side. Chemical composition of the material formed in-situ as well as its electrochemical property was investigated and possible reaction mechanism, corresponding cell performance and desirable structure of additive will be suggested.

EN02.14.18
Large Three-Dimensionally Interconnected Mesopore Carbon and Solid Polymer Electrolytes for All-Solid-State Flexible Supercapacitors with Ultra-High Energy Storage Performance

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All solid-state supercapacitors (SCs) have received significant research interest as a shape deformable power supply device owing to the recent progress in portable, lightweight, and flexible electronics/optoelectronics. SCs typically exhibit fast power delivery rates, long life cycles, a wide range of operating temperatures, and good operational safety compared to rechargeable batteries. However, their low energy density limits the use of SCs in broader applications. To overcome the low energy density of the SCs, we employed three-dimensionally interconnected large mesoporous carbons (49 nm) to electrochemically stable ionic-liquid (IL) based solid polymer electrolytes (referred to as ionic gels). Precisely designed large mesopores interconnected through windows provide effective transport pathways for the electrolyte ions, while the well-developed micropores render a large active area for capacitive charge storage. The resulting SCs showed excellent energy storage performance such as specific capacitance of 323 F g$^{-1}$ and record-high energy density of 179 Wh kg$^{-1}$. Furthermore, the high energy and power densities obtained in this work exceed the upper bound of Ragone plots constructed based on aqueous-, organic-, and IL-based EDLCs reported to date. We also demonstrated the flexible all-solid-state SCs with an outstanding energy storage density (115 Wh kg$^{-1}$) that are suitable for bendable and foldable electronic devices. We believe these results provide design principles for developing high-performance SCs using electrochemically stable but dynamically slow ILs or IL-based solid electrolytes.

EN02.14.19
Electrochemical Properties of LiMn$_2$O$_4$ under High Pressure

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Owing to their highest energy density compared to other commercially available energy storage devices, rechargeable lithium-ion batteries (LIBs) are indispensable device in modern society. In addition to the daily applications, LIBs are also expected to be used for cutting-edge fields such as deep-see, space, and other planets. In order to extend the application filed of LIBs, understanding of electrochemical behavior of LIBs at extreme environments is required. In addition, basic understanding of effects of pressure for battery operation is very important to improve reliability and safety of LIBs. Here, we report Li-ion storage properties of LiMn$_2$O$_4$ electrodes under extremely high-pressure condition up to 100 MPa.

In order to perform electrochemical experiments under high-pressure condition, we developed a two-electrode-type
cell in this study. The cell was immersed in an insulating silicone-oil (pressure medium) and hydrostatic pressure generated by a hand-pump was applied through a free-piston. Galvanostatic charge-discharge tests, galvanostatic intermittent titration measurements (GITT), and electrochemical impedance spectroscopy (EIS) were performed. In the measurements, a Li-metal foil, and LiMn$_2$O$_4$ coated on Al foil (LiMn$_2$O$_4$ : carbon black : PVdF = 6 : 3 : 1 in weight ratio) were used as anode and cathode, respectively. A mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) solution (EC : DEC = 1 : 1 in volume ratio) containing LiClO$_4$ (1 mol L$^{-1}$) was used as the electrolyte. A glass-fiber filter was used as separator. All test cells were constructed in high-purity Ar-filled glovebox.

We confirmed that the reversible capacity of LiMn$_2$O$_4$ electrode at 25°C was not changed up to 100 MPa. In the meantime, plateau potentials corresponding to Li-insertion/extraction reaction was changed by the pressure. It was found that charge transfer resistance of the LiMn$_2$O$_4$ was clearly decreased with increasing pressure. It was also found that the thermal stability of LiMn$_2$O$_4$ was dramatically improved under high pressure condition: Under 100 MPa condition, the LiMn$_2$O$_4$ electrode showed good cyclability even at 55°C. On the other hand, reversible capacity of the electrode was dropped within 2 cycles at 0.1 MPa-55°C condition. These results indicate that LiMn$_2$O$_4$ cathode has great potential for special batteries for high-pressure application (deep-sea exploration etc.).

EN02.14.20
Rational Engineering of Silicon–Carbon Materials for Lithium-Ion Batteries—Influence of the Carbon Coating Graphitization Degree
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Since its introduction, the research community has been engaged in efforts to replace the state-of-the-art graphite anode used in commercial Li-ion batteries with novel high-capacity materials. Among several candidates, silicon-core carbon-shell nanoparticles -NPs- are considered one of the most promising choices due to their good electrochemical performance and high gravimetric and volumetric storage capacities. Although a wide range of different Si-C nanocomposites have been proposed over the years, establishing a rational understanding of how the material structure and properties influence the battery performance is far from trivial. For instance, the influence of the presence and quality of the carbon (i.e. graphitization degree) on the electrochemical performance of the synthesized materials is still not well understood. We have investigated a novel approach to address this question through a modified Chemical Vapor Deposition -CVD- approach that enables a fine and precise tailoring of carbon coating graphitization degree on Si NPs. Our composite Si-C materials are produced by starting from the same raw silicon nano-powders, which allows for direct comparison of carbon shell contributions as the silicon cores are identical. The NPs are coated in a conformal layer of amorphous carbon resulting from the thermal cracking of C$_2$H$_2$ at 650 °C. After removing C$_2$H$_2$ from the reaction zone, the temperature is increased to 1000°C in Ar permitting controlled graphitization of the C-shell. Notably, both TEM and Raman analysis have shown no detectable presence of silicon-carbide in the synthesized materials. The as-produced composites have been tested in Li-ion battery half-cell assemblies. Both the amorphous-C-coated and graphitic-C-coated Si NPs exhibit a high first cycle coulombic efficiency of 87% with capacities around 1800 mAh g$^{-1}$. However, after 100 cycles the amorphous-C-shell rapidly decays to a capacity retention of 34% while the graphitic-C-shell drastically enhances the cycling stability showing a capacity retention above 71%. To explain this phenomenon, we then observed the lithiation process through in-situ TEM measurements. Highly graphitic carbon markedly improves the structural stability of the composite particles and strongly favours the passage of lithium ions into the silicon core with respect to a purely amorphous carbonaceous material. This interpretation is confirmed by EIS analysis, displaying a stark reduction of both SEI and Charge Transfer impedances for a carbon layers with high a graphitization degree. Finally, we demonstrate that the silicon-graphite composites produced also work as a functional “drop-in” additive in graphite dominant anodes. The addition of 10% in wt of the Si-based active material enables the fabrication of electrodes with areal capacity around 3 mAh/cm$^2$, gravimetric capacity 60% higher than the one of a pure graphite electrode, first cycle CE of 90% and capacity retention of 81% over 100 cycles.

EN02.14.21
TiO$_2$ as a Stable Catalyst-Support for Lithium–Oxygen Batteries
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Lithium-oxygen batteries (LOBs) can achieve a large energy density (> 3500 Wh/kg) through the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) during the discharge and charge processes. In the LOBs,
the oxygen-cathodes can improve the efficiency of discharge-discharge cycle through effective ORR and OER. Carbon is used as a support for the catalyst applied to the conventional air electrode. However, the carbon-electrolyte interface causes side-reactions such as the formation of by-products and then exhibits a large overpotential between charge-discharge. Therefore, a carbon-free catalyst supports capable of suppressing side-reactions is required. Transition metal oxides have attracted interest to replace carbon-based catalyst supports. This work investigated the Ti\textsubscript{4}O\textsubscript{7} crystal structure as a chemically/physically stable catalyst support. Initially, anatase-TiO\textsubscript{2} was synthesized by sol-gel synthesis method. Thereafter, in order to control the anatase-TiO\textsubscript{2} phase to the Magnéli-Ti\textsubscript{4}O\textsubscript{7} phase, reduction heat treatment was performed in an H\textsubscript{2} gas atmosphere. Magnéli-Ti\textsubscript{4}O\textsubscript{7} has the best electrical conductivity among titanate crystal structures. The electric conductivity of Magnéli-Ti\textsubscript{4}O\textsubscript{7} is improved due to oxygen vacancies with Ti\textsuperscript{3+} cations on the (110) surface plane. Therefore, since the characteristics that can efficiently transfer electrons to the catalyst are obtained, Magnéli-Ti\textsubscript{4}O\textsubscript{7} can exhibit excellent charge-discharge performance with the stable charge-discharge overpotential than anatase-TiO\textsubscript{2}.

We investigated the phase transition of Magnéli-Ti\textsubscript{4}O\textsubscript{7} with anatase-TiO\textsubscript{2} through XRD, TEM, XPS, etc. In electrochemical properties such as cyclic voltammetry and galvanostatic cycle tests, Magnéli-Ti\textsubscript{4}O\textsubscript{7} was proved an excellent catalyst support through the introduction of RuO\textsubscript{2} catalyst.

Energy storage systems can be the most plausible solution since we are on the verge of a global energy crisis due to the rapid dissolution of fossil fuels. Finding environmentally benign fossil fuel replica with a broad performance spectrum is still a very encouraging field of research. In recent times, a tremendous effort related to the energy storage device has been put by our research groups. Few-layer graphene (FLG) achieved via mechanical exfoliation method from agricultural waste biomass: peanut shell. We have explored that the electrochemically deposited three-dimensional graphene oxide (ErGO) has a crucial role to act as binder-free electrode material for supercapacitor application. A facile electrochemical method can have advantages to grow reduced graphene oxide-polypyrrole hybrid platform on a pristine nanoporous gold chip for microsupercapacitor (MSC) application with outstanding cycle life.

Recently, electrochemical followed by laser-induction have shown the advancement for the fabrication of conductive and robust and flexible metal-free MSC. The LIG film on flexible substrate was patterned with the aim to develop on-chip flexible MSC, which offers large working voltage of 1.2 V in aqueous solid electrolyte. The MSC, without any metal current collector, interestingly shows unique electrical-double layer behavior and unprecedented cycling stability. Notably, the retention of initial capacitance after 1,00,000 continuous cycle was 100\% and after 150 days was more than 99\%, respectively. This study provides an effective strategy to build up metal-free supercapacitor with exceptional life cycle and facilitates progress toward a sustainable energy future.

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3D printing is an additive manufacturing (AM) technique that has attracted extensive attention for both industry and academia because it enables direct printing of multifarious, delicate, and complex structures in a low-cost, adjustable and scalable way. 3D printing also provides a facile route to fabricate advanced architectures and systems for a broad range of applications: energy, biotechnology, microfluidics, electronics, and engineered composites. In this work, we demonstrated electrical double layer supercapacitors using 3D printed activated carbon-based porous materials. Supercapacitors typically show intermediate characteristics of conventional electrolytic capacitors and secondary batteries and have outstanding advantages such as rapid charge/discharge rates, high efficiency, a wide operating temperature range, and a semi-permanent lifetime. The porous carbon-based electrode inks developed in this work were printable in various shapes: lattice, rectangular, circle, pyramid, spiral and so on. They can also be
stacked in multiple layers to increase electrode surfaces for capacitive energy storage. For the device fabrication, multi-stacked/interdigitated electrodes were designed and generated and the resulting energy storage performance was studied. As an electrolyte layer solid-state polymer gel electrolytes consisting of ionic liquid and host polymer networks were employed. To evaluate the electrochemical performance, cyclic voltammetry measurements were performed at various scan rates and the devices showed the reversible energy storage characteristics in the investigated operating voltage window. In addition, galvanostatic charge/discharge properties of the supercapacitors were examined at various current densities and the devices exhibited triangular shaped charge/discharge profiles.

**Improving Fluorinated Separator Membranes Performance for Lithium-Ion Batteries by Surface Micropatterning**

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The constant technological development and the increasing mobility lead to the necessity of new ways of energy generation and storage [1]. Lithium ion batteries are increasingly used in portable devices and show some advantages when compared to other battery systems, due to higher energy storage, high capacity and higher number of charge-discharge cycles. Membrane separators are one of the key components of battery systems, the most important characteristics of these membranes being porosity, ionic conductivity, good mechanical properties and chemical stability [2]. Poly(vinylidene fluoride) (PVDF) and (vinylidene fluoride) (VDF) copolymers such poly(vinylidene fluoride – co – trifluoroethylene) (PVDF-TrFE) are known for its excellent chemical resistance, mechanical properties and outstanding electroactive properties [3].

In the present work, porous poly(vinylidene fluoride-cotrifluoroethylene) (PVDF-TrFE) separators with different patterned surfaces constituted by arrays of hexagons, lines, zig-zags and pillars microstructures and their influence on battery performance. In addition, computer simulations allow to deeper understae the influence of the patterned surface on battery response.

The discharge capacity efficiency of batteries with zig-zag micropatterned separators is the largest among the patterned separators, being 804% higher than the one for batteries with non-patterned separators.

**Two-Dimensional SiOₓ Nanosheets-Zero-Dimensional Silicon Nanoparticles Hybrid for High Capacity Lithium Storage Materials**

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Si based anode materials for lithium-ion batteries have high theoretical capacity(3,580 mAhg⁻¹), but they have critical limit for commercial use because of their poor cycle performance associated with severe volume changes during lithium insertion and desertion. Our previous work, two-dimensional(2D) SiOₓ nanosheets electrode showed highly stable cycle performance and excellent dimensional stability because of physical nature of 2D nanostructure such as short diffusion length and abundant pore formed between stacked 2D nanosheets. However, their low reversible capacity has been a drawback to compete with other commercial material. In this work, we suggested 2D SiOₓ nanosheets and 0D Si nanoparticles hybrid materials using abundant intra-nanosheets pores in the stacked 2D SiOₓ nanosheets. The hybrid material delivered much improved reversible capacity more than 825 mAhg⁻¹ with higher initial efficiency compared to those of 2D SiOₓ nanosheets without sacrificing other anodic performances.

**High-Performance Lithium-Ion Battery Anodes Based on SiN, Nanoparticles from Gas-Phase Synthesis**

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With the current target of numerous countries to push electro mobility to the mass market, the demand for high performance batteries has increased drastically. Currently, the next goals on the roadmap are to achieve sufficient mileage and to reduce charging time of electrical vehicles. To accomplish these goals, the energy density as well as rate capability of lithium-ion batteries (LIBs) needs to be increased.
Silicon is widely recognized as the most promising component in high-capacity anode materials for next-generation lithium-ion batteries (LIBs) owing to its natural abundance, relatively low working potential, and its high theoretical storage capacity of 3579 mAh/g. However, the practical application of Si-based anodes is severely hindered by its low intrinsic electrical conductivity and its large volume change (>300%) during charging and discharging. The resulting mechanical stress causes rapid pulverization of the silicon and insulation and disconnection of the active material from the current collector. These failure events can cause rapid degeneration of the Si electrode and is especially prominent for silicon particles exceeding the size of a few hundred nanometres. Thus, recent research mainly focuses on nanostructures and nanocomposites that can tolerate the volume change.

A very promising way to stabilize silicon in LIB anodes is the incorporation of nitrogen, which has been shown to significantly improve the cycle performance. We therefore developed a gas-phase synthesis method based on the pyrolysis of monosilane in ammonia-rich atmosphere. Production rates are as high as 30 g/h and can be easily scaled. Based on this technology we are able to synthesize high-performing SiNx nanoparticles for lithium-ion battery anode. Moreover, their electrochemical properties can be designed by adjusting the synthesis parameters, thus affecting Si/N stoichiometry, particle morphology, size, and crystallinity.

We further demonstrate that SiNx nanoparticles with medium nitrogen content show significantly enhanced cycling performance of LIB-electrodes compared to pristine silicon. They show an initial specific discharge capacity as high as 1400 mAh/g and a highly stable cycle performance with a capacity retention of 96% after 100 cycles and over 80% after 500 cycles. Rate capability tests show that more than 60% of their capacity can be retained at a charging/discharging rate of 10 C. These results imply that silicon-rich SiNx based LIB electrodes are promising candidates for high-performance lithium-ion batteries with very high durability.

EN02.14.27
Highly Ordered Mesoporous Niobium Nitride for High-Performance Anode Material in Potassium-Ion Batteries Jae-Hyuck Park1,2, Jisung Lee3, Seongseop Kim1, Eunho Lim4, Jinwoo Lee3 and Yung-Eun Sung1,2; 1Seoul National University, Korea (the Republic of); 2Institute for Basic Science, Korea (the Republic of); 3Korea Advanced Institute of Science and Technology, Korea (the Republic of); 4Korea Research Institute of Chemical Technology, Korea (the Republic of)

Although Lithium-ion batteries (LIBs) have been regarded as fascinating energy storage device, the scarcity and high cost of lithium resources intrigue researchers’ interest in the next-generation batteries such as Potassium-ion batteries (KIBs) which have similar electrochemical characteristic of LIBs and use abundant potassium resources. However, to date there are still significant problems about searching suitable anode materials for KIBs because of hazardous of potassium metals and unstable cycle performance of carbonaceous materials due to large ionic size of potassium. Herein, we report ordered mesoporous niobium nitride/N-doped carbon composites hybrids (m-NbN/NC) as anodes for KIBs with superior cyclability and rate capability. The electrode delivers reversible capacities of 143 mA h g⁻¹ at 0.01 A g⁻¹ and 49 mA h g⁻¹ at 1 A g⁻¹. More impressively, the capacity retention of 100% at 0.5 A g⁻¹ after 2000 cycles could be achieved. In situ X-ray diffraction and ex situ SEM analysis indicates that m-NbN/NC electrode retains its structural integrity during potassiation and is accompanied by small strain, which is ascribed to high proportion of surface-controlled reaction. This work may suggest feasible new class of anode materials for ultra-stable KIBs.

EN02.14.28
All Printed Flexible Micro-Supercapacitors Based on Carbon Nanotubes Current Collectors and Exfoliated Manganese Oxide Nanoshhets Electrodes João Coelho, Lorcan Mckeon and Valeria Nicolosi; Trinity College Dublin, Ireland

In the last few years the concept of self-powered systems (SPS) has gained momentum in the fields of portable flexible technology. SPS usually refers to devices that are powered up by harvesting energy from external sources, such as solar radiation and body movement.[1] In a society where portable devices become an indispensable part of modern life, the development of SPS is of major importance.[2] These systems not only reduce the pressure on the electrical grid, but also help society moving towards sustainable and renewable energy sources. When integrated with energy storage devices, such as batteries and supercapacitors, SPS are also capable of storing energy under normal circumstances, thus assuring energetic self-sufficiency, even when surrounding conditions are less favourable for energy harvest.[1] In fact, the development of energy autonomous SPS is anticipated to bring
unforeseen ubiquitous innovations in our daily lives. Current thin-film batteries, still suffer from several technical disadvantages, as their energy per volume tends to rapidly decrease in the micrometre scale.[2] Moreover, they also raise safety concerns. On the other hand, micro-supercapacitors are highly desired as power sources for flexible devices as they present an enhanced power density, optimal cyclability, long shelf life and capability of direct on-chip integration.[2–4] However, to be fully integrated into wearable and flexible technologies, supercapacitors need to be flexible enough to undergo large mechanical deformations, without compromising their performance.[5] Commercially available supercapacitors do not present the most suitable configuration for devices meant to be bent or even rolled up, due to the presence of rigid components and the constant risk of harmful electrolyte leakage. The transition from current supercapacitor technology to fully printed, planar, ultra-thin and light supercapacitors will be disruptive.

In this work, inks based on carbon nanotubes (CNTs) and two dimensional manganese oxide nanosheets (MnO₂) processed by liquid phase exfoliation will be used as promising material platforms for flexible in-plane printed micro-supercapacitors. Owing to their superior mechanical and electrical properties, CNTs were implemented as highly efficient current collectors, thus removing the need for bulky and heavy metallic components. UV-Vis analysis revealed that the electrical conductivity of CNT films, as thin as 12 nm, is suitable for supercapacitor applications. Energy storage active materials, such as 2D - manganese oxide nanosheets, were then printed on top of the CNT films. Preliminary cyclic voltammetry experiments exhibited a characteristic supercapacitor behaviour. In order to maximize the exploitation of these devices properties, optimized inks, formulations and printing patterns will be carefully designed and characterized.

The proposed combination of liquid phase exfoliation and printing technologies will open the venue for the large-scale manufacture of ultra-light and thin flexible energy storage devices.

References


EN02.14.29

Structural and Chemical Evolution of nSi-cPAN Electrodes after Extensive Cycling Harvey Guthrey¹, Chun-Sheng Jiang¹, Andrew G. Norman¹, Se-Hee Lee², Nathan Arthur Dunlap² and Mowafak Al-Jassim³; ¹National Renewable Energy Laboratory, United States; ²University of Colorado Boulder, United States

Coating silicon nanoparticles (nSi) with cyclized polyacrylonitrile (PAN) is one approach to address the large volume expansion of silicon when used as an electrode material in solid-state batteries. This also enables the use of industrial processing techniques and inexpensive materials that can provide high active material mass loading with large reversible capacity. While previous studies have demonstrated success in using these materials to maintain high energy densities over long cycling life, comprehensive characterization is still needed to supply critical details needed for further optimization and extension to different material systems. In this work we focus on analysis of solid-state sheet style electrodes (nSi-PAN) and the interface with the LPS (Li₂S-P₂S₅) solid electrolyte. This analysis was performed in cross-section after fracturing and polishing the exposed surface using Ar⁺ ion milling. All sample preparation and subsequent characterization was performed without exposure to atmosphere so that no unintentional oxidation of the material would obscure true material properties. Devices were studied in the initial uncycled state and also at full delithiation after extensive cycling. SEM-based EDS mapping has revealed that there are changes in the spatial distribution of the nSi particles after cycling devices extensively. Additionally, sulfur from the solid electrolyte appears to have migrated into the nSi-PAN layer after cycling. No sulfur was observed in this layer prior to device cycling. A more complete understanding of how these changes relate to device performance was attained by correlation with electronic characteristics (scanning spreading resistance microscopy (SSRM)) and
The Effect of Li Salt Concentration on the PEO-Base Solid Polymer Electrolyte

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To achieve improvement in the performance and energy density of lithium ion batteries, there is a high demand for novel electrolytes. Solid polymer electrolytes (SPEs) are now becoming increasingly attractive for LIBs because of their excellent properties such as high safety, easy fabrication, low cost, high energy density, good electrochemical stability and excellent compatibility with lithium salts. Polymers may also act as hosts for ions.

PEO is a polyether compound with low toxicity and is thus used in a variety of applications. PEO can complex with lithium salts (Li⁺) to form polymer electrolytes. Its ethylene oxide (EO) units have a high donor number for Li⁺ and high chain flexibility, which are responsible for ion transport. The ions can move in the space provided by the free volume of the polymer host, and conductivity is thus possible above the glass transition temperature (Tg) of the polymer where the polymer molecules are free to move. The ionic conductivity displays a diffusive liquid-like behavior in the solid electrolyte. The design criteria for PEO-based electrolytes is the suppression of PEO crystallinity to increase the percentage of amorphous phase of PEO for ion transport. Various strategies have been employed to improve the ionic conductivity of PEO based electrolytes.

The challenging and critical issue with solid polymer electrolytes are to improve the ionic conductivity, interfacial contacts between electrodes and electrolytes and electrochemical stability window

In order to above requirements, recent research in PEO-based solid-state electrolytes (SSEs) has focused on the design of additive for solid polymer electrolytes (SPEs). The additives include ionic liquid, oxide particles, etc. The addition of ionic liquid and organic solvent could serve as the plasticizers, which were found to be efficient on improving the ionic conductivities of SPEs. On the other hand, various modification methods of SPEs by introducing oxide particles have been published. It was reported that the addition of oxide nanoparticles to the SPEs, such as SiO₂, TiO₂, Al₂O₃, LAGP, YSZ can improve ionic conductivity. Researchers attributed the enhanced ionic conductivity to that the highly dispersed nanoparticles be able to inhibit the recrystallization of polymer segment and further accelerate Li⁺ transport. The nanoporous materials such as nanosized mesoporous SiO₂ and metal–organic framework (MOF) can be used to achieve high Li ion conductivities. One material containing porous channel was used as an additive to a high ionic conductivity composite electrolyte.

These results indicated the porous nanoparticles may be a relatively effective additive to increase the ionic conductivity than the nonporous particles, which is mainly attributed to the pores creating more space charge regions to facilitate Li⁺ transport. The implanted materials with rich nanoporous structure can effectively promote the formation of an Li⁺ enrichment area through the adsorption effect. In the newly formed percolated interface between additives and polymer, the continuous area could act as a high-speed pathway for fast lithium ion diffusion.

In this study, we mixed PEO and Si and Al based 3-dimensional nanoporous oxide structures (NOPSs) to make composite solid electrolytes. Because the choice of lithium salt also plays a crucial role in solid polymer electrolyte, lithium hydroxide (LiOH) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were used to investigate the effect of different kind of Li salt on the Li ion conductivity. The most important requirement of lithium salt is their solubility in polymer matrix. We varied the drying temperature of the composite solid state electrolytes. The drying temperature range is from 25 °C to 60 °C. We also changed the ration of EO:Li. Different molar concentration of PEO is utilized such as, EO:Li = 16:1 & 18:1 ratios. The best lithium ion conductivity was obtained in the temperature of 50 °C.

Enabling Rapid Charging Lithium-Metal Based Rechargeable Batteries through Suppression of Dendrite Growth and Ion Depletion in the Electrolyte via Surface Acoustic Wave-Driven Mixing

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Lithium metal is an attractive material for use as anodes in batteries due to its high electronegativity, low density, and high energy density. Because it is unstable during recharging, with non-uniform Li deposition that leads to porosity, dendrites, and dead Li, rechargeable lithium metal batteries have been unrealistic for nearly fifty years with
serious safety problems and low Coulombic efficiency. Over this time, research on electrolyte additives, solid-state electrolytes, artificial SEI modifications, and separators have produced modest improvements, but none that have justified considering lithium metal batteries over lithium-ion batteries in rechargeable applications. Battery stability, ionic conductivity, and interfacial issues remain key challenges.

Nonuniform lithium deposition during charging occurs due to a Li ion depletion layer adjacent to the anode, especially at modest to high charge rates of 1C or above. By including a small, 100 MHz surface acoustic wave device into the lithium metal battery that produces intense acoustic waves in the electrolyte, rapid submicron boundary layer mixing flow may be generated during charging. This flow largely eliminates the Li ion depletion layer, and because the SAW device is small, solid state, and requires only 10 mWh/cm² during battery charging, there is a realistic possibility of incorporating this technology into current batteries under consideration for an electric vehicle, consumer device, and medical applications. The elimination of the ion depletion layer furthermore allows high-rate charging, as we will demonstrate in our electrochemistry and morphological results. The underlying physics will be explained using a closed-form model formed from intermediate asymptotics, and will show the crucial impact of the Peclet number in avoiding the ion depletion layer.

EN02.14.32
Improved Ionic Conductivity Achieved via Sr Doping with Amorphous LLTO as Solid Electrolyte Yubin Zhang¹, Daxian Cao², Hongli Zhu² and Yan Wang¹; ¹Worcester Polytechnic Institute, United States; ²Northeastern University, United States

Amorphous Li₀.₃₅La₀.₅₅TiO₃ (LLTO) shows great promise for solid electrolyte in all-solid-state Li-ion batteries (ASSLiB), amorphous LLTO thin films have also been successfully synthesized by sol-gel process in our previous work. The ionic conductivity can reach up to 1.88*10⁻⁵ S/cm at 30 °C. However, one key requirement for solid electrolyte is high ionic conductivity. In order to further increase the ionic conductivity to fit the demand of ASSLiB, doping method was applied in our research. In specific, Strontium (Sr) was introduced as dopant. The ionic conductivity of Li₀.₃₅La₀.₅Sr₀.₀₅TiO₃ (LLSTO) is one order’s higher than LLTO. In this study, we successful prepared amorphous LLSTO thin film via sol-gel procedure, moreover, differences are introduced with Sr ratio in order to understand the relationship of ionic conductivity change and structure difference. We also proved the LLSTO came with promising electrochemical stability window and stability in contact with Lithium metal. In this case, we are able to better reveal the fundamental relationship between structure and ionic conductivity in a variety of solid-state electrolytes and Li-ion transport mechanism.

EN02.14.33
Fabrication of the Guest Li⁺ Ion Conductors Based on NaI-NaBH₄ System Reona Miyazaki¹, Yasuto Noda² and Takehiko Hihara¹; ¹Nagoya Institute of Technology, Japan; ²Kyoto University, Japan

Solid electrolytes for the all-solid-state lithium batteries have been mainly developed based on Li compounds in which the host Li⁺ ions are the main conduction species. On the other hand, our group has been focused on the “Li-free” compounds as the base materials for the solid electrolytes, where the foreign ions, or “guest Li⁺ ions” play a major role for the ionic conduction. From our previous research, it has been shown that NaI, NaBr and KI become guest Li⁺ ion conductors via forming the solid solution with LiBH₄ (6 mol%) [1-3]. While the guest Li⁺ ions are the major conduction carriers, the contribution of the host Na⁺ ion conduction in NaI-LiBH₄ systems was proven to be quite small [4]. The solid solutions of NaI-LiBH₄ were fabricated by mechanical milling of NaI and LiBH₄, however, it was suggested that the as-milled samples include unreacted LiBH₄ as the secondary phase [5]. The difference of the crystal structures would be one of the reasons for the slow kinetics for the formation of the solid solution (rock-salt and wurtzite structures for NaI and LiBH₄, respectively). Therefore, it is expected that the fraction of the secondary phase can be reduced if the guest Li⁺ ions in NaI lattice are introduced by the doping of LiI (rock-salt structure). In the present work, both BH₄⁻ and Li⁺ ions are doped into NaI by the mechanical milling of NaI, NaBH₄ and LiI all of which are the rock-salt type compounds. The guest Li⁺ conduction properties in NaI-NaBH₄-LiI systems will be also presented.

NaI, NaBH₄ and LiI were purchased from Aldrich Co. The mechanical milling was conducted with 10 pieces of balls in a chrome still pot (45 ml). First, several composition of NaI-NaBH₄ solid solutions were fabricated with the different f/BH₄⁻ ratios. Subsequently, LiI was milled with NaI-NaBH₄ systems in a given molar ratio. The concentration of Li⁺ and BH₄⁻ ions were changed by adjusting the doping amount of LiI and NaBH₄, respectively. The crystal structures of the obtained samples were analyzed by XRD measurement using Cu Kα radiation source.
The local structure around guest Li+ was investigated by 7Li NMR measurement. For the conductivity measurement, the powder sample was pelletized under ca. 400 MPa, resulting in the dense pellet with the thickness of 1 mm. Stainless steel was used as the both sides of electrodes and the three layered cell was sealed into air-tight cell. Electrical conductivity of the sample was measured by AC impedance methods from the frequency range between 1 MHz and 1 Hz. From the results of 7Li NMR measurement for NaI-NaBH4-LiI systems, it was clearly confirmed that the fraction of the secondary phase was successfully reduced by using LiI as the starting material. The Li+ conductivity is increased by the reduction of the secondary phase; the conductivity of 9(15NaI-NaBH4)-LiI was reached to be 1.5 × 10⁻⁵ S/cm at room temperature while the conductivity of the sample with unreacted LiBH₄ (9NaI-LiBH₄) was remained to 3.0 × 10⁻⁶ S/cm. The conductivity results of the samples with the different cation and anion ratios will be presented at the meeting.

References

EN02.14.34
MXenes' Terminations Engineering and Intercalation for Energy Storage Applications
Frederic Le Goualher, Liu Zheng and Martial Duchamp; Nanyang Technological University, Singapore

The sharp growth of the energy storage business - 30 % in the US in 2018, dominated by lithium ion battery - urges to find new alternatives for fast, safe and reliable devices. Existing solutions rely either on batteries or supercapacitors: the former stores energy with a high density but suffer from slow energy delivery and irreversible capacity fading; the latter stores less energy but higher power densities, with charging times of seconds to minutes and excellent cyclability.

But what if we could combine the best of both worlds?

This promise may be kept by using new pseudocapacitive materials known as MXenes. They are a rapidly growing family of transition carbides and/or nitrides with the general formula Mₙ₊₁XₙTₓ (n = 1, 2 or 3; M = transition metal, e.g. Ti, V, Nb, Mo; X = C and/or N; T = surface termination, e.g., -OH, -F, =O). Their potential in energy storage devices has already been intensively studied since their discovery in 2011. They exhibit a 2D layered structure, a very high conductivity, can intercalate ions or molecules in order to trigger or enhance ion insertion, show low diffusion barriers for Li+ ions or other multivalent ions. Another key aspect is that they use fast surface redox reactions to store more energy than traditional electrical double layer capacitors and at a higher rate than traditional batteries.

But the real potential of MXenes lies in their versatility. Researchers primarily focused on finding new Mₙ₊₁Xₙ chemistries, with great success. But another way to control their performances is to engineer surface terminations: they are introduced during the synthesis process and strongly influence Fermi's level density of state. Conductivity is thus strongly impacted as well as electrochemistry. Removing them or finding strategies to modify them is of great importance and can lead to boost performances.

In addition, intercalating molecules and/or ions between MXenes sheets is another mechanism that can be used. Interplanar distance and thus, storage capabilities, will be modified. We could think that 'the wider, the better' but this would be a false assumption. Indeed, as it has recently been proven, solvent plays a key role in this mechanism. A balance has to be found.

In this study, we demonstrate that for a given battery electrolyte, it is possible to enhance electrochemical storage in MXenes by choosing the right intercalant. Our results showed a 30 % improvement in performances by finding the correct balance between inter planar distance and ion insertion (with or without solvation shell). Moreover, we will also evaluate the impact of surface terminations modifications on battery performances and provide insight using electron microscopy.

EN02.14.35
Ideal Li-Metal Anodes with *Ex Situ* Artificial Layers for the Realization of Highly Stable Lithium-Metal Batteries Jung-In Lee and Soojin Park; Pohang University of Science and Technology (POSTECH), Korea (the Republic of)

The new technological breakthrough of battery systems is essential to spurring the development of energy-storage systems with a high energy density for electric vehicles and various electronic devices, albeit many advances since the commercialization of Li-ion batteries in 1991. At present, the employment of Li metal as a battery anode has attracted enormous attention because of its high capacity (3860 mA h g⁻¹), lightweight (0.59 g cm⁻³), and a low working voltage as crucial factors to fabricate high energy density batteries (e.g., Li-air batteries, Li-S batteries, and Li-metal batteries). Nonetheless, there are serious problems hanging over the system including the volume expansion and dendrite growth of Li anodes, safety issue, unstable interphase between Li metal and electrolytes, low round-trip efficiency, and short cycle life. Thus, it is necessary to seek a solution for suppressing the Li dendrites and then finally leading to advancing the development of practical Li metal batteries. In this work, we propose practical approaches for enhancing the electrochemical performances of Li metal batteries using two ways. One is a Li₂TiO₃ layer, (LT) which has the 3D pathway inside the particles for Li-ions, along with a simple, secure, and scalable fabrication method. The other is a polymer layer on a Li metal surface, which transports Li ions and screens Li metal from oxygen and moisture. Additionally, these works include indisputable evidence for verifying the superiority of these ways and practical demonstrations of full cells using high-energy cathodes.

EN02.14.36
The Impact of Charging Pulse on the Diffusion-Induced Stress on a Thin-Film Electrode Pavan Kumar Polkampally¹, Ashish Vineet¹, Jay Krishan Dora¹, Debashis Khan², Tarun K. Kundu¹ and Sudipto Ghosh¹; ¹Indian Institute of Technology, India; ²Indian Institute of Technology BHU, India

All solid-state thin film batteries are promising candidates for applications ranging from medical implants to micro-power sources for portable electronic devices. The structural durability and reliability of thin film batteries depend on the volume change in the electrodes. In order to make further improvements in the thin film battery technology, an in-depth understanding of the electro-chemo-mechanical processes involved in these batteries is necessary. To enhance the cyclic performance of thin film batteries, a fully coupled diffusion-stress modeling in continuum scale with various operating conditions are essential. In this work, we have incorporated coupling of diffusion and stress in a Si thin film and analyzed the impact of the nature of charging pulse on the evolution of hydrostatic and principal stresses.

EN02.14.37
Synthesis and Characterization of V₂O₅ Microstructures as Advanced Cathode Material for High-Performance Lithium-Ion Batteries Hemlata Dhoundiyal, Mukesh C. Bhatnagar and Pintu Das; Indian Institute of Technology Delhi, India

In recent time transition metal oxide vanadium pentoxide (V₂O₅) is considered as an excellent energy storage device material for Li-ion batteries (LIBs) with reference to its high charge storing capacity, low cost, rich layered structure, and abundant material. With respect to its rich layered structure, which can reversibly accept the intercalation and deintercalation of Li-ions in the process of charging and discharging of LIBs. In this study, we report a simple hydrothermal procedure to synthesize the porous microstructure of V₂O₅ as a cathode for LIBs with subsequent annealing temperature. The structural analysis stands for the orthorhombic phase of V₂O₅ and other suboxides phase of vanadium are absent. The RAMAN analysis justifies the layered structure of V₂O₅. The morphological study of V₂O₅ shows the flower-like three-dimensional micro flowers (having diameter ~1.2 to 2.6µm) self-assembled by Nanorods. In electrochemical cyclic voltammetry measurement three cathodic peaks were observed corresponds to 3.27V, 3.05V, and 2.08V as Li/Li⁺ refer to three crystal phase α-V₂O₅ to β- Li₀.₅V₂O₅; β- Li₀.₅V₂O₅ to δ-Li₂V₂O₅ and δ -Li₂V₂O₅ to γ-Li₂V₂O₅ respectively. And also three anodic peaks correspond to Li-ion deintercalation. Which indicate the good reversibility of the electrode. In this report, V₂O₅ micro flowers deliver very high specific discharge capacity of 290mAhg⁻¹ and after 50cycles the capacity reduced to 198mAhg⁻¹ cycled between the voltage range 2.0-4.0V at the current rate 0.1C.

EN02.14.38
Hierarchical Porous Nickel-Doped Vanadium Dioxide (B) Nanobelts with Ultrahigh Rate Capability and Long Cycle Life for Aqueous Rechargeable Zinc-Ion Batteries Yi Cai, Rodney Chua and Madhavi Srinivasan;
Nanyang Technological University, Singapore

Recently, aqueous rechargeable zinc-ion batteries (ARZIBs) have attracted great attention as compared to commercial lithium-ion batteries due to their unique advantages of high intrinsic safety (non-flammable water-based electrolyte) and low cost. [1-3] Over the past few decades, much progress has been focused on the exploration of suitable cathode materials. Among them, vanadium dioxide (B) has been considered as a potential cathode for ARZIBs owing to its unique double layers of V₂O₆ type with tunnels, which can facilitate rapid zinc-ions de/insertion processes. [4] However, the reported VO₂ (B) displays a high initial capacity but noticeable capacity fading and especially declines drastically at a high current rate. Compositing VO₂ (B) with an electrically conductive matrix has recently been introduced as an effective way to improve the power capability. However, it can only improve the external electric conductivity and the usage of expensive carbon (graphene) negates the cost advantage of vanadium oxides. Therefore, it is of great importance to construct novel VO₂ (B) electrode materials with excellent electrochemical performance.

Herein, we report an alternative approach to designing and engineering a hierarchical porous Ni-doped vanadium dioxide (B) nanobelts for ARZIBs. The as-synthesized samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy and transmission electron microscopy (TEM). The existence of Ni dopant was confirmed by the X-ray absorption near-edge structure studies (XANES) and X-ray photoelectron spectroscopy analysis. Electrochemical studies indicate that the Ni-doped VO₂ nanobelts electrode exhibits superior cycling stability and ultrahigh rate capability with long cycle life, which is significantly higher than that of the undoped VO₂ (B). This can be attributed to the utilization of Ni dopant to electrical wiring the electroactive material, the intrinsic conductivity of VO₂ can be effectively increased. In-operando XRD measurements coupled with ex-situ TEM micrographs taken at specific potentials were exploited to gain a further understanding into the structural evolution upon cycling and ions storage mechanism. The results of the study can potentially open the doors for the widespread application of constructing other elemental doping materials as cathodes with high rate capability and long cycle life for aqueous rechargeable batteries.

References:

EN02.14.39

Phase Transformation of Copper Hexacyanoferrate Cathode in Aqueous Zn-Ion Battery Joohyun Lim¹, Rajib Sahu¹, Kevin Schweinar¹, Gholnecheh Kasiri², Katharina Hengge¹, Dierk R. Raabe¹, Fabio La Mantia² and Christina Scheu¹; ¹Max-Planck-Institut für Eisenforschung GmbH, Germany; ²Universität Bremen, Germany

Prussian blue analogs (PBAs) are polynuclear transition metal cyanides with the general chemical formula of AMₙ[Mₙ(CN)₆]xH₂O, where A represents monovalent cations and M transient metal cations. The PBAs have been considered as promising electrode materials for multivalent metal-ion batteries as well as monovalent metal-ion batteries because of their robust and large 3D channel framework.¹ In particular, copper hexacyanoferrate (CuHCF) has shown promising performances in aqueous Zn-ion batteries with specific energy and power comparable to organic Li-ion batteries.² However, the CuHCF suffers from decreasing capacity upon cycling. The exact mechanism of the CuHCF upon Zn ions insertion is still difficult to understand.

Here, we investigate the change of the CuHCF cathode in aqueous Zn-ion battery in terms of morphology, chemical composition, and oxidation state. Advanced electron microscopy techniques such as scanning electron microscopy, (scanning) transmission electron microscopy, energy dispersive X-ray spectroscopy, electron energy loss spectroscopy, and focused ion beam are applied in order to unravel the underlying mechanism. We observed the formation of wire and cubic morphologies of the Zn₅Cu₆HCF upon cycling the CuHCF cathode in Zn ions-containing electrolytes. A substitution mechanism is proposed to explain the increasing Zn content of the cathode material while simultaneously the Cu content is lowered during the Zn-ion battery cycling. The detailed degradation
mechanism and its relationship with the electrochemical performance will be discussed.


EN02.14.40
Visualization of Inhomogeneity Formation on the Cathode Materials of Lithium-Ion Battery by X-Ray Micro-Diffraction Chao Li, Mark Wolfman and Jordi Cabana; University of Illinois at Chicago, United States

Layered transition metal oxide family of cathode materials for Lithium-ion battery (LIB) has been exclusively studied due to their high theoretical capacities and chemical stability. Their performance is limited by the capacity degradation during cycling as irreversible reaction occurs. The irreversible reaction resulting from the crystal structural change of the cathode materials is due to the movement of lithium ions between electrodes while cycling at different rates. As a result, different phases can be observed by X-ray Powder Diffraction (PXRD). In order to understand the mechanism of different phases formation during cycling, it is necessary to locate the regions where the inhomogeneity is formed within the cathode. LiNi0.80Co0.15Al0.05O2 (NCA) was used as an example to develop an ex-situ methodology by using X-ray Microdiffraction (μ-XRD) at the scale from 1mm to 100µm to visualize the distribution of inhomogeneity within the cathode by generating a map of distribution of unit cell parameters of crystal lattice. Applying this approach, NCA has been examined under different discharging rates (C/10, C/5, C/2, 1C and 5C) with different sizes of lithium anode. The maps clearly show the distribution patterns of rate-depend inhomogeneities due to kinetic limitation within the cell. This methodology will be further developed to investigate the inhomogeneity formation on secondary particles.

EN02.14.42
Investigation of the Interface Structure between a Solid Electrolyte and a Battery Electrode through Neutron Reflectometry Patrick Kim and Joseph A. Dura; National Institute of Standards and Technology, United States

Lithium phosphorus oxynitride (LiPON) has attracted significant interest in solid-state batteries, due its wide potential window, high ionic conductivity, and fairly good mechanical stability. However, several issues which are associated with the formation of an interfacial layer between LiPON and battery electrodes (e.g. LiCoO2) and the structural degradation of electrodes significantly affect the electrochemical performances in solid-state batteries. Several techniques (such as HRTEM, STEM, SEM etc.) have been employed to look into the interfacial layer between solid-state electrolytes and electrodes; but it was technically difficult to analyze the same spot of sample without damage, due to its high energy beam. In operando neutron reflectometry (NR) is a non-destructive technique which enables the investigation of the evolution of nanometer-scaled interfacial layers as a function of working potential. In addition it is very sensitive to the light elements such as Li and H, which facilitates the qualitative analysis of thin films. Due to these fascinating characteristics, it has been used to study the by-products (e.g. solid electrolyte interphase) formed at the interface of battery electrodes. Through this study, we investigated the interface of LiCoO2 electrode before and after sputtering LiPON via NR and studied how Li-impregnated solid-state electrolyte affects the structural characteristics of LiCoO2 electrode. Moreover, we looked into the structure and composition of the co-diffused layer between LiPON and LCO using NR. These results may explain the reason for the capacity fade and power fade of solid-state batteries. In future work, we will explore the possibility that a thin layer of Al2O3 can improve the structural integrity of each LiPON and LCO. These fundamental studies will lead us to understand the inherent problem of solid-state batteries and provide guidelines to design the suitable electrode for thin film solid-state batteries.

EN02.14.43
Nitrogen-Doped Graphene/CNTs/Li2S Composites as Cathode for High-Performance Lithium-Sulfur Batteries Gaind P. Pandey, Joshua Adkins and Lamartine Meda; Xavier University of Louisiana, United States

Lithium sulfide (Li2S) is one of the most promising cathode materials for the next-generation advanced lithium-ion batteries as it allows for the use of lithium-free metal-based high capacity lithium-ion anodes such as silicon-based anode etc. It has high theoretical capacity (1167 mA h g⁻¹) and large energy density to match with high capacity metal anodes. However, Li2S suffers from poor rate performance and short cycle life due to its insulating nature (very low electronic and ionic conductivity) and shuttle effect of lithium polysulfides during charge-discharge.
cycles. In this work, we report a facile and scalable ball milling synthesis method to synthesize nitrogen-doped graphene/carbon nanotubes (CNTs)/Li$_2$S composites with 80 wt% Li$_2$S loading. In this composite cathode, two-dimensional (2D) N-doped few layer graphene nanosheets and one-dimensional (1D) CNTs provides efficient channels for electron transfer and ionic diffusion, and leads to a low solubility of polysulfides in electrolytes during charge-discharge cycles. The N-doped Graphene/CNTs/Li$_2$S composites cathode yields an exceptionally high initial capacity of 847 mAh g$^{-1}$ after 3 cycles at the C/20 rate based on the mass of Li$_2$S. The mass loading of active material (Li$_2$S) was ~4 mg cm$^{-2}$ in the cathode. The cell also shows good cycling stability with an average decay rate of 0.23% per cycle over 150 cycles at C/3 rate, and improved rate capability of 470 mAh g$^{-1}$ at C/2 rate. The reported facile and scalable synthesis method of N-doped Graphene/CNTs/Li$_2$S composites cathode with high Li$_2$S content presents promising application potentials in high-performance lithium-sulfur batteries.

EN02.14.44  
Electrospun Nanofibric Network of Ca$_2$Fe$_2$O$_5$ as Durable Anode for Advanced Li-Ion Batteries  
Sandeep K. Sundriyal$^1$ and Yogesh Sharma$^2$; $^1$Indian Institute of Technology, Roorkee, India; $^2$Indian institute of Technology, Roorkee, India

Recently, iron based metal oxides have attracted much attention for advanced lithium ion batteries (LIBs) anode. However, rapid capacity fading and poor rate capability caused by drastic volume variations during cycling process hinder their practical applications. To circumvent these issues, one dimensional nanofibric architecture consisting voids/gap present in between individual nanoparticles may play a vital role to prevent the volume variation during long term cycling. In this regard, nanofibers of Ca$_2$Fe$_2$O$_5$ have been fabricated by facile, environment friendly and cost-effective electrospinning technique, and thoroughly characterized by FE-SEM, TGA, XRD, XPS and BET. Further, the advantages and importance of Ca$_2$Fe$_2$O$_5$ nanofibers as LIBs anode is demonstrated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). Ca$_2$Fe$_2$O$_5$ nanofibers exhibit remarkable lithium storage performance such as high initial reversible capacity (650(±10) mAh.g$^{-1}$), excellent cyclic stability (600(±10) mAh.g$^{-1}$ up to 100 cycles) and good rate capability. Moreover, Nanoparticles of Ca$_2$Fe$_2$O$_5$ were also investigated as LIBs anode, however, nanoparticles performance are found to be inferior to the nanofibers. The better performance of Ca$_2$Fe$_2$O$_5$ nanofibers is attributed to the unique features of nanofibric architecture such as one dimension, porous, high aspect ratio and presence of voids/gap between interconnected nanoparticles.

References:  

EN02.14.45  
N-doped, Microporous Carbon Coating Synthesized via Carbonization of Electrospray-Deposited Metal-Organic Framework for Lithium-Sulfur Battery  
Clayton T. Kacica and Pratim Biswas; Washington University in St. Louis, United States

Next-generation battery technologies with higher capacities and longer lifetimes compared to current lithium-ion batteries (LIBs) are vital for portable devices and electric vehicles. Lithium-sulfur batteries have received significant attention due to their ultrahigh theoretical capacity of 1675 mA g$^{-1}$ and the environmental availability and benignity of sulfur. However, several issues currently prevent their more widespread utilization, including the low electronic conductivity of sulfur (S$_8$) and its lithiated products (Li$_2$S$_x$). Additionally, the “shuttle effect” resulting from the soluble intermediate polysulfides Li$_2$S$_n$ (4 ≤ n ≤ 8) formed during charging and discharging in organic electrolytes has been shown to cause rapid capacity fade and battery failure.

Various strategies have been utilized to mitigate these issues, such as forming composites with conductive and adsorptive hosts to confine sulfur. However, the shuttle effect and resulting electrode instability has yet to be eliminated. Herein, we designed a metal-organic framework (MOF) derived N-doped microporous-carbon coated electrode consisting of sulfur and nanostructured titanium dioxide (S-TiO$_2$). The N-doped carbon coating is formed from the carbonization of an electrospray deposited Zn-MOF, and possesses a suitable pore size to prevent polysulfides from passing while not inhibiting the movement of Li$^+$. Meanwhile, the TiO$_2$ nanostructures provide efficient electron pathways to enhance the high-rate performance of the electrodes. The resultant electrodes deliver a high specific capacity and excellent rate performance.
Development of Novel Polymer Electrolyte for 3D Printed Free Form Factor Battery

Nishani Jayakody1, Steven Greenbaum1, Diana Golodnitsky2, Heftsi Ragones2, A. Vinegrad2 and G. Ardel2; 1Hunter College of CUNY, United States; 2Tel Aviv University, Israel

The high areal-energy and power requirements of advanced microelectronic devices favor the choice of a lithium-ion system, since it provides the highest energy density of available battery technologies. Several attempts have been made to produce primary and secondary thin film batteries utilizing printing techniques. These technologies are still at an early stage, and most currently printed batteries exploit printed electrodes sandwiched with self standing commercial polymer membranes, produced by conventional extrusion or papermaking techniques, followed by soaking in aqueous or non-aqueous liquid electrolytes.

In this work we report on the development and fabrication of novel 3D-printed solid-state or quasi-solid electrolytes by fused filament fabrication (FFF). The electrolytes are composed primarily of polyethylene oxide (PEO) and polyethylene glycol (PEG) which are known ionic conductors, and polylactic acid (PLA) for enhanced mechanical properties and high temperature durability. Flexible quasi-solid-state printed electrolyte plasticized by the ionic liquid (IL) 1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR14TFSI) with 0.3M concentration of LiTFSI exhibited an ionic conductivity of 2.8 × 10–4 S/cm at 60°C.

The 3D printed electrolytes were characterized by means of SEM imaging, differential scanning calorimetry (DSC) and electrical impedance spectroscopy (EIS). We have also investigated the charge transport dynamics in this printed electrolyte material by pulsed field gradient diffusion nuclear magnetic resonance (NMR) using the probe nuclei 1H, 7Li, and 19F, corresponding to the PYR14, Li, and TFSI ions. All ionic diffusivities in the IL-plasticized PLA/PEO/PEG electrolyte were reduced compared to their values in the IL with 0.3M LiTFSI, even though the ionic conductivity exhibited an acceptable value. Interestingly, a sample consisting of the IL LiTFSI mixture imbibed into the PLA matrix exhibited no reduction in ionic diffusivity compared to the liquid sample.

These results pave the way for a fully printed battery, which enables free-form-factor geometries and is far superior in terms of safety compared to standard Li ion batteries which contain volatile liquid electrolytes.

Reduced TiO2 as a Stable Cathode Material for Sodium-Air Batteries

Christopher J. Franko, Z. Blossom Yan and Gillian R. Goward; McMaster University, Canada

Sodium-based battery chemistries have potential for use as competitive energy storage alternatives to Li-ion batteries (LIBs), largely due to the low cost and wide availability of raw sodium materials compared to their lithium counterparts (150 USD t⁻¹ vs 5000 USD t⁻¹ for Na and Li carbonate respectively).1 Unfortunately, the development of Na-ion batteries (NIBs) has been limited by the intrinsic gravimetric barriers that come from moving toward Na-based intercalation. Na-air batteries (NABs) on the other hand, do not suffer from these barriers, reaching high theoretical capacities of 1108 Wh kg⁻¹.2 The comparatively high energy density of the NAB arises from a fundamentally different cell chemistry, where energy is gained through chemical synthesis rather than intercalation. Typically, a sodium metal anode is oxidized upon discharge to give Na⁺ ions which travel across a liquid electrolyte toward a porous carbon cathode, where O₂ gas is reduced to form either sodium superoxide (NaO₂) or sodium peroxide (Na₂O₂) in competing oxygen reduction pathways. Although theoretical gravimetric capacity is high in these batteries, cell lifetime is hindered by the oxidative instability of the carbon cathode toward NaO₂, forming sodium carbonate in a parasitic side reaction (Na₂CO₃).³

In this work, titanium dioxide (TiO₂) is investigated as a starting material for alternative cathode substrates in long cycle life, chemically stable, NABs. Electrically insulating TiO₂ is reduced via hydrogen gas to produce highly conductive single phase Ti₄O₇. The stability of Ti₄O₇ toward NaO₂ is confirmed by monitoring a ground mixture of the two by solid state ²³Na magic angle spinning nuclear magnetic resonance (MAS NMR), where no reaction is observed. A comparison mixture of NaO₂ and graphitic carbon is also monitored, and a distinct reaction to form Na₂CO₃ is seen.

Porous, carbon-free, Ti₄O₇ electrodes are fabricated and tested in Swagelok style Na-air cells. Cells are discharged, halted, stripped, and have their cathodes removed to examine the electrochemical products formed. ²³Na MAS NMR is used at spinning speeds of up to 40 kHz and at fields of up to 19.9 T in tandem with the multiple quantum MAS (MQMAS) pulse sequence to give optimal separation of the complex electrochemical mixture. Both NaO₂ and Na₂O₂ are detected by form on the Ti₄O₇ cathode, and are found to be relatively stable over time when compared to the carbon-based system. Continuous wave, x-band, electron paramagnetic resonance (EPR) is also used to characterise NABs. Both NaO₂ and Ti₄O₇ resonances are visible in the EPR spectrum of discharged cathodes. The EPR signature
of Ti₄O₇ is measured before and after an oxidative stress test where the cathode is kept at 4 V (Na/Na⁺) in an oxygen atmosphere to mimic the most extreme conditions faced in the NAB, and little to no change is observed. The long-term cycle life of Ti₄O₇ NABs is tested by monitoring capacity retention of cells over 50 charge/discharge cycles with varying cut-off voltage windows. Measurable improvement is seen over the carbon system. Ti₄O₇ is shown to be a highly stable cathode material for NAB systems, while tandem ²³Na MAS NMR and EPR are proven to be an encompassing toolkit for the disentanglement of the complex chemistries found in metal-air batteries.


**EN02.14.48**

**Thermal Stability in High Nickel Layered Oxides**

Carol M. Kaplan, Hui Zhou, Anshika Goel, Natasha Chernova and M. Stanley Whittingham; Binghamton University, United States

Layered oxides are among one of the leading cathodes for lithium ion batteries due to their high energy density. They are one of the more attractive options for use in electric vehicles which makes their safety a top priority. It is well known that layered oxides produce oxygen upon heating which can lead to exothermic reactions within the cell aiding in thermal runaway. This presentation will discuss the thermal stability of the high nickel layered oxides LiₓNi₀.₈Mn₀.₁Co₀.₁O₂ (NMC) and LiₓNi₀.₈Co₀.₁₅Al₀.₀₅O₂ (NCA) in different charged states. The effect of composition of the layered oxides as well as their interaction with the electrolyte components will be explored in order to isolate the cause of the thermal output present upon heating. Differential scanning calorimetry (DSC) was used to study the exothermic reaction between the cathode materials and the electrolyte. To further understand these reactions, the individual components of both the cathode and the electrolyte were studied to identify what interactions were causing the heat release. X-ray diffraction (XRD) was used after DSC to identify products of the reaction to gain better insight on what is going on within the cell. While high nickel content in layered oxides is known to destabilize the material, the onset temperatures for these reactions is not below 200°C and the total heat released does not exceed 1400 J/g. By using a more stable electrolyte, the total heat released drops to roughly 400 J/g.

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**EN02.14.49**

**Garnet-Rich Composite Solid Electrolytes for Dendrite-Free, High-Rate, Solid-State Lithium-Metal Batteries**

Chaoyi Yan; North Carolina State University, United States

Composite solid electrolytes (CSEs), which are composed of inorganic fillers and organic polymers, show improved safety and suppressed lithium dendrite growth in Li-metal batteries, as compared to flammable liquid electrolytes. However, the performance of current CSEs is limited by the agglomeration effect, with low content of inorganic Li⁺-conducting fillers and ineffective Li⁺ transport between the inorganic fillers and the polymer matrix. We therefore set out to design a CSE toward high-performance, solid-state Li-metal batteries based mainly on inorganic Li-conductors, with supplementary polymer content for improving interfacial contact. A new type of CSE with enriched inorganic Li-conductors and well-percolated network was introduced utilizing one dimensional L₆₂.₉₃La₃Al₀.₂₄Zr₂O₁₂ (LLAZO) nanofibers to provide long-range and fast Li⁺ conduction. Additionally, acrylate functional groups (CH₂=CHCOO⁻) were covalently bonded on the surface of LLAZO nanofibers, which enabled the chemical grafting of functional monomers directly from the nanofiber surfaces. In the resultant composite electrolytes, silane-decorated LLAZO nanofibers (s@LLAZO nanofibers) were cross-linked along with polymerization of monomers. This controlled fabrication of composite structures led to a well-percolated network, forming continuous, 3-dimensional, and fast Li⁺ conductive pathways within the CSE. The silane coupling agent significantly prevented the inhomogeneous distribution of inorganic Li⁺ conductors and enhanced the interaction between the LLAZO nanofibers and the polymer matrix, which improved the mechanical strength of CSE, favored the amorphization of polymer, and reduced the activation energy of Li⁺ conduction between the filler and polymer.
Consequently, the silane coupling agent successfully eliminated the agglomeration effect, and the introduced CSEs (LLAZO nanofibers > 60 wt.%) exhibited higher ionic conductivity, larger lithium transference number, and wider electrochemical stability window. Excellent cycling stability and extraordinarily high rate capability (up to 10C) was demonstrated in the all-solid-state Li-metal batteries with LiFePO4 and high-voltage Li[Ni0.3Mn0.3Co0.4]O2 cathodes at ambient temperature. This novel design of CSEs with s@LLAZO nanofibers paves the way for a new generation of improved functioning all-solid-state Li-metal batteries.

**EN02.14.50**

**Tunable D-spacing of Ammonium Vanadium Bronze for High-Performance Rechargeable Aqueous Zinc-Ion Batteries** Jianwei Li; University College London, United Kingdom

Driven by safety concern and cost-efficient demand of the commercial market, Rechargeable aqueous zinc-ion batteries (ZIBs) has drawn many attentions in last few years due to high energy/powder hubs and eco-friendly features for facile massive production and large-scale applications. However, considering the highly reversible and superior capacity of ZIBs, the researches of vanadium-based cathode materials are still in its infancy and suffering from a deficient investigation of zinc ion diffusion kinetics and deep insight of intercalation mechanism within a crystallographic configuration. Herein, we elaborately fabricated tunable d-spacing expansion of ammonium vanadium oxide (NVO) with various amount of ammonium ions as cathode material in ZIBs. The hydrogen bond of NH4+ within interlayer of V2O5 framework possesses superior behaviour on zinc ion diffusion as “lubricant” like water molecule which is highly different from metal pre-intercalated V2O5 in previous reports. Thus, the as-obtained NVO presented 252 mAh g\(^{-1}\) at a high current density of 10A g\(^{-1}\) with excellent retention of 95% after 1000 cycles. The electrochemical reaction kinetics, structure evolutions and zinc storage mechanism are discussed in detail. This work may stimulate future exploitation of vanadium-based cathodes in ZIBs and bring more insights into the mechanisms of zinc-ion storage.

**EN02.14.52**

**A Safe and Fast-Charging Lithium-Ion Battery Anode Using MXene Supported Li3VO4** Nian Liu and Haochen Yang; Georgia Institute of Technology, United States

During fast charging, the commonly used Li-ion battery anode material, graphite, has a significant shortcoming: its discharge potential is too low to guarantee the safety of batteries. Li3VO4 (LVO), an alternative anode material, has a safe discharge potential window of 0.5 V to 1.0 V vs. Li+/Li and high theoretical capacity (~394 mAh/g). However, the poor conductivity of LVO (~10\(^{-10}\) S/m) constrains its further applications. This presentation will show our recent efforts embedding LVO uniformly onto a multilayered material, Ti3C2Tx MXene, by a sol–gel method. The Ti3C2Tx MXene nanolayers with high electrical conductivity (2.4 × 10\(^5\) S/m) served as a scaffold to load LVO nanoparticles. The LVO/Ti3C2Tx MXene composite exhibited remarkable electrochemical performance in terms of rate capability and long-term cycle stability in comparison with bare LVO and commercial graphite anodes. The LVO/Ti3C2Tx MXene composite delivered an initial capacity of ~187 mAh/g and 146 mAh/g after 1000 cycles at 5C, compared to bare LVO (an initial capacity of ~41 mAh/g and ~40 mAh/g after 1000 cycles at 5C) and graphite (~71 mAh/g after 1000 cycles at 5C). We believe this work opens new possibilities of anode materials for safe and fast-charging Li-ion batteries. This presentation is based on our recent publication: *J. Mater. Chem. A*, 2019, 7, 11250-11256

**https://doi.org/10.1039/C9TA02037C**
A novel and facile polymer-assisted chemical solution (PACS) method is successfully developed for the synthesis of LiMn$_2$O$_4$, LiMn$_{1.5}$Ni$_{0.5}$O$_4$ and LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (NCM523) with unique morphology and nanoparticle nature as cathodes for lithium-ion batteries. PACS uses polymers polyethyleneimine and ethylenediaminetetraacetic acid to bind with metal salts, such as metal nitrate. PACS is unique compared with other solution methods in that water-soluble polymers bind with the metal ions to prevent them from hydrolysis. Therefore, these metal-polymer solutions are stable for years. The compositions and particle sizes of cathode materials can be tuned by simple controlling different heating temperatures from metal-polymer solutions. At low heating temperature of 550 °C, LiMn$_{2-x}$Ni$_x$O$_4$ nanoparticles are covered by a thin layer of carbon from in situ incomplete depolymerization of the polymers. The LiMn$_{2-x}$Ni$_x$O$_4$ cathode exhibited better durable rate capability with 100% of the capacity retained (∼100 mAhg$^{-1}$) after 400 cycles at 10 C rate. However, for NCM materials, higher calcination temperature of above 800 °C is necessary for layered structure formation with a lower degree of Ni/Li cation mixing thus for better electrochemical performance. As compared with the NCM prepared at 800 °C, the sample heated at 900 °C exhibits a higher initial discharge specific capacity of 189 mAh g$^{-1}$ being charged to 4.5 V at a current rate of 0.05 C, and better cyclability at 4.3 V cutoff voltage and a current density of 1 C.

8:30 AM EN02.15.02
**Short-Range Order and Li Transport in Fluorinated Disordered Rocksalt Cathode Materials** Bin Ouyang$^1$, Nongnuch Artrith$^2$, Zhengyan Lun$^1$, Zinab Jadidi$^1$, Daniil Kitchaev$^3$, Huwen Ji$^1$, Alexander S. Urban$^2$ and Gerbrand Ceder$^1$; $^1$University of California, Berkeley, United States; $^2$Columbia University, United States; $^3$University of California, Santa Barbara, United States

The discovery of Li-excess disordered rocksalt (DRX) materials has opened up a diversified chemical space for the development of low-cost high-energy-density cathodes. However, because of the Li excess, DRX oxide materials typically suffer from unsatisfactory capacity retention due to irreversible oxygen loss, a problem which can be mitigated by fluorination as it lowers the average cation charge states and makes more transition metal capacity available. In this work, we use ab-initio models to understand the short-range order and Li transport in fluorinated DRX (F-DRX) across different cation chemistries and fluorine contents. We find that the percolation of Li in F-DRX is governed by both Li-F attractions and cation mixing. To provide rational design principles for F-DRX, a synthesis map that combines expected electronic capacity, 0-TM percolation, and synthetic accessibility of fluorinated DRX materials is presented. Finally, we experimentally verify the fluorination effect in DRX materials and propose several promising F-DRX systems that combine high capacity and good cycle life.

8:45 AM EN02.15.03
**Developing High-Ni Layered Cathodes for Li-Ion Batteries through Synthesis by Design** Feng Wang, Mingjian Zhang, Chong Yin and Jianming Bai; Brookhaven National Laboratory, United States

There has been considerable interest in developing low-cost, high-energy electrodes for batteries. However, synthesizing materials with the desired structure and properties has proven difficult due to the complexity of the reaction involved in chemical synthesis. Additional challenge comes from the fact that synthesis is often undertaken under non-equilibrium conditions and, hence, the process is hard to be predicted by theoretical computations. In situ, real-time probing of synthesis reaction allows for identification of intermediates and determination of thermodynamic/kinetic parameters governing kinetic reaction pathways, thereby enabling synthetic design of materials with desired structure and properties. In this presentation, we will report our recent results from in situ probing and synthetic control of local structural ordering during synthesis of high-Ni layered LiNi$_{1-x}$Mn$_x$Co$_2$O$_4$ ($x>0.7$). Findings from this study, along with its implication to designing surface-stabilized high-Ni layered oxide cathodes, will be discussed.

9:00 AM EN02.15.04
**Cycling and Structural Evolution of KNb$_3$O$_7$ and NaNb$_3$O$_7$ as Li-Ion Battery Electrode Materials** Megan M. Butala$^{1,2}$ and Igor Levin$^2$; $^1$University of Florida, United States; $^2$National Institute of Standards & Technology, United States

As batteries are employed in larger numbers and for increasingly diverse applications, there is interest in alternative electrode materials, especially with improved safety, availability, and cost relative to the layered materials employed in commercial Li-ion batteries (LIBs). Early transition-metal oxides, one class of promising alternatives, have
demonstrated compelling performance for high-rate LIBs and even multivalent-ion-based energy storage. However, as this family of compounds is chemically and structurally distinct from the layered and olivine materials employed in commercial LIB electrodes, we are just beginning to understand the origins of their promising charge storage capabilities.

To bring new understanding to this class of materials and how they store charge, we analyze the cycling and structural evolution of KNb$_3$O$_8$ and related NaNb$_3$O$_8$, which comprise complex layers of edge- and corner-sharing [NbO$_6$] octahedra. On the first discharge, these materials react with 2 moles of Li per mole of Nb, resulting in relatively disordered products. Only half of the first discharge capacity is reversible on charge, yet long-range order is recovered and the structures of charge products resemble the initial materials. Using ex situ and operando XRD and PDF, we describe the evolution of the structure, focusing on changes in the [NbO$_6$] layers during cycling and the role of the counteration.

Our findings on how these materials store charge and their unexpected recovery of long-range order can inform the selection and design of new materials for energy storage, with relevance for early transition-metal oxides as well as conversion electrodes.

9:15 AM *EN02.15.05
Single Crystal Ni-Rich Cathode for Advanced Li-Ion Batteries Jie Xiao; Pacific Northwest National Lab, United States

Lithium ion battery (LIB) has been intensively investigated in recent years for vehicle electrification and its cost has been significantly reduced. For the long-range electrical vehicles, however, the cell energy and durability still need to be further improved to go beyond that of conventional Li-ion batteries. Among different cathode materials, Ni-rich NMC (LiNi$_{1-x}$Mn$_{x}$Co$_{1-x-y}$O$_2$, x $\geq$ 0.6) has a specific capacity greater than 200 mAh g$^{-1}$, high operating voltage (ca. 3.8 V) and low cost, and is therefore deemed as one of the most promising cathode candidates for next-generation Li-ion batteries.

Unlocking the full potentials of Ni-rich NMC cathodes demands to push the limit of this class of materials to achieve good cycling stability at elevated voltages to extract maximum reversible capacity, prevent Ni-catalyzed electrolyte decomposition, structural degradation and cracking during cycling, improve thermal stability and reduce moisture sensitivity, as well as overcome practical limitations to maximize the accessible capacity in the full cells. Although fundamental understandings of Ni-rich cathode have been deepened, an effective method to address the cathode problems is still lacking and even the failure mechanism of Ni-rich cathode is arguable. There is still a significant knowledge gap between materials research and cell-level need of the materials properties. For example, although many attractive attributes have been displayed from nano-sized cathode materials, the direction towards higher energy cathode is the opposite i.e., micron-sized large particles with high tap density and press density when being calendared into electrodes. The desired particle size, morphology and tap density of Ni-rich NMC that will benefit the porosity control and the electrochemical performances of the thick electrodes are not well studied from the synthesis point of view. The synthesis approach that help to extract greater than 210 mAh/g capacity from Ni-rich NMC without increasing the cutoff voltage is also critical and a necessity in improving the energy of next-generation Li-ion batteries which are, however, not well studied.

This talk will discuss the synthesis, understanding and implementation of single crystal Ni-rich cathode in lithium ion batteries. While polycrystalline is the common form of traditional LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, single crystal is preferred when Ni content becomes dominant (>70%) in the cathode material. Single crystal Ni-rich cathode may have reduced gas evolution, reduced sensitivity to moisture, lower surface area and increased tap density, all of which will play a key role for high performance advanced Li-ion batteries.

9:45 AM BREAK
Can a Glassy Interface Suppress Li Filaments in Ceramic Solid-State Electrolytes?  
Andrew S. Westover and Nancy J. Dudney; Oak Ridge National Laboratory, United States

Electric vehicles, consumer electronics, and the possibility of electric aviation demand energy storage with extremely high specific and volumetric energy densities. Incorporating Li metal as the anode in a Li ion battery to make Li metal batteries has the potential to fill this demand. To integrate Li metal into a battery, an electrolyte that is chemically stable with Li, and can suppress Li dendrites is required. Some of the most promising electrolytes are the ceramic electrolyte which have good ionic conductivity and electrochemical stability but are particularly prone to penetration by Li filaments. The glassy electrolyte Lipon on the other hand has a moderate ionic conductivity but can completely suppress Li filaments. The aim of this research is to answer the question: if ceramic electrolytes had a glassy interface like Lipon could they suppress Li dendrites at high current densities? To test this hypothesis, we deposited a Lipon layer on the surface of lithium lanthanum zirconium oxide (LLZO) and lithium aluminum titanium phosphate (LATP) ceramic electrolytes and cycled Li metal at increasing current densities. The answer to this question gives us great insight into the origin of Li filament formation and what is needed to suppress them in solid-state electrolytes with high ionic conductivities.

Inorganic Lithium Conductors for All-Solid-State Batteries—The Link between Crystal Chemistry, Transport Properties, Electrochemical and Chemical Stabilities in the Li2S - P2S5 System  
Omer U. Kudu1,2, Theodosios Famprikis1,3,4, Marc David Braida5, Thierry Le-Mercier5, Benoit Fleutot1,2 and Christian Masquelier1,3,2; 1Université de Picardie Jules Verne, France; 2Réseau sur le Stockage Électrochimique de l’Énergie (RS2E), France; 3ALISTORE European Research Institute, France; 4University of Bath, United Kingdom; 5SOLVAY R&I, France

Requirements for higher energy density and better safety in demanding applications such as grid storage and electric vehicles call for next-generation battery technologies. All Solid State Batteries (ASSBs) might enhance the safety and the energy density of conventional LIBs by removing flammable organic electrolytes and allowing the use of metallic lithium anodes [1]. In this context, solid sulfide-based solid electrolytes have drawn a lot of attention owing to their high ionic conductivities (10^-2 – 10^-4 Scm^-1 at RT) [2–5]. Few compositions in the Li2S – P2S5 binary system, particularly Li3PS4 and Li7P3S11, are being heavily investigated as glass-ceramic materials synthesized by mechanochemistry and subsequent annealing [4]. However, varying ball-milling parameters and annealing procedures were rarely systematically investigated [5].

In this work, we will report on the synthesis of various materials in the Li2S – P2S5 system (Li3PS4, Li7P3S11, Li2P2S6, …) via a systematic synthesis approach: the individual effects of pre-selected ball-milling and subsequent annealing parameters will be presented, as characterized in details through X-ray and neutron diffraction, and various techniques of spectroscopy such as Raman, NMR and complex impedance. The latter technique is quite powerful to discriminate between crystalline and amorphous contributions to the total ionic conductivity, which may be strongly affected as well by the relative amounts of local units such as P2S6^4-, P2S7^4- and PS4^3- in the material. Additionally, the chemical stabilities in air and the electrochemical stability windows of the aforementioned materials were assessed with the help of specialized experimental setups. These results will be comparatively presented along with the discussion of the link between the electrochemical and the chemical stabilities and the structure.

The vast majority of solid-state electrolyte (SSE) materials are unstable in contact with lithium metal, and (electro)chemical reactions between SSEs and lithium result in the formation of an interphase region [1]. Understanding the growth kinetics and chemo-mechanical consequences of interphase formation is key for controlling solid-state interfaces, which may enable the use of a wider variety of SSE materials within lithium metal batteries. Here, we investigate NASICON-structured L1+xAlxGe2-x(PO4)3 (LAGP), as well as sulfide-based SSEs. For LAGP, multi-modal \textit{in situ} investigation of interfacial reactions combined with electrochemical experiments reveal how the formation of the interphase is linked to cell failure. \textit{In situ} transmission electron microscopy (TEM) shows that the reaction of LAGP with lithium is similar to a conversion reaction, in which lithium insertion causes amorphization and volume expansion of ~130\% [2]. The interphase is a mixed ionic-electronic conductor, resulting in continuous growth. \textit{In situ} X-ray tomography experiments of operating LAGP-based cells reveal that the growth of the interphase causes fracture of the SSE, and quantification of the crack network shows that the extent of fracture with time is directly correlated to impedance increases within the cell [3]. Finite-element analysis is used to model stress evolution during interphase formation, and the initial fracture locations predicted from modeling correspond well to experimental observations. Interestingly, we have found that interphase growth trajectories can be modulated through the deposition of interfacial protection layers. Controlling the morphology of the interphase with protection layers results in the ability to extend cycling stability of symmetric cells from ~30 hours with unprotected SSEs to >1000 hours with protected materials. Overall, these results provide fundamental insight into interfacial transformations in SSEs, and they show that control over interfacial transformation processes could enable a wider variety of materials to be used in solid-state lithium metal batteries.

This work was supported by the Nanostructures for Electrical Energy Storage (NEES) center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award number DESC0001160.

11:00 AM EN02.16.05
First Principles Modelling of Defect Chemistry and Electronic Properties of Lithium Garnets Alexander Squires¹, Daniel W. Davies², David O. Scanlon¹,⁴,⁵, Aron Walsh²,⁶,⁵ and Benjamin J. Morgan¹,⁵; ¹University of Bath, United Kingdom; ²Imperial College London, United Kingdom; ³University College London, United Kingdom; ⁴Diamond Light Source, United Kingdom; ⁵The Faraday Institution, United Kingdom; ⁶Yonsei University, Korea (the Republic of)

One of the key challenges in the development of high energy-density solid-state lithium batteries is the development of an electrolyte that is chemically stable with respect to a lithium metal anode. Lithium-rich garnets have been shown to possess the required electrochemical stability window to interface with lithium during battery cycling and consequently are highly promising candidate solid-state battery electrolytes [1,2]. Despite this, garnet-based batteries are yet to achieve commercialisation. Questions remain around how best to optimise lithium conductivity in the garnet framework to make them truly competitive with conventional liquid electrolytes, and how to prevent the formation and propagation of lithium dendrites, which cause batteries to fail by short circuit.

A number of recent works have suggested that defect chemistry of lithium garnets is non-trivial, with experimental evidence for the presence of oxygen vacancies in the as-synthesised materials [2]—This raises questions about both the native defect chemistry, and how native defect chemistry interacts with extrinsic dopants used to control lithium content in an attempt to optimise conductivity. Other work has suggested that electronic conductivity in lithium garnets is the reason behind ruinous dendrite formation [3]; in this work it was proposed that electronic conductivity facilitates the reduction of lithium within the garnet structure, causing dendrites to nucleate within the electrolyte, rather than propagating out from the anode. As the defect and electrical properties of semiconductors are inextricably linked, we have used first principles techniques to investigate both in this work, in an attempt to determine to what extent these can be controlled by synthetic design.

We have used hybrid density functional theory calculations to determine defect formation energies in the prototypical lithium garnet Li₇La₃Zr₂O₁₂ (LLZO). We use these defect formation energies to solve for grand canonical defect and carrier concentrations self-consistently as a function of chemical growth conditions [4].

Analysis of these results suggests that the defect chemistry of LLZO is indeed more complex than previously suggested. We report potential synthesis regimes in which the charge introduced by donor doping to control lithium content is compensated by the formation of LiZr anti-sites as opposed to the expected lithium vacancy [6]. Calculation of electronic charge carrier concentrations, in addition to further first principles analysis of dielectric response and charge carrier effective mass, allow for us to estimate electronic conductivities using the Feynman polaron mobility model [7]. These results provide insight into the nature of electronic conductivity and the extent to which synthetic control can be used to minimise electronic conductivity, finding that under the range of temperatures LLZO is typically synthesised under, charge carrier concentrations can vary by 6 orders of magnitude. This work may aid in understanding what synthesis regimes reduce electronic conductivity, with the potential consequence of inhibiting dendrite formation.

References

11:15 AM EN02.16.06
Phonon Contributions to Ionic Transport—A Guide to Achieving High Performance Solid Electrolytes
The application of solid-state ionic conductors is vast, ranging from next generation solid-state Li-ion batteries, to solid oxide fuel cells and different families of sensors. However, the realization of these applications is mostly impeded by the slow diffusion of ions in the lattice. One of the factors that directly impact the conduction of ions in solid materials is the vibration of atoms in the lattice. In the classical theory of diffusion, the effect of these vibrations only enters the formulations through a set of proxy parameters such as the attempt frequency. Such oversimplification of the vibrational effects neglects all the individual contribution that each phonon/mode of vibration can have on the hopping of ions between different lattice sites. In this study, we introduce a formalism that allows us to better understand the effect of individual phonons on the diffusion of ions through the lattice. Specifically, after calculating the modes of vibration for different configurations of the system using lattice dynamics calculations, we determine their contribution to the ionic diffusion using (i) molecular dynamics simulations and (ii) Nudge Elastic Band calculations. Our obtained results on the example structure of Ge-doped Li3PO4 revealed that >90% of the Li-ion diffusion in the lattice originates from the vibrational modes with frequencies in the 10-15THz region. Analyzing the distribution of eigen-vectors for these contributing modes shows that the P atom in all these vibrations is frozen and does not participate in the vibrations. Such a high resolution understanding of the contribution of phonons to the ionic conduction opens new gates for (i) improving the performance of the existing electrolytes by engineering the vibrations of phonons in their respective structures, and (ii) searching for better performing solid-state ionic conductors, using methods such as high-throughput computational approaches.

Can Battery Material Morphology be Controlled by a Guided Synthesis Approach? Pallab Barai, Juan C. Garcia, Tim Fister, Hakim Iddir and Venkat Srinivasan; Argonne National Laboratory, United States

New battery materials hold the key for an electrified future by enabling electrification of transportation and integration of storage on the electric grid. While there is a robust and growing effort to accelerate the discovery of new materials, the next frontier is identifying synthesis pathways to ensure that these materials can be made. Recently, new approaches focused on precision synthesis have gained a lot of attention in the materials field, including battery materials. While the focus of much of these efforts is around developing predictive routes to synthesis materials of a specific crystal structure, it has been clear for decades that the morphology of the material plays an equally crucial role in its behavior. An example is the layered LiNi0.5Mn1.5CoO2(NMC) layered oxide. In these materials the high reactivity of the cathode with respect to the electrolyte remains a key challenge that impedes their performance. It is well-established that the reactivity of these materials depends strongly on crystal facet, suggesting that shielding some primary particle facets from solution could be critical. Cathode secondary particle porosity can aid with fast-charging but also expose greater surface area to reaction. Graded secondary particles, wherein the outer regions are designed to be less reactive while the interiors are designed to be more energetic, have been advanced as an approach, but ensuring that the right gradation is achieved and the right structure is exposed to the electrolyte requires careful morphology control. Finally, while coatings (e.g., Al2O3) are known to protect the cathode surface, their coverage tends to differ on different facets. Controlling the reactivity of these materials requires control over the morphology of the cathode material in addition to the structure. Therefore, synthesis routes need to be tuned to achieve the right morphology, in addition to obtaining the right crystal structure.

Over the last two years we have been developing a methodology to link synthesis conditions to particle morphology with the aim of using predictive approaches to guide synthesis. The focus of the research has been around (i) linking synthesis conditions to morphology during the co-precipitation of the NMC-hydroxide precursor and the sintering to the lithiated oxide and (ii) linking the sintering of Li7La3Zr2O12(LLZO) solid electrolytes to the density of the final
structure. The methodology involves simulations at multiple scales to bring focus to preferred crystal orientation during synthesis, growth of primary and secondary cathode particles, understanding grain growth and grain boundary movement, and the formation of dense structures as a function of process conditions. The models are complemented with in situ synchrotron x-ray methods and other techniques to provide physical insights and use as comparisons to the models.

This talk to summarize the approach, and describe the physical insights that have been gained in these two material classes. Further, the talk will describe the various opportunities in this emerging new area in battery synthesis.

2:00 PM OPEN DISCUSSION

2:15 PM EN02.17.03
Investigation of the Transport in Li(Ni1/3Co1/3Mn1/3)O2 as Cathode Active Material in a Single Secondary Particle Set-Up Markus S. Friedrich, Simon Burkhardt, Janis K. Eckhardt, Matthias T. Elm and Peter J. Klar; Justus Liebig University Giessen, Germany

Lithium ion batteries (LIBs) are today's state-of-the-art power supplies for portable electronic devices as well as for electrical and hybrid vehicles. In addition, LIBs are a promising technology to store the excess energy generated from renewable energy sources which would otherwise be wasted. To meet the requirements of such applications, an optimization of the overall performance, i.e. life-time, cyclability, and energy as well as power density, of such batteries is crucial [1]. A deeper understanding of the transport in the active material used in the electrodes of the LIBs is key to such optimizations. State-of-the-art LIBs usually contain layered structured transition metal oxides, such as Li(Ni0.5Co0.5Mn1−x−y)O2 (NCM), as cathode active material (CAM) [2] [3]. To investigate the properties of such CAMs conventionally composite electrodes are prepared. In this composite electrodes micrometer sized spherical secondary particles (diameter of 10 to 30 µm) of the CAM, built from a complex porous network of nanometer sized single crystalline primary particles, are embedded in a network of organic binder and conductive agents. These additives might influence or superpose the properties of the pure active material [4].

To investigate the transport properties in the pristine active material we developed a technique that allows to perform electrochemical measurements on single particles of CAMs. The investigated NCM material was of the composition Li(Ni1/3Co1/3Mn1/3)O2 (NCM111). The particles were arranged in trap holes, formed via photolithographical structuring a photosist, on top of a noble metal coated substrate. The setup, on one hand, allowed us to perform experiments with ion-blocking electrodes [5] and, on the other hand, to assemble Lithium ion batteries, that contain a single secondary particle of NCM as cathode active material (SCAMP-LIB). We performed cycling experiments, cyclic voltammetry, and impedance spectroscopy on single secondary particles and agglomerates of NCM111 secondary particles. To resolve the influence of the measurement set-up systematically, different set-ups have been investigated. We found clear evidence, that the secondary particle’s diameter, and therefore its porosity, has an influence on the impedance of the cell system. Furthermore, it was possible to estimate the diffusion coefficient of Lithium ions in the bulk NCM111 during delithiation. This estimated diffusion coefficient was a few orders of magnitude lower than those reported by other groups [6][7]. We found clear evidence, that the investigated material undergoes severe surface degradation during cyclization.

Nevertheless, the presented method is a promising way to study the transport in pristine CAMs. The technique can be further improved by the application of solid electrolytes in the cell system or a controlled arrangement of many single secondary particles to achieve a better model of a real electrode.

References:

2:30 PM *EN02.17.04
New Power Technologies for Venus Atmospheric and Surface Missions Ratnakumar V. Bugga1, John-Paul Jones1, Michael Pauken1, Keith Billings1, Channing Ahn1, Brent T. Fultz1, Kerry Nock2, Abhijit Shevade1, Dharmesh Bhakta1, Eric Raub1 and James Cutts1; 1California Institute of Technology, United States; 2Global
**Aerospace Corporation, United States; 3Eagle Picher Technologies, United States**

*In-situ* exploration of Venus is seriously hampered by its severe environment, which is benign (28°C) at an altitude of 55 km, but rapidly becoming more hostile at lower altitudes, with temperature increasing initially at ~10°C/km eventually to reach ~465°C and the pressure attaining 90 bars at the surface. These challenging conditions have limited Venus in-situ exploration missions to high altitude balloons at 55 km (above the clouds) that lasted for 48 h, or even shorter duration of 2h for surface missions, even when the batteries were enclosed in thermal chamber. Both these types of missions were implemented using primary batteries. There is a need for more long-duration in-situ missions for a better understanding of the Venus atmosphere across the cloud layers and below, and even to the surface, as recommended by the Venus Exploration Analysis Group (VEXAG). Two types of mission concepts, i.e., i) long-duration variable-altitude balloons with extended range below the clouds, and ii) landers with lifetimes of a few days have gained particular interest. This talk will describe new power technology for a variable altitude balloon (VAB) that we have been developing under NASA-NIAC (NASA Innovative and Advanced Concepts) program for sustained Venus atmospheric exploration. The probe mission concept utilizes: i) Photovoltaics (PV), regenerative solid oxide fuel (SOFC), hydrogen storage bed for on-demand storage or release of hydrogen, and a balloon filled with hydrogen and with hydrogen buoyancy-based altitude control system. This novel architecture enables generation of fuel from in-situ resources at high altitudes, power at low altitudes, and provides transport gas for the balloon. In addition to this VAB, we have been developing high-temperature primary batteries for Venus surface missions under NASA’s HOTTech program. These batteries are based on lithium alloy (e.g., Li-Al) anodes, molten salt electrolytes based on binary/ternary mixtures of alkali metal halides, cathodes consisting of transition metal sulfides and designs similar to the aerospace thermal batteries.

**3:00 PM BREAK**

SESSION EN02.18: Scale-Up and Manufacture  
Session Chair: David Scanlon  
Thursday Afternoon, December 5, 2019  
Sheraton, 2nd Floor, Grand Ballroom

**3:30 PM *EN02.18.01**  
Transitioning Garnet Li-Ion Electrolyte into Manufacturable Li Metal Solid-State Batteries  
Jeff Sakamoto1,1, Regina García-Mendez1, Michael Wang1 and Arushi Gupta2; 1University of Michigan, United States; 2University of Michigan–Ann Arbor, United States

There is tremendous interest in making the next super battery, but state-of-the-art Li-ion technology works well and has inertia in several commercial markets. Supplanting Li-ion will be difficult. Recent breakthroughs in Li metal solid-state electrolytes could enable a new class of non-combustible solid-state batteries (SSB) delivering twice the energy density (1,200 Wh/l) compared to Li-ion. Garnet-type ceramic electrolyte with the nominal formula Li7La3Zr2O12 (LLZO) satisfies many of the criteria necessary to enable Li metal electrodes. However, technological and manufacturing challenges remain. The discussion will consist of recent milestones and attempts to bridge knowledge gaps to include:

- Stability and kinetics of the Li metal-LLZO interface
- Stability and kinetics of the catholyte-LLZO interface
- Manufacturing and scale-up of thin film ceramic constructs and cells.

Despite the challenges, SSB technology is rapidly progressing. Multi-disciplinary research in the fields of materials science, solid-state electrochemistry, and solid-state mechanics will play an important role in determining if SSB will make the lab-to-market transition.

**4:00 PM EN02.18.02**  
Integration of Porous Semiconductor Nanocomposites in Advanced Energy Storage Systems—An Industrial Compatible Synthesis Process  
Arthur Dupuy1, Aude Roland2, Stéphanie Sauze3, Mohammad Reza Azizyan1,
The extension of Internet connectivity and interrelating physical devices, known as Internet of Things (IoT), has become an increasingly growing topic of research over the past few years. Because of rapid progresses in this filed, it is expected that successful implementation of IoT will revolutionize everyday human life within the coming decades. Therefore, it has become inevitably necessary to redesign the current power supplies to integrate them directly into the production line [1]. This has motivated many researchers for enhancing solid-state and on-chip storage systems, such as supercapacitor and lithium-ion battery [2]. In this respect, the significant specific capacity (4200 mAh/g) and high lithium-ion diffusion coefficient of silicon (Si) made it an attractive candidate for storage applications. However, it has been extensively discussed and proved that Si suffers from a low life cycle and large volume expansion. Nanostructuring of Si has been one of the viable solutions to reduce the stress during lithiation. As a matter of fact, porous silicon has been a favourable candidate as on-chip anode for supercapacitor [3], high power density [4] and high energy density device [5]. Although downsizing the active material can prevent volume expansion stress, it also increases specific surface, leading to formation of solid electrolyte interface, which is the origin of irreversible capacity. On this subject, functionalization of the semiconductor surface by carbon has been one of the most compelling alternatives for limiting SEI formation and the first cycle irreversible capacity. Compared to silicon, germanium (Ge) has better electrons and holes mobilities, faster Li-ion diffusion rate, lower charge/discharge potential, and an isotropic volume expansion less significant than silicon during lithiation process. Similar to porous silicon, macro- and mesoporous Ge anodes have shown outstanding performances, but they have been produced by an unscalable and expensive process; the thermal reduction synthesis. In parallel, progresses in the electrochemical etching of Ge provided conditions for the synthesis of low-cost and scalable porous layers [6]. Concerning graphene functionalization based on CVD technique, Ge offers a good catalytic surface, because of the low miscibility of carbon into Ge, to grow a graphene-like coating with higher quality compares to silicon. In this study, we have investigated a mesoporous Ge on-chip anode that was synthesized by electrochemical etching, and we have compared the improvement of the electrode life cycle and rate capability once the active material was coated with graphene-like layer grown by CVD. A coulombic efficiency above 98% was achieved and 1000 mAh/g capacity was reached during over 400 cycles for the graphene-coated porous Ge nanocomposite on-chip anode. In this presentation, we will discuss the crucial parameters and experimental conditions that allowed us to achieve such high-performance devices and will present a new type of anode which can reach a wide range of power density value.

improve the life of Li metal anodes, and that these properties are synergistic.

The final structure for use as a Li metal coating is a dynamic, single-ion-conducting network (DSN) with room temperature Li ion conductivity of $3.5 \times 10^{-5}$ S cm$^{-1}$. When cut, the material self-heals at room temperature in 12 hours. Molecular dynamics simulations combined with DFT calculations show that the labile bonding between the anionic centers and the coordination ligands impart the dynamic self-healability and high ionic conductivity. When used as a coating on Li metal, 1 mAh cm$^{-2}$ of lithium can be reversibly plated and stripped at rate of 0.5 mA cm$^{-2}$ for a record high 300 cycles with a high coulombic efficiency of 96.5%. In contrast to other lithium coatings, synthesis of DSN emerges from a facile, scalable, one-pot process with only hydrogen gas as the by-product. Furthermore, the coating can be directly applied to Li metal via a dip-coating process at a cost of only 0.02 $ cm^{-2}$. Using this scalable approach, a DSN-coated Li metal anode was used in a high-voltage NMC-532 full-cell with all commercial components. The coated Li metal anodes show dramatically increased cycle life (160+ cycles) over uncoated Li (<100 cycles). The rational design of these scalable coordination polymers offers a promising approach to enable next-generation batteries with Li metal anodes.

4:30 PM EN02.18.04
Time-Temperature-Transformation-Conductivity (TTTC) Diagrams for Li-Garnet Films from Solution Processing – Giving Manufacturing Guidelines and Insights on Phase Stabilization
Yuntong Zhu1, Zachary D. Hood1, Won Seok Chang2, Lincoln J. Miara3 and Jennifer L. Rupp1; 1Massachusetts Institute of Technology, United States; 2Samsung Advanced Institute of Technology, Korea (the Republic of); 3Samsung Research America, United States

Li-garnets have been considered as the candidate ionic conductors for multiple new technological applications, including all-solid-state batteries1 and very recently, electrochemical gas sensors,2 owing to their wide electrochemical stability window, high room temperature Li-ion conductivity, and good thermal stability. Very recently, research advancements have demonstrated the possibility of transferring Li-garnets to their thin-film forms with various crystalline and poly-amorphous states,3 giving room for researchers to redesign the structural and transport properties with alternatives of low-temperature film processing for grain-boundary-free polyamorphous Li-garnets to compete with state-of-the-art electrolytes, such as LiPON, and prevent dendrite penetration.3-4 Despite the promises, there is still a lack of understanding on the crystallization kinetics and its effects on Li-ion transport properties. In this study, garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO), is processed as thin films by spray pyrolysis. The crystallization and phase transitions of the LLZO thin films were studied by DSC together with Raman spectroscopy and in situ TEM. Johnson-Mehl-Avrami-Kolmogorov (JMAK) crystallization theory and Kissinger analysis are applied here, for the first time, to study the fundamentals of the crystallization involving chemical reactions and enthalpy changes during the phase formation process of LLZO. We develop Time-Temperature-Transformation-Conductivity (TTTC) diagrams for Li-garnet films to connect the transport properties with phase formation kinetics. Inspired by the TTTC diagram, crystallization temperature for the cubic phase LLZO is successfully lowered via an isothermal annealing step. Role of structural compaction on ionic conductivity is discussed for the crystalline and poly-amorphous LLZO and compared to the structure-transport characteristics of other Li-glass conductors. Our methodology and results highlight a new opportunity of tuning Li motion and lowering the crystallization temperature by precisely controlling the processing history with a cost-effective processing method. The insights from this work are expected to serve as fundamental guidelines for understanding the processing-structure-property relationships of amorphous and crystalline Li-garnet. Technologically, the work demonstrates new opportunities to stabilize amorphous and crystalline cubic films at low temperatures, and sets process temperature windows for next-generation solid-state batteries.

Acknowledgments
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References

Final Program 1/13/2020  442
Advanced Microfabrication Process for All Solid-State Thin-Film Batteries

Arnaud Bazin, Francoise Geffraye, Sami Oukasi, Séverine Poncelet, Christophe Secouard and Raphael Salot; CEA-LETI, France

Over the last years, the continuous miniaturization of nomadic electronic systems such as sensors, actuators or medical devices, has put a focus on the growing need for miniaturized energy sources with high power densities. All solid-state thin film batteries have proved to be of particular interest for such applications as they can be directly integrated onto the device. Moreover, the absence of liquid electrolyte is particularly advantageous in terms of safety, particularly for the numerous medical applications that are emerging today.

In this work we propose to present our latest progress on microfabrication process for thin film batteries. Microbatteries are manufactured on 8 inches silicon wafers using standard semiconductors processes such as physical vapor deposition, photolithography and etching. The fabrication process flow is carried out in a clean room environment using the TINY platform. Lithium based materials are particularly challenging when it comes to patterning processes due to their high reactivity. Moreover, the need for higher battery capacity induces an increase of the materials thickness, which brings also great challenges in terms of process development.

Microfabricated thin film batteries presented in this work are composed of the following layers (bottom-up):
- Platinum as current collector, LiCoO2 as the cathode, LiPON as solid electrolyte, Silicon as anode and Titanium as anodic current collector and redistribution layer.
- In order to improve the capacity of the battery, the thickness of the LiCoO2 cathode is increased up to 20 µm, leading to a high defectivity in the film due to coating process limitations. We propose to optimize the patterning process to cope with the high defect density.
- After fabrication, the wafer is thinned down to about 50 µm in order to obtain a total thickness of less than 100 µm for the battery. Wafer dicing is then carried out to obtain single batteries ready to be tested and integrated in the final component.
- The 5.3 millimeter square batteries demonstrate excellent electrical performances with a discharge capacity of 20µAh (680 µAh.cm-2, galvanostatic cycling, 3-4.2V potential range, 0.2C rate). The average capacity loss is limited to 0.1%/cycle, with a state of the art coulombic efficiency of 99%.

EN02.19.01

Liquid Electrolyte with a High Dielectric Constant for Stable Operation of Lithium-Metal Anode

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Lithium metal is considered one of the most promising anode materials for realizing high volumetric and gravimetric energy density, owing to the high specific capacity (~3860 mAh g−1) and the low electrochemical potential of lithium (~3.04 V vs. the standard hydrogen electrode)[1]. However, undesirable dendritic or mossy lithium growth and corresponding instability of the solid electrolyte interphase prevent safe and long-term use of lithium metal anodes[2-3]. This work presents an easy electrolyte approach to improve the performance of lithium metal batteries by tuning the dielectric constant of the liquid electrolyte. Electrolyte formulations are designed by changing the concentration of ethylene carbonate to have various dielectric constants. This study confirms that high ethylene carbonate content in a liquid electrolyte enhances the cycling performance of lithium metal batteries because the electric field intensity applied to the electrolyte is reduced in relation to the polarization of the electrolyte and thus allows smooth lithium plating by the formation of stable solid electrolyte interphase. We believe that this approach provides an important concept for electrolyte system design suitable for lithium metal batteries.


**EN02.19.02**
Highly Active Metal Pyrites Catalysts for a Low-Cost, High-Performance Polysulfide/ferrocyanide Redox Flow Battery Yifan Dong¹,², China University of Geosciences, China; ²University of Wisconsin, United States

Polysulfide is a promising redox couple employed in various aqueous redox flow batteries (RFB) for large scale electrochemical energy storage due to its high solubility and low cost. However, polysulfide has much lower rate constant in comparison with other commonly used redox couples in RFB. Therefore, efficient electrocatalysis is a key to achieving high performance for polysulfide-based RFB. Here we first systematically investigated the electrocatalytic activity of various pyrite phase metal disulfides (FeS₂, CoS₂, NiS₂) as thin film electrodes towards polysulfide redox reactions under steady state condition. Then we further demonstrated a high-performance polysulfide/ferrocyanide RFB using optimized high surface area NiS₂ nanostructures grown on carbon paper as the electrode. The NiS₂/carbon paper electrode showed a high exchange current density of 9.3 mA cm⁻² and was able to achieve a current density of 38.6 mA cm⁻² at an over potential of 100 mV. An aqueous polysulfide/ferrocyanide RFB employing NiS₂/carbon paper as anode and plain carbon paper as cathode was further evaluated by constant current cycling test and electrochemical impedance spectroscopy to demonstrate high charging-discharging cycling performance and low charge transfer impedance.

**EN02.19.03**
Room-Temperature, Ambient-Pressure Chemical Synthesis of Amine-Functionalized Hierarchical Carbon–Sulfur Composites for Lithium–Sulfur Battery Cathodes Changju Chae, Youngmin Choi and Sunho Jeong; Korea Research Institute of Chemical Technology, Korea (the Republic of)

Recently, the achievement of newly designed carbon–sulfur composite materials has attracted a tremendous amount of attention as high-performance cathode materials for lithium–sulfur batteries. Compared with commercialized lithium-ion batteries, the Li–S batteries possess a characteristic advantage in storing an electrical energy (2.6 kWh/kg). To date, sulfur materials have been generally synthesized by a sublimation technique in sealed containers. This is a well-developed technique for the synthesizing of well-ordered sulfur materials, but it is limited when used to scale up synthetic procedures for practical applications. In this study, we design a room-temperature, ambient-pressure chemical synthetic method by which to obtain multistacked, amine-functionalized carbon–sulfur composite materials. By an aqueous chemical conversion from sodium thiosulfate (Na₂S₂O₃), sulfur layers are deposited on preformed two-dimensional carbon templates, which are synthesized through the electrostatic interaction between negatively charged graphene oxides and positively charged amine-terminated multiwalled carbon nanotubes. It is demonstrated that stable cycling performance outcomes are achievable with a capacity of 730 mAhg⁻¹ at a current density of 1 C with good cycling stability by virtue of the characteristic chemical/physical properties of composite materials. The critical roles of conductive carbon moieties and amine functional groups inside composite materials are clarified with combinatorial analyses by X-ray photoelectron spectroscopy, cyclic voltammetry, and electrochemical impedance spectroscopy.

**EN02.19.04**
Development of Novel and Versatile Polyl Method to Synthesize High-Performance Cathode Materials Hyeseung Chung¹, Antonin Grenier², Zachary W. Lebens-Higgins³, Peter Ercius⁴, Minghao Zhang¹ and Shirley Meng¹; ¹University of California, San Diego, United States; ²Stony Brook University, The State University of New York, United States; ³Binghamton University, The State University of New York, United States; ⁴Lawrence Berkeley National Laboratory, United States

To develop high-performance cathode materials in Li-ion batteries, diverse synthetic methods have been explored with the overall goal of producing a product with controlled morphology and without local compositional and crystallographic inhomogeneities. Polyl method is a promising synthetic technique, when properly designed, that can offer these advantages. The unique properties of polyl solvent allow for monodispersed nanoparticle morphology while maintaining scalability for industrial applications. In this work, we introduce this novel synthesis method to produce cathode materials with three different crystal structures - layered LiNi₀.₃Mn₀.₃Co₀.₄O₂, spinel
LiNi_{0.5}Mn_{1.5}O_{4}, and olivine LiCoPO_{4}. Each of the synthesized material shows high crystallinity and competitive electrochemistry due to stable surface structure. After confirming the versatility of this synthetic method, our study extends to the detailed synthesis reaction mechanism that explores nanoscale dynamics occurring during polyol synthesis. With a combination of in situ and ex situ characterizations, including STEM/EELS, soft XAS, synchrotron XRD, and pair distribution functions (PDF) analysis, we directly observe the structural and chemical transformation during each step of the reaction. Our work highlights the deep insights in designing and optimizing synthesis procedure for cathode materials and possibly a wide range of intercalation compounds in the future.

**EN02.19.05**

*Ab Initio* Non-Covalent Interaction Energies to Quantify Structure-Property Relationships in Lithium-Conducting Oligomers

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Polymer electrolytes for lithium ion batteries offer superior mechanical stability and lower risks than liquid organic solvents, but are challenged by a lower ionic conductivity. The addition of secondary modifications to the polymer backbone opens up an additional degree of freedom for design to enhance the transport properties, by modulating the polymer-ion and counterion interactions. In this work, we explore how non-covalent interactions govern the interplay between conductivity and viscosity of a series of ethylene-oxide oligomers with secondary modifications. DFT calculations were used to quantify the additional non-covalent interactions introduced by the secondary modifications. A multi-dimensional regression was then fit to experimental conductivity and viscosity data at different temperatures. The binding energies of the secondary site towards lithium ion, counteranion, glyme, and the same secondary site through intermolecular interaction were used as the inputs to the regression. Since all inputs to the predictor are available from affordable simulations, this multi-dimensional free energy relationship was then used to screen for new secondary sites that maximize conductivity, which were then realized in the lab and shown to have 13% higher molar conductivity than baseline at room temperature.

**EN02.19.06**

Liquid Phase Sintering Effect of Composite-Electrode Containing Li_{2.2}C_{0.8}B_{0.2}O_{3} Solid Electrolyte for All-Solid-State Batteries

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All-solid-state batteries have received significant attention around the world because of high safety, reliability and energy density. Up until now, all-solid-state batteries are produced by vacuum deposition techniques, such as RF-sputtering like physical vapor deposition (PVD) or pulsed laser deposition (PLD), and thermal evaporation. These batteries are developed to use micro-batteries because their specific capacities are only between 5 and 100 μAh cm⁻², depending on the thickness of electrode. The main challenge facing all-solid-state batteries is to enhance the surface capacity influenced by the thickness of electrode. However, many attempts to increase the electrode thickness have not been successful because of micro-cracks between the components by stress generated at the solid electrode-electrolyte interface. In addition, strong kinetic limitations due to the low mobility of the ions and electrons in the increased electrode is also another problem. To overcome these problems, a composite-electrode made of multifunctional materials should be used as electrode. The composite-electrode contains the electrochemically active material, solid electrolyte, and conducting additive to transport electrons and ions in the electrode.

In this study, a Li_{2.2}C_{0.8}B_{0.2}O_{3} solid electrolyte is used for Li⁺ conduction pathway in the composite-electrode because it has a low melting point (> 500 °C) and is expected to act as a bonding material at the interface resulted from liquid phase sintering. Moreover, the composite-electrode with a strong mechanically framework was fabricated by a simple one-step spark plasma sintering (SPS) technique. To apply composite-electrode of all-solid-state batteries, optimized parameters are scrutinized, such as SPS conditions to protect decomposition of active material and the composite-electrode formulation (active material/solid electrolyte/electrical conductor ratio) to ensure good ionic and electronic percolation. The composite-electrode was very dense with very few voids as a result of the microstructure analysis. The Li_{2.2}C_{0.8}B_{0.2}O_{3} solid electrolyte was in close contact with the active materials due to liquid phase sintering. A Li-ion conduction path was formed along the electrode particles. In order to analyze the effects of liquid phase sintering systematically, the electrochemical performance of the composite-electrode is discussed in detail.
Development of Highly Heat-Resistant Battery Separator Based on Boron Nitride Nanotubes

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A separator is a key component for the safety of batteries. The conventional separator is made of polypropylene (PP), that has a shut-down function by closing its pores at an elevated temperature. But its fundamental thermal stability is low; it shrinks largely over melting point (PP: 160 °C), resulting in direct contact and short circuit between cathode and anode. We here propose and report a highly heat-resistant separator based on boron nitride nanotube (BNNT), which has high chemical and thermal stabilities (stable in air up to 900 °C) [1].

Self-supporting BNNT papers (thickness: 25 µm) were fabricated by dispersion and filtration without using binder. Similarly, self-supporting electrodes based on carbon nanotube (CNT) with lithium cobalt oxide (LCO) and graphite for cathode and anode, respectively, were fabricated [2]. The cathode/separator/anode stack was prepared, heated to and kept at a given temperature for 10 min. After cooled down, the insulation between the cathode and anode was checked. Then the charge-discharge test was performed by fabricating a 2032-coin cell using the stack and fresh electrolyte.

The PP separator shrank significantly, resulting in short-circuit at 225 °C. In contrast, the BNNT separator showed little thermal shrinkage and kept insulation even at 500 °C. Furthermore, the stack with BNNT showed no degradation after heating in the charge-discharge test. This showed that BNNT separator as well as the CNT-based electrodes worked without problem after heating at 500 °C.


Controllable Electrochemical Fabrication of KO₂-Decorated Binder-Free Cathodes for Rechargeable Lithium–Oxygen Batteries

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Understanding the electrochemical property of superoxides in alkali metal oxygen batteries is critical for the design of a stable oxygen battery with high capacity and long cycle performance. In this work, a KO₂-decorated binder-free cathode is fabricated by a simple and efficient electrochemical strategy. KO₂ nanoparticles are uniformly coated on the carbon nanotube film (CNT-f) through a controllable discharge process in the K–O₂ battery, and the KO₂-decorated CNT-f is innovatively introduced into the Li–O₂ battery as the O₂ diffusion electrode. The Li–O₂ battery based on the KO₂-decorated CNT-f cathode can deliver enhanced discharge capacity, reduced charge overpotential, and more stable cycle performance compared with the battery in the absence of KO₂. In situ formed KO₂ particles on the surface of CNT-f cathode assist to form Li₂O₂ nanosheets in the Li–O₂ battery, which contributes to the improvement of discharge capacity and cycle life. Interestingly, the analysis of KO₂-decorated CNT-f cathodes, after discharge and cycle tests, reveals that the electrochemically synthesized KO₂ seems not a conventional electrocatalyst but a partially dissolvable and decomposable promoter in Li–O₂ batteries. In general, tailoring a promoter-loaded binder-free cathode by a simple electrochemical process in a battery provides a feasible route to construct a multifunctional electrode not only for the alkali metal oxygen battery but also for other energy devices, such as sulfur batteries and ion batteries.

Understanding Low-Temperature Cycling of Lithium-Metal Anodes

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Efficient operation of batteries at low temperature is crucial to enable technological development in the areas of electric aircraft, interplanetary space exploration, and advanced robotics. For these high energy applications, Li metal batteries are the superior choice as they can deliver significantly higher specific energy than conventional Li-ion cells with graphite anodes. However, the electrochemical behavior of Li metal anodes at low temperatures is largely unknown. In this work, we investigate the effect of sub-zero temperatures on electrochemical behavior, morphological evolution, and solid-electrolyte interphase (SEI) formation of Li metal anodes in carbonate and ether solvents. We find that electrolytes containing carbonates tailored for low-temperature operation exhibit severe transport limitations at low temperatures, while ether-based electrolytes show promising Li cycling ability down to -80 °C. Interestingly, ex situ investigation after cycling revealed that distinct Li morphologies form at different temperatures, which is likely due to different nucleation and growth behavior, as well as differences in SEI.
chemistry and structure. Detailed SEI characterization by x-ray photoelectron spectroscopy and cryogenic electron microscopy reveal distinct structures of the SEI formed at room temperature compared to temperatures less than -40 °C. These results provide a fundamental understanding of how Li metal anodes behave at low temperatures, which could enable high-energy batteries for a range of operating conditions and environments.

EN02.19.11
Boost-Up Electrochemical Performance of MOFs via Confined Synthesis within Nanoporous Carbon Matrices for Energy Storage and Conversion Applications Min Seok Kang, Hyuna Kyung and Won Cheol Yoo; Hanyang University, Korea (the Republic of)

Utilizations of metal-organic frameworks (MOFs) for electrochemical applications are significantly limited by insulating nature and mechanical/chemical instability. One promising approach for the deployment of conventional MOFs in electrochemical applications is to fabricate MOF-based hybrids (MBHs) with conductive materials, which facilitate effective electron transfer via conductive additives between MOFs. Herein, we present a facile method for effective filling of Cu- and Ni-HKUST-1 (Cu-/Ni-MOF) inside 3D ordered mesoporous carbon (24nm, mC), 3D ordered N-doped macroporous carbon (300 nm, NMC), and 3D ordered macroporous carbon (300 nm, MC), denoted as MOF@mC, MOF@NMC, and MOF@MC, respectively. The MOF@carbon matrix (MOF@CM) composites were intended for use as electrodes for electrical double layer capacitors (EDLCs) and Li-S battery (LSB) and as electrocatalysts for the oxygen reduction reaction (ORR). EDLC performance of MOFs can be significantly improved by facilitating electron transfer through 3D conductive CM, reducing the electron pathway within insulating MOF using CM with small pores, and choice of metal center with pronounced faradaic nature. Ni-MOF@mC exhibited superior specific surface area normalized are capacitance (26.5 μF/cm²), exceeding most carbons and MOF-based EDLCs and outstanding long-term stability (91%@5000th). Furthermore, Cu-MOF@mC resulted in pronounced ORR activities, excellent methanol tolerance, and long-term stability. For LSB, Cu-MOF@mC presented superior performances compared to Ni-MOF@mC probably due to more preferential coordination bonding of S toward Cu center. It is clearly demonstrated that conventional MOFs can be utilized for EDLC, ORR, and LSB when conjugated with a 3D-connectednano-sized CM.

EN02.19.12
High-Performance Garnet-Based Lithium-Metal Batteries with Optimized Electrolyte/Electrode Interfaces Bingkun Hu, Wei Yu, Bingqing Xu, Liangliang Li and Ce Wen Nan; Tsinghua University, China

Garnet-type solid electrolytes are suitable for solid-state batteries with a lithium metal anode due to their high ionic conductivity, good stability against the lithium metal, and wide electrochemical window. The interfaces between the garnet electrolytes and the anode/cathode play an important role in the performance of garnet-based lithium metal batteries. In this study, at first, we applied some metal or alloy coating layers on the surface of garnet-type LixLi1/2La2/3Er1/3Ta2/3O2 (LLZTO) pellets that were synthesized by pressureless solid-state sintering and assembled LiFePO4|| LLZTO||Li cells. These LLZTO-based cells showed a long cycle life with a large current density of a few hundreds of μA/cm² at room temperature and an excellent rate performance, because the interfacial resistance between the electrolyte pellets and the Li anode was significantly reduced by 1-2 orders and the lithium dendrite growth was suppressed. The microstructure and composition of the interfacial layers formed at the LLZTO/Li interfaces were systematically investigated by high-resolution TEM and XPS. Next, based on the optimized LLZTO/Li interface above, the interface between the garnet electrolytes and the cathode was studied. Ionic liquid was adopted to improve the contact between the LiCoO2-based cathode and LLZTO. With an optimal cathode composition, LiCoO2||LLZTO||Li solid-state cells were fabricated and the influence of the concentration and type of Li salts in the ionic liquid on the performance of these cells was studied. The cells can be steadily cycled at room temperature. It is worth noting that our cathode design is applicable for other active materials when they are combined with garnet electrolytes. Our work provides proper interfacial optimization methods for garnet-based lithium metal batteries and paves the way for developing high-performance solid-state batteries.

EN02.19.13
Enhancement of Electrochemical Performance in Boron-Doped Si Micron-Rod aNode Fabricated Using a Mass-Producible Lithography Method for a Lithium-Ion Battery Sungjun Cho, Gun Young Jung and Kwangsup Eom; Gwangju Institute of Science and Technology, Korea (the Republic of)

Studies on the high specific capacity of silicon (Si) based anodes for lithium ion batteries (LiBs) have recently been
conducted, despite a large volume being expanded during electrochemical cycling\cite{1}, which is a significant problem. Although a variety of Si structures have been incorporated into the anode to prevent this problem\cite{2}, such structures have difficulties in terms of mass production. Herein, we present a new way to repetitively produce micron Si rods at different boron (B) doping levels using laser interference lithography (LIL) and metal assisted chemical etching (MACE), enabling the mass-production of multiple Si rods at low cost. The micron rod shaped Si anodes showed a higher rate capability and capacity retention than powdery Si particles. These characteristics are attributed to an increase in the surface-to-volume ratio, and a short radial lithium (Li) ions diffusion path, leading to alleviated pulverization during the de/lithiation process. In addition, the effects of the B-doping level on the electrochemical battery performance are studied for the first time. In particular, lightly B-doped Si rod (~10^{15} atoms cm^{-3}) anodes exhibit the highest capacity and cycling performance, showing a high initial coulombic efficiency (CE) of 98.1% and a capacity fading rate of 0.11% during 500 cycles owing to the high kinetics of de/lithiation relevant to the phase transition and diffusion. Through a CV analysis, it was confirmed that the lightly B-doped Si rod have a low over-potential, implying outstanding kinetics for the de/lithiation process. Whereas the heavy B doping hinders the de/lithiation kinetics because a number of Li atoms are trapped from the outermost side of the Si rods even after being fully delithiated with an increase in B-doping densities. This study provides a new approach for easy and rapid preparation of the electrode material and elucidates the dependence of the electrochemical performance on the level of B doping.

References

EN02.19.14
Polyethylene Oxide/Garnet-Type Li_{6.4}La_{3}Zr_{1.4}Nb_{0.6}O_{12} Composite Electrolytes with Improved Electrochemical Performance for Solid-State Lithium Rechargeable Batteries
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Next generation lithium batteries require new electrolytes with good safety, excellent ionic conductivity, high electrochemical stability and good cycling performance. Herein, we first report a solid composite polymer electrolyte comprises of Li_{6.4}La_{3}Zr_{1.4}Nb_{0.6}O_{12} fillers and polyethylene oxide matrix. The ionic conductivity of the solid composite electrolyte is significantly improved to 1.4 × 10^{-3} S cm^{-1} (60 °C) and the electrochemical window is enhanced to 5.2 V, respectively, by incorporation of Li_{6.4}La_{3}Zr_{1.4}Nb_{0.6}O_{12} powder at a weight ratio of 0.5:1 with respect to polyethylene oxide. The solid batteries employing the composite electrolytes are able to work at room temperature and have a capacity retention of 99% after cycle. The performance improvement is primarily due to the combined functions of each component in the composite: (i) the incorporation of fillers effectively decreases the crystallinity of PEO, providing more amorphous region for ion conduction; (ii) Li_{6.4}La_{3}Zr_{1.4}Nb_{0.6}O_{12} serves as a fast ion conductor in the composite and enhance the electrochemical stability; (iii) the polymer matrix forms intimate surface contact with fillers and electrodes, reducing the bulk and interfacial resistance. The composite polymer electrolyte in this work would be a competitive alternative for the next generation solid state lithium rechargeable batteries.

EN02.19.16
Phase Change Materials Encapsulated in Reduced Graphene Aerogel Beads for Lithium-Ion Battery Thermal Management
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Over last few decades, lithium ion battery (LIB) has been extensively explored and has dominated the power source market for portable electronic devices since Sony Co launched their first LIB in 1992. Recently, as a result of depletion of coal fuels, it triggered cleaner and more sustainable energy technology development including the invention of electrical vehicles (EVs), hybrid electrical vehicles (HEVs) and plug-in hybrid electrical vehicles (PHEVs). The challenges of developing EV, HEV and PHEV are short calendar and cycle lifetime, high weight, high volume and safety issues. LIBs provide the solutions for these technologies due to its high gravimetric and volumetric energy density, rechargeability, temperature stability and capability of scale-up. In most cases, a certain
Recent researches on the production and utilization of renewable energy (solar, wind, geothermal, etc.) have attracted attention as environmental pollution problems caused by depletion and use of fossil energy are emerging. The development of the renewable energy sector is essential to build an energy storage system (ESS) to secure the elasticity of energy production and consumption. Therefore, although lithium-ion battery systems widely used today are in the spotlight, the development of new material-based battery systems is required for long-term demand response and stability of supply and demand. Na-ion batteries have similar electrochemical mechanisms to Li-ion batteries and are actively being studied as candidates for energy storage systems due to their abundant amount and price stability. Na$_3$V$_2$(PO$_4$)$_3$ (NVP) is one of the promising cathode materials among Na ion storage materials due to its excellent structural and thermal stabilities due to its strong polyanion network. However, it is difficult to secure a reversible capacity close to the theoretical capacity (117.6 mAh g$^{-1}$ at 3.4 V vs. Na/Na$^+$) owing to NVP's poor electrical conductivity. There have been many attempts to improve the mass and charge transport of NVP materials by decreasing the NVP particles size or introducing conductive materials. In particular, many attempts have been made to synthesize carbon-NVP composites by forming carbon coatings using hydrocarbons, organic solvents, organic acids and surfactants on the surface of NVP. However, these methods require a high carbon weight of at least 10% to achieve high rate performance. Recently, the use of graphene or graphene oxides enabled ultra-high speed movement with a relatively small amount of carbon (less than 5%), but the use of related materials limits the practicality of using Na-ion battery systems instead of lithium.

In this study, we have developed carbon-containing Na$_3$V$_2$(PO$_4$)$_3$ (NVP) as an active cathode material for Na-ion batteries using carbon-methyl cellulose (CMC) and sucrose as dual carbon sources. The interaction between CMC and sucrose formed a porous structure (surface area: 58.998 m$^2$ g$^{-1}$) with increased sp$^2$ carbon species, promoting mass and charge transport. The specific capacity (104.99 mAh g$^{-1}$) of the carbonized CMC/sucrose NVP (CS-NVP) was obtained close to the theoretical capacity (117.6 mAh g$^{-1}$). Also, CS-NVP exhibited stable cyclability with a specific capacity of 75.04 mA g$^{-1}$ at a rate of 20 C.
**EN02.19.18**

**Electrochemical Property of Yb-F-S Multiple-Anion Compounds**  Shintaro Tachibana¹, Kazuto Ide², Takeshi Tojigamori², Hisatsugu Yamasaki², Yukinari Kotani² and Yuki Orikasa¹; ¹Ritsumeikan University, Japan; ²Toyota Motor Corporation, Japan

Fluoride-ion batteries using solid-state electrolytes are expected as one of the candidates for next-generation rechargeable batteries [1]. For fluoride-ion batteries, the ion carrier is monovalent fluoride ion, which can realize the multi-electron reactions of counter cations in active materials of fluoride compounds. However, it is far from practical use mainly due to lack of solid electrolytes which have high ionic conductivity and a wide electrochemical potential window like lithium-ion conductors. The previously reported fluoride-ion conductors such as PbSnF₄ [2] and La₀.₉Ba₀.₁F₂.₉ [3] contain one type of anion, fluoride ions. To our best knowledge, there is no report on the solid electrolyte materials containing multiple-anion compounds. Fluoride-based multiple-anion compounds have the potential to exhibit abundant functionality (electrical, optical, and magnetic properties, etc.) because of a variety of crystal structures [4]. However, their stability of fluoride compounds is low because the activity of fluorine in the air is extremely low compared to that of oxygen. Therefore, in many cases, controlling the synthesis atmosphere is required, resulting in few research examples of multiple-anion compound using fluoride ion.

In this study, we prepared Yb-F-S compounds containing fluoride and sulfides ions as anions by solid-state reaction under vacuum. In order to identify the phase of the prepared samples, powder XRD measurement was performed. F K-edge and O K-edge XAS measurements were performed at BL-2 in Ritsumeikan University SR Center. Electrochemical impedance spectroscopy and the two-probe conductivity measurement were performed. In addition, the charge-discharge properties of the prepared compounds were examined.

The synthesized sample contains the ytterbium fluoride sulfide as the main phase and ytterbium oxyfluoride as an impurity. One of the reasons for the appearance of this impurity is that the oxygen source which was initially contained in the starting materials could not be removed during the synthesis process and remained in the resulting sample. Electrochemical measurements indicate that the prepared compound exhibits electric conductivity. This is because ytterbium ion in this compound is a mixed valence state with divalent and trivalent.

Reference:

**EN02.19.19**

**Ion Transport in Sputter-Deposited Li₂O and Li₂S Thin Films**  Simon Lorger, Dieter Fischer, Robert E. Usiskin and Joachim Maier; Max Planck Institute for Solid State Research, Germany

Dense thin films of Li₂O and Li₂S grown by r.f. sputtering are found to exhibit ionic conductivities at 25 °C that are multiple orders of magnitude higher than expected from the bulk defect chemistry. The enhancement appears not to be due to the substrate - film interface, nor to doping, nor to the presence of impurity phases. Instead, the evidence points to higher-dimensional defects as enabling the faster ion transport. The resulting conductivity values are consistent with those typically observed from composite SEI layers that contain Li₂O or Li₂S. This work may help explain the rate-limiting process for ion transport through some SEI layers.

**EN02.19.20**

**N-doped Nanoporous Carbon Coated Graphite as a Anode Material for Lithium-Ion Batteries**  Junyoung Kim, Dong Young Rhee and Min-Sik Park; Kyung Hee University, Korea (the Republic of)

Lithium-ion batteries (LIBs) have been successfully utilized as a main power source for various energy storage applications owing to their high energy density and excellent power characteristics. Unfortunately, current LIBs cannot fulfill the requirements of the rapidly growing electric vehicle (EV) market due to their limited energy density based on conventional electrode materials [1]. Therefore, the development of advanced materials for LIBs has become very important. In practice, graphite is the most popular anode material of commercialized LIBs owing to a low reaction potential (~0.2V vs. Li/Li⁺) and a high reversibility toward Li⁺ intercalation and de-intercalation.
However, the practical use of graphite in EV applications is hindered by poor rate capability and cycle performance because Li\(^+\) intercalation into graphite is allowed only through the edge-plane of graphite so that uncontrollable metallic Li is deposited on the surface of graphite anode under high-rate cycles [2]. In this respect, it is crucial to develop a robust design of graphite to make it more suitable for EV applications. With a purpose of improving the rate capability and cycle performance of graphite, herein, we propose a bi-phasic graphite decorated with N-doped nanoporous carbon (NPC) nanoparticles. It can be obtained by a direct growth of ZIFs (Zeolitic Imidazolate Framework) on the surface of graphite followed by a carbonization process. The large specific area and high electrical conductivity of NPC offer additional reaction sites of Li\(^+\) as well as promote charge-transfer reactions [3-4]. Furthermore, the porous structure of NPC is advantageous for securing the tortuosity of electrode and facilitating Li\(^+\) migration in the electrode during cycles. Based on the electrochemical and structural analyses, further discussion on the positive effects of NPC decoration on the rate capability and cycle performance of graphite will be presented.

References

EN02.19.21
Fluorinated-O\(_2\) Selective Membranes as Gas Diffusion Electrodes for Metal-Air Batteries
Gizem Cihanoglu and Ozgenc Ebil; Izmir Institute of Technology, Turkey

Fluctuation of oil prices and the effects of global warming have resulted in increased research in alternative energy storage and conversion systems, especially in battery technologies. Development of cost effective and environmentally safe battery technologies for a variety of applications ranging from small portable electronic devices to electric vehicles are also driven by increased public awareness of fire, explosion and toxicity risks associated with today’s Li-ion batteries. Metal-air batteries are considered as cheaper and safer alternative to Li-ion batteries due to their theoretically higher energy densities (1000-13000 Wh kg\(^{-1}\)) for a wide range of applications. However, metal-air batteries have not reached their full potentials as they suffer from limited capacity and lifetime mostly due to catalyst corrosion, anode passivation and corrosion, electrolyte loss and pore clogging leading to performance loss and reduced cycle life.

Here we present an improved Gas Diffusion Electrode (GDE) based on CVD deposited hydrophobic and oxygen selective polymeric thin films as gas diffusion layers to increase energy and power densities of metal-air batteries. Oxygen selective and highly hydrophobic copolymer thin films containing tetravinyltetramethylecyclohexasiloxane (V4D4), 2-(perfluorohexylethyl) acrylate and 2-(perfluoroalkyl)ethyl methacrylate were fabricated via Initiated-CVD. Fabricated copolymer films minimize the accumulation of excess water and prevent flooding of GDE during battery operation. In addition, higher oxygen permeability leads to higher current densities resulting in improved battery performance.

EN02.19.22
Direct Analysis of Lithium in LIB Cathode Using Soft X-Ray Emission Spectrometer
Yusuke Uetake\(^1\), Shunsuke Asahina\(^1\), Natasha Erdman\(^2\), Tamae Omoto\(^1\) and Hirokazu Munakata\(^3\); \(^1\)JEOL Ltd., Japan; \(^2\)JEOL USA, United States; \(^3\)Tokyo Metropolitan University, Japan

Both distribution and composition of Lithium in a charged cathode affect the capacitance and the efficiency of Lithium ion battery (LIB). Auger Electron Microscopy (AES) is one of the common methods to analyze distribution and composition of Lithium in the battery with high spatial resolution by using focused electron beam for surface analysis of the specimen. Since the energy of Auger electrons is a few electron volts, it is possible to analyze with surface sensitive information. In addition, AES is also capable of providing depth profiling by using Ar ion sputtering, making AEM a quite useful method for LIB analysis. However, there are issues with AES analysis for LIB. The Auger electrons are very sensitive to the electrostatic field on the surface. The user should therefore create a condition of ‘floating’ Cathode with respect to the specimen holder during AES analysis. Otherwise, the Cathode will discharge Lithium ion during the analysis.

Currently we are focusing our efforts on using SXES (Soft X-ray Emission Spectrometer) method, which was...
Recently developed, this method allows analysis of characteristic X-ray of Lithium by charging on the sample surface. The SXES is installed on Field Emission SEM (Scanning Electron Microscope) that is able to detect soft X-rays with high spatial resolution. The acquisition energy range of SXES is less than 250 eV, which means that this SXES enables the use of low landing voltage with small interaction volume for X-ray excitation such as 2 kV or below. Such setup makes SXES a surface analysis method like an AES. In addition, using SXES is sufficient to generate soft X-rays with low landing energy such as 2 kV, which suppresses the charging of the sample by the irradiated electrons.

JEOL FE-SEM (JSM-7200F) equipped with SXES (SS-94000) was used for analyzing Lithium distribution in LIB Cathode. Sample was prepared in a glove box and transferred without air exposure into the SEM to avoid any oxidation. The soft X-ray spectra were acquired at an accelerating voltage of 2 kV and a beam current of 40 nA. As a result, a characteristic X-ray of a Lithium peak around 48 eV was detected from the surface of fully charged LIB cathode.

In this study, we will report that we examined the distribution of Lithium by direct analysis from the surface of charged Lithium ion battery cathode using SEM-SXES.

**EN02.19.23**  
**Surface Coated Graphite Anode with Non-Stoichiometric Metal Oxides for Lithium-Ion Batteries**  
Dong Young Rhee, Junyoung Kim and Min-Sik Park; Kyung Hee University, Korea (the Republic of)

Recently, lithium ion batteries (LIBs) have been considered as the most suitable power source for various energy storage applications. In the LIBs, graphite is widely used as a commercial anode material because it offers a low reaction potential (~0.2 V vs. Li/Li⁺) and high theoretical capacity (~372 mAh/g) [1]. However, because of the layered structure of the graphite, graphite does not offer sufficient cycle performance and rate-capability for practical use in electric vehicles (EV) applications [2]. Therefore, it is of great importance to develop advanced anode materials with improved electrochemical performance in this research field. To overcome these technical limitations, various structural modifications of the graphite have been proposed to make it more favorable for securing a long term cycle stability as well as excellent power characteristic. In this respect, we focused on advantages of non-stoichiometric metal oxides with distinctive electronic properties because they can play an important role as a functional additive for improving the electrochemical performance of the graphite [3]. Herein, we propose a new material design with a core-shell structure in which graphite core is encapsulated by a functional surface layer (shell) composed of non-stoichiometric MeOₓ and amorphous carbon. The functional layer can be successfully introduced on the surface of graphite by a simple solution process combined with a carbothermal reduction using MeO₂ nanoparticles and coal-tar pitch precursors. Tailoring the surface structure of graphite with a functional layer is effective for suppressing structural degradation and lowering the overpotential at the surface of graphite even at high current densities. In addition, cycle performance of the proposed anode material can be notably improved compared with commercial graphite. Based on a range of structural and electrochemical analyses, fundamental roles of the functional layer on the surface of graphite will be discussed.

**References**


**EN02.19.24**  
**Mesoporous Carbon as a Potential Reservoir of Metallic Li**  
Seung Hyun Choi, Junyoung Kim and Min-Sik Park; Kyung Hee University, Korea (the Republic of)

During the last decade, lithium ion batteries (LIBs) have shown great promise as a potential power source for various application such as portable electronic devices and electric vehicles (EVs) [1]. Responding to growing demand for high-energy LIBs, it is crucial to develop materials which provide a higher energy density than commercial materials currently available.

Li metal has been considered as a future anode material for LIBs because of its extremely high theoretical capacity (~3,860mAh/g) and low redox potential. Despite these benefits, the practical use of Li metal is limited by several technical issues as follow; i) inevitable growth of dendritic Li and ii) infinite volume changes during cycling are...
regarded as drawbacks causing rapid performance degradation and safety issues [2]. Recently, porous carbon materials with well-distributed pore that can serve as Li storage reservoir have been proposed to suppress unfavorable volume changes [3-4]. Herein, we design a disordered mesoporous carbon (DPC) as a potential Li storage material, allowing a dual-phase reaction (i.e. lithiation and metallization). It can be synthesized via a direct carbonization of silica-embedded zeolitic imidazolate frameworks (SEZIFs) combined with a chemical etching process. The DPC exhibits a great potential for accommodating a large amount of metallic Li thanks to its highly mesoporous structure. In practice, we confirm that Li can be reversibly stored in the structure based on various electrochemical and structural analyses. Furthermore, a correlation between pore structure and Li storage behavior is thoroughly investigated to examine the feasibility of DPCs as the next generation anode for high-energy LIBs.

References

EN02.19.25
[S8 | Li-Doped Graphite] Cells for Long-Cycle-Life Li-S Batteries Yusuke Ushioda1, Yuki Ishino1, Keitaro Takahashi1, Kohei Inaba1, Tatsuya Kawamura1, Masayoshi Watanabe2 and Shiro Seki1; 1Kogakuin University, Japan; 2Yokohama National University, Japan

Recently, demands of renewable energy are increasing with against lack of energy resources. However, power generation of renewable energies (solar and wind-power) drastically change with meteorological variation, and have poor stability of output performances. Therefore, large-scale and high-energy-density energy storage devises are strongly desired for power system stabilization, and lithium-sulfur (Li-S) batteries are expected as the one candidates. Main advantages of Li-S batteries are low-cost of elemental sulfur (S8) and their high capacity (1,672 mAhg⁻¹). On the other hand, intermediate compound of positive electrode material with charge-discharge process (Li2Sₓ) can be easily dissolved into electrolyte solution with significant degradation of cells. Moreover, lithium dendrite grows up at the Li metal and causes internal short-circuit. In this study, to prevent the Li dendrite, Li-incorporated negative electrode, such as C6Liₓ (Li-doped graphite electrode) was proposed as a stable electrode. C6Liₓ electrodes were prepared by reconstructed process of electrochemical cells (C6 | electrolyte | Li). In order to improve the efficiency of Li dope process, we investigated the electrolyte species (glyme and sulfolane) and composition dependencies for electrochemical performances. Moreover, preparation process of cells (annealing temperature) affected electrical coulombic efficiency. In the presentation, we will also report Li-S battery performances of [S8 | electrolyte | Li-doped C6 (C6Liₓ)] cells, and their related applied systems.

EN02.19.26
Optimization of NMC Electrode for High-Voltage Lithium Batteries Maciej J. Boczar1, Hui Wang2, Dominika A. Ziolkowska1 and Andrzej Czerwinski1; 1University of Warsaw, Poland; 2University of Louisville, United States

In recent years, lithium-ion cells have been introduced into electric vehicles. Presently, one of the most promising cathode materials for lithium batteries industry are mixed manganese nickel cobalt oxides (NMCs) due to their high specific capacity and high cycle stability. In this work, we present how the application of different electrolyte mixtures influences safety and stabilizes the NMC cathode material with upper cutoff potential exceeding 4.2 V. Next, we will demonstrate all-solid-state battery (ASSB) design using S-based solid electrolyte. The structure and morphology of the materials will be examined using Raman spectroscopy, scanning electron microscopy, X ray powder diffraction and specific surface area by (BET). Electrochemical measurements are carried out in three-electrode Swagelok® systems with Li metal as counter and reference electrodes and a working electrode composed of NMC active material. In order to determine the optimal potential window of NMC without a significant specific capacity drop electrolytes based on LiPF6, LiTFSI, LiTDI and LiBOB in various organic solvents were tested. Those cells are characterized by chronopotentiometry and cyclic voltammetry. As most of the batteries with liquid electrolyte are flammable and unstable and therefore are not a reliable solution for various applications, especially in higher voltage systems, we present an alternative design characterized by higher safety and energy density thanks to application of S-based solid electrolytes to our exemplary ASSB system.
Thin layered ASSB design will be possible thanks to our recently discovered liquid synthesis approach of producing lithium thiophosphates. This new generation of all-solid-state batteries creates new possibilities. It may be attractive, efficient and safer for several energy storage systems, especially for automotive industries due to the large potential window, higher energy density, and its inflammability.


EN02.19.27

Engineering the Cathode-Li Garnet Interface—How Phase Stabilities and Temperature Windows in Processing Affect Solid-State Battery Performances Kunjoong Kim and Jennifer L. Rupp; Massachusetts Institute of Technology, United States

Solid State Batteries offer safe alternatives to classical Lithium-ion batteries (LIBs) due to the non-liquid nature of the electrolyte and give perspective to assure both, high energy and power densities. Despite the fast-growing field of solid-state batteries, the high-temperature manufacturing of the battery cell components and co-assembly of solid electrolyte/cathode interfaces define largely by structures and kinetics the battery characteristics for technology. Till date, interface fabrication in Li-garnet (LLZO) based cathode/electrolyte interface is reported for high-temperature sintering (600-1050 °C) and also implicate its electrochemical storage capability. However, interfacial resistances for the Li⁺ transfer between the active material and the LLZO electrolyte and corresponding overpotential are still high which limits overall performance. Through this work, we focus on fabrication and characterization of all solid state cathode/LLZO electrolyte interfaces using most popular oxide cathode material, LiFePO₄, and LiCoO₂. Critical discussion is placed on how to enhance contact quality at low temperature in the co-assembly manufacturing vs. phase stability. We highlight the need to control the number of the reaction site and assure efficient electro-ionic percolation pathway by comparing classic co-sintered and infiltration manufactured cathode/electrolyte assemblies, and also discuss the findings towards other three-dimensional composite cathodes processed with and without additives. Ultimately, this work provides guidelines on the phase stability of LLZO and cathode interfaces, and temperature window for processing depending on the manufacturing route (classic sintering vs. infiltration) for the engineering of future solid-state batteries based on Li-garnets for safe energy storage.


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**EN02.19.29**

**N, S-Codoped and Size-Controlled Porous Carbon Derived from MOF-5 as Lithium-Sulfur Battery Cathodes**
Geonho Kim, Seoyeah Oh and Jiwon Kim; Yonsei University, Korea (the Republic of)

Lithium-sulfur batteries have been actively studied as one of the future energy storage devices because they have higher theoretical capacity values compared to commercial lithium-ion batteries. Since sulfur is abundant in nature, it is low in price and environmentally safe. However, when sulfur is used as an anode material for lithium-sulfur batteries, it often lowers the conductivity and the reaction intermediates (ex. Li₂S, Li₂S₂) cause expansion in volume. The reaction intermediates also show high solubility in electrolytes reducing the cell cycles. Porous structured carbon with high content of sulfur can suppress volume expansion and also improve conductivity. Porous carbon can easily be synthesized by carbonization of metal-organic framework (MOF) with controllable porosity facilitating charge transfer. Heteroatom doping can also enhance the conductivity and prevent dissolution of polysulfide into electrolytes due to an electronegativity of the doped atoms.

Herein, we synthesized MOF-5 derived N, S-codoped porous carbon via microwave-assisted solvothermal method. The microwave-assisted solvothermal process can drastically reduce the time (<30min) required for heteroatom (N, S) doping compared to conventional solvothermal methods (several hours). When thiourea was used as a doping source, 1~3 at% and 2~5 at% of N and S in porous carbon were obtained, respectively. Furthermore, when it was used as a cathode of Li-S battery, it showed high initial capacity of ~1300 mAhg⁻¹ and excellent cell cycle retention of 60% at 0.1 C after 150 cycles. In addition, the crystal size of MOF was controlled by stirring speed. As a result of controlling the stirring speed from 0 to 300 rpm, it was confirmed that the crystal size of the MOF changed to a size of about 10 μm to 100 μm (higher speed results in smaller crystal size). As a result of reduced-size crystal applied to Li-S battery, the initial capacity was improved to ~1400 mAhg⁻¹ at 0.1C compared to ~1000 mAhg⁻¹ at 0.1C for non-stirred MOF. Therefore, we can greatly improve the performance of Li-S batteries by optimizing structure and composition of porous carbon which can contribute to commercialization of Li-S batteries.

**EN02.19.30**

**Nano-Electrodes for Na-Ion Batteries—New Insights from Ab Initio Calculations**  
Arianna Massaro, Ana B. Munoz-Garcia and Michele Pavone; University of Naples "Federico II", Italy

Na-ion batteries (NIBs) [1] are attracting widespread interests as convenient alternatives to current state-of-the-art Li-ion batteries (LIBs) [2] for large-scale grid energy storage applications [3]. Despite similar working principles, the larger sodium ion needs different component materials than LIBs, especially at the negative electrode [4]. In this context, recent studies have proposed new electrodes based on nano-structured materials like TiO₂ anatase nanoparticles, and the reported results are very promising in terms of both performance and stability [5]. However, a deep comprehension of the surface-related mechanism for insertion/de-insertion of Na into the specific materials surface/interface termination is still missing. Within this context, in this contribution we report state-of-the-art first-principles calculations on two prototypical systems that can be applied as nano-electrodes in NIBs, namely the TiO₂ anatase nanoparticles, and the MoS₂-Graphene hybrid 2D heterojunction [6].

First, we rationalize the adsorption and insertion of Na at the different (101), (100) and (001) surface termination of TiO₂ anatase nanoparticles, and the MoS₂-Graphene hybrid 2D heterojunction. Our results provide an unambiguous explanation of recent relevant experiments. Second, we will highlight the potentiality of molybdenum disulfide 2D nano-layer supported on Graphene for the inclusion and diffusion of the sodium cation at such hybrid interface.

In conclusion, the new insights on the structural features that determine the observed electrochemical behavior can be easily exploited further for the design of new and more effective nano-structured electrodes for NIBs. Authors wish to thank European Union (FSE, PON Ricerca e Innovazione 2014-2020, Azione I.1 “Dottorati Innovativi con caratterizzazione Industriale”), for funding a Ph.D. grant to Arianna Massaro.

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EN02.19.31
Flow Batteries Using Manganese, Cerium and Related Redox Couples
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Grid-scale implementation of redox flow batteries (RFBs) has been hindered by the availability of cost-effective redox couples within the solvent window of aqueous electrolytes. Vanadium is the predominant active species in RFBs because it is highly reversible over many cycles and it possesses multiple oxidation states, allowing it to be used in both sides of the battery (positive electrolyte: \( V^{5+} \leftrightarrow V^{4+} \), negative electrolyte: \( V^{2+} \leftrightarrow V^{3+} \)). However, the cost of vanadium is too high, resulting in a high capital cost that is not competitive for grid-scale energy storage. While other redox active species are frequently reported, such as Fe, Cr, and Br, there are few that are compatible with the aqueous solvent window while utilizing graphite electrodes, commonly used in the standard RFB configuration.

In this presentation, boron-doped diamond (BDD) is shown to be an exceptional alternative to the standard graphite electrode by enabling a wide range of redox couples that are more cost effective, environmentally friendly, and sustainable, while also offering improved efficiencies and energy densities than the current state-of-the-art. Diamond has proven itself to be a superior material for a variety of applications and its utility in electrochemistry has become increasingly apparent over the past decade. In addition to diamond’s ability to resist fouling and corrosion in extreme environments, it’s most critical advantage for flow batteries is it’s extremely high overpotential for both hydrogen and oxygen evolution (-1 V to 2.5 V, respectively). This large solvent window enables the use of redox couples that would occur with common electrodes, such as graphite or platinum, in either the hydrogen or oxygen evolution regime. Despite these advantages, it has not been until now, that BDD has been considered for use in RFB technology. This has led to the identification of several additional relevant redox couples that were previously out of reach. This research represents a monumental advancement of RFB technology and could be the solution to grid-scale energy storage challenges.

EN02.19.32
Two-Dimensional Metal Chalcogenides for Li-Ion Battery Applications
Meiying Liang and Valeria Nicolosi; Trinity College Dublin, Ireland

Metal chalcogenides (MCs), including metal sulfides and metal selenides, have attracted tremendous attention for energy storage applications and development of rechargeable lithium-ion batteries due to their unique physicochemical properties (e.g. high electrical conductivity, good thermal stability, earth abundance, etc.).\textsuperscript{[1-3]} Especially, MCs possess higher theoretical specific capacities for rechargeable lithium-ion batteries compared to traditional intercalation electrode materials. In addition, metal chalcogenides tend to be more electrochemically reversible as compared to metal oxide counterparts due to their faster charge transfer kinetics. Recently, as an alternative anode material for replacing currently commercialized graphite or carbon-based anode materials, many kinds of layered inorganic materials are investigated because of their large theoretical capacity. Similarly large numbers of layered MCs are explored as intercalation anode materials for lithium-ion batteries. However, there is still a plenty of room for the development of new efficient anode materials from non-layered MCs such as two dimensional (2D) MC nanosheets operating in terms of non-intercalative mechanism, since only a few studies are carried out for this type of materials.\textsuperscript{[3,4]}

In this work, 2D MCs nanosheets (such as GaS, GaSe, GaTe and InSe) were prepared via LPE approach. And their application as anodes of Li-ion batteries was investigated in detail. Among these 2D MC nanosheets, InSe displays the most excellent rate capability and high specific capacity (926 mAh g\textsuperscript{-1} and 595 mAh g\textsuperscript{-1} at 50 mA g\textsuperscript{-1} and 2 A g\textsuperscript{-1}, respectively). In addition, it shows exotic cycling stability. The capacity of it has increased with the increase of cycling numbers, which means the quality of a battery will be improved when the battery is used. This work opens up vast opportunities for InSe and other families of MC nanosheets to be scalably processed into flexible conductive composite films with a broad range of applications such as wearable electronics, optoelectronics, and other energy storage systems.
Improved Cyclability of Nickel Rich Layered Oxides

Nils Wagner\textsuperscript{1,2}, Julian Tolchard\textsuperscript{1}, Artur Tron\textsuperscript{1}, Sidsel Hanetho\textsuperscript{1}, Harald Pollen\textsuperscript{2} and Paul Dahl\textsuperscript{1}; \textsuperscript{1}SINTEF Industry, Norway; \textsuperscript{2}Norwegian University of Science and Technology, Norway

Secondary Li-ion batteries are the battery concept with the highest energy density both per volume and weight currently on the market and have driven the electric mobility transition. A difficult compromise between energy density and safety has to be found for electric vehicle (EV) Li-ion chemistries. The most common positive electrode for EV applications is based on the LiNi\textsubscript{x}Mn\textsubscript{y}Co\textsubscript{z}O\textsubscript{2} (NMC) system, as this is the only system that can meet the power and range requirements. Increasing the Ni content with NMC oxides results in higher capacity values but is detrimental to the capacity retention and the thermal stability. This work explores a simple acidic co-precipitation route as a "one-pot" synthesis for high energy layered oxide cathodes by oxalate precipitation, adapted from a method described by Zhen Chen \textsuperscript{[1]}. This versatile synthesis route allows for the preparation of single phase high Nickel oxides such as LiNi\textsubscript{0.8}Mn\textsubscript{0.1}Co\textsubscript{0.1}O\textsubscript{2} (NMC 811), and more complex composites such as LiNi\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2} decorated LiNi\textsubscript{0.8}Mn\textsubscript{0.08}Co\textsubscript{0.12}O\textsubscript{2} in core-shell structure with improved capacity retention compared to NMC 811. This study further includes the implementation of protective surface coatings to further improve the cycle-life and increase the thermal stability of Ni rich layered oxides by lowering the reactivity of the material surface. Most reported coating methods rely on expensive fluidised bed atomic layer deposition. \textsuperscript{[2-4]} Here we compare FB-ALD with wet chemical methods that can be implemented into the material synthesis.

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Neutron Depth Profiling (NDP) Technique for Studying Dynamic Short-Circuit Behaviors in Garnet-Based Solid-State Batteries

Chengwei Wang, Weiwei Ping, Howard Wang and Liangbing Hu; University of Maryland, United States

Wide electrochemical window, high ionic conductivity, and excellent stability to the lithium metal make the garnet-based solid-state electrolytes (SSEs) attractive for solid state lithium metal batteries. However, the hazard of short-circuit in garnet-based solid-state batteries has encumbered the cycle life and capacity of the full cells with the blurred reason and mechanism. In this work, we report a dynamic short-circuit process in the garnet-based solid-state batteries and study the mechanism with in situ neutron depth profiling (NDP) technique. The quantitative NDP measurements could perceive the transferring Li ions within the cell sensitively, which can forecast and confirm the dynamic behavior of the short-circuit in the garnet-based batteries. A real-time Li accumulation monitoring system of CNT/NMC/garnet/Li is also designed to reveal the charging problem in the garnet-based full cells. The voltage drops of the CNT monitoring electrode during the charging process of NMC/garnet/Li full cell indicate the Li accumulation on the garnet surface through Li dendrite inside garnet bulk, while the flat and smooth voltage profile of the CNT electrode during the discharging process demonstrates the disappearance of the short-circuit. The results indicate that this dynamic short-circuit behavior is mainly due to the low ionic conductivity and high electronic conductivity of garnet SSEs. Increasing ionic conductivity while decreasing electronic conductivity is the key to
achieve electrochemically stable garnet SSEs for solid state batteries.

EN02.19.35
New Insights into the Relationship between Structure and Transport Properties of Oxide Glasses  
Mirza C. Beg and John Kieffer; University of Michigan, United States

Combining a recently developed variant of transition state theory (TST) for ionic transport in amorphous structures with molecular dynamics (MD) simulations facilitates unprecedented insights into the local and medium-range structure of these glasses. Realistic structural models of network glasses are generated using MD simulations based on a reactive force field, which allows for the accommodation of dynamically variable coordination numbers for a given network former and dynamic charge transfer upon formation or breakage of covalent bonds. The TST model, which relies on mean-field statistical measures, allows us to identify the size of the spatial region affected by the activated ion hopping process. In combination with MD simulations, we can identify the specific molecular configurations that participate in the jump process and onto which the thermal energy for activation must be focused. Thus, MD simulations allow us to observe the behavior of all atoms involved in the ionic transport process, and identify the underlying mechanisms in the context of glass structure, its chemical character, and its bonding topology. This knowledge is used towards the development of a materials design criteria for solid-state electrolytes. (Acknowledgement: NSF-DMR 1610742.)

EN02.19.36
High Entropy Materials as Anode and Cathode for Advanced Li-Ion Batteries  
David Stenzel, Abhishek Sarkar, Qingsong Wang and Ben Breitung; Karlsruhe Institute of Technology (KIT), Germany

In recent years, a new class of high entropy materials has gained scientific interest besides the already known high entropy alloys, namely, the “high entropy oxides” (HEOs). These compounds are based on the concept of entropy stabilization of crystal structures in oxide systems by embedding multiple metal cations into single-phase crystal structures. The interactions among the various metal cations lead to interesting and often unexpected characteristics. Some of the compounds show electrochemical and structural properties, which improve the capacity retention of conversion materials for Li-ion batteries. Another promising material class are the high entropy oxyfluoride systems (HEOFs), showing great potential to be part of next generation cathode materials. The modular building approach for these high entropy materials allows tailoring the composition to develop customized electrode materials, e.g. with reduced Co content.

In our report we present different approaches, which utilize the high entropy concept, for novel high entropy electrode materials. The compounds (Co0.2Cu0.2Mg0.2Ni0.2Zn0.2)O and Li(Co0.2Cu0.2Mg0.2Ni0.2Zn0.2)OF are used as anode and cathode materials, respectively. By replacing, adding or subtracting elements, the electrochemical properties can be tailored and the influence of different elements evaluated.

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EN02.19.37
Investigations of Ionic Conduction Mechanism and Charge-Discharge Property of  
Polyether/Li7La3Zr2O12(LLZO) Composite Solid Electrolytes  
Masaki Kato, Shiro Seki and Koji Hiraoka; Kogakuin University, Japan

Li-ion secondary batteries are widely used in many applications from various of electric devices, including mobile phones and electric vehicle to large scale power storage system due to high capacity, cycle ability and in/out put ability. Conventional electrolytes of Li-ion battery are mainly used flammable organic liquid electrolyte such as ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC). Not only performance improvement of batteries but also securing of essential safety of Li-ion batteries are also important. All solid-state Li
ion battery can solve the safety problem and higher energy density by stacking, weight saving of device by thinning of electrolyte layer are also possible. Our group focused on solid polymer electrolyte with high flexibility and oxide-based inorganic solid electrolyte with high ionic conductivity and chemical stability in air. We prepared polymer/inorganic composite solid electrolyte has high autonomy at thinning by using polyether-based solid polymer electrolyte and cubic-Li$_7$La$_3$Zr$_2$O$_{12}$(LLZO), one of the most candidate Li-ion conductive inorganic electrolyte with garnet structure. Preparation of samples and cell were carried out in Ar-filled groove box. LiN(SO$_2$CF$_3$)$_2$ and DMPA (photo initiator) were dissolved in polymer-based macromonomer solution ([Li] / [O] =0.1, amount of O was based on oxide unit from polyether and DMPA is 1000ppm based on weight of macromonomer). Cubic-LLZO were mixed in weight ratio of macromonomer: LLZO = 1: x (x =0, 0.2, 0.33, 0.42, 0.5, 0.6, 0.66) and a little acetonitrile were added to the solution to obtain homogeneous solution. The solutions were vacuum dried over 12h. The solutions were casted on glass plate and covered by two glass plate and 0.5mm teflon spacer. Composite solid electrolyte films were fabricated by radical polymerization under UV at 5 min. Ionic conductivity, Li/electrolyte interfacial behavior using Li/Li symmetrical cell, Li ion transport number were measured by AC impedance method (VSP, Bio-logic). Temperature dependence of ionic conductivity and Li/electrolyte resistance were carried out and Li-ion transport number were also measured at 333K. We consider that there are two Li ion conduction pass of polymer phase and LLZO particle in polyether/LLZO composite system from changing of impedance spectra. Li-ion conduction in LLZO particle and grain boundary is more preferentially than polymer phase because of ionic conductivity and amount of Li-ion career are much higher than polymer phase. Thermal properties of polyether/LLZO composite solid electrolytes were measured by differential scanning calorimetry (THRMO PRO EVO2, Rigaku). Heat capacity changes with glass transition of polymer electrolyte were observed -243K. All solid-state Li batteries were prepared using LiCoO$_2$ for positive electrolyte and Li metal for negative electrolyte. Charge-discharge measurements were performed in the operating voltage 4.2~2.5V and 0.05C rate at 333K and showed initial capacity of 120mAh/g. We will present about charge-discharge property and ionic conduction mechanism of polyether/LLZO composite system in detail on conference.

EN02.19.38

Developing Low-Potential Prussian Blue Analogues

Samuel J. Wheeler and Mauro Pasta; University of Oxford, United Kingdom

Prussian blue analogues (PBA) are some of the most promising cathode materials for sodium-ion and potassium-ion batteries operated in both aqueous and non-aqueous electrolytes. They have an open-framework structure that exhibits minimal structural change during ion insertion/extraction and enables fast ionic conduction. This leads to high power and long cycle life electrodes. However, the excellent properties of PBA cathodes can only be fully utilised in a full cell with an anode of comparable performance. One pathway to high performance anodes is to develop low-potential PBA materials by tuning the composition. This has successfully led to the development of anodes based on manganese hexacyanomanganate with a reduction potential of ~0.70 V vs. SHE.

In search for lower potential PBA compositions we recently reported a thorough characterisation of manganese hexacyanochromate which has a reduction potential of ~0.86 V vs. SHE, giving full cell voltages against common PBA cathodes approaching 2 V. This material had a modest specific capacity of 63 mAh g$^{-1}$, much lower than its theoretical value (~170 mAh g$^{-1}$) due to high vacancy and water content, and only one transition metal being electrochemically active. Improving its capacity is a scientific challenge as the material is unstable in the reduced state in water, which prevents the use of common strategies to reduce the vacancy and water content during synthesis. In my talk, I will present our efforts to improve the specific capacity and stability of low-potential Prussian blue analogues by exploring the wider transition-metal hexacyanochromate composition space and by developing novel synthetic strategies.

EN02.19.39
Phosphorene Based Composites as Anode Material for Potassium-Ion Battery Rishabh Jain, Prateek Hundekar and Nikhil Koratkar; Rensselaer Polytechnic Institute, United States

Potassium ion battery has recently gained considerable interest in energy storage systems. We report, for the first time, phosphorene as an anode material for K ion battery. Phosphorene showed very high initial capacity of 865 mAhg\(^{-1}\) which is attributed to alloy formation with potassium (K\(_{3-x}\)P) but also lead to tremendous increase in volume (200%). This lead to delamination of phosphorene anode which lead to very quick decay in specific capacity. In order to prevent huge loss in capacity decay, we investigated two different type of materials as buffer layer: reduced graphene oxide (2D) and single walled carbon nanotubes (1D). Phosphorene composite with reduced graphene oxide in proportion of 1:3 showed high specific capacity of 762 mAh g\(^{-1}\) and 72% capacity retention after 100 cycles. In comparison to that phosphorene composite with single walled carbon nanotubes (1:3) showed capacity retention of 40%. Phosphorene/reduced graphene oxide (P/rGO) also showed high rate capability (~400 mAhg\(^{-1}\) at 1C) and stable cycle life up to 300 cycles. Furthermore, P/rGO using spherical potassium cobalt oxide (s Koch) as cathode showed almost similar specific capacity (~400 mAhg\(^{-1}\) at 1C) and a long cycle life (100 cycles).

EN02.19.40
Reassessing the Charge Transfer Transition of Layered LiMO\(_2\) Electrodes Christopher Savory\(^1\), Aron Walsh\(^2\), Benjamin J. Morgan\(^3\) and David O. Scanlon\(^1\); \(^1\)University College London, United Kingdom; \(^2\)Imperial College London, United Kingdom; \(^3\)University of Bath, United Kingdom

Ab initio modelling is a useful tool in the study of battery electrodes, able to support experimental findings and predict new phases and behaviours, providing a suitable and accurate method is used. Regular Density Functional Theory (DFT) functionals such as the commonly used PBE, however, are impacted by the ‘self-interaction error’ which severely impacts the accuracy of calculations involving the highly-correlated 3d valence electrons in transition metals.\(^1\)

Historically, the study of battery cathodes using DFT has been improved through the addition of ‘U’ parameters, which correct for the self-interaction error,\(^2\) however these parameters require tuning to experimental measurements on the specific system in question, while also need to be varied during intercalation (with changes in oxidation state) and can be highly sensitive to changes in transition metal composition. This makes them unideal for the description of complex cathode systems such as NMCs and as a predictive tool for new systems.

Additionally, with the increased development behind the theory of anionic redox, accurate assessment of the charge transfer transition, which standard DFT tends to underestimate, is crucial.\(^3\) Minimally-parameterised hybrid DFT functionals such as HSE06 are routinely used to accurately predict the band gaps of semiconductors, however previous studies have highlighted disagreement between hybrid DFT and the band gap of LiCoO\(_2\) recorded from XPS-BIS, as well as overestimation of its predicted intercalation voltage.\(^4,5\)

In this study, we address this issue, demonstrating through a combination of HSE06 and high-level quasiparticle self-consistent GW calculations that the perceived value of the LiCoO\(_2\) charge transfer transition is underestimated, and that HSE06 represents an accurate, transferable standard method for describing the structural and electronic properties of LiMO\(_2\) cathode materials (M=Mn, Co, Ni). We also consider the issue of dispersion effects on estimated intercalation voltages, and explore the impact of the reassessed charge transfer gap on the defect chemistry of these materials, with a view to wider study of degradation and anionic redox in NMC cathodes.


EN02.19.41
Highly Porous Carbon in Multiscale as a Lithium-Sulfur Battery Cathode Seoyoung Yoon, Jihyeon Park and
Porous carbon is known for its strong mechanical stability, excellent electrical conductivity, high surface area and porosity. Therefore, it is utilized in various fields such as electrodes for electrochemical reactions or supports for gas storage. When applied as an electrode, its porous structure provides increased active sites and efficient electrolyte infiltration resulting in an enhanced performance of batteries. More specifically, porous structure reduces volume expansion of a cathode minimizing deformation and shuttle effect caused by migration of intermediates during reduction-oxidation reaction via sequestrating intermediates inside the pores. Furthermore, multiscale porous structure with macro-, meso-, and micro-pores allows an effective ion diffusion and charge transfer by shortening the ion diffusion path.

Herein, we synthesized metal organic framework (MOF) derived multiscale porous carbon by varying the ratio of more than one solvent and MOF-5 precursor, respectively. Dimethylformamide (DMF) and water were used as solvents, whereas benzene-1,4-dicarboxylic acid (BDC, C₆H₄(COOH)₂) and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) were MOF-5 precursors. Varying the ratios of solvents and ligand to metal led to changes in morphology of MOF via competition between water and BDC ligands for coordination with [Zn(NO₃)₂]⁶⁺ units. Afterwards, carbonization of MOF resulted in porous carbon with high specific surface area (837~2990 m²/g) and porosity (pore volume of 0.582~3.281 cc/g). Batteries with the controlled porous carbon as an electrode showed a broad range of performances: an initial capacity was 1123 mAh/g when water to DMF ratio was 11:1 and the metal-ligand ratio was 1:6, and the coulombic efficiency maintained over 98% even after 200 cycles. We believe a facile way to synthesize multiscale porous carbon with both meso- and micro-pores can pave a way for many other application areas including energy/conversion devices, catalysis, and gas storage.

Molecular Level Insight into the Lithium Coordination Structure and Lithium Transport Properties in Polyether-Based Polymer Electrolytes

Koki Yamada, Ryansu Sai, Yu Katayama and Hiromori Tsutsumi; Yamaguchi University, Japan

There has been much effort to develop solid-state electrolytes, including polymer electrolytes, with high energy and power densities, long cycle lives, and safety for next-generation lithium batteries. However, the ionic conductivities of current polymer electrolytes are orders of magnitude less than those of liquid electrolytes, and they are still insufficient for practical battery applications. In this study, a series of polyether-based polymers having different number of cyanoethoxy side chains are newly synthesized and compared. The contribution of the cyanoethoxy group to the Li⁺ coordination structure as well as electrolyte properties, such as the ionic conductivity and lithium transference number, are studied by various (electro)chemical and spectroscopic techniques. Here, we verify that the molecular structure of the repeating monomer unit of the polymers (i.e. the number of the cyanoethoxy group on the main chain) alter the Li⁺ coordination structure, which in turn affects the thermal stabilities and ionic transport properties. The result thus indicates the importance of the Li⁺ coordination structure in the polymer electrolyte in order to understand electrolyte properties. Our findings pave the way toward a design strategy for polymer electrolytes with improved conductivity, based on the Li⁺ coordination structure that has been experimentally identified.

Polymer Based Solid State Electrolyte for Safe Energy Storage Application

Samuel Danquah, Sangram K. Pradhan and Messaoud Bahoura; Norfolk State University, United States

Polymer solid electrolyte such as polyethylene oxide (PEO) could influence solid-state battery chemistries with desirable performance and safety due to their high ionic conductivity of 10⁻⁴ S.cm⁻¹ (65°C - 78 °C), low glass transition temperature, flexibility and its stability with lithium metals and conductive with lithium salt. In addition, it is environmentally stable and has an electrochemical window wide enough to overpower surplus electronic transport. However, limited thermal stability of PEO makes it more challenging for commercial use, which consequently, hinders the fast charging and discharging behavior of the battery. This work investigates the synthesis of polyethylene oxide solid electrolyte by a simple melting technique. A remarkable reduction of the interfacial impedance was noticed at room temperature. The structure and surface morphology of PEO was characterized by X-ray diffraction (XRD) and FESEM, respectively. Interestingly, field emission scanning electron microscope (FESEM) images show a porous nature of the electrolyte which promotes the movement of lithium ions through the
The electrochemical performance of the battery shows outstanding performance with large charge storage capability. The battery shows improved capacitance with higher number of charging and discharging cycles. This improvement in the rate ability is a result of the reduction in the interfacial impedance. This work is supported by the NSF-CREST (CREAM) Grant Number HRD 1547771, and NSF-CREST1 (CNBMD) Grant number HRD 1036494.

**EN02.19.44**

**Thin Solid Composite Electrolyte with Three-Dimensional Interconnected Structure**

Xi C. Chen¹, Max J. Palmer¹, Marm Dixit², Sergiy Kalnaus¹, Andrew S. Westover¹, Kelsey B. Hatzell² and Nancy J. Dudney¹; ¹Oak Ridge National Laboratory, United States; ²Vanderbilt University, United States

Composite solid electrolytes consisting of a processible soft polymer phase and a highly conductive hard ceramic phase are promising in enabling lithium metal anode to achieve high energy and power density. In order to achieve energy density goals, the electrolyte film must be thin (< 30 μm). In previous work, we discovered that composite electrolytes with high ceramic loadings suffer from low ionic conductivity due to a large interfacial resistance for ion transport across the polymer-ceramic interface.¹⁻² In a composite electrolyte where discrete ceramic particles are dispersed in the polymer host, ions do not transport through the ceramic phase due to large interparticle resistance.

Here we introduce an approach that creates a 3D interconnected structure of the ceramic with greatly reduced interparticle resistance.³ Furthermore, we fabricate a solid composite electrolyte film that is thin (20-30 μm in thickness), ionically conductive, and mechanically robust. Without the use of plasticizers, our composite film has an ionic conductivity of approximately 0.03 mS/cm at 30°C. Ion conduction path in the composite electrolyte is investigated by synchrotron X-ray tomography and finite element analysis.

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**EN02.19.45**

**Accurate Sub Nanometer Thin, Pristine 2D Channels for Electrochemical Applications**

Gangaiah Mettela, Pawin Lamprasertkun, Ashok Keerthi, Robert Dryfe and Radha Boya; University of Manchester, United Kingdom

Electric double layer capacitors (EDLC) are energy storage devices which fall between dielectric capacitors and batteries.¹ EDLC store the energy by ion adsorption on the electrode surface, and the criteria for a high performance electrode is high surface area to maximise the charge storage. In spite of numerous studies on porous electrodes particularly involving carbon, there still remains a lack of understanding on the precise relationship of confinement to EDLC, due to the distribution of pore sizes, and uncontrolled surface charge on electrodes.² A fundamental study establishing the relation between the capillaries/pore size in electrode to EDLC is a potential way to improvise the performance of a capacitor. We have fabricated sub nm thin channels through a modified of the fabrication method reported by Radha et al.³ Briefly, three components, namely- top, channel and bottom are assembled through the van der waals interactions. The thickness of the channels has been varied from 0.68 nm to a few nm, while channel length is of a few tens of microns. The obtained channels possess ultra-smooth pristine surfaces, nearly free from the rough edges. The specific capacitance and cation size effect of the electrolyte have been studied.

Thermal and Electrochemical Characterization of Adiponitrile (ADN) LiXF₆ (X = P, As, Sb) Cocrystals

Laura Sonnenberg, Birane Fall, Stephanie Wunder and Michael J. Zdilla; Temple University, United States

Cocrystals of adiponitrile (ADN₂LiXF₆ (X = P, As, Sb) can be formed by dissolving the LiXF₆ salts in excess ADN at elevated temperature and cooling to room temperature, resulting in the formation of cocrystals. The cocrystals all have the same crystal structure. Temperature-dependent ionic conductivities (σ) and lithium ion transference numbers, tₐ⁺, show that tₐ⁺(Sb) > tₐ⁺(As) > tₐ⁺(P), that is there is a greater contribution from the Li⁺ ion to the conductivity as the anion becomes larger (greater mass). Thermogravimetric analysis data indicate that the ADN is removed first (T_d ~ 100 °C) and that it comes off at the same temperature as ADN for LiPF₆ but at a higher temperature (T_d ~ 150 °C) for LiAsF₆ and LiSbF₆. Further, the residual weight loss of the anion increases as the anion size increases in mass. DSC data for (ADN) LiXF₆ indicates no melting of the sample below the T_d. However, there is a small melt and crystallization of the ADN. As previously observed, this is attributed to liquid regions around the co-crystallites. Similar DSC results are observed for the LiAsF₆ and LiSbF₆.

Improving Electrochemical Performance of LiNi₀.₈Mn₀.₁Co₀.₁O₂ Cathode by a Li-Nb-O Combined Coating/Substitution for High-Energy-Density Lithium-Ion Battery

Fengxia Xin, Hui Zhou, Xiaobo Chen, Carol M. Kaplan, Natasha Chernova, Guangwen Zhou and M. Stanley Whittingham; Binghamton University, United States

High-nickel NMCs are very attractive high capacity cathode material for practical applications, especially in automotive industry. However, many obstacles caused by the high nickel content, such as high surface reactivity, structural instability, etc., must be overcome before this type of compounds can become the material of choice for application. Through a wet chemistry method, a Li-Nb-O coated and substituted co-modified NMC 811 was prepared by single step treatment. The Li-Nb-O coating/substitution not only supplies a protection on surface but also optimize the material itself by Nb⁵⁺ incorporation. With this treatment, the 1st capacity loss was significantly reduced (13.7 vs. 25.1 mAh/g), which can contribute at least 5% increase on the energy density of full-cell level. In addition, both rate (158 vs. 135 mAh/g at 2C) and cycling (89.6 vs. 81.6% after 60 cycles) performance were greatly enhanced as well.

Acknowledgement: This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy, through the Advanced Battery Materials Research Program (Battery500 Consortium).

Simultaneous Exfoliation and Functionalization of Graphene for Supercapacitors

Yuling Zhuo; University of Manchester, United Kingdom

Aryl diazonium salts have been widely reported in the research of surface chemistry and they are believed to increase the specific capacitance of pristine graphene electrodes by introduction of pseudocapacitance as well as increased surface area due to prevention of graphene restacking. In this work functionalized graphene for use in supercapacitors was prepared by a two-step process, where graphene was functionalized with two different aryl diazonium salts (4-nitrobenzenediazonium tetrafluoroborate (NBD) or 4-bromobenzenediazonium tetrafluoroborate (BBD)) simultaneously during electrochemical exfoliation. Characteristic peaks identified from Raman and X-ray photoelectron spectroscopy demonstrate that the simultaneous functionalization and exfoliation of the graphene with NBD and BBD was successful. Cyclic voltammetry, galvanostatic charge-discharge measurements and electrochemical impedance spectroscopy were performed to study the electrochemical properties of the functionalized graphene electrodes. It was found that graphene NBD functionalized for 30 minutes (N30) exhibited superior energy storage properties with 5 times increase in specific capacitance compared to pristine graphene.
**EN02.19.50**

**Bismuth Nanowire Array Electrode for a Dual-Function Battery for Desalination and Energy Storage** Jun-Bin Wu¹, Shih-Hsun Chen², Shao-Sian Li¹ and Pochun Chen¹;¹ National Taipei University of Technology, Taiwan; ²National Taiwan University of Science and Technology, Taiwan

With the increasing demands of the green energy and fresh water, it is necessary to develop a more efficient approach to provide sustainable resources for human use. Seawater is an abundant resource to produce clean water and to store energy by desalination process. Among several types of desalination, electrochemical salt removal is a promising approach to separate dissolved salt ions from seawater and to selectively store sodium and chloride ions in cathode and anode. The development of desalination batteries depends critically on the discovery of high performance chloride-storage electrodes. Among all types of anode materials, bismuth-based electrodes, with a comparable theoretical specific capacity, as new high efficient electrode materials for chloride storage.

In this study, we designed and fabricated bismuth nanowire arrays with various aspect-ratios serving as chloride-storage electrodes by a template-assisted process. Chloride ions can be efficiently stored in the high-aspect-ratio bismuth nanowire structures in the form of BiOCl. We characterized and evaluated the bismuth nanowire array electrodes for application of seawater desalination. We carried out linear sweep voltammetry (LSV) and galvanostatic charging/discharging tests for half-cell reactions of bismuth nanowire array electrode to examine its chlorination/dechlorination behavior. In addition, we discussed the effects of the dimensional parameters of the bismuth nanowire arrays and the surface treatments on the bismuth nanowire arrays.

**EN02.19.51**

**Modeling the Mechanisms of Dendrite Growth and Suppression in Lithium-Ion Batteries** Zhuolin Xia¹, Feiyang Yu² and Dilip Gersappe¹;¹ SUNY-Stony Brook, United States; ²Columbia University, United States

The choice of an anode material for Li-Ion batteries is critical, since the formation of dendrites, which will result in safety problems and self-discharge, usually occurs on the anode. Thus, the choice of anode materials, the charge-discharge conditions and the additives inside of the electrolyte is critical to the formation of dendrites. Here, we focus our study on the use of Li metal anodes. To study the process of dendrite formation on Li anodes, we have developed a Lattice Boltzmann model. The model is used to study the mechanism of these processes, and the effects of applied potential and morphological features on the local concentration distribution and structure evolution. Our model is also able to capture the effect of charge-discharge cycles on the morphology of the anode. We also study the effect of pulsing on the formation of dendrites in the battery. These results can be used to build a relationship between design parameters and battery performance in order to improve the stability and the capacity of the battery.

**EN02.19.52**

**Abuse Tolerant 300 Wh/Kg High Energy Density Li-Ion Batteries** Jun Wang, Xiangyang Zhu, Hong Yan, Ryan Laplante, Jongho Jeon, Jordan Rubio, Qiguo Chen, Yao Chen, Kitae Kim, Maha Hammoud and Derek C. Johnson; A123 Systems LLC, United States

Rechargeable Li-ion batteries with energy density ≥ 300 Wh/kg (650 Wh/L) have become increasing important to extend driving range beyond 250 miles per charge for electric vehicles. While cell level energy density target may be achieved with commercial grade high nickel content (≥80%) NCM cathode when paired with Si/graphite composite anode, how to ensure such high nickel chemistry can deliver on cell safety requirements is a major hurdle to the vehicle electrification roadmap. Therefore, a number of techniques have been studied in order to improve Li ion battery safety at component level, such as active materials engineering and safer electrolyte formulation. The main purpose of this research is to demonstrate a technology path which can deliver cell level energy density of 300 Wh/Kg as well as meet very stringent abuse tolerance tests including nail penetration, overcharge, hotbox and crush. Due to intrinsically low first cycle columbic efficiency of the Si/graphite anode, prelithiation emerges as an indispensable process to reach 300 Wh/Kg energy density target. Cell safety is primarily achieved by combining A123’s for proprietary safety technologies with commercially available cathode materials such as NCM 811. As expected, the composite cathode materials exhibited improved thermal stability as onset temperature shifted to higher degree with split exothermal peaks as revealed by differential scanning calorimetry (DSC) characterization. Subsequent validation experiments conducted through production intent large format cell testing confirmed the
effectiveness of the A123 safety technologies while maintaining target energy density, as cells without those safety additives failed nail penetration (Hazard level 5.0) whereas those with safety additives passed convincingly (Hazard Level 3.0). Not surprisingly, this study also demonstrates that nail penetration, the most challenging one among all abuse tolerance tests, shows a strong dependence on testing conditions such as size and speed of the nail. Those results shed light on how high energy density Li ion batteries (≥300 W/kg) can be made safe through innovative engineering of commercial NCM cathode materials.

EN02.19.53
The Exploration on the Promising Performance of Epitaxial Li$_{1-x}$CoO$_2$ Thin Film  
Justin S. Pearson, Heshan Yu, Ren Yaoyu and Ichiro Takeuchi; University of Maryland, United States

Li$_{1-x}$CoO$_2$ (LCO) is a promising material for the application in lithium batteries as cathodes as well as the new type of transistor devices. Fabricating the epitaxial LCO thin films is considered to be a potentially effective method to raise the ionic conductivity and to optimize the interface between the solid electrolyte and electrode. In order to improve the performance of the LCO, the high-quality epitaxial thin films with different orientations, e.g., (104), (110), and (001) were grown on (100), (110), and (111) - oriented SrTiO$_3$ substrates utilizing the Pulsed Laser Deposition (PLD) technique with deposition temperature of 650 – 700 °C, respectively. By tuning the oxygen pressure and laser repetition precisely, the epitaxial LCO thin films with different grain sizes were fabricated. As shown in the X-ray diffraction results, the crystallization varies with changing oxygen pressure, e.g. intensity of the LCO diffraction peaks of each orientation firstly increases with raising oxygen pressure from 50mTorr to 150mTorr and then decreases at higher pressure. The surface geometry mapped by AFM and SEM also reveals that the grain size is the maximum at 150mTorr and would decrease with both raising and reducing the oxygen pressure. This may be related to the different growth modes: the level of interaction between the ablated material and the oxygen environment effectively enhanced the diffusion and growth of the film until the interactions increased past a critical point to change the growth mode leading to smaller uncoalesced grains at higher pressure. In order to maximize the grain size, the laser frequency is then carefully tuned at the most promising oxygen pressure of 150 mTorr. There exists approximately an order of magnitude change in the grain size with changing repetition. The grain size could be almost 1 micron with the laser frequency of 2Hz. Recently, the Lithiation and de-lithiation process is taken in a sealed cell at room temperature to investigate the function of the LCO with different grain sizes.

EN02.19.54
Ionic Liquid-Polymer Interaction in Fully Zwitterionic Ionogels Using Thermal Analysis  
Andrew G. Clark, Morgan Taylor, Matthew Panzer and Peggy Cebe; Tufts University, United States

In this study, the thermal properties of a group of zwitterionic copolymers containing ionic liquid designed for electrochemical energy storage are investigated using temperature modulated differential scanning calorimetry (TMDSC) and thermogravimetry (TG). Investigating the thermal properties will reveal how the zwitterionic moieties affect transition phenomena and interact with ionic electrolytes. Sulfo betaine vinylimidazole (SBVI) and 2-methacryloyloxyethyl phosphorylcholine (MPC) were dissolved in the commercial ionic liquid EMI TFSI in varying molar ratios and subsequently polymerized to produce fully zwitterionic random copolymers. TG reveals two degradation steps at 290 °C and 390 °C due to MPC degradation, and one step at 350 °C due to SBVI degradation. TMDSC at 5 °C/min was used to identify the glass transition of these materials, showing a decrease in $T_g$ from 60 °C to 10 °C with increasing addition of SBVI. A melting endotherm at -18 °C was observed on heating, attributed to the presence of residual ionic liquid. The solid state heat capacity of the polyzwitterions with ionic liquid was measured and compared to predictions assuming additivity of the heat capacities of the ionic liquid and polyzwitterions. The assumption of additivity was valid for only a few of the polyzwitterion compositions, suggesting that some of these materials were still in the liquid or partially liquid state, even down to -80 °C.

EN02.19.55
Transition-Metal-Mediated Instability of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ Spinel by In Situ Neutron Scattering  
Yan Chen and Ke An; Oak Ridge National Laboratory, United States

Transition metal (TM) substitution has been widely applied to tune the complex oxides crystal structures to create high energy density electrodes materials in high performance secondary rechargeable lithium-ion batteries. The LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel, which is obtained by substituting one fourth of the Mn with Ni in the LiMn$_2$O$_4$ spinel, is a candidate cathode material for electric vehicle applications because of its high operating voltage and large energy
density. The distribution of Ni and Mn at the octahedral sites plays a key role in the electrochemical performances such as capacity and cyclability, and it brings complexity in the material synthesis, thermal treatment and structure tuning. Thanks to its high sensitivity in detecting lithium ions and distinguishing transition metals, in-situ neutron scattering is used here to study the TM-mediated structure transition during the synthesis, as well as crystal structures in global and local scales, which is correlated with the electrochemical behaviors. In-situ neutron diffraction monitors the TM activities at elevated temperature, which are found to be significantly influenced by the atmosphere. In air, Ni and Mn reversibly exchange at the octahedral sites between 700~750 °C, mediating the “ordered” and “disordered” TM arrangement. The spinel-to-rocksalt structural transition occurs at higher temperatures, and it is reversible upon cooling. In contrast, in oxygen-deficient atmosphere it is found that the TM atoms not only exchange at the octahedral site but also migrate to the Li tetrahedral sites, resulting in the formation of a tetragonal spinel phase with the cubic spinel phase reserved. In-situ neutron diffraction reveals the kinetics of the TM migration, and the in-situ neutron pair distribution function evidences the TM valence change during the phase transition. The results will further guide and accelerate the novel material finding for high performance Li ion batteries.

Chitosan Based Gel Electrolytes for Zn-MnO2 Alkaline Rechargeable Batteries
Aswani Poosapati, Karla Negrete and Deepa Madan; University of Maryland, United States

Our study focuses on the use of Chitosan, a naturally available polysaccharide to form flexible films that act as gel electrolytes. Chitosan was chosen among various polysaccharides for testing due to natural abundance, renewability, biodegradability, cost-effectiveness, eco-friendly nature and a high degree of functionality, which is not available in most synthetic polymers. During initial testing, the ionic conductivity value obtained for pristine chitosan was approximately 10^{-6}S/cm, which is at least two orders of magnitude higher than the conventional synthetic polymers (PEO, PVP, etc.). This inherent advantage encouraged us to explore the possibility of their use as an electrolyte layer in batteries. It was noted that a semi-stable gel is formed when these biopolymers were vigorously mixed with minute amounts of acetic acid and dissolved in deionized water and allowed to sit for a while. It was also noted from the literature that chitosan films have an enormous surface area per unit volume (high aspect ratio), which makes us anticipate higher efficiencies. In our effort to make stable yet flexible organic films, various amounts of PVA (x=0.2, 0.4, 0.6, 0.8, 1) were added individually to Chitosan (CPx, CP=Chitosan: PVA), vortex mixed, cast into films, dried and then tested against SS blocking electrodes. Ionic conductivity studies on the various films provided a best average ionic conductivity value of 6.8mS/cm for CP0.2. This sample was then chosen and used for future experimentations due to enhanced conductivity and flexibility properties in comparison to pristine chitosan. To further enhance the ionic conductivities, varying amounts of KOH (y=0.1, 0.2, 0.3, 0.4, 0.5) were added individually to CP0.2 (CPKy, CPK=CP0.2: KOH) and cast into films and tested in a similar process as earlier. An average highest ionic conductivity of 105mS/cm was obtained for CPK0.3 (Chitosan: PVA: KOH= 1:0.2:0.3) sample. This sample CPK0.3 is then further analyzed for application in Zn-MnO2 batteries. Zn-MnO2 chemistries are chosen for testing the alkaline electrolyte due to their high-rate capabilities and mercury-free nature. Also, MnO2 is inexpensive, nontoxic and readily available. Prior to complete battery testing, the electrolyte is tested for electrochemical stability by conducting the linear scan voltammetry for SS/CPK0.3/Zn configuration. It was observed that the electrolyte was stable under 1.5V potential. This operating voltage window is a generic for Zn based systems. Then a cyclic voltammetry was performed between -0.5V and 1V, at a scan rate of 10mV/s for a Zn/CPK0.3/Zn configuration. It was observed that the electrolyte actually facilitates the oxidation and reduction at 0.5V and -0.35V potentials respectively. After these preliminary electrochemical studies, the prepared chitosan based gel electrolyte is then tested in a Zn-MnO2 system by using a Zn foil as anode and a MnO2 film prepared in-house after optimizing the ratios of MnO2, carbon and chitosan as cathode. Cyclic voltammetry and charge-discharge studies were then performed on this Zn/CPK0.3/MnO2 configuration battery. It was found that the cell stabilizes after the initial 3 cycles. A rapid galvanostatic charge-recharge study was also conducted at 50C rate for 15 cycles. The capacity attained was approximately 140 mAh/g and is relatively stable for the 15 cycles obtained. Further experiments with lower rates and more cycles need to be conducted and analyzed.

Structural Analysis of Li1+xAlxTi2-x(PO4)3 Thin Films for All-Solid-State Li-Ion Battery Applications
Marie
Francoise C. Millares1, Hunter Frost1, Matthew Chebuske1, Kevin Shah1, Yashashvini Andugula1, Spencer Flottman2,3, Seiichiro Higashiy4, Devendra K. Sadana4 and Harry Efstratiadis1; 1SUNY Polytechnic Institute College of Nanoscale Science and Engineering, United States; 2Oak Ridge National Laboratory, United States; 3Eonix, LCC, United States; 4IBM T.J. Watson Research Center, United States

Significant interest has arisen in all-solid-state lithium-ion batteries due to benefits in safety and cost. The electrolyte compounds used have many other benefits over traditional liquid electrolytes. One solid-state electrolyte of interest is the NASICON-like solid compound lithium aluminum titanium phosphate (Li1+xAlxTi2-x(PO4)3, LATP), due to its demonstrated high ionic conductivity of ~3x10^-3 S cm^-1. In this study, LATP thin films were successfully prepared through RF-magnetron sputtering of a 99.9% pure single LATP target onto a variety of substrates. LATP thin films (~100-150nm) were deposited at a range of temperatures varying from room temperature to 300°C, and annealed post-deposition at a variety of temperatures ranging from room temperature to 400°C. These alterations in process temperature have a significant impact on the resulting crystal structure of the thin films, as well as affecting both its ionically conductive and electrically resistive properties. The films' structural and compositional properties were characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM) and secondary ion mass spectroscopy (SIMS). The resulting XRD spectra depict a primarily polycrystalline structure with peaks at 35° and 50°, which can be attributed to the presence of LiOTi and AlTi alloy, respectively. SEM analysis shows crack-free films with clear surface morphology, which is ideal for minimizing electrolyte-electrode interface resistance, and SIMS analysis shows films with uniform composition.

EN02.19.58
Xerion’s Disruptive Battery Technology for Electrical Vehicle and Consumer Electronics Chadd Kiggins and John Cook; Xerion Advanced Battery, United States

As the demand for Li-ion battery technologies increase, transformative battery materials are desperately required. Cost, performance, and safety are major driving forces that determine the mass adoption of new materials by industry and consumers alike. Xerion Advanced Battery Corporation (XABC) produces low cost, high performance Li-ion batteries with increased safety by using a revolutionizing electroplating method. Cathode chemistries such as LiCoO2 and anode chemistries such as silicon can be directly electroplated onto current collectors yielding binder and carbon free electrodes. This architecture leads to a drastic increase in battery safety as it can shut down conductive pathways during a hard short since active materials like LiCoO2 are much less electrically conductive than carbon. This electrodeposition method doesn’t use highly purified starting raw materials, which reduces the cost of a cell by up to 50%. The unique electrode architectures are directly adhered to the current collector thereby reducing interfacial resistance and enhancing the power and energy of a given battery chemistry. This poster will give an overview of what Xerion’s battery technology is currently capable of delivering. The technology will be discussed from a cost and performance perspective.

EN02.19.59
Analytical Microscopy Studies of SEI Formation on Model Si Electrodes Andrew G. Norman1, Caleb Stetson2,1, Yanli Yin1, Manuel Schnabel1,2, Sang-Don Han1, Chun-Sheng Jiang1, Mowafak Al-Jassim1 and Anthony Burrell1; 1National Renewable Energy Laboratory, United States; 2Colorado School of Mines, United States

Lithium ion batteries are becoming an increasingly important part of everyday life with diverse applications from low emission electric vehicles to consumer electronics. Si anodes offer the potential for approximately ten times higher capacity than the presently used graphite electrodes. However, Si anodes have several challenges that have so far prevented their commercial application on a large scale. These include high capacity fade, a poor shelf life, and the long-term stability of the electrode materials. Solid electrolyte interphase (SEI) formation and stability is poorly understood in Si anodes as compared to graphite anodes. Problems faced include the large volume expansion/contraction on lithiation/delithiation and extensive gas formation during cycling.

In this work, we report on analytical scanning transmission electron microscopy (STEM) studies of the lithiation behavior and SEI formation on various model Si electrode structures. These include bare wafer Si and wafer Si with different thickness native and thermally grown SiO2 layers. We report data on the structure and chemistry of the lithiated electrodes and SEI layers formed. The results are correlated with results obtained by other techniques on the same samples including electrochemical cycling data and scanning spreading resistance microscopy (SSRM).
measurements on SEI thickness and resistivity. We have observed that resistance changes of the SEI measured by SSRM correlate with compositional differences in the SEI as determined by STEM electron energy loss spectrometry (EELS) and energy dispersive x-ray spectrometry (EDS) measurements.1


EN02.19.60
Comparative Study of Sulfide Solid Electrolytes for All-Solid-State Lithium-Ion Batteries—Chemical and Thermal Stability, Conformity with Cathode Material Jae-Ho Park1,2, Jiwon Jeong1,2, Jun Tae Kim1, Hun-Gi Jung1,2, Hwa Young Lee1, Woo Young Yoon2 and Kyung Yoon Chung1,3; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Korea University, Korea (the Republic of); 3Korea University of Science and Technology, Korea (the Republic of)

Recent studies on lithium-ion batteries (LIBs) have focused on satisfying the electrochemical performance that required for their applications such as electric vehicles and energy storage systems. Along with this research trend, there is also growing interest in preventing the risk factors on present LIBs caused by excessive improvement. In this respect, all-solid-state lithium-ion batteries (ASLBs) are one of the attractive candidate for next generation batteries that can improved both performance and safety compared to conventional LIBs.

Among various types of solid electrolyte (SE) candidates, sulfide-based SEs are promising due to high ionic conductivity which is comparable to commercial liquid electrolytes (~10⁻² S cm⁻¹ at room temperature) and high-formability which enables favorable inter-particles contact on composite electrode for ASLBs. Despite the advantages of sulfide-based SEs, there are several problems that should be solved such as chemical and oxidation instability, diffusion of mutual elements on interface with cathode materials.

In this work, we synthesized Li₇P₃S₁₁ and Li₆PS₅Cl sulfide-based SEs which have been widely studied, and we have conducted a comparative study on their chemical and thermal stability. To compare them, we performed optical observation and advanced X-ray diagnostics. Further more, we also confirmed the conformity between sulfide-based SEs and commercialized cathode material. The details will be discussed at the conference.

EN02.19.61
Tin Nanoparticles Embedded in Carbon Buffer Layer as Preferential Nucleation Sites for Stable Sodium Metal Anodes Huan Wang, Edward Matios, Chuanlong Wang and Weiyang Li; Dartmouth College, United States

Sodium (Na) metal is one of the most appealing anode materials for grid-scale energy storage systems owing to the high earth abundance and low cost of Na resources. Nevertheless, the implementation of Na metal anode is hindered by two primary issues associated with Na dendrite growth and volume expansion, resulting in low Coulombic efficiency and poor cycle life. Herein we present a facile and scalable method to synthesize tin (Sn) nanoparticles (NPs) that are uniformly embedded within carbon network (denoted as Sn@C composite), which can address the two issues simultaneously. Specifically, Sn NPs can serve as preferential nucleation sites to guide Na nucleation and thereby lower the Na deposition overpotential, while the carbon network can act as buffer layer to effectively minimize the volume change and alleviate the exfoliation of Sn NPs over repeated cycles. Consequently, high-capacity Na anodes can be realized with long-term reversibility and stability. Moreover, a room-temperature Na-sulfur battery based on the Sn@C composite as anode coupled with commercial sodium sulfide as cathode was demonstrated with significantly improved electrochemical performance. We believe this work provides a new pathway in designing high-energy Na metal batteries.

EN02.19.62
Exploiting Lewis Basic Nature of Boron-Containing Polymers to Improve Ionic Conductivity in Solid-State Electrolytes Megan Van Vliet; Temple University, United States

To improve the safety of Lithium Ion Batteries (LIBs) more desirable, non-flammable, highly conductive solid-state electrolytes are needed for commercial use. One promising alternative is the synthesis of highly conductive and flexible polymer electrolytes. Current polymers often suffer from low ionic conductivities that cannot meet current
standards for operation in LIBs. In order to increase performance and longevity, materials that only admit the electrochemically active cation are desirable. For this reason, synthetic efforts toward single-ion conducting polymers are necessary. A promising synthetic pathway is with the exploitation of the Lewis basic nature of borane compounds. With matching salts with Lewis basic anions to Lewis acidic boron-containing polymers, the interaction of the anions with the boron-containing polymer backbone are likely to hinder anionic movement. Meanwhile this allows the cations to be the most likely ionic conductor and help improve overall ionic conductivity of the system. The preparation of step-growth or Ziegler-Natta catalyzed boron-containing electrolyte polymers will be synthesized and analyzed via thermal gravimetric analysis, differential scanning calorimetry and electrochemical impedance spectroscopy for preliminary characterization.

EN02.19.63
An Alternative Route to Single Ion Conductivity Using Multi-Ionic Salts Sumanth Chereddy; Temple University, United States

One of the major problems with the Li metal batteries is the safety issues associated with dendrite growth when using metallic Li0 anode. There has been extensive research on the prevention of dendritic growth, including mechanical inhibition and limiting concentration gradients that result in anion depletion near the anode. The latter can be achieved by the use of electrolytes with high ionic conductivities and low anion mobility, i.e. high Li+ ion transference numbers (tLi+). Concentration gradients are avoided in polymer single ion conductors (SICs) with tLi+ ~ 1. However, conductivities of polymer SICs have remained low (< 10^{-5} S cm^{-1}). One of the reasons for low conductivity in polymer SICs is extensive ion aggregation. In this work we proposed the use of multi-ionic polyhedral oligomeric silsesquioxane (POSS) with dissociative lithium salts [POSS-(LiNSO2CF3)$_8$] dissolved in tetruglyme (G$_4$), CH$_3$-O-(CH$_2$CH$_2$O)$_4$-CH$_3$, as electrolytes having both high ionic conductivity and high lithium ion transference numbers. [POSS-(LiNSO2CF3)$_8$] can be dissolved at very high loadings into G$_4$, where they can be considered solvent-in salt electrolytes. Two systems were investigated, neat [POSS-(LiNSO2CF3)$_8$] in G$_4$ and mixtures of [POSS-(LiNSO2CF3)$_8$] with LiPF$_6$ or lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI). PFG-NMR indicates that Li can be un-dissociated, completely dissociated and surrounded by G$_4$ molecules, or as contact ion pairs (in which there are 3–4 ether oxygen contacts and one contact with the oxygen from the anion). Equilibria exist between the species of [POSS-(LiNSO2CF3)$_8$] and if there is rapid equilibration between the Li states and close enough proximity between the POSS-(LiNSO2CF3), then the Li$^+$ ions can migrate by a Grothuss-type coordinated hopping mechanism, as well as by a purely diffusive motion. Unlike polymer single ion conductors, where the backbone flexibility permits cluster/aggregate formation, which inhibits escape and mobility of the Li$^+$ ions, the rigid POSS cube and its colloidal structure in G$_4$ prevents formation of POSS-(NSO$_2$CF$_3$)$^-$ Li$^+$ (CF$_3$NSO$_2$) POSS triplets. Instead, the solvated Li$^+$ in POSS-(NSO$_2$CF$_3$)$^-$ Li$^+$ G$_4$ can be more easily removed to form conductive G$_4$ Li$^+$ G$_4$. Good ionic conductivities (< 10^{-4} S cm^{-1}) and lithium ion transference numbers of tPP = 0.65 can be achieved in these systems. Mixtures of 80 wt% LiTFSI and 20 wt% [POSS-(LiNSO2CF3)$_8$] in G$_4$ at an O/Li ratio of 20/1, yield both high conductivity (3.3 x 10^{-3} S cm$^{-1}$) and high (tPP = 0.65) transference number. Stable cycling at C/4 with high capacity retention was achieved using Li$^0$/[G$_4$/80 wt% LiTFSI/20 wt% [POSS-(LiNSO2CF3)$_8$]/LiFePO$_4$ half-cells.

S.Chereddy et.al., Materials Horizons, 2018 , 5, 461

EN02.19.64
Constructing Electrode/Electrolyte Interfaces with Low Resistance for All-Solid-State Batteries Nataly C. Rosero Navarro, Ryunosuke Kajiura, Akira Miura and Kiyoharu Tadanaga; Hokkaido University, Japan

All-solid-state lithium batteries based on oxide solid electrolytes are a practical proposal for large-scale energy storage applications because of chemical stability and ease to handle of oxide solid electrolytes (e.g. Li$_7$La$_3$Zr$_2$O$_{12}$, LLZ). The high interfacial resistance between electrode and electrolyte remains a major concern for their application. Here, an amorphous layer of lithium silicate is proposed as a suitable conductive material to construct a low interfacial resistance between garnet solid electrolyte and lithium metal. An adequate thickness of the lithium silicate layer allows obtaining an interfacial resistance as low as 50 Ω cm$^2$. Moreover, the symmetric cell of the Li$_2$SiO$_3$ modified garnet solid electrolyte and lithium metal shows a stable plating-stripping cycling behavior at a current density of 0.1 mA cm$^{-2}$ with a voltage response of less than 5 mV for up to 500 cycles.
Acknowledgments
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EN02.19.65
Liquid-Phase Syntheses of Sulfide Electrolytes and Application in All-Solid-State Lithium Battery Nataly C. Rosero Navarro, Akira Miura and Kiyoharu Tadanaga; Hokkaido University, United States

Sulfide-based solid electrolytes are promising for all-solid-state batteries because of their high ionic conductivity and good mechanical properties that allow an intimate contact at the interface between electrode and electrolyte by using only room temperature pressing [1,2]. A sulfide-based solid electrolyte with high ionic conductivity and small particle size is desirable to improve the charge transfer and to obtain a large interfacial contact area between the electrolyte and active material.

The synthesis of sulfide solid electrolytes by a liquid-phase process using an organic solvent has been recently reported. Reaction times from 24 h to more than 3 days are required. Here, we report an efficient synthesis of sulfide solid electrolytes by a simple procedure involving a liquid phase process under ultrasonic irradiation, with the short reaction time of 30 min, and heat treatments at low temperatures [3]. Sulfide solid electrolytes, such as Li7P3S11 and argyrodite Li6PS5Cl, with high ionic conductivity up to 1 mS cm-1 can be prepared. The control of the morphology was found to be essential to achieve high ionic conductivity.

Acknowledgements
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References

EN02.19.66
Ab Initio Investigation of the Diffusion Mechanism Lithium in Li4Ge1-xSnxS4 Hamidreza Seyf, Partha Mukherjee and Vilas G. Pol; Purdue University, United States

All-solid-state lithium-ion battery is regarded as the next generation battery to replace the current commercial lithium-ion battery. As one critical component in solid-state lithium-ion battery, solid-state electrolyte should possess superior operational safety and high ionic conductivity. Recently experimental studies have shown that substitution of Ge4+ by Sn4+ within Li4Ge1-xSnxS4 broaden the diffusion bottleneck, modify the lithium distribution, and enhance connectivity between the conduction channel, hence leading to an increase of the ionic conductivity for Li4SnS4. In this work, we have conducted an expensive ab initio molecular dynamics simulation to systematically study the diffusion mechanism of lithium ions in Li4Ge1-xSnxS4 at different Sn composition and temperature. Mean square displacements, pair correlation functions, diffusion coefficient, activation barrier, and pair correlation functions are calculated and their relation to the structural modification and transport properties are discussed.

EN02.19.67
A Theoretical Investigation of Enhanced Electrochemical Performance of Birnessite-Type MnOx Nanosheets Assembled on Reduced Graphene Oxide Template Yoon-Su Shim1, Segi Byun2, Jong Min Yuk1, Chan-Woo Lee2, Jungjoon Yoo2 and Jin Yu1; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2Korea Institute of Energy Research, Korea (the Republic of)

Graphene-based micro-supercapacitors have drawn valuable attention as a new class of micro-energy storage devices. However, due to their low volumetric energy densities, they have been limited for the use in micro-power sources. Here, we propose the densely packed manganese oxide/reduced graphene oxide hybrid film (MnOx/rGO) consisting of multi-valent Mn ions as the promising electrode material for high energy density. To study K ion storage behavior of MnOx/rGO nanosheet, density functional theory (DFT) calculations are employed. With the DFT calculation, we expect high thermodynamical stability of K-MnOx/rGO capacitor and its enhanced
We investigate the origin of the performance enhancement in terms of the charge gain from rGO and the increased electronic states near the Fermi level.

The charge gain is triggered by the formation of an interface between MnOx and rGO, which implies the changes of the oxidation state facilitating K-ion storage reaction. The enhancement of conductivity is also expected as a result of increased electronic states near the Fermi level. We believe that our finding will provide an invaluable insight on metal oxide/rGO composite for super capacitor.

**EN02.19.68**

**Nanoscale Morphology Evolution in Nanoporous Alloy-Type Lithium-Ion Anodes Elucidated by Transmission Electron Microscopy** John Corsi and Eric Detsi; University of Pennsylvania, United States

With the increasing adoption of solar and wind energy technologies, a large demand exists for energy storage with high energy density to accommodate the intermittency of these technologies. Although intercalation type battery lithium-ion electrodes have been highly successful due to their reliability, these chemistries have limited capacity. Alloy-type lithium-ion battery electrodes are an attractive alternative due to their large theoretical energy densities. However, these electrodes often experience poor cycle stability. This is due to the large volume changes (~300%) which occur during lithiation, causing the active material to crack during delithiation, and inducing delamination of this active material from the current collector.1 Previous work demonstrated that nanoporous electrode materials, consisting of an open three dimensional bicontinuous network of nanoscale ligaments and pores, have improved cycling performance compared to their bulk counterparts. Currently, it is hypothesized that this lithiation induced volume change is minimized due to a buffering mechanism in which the ligaments expand while the pores shrink, resulting in a smaller lithiation-induced net volume change.1 In an attempt to verify this hypothesis, synchrotron-based transmission X-ray microscopy (TXM) has been used to image these volume changes in nanoporous Sn (NP-Sn) and it was found that NP-Sn particles accommodate the lithiation-induced volume changes better than dense Sn.2 However, the TXM is only able to accurately probe the volume change in sub-micrometer sized Sn particles. My work seeks to build on this understanding by probing the structure at the nanoscale with transmission electron microscopy (TEM) using nanoporous gold (NP-Au) as a model material system for Li storage. The lithiation and delithiation of NP-Au electrodes were imaged *ex situ* using TEM at different stages of the process, to observe the structural evolution of the nanoporous ligament-pore structure. The next step will involve an *operando* study in which the NP-Au is imaged in real-time in the TEM. Through this methodology, this experiment will be able to address fundamental questions involving structural changes in nanoporous alloy-type lithium-ion battery anodes during (de)lithiation cycling. Although NP-Au was studied because it is considered a model nanoporous material, this methodology can be applied to earth-abundant candidate battery materials such as tin and aluminum.


**EN02.19.69**

**Intercalation-Conversion Hybrid Strategy Enabling Li-S Full-Cell Architectures with High Energy Density** Weijiang Xue; Massachusetts Institute of Technology, United States

A common practice in research of Li-S batteries is to use high electrode porosity and excessive electrolytes to boost sulfur-specific capacity. Here we propose a class of dense intercalation-conversion hybrid cathodes by combining intercalation-type Mo6S8 with conversion-type sulfur, to realize a Li-S full cell. The mechanically hard Mo6S8 with fast Li-ion transport ability, high electronic conductivity, active capacity contribution and high affinity for lithium polysulfides is shown to be an ideal backbone to immobilize the sulfur species and unlock their high gravimetric capacity. Cycling stability and rate capability are reported under realistic conditions of low carbon content, low electrolyte/active material ratio, low cathode porosity and high mass loading. A pouch cell assembled based on the hybrid cathode and 2× excess Li metal anode is able to simultaneously deliver a high gravimetric and volumetric energy densities.

**EN02.19.70**

**MXene-Based Nanomaterials as a Stable Matrix for High Performance Sodium Metal Anodes** Jianmin Luo
Sodium (Na) metal is a promising alternative to lithium metal as an anode material for the next-generation energy storage devices due to its high theoretical capacity, low cost, and natural abundance. However, dendritic/mossy Na growth caused by uncontrollable plating/stripping results in serious safety concerns and rapid electrode degradation. These studies present Sn²⁺ pillared Ti₃C₂ MXene/pillared MXene-derived porous nanocomposite serving as stable matrixes for high-performance dendrite-free Na metal anodes. 1) The intercalated Sn²⁺ between Ti₃C₂ layers not only induces Na to nucleate and grow within Ti₃C₂ interlayers, but also endows the Ti₃C₂ with larger interlayer space to accommodate the deposited Na by taking advantage of the “pillar effect” that leads to uniform Na deposition. 2) The obtained matrix facilitates Na nucleation and growth within interconnected nanopores promoted by the preferential chemical interaction between deposited Na and the matrix. As a result, the pillar-structured MXene-based Na metal anode exhibits superior electrochemical performance than that with host-less commercial Na. It is believed that the well-controlled MXene-based Na anode not only extends the application scope of MXene, but also provides guidance in designing high-performance and safe Na metal batteries.

EN02.19.71
Salt-Organic Cocrystals as Soft-Solid, Melt- and Press-Castable Solid Electrolytes for Lithium- and Sodium-Ion Batteries
Michael J. Zdilla¹, Stephanie Wunder¹, Birane Fall¹, Prabhat Prakash², Arun Venkatnathan² and Abdel Aziz Jalil¹; ¹Temple University, United States; ²IISER Pune, India

The cocrystalization of weakly-ligating organic molecules with lithium and sodium salts is a general phenomenon. Most of the time, these structures contain channels of weakly-bound cations that are highly mobile, giving conductivities as high as 5 x 10⁻⁴ S/cm, high for solid organic electrolytes. Preparation and characterization are described. Examples are given with high conductivity, good anode stability, and high cycle life. A unique feature of this class of electrolytes is an ionically conductive nanoliquid layer at the surface of the crystallites that facilitates grain binding and self-healing. This nanoliquid layer is additionally characterized by SEM, XRD, DSC, and its dynamical properties are described using molecular dynamics simulation.

EN02.19.72
Expanded Graphite Anodes Employing Atomic Metallic Pillars for High Capacity Sodium-Ion Batteries
Yoo Jin Kim and Won-Hee Ryu; Sookmyung Women's University, Korea (the Republic of)

Na-ion battery is a substitutional energy storage system for future large scale applications because of economic virtue and rich deposits of Na resource.[1, 3] However, low electrochemical performance (e.g. capacity, cycle life, and rate capability) of the electrode materials in Na-ion cell, originated from a large radius of the sodium ion, should be improved. Previous studies regarding anode materials for Na-ion batteries have further focused on improving affordable sites for Na ions and consequent reversible electrochemical reaction in Na accommodation layer. Improving anode materials is the important key to realize high capacity and stable cycle life of Na-ion batteries.

Graphite has been extensively used as an anode for commercialized lithium-ion batteries.[2] The graphite known as a long range and high crystalline carbon material can deliver a good capacity of ~350 mAh/g in Li-ion cells, yet poor capacity in terms of sluggish intercalation of large Na ion is shown in Na-ion cells.[3, 4] In this regard, non-graphitic hard carbon materials have been utilized as an alternative instead of the graphite due to high capacity around 300 mAh/g. However, their expensive material cost and low structural stability resulted from low crystallinity are a critical reason why we should seek better carbon alternatives.

Directly expanding interlayer of graphite is a preferred solution to develop carbon-based anode material for Na-ion batteries. Larger interlayer space and stable long-range order of the expanded graphite anodes enable excellent electrochemical performance.[5] Although there are many advantages of the expanded graphite anodes, side reactions easily occur between Na ions and a lot of oxygen contents in the carbon layers. The proper pillar components should be applied for developing high performance expanded graphite anodes.

In this work, we synthesized expanded graphite anode materials for Na-ion batteries using the functional introduction of atomic metallic pillars between graphene layers. We examined its morphology and structures of the
expanded graphite anode materials. Finally, we successfully achieved improved electrochemical properties of Na-ion batteries employing the expanded graphites, in comparison with reference samples due to the generation of sufficient Na-ion sites by functional pillar species.

References

EN02.19.73
A Solid-State Electrolyte Lithium Phosphorus Oxynitride Films Prepared from Li3PO4 Sintered Target for Li-Ion Batteries Prashanth Kumar Kodhamda1, Thulasi Raman K H2, Divya Bharathi M S1, Balasundaraprabhu R1, G Mohan Rao2 and Prasanna S1; 1PSG College of Technology, India; 2Indian Institute of Science, India

In the present work Lithium phosphorus oxynitride (LiPON) thin films which is used as solid electrolytes for Li-ion batteries, were deposited by reactive radio frequency (rf) magnetron sputtering technique using Li3PO4 sintered target under N2 atmosphere. It was observed that sintered target provides higher deposition rates, enhanced ionic conductivity, porous free thin films and could be used for more no of depositions using single target when compared to compact Li3PO4 powder targets. The non-porous nature of the film prevents the degradation of LiPON when exposed to moisture. Moreover, the deposited LiPON films exhibit good chemical stability for more no of charge/discharge cycles during full battery testing. It shows the superior interfacial compatibility with Li metal anode and it does not decompose when it comes into contact with Li, like other electrolytes. The electrochemical impedance spectroscopy of LiPON films showed an ionic Conductivity of $2.3 \times 10^{-6}$ Scm$^{-1}$ for sintered target thin films. Therefore we strongly believed that LiPON films deposited from sintered target are best suitable for solid state battery fabrication.

EN02.19.74
Printed Miniature Lithium-Ion Batteries for IoT Devices Anju Toor, Albert Wen and Ana Claudia Arias; University of California, Berkeley, United States

The rapid growth of the electronics industry has stimulated ever-increasing needs for both the amounts and types of portable electronics. Intensive efforts have been made to continuously develop miniaturized wireless devices, which can be used for smart medical implants, micro-electromechanical systems (MEMS). Such onboard autonomous devices need integrated power supplies or standby power sources to guarantee a stable current supply, and the size requirements for such kinds of power supplies are in a volume smaller than 10 mm$^3$.

Portable electronic devices evolved and incorporated several different types of rechargeable batteries, including lead-acid, Ni-Cd, Ni-MH, and Lithium-ion batteries. A Lithium-ion battery system is a preferred candidate for microscale power sources that can be integrated into autonomous on-chip electronic devices. They are not only able to provide relatively high power and energy density simultaneously, but also make the energy/power ratio and operation temperature adjustable by changing the electrode components and structures under the requested conditions.

Printed batteries incorporating additive manufacturing methods to achieve low-cost fabrication$^{[1-3]}$ and high throughput are excellent candidates for powering wireless electronic systems. Printing techniques such as stencil and screen printing offer the flexibility to customize battery active area as per the device layout and size requirements while also accommodating a wide range of substrate materials, ranging from flexible plastics to rigid substrates e.g. silicon. Although a significant amount of work has been performed on printed batteries for large-area applications, reports emphasizing on scaling battery size and power for typical IoT system requirements are limited$^{[4-6]}$.

In this contribution, a stencil-printed Lithium-ion battery with an electrode area scaled down to 1mm$^2$ is demonstrated. This work investigates the electrochemical limitations of Lithium-ion batteries as the active areas are
scaled-down. The battery consists of graphite and lithium cobalt oxide (LCO) as the respective anode and cathode layers printed on thin evaporated current collectors. For the fabrication of miniature batteries, a thin film configuration is adopted where single layers of anode, separator, and cathode are stacked together and sealed. A novel bonding strategy is developed to achieve a hermetic seal between (1) glass-glass and (2) silicon-glass substrates each having respective (cathode/anode) printed active layers. The batteries demonstrate an areal capacity of ~4 mAh/cm² and capacity retention of >95% under 100 charge/discharge cycles. Preliminary experiments show that a 5mmx5mm printed battery can easily power a micromote[7] that consumes a baseline current of 500-600μA. Further efforts to enhance the battery capacity at higher C-rates are currently in progress.

References:

EN02.19.75
All-Solid-State Asymmetric Supercapacitors with Metal Selenides Electrodes and Ionic Conductive Composites Electrolytes Yongrui Yang, Tao Zhu, Lei Liu and Xiong Gong; The University of Akron, United States

All-solid-state flexible asymmetric supercapacitors (ASCs) are developed by utilization of the graphene nanoribbon (GNR)/Co0.85Se composites as the positive electrode, the GNR/Bi2Se3 composites as the negative electrode and the polymer-grafted-graphene oxide membranes as solid-state electrolytes. Both GNR/Co0.85Se and GNR/Bi2Se3 composites electrodes are developed by a facile one-step hydrothermal growth method from graphene oxide nanoribbons as the nucleation framework. The GNR/Co0.85Se composites electrode exhibits a specific capacity of 76.4 mAh/g at the current density of 1 A/g and the GNR/Bi2Se3 composites electrode exhibits a specific capacity of 100.2 mAh/g at the current density of 0.5 A/g. Moreover, the stretchable membrane solid-state electrolytes exhibit superior ionic conductivity of 108.7 mS/cm. As a result, the flexible ASCs demonstrate an operating voltage of 1.6 V, an energy density of 30.9 Wh/kg at the power density of 559 W/kg, and excellent cycling stability with 89% capacitance retention after 5000 cycles. All these results demonstrate that we provide a simple, scalable, and efficient approach to fabricate high performance flexible all-solid-state ASCs for energy storage.

EN02.19.76
Predicting the Open Circuit Potential Curve for a Class of Ni-Rich Cathode Materials Kevin W. Kimura1,2, Rebecca Wilhelm3,4, Soo Kim2, Munir Besli2,4, Camille Usubelli2,4, Joerg Ziegler4, Reinhardt Klein2, Jake Christenson2 and Yelena Gorlin2; 1Cornell University, United States; 2Robert Bosch LLC, United States; 3Technical University of Munich, Germany; 4Karlsruhe Institute of Technology, Germany; 6University of Strasbourg, France; 6Robert Bosch GmbH, Germany

From consumer products to the automotive industry, lithium ion batteries (LIB) are playing an ever-increasing role in the electrification of our society. In particular, the automotive industry has seen exciting growth in the demand for batteries to meet the needs of an expanding battery electric vehicles (BEVs) market. Li[Ni0.80Co0.15Al0.05]O2 (NCA) is a cathode composition, which is of significant interest to BEVs, due to its high energy density and suitable thermal stability. A significant drawback of this material, however, is that one of its constituents, Co, continues to be a substantial contributor to cost. As a result, the recent industry trend has been to raise Ni and lower Co content in NCA, to decrease the cost and further increase the energy density of the battery. Effective adoption of these emerging Ni-rich NCA cathode materials requires improved understanding of their electrochemical properties, such as the open circuit potential (OCP) curve. To address this point, we show how Ni stoichiometry influences the OCP curve and identify a methodology for predicting OCP curves for a class of Ni-rich cathode materials.
Dry Pressed, High Mass Loading Electrode Architectures Enabled by Holey Graphene Yi Lin\textsuperscript{1} and John W. Connell\textsuperscript{2}; \textsuperscript{1}National Institute of Aerospace, United States; \textsuperscript{2}NASA Langley Research Center, United States

For future electric aviation, advanced battery cell chemistry beyond lithium ion batteries are required to meet mission requirements. High energy density battery concepts such as lithium-sulfur (Li-S) and lithium-oxygen (Li-O\textsubscript{2}) chemistries are being intensively investigated to realize their extraordinary theoretical promise in terms of energy density. Most fabrication methods of cathodes for these novel battery chemistries followed a conventional approach. In this approach, the active material is mixed with a polymer binder and a conductive carbon in a high-boiling organic solvent to form a slurry, followed by casting onto a current collector and solvent evaporation. The process is usually lengthy and poses environmental hazards due to the use of organic solvents.

Graphene is known to be an advanced carbon additive in novel battery electrodes with good electrical conductivity, high surface area, and mechanical robustness to maximize the electrochemical function of the active materials. Holey graphene, a structural derivative of graphene with an array of through-the-thickness holes across the lateral surface of the nanosheet, allow more facile cross-plane ion and gas transport than intact graphene, making it an ideal electrode material for electrochemical energy storage.

In this presentation, we will discuss our recent progress based on a unique property of holey graphene in that it can be compression molded into robust articles or architectures under solvent-free conditions without the need for parasitic binders. This unique dry compressibility of holey graphene has enabled facile dry fabrication of high mass loading electrodes with both high density and high porosity and controlled architectures, which have found use in a variety of energy storage applications including, but not limited to, supercapacitors and Li-O\textsubscript{2}, Li-S, and lithium-selenium (Li-Se) battery systems.

Enhanced Electrochemical Stability of NCM811 Solid-State Batteries by Surface Altering Processes Qing Zhang\textsuperscript{1}, Peter Aurora\textsuperscript{1}, Joshua Gallaway\textsuperscript{2} and Alyssa Stavola\textsuperscript{1}; \textsuperscript{1}Kostas Research Institute at Northeastern University, United States; \textsuperscript{2}Northeastern University, United States

Solid-state electrolytes (SSEs) are nonflammable and have a wider operation temperature range, making them much safer than their liquid counterparts. An ideal all solid-state Li ion battery (ASSB) made with high-energy electrode materials and superionic Li ion conductors has the potential to meet the high-energy and safety requirements of existing and new battery applications. Among various categories of SSEs, the sulfide family demonstrates the highest Li ion conductivity because sulfur has small binding energy to Li ions and large atomic radius. However, the stability of the interface between sulfide electrolyte and oxide cathode materials such as LiCoO\textsubscript{2} (LCO) and LiNi\textsubscript{1-x-y}Co\textsubscript{x}Mn\textsubscript{y}O\textsubscript{2} (NCM) is poor due to the large reaction energy between sulfide electrolytes and transition metal oxide materials. Chemical reactions at the interface as well as the formation of a space-charge layer result in large interfacial resistance. The goal of our study is to build an ASSB with high-energy NCM811 material which has a theoretical capacity of \textasciitilde200 mAh\textpermg\textsuperscript{2} and Li\textsubscript{6}PS\textsubscript{5}Cl sulfide electrolyte which has an ionic conductivity of 1.6 mS\textpercm\textsuperscript{2} at room temperature. We employed various methods to coat NCM811 material with oxide protective coatings, which are stable with both sulfide electrolytes and NCM811. LiNbO\textsubscript{3} coating was prepared by a sol-gel method and TiO\textsubscript{2} coating was prepared by dry-mixing. Characterization results showed that both methods produced a uniform coating. By altering the surface chemistry of NCM811, the cyclic stability of the ASSB was significantly improved compared to bare NCM811.

Surface Modification of Copper Current Collector Using Graphene Oxide as a Buffer Layer to Impede Lithium Dendrites Growth in LMBs Zewdu T. Wondimkun\textsuperscript{1}, Wei-Nien Su\textsuperscript{1} and Bing-Joe Hwang\textsuperscript{1,2}; \textsuperscript{1}National Taiwan University of Science and Technology, Taiwan; \textsuperscript{2}National Synchrotron Radiation Research Center, Taiwan

Lithium (Li) metal anodes have attracted considerable interest due to their ultrahigh theoretical gravimetric energy density and very low redox potential. However, the issues of nonuniform lithium deposits (dendritic Li) during cycling are hindering the practical applications of Li metal batteries. Herein, we propose a surface modification of the copper current collector with ultra-thin spin-coated GO as buffer layer to regulate the movement of Li ions. The as-prepared GO coated film enables smooth, uniform, and dendrite-free lithium plating. Moreover, the cell with the
GO-coated electrode displays superior reversible plating/stripping efficiency, low plating/stripping polarization and stable voltage profile than the bare copper electrode. Thus, Li/Cu@GO exhibit a CE of ~ 98% and that of the Li/Cu half cells show ~75% within 1 M LiPF₆ (1:1 v/v) (EC/DEC) after 50 cycles. Our results demonstrate the GO-coated buffer layer can be a promising strategy to improve inhibiting the growth of Li dendrites and the performance of LMBs.

EN02.19.81
Next-Generation Zn-Ion Batteries with Enhanced Rechargeability and High-Rate Operation via 3D Nanostructured Electrodes and Mixed Salt Electrolytes
Maya Helms¹, Megan Sassin¹, Joseph Parker¹, Christopher Chervin¹, Jesse S. Ko², Debra R. Rolison¹ and Jeffrey W. Long¹; ¹U.S. Naval Research Laboratory, United States; ²SLAC National Accelerator Laboratory, United States

The low cost and safety advantages of primary Zn/MnO₂ batteries can be translated to next-generation “zinc-ion batteries” by replacing the alkaline electrolyte with a near neutral-pH Zn²⁺-based electrolyte. The functionality of such Zn-ion batteries can be extended to include rechargeability (100s of cycles) and high-rate operation (300 mAh g⁻¹ at 1C and 100 mAh g⁻¹ at 20C) by using a 3D nanoarchitectured MnOₓ@carbon nanofoam-paper (CNF) electrode and a mixed salt electrolyte (e.g., ZnSO₄ + Na₂SO₄). The MnOₓ stores charge via pseudocapacitance at potentials not associated with Zn²⁺-based redox reactions, while Zn₄(OH)₆SO₄.5H₂O precipitates during discharge and dissolves during recharge. This complex charge-storage reaction is reversible over hundreds of cycles, which is attributed to structural features of the 3D CNF electrode and the use of a mixed-salt electrolyte. Recently, we developed an in-place conversion to create nanocrystalline ZnMn₂O₄ spinel from the 10-nm–thick birnessite-like MnOₓ coating on the CNF and demonstrated that the ZnMn₂O₄@CNF electrode also undergoes precipitation/dissolution reaction when cycled in 1M ZnSO₄, but offers benefits in terms of discharge voltage and long-term cycling stability.

EN02.19.82
Activation of Asphaltene Using Melamine Sponge for Applications in High Performance Supercapacitors
Shayan Enayat¹, Mai K Tran¹, Devashish Salpekar¹, Mohamad Kabbani², Ganguli Babu¹, Fransisco Vargas¹ and Pulickel Ajayan¹; ¹Rice University, United States; ²Shell, United States

Asphaltene is the heaviest fraction of crude oil consisting of a mixture of organic compounds. During oil production, the asphaltene fraction can get destabilized due to the changes in pressure, temperature, and composition, allowing its precipitation out of the crude oil. These precipitated asphaltene aggregates can cause surface deposition within oilfield wellbores, leading to a significant reduction in the well productivity.

In this work we report a novel technique for converting crude oil asphaltene into an interconnected porous carbon network material using melamine sponge as template. Dispersed pristine asphaltene powder in toluene is mixed with aqueous KOH solution, then sonicated and homogenized. The melamine sponge is saturated with the homogenized emulsion and heated to burn off the melamine resulting in a porous activated asphaltene of BET specific area of 3868 m²/g as compared to that of 2466 m²/g for that of activated carbon obtained under the same conditions. Electrochemical measurements of activated asphaltene-based supercapacitors in a standard aqueous electrolyte gives a high-performance specific capacitance of 197.3 F/g. Moreover, the activated asphaltene electrodes with “water-in-salt” electrolyte showed potential for higher voltage operating up to 2.5 V, with an energy density up to 31Wh/kg.
in many technical parameters, beyond Li-ion chemistries (Na, K, or multi-valence ions like Zn and Mg etc.) were considered as alternative bypasses to higher energy densities. These efforts have encountered various challenges, with electrolytes being the most frequent obstacles. Replacing non-aqueous solvents with water could bring significant benefits in both safety and environmental friendliness, but nonetheless increasing some of the challenges for the efforts to increase energy densities. One such conspicuous challenges has been the electrochemical stability window of water. This talk will summarize our recent efforts in this direction, and the various high voltage aqueous beyond Li-ion chemistries thus enabled.

8:30 AM EN02.20.02
Designing Safer Electrode Materials Using Coupled High Throughput Ab Intio Calculations and Experimental Characterization Maxim Makeev1, Sourav Ghosh2, Vilas G. Pol2 and Nav Nidhi Rajput1; 1Tufts University, United States; 2Purdue University, United States

Developing sustainable and safe energy storage devices is inherently a materials problem, which requires design of optimal electrode and electrolyte materials, alike. The aspects of the problem related to design and development of novel materials for energy storage have been and remain to be of utmost importance. In the Materials Science domain, a serious consideration is given to potential application of organic materials in energy storage devices, including – but not limited to – batteries. Also, recently, sodium-ion batteries (SIB) have attracted much attention as a cheap alternative to their conventional lithium-based counterparts. For SIBs, various carbon-based anode materials have been under intense scrutiny, aimed at finding a solution with improved electrochemical performance and cycle life [1]. While significant benefits of such a paradigm shift is evident, a number of materials-related problems still remain to be solved. Thus, it is well realized by now that sodium-based batteries require a different set of materials to be used in battery architectures than their conventional counterparts, with organic materials being regarded as promising possible solution [2]. In this work, we focus on sodium terephthalate (Na2C8H2O4) as a material for electrodes, as it offers high flexibility in design and has been previously shown to be a good candidate for sodium-based batteries. It has also been noticed, however, that electron conductivity of the compound is below the desirable limit. Correspondingly, the purpose of the theoretical part of the present work is to understand the electronic properties of sodium terephthalate-based matrices and their response to intercalation of different types of ions. Within the framework, we restrict ourselves to three types of ions: sodium, lithium, and potassium. The comparative analysis of the structural and electronic properties of sodium terephthalate during sequential intercalation of ions of the three above types will be presented. The electronic structure calculations have been performed on both single molecule and unit cells of Na2C8H2O4 crystalline phase with periodic boundary conditions. All the computations, reported in this study, have been performed with high throughput screening paradigms; the method and its extensions developed for this work will be highlighted in the presentation [3]. The obtained theoretical results will be presented, discussed, and analyzed in the context of experimental data obtained on sodium terephthalate. This includes structural analysis performed using both XRD and SEM, and electrochemical characterization of lithium, sodium, and potassium ion batteries performance.


8:45 AM EN02.20.03
Humidity-Induced Degradation and Surface Reconstruction of Ni-Rich Layered Oxides Leiting Zhang1, Christoph Bolli1, Heino Sommer2, Petr Novák1 and Sigita Trabesinger1; 1Paul Scherrer Institut, Switzerland; 2BASF SE, Germany

There is a pressing need for improving the energy density and lowering the cost for next-generation Li-ion batteries. Ni-rich layered oxides, in a general term of Li(Ni\textsubscript{x}Co\textsubscript{y}Mn\textsubscript{1-x-y})O\textsubscript{2} (x > 0.5), are widely recognized as a competitive candidates. However, the high surface reactivity of the materials results in parasitic side reactions in contact with electrolyte and notable gas release when the cell is charged to higher potentials. Furthermore, the oxygen-loss leads to formation of a MO\textsubscript{x} spinel/rock-salt-like phase on the surface of the pristine material, accounting for significant internal resistance growth and, hence, quick capacity loss.
In this study, we embarked on a systematic investigation of the moisture-sensitivity of the LiNi_{0.85}Co_{0.1}Mn_{0.05}O_{2} material by aging it in a controlled environment with constant relative humidity (RH) of 63 % for different periods of time. Online electrochemical mass spectrometry (OEMS) was used as a main tool to investigate the gas release behavior of the aged samples. A thorough understanding of the interfacial degradation phenomena was gained by additional electrochemical and physiochemical characterization, such as experiments with isotopically-labelled electrolyte, surface carbonate titration, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). A reaction scheme accounting for the origin of CO_{2} evolution will also be elucidated.

Reference

Acknowledgment
BASF SE is acknowledged for financial support.

9:00 AM EN02.20.04
Enhancing the Structural and Li Transport Properties of Li_{4-2x}Fe_{x}SiO_{4} via Composition Engineering Yan Zeng¹, Karim Zaghib² and George P. Demopoulos¹; ¹McGill University, Canada; ²Hydro Québec, Canada

Compositional engineering can serve as an effective strategy to tune the electronic and crystal structures of intercalation compounds, hence enhancing their electrochemical properties. The recent development in advanced Li-rich layered oxides has shown the benefits of non-stoichiometry particularly in enhancing the energy density of Li-ion cathodes. We apply this strategy in improving another type of cathode material, Li_{2}FeSiO_{4}, which although possesses attractive properties in terms of safety and sustainability, has been suffering from low electronic and ionic conductivities and the difficulty in utilizing more than one Li-capacity per formula unit. We synthesized non-stoichiometric compounds Li_{4-2x}Fe_{x}SiO_{4}, in two directions– Li-rich and Fe-rich, via a hydrothermal method. X-ray diffraction with Rietveld refinements and elemental analyses reveal that there are solubility limitations to the extent of non-stoichiometry that can be sustained in Li_{2}FeSiO_{4} synthesized at 200°C. We demonstrate that Fe-rich Li_{2}FeSiO_{4} not only delivers higher capacity vis-à-vis the stoichiometric composition because of the higher Fe content but also shows promises in facilitating electronic and ionic transport. An evaluation integrating the experimental electrochemistry tests, including Cyclic Voltammetry (CV) and Galvanostatic Intermittent Titration Technique (GITT), with \textit{ab initio} DFT calculations suggests that the enhanced electrochemical performance is mainly attributed to the new Fe–O–Fe configurations and the pre-existing Li-vacancies.

Acknowledgments: This research is supported by a Hydro-Quebec/NSERC CRD grant and the McGill Sustainability Systems Initiative (MSSI).

9:15 AM EN02.20.05
Rational Design of Cathode Materials Operated by Anionic Redox Reactions for Advanced Sodium-Ion Batteries Duho Kim; Kyung Hee University, Korea (the Republic of)

In recent years, sodium-ion batteries (SIBs) have been identified as the most promising alternative to lithium-ion batteries (LIBs) owing to the low-cost and abundance of sodium resources. Therefore, numerous efforts have been invested in the development of SIBs for large-scale energy storage applications. Among various cathodes, Mn-based layered oxides have been considered to be promising materials to achieve high-energy-density cathodes owing to their low cost, abundance, and eco-friendliness. Considering the fact that the standard redox potential of Na/Na^{+} is lower than that of Li/Li^{+} (by ~0.3 V), many research groups have focused on the introduction of different transition metals (M) or non-M atoms with varying compositions in Mn-based layered oxides in order to gain high-redox-potential. Recently, anionic redox reactions have attracted great attention due to their potential to improve energy density of battery cathode materials for LIBs and SIBs. These anionic redox reactions have been considered to be a more crucial factor to overcome the limitation of energy density for SIBs than those for LIBs because the anion-based redox behavior induced by the pure lattice oxygen (O_{2}/O^{2-}) occur at a high-voltage of 4.2 V versus Na/Na^{+}. However, the only anion-based redox mechanism leads to structural instabilities resulting in severe phase separations and chemomechanical stresses, which reflect significant irreversibility in the first cycle, capacity and
voltage fading upon cycling. In this talk, we in detail present that Na[Li\textsubscript{1/3}Mn\textsubscript{2/3}]O\textsubscript{2} is rationally designed as an example of a new class of promising cathode materials through a fundamental understanding of the redox reaction mechanism in Li\textsubscript{3}MnO\textsubscript{3} exhibiting a high redox potential of ~4.2 V versus Na/Na\textsuperscript{+} with high charge capacity (190 mAh g\textsuperscript{-1}). In spite of the rigorously designed Na[Li\textsubscript{1/3}Mn\textsubscript{2/3}]O\textsubscript{2} utilizing the anionic redox of O 2p-electron of Na-O-Li configuration, two major challenges regarded as the phase separation and the chemomechanical stress remain to improve the electrochemical performance. Herein, we propose the rational use of anion-based redox reactions to mitigate the two drawbacks and attain high-energy-density cathodes with cyclic stability for SIBs, which enables the development of rechargeable sodium battery materials for high-energy-density.

9:30 AM BREAK

10:00 AM *EN02.20.06

Unsuitable Electrolytes Made Suitable for Li-O\textsubscript{2} Batteries with the Use of Redox Mediators Nuria Garcia-Araez, J. Padmanabhan Vivek, Tom Homewood, James Frith and John Owen; University of Southampton, United Kingdom

Redox mediators have demonstrated dramatic improvements in performance of Li-O\textsubscript{2} batteries. However, degradation reactions triggered by reactive intermediates in the oxygen reduction and evolution reactions (singlet oxygen, superoxide, etc.) are still the main cause of poor performance. This talk specifically addresses the development of redox mediators to prevent Li-O\textsubscript{2} battery degradation. The synergetic combination of redox mediators with water is shown to produce step change improvements in all performance metrics [1], which is attributed to an alteration of the reaction mechanism bypassing problematic reaction intermediates. In further work, a new type of inorganic redox mediator, polyoxometalates, is shown to exhibit high catalytic activity towards Li-O\textsubscript{2} battery reactions and unprecedented resistance against degradation [2]. In addition, redox mediators are also used to suppress the degradation of electrolytes in such a way that unsuitable electrolytes (e.g. prone to degradation by the attack of superoxide species) are transformed into suitable electrolyte candidates for Li-O\textsubscript{2} battery applications [3].

References:

10:30 AM EN02.20.07

Is Nickel Hydroxide Charging Only Skin Deep? Joseph H. Hadden, D. Jason Riley and Mary P. Ryan; Imperial College London, United Kingdom

Renewable energy sources, which do not continuously produce power, rely on charge storage devices to hold excess energy when supply is high and provide energy when demand is high. Understanding the charging mechanism of energy storage materials is critical for further improving the performance of these devices. This work demonstrates a method of analysing the charging surface layer using time of flight secondary ion mass spectrometry in a model energy storage material, Ni(OH)\textsubscript{2}. Since Ni(OH)\textsubscript{2} exchanges protons with the electrolyte on charging and discharging in alkaline media, deuterated solvents were used to load the charging layer with deuterium, which could then be analysed using a depth profile. Electrodeposited Ni(OH)\textsubscript{2} was initially used, however the density was too low to provide a single flat surface for the reaction. Low melting point paraffin wax was used to fill all pores in the material, preventing electrolyte ingress. The surface was then ground down to allow electrolyte access to the top face of the electrodeposited Ni(OH)\textsubscript{2} only. Time of flight secondary ion mass spectrometry after potential cycling in deuterated aqueous alkaline electrolyte was performed on the samples before and after the wax deposition. It was found that despite an expected substantial deuterium background signal from the wax, a noticeable increase in deuterium was observed after cycling. This increase was proportional to the theoretical 50% exchange per cycle. Measuring the sputter crater depth using AFM allowed the decay with depth to be measured. It was found that the increase in deuterium only occurred over the first 20-30 nm, which agreed well with observations of a charging surface “skin”.

10:45 AM EN02.20.08
Electrostatically Tuned Microdomain Morphology and Phase-Dependent Ion Transport Anisotropy in Single-Ion Conducting Block Copolyelectrolytes

Chenxi Zhai¹, Huanhuan Zhou¹, Teng Gao², Lingling Zhao² and Shangchao Lin³; ¹Florida State University, United States; ²Southeast University, China; ³Shanghai Jiao Tong University, China

Block copolyelectrolytes are solid-state single-ion conductors which phase separate into ubiquitous microdomains to enable both high ion transference number and structural integrity. Ion transport in these charged block copolymers highly depends on the nanoscale microdomain morphology; however, the influence of electrostatic interactions on morphology and ion diffusion pathways in block copolyelectrolytes remains an obscure feature. In this paper, we systematically predict the phase diagram and morphology of diblock copolyelectrolytes using a modified dissipative particle dynamics simulation framework, considering both explicit electrostatic interactions and ion diffusion dynamics. Various experimentally controllable conditions are considered here, including block volume fraction, Flory–Huggins parameter, block charge fraction or ion concentration, and dielectric constant. Boundaries for microphase transitions are identified based on the computed structure factors, mimicking small-angle X-ray scattering patterns. Furthermore, we develop a novel “diffusivity tensor” approach to predict the degree of anisotropy in ion diffusivity along the principal microdomain orientations, which leads to hitherto missing mapping of phase-dependent ion transport properties. Inclusion of ions leads to a significant leftward and upward shift of the phase diagram due to ion-induced excluded volume, increased entropy of mixing, and reduced interfacial tension between dissimilar blocks. Interestingly, we discover that the inverse topology gyroid and cylindrical phases are ideal candidates for solid-state electrolytes in metal-ion batteries. These inverse phases exhibit an optimal combination of high ion conductivity, well-percolated diffusion pathways, and mechanical robustness. Finally, we find that higher dielectric constants can lead to higher ion diffusivity by reducing electrostatic cohesions between the charged block and counterions to facilitate ion diffusion across block microdomain interfaces. This work significantly expands the design space for emerging block copolyelectrolytes and motivates future efforts to explore inverse phases to avoid engineering hurdles of aligning microdomains or removing grain boundaries.

SESSION EN02.21: New Materials and Methods III
Session Chair: Hao Bin Wu
Friday Afternoon, December 6, 2019
Hynes, Level 2, Room 207

1:30 PM *EN02.21.01
Point Defects in Lithium-Rich Layered Oxides for Energy Storage
William C. Chueh and Peter Csernica; Stanford University, United States

Layered LiₓMO₂₋ₓ (e.g., LiCoO₂) is a key component in lithium-ion batteries and is one of the most utilized nonstoichiometric oxides. The most studied point defect is the Li that occupies the van der Waals gap; its concentration is thoroughly studied as a function of lithium activity through coulometric titration. However, there are several additional point defects that are less investigated. They are: (1) Vₓ cation vacancies, (2) Liₓ/MₓLi antisites, and (3) Vₒ oxygen vacancies. In these oxides, metal vacancies can form by migrating a metal into the van der Waals gap. X-ray and neutron scattering measurements confirmed that introducing metal vacancies can substantially contract neighboring M-O bond length, transforming single bonds to double bonds (i.e., terminal metal oxo ligand). In select local configurations, even the peroxo species (O-O)²⁻ can form. These variations of oxygen bonding leads to dramatic modification of the Li and O redox potentials. Oxygen vacancies also exhibit coupling to other point defects, mainly through partial Schottky disorder. In this talk, I will discuss the characterization of these point defects for M = Ni, Mn, Co, Ru and Ir, their interactions amongst one another, and implications for engineering better lithium-ion batteries.

2:00 PM EN02.21.02
Achieving Superior Interfacial Stability from Well-Designed Artificial Lithium-Metal Interphase with Polymers of Intrinsic Microporosity
Hyun Jong Kim, Moon G. Hyeon, Dong Jae Chung, Hyun Dong Yoo, Hansu Kim and Yong Soo Kang; Hanyang University, Korea (the Republic of)
Li metal has been in the spotlight as the most promising anode material because it has the highest specific capacity and the lowest working potential. However, including fast capacity fading and dendrite formation derived from their high reactivity still remain challenges for practical application. In this work, we have investigated the artificial solid interphase with polymers of intrinsic microporosity which improving electrochemical performance and the associated morphological changes by various analytical techniques as well as electrochemical characterization techniques. As a result, we found a desolvation effect of electrolyte through the PIM-1 coating, thereby forming the uniform and stable lithium deposition during cycling. Adopting a highly stable artificial solid interphase with polymers of intrinsic microporosity can improve interfacial stability and electrochemical characteristics of lithium metal battery, encouraging the development of lithium metal-based rechargeable batteries.

2:15 PM EN02.21.03
Impact of Liquid Phase Formation on Microstructure and Conductivity of Li-Stabilized Na-β"'-Alumina Ceramics Marie-Claude Bay, Meike V. Heinz and Corsin Battaglia; Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Ceramic Na-β"'-alumina is a fast solid-state sodium-ion conductor deployed as electrolyte in commercial high-temperature NaNiCl and NaS batteries (0.2 S/cm at 300 °C). Furthermore, it is gaining attention as interesting candidate for all-solid-state batteries (1 mS/cm at room temperature). Processing of Na-β"'-alumina is, however, challenging and results in large variations in reported values for the ionic conductivity. We systematically reexamine the impact of sintering conditions on microstructure and sodium-ion conductivity of Na-β"'-alumina ceramics.[1] Depending on sintering temperature and sintering time, we measure conductivities between 0.04 and 0.37 S/cm at 300 °C on ceramics prepared from identical starting powders. During sintering, formation of a liquid phase is observed above 1500 °C, which promotes densification, but leads to abnormal grain growth for extended sintering times. While such conditions result in the highest conductivities measured for our sample series (0.37 S/cm at 300 °C), the corresponding microstructures are mechanically fragile. For mechanically robust, densely sintered samples, we identify the average grain size as the dominating factor controlling ion conductivity. For average grain sizes between 1 and 6 μm, we obtain conductivities between 0.17 and 0.27 S/cm at 300 °C. The influence of porosity in under-sintered, highly porous samples is well accounted for by Archie’s law and results in low ion conductivities down to 0.04 S/cm at 68% density. Our insights into microstructural factors controlling ionic conductivity such as grain size and density are instrumental for the successful integration of Na-β"'-alumina ceramic electrolytes into next-generation batteries.


2:30 PM EN02.21.04
Lithiated Lithiophilic (Li,Si) Layer Induced Li Host Materials for Next Generation High-Energy Li-Metal Batteries YoonKwang Lee and Jaephil Cho; UNIST, Korea (the Republic of)

Li-ion battery application has been simultaneously widened with the development of portable devices. In particular, high volumetric/gravimetric energy density LiB has attracted attention due to increasing demands for mass energy storage devices such as electric vehicles and Energy Storage System. Li metal has been reinspired as next generation preeminent promising anode materials because extensive researches of high-energy silicon anodes to commercialize it was insufficient to substitute graphite in terms of cycle stability. Li metal facilitates extremely high specific capacity (3860 mAh/g) and lowest electrochemical potential (~3.04 V) that it features its high power and energy density. However, the use LMB was hindered from severe safety issues related to volume expansion from non-uniform deposition, uncontrollable dendrite growth and crack induced repeated SEI formation. The above-mentioned reasons cause electrolyte consumption, low Coulombic efficiency, resulting in capacity deterioration and, more seriously internal short circuits and explosion. Regulating Li plating and suppression of Li dendrites should be realized to solve the problems.

In this study, we synthesized ion and electron conductive carbon structure, which contains sufficient space to accommodate Li during plating and striping. Li is intensely light metal denoting 0.534 g/cm³ density that the required dense lithium thickness is 14.6 μm for commercializable areal capacity (≥3 mAh/cm²). The interconnected porous structure containing 200 nm pore and showing 0.2 g/cm³ tap density takes merits in expanded potentious area
for Li deposition. To incorporate lithiophilic surface layer, thermal decomposed artificial interfacial Si nano-layer was deposited uniformly with 5 nm. The lithiophilic lithiated Si (LixSi) alleviated the polarization that it could induce planar Li nucleation and continuous Li accumulation at inner pore and outer surface region, followed by dense and smooth Li plating in electrode. The volume expansion of the electrode at lithiated state of 3 mAh/cm² was just 30% from 27 um to 35 um because of the adequate pore volume. And lithiophilic layer induced electrode exhibited prolonged lifespan and high power performances at high current density comparing to solely carbon frame.

2:45 PM EN02.21.05
Role of Solid Electrolyte Interphase in Sodium Electrodeposition Revealed through Liquid Cell Electron Microscopy Zhiyuan Zeng; City University of Hong Kong, Hong Kong

Solid-electrolyte interphase (SEI) plays a vital role in the performance of an electrochemical device, such as batteries and capacitors. Much progress has been made in the understanding of SEI formed on lithium metal, however little information is available on sodium SEI. Here, we report an in situ study of Na deposition with our development of electrochemical liquid cells, in which the electrodes within a cell are patterned in different configurations to produce a flat or sharp curvature. Real time observation using transmission electron microscopy (TEM) reveals an unprecedented level of detail on Na electrodeposition. The Na deposition shows granular growth. Variations in the SEI thickness on a Na nanograin introduce differences in the local growth rate and disparities in the morphology. The newly formed Na grains preferentially deposit at the base of existing grains close to the electrode. Such “base growth” behavior is more dramatic on the electrode with sharper curvature. Further studies using continuum-based computational modeling show the deposition behavior of an alkali metal is strongly influenced by the transport properties of SEI, thus the growth mode, either “tip growth” or “base growth”. Our direct observation of Na deposition in combination with the theoretical modeling provides critical insights for comprehensive understanding of SEI effects on the electrochemical deposition of an alkali metal.

SYMPOSIUM EN03

Green Electrochemical Energy Storage Solutions—Materials, Processes and Devices
December 2 - December 5, 2019

Symposium Organizers
Clara Santato, Ecole Polytechnique de Montreal
Francesca Soavi, University of Bologna
Min–Kyu Song, Washington State University
Hongli Zhu, Northeastern University

Symposium Support
Bronze
MilliporeSigma

* Invited Paper

SESSION EN03.01: Green Electrochemical Energy Storage Solutions—Materials, Processes and Devices I
Session Chair: Clara Santato
Monday Morning, December 2, 2019
Sheraton, 2nd Floor, Republic A

8:30 AM *EN03.01.01
Bioinspired Energy Storage Devices  Magdalena Titirici; Imperial College London, United Kingdom

Building a healthy and wealthy society fuelled by clean energy is the most important challenge of the 21st Century. New energy technologies rely heavily on materials, while materials production relies on energy. It is crucial we will address the fine balance between the development of emerging energy technologies and the materials we use to build them. Today, scarce metals are the most important components of energy storage and conversion systems. The current available supply for these metals cannot sustain the expansion of such technologies at a global scale. Sustainability means avoiding the depletion of natural resources to maintain an ecological balance. Sustainable development means meeting the needs of the present without compromising the well-being of future generations. Based on these definitions, the approaches we currently use to build renewable energy technologies are not sustainable, as we rely on materials choices that are limited and geographically constrained. We need to learn from past mistakes made with fossil fuels to build a future society based on clean energy. In this talk I will present new concept is making and manufacturing sustainable materials and their assembly into energy storage devices which are flexible, self-healing and compostable.

9:00 AM EN03.01.02
A Biomass-Derived Polyhydroxyalkanoate Biopolymer as Safe and Environmental-Friendly Skeleton in Highly Efficient Gel Electrolytes for Lithium Batteries Eliana Quartarone1, Piercarlo Mustarelli2, Davide Ravelli1 and Chiara Samorì3; 1University of Pavia, Italy; 2University of Milano-Bicocca, Italy; 3University of Bologna, Italy

The massive use of lithium batteries in industries, such as automotive and electrical network accumulation, requires the development of safer electrolytes, economic and possibly made from renewable resources using eco-friendly processes. In this work, we reported the synthesis and the physico-chemical and functional characterization of a polymer gel electrolyte (GPE) based on a skeleton of polyhydroxyalcanoate obtained from biomass by means of an easy and environmentally friendly chemical process. The GPE has an ionic conductivity of 0.8 mS cm\(^{-1}\) at room temperature, is thermally stable up to over 100°C and is not flammable. The electrochemical stability window is higher than 5V. The cell Li/GPE/LiFePO4 shows specific capacity of 100 mAhg\(^{-1}\) at 3C with 100% coulombic efficiency. These results demonstrate that the GPE based on polyhydroxyalcanoate is very promising for use in lithium batteries of high power density.

9:15 AM EN03.01.03
3D Architected Li\(_2\)S Composites Fabricated via Emulsion Stereolithography Max Saccone and Julia R. Greer; California Institute of Technology, United States

Additive manufacturing is a promising route towards the development of mechanically resilient 3D electrodes with complex architectures, high active material loadings, and large areal capacities relative to conventional 2D film electrodes. These types of processes for fabricating lithium-sulfur (Li-S) cathode materials are beginning to be explored; currently only extrusion methods have been reported, which are limited in resolution to >150 µm and offer limited control over the final morphology and microstructure of the printed material\(^1,2\).

We report an additive manufacturing process which enables fabrication of 3D architected lithium sulfide (Li\(_2\)S) carbon composite cathodes for Li-S batteries via digital light processing stereolithography and subsequent pyrolysis. The composites have feature sizes of ~50 µm and are comprised of a porous glassy carbon matrix containing crystalline Li\(_2\)S deposits within the pores. We 3D print porous polymer composites using water-in-oil emulsions of aqueous lithium sulfate dispersed in a UV-curable photopolymer resin. Pyrolysis converts the porous polymer matrix to glassy carbon and the lithium sulfate deposited within the pores to lithium sulfide via carothermal
reduction. We investigate the effects of surfactant concentration and emulsion composition on pore size, pore connectivity, and Li$_2$S morphology via SEM image analysis and show that pore size and Li$_2$S crystal size can vary from ~10 nm to ~5 µm and are related to the size of aqueous domains in the emulsion. We also report the effects of cathode architecture and microstructure on battery cycling performance and mechanical properties and discuss general design considerations for 3D structured electrodes.

References

9:30 AM *EN03.01.04*
**MXenes—From Active Material to Passive Components for Electrochemical Energy Storage** Xuehang Wang, Narendra Kurra and Yury Gogotsi; Drexel University, United States

MXenes are an emerging large family of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides, that were discovered at Drexel in 2011 and have become versatile materials due to a combination of hydrophilicity and metallic conductivity. About 30 different MXenes have been experimentally synthesized already. Many more MXene compositions and their properties have been predicted computationally. Given their compositional diversity, tunable surface chemistry, existence of various ordered structures and solid solutions, MXenes may well be the largest family of 2D materials known to date. MXenes are usually produced by top-down synthesis, namely wet chemical extraction of ‘A’ atomic layers from the layered ternary carbide precursors, such as MAX phases. The resulting MXenes with surface terminations (-O, -F, -OH) impart negative surface charges, key for stable MXene dispersions in water and organic solvents which enable solution processing to ease the design of electrode architectures.

The available for intercalation 2D gallery spaces, accessible redox sites at the transition metal oxide-like surface, and metallic conductivity make MXenes promising as potential candidate materials for high rate capacitive energy storage applications. The ability of MXenes to intercalate a variety of cations while promoting fast charge transfer rates, expanding their widespread usage in a variety of electrochemical energy storage applications including hybrid metal-ion capacitors and battery applications. Besides the role of active charge storage matrix, MXenes have been explored as passive component in the form of current collectors and functional binders for designing degradable green electrochemical energy storage devices. Given the high electrical conductivity of titanium carbide MXene (beyond 10,000 S/cm), it was employed as current collector, replacing metal in fabrication of microsupercapacitors and hybrid energy storage devices. Functionalized surfaces of MXenes have shown the ability for binding carbon, silicon particles and organic systems, playing a role of conductive binder, replacing fluorinated polymers and improving the mechanical and electrochemical stability of the electrodes. Titanium carbide MXenes and also degradable in the environment, producing just titania and carbon dioxide and allowing development of green electrochemical energy storage devices.

10:00 AM BREAK

10:30 AM *EN03.01.05*
**Coupling Energy Capture and Storage—Endeavoring to Make a Solar Battery** Deepa Khushalani; Tata Inst of Fundamental Research, India

Storage of solar radiation is currently accomplished by coupling two separate devices, one that captures and converts the energy into an electrical impulse (a photovoltaic cell) and another that stores this electrical output (a battery or a supercapacitor electrochemical cell). This configuration however has several challenges that stem from a complex coupled-device architecture and multiple interfaces through which charge transfer has to occur. As such presented here is a scheme whereby solar energy capture and storage have been coupled using a single bi-functional material. Two electroactive semiconductors BiVO$_4$ (n-type) and Co$_3$O$_4$ (p-type) have been separately evaluated exclusively for their energy storage capability in the presence and absence of visible radiation. Each of these have the capability to function as a light harvester and also they have faradaic capability. An unprecedented aspect has been observed in that upon photo-illumination of either of these semiconductors, *in situ* charge carriers being generated play a pivotal role in perturbing the electroactivity of the redox species such that the majority charge carriers, *viz.* electrons in BiVO$_4$ and holes in Co$_3$O$_4$, influence the redox response in a disproportionate manner. More importantly, there is an
enhancement of ca. 30% in the discharge capacity of BiVO₄ in the presence of light and this directly provides a unique route to augment charge storage during illumination.

10:45 AM EN03.01.06
Artificial Neuron Network Assisted On-Demand Device-Level Design of Graphene Membrane-Based Supercapacitors Longbing Qu, Dan Li and Zhe (Jefferson) Liu; The University of Melbourne, Australia

Supercapacitors, also called electrochemical double layer capacitors (EDLCs), store and deliver energy through ion adsorption/desorption at the electrical double layers. They have attracted intensive attention in the energy storage field in light of their fast charging capability, high power density, and long-life span. The low volumetric energy density (amount of energy stored per unit volume) is a crucial drawback index for impeding the broad application of EDLCs. The strategies used to increase EDLC energy density include developing new capacitive materials, applying high working voltage electrolytes, and designing asymmetric supercapacitors. The main task is thus to optimally match suitable positive and negative active materials with selected electrolyte. However, the optimal design of supercapacitors on device-level is still a tremendous challenge because of the high dimensional design space consisting of pore size (or packing density) and thickness of both electrodes, working voltage, and operation charging rate.

In this work, we will present that utilizing an artificial neuron network (ANN) can successfully establish the quantitative structure-property relation of supercapacitor electrodes and thus efficiently guide the supercapacitor device design. We adopted the tunable chemically converted graphene membrane (CCGM) as a suitable experimental platform with the standard KCl (1M) electrolyte. Using the capillary compression technique developed in our group, we tuned the pore size of CCGM from 1.7 down to 0.8 nm. The thickness of the electrodes was varied from 11 to 276 um. We did about 200 separated experiments to measure the capacitance of electrodes with different thickness and pore size under different charging rates. The obtained experimental database was used to train the ANN. Then, we apply the well-trained ANN model to predict the capacitance of positive and negative electrodes with various electrode structures, establishing a comprehensive and continuous quantitative relationship between CCGM structure and capacitance of both electrodes. After that, the numerical method was applied to explore the high dimensional design space modeled by ANN for the optimized matching of positive and negative electrodes on device-level. The results indicate that there are more than 1 million matching combinations for positive and negative electrodes that meet the general design rules. This result shows that it is an extremely complicated task for optimized supercapacitor design based on a conventional method. We then carried out experiments to successfully confirm the validity of our optimized supercapacitor device design. In the optimal device designs, the positive and negative electrode structures, including pore size and thickness, are hard to determine quantitatively from conventional trial-and-error experiments. Besides, the optimal designs depend on the charging rate. Our method provides a general solution to design CCGM based supercapacitor devices under different charging conditions. Our study indicates that the machine learning method offers computer models an ability to learn from the experiment database and make a reliable prediction of electrode capacitance, enabling the on-demand quantitative device-level supercapacitor design for practical applications.

11:00 AM EN03.01.07
Challenges and Opportunities for Thick Electrode Batteries and Supercapacitors Chaoji Chen and Liangbing Hu; University of Maryland College Park, United States

The fast growing demand of portable electronics and electric vehicles has driven the rapid development of rechargeable batteries and supercapacitors in the past forty years. Energy storage devices with higher energy density is desirable for a longer using time or driving range. In pursue of higher energy density, tremendous efforts have been made in the past few decades, mainly via the developing of novel battery chemistries and/or structural engineering. Battery structural engineering is able to improve the energy density of the energy storage devices via optimizing the configurations of electrode and/or battery architecture yet without changing the electrode chemistry, representing a promising direction towards high-energy battery and supercapacitor development. One most attractive battery structural engineering strategy is thick electrode design that is able to increase the ratio of active material and reduce the manufacturing cost by reducing the use of nonactive components in batteries (e.g., current collector, separator, binder, packaging material, electrolyte, etc.). Given the opportunities thick electrode design offered, intensive efforts from the energy storage community have been dedicated, and great progresses have been made recently. However, constructing thick electrode still faces several challenges, including the delamination of electrode slurry from metal current collector during the drying process, scalable manufacturing, and the sluggish
charge kinetics.

To address these challenges, Hu’s group has developed several strategies in constructing better thick electrodes for high-energy batteries and supercapacitors. One strategy is constructing three-dimensional (3D) conductive framework with low-tortuosity pores via direct carbonization of natural wood, where various active electrode materials (e.g., lithium iron phosphate, sulfur, manganese dioxide cathode, lithium metal, porous carbon anode) can be infiltrated or deposited with high active material mass loadings [1-3]. To maintain the mechanical robustness of wood, a new strategy was developed to convert natural wood into flexible wood electrode via partial delignification and multiple coating processes, where carbonization is avoided [4]. A cellulose based densified 3D electrode structure was also proposed via conformal coating of carbon black particles on each cellulose nanofiber to impart decoupled pathways for the fast transport of ions and electrons, followed by active material incorporation into the conductive framework and mechanical compression [5]. We will discuss these progresses in thick electrode development from our lab, challenges, and future research opportunities in this field.

References

11:15 AM EN03.01.08
Biomass Derived Hard Carbon as Sodium-Ion Battery Anode Arka Saha, Rosy Sharma, Malachi Noked and Gilbert D. Nessim; Bar Ilan University, Israel

In the last few years, sodium-ion batteries (SIBs) emerged as an economical, high energy alternative to lithium-ion batteries (LIBs) for large-scale energy storage applications. Nevertheless, even after a decade of research, the anode remains the biggest challenge towards its practical applications. Consequently, for acquiring higher energy density, superior power performances, and meaningfully prolonged stability from SIBs, we need a stable, efficient and cost-effective anode material.

Here, in our proposed research work, we utilized a variety of biomass waste like fruit peels, rice husk, etc. as a precursor to synthesize some new carbon- electrode materials for their application in SIB. The carbon materials were synthesis through H3PO4 acid treatment of the dried powdered biomass materials accompanied by washing and annealing at 900 °C at Ar atmosphere. The synthesized material exhibited a capacity as high as ~180 mAh/g. To further improve the electrochemical behavior of the material, we exploited different percentages of hetero-atom and found that if doping percentages are carefully optimized, they can, not only help in mitigating the material instability but also leads to significant improvement in rate performance. We further characterized the surface of the carbon material with high-resolution scanning electron microscopy, X-ray diffraction, and Raman spectroscopy before and after cycling to investigate the structural stability. We believe that the results presented herein opens a promising direction to exploit the bio-waste as precursors to fabricate carbon materials with promising electrochemical activity.

Reference:

11:30 AM EN03.01.09
SiC Passivation Layer for Scalable One-Pot Hollow Nanostructured Si-Based Anodes Seungkyu Park and
Silicon has been considered as the most promising alternative for the conventional graphite anode in lithium-ion batteries, due to its high gravimetric capacity. There are tremendous approaches to alleviate the large volume change considered as the main reason of cycle degradation upon repeated alloying reaction. In particular, hollow nano-structure is one of feasible approach, in that free volume in hollow type of structure produces sufficient space to accommodate the large volume change stemming from alloying reaction. Nevertheless, fabrication procedure, involving toxic reagents and complicated reactions for removing sacrificial template hinders the commercial utilization. Here in, we develop technique enabling to synthesize silicon anodes with various morphologies such as sheet, tube and hollow typed-structure without any toxic reagents and complex reactions. In this technique, SiC$_x$ layer in which Si nanoparticles embedded in SiC passivation matrix acting as strong protection against oxidation, was coated on the carbonaceous templates (spherical, sheet and rod types) and etched via scalable one-pot thermal decomposition method using SiH$_4$, C$_2$H$_4$ and Air. Surprisingly, a few Si nanoparticles produced the silicon oxide even over 800°C owing to SiC passivation matrix. As a results, electrodes fabricated such anodes effectively alleviate large volume changes without pulverization during cycling with 100 cycle retention of 92%. In addition, it performs excellent initial coulombic efficiency compared with the previously reported Si hollow nanostructure. Specifically, SiC hollow nano-structure shows the high initial discharge capacity of 1862 mAh g$^{-1}$ with initial coulombic efficiency of 90.1%.

**SESSION EN03.02: Green Electrochemical Energy Storage Solutions—Materials, Processes and Devices II**

**Session Chair: Clara Santato**

**Monday Afternoon, December 2, 2019**

**Sheraton, 2nd Floor, Republic A**

**1:30 PM *EN03.02.01**

**3D Microsupercapacitors with High Areal Energy Density** Daniel Guay$^1$, Anais Ferris$^{1,2}$, David Bourrier$^2$, Sébastien Garbarino$^1$ and David Pech$^2$; $^1$INRS, Canada; $^2$LAAS-CNRS, France

The increasing need for onboard energy supply/storage in wearable electronics, wireless sensor networks, and the upcoming Internet of Things has pushed for the miniaturization of technologies, including energy harvesting and energy storage units that could be integrated directly onto microchips to achieve energy self-sufficiency. In this context, microsupercapacitors have attracted considerable attention for their use in various emerging micropower applications. A microsupercapacitor is a miniaturized supercapacitor that can be directly mounted on a chip to power integrated circuits. These small electrochemical energy storage devices are characterized by high power and excellent cyclability. However, they have moderate energy density because they rely on a charge storage mechanisms based on interfacial reactions. In order to improve their capacitance and energetic performances while maintaining reduced footprint, more active and accessible materials have to be loaded per unit area of the electrode. This can be obtained by designing 3D electrodes with high surface-to-volume ratio that achieves charge storage over an extended surface, thereby decoupling the direct relationship between power and energy density. Various strategies exist to fabricate these 3D nano-architected electrodes and they will be reviewed, with a special focus on disordered 3D architecture that has received increasing interest in recent years due to the impressive results obtained using this paradigm shift. These disordered 3D nano-architected electrodes rely on the deposition of pseudocapacitive materials, known for their large specific capacitance, onto a disordered 3D high-surface-area conductive support. The areal capacitance is improved from one to three orders of magnitude compared to the planar geometry.

**2:00 PM EN03.02.02**

**A 2 V Class Aqueous Sodium-Ion Battery with Low-Temperature Cycling Capabilities** David Reber$^{1,2}$, Ruben-Simon Kühl$^1$ and Corsin Battaglia$^1$; $^1$Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; $^2$École Polytechnique Fédérale de Lausanne, Switzerland

Rechargeable sodium-ion batteries based on non-flammable aqueous electrolytes are promising for large-scale energy storage for grid applications. Recently we reported a highly-concentrated 35 molal aqueous sodium
bis(fluorosulfonyl)imide (NaFSI) electrolyte with an extended stability window of 2.6 V on stainless steel current collectors.[1] However, such highly concentrated systems, often referred to as water-in-salt electrolytes, tend to crystallize already near room temperature, resulting in cell failure. Here, we report a ternary 25m NaFSI + 10m NaFTFSI electrolyte, which is kinetically robust against crystallization and allows long term cycling even at -10 °C. We show that the asymmetry of the FTFSI anion is crucial for efficiently suppressing crystallization in such supercooled electrolytes.[2] Taking into account the raw materials supply chain as an important challenge for scaling, we developed a 2 V class aqueous sodium-ion battery employing abundant raw materials, namely NaTi2(PO4)3 and Na3(VOPO4)2F on the anode and cathode side, respectively. With 64 Wh kg⁻¹, based on the masses of active materials of both electrodes, this battery displays an energy density that is almost twice as high as that of previously reported aqueous sodium-ion batteries. The cell displays excellent cycling stability at 30 °C with a capacity retention of 85% after 100 cycles at C/5 and 77% after 500 cycles at 1C. At -10 °C, we obtain a capacity retention of 74% after 500 cycles at C/5.

References:

In recent years, significant attention has been paid to the development of micro-devices as innovative energy storage solutions. For instance micro-sensor networks such as sensors actuators or implantable medical devices require power densities and cyclability that are several orders of magnitude higher than those of conventional Lithium-Ion batteries. For such applications, µSCs, a developing novel class of micro/nanoscale power source are rising alternatives, and their integration “on-chip” could allow significant innovations to emerge [1]. Therefore, a great deal of attention has been focused on µSCs, for which large series of nanostructured active materials have been developed.

In this work we focused to increasing the stability and the energy performance of the supercapacitors based on silicon nanostructures electrodes (nanowires and nanotrees) and in same time used safety and green electrolytes (aqueous) without lithium and ionic liquids. The nanostructures were grown by chemical vapor deposition (CVD) through a vapor-liquid-solid (VLS) process and take here advantage of a substantial increase of the developed surface of the electrode while structured at the nanoscale [2-4]. We realized a new nanocomposites electrodes based on silicon nanostructures/ protected nanometric layer/ electronic conducting polymer. This nanocomposite electrode is a real important lever for improving performance in terms of energy density and durability of devices that becomes possible via Atomic Layer Deposition (ALD) layers of Alumina [5]. We have demonstrated a clear gains of a layer of alumina of less than four nanometers which makes it possible to reach cyclability greater than 8 million cycles and retentions of capacities close to 100%. In addition, the first key steps in the process of producing flexible composite electrodes (Si nanowires / Al2O3 / conductive polymers) have recently been successfully completed. Thus a remarkably simple deposition of PEDOT-PSS by drop-casting of an aqueous solution of commercial polymer was used. Despite the poor control over the thickness of the deposit, the gravimetric performances proved to be excellent with a low capacity retention of 95% over 500 000 cycles for an initial gravimetric capacity 8.5 F. g⁻¹ and specific energies and powers of 8.2 mJ.cm⁻² and of 4.1 mW.cm⁻². Such cycling stability for a polymer-based nanocomposite in aqueous media combined with first-order electrochemical storage performance is unprecedented in the literature [6].
2:30 PM BREAK

3:00 PM *EN03.02.04
Nanocellulose Enabled Green Electrochemical Energy Storage Solutions Liangbing Hu; University of Maryland, United States

I will start by giving an overview of our work on assembly and functionalization strategies of nanocellulose aimed at specific properties, with an eye toward high impact applications including energy, electronics, building materials and water treatment, including nanomanufacturing and light management in transparent nanopaper for optoelectronics (as a replacement of plastics); mechanical properties of densely packed nanocellulose for lightweight structural materials (replacement of steel, Nature 2018); artificial tree for high-performance water desalination and solar steam generations; and radiation cooling (Science, 2019).

I will then focus on our work on applying nanocellulose/wood as building blocks for advanced energy devices, including flexible, thick battery electrodes with nanocellulose binder, three-dimensional carbon derived from wood for advanced batteries (replacement of metal current collectors for beyond Li-ion batteries); nano-ionic membranes for thermoelectrics (Nature Materials, 2019).

3:30 PM EN03.02.05
Li-Ion Capacitors and Li-Ion Battery/Capacitor Hybrid Energy Storage Devices Jim P. Zheng; FAMU-FSU College of Engineering, United States

As a new generation of supercapacitor, the Li-ion capacitor (LIC) is an advanced energy storage device which consists of an electric double-layer capacitor (EDLC) cathode and a pre-lithiated anode [1,2], between which the ions shuttle during charge and discharge processes. The LIC cell not only retains all the advantages of EDLC such as high specific power >10 kW/kg and long cycle life >100,000 cycles, but also exhibits a higher specific energy of 15-25 Wh/kg and a higher maximum cell voltage than that of the EDLC [3]. Because of using pre-lithiated and low surface anode materials, the LIC can be charged to a maximum voltage as high as 4.0 V, which is much higher than of EDLCs and comparable to Li-ion batteries (LIBs); therefore, it allows the LIC and LIB to be assembled in one package as a LIB/LIC hybrid energy storage cell.

We have demonstrated a new hybrid energy storage cell that combines the advantages of both the LIB and the LIC [4], thereby avoiding their inherent defects, while bridging the gap between the high energy densities offered by batteries and the high power densities seen in EDLCs. The energy density and power density of the hybrid cell can be designed to meet the requirements by a reasonable distribution of the ratio between LIB and LIC electrode materials in the internal hybrid cell. For example, we show a hybrid LIC consisting of a Li nickel cobalt manganese oxide (NMC)/activated carbon (AC) composite cathode in combination with an ultra-thin Li film (u-Li) pre-loaded hard carbon anode. Additionally, we show that by utilizing three design approaches: dry composite electrode fabrication method, cathode to anode capacity ratio design, and pre-lithiation method using u-Li, we can demonstrate an energy storage device with excellent cycle life, and that can be tailored by composite ratios within the cathode to fit different applications. Shown here is an in-depth look at various composite material ratios, pre-lithiation calculations and hybrid Li-ion battery-capacitor energy storage device creation based on targeting essential energy-power performance characteristics.

References
Emergent green conductive materials are pivotal to reduce harmful and long-lasting electronic waste [1, 2]. At the same time, the electronics industry has demand to transform rigid devices into soft, wearable and conformable structures [2-3]. A first achievement towards flexible and sustainable electronics would be blending biomaterials and conductive nanoparticles to produce electronic components. Following such an approach, we have realized conformable resistors, capacitors and inductors using a fibrous structural protein extracted from bio-waste as a “polymer” matrix for graphene nanoplatelets (GnPs). Furthermore, we have obtained flexible conductors (sheet resistance ≈ 10 Ω/sq) by functionalizing cellulose with bio-based conductive inks made by mixing GnPs with biopolymers and/or natural proteins. These conductive biocomposites were exploited in foldable circuits, passive electrical components (such as filters), organic photovoltaic devices, electromagnetic interference shielding films, portable antennas and electrodiagnostic sensors [2, 4, 5]. The success of conformable and sustainable conductors will simplify the fabrication of easily disposable devices with a low environmental footprint and, simultaneously, support the transition towards flexible electronics.

References:

4:00 PM OPEN DISCUSSION

4:15 PM EN03.02.08
Towards Electrochemical Synthesis of Cement—An Electrolyzer-Based Process for Decarbonating CaCO3 While Producing Useful Gas Streams Leah Ellis, Andres Badel, Mikki Chiang, Richard Park and Yet-Ming Chiang; Massachusetts Institute of Technology, United States

Cement production is currently the largest single industrial emitter of CO2, accounting for 8% (2.8 Gtons/year) of global CO2 emissions in 2015. Deep decarbonization of cement manufacturing will require remediation of both the CO2 emissions due to the decomposition of CaCO3 to CaO, and that due to combustion of fossil fuels (primarily coal) in the calcining (~900°C) and sintering (~1,450°C) processes. Here, we demonstrate an electrochemical process that uses neutral water electrolysis to produce a pH gradient in which CaCO3 is decarbonated at low pH and Ca(OH)2 is precipitated at neutral to high pH, concurrently producing a high purity O2/CO2 gas mixture (1:2 molar ratio at demonstrated stoichiometric operation) at the anode and H2 at the cathode. We show that the solid Ca(OH)2 product readily decomposes and reacts with SiO2 to form alite, the majority cementitious phase in Portland cement. Our electrochemical calcination approach produces concentrated gas streams from which the CO2 may be readily separated and sequestered, the H2 and/or O2 may be used to generate electric power via fuel cells or combustors, the O2 may be used as a component of oxyfuel in the cement kiln to further lower CO2 and NOx emissions, or the output gases may be used for other value-added processes including liquid fuel production. Analysis shows that in a scenario where the hydrogen produced by the reactor is combusted to heat the high temperature kiln, the electrochemical cement process can be powered solely by renewable electricity.

4:30 PM EN03.02.09
Architectural Design of Fully-Zwitterionic Copolymer Scaffolds for Nonvolatile Ionogel Electrolytes Morgan Taylor, Samuel Lounder, Ayse Asatekin and Matthew Panzer; Tufts University, United States

The strong interactions of zwitterionic polymers with ionic species and their self-assembly have been widely used for drug delivery, hydrogel materials, and membrane selective layer coatings, but little has been done to exploit their potential for electrochemical applications. Recent works within our group have focused on the development of polymer-supported ionogels containing one or more bio-inspired zwitterionic functional groups. By taking
advantage of the unique interactions between zwitterionic moieties and ionic liquid ions, we have developed a new class of ionogels with highly tunable properties that could provide several potential advantages for safer electrochemical devices. An important benefit to utilizing ionic liquids is that they can be recycled due to their nonvolatile nature, leading to the development of more environmentally friendly electrolytes. This presentation will describe the synthesis of fully-zwitterionic (co)polymer scaffolds for fabrication of ionogel electrolytes and reveal the importance of polymer selection and architecture on the observed gel properties. First, random zwitterionic copolymers were prepared in situ via free radical photopolymerization in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI TFSI). Spectroscopic characterization indicated different degrees of zwitterion/ion interactions and zwitterionic dipole—dipole physical cross-links depending on the zwitterion chemical identity. A wide range of ion transport and mechanical properties were obtained by tuning the copolymer ratio, which highlighted the benefits of combining more than one zwitterion chemistry.[1] Second, fully-zwitterionic ABA triblock copolymers were synthesized using sequential addition with a controlled radical polymerization method. While both polymeric subunits are zwitterionic, a difference in solubility drives copolymer self-assembly in various environments, including ionic liquids, which allows one to fabricate ionogels. Further tuning of the mechanical and ion transport properties of these ionogels can be achieved by changing the zwitterion identities of the polymeric subunits, or by adjusting the block lengths and molar ratio between the two functional groups. Incorporation of bio-inspired zwitterionic moieties in ionic liquid-based electrolytes is still relatively unexplored, and there is much room for additional investigation in order to build a deeper understanding of zwitterion behavior within ionic liquid environments. This work highlights some of the exciting possibilities of careful selection of zwitterion chemical identities and copolymer architectures towards the development of safer materials for electrochemical energy storage.

4:45 PM EN03.02.10
Electrochemistry, Solvation and Local Order in Mixed Cation Acetate-Based Water-in-Salt Electrolytes
Maria Lukatskaya1,2, Hans-Georg Steinrueck2, Christopher J. Takacs2 and Michael F. Toney2; 1ETH Zurich, Switzerland; 2SLAC National Accelerator Laboratory, United States

Electrolytes are an essential component of energy storage devices. Electrolyte composition has a significant impact on the safety, price and performance of the battery. Intrinsically nonflammable aqueous electrolytes can offer safer battery operation and decreased associated toxicity but suffer from a smaller electrochemical stability window (and hence energy density) compared to traditional organic electrolytes. To circumvent the small electrochemical stability window, highly concentrated “water-in-salt”, WIS, lithium organic imide systems which demonstrate significantly wider stability windows were recently proposed.1,2 However, the toxicity often associated with organic imides and high price make the practical implementation of current water-in-salt electrolyte chemistries into commercial energy storage devices challenging.

We address the challenge of developing new formulations of water-in-salt electrolytes caused by the lack of lithium salts having water solubility high enough to satisfy the water-in-salt condition. The proposed mixed cation strategy is whereby cheaper (by at least an order of magnitude) and more soluble salts featuring alkali cations beyond lithium, e.g. potassium acetate, are used to create the water-in-salt condition.3 We study co-dissolution of corresponding lithium and zinc acetate salts, we show that such highly concentrated electrolytes can provide the same benefits of the extended voltage window as imide-based electrolytes and, demonstrate compatibility with traditional Li-ion or Zn-ion battery electrode materials while being low-cost and environmentally benign. In addition, we demonstrate the strong effect of the solution concentration on the solvation structure of the cations and local order in the potassium acetate-based WIS systems and correlate it with the electrochemical response of different Zn-ion and Li-ion-based electrode systems.

References
SESSION EN03.03: Green Electrochemical Energy Storage Solutions—Materials, Processes and Devices III  
Session Chair: Hongli Zhu  
Tuesday Morning, December 3, 2019  
Sheraton, 2nd Floor, Republic A

8:00 AM *EN03.03.01  
Nanoscale Design for Lithium-Sulfur Batteries Yi Cui; Stanford University, United States

Lithium sulfur (Li-S) batteries have high theoretical specific energy for portable and stationary storage application. Sulfur is an earth abundant materials for potential green energy storage. However, Li-S batteries have many challenging issues at the materials level. Here I will present our recent progress on: 1) Nanoscale materials design for polysulfide binding, encapsulation and activation. 2) Discovery of liquid sulfur behavior at room temperature, leading to new guidance to materials design.

8:30 AM *EN03.03.02  
Sulfur Grafted Hollow Carbon Spheres for Potassium-Ion Battery Anodes David Mitlin; University of Texas at Austin, United States

Sulfur-rich carbons are minimally explored for potassium ion batteries (KIBs). Here, we chemically incorporate a large amount of S (38 wt. %) into a carbon host, creating Sulfur-grafted Hollow Carbon Spheres (SHCS) for KIB anodes. The SHCS architecture provides a combination of nanoscale (ca. 40 nm) diffusion distances and C-S chemical bonding to minimize cycling capacity decay and Coulombic efficiency (CE) loss. SHCS exhibits a reversible capacity of 581 mAh g⁻¹ (at 0.025 A g⁻¹), which is the highest reversible capacity reported for any carbon-based KIB anode. Electrochemical analysis of S-free carbon spheres baseline demonstrates that both the carbon matrix and the sulfur species are highly electrochemically active. SHCS also shows excellent rate capability, achieving 202, 160 and 110 mAh g⁻¹ at 1.5, 3 and 5 A g⁻¹, respectively. The electrode maintained 93% of the capacity from the 5th to 1000th cycle at 3 A g⁻¹, with steady-state CE being near 100%. Raman analysis indicates reversible breakage of C-S and S-S bonds upon potassiation to 0.01 V vs. K/K⁺. GITT analysis provides voltage-dependent K⁺ diffusion coefficients that range 10⁻¹⁰ to 10⁻¹² cm² s⁻¹ upon potassiation and depotassiation, with approximately five times higher coefficient for the former.

9:00 AM *EN03.03.03  
Assessing End-of-Life Options for Li-Ion Battery Cells and Materials—Materials Recycling and Second Use Duty Cycling Jay F. Whitacre¹, Rebecca Ciez² and Han Wang¹; ¹Carnegie Mellon Univ, United States; ²Princeton, United States

This presentation will compare and contrast various options in the quest for dealing with lithium ion batteries that have reached the end of their useful (first) lives. First, the economic and environmental impacts of recycling battery materials using multiple processing techniques will be examined and best practices will be suggested. We will then examine several different promising methods for direct recycling of cathode materials, as they have the most economic value and highest carbon footprint of the materials in most cells. Lastly, the durability of purposely aged second-use battery cells under several different application-specific duty cycles will be explored with the intention of understanding the likely benefits of using these aged cells in less taxing stationary applications such as intermittent renewable integration and for use in uninterruptible power supplies.

9:30 AM BREAK

10:00 AM *EN03.03.04  
Improved Charge Storage Performance of Nanostructured Organic Electrodes Using Surface-Controlled Charge Storage Mechanisms Seung Woo Lee, Byeongyong Lee, Michael Lee, Shikai Jin and Yongmin Ko; Georgia Institute of Technology, United States

Redox-active organic compounds have been attracting extensive attention as active electrode materials to replace conventional transitional metal based inorganic electrodes for rechargeable batteries.¹,² Potential advantages of organic electrode materials include their environmental benignity, sustainability, and high theoretical energy density,
which can be ideal for large-scale energy storage applications.\textsuperscript{1,2} Despite these advantages, organic electrodes have suffered from poor cycling stability and rate performance, limiting their practical applications.\textsuperscript{1-3} A promising strategy to overcome these issues is to incorporate redox-active molecules onto 3D conductive substrates.\textsuperscript{1-3} In this presentation, we will discuss our recent progress in designing nanostructured organic electrodes for Li-/Na-ion storage. The assembled organic electrodes using carbon nanotube or graphene substrates have multiple redox reactions with Li-/Na-ions in high potential regions. Based on the redox reactions, these organic electrodes delivered high capacity at high potential regions with superior rate-performance and cycling stability, which can be promising cathodes for large-scale rechargeable batteries or hybrid capacitors. Next, we will introduce a new self-assembly technique using ligand exchange reactions on nanoparticles. This technique was used to convert the insulating paper or fabric to highly porous metallic current collectors. Using such metallic current collectors, we demonstrate flexible and wearable energy storage and conversion devices.


10:30 AM EN03.03.05
3D Printed Biomass-Derived Hierarchical Porous Carbon Aerogels for Supercapacitors at Ultralow Temperatures Bin Yao and Yat Li; University of California, Santa Cruz, United States

Supercapacitors (SCs) represents an emerging class of fast-charging and stable energy storage devices and have been extensively studied in recent years. However, most of the previous research are focused on SCs in aqueous and room temperature conditions. Improving the performance of SCs, especially at low-temperature environments, is significantly important for prolonged space exploration. This talk will report our new findings of using 3D printing method to fabricate biomass-derived carbon aerogels for supercapacitors at ultralow temperatures. The 3D printed biomass-derived carbon aerogel electrodes with periodic large pores have shown significantly improved electrochemical performance than the non-3D printed counterparts at low temperatures. More importantly, hierarchical pore structure with large periodic pores, macropores, mesopores and micropores in the 3D printed carbon aerogels enable the porous electrodes to achieve an excellent capacitance of around 150 F/g even under -70°C. The kinetic analysis further reveals the favorable ion diffusion property in the 3D printed hierarchical porous electrodes. Moreover, the effects of each type of pore structure on capacitance at low-temperature will also be explained. This talk will for the first time demonstrate the superiority of 3D printed porous electrodes for ultralow temperature energy storage, which might open a new door for the future work on high-performance fast-charging energy storage systems for space missions.

10:45 AM EN03.03.06
Energy Harvesting and Storage by Indoor Light Using Dye-Sensitized Solar Battery (DSSB) Myeong-Hee Lee, Byung-Man Kim, Tae-Hyuk Kwon and Hyun-kon Song; UNIST, Korea (the Republic of)

Photo-rechargeable batteries (PRBs) have been developed as all-in-one energy devices having a merit that both energy harvesting and storage are realized in a single device. A major portion of the PRBs are based on non-faradaic processes (capacitive PRBs) for their energy storage. On the other hand, several works have focused on using faradaic processes (faradaic PRBs) because the faradaic PRBs are much superior in terms of energy densities. However, for the spontaneous electron transfer between the photo-electrode and the storage-electrode, the energy levels of the two active materials should be matched well, so that there are not so many storage materials having faradaic reaction. In addition, dim-light performances of the faradaic PRBs have not been reported as far as we know. Herein, we present an external-power-free single-structured faradaic PRB, named dye-sensitized solar battery (DSSB), developed specifically for indoor light harvesting. The DSSB was designed to be photo-charged by the photo-anodic process of dye-sensitized solar cells (DSSCs) and the cathodic process of LiMn$_2$O$_4$ (LMO). Redox mediators in electrolyte of the compartment to the photo-electrode are oxidized to regenerate activated dye molecules. The
charged DSSB can be discharged by returning to their original state of the two redox active materials. The performances of DSSBs were strongly dependent on the thermodynamic and kinetic parameters of redox mediators. At one sun condition, the kinetics of mediator determined the light-to-charge energy efficiency ($\eta_{\text{overall}}$). A kinetically-fast but thermodynamically-unfavorable (can make smaller cell voltage) mediator (I-/I$_3^-$) showed the best results in terms of photo-charging current ($J_{\text{Ch}}$) and discharge capacity ($Q_{\text{dCh}}$). However, in dim-light condition (200 ~ 2000 lux), a thermodynamically-favorable (can make larger cell voltage) mediator (Cu$_{\text{II}}$/$\text{Cu}^{\text{III}}$(dmp)$_2$) delivered the highest photo-charging energy density ($E_{\text{DCh}}$) corresponding to $\eta_{\text{overall}}$ of 11.5 % because kinetic limitation becomes negligible. The successful demonstration of the DSSB to operate an IoT sensor node only by an indoor light (500 lux) opens the possibility of realizing indoor-light-harvesting PRBs.

11:00 AM EN03.03.07
Charge-Transfer Complexes for Organic Rechargeable Batteries with High Redox Potential and Power Density Sechan Lee$^1$, Jihyun Hong$^2$, Sung-Kyun Jung$^1$, Kyojin Ku$^1$, Giyun Kwon$^1$, Won Mo Seong$^1$, Hyungsub Kim$^1$, Gabin Yoon$^1$, Inyeong Kang$^2$, Kootak Hong$^1$, Ho Won Jang$^1$ and Kisuk Kang$^1$; $^1$Seoul National University, Korea (the Republic of); $^2$Korea Institute of Science and Technology, Korea (the Republic of); $^3$Korea Atomic Energy Research Institute, Korea (the Republic of); $^4$Institute for Basic Science, Korea (the Republic of)

Organic redox compounds are potential substitutes for transition-metal-oxide electrode materials in rechargeable batteries because of their low cost, minimal environmental footprint, and chemical diversity.[1] However, their electrochemical performances could not reach the level of currently used electrode materials due to the relatively low redox potential, low electrical conductivity and high solubility in organic solvents. Those drawbacks have not been simultaneously overcome with the single molecule-based tuning such as chemical modification and hybridization with conductive scaffolds.[2] Herein, we report the novel design paradigm of organic charge-transfer complexes for the new type of organic electrode material candidates which can solve the existing shortcomings of single-moiety-based organic electrode materials.[3] Organic charge-transfer complexes are an association of two or more types of organic molecules in which a fraction of electronic charge is transferred between the molecular entities. Well-ordered stacking of the molecular layers in charge-transfer complexes creates a charge-transport path which electrons can move freely, and the strong intermolecular interaction such as hydrogen bonding and -interaction result in high structural stability.

We first developed the donor components of organic charge-transfer complexes, 5,10-dihydro-5,10-dimethylphenazine (DMPZ)[4] and dibenzo-1,4-dioxin (DD)[5], which are ready-to-charge and have high redox potential. DMPZ and DD successfully show reversible redox reaction and high redox potential of 3.4 and 4.1 V vs. Li/Li$^+$, respectively. Following with these results, organic charge-transfer complexes, a novel class of electrode materials with intrinsically high electrical conductivity and low solubility that can potentially overcome the chronic drawbacks, are constructed with the developed ready-to-charge organic electrode material.[3] Combination of DD and 7,7,8,8-tetracyanoquinodimethane (TCNQ) via a room-temperature process leads to enhancement in the electrical conductivity for 5 order magnitudes and reduction in the dissolution resulting in the high power and cycle performances that far outperform those of each single-moiety counterpart. Moreover, full redox activation of donor and acceptor molecules is revealed with the practical energy density of 560 Wh kg$^{-1}$. By applying an investigation on the relationship between the redox potential and the charge carrying ions with DMPZ and terephthalate derivatives, it is confirmed that there is still a room for enhancing energy density with optimizing the cell configuration such as electrolyte and counter metal.[4, 6] These findings demonstrate the general applicability of the charge-transfer complex and opens up an uncharged pathway toward the development of high-performance organic electrode materials via the exploration of various combinations of donor-acceptor monomers with different stoichiometry.

References

11:15 AM EN03.03.08
Green, Biodegradable and Implantable Energy Storage and Conversion Devices  
**Maher El-Kady** and Richard B. Kaner; University of California, Los Angeles, United States

As the world energy demand continues to rise and carbon dioxide emission reaching a dangerous level, many cities around the world have committed to replacing fossil energy with renewables. For this transition to take place, major improvements in current technology and investigation of new materials are essential. In this talk, I will discuss our efforts for the development of green energy storage and conversion devices including batteries, supercapacitors, and nanogenerators. We explore new materials and methods to store electricity using organic carbons and electrolytes to meet the growing demand for organic materials. The talk will be supported by several examples for green, biocompatible, biodegradable and metal-free energy storage devices. In addition, we have designed and tested supercapacitors that could make pacemakers and other implantable devices safer and more durable. On the other hand, nanogenerators have recently captured interest as an alternative for clean and sustainable energies. They could be used as a power source for self-charging batteries and supercapacitors. Here, we have developed an all-printable wearable device that can function as a stretchable energy harvester and a multifunctional sensor based on the principle of snow-electrification. These devices could potentially be integrated with solar panels to ensure continuous power supply in areas with frequent snowfall. In addition, we utilized this technology for fabricating self-powered, multifunctional electronic skin that is capable of detecting human physiological signals such as pressure, temperature, and humidity through an array of totally flat and lightweight sensors. When combined with a supercapacitor, this technology could potentially be used as a self-standing power source that is stretchable, breathable with excellent anti-bacterial properties, which is favorable for biomedical electronics.

Recent publications

V. Strauss et al., *Advanced Materials* 2018, 30, 1704449  
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M. Hashemi et al., *Nano energy* 2018, 44, 489  
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**11:30 AM EN03.03.09**  
Energy and Power Scaling between Coin and Prototype Devices—A Practical Study on Moving from Materials to Prototype Supercapacitors on Ragone Parameters  
**Alexander J. Roberts**; Coventry University, United Kingdom

With the increasing interest and research focus on energy storage devices such as batteries, hybrids and supercapacitors, more and more early stage materials and technologies are tested at small, usually coin cell, scale to screen materials and systems and assess their suitability for further scale-up. This small scale electrochemical testing is then often scaled through various factors and assumptions to inform likely behaviour at a larger commercial or prototype cell scale. This approach of testing and assessing at the small scale and applying the results to a larger device generally produces reasonable agreement with what follows in prototype devices in Li-ion battery systems, where many millions of cells are produced through standard processes and using standard materials each month. The wealth of knowledge and available data on such production and scaling has allowed models to be developed and parameterised, with extensive validation resulting. In EDLC supercapacitors, this is not the case. The vastly smaller scale of production of such devices, carried out almost exclusively in commercial entities rather than the wider academic community, has resulted in information on information on how to effectively scale from results in coin cells to larger devices being unavailable in the scientific literature. It is usually found that where a comparison is made between a coin cell (and materials properties) and how that would perform in a larger cell, parameters associated with batteries are used or parameters such as energy and power densities are quoted with no regard for the ‘parasitic’ but necessary cell components needed at a larger scale such as the mass and volume of current collectors, cans, electrolyte and the like.

In this study, the factors necessary to scale between material properties and those of prototype and commercial cells have been investigated. Commercial cells of various sizes between 100 and 3000F have been tested and characterised extensively before being disassembled into their component parts. The electrodes and separators have then been used to construct and fully characterise supercapacitor coin cells, with factors to scale between the coin
cell and the original commercial cells extracted. In addition, to investigate the effect changes in parameters such as electrode thickness would have on the scaling between cell sizes, prototype 100F pouch and cylindrical cells have been produced and extensively tested in parallel with their corresponding coin cells. Finally, through consideration of the Ragone plots generated at various sizes of cells, a realistic set of parameters to be applied to small scale tested materials is presented, along with insights into the effect of moving to larger cells on the expected lifetime of a material or system.

11:45 AM EN03.03.10
Stretchable Self-Charging Power Systems to Power Wearable Electronics Fang Yi; Sun Yat-sen University, China

Stretchable and wearable electronics have been an emerging class of electronics that enable a wide range of applications such as electronic skins, implantable devices, robotics, and prosthesis. Consequently, development of stretchable power sources for such devices is highly demanded with the possibility that it can harvest energy from the environment in which the device is deployed. Triboelectric nanogenerator (TENG), a biomechanical energy harvester, possesses the advantages of low cost, light weight, high efficiency, and eco-friendly feature. However, the electrical outputs generated by TENG are pulses and sometimes with irregular magnitudes owing to the uneven strength of the mechanical motion. To enable its ability to serve as a direct power source for most electronic devices that need a constant direct-current supply, it is necessary to integrate the TENG with energy storage devices. In addition, a self-protection from the external environment is preferable for stretchable power sources so as to adapt to real-world conditions.

Here, our recent studies on the flexible/stretchable self-charging power systems to power wearable electronics solely by harvesting biomechanical energy will be presented. The challenges, future directions and potential applications for wearable/stretchable electronics will also be discussed.

SESSION EN03.04: Green Electrochemical Energy Storage Solutions—Materials, Processes and Devices IV
Session Chair: Francesca Soavi
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Republic A

1:30 PM *EN03.04.01
Stretchable Rechargeable Lithium-Ion Batteries Soomin Park; Pohang University of Science and Technology, Korea (the Republic of)

Deformable, stretchable electronics are considered as next-generation devices; however, to realize highly flexible electronics, it is first necessary to develop a deformable energy device. Herein, a crumply and highly flexible lithium-ion battery is realized by using microfiber mat electrodes in which the microfibers are wound or webbed with conductive nanowires. This electrode architecture guarantees extraordinary mechanical durability without any increase in resistance after folding 1,000 times. Its areal energy density is easily controllable by the number of folded stacks of a piece of the electrode mat. Deformable lithium-ion batteries of lithium iron phosphate as cathode and lithium titanium oxide as anode at high areal capacity (3.2 mAh cm⁻²) are successfully operated without structural failure and performance loss, even after repeated crumpling and folding during charging and discharging.

As another deformable batteries, we demonstrate the fabrication of highly stretchable hybrid carbon/polymer (HCP) composite which was found to effectively retain its electrical conductivity, even when under high strain (~200%), due to the co-supporting network of hybrid nanofillers in its structure. We are the first to have developed a stretchable aqueous rechargeable lithium-ion battery (ARLB) that utilized this HCP composite as a stretchable current collector. The ARLB exhibited excellent rate capability (~90 mA h g⁻¹ at a rate of 20 C) and outstanding durability (capacity retention of 93% after 500 cycles).

2:00 PM EN03.04.02
Insights into Solid-State Electrochemistry of bi-Redox Organic Battery Materials Alae Eddine Lakraychi, Simon Kreijger, Deepak Gupta and Alexandru Vlad; Institute of Condensed Mater and Nanosciences, Belgium
The technological pressure on the present batteries, dominated by inorganic materials, has led to a sustainability dilemma, and therefore developing new battery chemistries has become of prime importance [1]. In this context, organic batteries are emerging as probably one of the most promising approaches to render the energy storage technology green and sustainable [2]. Presently, carbonyl-based electroactive materials are the most focused due to their potential to achieve simultaneously high energy/power density as well as extended cycling stability [3]. Within this framework, molecular engineering has played a big part in improving theirs electrochemical performances in terms of potential tuning [4] and preventing the unwanted dissolution [5]. However, these improvements usually partially penalize the gravimetric capacities and, in some cases, the exact origin of the operating potential shift as well as redox mechanism are still a matter of debates.

In this work, we will try to address both issues. Firstly, we will show how by using coordination chemistry, Ligand-Metal complexes with sustainable metals (Fe, Mn) as new multi-electron with bi-redox activity can be designed. These new materials can deliver capacities in excess of 200 mAh.g⁻¹ at an average working potential of 3 V vs. Li⁺/Li⁰. Secondly, we will detail on the electrochemistry of aromatic and heterocyclic dicarboxylate isomers. This study comprehends (i) the effect of N-heteroatom on the potential of the dicarboxylates, with a direct correlation between the operating potential and the ¹³C-chemical and vibration frequency shift of the carbonyl and (ii) the true redox mechanism that dictates the electrochemical activity in the case of bi-redox systems (pyrazine-dicarboxylate). This mechanistic investigation leads to the discovery of new nitrogen-related redox center that can be beneficially explored in the organic battery field.

References

2:15 PM EN03.04.03
“Water-in-Salt” Electrolyte Promises Green and Safe Al-Ion Based Electrochemical Energy Storage Systems
Zahid Ali Zafar¹,², Martin Silhavík¹, Ghulam Abbas² and Jiri Cervenka¹; ¹FZU-Institute of Physics of The Czech Academy of Sciences, Czechia; ²Faculty of Science, Charles University, Czechia

Electrochemical energy storage systems (EESS) with high energy density, safety, low cost, and low carbon footprint have become indispensable in the modern era of ubiquitous electronics, electric vehicles, and grid storage. Current EESS lack of these characteristics due to the utilization of critical materials which are precious, flammable and difficult to recycle. Whereas, aqueous electrolytes offer higher safety and lower costs. Nevertheless, their biggest bottleneck is the narrow electrochemical window (1.23V) that is preventing from attaining higher energy and power densities in most of the aqueous EESS. For instance, aqueous rechargeable aluminum ion batteries promise high energy density due to multivalent redox chemistry of aluminum ion (Al³⁺) but they exhibit much lower energy density in real experiments due to the limited electrochemical windows of the aqueous electrolytes. The water-in-salt based electrolytes (WiSE) can potentially eliminate this barrier by offering a larger electrochemical window by reducing the overall electrochemical activity of water on the electrodes. Here, we demonstrate a new concept using aluminum perchlorate based WiSE that is showing a stable and wide electrochemical window of nearly 3 V against Ag/AgCl. The electrochemistry tests of the electrolyte are performed using carbon-based redox-active electrode materials. We employ the new electrochemical system in aqueous rechargeable aluminum ion batteries and supercapacitors, revealing superior performance to standard aqueous electrolytes. Our findings provide new possibilities for widening the electrochemical window and enhancing the energy and power density in aqueous EESS.

References
The replacement of organic solvent-based electrode manufacturing by a water-based process offers an alternative processing route with regard to cost-reduction and more sustainability. However, the interaction of cathode materials with water changes their storage behavior and causes massive problems for electrode manufacturing and cell properties. Due to a Li⁺/H⁺ exchange reaction, the pH of the aqueous slurry is increased so that a corrosive attack of the aluminum foil takes place. The reduction of the pH value by the addition of an acid is one practical measure to prevent corrosion, but has also negative impact on slurry rheology, electrode conductivity or adhesion. These consequences are shown in an exemplary way for the addition of acetic acid. As especially the adhesion strength is influenced, this effect is investigated in detail for various acids. Best electrode properties are not found in the stable region of the aluminum foil, but at a higher pH of 9 to 10. Acetic acid treated cells show high capacities at their begin-of-life, but undergo stronger degradation than samples without acid addition.

Development of Conductive Organic Cathode Using Interface Charge-Transfer

Lithium ion batteries have become a mainstay as power storage devices with high energy densities. However, they contain heavy metal compounds such as LiCoO₂, which is constrained by limited resources and problems related to the processing of heavy metal waste. Moreover, the capacities of lithium ion battery cathodes are approaching their theoretical limit, since they rely on one-electron redox reactions of heavy transition metals. In order to increase the adoption of storage batteries in an environmentally friendly manner, the development of innovative electrode materials free of rare metals and having high output and high energy densities is necessary. In recent years, redox active organic compounds such as benzoquinone derivatives have attracted attention as candidate materials for battery electrodes. They exhibit excellent characteristics such as high capacities because of multi-electron redox reactions and their structures composed of light elements only. Moreover, their functional groups can be optimized by chemical modification. However, one of the problems in using an organic compound as cathode material is the insulating property of the organic molecule. The insulating property not only lowers the energy efficiency of the redox reaction but also requires the addition of a large amount of carbon material to ensure conductivity, which reduces the effective energy density.

In this study, we propose an organic cathode material based on a novel concept, the “Interface Charge-Transfer [1] (ICT)” phenomenon. In ICT, the electron transfer occurs at the interface between molecular solids that act as a donor and acceptor, respectively. Charge carriers are generated in the molecular solids, and electric conductivity is acquired. In order to realize an ICT “cathode,” we selected donor and acceptor molecules that are redox-active, that have a small molecular weight, so that both the donor and acceptor molecule can act as an active material, and that have a large theoretical capacity. Based on these criteria, we selected tetraphiafulvalene (donor) and 7,7,8,8-tetracyanoquinodimethane (acceptor). Powders of the molecules and polytetrafluoroethylene (PTFE) were mixed to form an electrode without adding any conductive filler such as carbon. The bulk resistivities were measured and it was revealed that the resistivity of the cathodes was very low (2-7 Ω cm). Then, we carried out charge-discharge cycle tests in a half cell system, and the batteries worked for at least 20 cycles while retaining more than 80% of the highest capacity value.

In summary, we succeeded in establishing a novel type of a cathode material, the “ICT cathode”, and examined its performance and characteristics. Since no additives are required to achieve electric conductivity, it is expected that this type of cathode has a high potential for future light-weight and environmentally friendly battery systems.

Reference:
We present the development of a zinc–polymer energy storage device where we employ redox–active polymers based on naphthalenetetracarboxylic diimides (NDIs) with large electron affinities as the cathode. We observe that electrodes made of the polymer can become reduced by zinc electrodes when both electrodes are immersed in aqueous electrolytes. To enable rapid charging in aqueous electrolytes, polar side chains are attached to the polymer backbone that facilitate fast cation transport from the electrolyte into the bulk of the polymer.[1] In addition, no additives or binders are required for the electrode to function in aqueous electrolytes which also enable to fabricate electrodes from solution. Due to the excellent charging properties of the polymers in aqueous electrolytes, we explore non–toxic aqueous electrolytes (salty water) and discuss pathways of how solid state electrolytes can be used in future devices. Finally, we will present how oxygen reduction reactions (ORRs) can be employed to develop a zinc–polymer–air energy storage devices where the redox-active polymer acts as the catalyst to reduce oxygen. We believe that our findings are of importance for the development of future zinc-air batteries, with the potential to use safe and environmentally friendly electrolytes.


It is known that the electrochemical performance of carbon-based supercapacitors depends on the porous structures of carbon-based materials. In this work, we prepare activated carbons (ACs) of different porous structures from xylose and use the prepared ACs as the electrode materials in coin-type supercapacitors with 1 mol/L Et4NBF4 solution in AN as electrolyte. The electrochemical performance of the coin-type supercapacitors is systematically studied. The largest specific capacitances obtained from the coin-type supercapacitors are 340 F/g at 0.5 A/g and 220 F/g at 50 A/g, which are much larger than the results reported for similar systems. The supercapacitors can maintain 86.8% of the capacitance after 10000 cycles at 50 A/g. The energy density is 48 Wh/kg at a power density of 13.6 kW/kg.

This work is supported by the NSF [CMMI-1634540].

One weakness of batteries is the rapid falloff in charge-storage capacity with increasing charge/discharge rate. Rate performance is related to the timescales associated with charge/ ionic motion in both electrode and electrolyte. However, no general fittable model exists to link capacity-rate data to electrode/electrolyte properties. Here we demonstrate an equation which can fit capacity versus rate data, outputting three parameters which fully describe rate performance. Most important is the characteristic time associated with charge/ discharge which can be linked by a second equation to physical electrode/electrolyte parameters via various rate-limiting processes. We fit these equations to ~200 data sets, deriving parameters such as diffusion coefficients or electrolyte conductivities. It is possible to show which rate-limiting processes are dominant in a given situation, facilitating rational design and cell optimisation. In addition, this model predicts the upper speed limit for lithium/ sodium ion batteries, yielding a value that is consistent with the fastest electrodes in the literature.

Self-Organization of Conducting Polymers on Nano-Scale Biopolymer Templates Dagmawi Belaineh1, Jens Wenzel Andreassen2, Justinas Palisaitis1, Sapiens Malti2, Karl Håkansson4, Aleksandar Mehandzhiyski2, Igor Zozoulenko1, Lars Wågberg3, Xavier Crispin1, Isak Engquist1 and Magnus Berggren1; 1Linköping University,
Renewable biomass-derived materials are the key to sustainable energy storage systems. Biopolymers derived from the forest have been blended with conducting polymers to produce green batteries and supercapacitors. In this work, we use cellulose, which is the most abundant biopolymer on earth, to study the critical intra-component interactions between the biopolymer and the seasoned conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). We report a remarkable self-organization of PEDOT:PSS on cellulose nano-fibrils (CNF) which leads to a continuous, linear array of PEDOT:PSS nano-beads, with an average diameter of 13 nm, along the length of individual nano-fibrils. Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) studies elucidate the self-aggregation of PEDO:PSS particles on cellulose. This self-organization leads to the enhancement of long-range electronic transport in the PEDOT which is confirmed by charge transport measurements. Furthermore, we utilize Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) to pinpoint the face-on π-stacked crystallographic orientation of the PEDOT:PSS on top of the CNF. We conclude our investigations by confirming our experimental study by the theoretical modeling of the physicochemical processes that lead to the aggregation of PEDOT:PSS on cellulose using coarse-grained molecular dynamics simulations. Significantly, the simulations also predict nano-beads of PEDOT:PSS aligned along the CNF.

4:45 PM EN03.04.10

W-Co-Fe Metal Oxide as a Carbon-Free Catalyst for the Cathode of Li-O2 Batteries
Ruizhi Yang and Xuecheng Cao; Soochow University, China

The rechargeable aprotic Li-O2 batteries hold great promise for electric vehicles because of their high energy density and environmental friendliness. However, the carbon-based cathodes commonly used in Li-O2 batteries are not stable due to their reaction with discharge products (Li2O2, Li2O), which leads to the formation of insulating lithium carbonate and fades the batteries’ efficiency and cycling stability. In this work, a WCoFe@Ni cathode consisting of sub-stoichiometric tungsten oxide (W18O49), cobalt oxide and ferric oxide as a carbon-free cathode for Li-O2 batteries is presented for the first time. The resulting WCoFe@Ni cathode delivers a high specific capacity (5800 mAh g⁻¹ at 200 mA g⁻¹) and remarkable cycling stability (more than 400 cycles at a capacity of 1000 mAh g⁻¹ under 500 mA g⁻¹). The electronic structures of Co and Fe are modified upon the adding of W in the oxides. The amount of Fe³⁺ in CoFe (37 %) is higher than that in WCoFe (20.2 %), while the amount of Co²⁺ in WCoFe (66.8 %) is higher than that in CoFe (41.3 %). Furthermore, the Fe at the high-valence in WCoFe stabilizes the Co at the low-valence, which facilitates the formation of CoO-like species that is highly active for the decomposition of discharge products in the Li-O2 batteries. The synergistic interaction between W, Co and Fe in WCoFe@Ni cathode plays a critical role in promoting the performance of Li-O2 batteries. Moreover, the sub-stoichiometric tungsten oxide provides high electronic conductivity and the unique 3D nanowire network structure is beneficial for the storage of discharge products. The WCoFe@Ni is a promising carbon-free cathode for Li-O2 batteries.
lignin itself is electronically insulating. Polymer, partially reduced graphite or graphene oxide and graphene have been investigated for energy storage devices. However, these preparation procedures are complicated and difficult for scalable production. Herein, we report a facile process to combine graphite and the lignin derivative lignosulphonate (LS) with the help of simple mechanochemistry; graphite flakes and LS are co-ground in the solid state followed by treatment with water, resulting in a readily processable lignin: graphite paste that can be coated on substrates and directly applied in electrical energy storage devices.

The materials and electrodes are characterized by UV-vis spectroscopy, FTIR spectroscopy, Raman spectroscopy, XRD, dynamic light scattering (DLS), thermogravimetric analysis (TGA), SEM, cyclic voltammetry (CVs) and galvanostatic charge-discharge measurements. The hybrid electrodes with different stoichiometry give two symmetric redox waves defined at 0.67 V and 0.34V versus Ag/AgCl, which is ascribed to the redox reactions of Q groups in LS, a conductivity range from 70 to 290 S m⁻¹ and a charge capacity from 30 to 35 mAhg⁻¹. Moreover, considering the charge capacity from Q groups and mass of LS in the LS/graphite hybrid material electrodes, the charge capacity of the hybrid materials due to LS can be as much as 70 mAhg⁻¹. IR results and UV-vis results prove the LS/graphite pellets and supernatant contain a mixture of LS and graphite. The Raman spectra, TEM pictures and XRD results suggest the presence of fewer layers, more defects, more disorder and smaller crystallite size of graphite in the hybrid material electrodes than in the pristine graphite. The TGA results confirm the range of the stoichiometry of the LS/graphite pellets of 0.55-1.25. The SEM results illustrate that the ball milling process can reduce the grain size of graphite and LS, and create nanoscale geometries in the hybrid materials. Furthermore, the morphology of the LS/graphite hybrid material electrodes can be effected by the stoichiometry of LS and graphite in the ball milling process.

In summary, mechanical ball milling combined with aqueous process is a way to fabricate sustainable, environmental friendly, low cost and scalable LS/graphite hybrid materials with high conductivity and moderate charge capacity. The molecular interaction and charge transfer between LS and graphite in the electrodes make these electrodes candidates for energy storage.


EN03.05.02
In Situ Interface-Forming Technique of Poly(ionic liquid)s with Plastic Crystal and Lithium Salt in Electrodes for Solid Lithium Batteries Hideyuki Ogawa1, Akihiro Orita1, Katsunori Kojima1 and Hideharu Mori2; 1Hitachi Chemical Co. Ltd., Japan; 2Yamagata University, Japan

Recently, solid lithium batteries using solid electrolytes have attracted considerable attention due to their potentially high energy density and safety. However, some key issues remain unsolved. The good interface formation between the solid polymer electrolyte and the solid active material is needed. Specifically, an adhesive and flexible electrolyte are favorable to follow the volume change of an active material in an electrode upon charging and discharging. Actually, the addition of solid polymer electrolyte (in general, around 20wt-%) into an electrode to form the above good interface causes the degradation of an energy density, hindering their commercialization.

To solve these problems, we propose in-situ radical polymerization of diallyldimethyl ammonium bis(trifluoromethanesulfonyl)imide (DADMA-NTf₂) in the presence of lithium bis(trifluoromethanesulfonyl)imide (LiNTf₂) and 1-ethyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (P12NTf₂) in an electrode with an active material. The ternary mixed solution (DADMA-NTf₂/LiNTf₂/P12NTf₂) is successfully permeated into pores of an electrode layer, and a solid-state ionogel is formed in the electrode after in-situ radical polymerization under air: without decreasing the ratio of the active material. In addition, there are no observable pores or defects by SEM and EDX measurements, suggesting that an ideal interface between the ionogel and the active material is formed. The ionic conductivity of such ionogel exceeds 1.0 x 10⁻³ S/cm at 50 °C, which is close to that of gel polymer electrolytes with ionic liquids as reported previously. The conversion of DADMA-NTf₂ during bulk polymerization decreases with increasing in the P12NTf₂ ratio in the feed, while the increase in P12NTf₂ leads to the improvement of the ionic conductivity. This result suggests that suitable content of the P12NTf₂ is crucial to obtain a solid-state ionogel with a high ionic conductivity. Batteries fabricated by simply stacking of a glass-fiber membrane between the positive and negative electrodes, all of which contain solvent-free in-situ formed ionogels, are successfully operated at a low current rate. Owing to no need of the volatile organic solvent and any special atmospheric control, this simple and environmentally-friendly procedure to prepare an electrode for solid batteries can help to ensure the wider practical use of solid lithium batteries.
EN03.05.03

Electrocatalytic Performance of Nitrogen and Oxygen Co-Doped Carbon Electrodes for Vanadium Redox Flow Battery

Doohwan Lee, Hyebin Lim and Seong-Cheol Kim; University of Seoul, Korea (the Republic of)

The electrocatalytic properties of graphite felt (GF) electrodes for vanadium redox flow battery (VRFB) are studied with N and O atomic dual doping on the GF surface by urea thermolysis. Simple impregnation of GF with urea and polyethylene glycol (PEG), followed by thermal treatment at elevated temperatures, results in significant N and O dual doping on the electrode with high surface uniformity and electrocatalytic activities. The correlation analysis on the electrocatalytic properties of the GF electrodes with respect to the configuration and elemental contents of the doped N and O functionalities suggests that the pyrrolic-N species on the carbon electrodes provide significant kinetic enhancement for vanadium redox reactions. The operando studies measuring the through-plane voltage losses in the VRFB single cell reveal that the N and O dual doping by urea thermolysis gives rise to approximately 3-fold improvement in the vanadium redox kinetics, particularly on the anode side, which greatly reduces the overall cell voltage loss. At practical charge–discharge condition, the N and O dual-doped GF electrode affords about 15 % increase in voltage efficiency and 2-fold increase in charge–discharge capacity of the VRFB over that obtained from the pristine-GF electrode. These results suggest the marked electrocatalytic effects of the N and O dual-doping on carbon electrodes for vanadium redox reactions, and the high effectiveness of urea thermolysis for the electrode functionalization for VRFB.

EN03.05.04

A Novel Ethanol/Water Binary Electrolyte Enabling Superior Cycle Stability of Na-Mn-O Cathode for Aqueous Rechargeable Sodium-Ion Batteries

Rodney Chua, Yi Cai, Sonal Kumar, Vivek Verma and Madhavi Srinivasan; Nanyang Technological University, Singapore

Aqueous rechargeable sodium-ions batteries (ARSIBs) have garnered extensive research interests due to its safety and abundant sodium resources towards sustainable large-scale energy storage applications. [1, 2] Among the various transition metal oxides employed in ARSIBs, Na0.44MnO2 (NMO) has been considered as an attractive cathode due to its unique tunnel structure that can facilitate fast transport of Na-ions during de/insertion processes.[3-6] However, the parasitic side reactions such as dissolution of active material, H2/O2 evolution reactions and water protons insertion into the NMO structure undermine the cycle life of NMO.[6] Therefore, the prevailing research challenge lies in maintaining the capacity over long cycles of NMO in an aqueous media.

Herein, for the first time, we propose a novel binary electrolyte for ARSIBs by using green and low-cost 1 m sodium acetate dissolved in the optimized ethanol/water cosolvents. Electrochemical behaviors are studied on NMO plates by using our binary electrolyte. Meanwhile, the NMO electrode was also tested in a single electrolyte (1 m sodium acetate dissolved in Di water) for comparison. The overlapping cyclic voltammetry curves of NMO cycled in binary electrolyte (NMO-Et/Di) indicate a highly reversible de/insertion processes of Na-ions. Furthermore, the NMO-Et/Di electrode exhibits a superior cycle stability, while the NMO-Di sample shows an obvious capacity fading after 1000 cycles. A combination of Fourier-transform infrared spectroscopy and nuclear magnetic resonance measurements carried at various cosolvents ratio coupled with ex-situ X-ray diffraction and scanning electron microscopy were conducted to further understand the dependence of the cathode/electrolyte interface, material stability and charge storage mechanism. It is noted that the intrinsic hydrogen-bonding interaction between ethanol and water protons in binary electrolyte is one of the main contributing factors towards a superior cycle stability of NMO. The results of the study provide insights into the electrode-electrolyte interactions and highlight the significance of electrolyte design and optimization in aqueous rechargeable batteries.

References
Typical fabrication methods, such as photolithography and rolling/stacking, that are commonly used in conventional electronics and energy storage systems respectively, have caused the devices to lack a variety of form factors and flexibility needed for countless new Internet-of-Things applications[1]. In the past decade, the development of digital printing technology in the field of printed electronics, has triggered an explosion of new ideas and alternative fabrication strategies that led to lean and cost-efficient manufacturing processes. In this work, the digital nature of inkjet printer was utilised to fabricate multifunctional energy storage sources in the form of casual letters in text. A new font style of the Latin alphabet was developed so that each character assembles a planar supercapacitor, able to be aesthetically and seamlessly connected, either in series or parallel configuration. A nanoparticle-based silver current collector, a nanoparticle-based nickel (II) oxide (NiO) active electrode material and a transparent ionic liquid/ultraviolet-cured triacrylate polymer-based solid-state electrolyte, were chosen as model materials to explore the feasibility of the proposed concept. The model letter-supercapacitors were able to deliver up to 27 mF cm\(^{-2}\) and handle scan rates up to 500 mV s\(^{-1}\) at a voltage window of 2.5 V. This approach underlines the exceptional applicability of the inkjet-printed letter-supercapacitors as a fabrication strategy towards multifunctional power sources with versatile form factors that lie far beyond what conventional fabrication technologies can achieve. The letter-supercapacitors can be used as energy storage units for electronic books, paper electronics and smart textiles with the potential of the proposed concept to be extended beyond interconnects and energy storage to seamless printed sensors and other electronic components.


Microporous Carbons from Different Lignin through Controlled Activation

Lu Yu\(^1\), David Harper\(^1\), Orlando Rios\(^2\), David Keffer\(^1\), David Alonso\(^3\), Kendhl Seabright\(^1\) and Valerie Garcia-Negrón\(^1\); \(^1\)University of Tennessee, United States; \(^2\)Oak Ridge National Laboratory, United States; \(^3\)University of Wisconsin–Madison, United States

With the awareness of sustainable development and solving the energy storage problem, convert woody biomass into carbon products for energy storage applications has attracted enormous attention. We extract high purity lignin from four different types of biomass materials, and then control the processing conditions to produce high-value carbon products. Chemical characterizations including TGA and DSC are conducted to get the thermal properties of the lignin, such as the glass transition temperature, average decomposition temperature, and char content. The lignin functionality and chemical composition were investigated by Fourier-transform infrared spectroscopy and nuclear magnetic resonance spectroscopy measurements. From this information, we optimized the carbonization conditions through control humidity, temperature and reducing environment needed for graphitization. Carbons after pyrolysis were activated to produce activated carbon foams. The physical and chemical activation were compared and explore the reactions during the activation. Brunauer–Emmett–Teller (BET) analysis was conducted to measure the surface area and pore size distributions (PSDs). The surface area and PSDs are significantly affected by the activation temperature and duration. Usually the higher temperature, the greater surface area and PSDs. In addition, various precursors also show different results under different activation duration. Changes in morphology were determined by SEM and TEM. Carbon morphology and composition were determined by x-ray diffraction and elemental analysis. Combined with these experiments results, the major reactions during the activation are clear and the way to control porosity through activation and produce microporous activated carbon are developed.

Dye-Sensitized Solar Cells Based on Tin and Zinc Oxide Composite Films Using Ionic Electrolytes

K.D.M.S.P.K. Kumaraasinghe\(^1\), G.R.A. Kumara\(^2\), Ajith DeSilva\(^2,3\), A.G.U. Perera\(^1\), Sunil Dehipawala\(^4\) and K. Tennakone\(^5\); \(^1\)National Institute of Fundamental Studies, Sri Lanka; \(^2\)University of West Georgia, United States; \(^3\)Georgia State University, United States; \(^4\)Queensborough Community College of CUNY, United States; 

Final Program 1/13/2020  503
After decades of research, long term stability of dye sensitized solar cells (DSCs) continue to remain a questionable issue. The observed instability is caused by dye and electrolytic degradation and gradual evaporative elimination of the volatile component of the electrolyte via unavoidable faults in the sealing. Degradation of the dye and the electrolyte is mainly due to photocatalytic reactions mediated by titanium dioxide. Of familiar high-band gap oxide materials, short wavelength (<300 nm) radiation initiated by photo-catalytic activity originating free radical generated by hole transfer to water molecules is strongest in titanium dioxide. Although DSCs made from less photo-catalytically active tin and zinc oxides are inefficient, composite tin-zinc oxide films yield efficiencies comparable to those fabricated out of titanium dioxide films. Studies conducted reveal that DSCs based tin-zinc oxide films are highly stable when moisture free high boiling point solvents are incorporated to solubilize the conventional iodide/tri-iodide redox system. Sensitized charge injection and transport in composite tin-zinc oxide films and the possible causes of enhanced stability will be discussed.

EN03.05.10
Controlled Phase Transformation of Ni-Co Layered Double Hydroxides and Their Effects on Electrochemical Performances for Wearable and Flexible Asymmetric Supercapacitors
Young-Min Jeong and Seong-Ho Baek;
DGIST, Korea (the Republic of)

Recently, due to the tremendous demand on wearable and flexible devices, there has been an urgent requirement for future energy sources that are compact, efficient, and implementable on small footprint. Supercapacitors (SCs) can supply higher capacity per unit area compared to traditional electrostatic or electric double layer capacitors (EDLCs) while they can provide faster power delivery and longer cycling ability than lithium ion batteries (LIBs). However, one of the biggest challenge of SCs is to find an efficient way to enhance energy density comparable to LIBs without sacrificing power density loss. To address these issues, much effort has been devoted on the improvement of electrode materials and novel structures in recent years. In this work, we demonstrate Ni and Co layered double hydroxides (NiCo–LDHs) on Ni–coated textile for wearable supercapacitor (SC) applications. LDHs are a group of two dimensional layered structures and have proven to be very promising due to high performance pseudocapacitive materials, high redox activity, and environmentally friendliness. In addition, we investigate that the crystal structure and electrochemical properties of NiCo-LDH can be controlled by adjusting the reaction time using hydrothermal method. We report on controllable phase transformation of NiCo-LDH and their morphology evolution from nanosheets to nanowires with increasing growth time. Lastly, an asymmetric pseudocapacitor is assembled with the graphitic carbon as negative electrode and the NiCo LDH as positive electrode. The best device result shows a high energy density of 55.8 Wh kg\(^{-1}\) at power density of 601 W kg\(^{-1}\) with a 1.2 V operating voltage.

EN03.05.11
Investigations of Thermal Processing of Nasicon-Like Lithium-Ionic Conductors for All-Solid Li-Ion Batteries
Hunter Frost\(^1\), Marie Francoise C. Millares\(^1\), Kevin Shah\(^1\), Yashashvini Andugula\(^1\), Spencer Flottman\(^2,3\), Seiichiro Higashiya\(^1\), Devendra K. Sadana\(^4\) and Harry Efthathiadis\(^1\), \(^1\)SUNY Polytechnic Institute College of Nanoscale Science and Engineering, United States; \(^2\)Oak Ridge National Laboratory, United States; \(^3\)Eonix LLC, United States; \(^4\)IBM T.J. Watson Research Center, United States

For decades, solid electrolyte thin films have opened up new avenues for power storage, as well as offering alternative applications, such as neuromorphic computing, and have represented many benefits concerning safety, cost, and energy efficiency compared to their liquid electrolyte counterparts. The NASICON-like solid compound, lithium aluminum titanium phosphate \((\text{Li}_{1.4}\text{Al}_{6.6}\text{Ti}_{2.4}(\text{PO}_{4})_3)\), LATP has shown promise as a solid electrolyte, with a demonstrated ionic conductivity of \(\approx 3 \times 10^{-3} \text{ S cm}^{-1}\). Here, LATP thin films were deposited via RF-magnetron sputtering; this method is more suitable for large scale implementation and reproducibility, unlike the commonly utilized sol-gel method. This study focuses on the effect of thermal processing on electrical resistance for both micrascale batteries and unique MIM structures created with the sputtered LATP thin films. The two thermal processes studied here are the effects of both mid-deposition heating and post-deposition annealing on these devices. During the fabrication process, a range of mid-deposition heating temperatures and post-deposition annealing temperatures are examined to determine optimal processing conditions for maximizing electrical resistivity. It has been found that optimal electrical resistivity (~150 M\(\Omega\)) is achieved only through post-deposition annealing at >350\(^\circ\)C, with notable resistivity improvements arising from mid-deposition heating. Microscale half-cell batteries (~100 \(\mu\)m x 100 \(\mu\)m) created with the annealed LATP films show behavior typical of half-cell batteries, with minimal to no signs of leakage.
EN03.05.12
A Novel, Water-Stable 2D Sheet-Like Neutral Cu(i)-Sulfonate MOF Containing π-Acidic Naphthalenediimide (NDI) Ligand Dillip K. Panda; Clemson University, United States

In this study, we report the design, synthesis, and characterization of a novel, water-stable 2D sheet-like neutral Cu(I)-sulfonate metal-organic framework (MOF) having π-acidic naphthalenediimide (NDI) disulfonate as ligands. This NDI-based ligand has an ability to bind the guest lithium ions (Li+) with its carbonyl and sulfonate oxygen atoms, and whereas, the diffuse perchlorate anions (ClO4-) binds via anion−π and CH...anion interaction. The measured ionic conductivity of this MOF [Cu2(BPY)2(NDIDS)] has significantly enhanced to 10^6 times (2.3x10^{-4} S/m) by inserting LiClO4 dopant. This Lithium-ion conducting (MOFs) act as an ion permeable electrode separators and useful for rechargeable batteries. For the first time, such enhancement of lithium-ion conductivity is observed in a neutral, and solvent-free, not post-synthetically modified MOF. Moreover, the determined low activation energy (E_a =0.167 eV) and high Li-transference number (τ_{Li} =0.749), suggest that the newly developed ion-conducting disulfonate could be a potential solid-electrolyte for battery applications. To demonstrate further the influence of the Li^+ binding, the MOF was also treated with Bu4NClO4 salt which shows the poor electrical conductivity (4.55x10^{-10} S/m) similar to the pristine untreated MOF (4.65x10^{-10} S/m) at room temperature. The same conductivity properties could be attributed to the size exclusion and facile removal of large uncoordinated Bu4N^+ cations. The impact of ionic conductivities of this MOF upon doping with various cations such as (K^+, Na^+, Mg^{2+}) and anions (BF_4^-, I^-, PF_6^- TfO^-) with this [Cu2(BPY)2(NDIDS)] MOF are under investigation in our lab.

EN03.05.13
Value-Addition Recycling Process for Electric Vehicle Battery Cathode Materials Linsen Li, Guannan Qian, Zi-Feng Ma and Yushi He; Shanghai Jiao Tong University, China

The word is embracing a new electrification revolution sparked by the rapid development and mass deployment of lithium-ion batteries. LIBs based on lithium nickel manganese cobalt (NMC) or lithium nickel cobalt aluminum oxide (NCA) cathode materials are now dominant power sources for electric vehicles. Ni and Co are expensive heavy metals that are attractive for recycling. Currently, Ni and Co are recovered from the used batteries either by pyrometallurgy or hydrometallurgy method. Hydrometallurgy method is more widely used because it can be integrated into the production of hydroxide precursors for NMC or NCA. This is a profitable process thus goverment subsidies are no longer necessary. However, this recycling method consists of many steps (>10) and generates a large amount of heavy-metal containing acid-waste and base-waste. To better address the NMC battery recycling challenge, it is necessary to develop greener and more cost-effective methods. We have recently developed a convenient and scalable method based on advanced molten-salt chemistry to convert the structurally damaged and lithium deficient polycrystalline NMC materials in the used batteries into high-performance single-crystal NMC cathode materials. During the conversion, it is also possible to increase the Ni content in the cathode materials to further boost the energy density and increase the value. Cost analysis are performed to confirm that the new method is a value-addition process. This work reveals a promising new path toward better recycling used battery cathode materials at a large scale and with much less environmental impact.

SESSION EN03.06: Green Electrochemical Energy Storage Solutions—Materials, Processes and Devices V
Session Chair: Francesca Soavi
Wednesday Morning, December 4, 2019
Sheraton, 2nd Floor, Republic A

8:30 AM *EN03.06.01
Structural Water Containing Materials for Aqueous Post-Lithium-Ion Batteries Jang Wook Choi; Seoul National University, Korea (the Republic of)

Although Li-ion batteries have been successful in various applications, their shortcomings with regard to high cost and global maldistribution of raw materials, as well as safety concerns have promoted alternative rechargeable batteries based on other carrier ions represented by sodium and magnesium ions, targeting grid-scale energy storage
systems (ESSs). However, many electrode materials in these emerging systems often suffer from sluggish kinetics due to the larger size or bivalency of carrier ions, limiting electrochemical performance particular in specific capacity and operation voltage. In this talk, I will introduce a new approach of engaging intercalated water in layered cathode materials. The intercalated water improves the performance of the given materials substantially by shielding electrostatic interactions or maintaining the crystal frameworks over repeated cycles. Detailed effects of intercalated water will also be described, along with promising potentials towards aqueous operations. Electron microscopy characterization for in-depth understanding of these materials will also be introduced.

9:00 AM *EN03.06.02
Facile-Processed Sulfur Cathodes for High Performance Sodium-Sulfur Batteries Weiyang Li; Dartmouth College, United States

Room-temperature (RT) sodium-sulfur (Na-S) batteries using all earth-abundant resources as electrode materials are considered to be the next-generation cost-effective energy storage devices. However, their practical applications are still plagued by the low reversible capacity of commercial S, low Coulombic efficiency, and poor cycling stability caused by sluggish kinetics of Na-S electrochemical reactions and severe shuttle effect of polysulfides. Here we present our most recent works on developing high-performance RT Na-S batteries using facile-processed S-based cathodes. A simple and scalable approach has been developed to synthesize hollow sodium sulfide nanospheres embedded in a highly hierarchical and spongy conductive carbon matrix, forming an intriguing architecture similar to the morphology of frogspawn coral, which has shown great potential as a cathode for high-rate performance RT Na-S batteries. The shortened Na-ion diffusion pathway benefits from the hollow structures together with the fast electron transfer from the carbon matrix contributes to high electrochemical reactivity, leading to superior electrochemical performance at various current rates. A Na-metal-free Na-S battery is demonstrated by pairing the hollow sodium sulfide cathode with tin-based anode. Besides using sodium sulfide as cathode, we also develop a highly stable RT Na-S battery using a facile-processed commercial S cathode and gel polymer electrolyte, which delivers a reversible capacity of >700 mAh g\(^{-1}\) with near 100% Coulombic efficiency and an ultrahigh capacity retention of 98.2% at 0.2C after 200 cycles.

9:30 AM BREAK

10:00 AM *EN03.06.03
Materials and Processes for Sustainable Batteries Stefano Passerini; Karlsruhe Institute of Technology, Germany

Our society is presently facing the great challenge to switch from depleting energy sources like oil, coal, or gas, to renewables such as solar and wind. With regard to their inherent intermittency and commonly decentralized generation, however, efficient and sustainable energy storage is of utmost importance. Beside large-scale solutions like hydropower or compressed air, electrochemical energy storage, in particular secondary batteries, is currently considered to be the most suitable technology, particularly for relatively smaller applications like transportation or short- to mid-term stationary energy storage.[1–4] As a matter of fact, the number of electric vehicle (EV) sales is steadily increasing within the past years and the same trend is observed for the implementation of secondary batteries for buffering the intermittent energy supply by solar and wind.[1–4] Consequently, batteries play a vital role for moving towards a more sustainable “energy future”, raising, however, concerns about the impact that their production and disposal could have on the environment.[5] Renewable materials, environmentally-friendly processes and safer batteries are needed for the sustainable development of electrochemical energy storage [6].

The sustainable use of natural resources is indispensable for future energy storage. As a step towards the utilisation of biowaste, hard carbon produced from waste apples is demonstrated to be a high performance active material for Na-ion batteries [7].

The aqueous processing of lithium-ion battery (LIB) electrodes has the potential to notably decrease the battery processing costs and paves the way for the sustainable production (and recycling) of electrochemical energy storage devices. In this study, we show that the addition of small quantities of phosphoric acid into the cathodic slurry yields NMC electrodes with outstanding electrochemical performance in lithium-ion cells [8]. Another example is the excellent performance of graphite/LNMO cells with both electrodes made using water-soluble binder [9].

References:
A Photochemical Artificial Photosynthesis of CO₂ Reduction into Syngas Production

Roksana Rashid¹, Mohammad Faqrul Alam Chowdhury¹ and Zetian Mi¹,²; ¹McGill University, Canada; ²University of Michigan–Ann Arbor, United States

In this study, we have demonstrated for the first-time, enable, efficient, unassisted photochemical reduction of carbon dioxide (CO₂) into syngas using wafer scale multiband InGaN/GaN nanowire structures without using any sacrificial reagent. The effective manipulation and control of charge carrier flow in nanostructured photocatalysts provides critical insight in achieving high efficiency artificial photosynthesis, which includes the efficient and selective reduction of CO₂ into solar fuels.

Supercapacitors within the Water-Energy Nexus

Francesca Soavi¹, Federico Poli¹, Francesca E. Spina¹, Alessandro Brilloni¹, Jacopo Seri¹, Mehrdad Mashkour¹,², Mohammad Said El Halimi¹,³, Maria L. Focarete¹, Clara Santato⁴, Carlo Santoro⁵, Bridget K. Mutuma⁶, Amanda Bubu⁶ and Ncholu Manyala⁶; ¹University of Bologna, Italy; Babol Noshirvani University of Technology, Iran (the Islamic Republic of); ³University Abdelmalek Essaadi, Morocco; ⁴Polytechnique Montréal, Canada; ⁵University of West of England, United Kingdom; ⁶University of Pretoria, South Africa

Supercapacitors (SC) are playing a key role within the so called Water-Energy Nexus. Indeed, SCs can improve the quality of electric energy harvested from intermittent renewable energy source and from microbial fuel cells (MFC) that are bio-electrochemical devices that convert the chemical energy of wastewater organic compounds directly into electrical energy.

In this scenario, lowering the price and minimizing the environmental and economic impact of disassembly and recycling of end-of-life SCs are is mandatory.

The use of water-processable electrode binders and new membrane production techniques like electrospinning are viable approaches to decrease cost and environmental footprint.

A study on the development of bio-inspired supercapacitors and their integration with MFCs is reported and discussed.

Specifically, a pullulan-based supercapacitor featuring carbon electrodes obtained by the pyrolysis of pepper seeds and working with ionic liquid electrolyte is hereby proposed. The use of a water soluble, biodegradable polymer as binder and separator along with a hydrophobic ionic liquid brings about a novel approach for device end-of-life management. The use of melamine as pseudocapacitive electrode material is also presented.

Acknowledgments

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References


11:15 AM EN03.06.07
Greener Process for Greener Batteries—Application of Use of Water Processable Binders in Aqueous Rechargeable Lithium-Ion Batteries

Steeve Rousselot, Lida Hadidi, Jacopo Profili, Erica Tomassi, Maxime Nicolas and Mickael Dollé; Université de Montreal, Canada

Sustainability for energy storage systems and environmental protection imply both the use of environmentally benign materials and the development of green processes. Rechargeable lithium ion battery (LIB) with organic electrolyte has found many applications. Its high energy density and long cycle life make it the best option compared to other secondary batteries. However, environmental impact throughout their fabrication and disposal, safety concerns during their use, and cost remain the main drawbacks for large-scale applications. Hence, interest in aqueous electrolyte rechargeable LIB (ARLB) has grown, particularly for safe and cost effective large scale devices.

To reduce the adverse environmental/human impact of LIB production, the electrode preparation process needs to be revisited. In this regard, replacing common binders (e.g. fluorene-containing polymers; polyvinylidene difluoride (PVDF)) and noxious organic solvents (e.g. N-methyl-2-pyrrolidone (NMP)) by non-toxic and aqueous processable binders is a must. Water soluble binders such as carboxymethyl cellulose (CMC) have gained considerable attention due to their natural abundance, water processability and lower cost.

Nevertheless, using water soluble binders in electrodes for aqueous batteries is challenging because of their solubility in aqueous electrolyte with low salt concentration. In our group, we successfully addressed this issue by developing a strategy to prepare electrode employing CMC usable in ARLB. A chemical modification of the electrodes prevents the loss of electronic percolation and allows the cycling over a prolonged number of cycles in low concentrated aqueous electrolytes.

In this presentation, the physiochemical properties and electrochemical performance of such electrodes were investigated and compared to that of electrodes prepared with typical binders in organic electrolytes.

11:30 AM EN03.06.08
Pillared and Hetero-Layered 2D Metal Carbides (MXenes) for Electrochemical Energy Storage

Armin VahidMohammadi1, Weiqian Tian2, Wentao Liang3, Mehrnaz Mojtabavi3, Meni Wanunu3, Mahiar M. Hamedi2 and Majid Beidaghi1; 1Auburn University, United States; 2KTH Royal Institute of Technology, Sweden; 3Northeastern University, United States

Two-dimensional (2D) materials have shown promising performances as electrode materials for electrochemical energy storage devices. Most individual 2D materials, however, suffer from certain limitations and therefore, cannot be individually considered as practical electrode materials for supercapacitors or batteries.[10] Controlled pillaring of 2D materials into multilayers and vertical stacking of different 2D layers into heterostructures have shown to be effective methods to avoid their self-restacking and overcome drawbacks of individual 2D materials. Such pillared 2D multilayers or superlattice heterostructures built by sequential stacking of single or multiple 2D layers can
display new and improved electrochemical responses and offer a combination of their building blocks’ best properties. 2D metal carbides (MXenes) have recently received huge attention for energy storage applications due to their diverse compositions, ability to intercalate a variety of cations, and high rate pseudocapacitive properties. Self-restacking of MXenes and their lower capacitances compared to other pseudocapacitive materials, however, have hindered their further development. Also, because of instability and rapid structural degradation of the delaminated form of various MXene compositions, most studies on MXenes have been limited only to Ti$_3$C$_2$Tx. Here in this presentation, we demonstrate new pillared and heterostructure MXene architectures fabricated by controlled self-assembly of individual MXene sheets. The fabricated pillared MXene multilayers and MXene heterostructures show stable and superior electrochemical performances in aqueous and organic electrolytes. For example, alkali-cation pillared multilayers of V$_2$CTx could deliver volumetric capacitances of over 1300 F cm$^{-3}$ and maintain ~78% of their initial capacitance after one million cycles at a rate of 100 A g$^{-1}$ in aqueous supercapacitors. In addition, all-solid-state supercapacitors based on pillared Ti$_3$C$_2$Tx electrodes fabricated by a precise layer-by-layer (LBL) self-assembly method delivered high energy and power densities of 3.0 Wh L$^{-1}$ and 4400 W L$^{-1}$, respectively. This is while Ti$_3$C$_2$Tx and V$_2$CTx MXene heterostructures showed new features in their cyclic voltammetry profiles and could deliver the highest volumetric capacitance of ~1470 F cm$^{-3}$ in 3M H$_2$SO$_4$ electrolyte. This study paves the way for the preparation of high-performance pillared and hetero-layered MXene structures for electrochemical energy storage applications and beyond.

References

11:45 AM EN03.06.09
NMC Cathode Materials with Outstanding Performance Generated by a Closed-Loop Recycling Process
Mengyuan Chen$^1$, Bin Chen$^1$, Xiaotu Ma$^1$, Zifei Meng$^1$, Dennis Bullen$^2$, Jun Wang$^2$, Zhangfeng Zheng$^3$, Eric Gratz$^3$ and Yan Wang$^1$; $^1$Worcester Polytechnic Institute, United States; $^2$A123 Systems, United States; $^3$Battery Resources, United States

Lithium-ion batteries (LIBs) is widely used in every aspect of our life due to its high energy density and long cycle life. However, the large demand of LIBs will also lead to a substantial end-of-life (EOL) batteries which requiring proper treatment. Recycling EOL LIBs not only mitigates the production of hazardous waste caused by improper disposal, it also can recover the value from strategic materials. A closed-loop recycling process developed in WPI has demonstrated its successful in synthesizing recycled NMC 111 with excellent electrochemical performance when compared with a commercially available cathode. Now, WPI moves forward to demonstrate its feasibility to synthesize high-nickel NMC cathode powder-NMC 622. Here, recycled NMC 622 shows better rate and cycle performance comparing to a commercially and chemically equivalent. In addition to that, NMC 622 cathode is coated with alumina oxide using two coating methods (dry coating and wet coating) and its cycle stability is improved.


1:30 PM *EN03.07.01
Electrolyte Dictated Organic Electrode Materials Design for Energy Storage
Yan Yao; University of Houston, United States
The quest for cheaper, safer, higher-density, and more resource-abundant energy storage has driven significant battery innovations. Existing lithium-ion batteries (LIBs) use cobalt-heavy active electrode materials that are predicted to see supply constraints going down the path and can be too expensive to meet long-term capital cost goals for grid storage and electric vehicle systems ($100 kWh^{-1}$). On the other hand, the safety issues with commercial LIBs mainly originate from the flammable and volatile nonaqueous electrolytes. Safer systems with solid-state and aqueous electrolytes are being actively developed, but today’s active electrode materials are not optimized for these electrolytes in terms of chemical and electrochemical compatibility. In the course of overcoming the above limitations, considerable innovations are taking place in the development of active materials featuring sufficiently high energy, Earth-abundant elements, and unique electrolyte-dictated properties. A notable family of such materials is organic battery electrode materials (OBEMs), which comprise electrochemically redox-active organic compounds including molecules, polymers, and organometallics where the organic components contribute to redox activity. In this talk, I will compare OBEMs with dominating/competing inorganic materials through analyses of charge storage mechanism, working potential, specific capacity, resource availability. We show that from high-energy lithium batteries to aqueous, Mg-ion, and all-solid-state batteries, OBEMs can be designed to be sufficiently capable and offer unique feature sets unmatched by other materials.

2:00 PM EN03.07.02
How Protective Layer Forms in High-Concentrated Sodium Aqueous Electrolyte for High-Voltage Aqueous Rechargeable Battery

Myeong Hwan Lee, Sung Joo Kim and Kisuk Kang; Seoul National University, Korea (the Republic of)

In the non-aqueous based conventional Li-ion battery (LIB) system, solid-electrolyte interphase (SEI) layer have been successfully prevented the electrolyte decomposition on the electrode surface, which enables the representative reversible electrochemical reaction, while the aqueous electrolyte could not form a stable protective layer on the electrode. However, the recent invention of highly concentrated aqueous electrolytes has outperformed conventional electrolytes by producing the SEI layer with anion decomposition and suppressing water splitting. Nevertheless, the high-concentrated aqueous electrolyte systems give a widened stability window and cycle stability with a robust protective layer, it still has a significant economic issue for their commercialization regarding the use of high-cost imide based organic solutes. In this study, we focused on finding a new low-cost high-concentrated aqueous electrolyte and studying how SEI layer forms in this newly investigated aqueous electrolyte. For evaluating these issues, we revisited all the commonly used low-cost inorganic salts and demonstrate them for their use in high-concentrated aqueous electrolytes. The reinvestigated highly concentrated aqueous electrolyte offers a wide electrochemical stability window of up to 2.7 V with forming a stable protective layer without involving the reduction of salt anions. In addition, we proposed a new mechanism of the protective layer formation on the electrode surface involving the residual gas reduction in different from the model of the anion decomposition. It was noted that the relative stability of this protective layer in the high-concentration aqueous electrolyte assists the stability of the electrode in the cell, resulting to exhibit the extraordinary electrochemical storage stability of the full-cell for over 900 hours.

2:15 PM EN03.07.03
Highly Porous Anisotropic Wood Aerogels

Jonas P. Garemark, Yuanyuan Li, Xuan Yang and Lars Berglund; KTH Royal Institute of Technology, Sweden

Highly porous aerogels with anisotropic structural properties are highly demanded in many areas, ranging from thermal insulators in buildings to supercapacitors in electrical devices. Currently, aerogels are often made from synthetic polymers. With the depletion of fossil energy and increasing environmental concerns, the research focus has been shifted to biomass-based materials. In this work, a highly porous anisotropic wood aerogel is prepared from a top-down synthesize method. The preparation comprises removal of lignin followed by a cellulose dissolution/regeneration regime with DMAc/LiCl. The co-solvent partially dissolves the cell wall and the regeneration results in a porous cell wall with fibrillated networks inside the fibres lumen. The aerogels retain the structural anisotropy of natural wood, exhibits a high specific area of 247 m²/g, whilst remaining mechanically strong. As a demonstration, the aerogels are carbonized to yield electrodes towards supercapacitor applications. This top-down approach is found to be a novel preparation method for porous materials towards energy storage and harvesting.

2:30 PM BREAK
Exploratory Studies of an Alkaline Polysulfide-Permanganate Redox Flow Battery

Jesse Hinricher and Fikile Brushett; Massachusetts Institute of Technology, United States

Energy storage has emerged as a key technology for improving the sustainability of electricity generation by improving the efficiency of existing fossil-fuel infrastructure through load-leveling, alleviating the intermittency of renewables, and providing high-value services (frequency regulation, voltage support, or back-up power) [1]. Redox flow batteries (RFBs) are promising devices for low-cost grid energy storage due to decoupled capacity and power scaling, long operational lifetime, easy thermal management, and reliable safety features. While a variety of redox chemistries have been investigated over the years, the all-vanadium RFB has been the most successful as it is based on four stable, water-soluble oxidation states of vanadium that enable both high cell potential and crossover tolerance. Despite these favorable attributes, the technology is considered too expensive for broad adoption, motivating efforts to advance new redox chemistries, separation strategies, and reactor formats which may offer pathways to lower-cost RFB systems.

In this presentation, I will describe an alkaline polysulfide-permanganate RFB whose cell voltage, solubility, and potentially-inexpensive constituent components make it a promising candidate redox chemistry [2, 3]. Cell performance and durability will be evaluated as a function of component material selection (electrodes, membranes), electrolyte composition, and operating conditions. In addition, failure mechanisms will be assessed and performance recovery strategies proposed.

References

Sustainable Free-Standing N-Containing Bubbled 3D Carbon Sponge for Supercapacitor Application

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To overcome the increased demand in energy consumption and fossil fuel depletion, there’s a huge requirement for sustainable energy storage devices. Supercapacitors play a vital role compared to batteries and fuel cells in terms of high-power density, long cyclic stability and environment friendly. The simple, low-cost N-containing bubbled 3D carbon sponge was prepared by the carbonization of polyaniline nanofibers coated onto pre-carbonized carbon sponge as scaffold. In this material, the 3D carbon sponge derived from kitchen sponge acts as a base framework for polyaniline fibers growth by chemical synthesis. The further carbonization of fibers on carbon sponge results in bubble formation at the nodes of network with nitrogen doping that leads to increasing the specific surface area from 75 m² g⁻¹ for carbon sponge to 212 m² g⁻¹ for bubbled carbon sponge. The morphology and N-doping of the material was confirmed by scanning electron microscope and energy dispersive spectroscopy respectively. It was found that this free-standing 3D nitrogen doped carbon sponge in symmetric cell exhibits high specific capacitance of 273 F g⁻¹ at 0.5 A g⁻¹ of current density with excellent cyclic stability. This high specific capacitance of the material was due to the interconnected microporous structure of carbon framework with bubbled structure at nodes that provides pathway for the rapid electron transfer kinetics during electrochemical reaction, N-doping and its high electrical conductivity. The high electrochemical performance makes this free-standing 3D all carbon framework a material promising for developing nanocomposites coated with metal oxides, sulfides etc. for practical potential energy storage applications.

Charge Transport Properties of the Biopigment Sepia Melanin Towards Sustainable Electronics

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The intermittent nature of the most reliable energy source, the Sun, requires high performance energy storage technologies [1]. Organic electrode materials operating in aqueous electrolytes offer the opportunity to use
abundant, nontoxic, low cost materials, avoiding the use of critical elements. Unfortunately, organic materials often feature limited cyclability [2, 3].

Among organic materials, eumelanin is a bio-sourced, redox active, quinone-based macromolecule, ubiquitous in flora and fauna. Eumelanin originates from the oxidative polymerization of L-3-(3,4-dihydroxyphenyl)-alanine (L-dopa) via 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2 carboxyl acid (DHICA) building blocks [4]. It has fascinating properties beyond the redox activity, such as strong broadband UV-visible absorption, metal binding affinity and radical quenching [5]. The redox activity of the building blocks and the capability to reversibly bind cations constitute the foundation for the use of eumelanin in energy storage [2, 6].

In this work, we report on the electrochemical energy storage performance of composites of N-doped and pristine Carbon Quantum Dots (CQDs) with eumelanin. The composites were prepared at different weight ratios (eumelanin building block:CQD 1:0, 1:0.4, 1:1, 1:2) through a solution-based process followed by in situ polymerization [7]. From the cyclic voltammetry, galvanic charge/discharge and electrochemical impedance spectroscopy characterizations of the composite electrodes in nearly neutral aqueous electrolyte solutions, it has been possible to deduce, with respect to bare melanin electrode, that the composite electrodes feature an increase of the areal capacitance from 0.02 mF/cm² to 0.84 mF/cm² and a decrease of the charge transfer resistance from 42 Ohms to 20 Ohms. Composite electrodes also feature a capacitance retention of ca. 99.5% and coulombic efficiency of ca. 100% during 4000 cycles.


4:30 PM EN03.07.07
Stable Thiophosphate-Based All-Solid-State Lithium Batteries through Conformally Interfacial Nano Coating Daxian Cao¹, Yubin Zhang², Adelaide M. Nolan¹, Yifei Mo³, Yan Wang² and Hongli Zhu¹; ¹Northeastern University, United States; ²Worcester Polytechnic Institute, United States; ³University of Maryland, United States

All-solid-state lithium batteries (ASLBs) are promising for next generation energy storage system with critical safety. Among various candidates, thiophosphate-based electrolytes have shown great promises because of their high ionic conductivity. However, the narrow operation voltage and poor compatibility with high voltage cathode materials impede their application in the development of high energy ASLBs. In this work, we studied the failure mechanism of Li₆PS₅Cl at high voltage through in situ Raman spectra and investigated the stability with high-voltage LiNi₁/₃Mn₁/₃Co₁/₃O₂ (NMC) cathode. With a facile wet chemical approach, we coated a thin layer of amorphous Li₀.₃₅La₀.₅Sr₀.₀₅TiO₃ (LLSTO) with 15-20 nm at the interface between NMC and Li₆PS₅Cl. We studied different coating parameters and optimized the coating thickness of the interface layers. Meanwhile, we studied the effect of NMC dimension to the ASLBs performance. We further conducted the first principles thermodynamic calculations to understand the electrochemical stability between Li₆PS₅Cl and carbon, NMC, LLSTO, NMC/LLSTO. Attributed to the high stability of Li₆PS₅Cl with NMC/LLSTO and outstanding ionic conductivity of the LLSTO and Li₆PS₅Cl, at room temperature, the ASLB exhibit outstanding capacity of 107 mAh g⁻¹ and keep stable for 850 cycles with a high capacity retention of 91.5 % at C/3 and voltage window 2.55-4.0 V (vs. Li-In).

4:45 PM EN03.07.08
Structural Influences on the Performance and Storage Mechanisms in Hard Carbons for Sodium-Ion Batteries Heather Au¹, Hande Alptekin¹, Anders Jensen², Alan Drew² and Magdalena Titirici¹; ¹Imperial College London, United Kingdom; ²Queen Mary University of London, United Kingdom
Sodium-ion batteries have shown potential as a cost-effective successor to lithium-ion batteries, but the performance is still limited by their low energy density and poor cycleability compared with lithium-ion analogues. The development of suitable electrode materials is crucial for the realisation of sodium-ion batteries as a feasible replacement. Disordered carbons, also known as ‘hard carbons’ (i.e. those with some degree of graphitisation but randomly oriented graphitic domains) are considered promising anode materials due to negligible volume change during the sodiation/desodiation cycles, essential for achieving a long cycle life.

A range of materials were prepared via hydrothermal carbonisation of various biomass precursors followed by further heat treatment; by tuning the carbon source, the nature and amount of dopant, the templating agent and the treatment temperature, carbon anodes with varying degrees of graphitisation and tailored pore size, wall thickness and heteroatom functionalities were obtained. The pore structure, particle size, nature of defects and degree of doping were found to have a significant effect on the storage capacity and cycleability of the batteries. The ability to tailor these hierarchical nanostructures therefore makes this process a promising route to achieving new electrode materials.

EN03.08.01

Carbon Nanomaterials with Dominant Micropore Texture Parameters for Capacitive De-Mineralization
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With a growing number of studies providing credible evidence that the highest capacitance in carbon nanomaterials is attainable only when the pore size is 0.7 nm, the special attention in porosity engineering is strongly biased towards micropore. Microporous carbon materials are thus extremely promising in the development of high-performing capacitive devices compared to their meso and macroporous counterparts. In this study therefore, carbon materials with extremely high micropore content was derived from *parinari curatelifolia* (PC) waste seeds via pyrolysis and chemical activation. Characterization using SEM, EDAX, TEM, Raman, and XRD techniques show that the microstructure and composition of the as-prepared carbon materials are strongly dependent on the KOH to carbon mass ratio. High BET surface area of 1898 m² g⁻¹, type I isotherm, and 99% micropore content were obtained for the carbon materials. The electrodes made from these carbon materials showed high specific capacitances of 423 F g⁻¹ at 5 mV s⁻¹ and cyclic stability of 98% after 50000 cycles both of which are indicative of our carbon materials huge potential in making high performance capacitive demineralization devices. The high specific capacitance the PC carbon materials deliver is due to the enhancement of diffusion and charge storage stemming from the synergetic interplay of the aforementioned textural parameters.

EN03.08.02

Dehydrogenation Kinetics of Mg2FeH6 by In Situ Transmission Electron Microscopy
Juyoung Kim1,2, Julien Fadonougbo2, Jae-Hwan Bae2, Jaeyoung Hong2, Young Whan Cho2, Gyeung Ho Kim2, Jin Yoo Suh2 and Dongwon Chun2; 1Yonsei University, Korea (the Republic of); 2Korea Institute of Science and Technology, Korea (the Republic of)

Hydrogen is considered as a promising alternative energy sources because it can potentially replace fossil fuel to clean energy due to its high energy density (142MJkg⁻¹) as well as no harmful gaseous by-products after combustion [1]. Nevertheless, the lack of efficient storage system hinders its widespread application. For the efficient hydrogen system, storage materials must readily take up hydrogen and subsequently release it again at a sufficiently high rate.
of hydrogenation / dehydrogenation process. Thus, understanding the kinetics of hydrogen storage materials during the process is indispensable.

Magnesium ternary hydrides Mg$_2$FeH$_6$ have been extensively studied as a candidate hydrogen storage materials due to its hydrogen gravimetric density (150 kg/m$^3$) as well as a good cycling ability (~1000 hydrogenation / dehydrogenation cycles) [2,3]. However, kinetics during hydrogenation / dehydrogenation process in Mg$_2$FeH$_6$ is unrevealed by the limitation of in-situ observation analytical method.

In this study, we investigated the dehydrogenation kinetics of Mg$_2$FeH$_6$ by in-situ transmission electron microscopy (TEM) holder system (Fusion, Protochips). We placed nanostructured Mg$_2$FeH$_6$ sample on the chip and heated up the temperature 300 °C for 30 minutes to trigger the hydrogen decomposition in Mg$_2$FeH$_6$. We acquired high-resolution images and diffraction patterns (25 frames every second) of Mg$_2$FeH$_6$ during dehydrogenation process by one-view camera (One-view, Gatan) attached on Titan (G2, FEI). In addition, EDS analysis was performed by super-EDS embedded TEM (Talos F200X, FEI) to investigate particle size of Fe and Mg after dehydrogenation.

As expected, Mg$_2$FeH$_6$ diffraction patterns were observed in as-prepared Mg$_2$FeH$_6$ sample. Upon heating, intensities of Mg$_2$FeH$_6$ diffraction patterns decrease and eventually disappeared due to the hydrogen desorption. On the other hands, new Mg and Fe diffraction patterns were produced in the beginning of dehydrogenation process due to the phase segregation of Mg and Fe from Mg$_2$FeH$_6$. In addition, oxide phases such as MgO and Fe$_2$O$_3$ were observed possibly due to the oxidation inside TEM column.

We estimated dehydrogenation speed from the diffraction patterns of Mg$_2$FeH$_6$ and it rapidly increases up to the process temperature of 300 °C. For example, diffraction patterns of Mg$_2$FeH$_6$ were disappeared within 120 sec at 260 °C and it was shorten to 12 sec. At the process temperature of 280 °C. Also, average particle size of Fe after the dehydrogenation process was investigated through EDS results because hydrogenation speed largely depends on its dimension. It was revealed that estimated average particle size after the process is ~ 10 nm at 260 °C and 15 nm at 280 °C.

References

EN03.08.03
Sulfur-Doped Biomass-Derived Graphene-Based Carbon for Supercapacitor with High Energy Density and Ultra-High Power Density SungHoon Jung, Yusik Myung and TaeYoung Kim; Gachon University, Korea (the Republic of)

Here, we report a facile method to produce sulfur-doped graphene based-carbon with three-dimensional (3D) open structure from a biomass. The 3D graphene-based carbons were produced via the transformation of glucose-derived polymers and organosulfur compounds with starting materials provide additional properties of the graphitic carbon such as sulfur doping and coral-like open structures. In-situ physical activation was performed on this method and the open structures contributed hierarchically porous and sulfur doped biomass-derived graphene-based carbon with Brunauer-Emmett-Teller theory specific surface area of 3,426 m$^2$/g, providing a defined-mesoporosity without additional chemical activation. On organic electrolyte system, this carbon showed a high specific capacitance of 143 F/g for its high surface area, unique and interconnected structure and a highly graphitization with sulfur doping. Furthermore, this carbon-based supercapacitor electrodes exhibited high energy density of 33 Wh/kg and ultra-high power density of 1,732 kW/kg derived from its specific capacitance of 133 F/g at the high current density of 256 A/g.

EN03.08.04
2D Hexagonal Boron Nitride - Molybdenum Disulfide Nanocomposite Supercapacitor Electrodes Alptekin Aydinli$^{1,2}$ and Husnu E. Unalan$^{1,2}$; 1Middle East Technical University, Turkey; 2Energy Storage Materials and Devices Research Center (ENDAM), METU, Turkey

Two-dimensional (2D) materials are very promising as supercapacitor electrodes due to their high specific surface
area. In recent years, significant attention has been focused to environmentally friendly 2D hexagonal boron nitride (h-BN), since pristine 2D h-BN has many applications in high-temperature instruments and as a substrate for the growth of other 2D materials. However, its electrically insulating character in pristine form limits its utilization in electrochemistry and in electronic applications. Formation of nanocomposites with a conducting complementary materials offers a solution to this problem. In this study, we fabricated 2D h-BN/MoS$_2$ nanocomposite electrodes using solution phase synthesis routes and evaluated their electrochemical performance for supercapacitors. Prior to preparation of the electrodes both h-BN and MoS$_2$ were chemically exfoliated. Electrochemical properties such as specific capacity and capacity retention of the fabricated nanocomposite electrodes were examined through cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy in three electrode configuration. Obtained results were compared to that of the control sample fabricated from bare MoS$_2$ nanosheets. In order to determine the effect of electrolyte type on the electrochemical properties of the nanocomposite electrodes, various aqueous solutions, such as sodium sulfate (Na$_2$SO$_4$), hydrochloric acid (H$_2$SO$_4$) and potassium hydroxide (KOH) were investigated. Fabricated supercapacitor electrodes showed encouraging specific capacitance values exceeding 100 F/g. A comprehensive analysis on the electrochemical properties of the fabricated supercapacitor will be presented.

EN03.08.05
Green Electrodes Material, Electrolyte and Separator for High-Performance Supercapacitor
Mohammad Said El Halimi$^{1,2}$, Federico Poli$^1$, Mehrdad Mashkour$^1$, Alessandro Brillon$^1$, Nicola Mancuso$^1$, Alessandro Olivieri$^1$, Tarik Chafik$^3$ and Francesca Soavi$^1$; $^1$Alma Mater Studiorum University of Bologna, Italy; $^2$Abdelmalek Essaadi University, Morocco; $^3$Abdelmalek Essaadi University, Morocco

The global demand for clean energy and water combined with the rising market of supercapacitors requires materials, components, and systems to be developed with a green approach. Recently scientists making great efforts towards the development of sustainable materials for the future generation of supercapacitors, considering the environmental and economic impacts.

The present work investigates some green materials for supercapacitor such as: using Argan fruits shell (agriculture wastes) to obtain porous carbon electrodes material, ammonium acetate (salt in water electrolytes) and bacterial cellulose (biomaterial separator).

Carbon electrodes were obtained from the carbonization of Argan shells followed by activation using wet impregnation or dry physical mixing. The as-prepared samples have been subjected to textural investigations and comprehensive characterizations using SEM, XRD, Raman, FTIR, and BET. After selecting the sample with desired structural and textural proprieties, their electrochemical response was investigated ammonium acetate electrolyte with different concentration (from 1m up to 30m). Specifically, electrodes were obtained by using carbon-coated bacterial cellulose (BC) film as a current collector. The results of Electrochemical Impedance Spectroscopy (PESI), Cyclic voltammetry (CV) and Galvanostatic charge-discharge (GCPL) of the BC-electrodes and the BC-Supercapacitor making use of ammonium acetate solutions are here reported and discussed.

Acknowledgments
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EN03.08.06
Hydrogenase-Assisted Catalysis on Titania Electrodes Xin Liu1, Patricia A. Carvalho2, Paul Hoff Backe3, Mingyi Yang3, Truls Norby1 and Athanasios Chatzitakis1; 1University of Oslo, Norway; 2SINTEF, Norway; 3Oslo University Hospital, Norway

The widespread use of fuel cells and water splitting devices for energy generation and storage is limited by the dependence on noble metal catalysts. There is thus a tremendous need for the development of efficient electrocatalysts based on Earth-abundant elements. Nature inspired hydrogenases (HydA) are metallo-enzymes that catalyze the reversible reaction of H2 to protons and electrons. Hydrogenases containing Fe at the active sites, known as [FeFe]-HydA, show activities comparable to that of Pt. This work addresses a new class of electrodes for [FeFe]-HydA attachment and bio-assisted catalysis based on TiO2 nanotubes. The conducting oxide material provides suitable electronic conduction and hydrophilicity, while the nanostructure ensures tunability (tube length, crystal orientation and pore diameter) and high surface area for HydA attachment. In this work, transmission electron microscopy and atomic force microscopy are used to characterize the bio-electrodes. Based on the experimental findings, density functional theory (DFT) calculations are used to probe the catalytic reaction sites on the HydA and address the interaction between enzymes and TiO2. The novel bioelectrode will be employed in a system of artificial photosynthesis and generation of solar fuels by simultaneous water splitting and CO2 capture and utilization.

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EN03.08.07
Determination of Charge Carrier Transport Parameters in a Polymer Electrolyte Using Electrochemical Impedance Analysis T.M.W.J. Bandara1, Ajith DeSilva2, B.-E. Mellander1 and Sunil Dehipawala4; 1University of Peradeniya, Sri Lanka; 2University of West Georgia, United States; 3Chalmers University of Technology, Sweden; 4Queensborough Community College of CUNY, United States

Polymer electrolytes are key components in many electrochemical devices such as dye sensitized solar cells (DSC), fuel cells, batteries super-capacitors, sensors and biomedical applications. In order to characterize such electrolytes, we developed a method to determine the charge carrier density (n), mobility (µ), and diffusion coefficient (D) of ionic conductors with the help of dielectric analysis of electrolytes [1,2]. The method previously proposed by our group is further simplified making it possible to calculate these parameters by just using electrochemical impedance analysis (EIS). The method has been tested with gel polymer electrolyte based on polyacrylonitrile host polymer and alkaline iodide at deferent temperatures. The temperature dependence of n, µ, and D have also been studied. The results are in agreements with those available for the ionic electrolytes.


EN03.08.08
High Electrochemical Stability of Ag-Pt Core-Shell Nanowires in a Wide Potential Window Sensu Tunca1,
Silver nanowires (Ag NWs) are appealing candidates for supercapacitor electrodes due to their high conductivity in addition to their allowance for all active materials to be in close contact to facilitate charge transport. These are very important to attain maximum charge accumulation provided that Ag NWs are electrochemically stable within the utilized potential window. The potential window of bare Ag NWs was found as 0-0.5 V, where irreversible oxidation takes place at 0.6 V, limiting not only the potential window but also the power and energy density of supercapacitors in consequence. In this work, in order to extend the potential range, Ag NWs were coated with a thin platinum (Pt) shell layer using a simple solution based, green method. Fabricated core-shell nanowires were then deposited onto glass substrates in the form of networks via spray coating. Ag-Pt core-shell NW network electrodes were electrochemically tested and the potential window was found to be extended up to 1.2 V. The true potential of Ag-Pt core-shell nanowire network electrodes were further evaluated in coaxial nanocomposite form, which is simply achieved through cathodic electrodeposition of pseudocapacitive nickel hydroxide (Ni(OH)2) layers onto the networks [1]. Capacitive behavior of the coaxial nanocomposites was investigated through cyclic voltammetry, galvanostatic charge-discharge and impedance spectroscopy. Thorough analysis on the electrochemical stability and capacitive behavior of the fabricated nanocomposite electrodes will be presented in conjunction with different electrochemical coating parameters.


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EN03.08.09
Rehydroxylation Methods on Mesoporous Silica with Impact on Fuctionalisation Tom F. O'Mahony; Trinity College Dublin, Ireland

Ordered mesoporous silica materials are used as supports for various applications from catalysts, chromatography and enzyme immobilisation. In this work, the impact of surface silane functionalisation was examined by various pre-treatment methods. The surface chemistry and physical properties were examined pre and post ‘cleaning’ of the supports.

The impact of these changes were then examined by functionalisation of the support with (3-aminopropyl)triethoxysilane with potentially increasing the efficiency of attachment and robustness of the end application.

SBA-15 was synthesised, calcined and characterised. The support was then rehydroxylated or ‘cleaned’ by various routes (H2O, H2SO4, H2O2/H2SO4 solution and UV/Ozonolysis) and then functionalised.

The results showed that using pre-treatment methods allowed for higher attachment of the silane.

Surface energy measurements were also determined showing the changes after pretreatment methods and after grafting with the silane.

EN03.08.10
Water-in-Salt Electrolytes for High-Voltage Aqueous Sodium-Ion Batteries David Reber1,2, Ruben-Simon Kühnel1 and Corsin Battaglia1; 1Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; 2École Polytechnique Fédérale de Lausanne, Switzerland

The potential low cost and non-flammability of rechargeable batteries based on aqueous electrolytes make them a promising option for large-scale energy storage for grid applications. Using a highly-concentrated (35 molal) aqueous sodium bis(fluorosulfonyl)imide (NaFSI) electrolyte we recently reported a stability window of 2.6 V.[1] Using asymmetric FTFSI anions as solution to suppress the commonly encountered crystallization of highly concentrated aqueous electrolytes we further demonstrated that an electrolyte consisting of 25m NaFSI + 10m NaFTFSI is robust against crystallization at low temperatures and enables long-term cycling of 2 V class full cells even at -10 °C.[2]

Besides the electrochemical stability of an electrolyte, the chemical stability of its constituents is crucial for stable
Here, we explore the chemical stability and physicochemical properties of aqueous solutions of FSI salts as electrolytes for lithium-ion and sodium-ion batteries. We demonstrate that the rate of hydrolysis of this anion is strongly dependent on the salt concentration as well as the nature of the cation. We relate the stability of FSI to the interaction with the cation and the charge density of the latter, and show that also at elevated temperatures highly concentrated NaFSI electrolytes are significantly more stable than their lithium analogues. Yet, hydrolysis is still observed in the NaFSI electrolytes to some degree and we emphasize that major efforts are needed to develop new, highly soluble, stable salts in order to push the long-term performance of such aqueous systems towards competitive levels. [3]

References:

EN03.08.11
Analysis of Crucial Parameters in the Solution Chemistry and Deposition Conditions Leading to the Synthesis of Pure Phase SnSb Electrodeposited From an Ethaline Solution
Jeffrey Ma and Amy L. Prieto;
Colorado State University, United States

Lithium-ion batteries are currently being used in majority of portable applications ranging from cell phones to electric vehicles. While the use of graphite as an anode has been successful for the last 30 years, there is currently a wide variety of research in new materials and architectures that can increase a lithium-ion battery’s overall energy density, cycle life, or rate capabilities. Intermetallic alloys have been promising due to their ability to improve the energy density when compared to graphite. Of these alloys, SnSb has been heavily studied and can be a potential candidate in replacing graphite.

We herein report on the synthesis of pure phase SnSb from ethaline solution. Previous reports on electrodeposition of SnSb resulted in the presence of a Sn rich product. While the synthesis may be described simply, specific parameters (in the solution composition as well as the method of deposition) must be achieved to form this material in the pure phase. An in depth analysis with multiple characterization techniques will be used to clarify what is occurring with changes to specific parameters in the synthesis. Lithium battery cycling studies will also be presented, showing the material’s performance compared to Sn-rich production seen in previous electrodeposition reports.

EN03.08.12
Preparation and Electrochemical Property Measurement of Monolithic Carbon Xerogel from Resorcinol-Formaldehyde-Graphene Oxide via One-Step, Template-Free and Catalyst-Free Hydrothermal Reaction
Minhu Huang, Jae-Suk Lee and Tae-Ho Yoon; Gwangju Institute of Science and Technology, Korea (the Republic of)

Monolithic carbon xerogel with co-continuous hierarchical porosity was prepared via one-step, template-free and catalyst-free hydrothermal polycondensation reaction with resorcinol(R), formaldehyde(F) and mildly oxidized graphene oxide. The gels were prepared in a pressurized Teflon mold at 100 °C for 6 h, followed by drying at 60 °C for 36 h and then 100 °C for 12 h, generating xerogels. The R/W ratio and loading of graphene oxide were varied to optimize pore size with co-continuous hierarchical pore structure. Next, the xerogels were subjected to pyrolysis at 900 °C for 2 h, followed by KOH infiltration and activation at 800 °C for 1h. The gels, before and after the activation, were subjected to N2 sorption study and also to electrochemical property measurement via cyclic voltammetry, while the samples for the latter were prepared via cutting the monolithic xerogels rwithout involving polymeric binder and solvent. In addition, XRD, Raman and SEM were also utilized for characterization.

EN03.08.14
Optimization of Nano Sized Silicon-Based Graphene Anodes for Lithium-Ion Batteries
Gunisha Jain, Sara Abouali, Vittorio Pellegrini and Fabio Di Fonso; Istituto Italiano di Tecnologia, Italy
Silicon graphene based composites can be very promising next generation lithium ion battery (LIB) anodes because of silicon having high capacity ($4200 \text{ mA h g}^{-1}$ and $2400 \text{ mA h cm}^{-3}$) and lower electrochemical potential with respect to Li ($< 0.35 \text{ V vs. Li/Li}^+)$.

Unfortunately, bulk silicon anode faces other problems, e.g. poor cycle stability and great volume expansion. However, reports have suggested that silicon nanoparticles can overcome these issues by relieving larger stress/strain and facilitated by the short Li$^+$/electron transfer length. Extensive research has been performed with nano silicon-based anodes and major complexities rely with the optimization of silicon particle size, degree of crystallinity, dispersion of silicon particles in graphene matrices, nano silicon percentage in the composite etc. In this report, optimization of oxidation and degree of crystallinity of silicon nanoparticles is studied for better battery performance. A simple and scalable plasma enhanced chemical vapor deposition technique is used to produce silicon nanoparticles with variable range of crystallinity. A detailed characterization is performed to investigate chemical, structural and morphological characteristics of these particles. Later, these particles are used as anode material in LIBs. Anodes are prepared with conductive few layers graphene and polyacrylic acid binder. These anodes showed excellent stability over 250 cycles with clear correlation between particle size, crystallinity and oxygen content. Results are very promising with these silicon NPs, with the capability of scalable production process.


EN03.08.15
Sulfurized Anodic TiO$_2$ Nanotube Layers for Energy and Catalytic Applications
Milos Krbal$^1$, Girish D. Salian$^2$, Siow Woon Ng$^3$, Ludek Hromadko$^{1,3}$, Hanna Sophie$^{1,3}$, Alexander T. Tesfaye$^2$, Jan Michalicka$^4$, Thierry Djenizian$^5$ and Jan M. Macak$^{1,3}$; $^1$University of Pardubice, Czechia; $^2$Center of Microelectronics in Provence, France; $^3$Brno University of Technology, Czechia

The self-organized TiO$_2$ nanotube (TNTs) layers have attracted considerable scientific and technological attention for the last two decades. Nowadays, they perform very well in a wide range of applications including photocatalysis, solar cells, hydrogen generation and energy storage [1]. The synthesis of 1D TNTs layers is carried out by a conventional electrochemical anodization of valve Ti metal sheet. The main drawback of TiO$_2$ is its applicability in the UV light (wavelengths < 390 nm). In order to obtain also visible light photoresponse, TiO$_2$ has to be doped or sensitized. For example, N [2] or C [3] were used as very effective TiO$_2$ dopants. Except the extension of the VIS light response, one of the major issues to extend the functional range of nanotubes is to coat homogenously the nanotube interiors by a secondary material. It has been shown that additional ultrathin surface coating of TNTs by secondary materials using Atomic Layer Deposition (ALD) significantly improves the functionality of the resulting hetero-structure for various applications [4]. Next to the ALD, sulphur treated 1D anodic TNT layers possess improved photo-electrochemical and catalytic properties and the energy storage compared to the blank TNT layers [5, 6]. This treatment was performed in the evacuated quartz ampoules in the temperature range from 250 to 450°C. An inspection of the sulfurized nanotube layers via scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) has disclosed a gradual crystal growth within nanotube walls, represented by TiS$_2$ or TiS$_3$ phases. It was found that each application requires a different optimum condition of sulfurization.

The presentation will focus on the sulfurization process of TNTs and their characterization. The potential applications in various fields (such as batteries, photocatalysis) of prepared TiS$_x$/TNTs heterostructures will be discussed.

References

EN03.08.16
Iron Layered Vanadate Nanocomposite with Fluorine Free-WIS Electrolyte for Low Cost and Green Energy
Supercapacitor Fitri Nur Indah Sari¹ and Jyh-Ming Ting¹,²; ¹National Cheng Kung University, Taiwan; ²Hierarchical Green-Energy Materials (Hi-GEM) Research Center, Taiwan

In this study, low-cost, environmental friendly “water in salt (WIS)” electrolyte was introduced to replace the expensive and toxic organic electrolyte of supercapacitor. Very recently, potassium acetate (CH₃CO₂K) electrolyte was found to be able to replace the LiTFSI in LiB. To our best knowledge, this new WIS electrolyte has not been demonstrated in aqueous supercapacitor. Moreover, CH₃CO₂K is safer and cheaper than LiTFSI-based WIS electrolytes. Therefore, in this study, we open up new opportunities of using acetate-based WIS electrolyte in the supercapacitor. We demonstrated that acetate-based WIS able to obtain wide potential window up to 2.5V. We investigated several acetate-based WIS, such as CH₃CO₂K, CH₃CO₂Na, CH₃CO₂Li, and its combination. The result shows that mixing two WIS leads to wider potential window up to 3V. We investigated the performance of CH₃CO₂K-CH₃CO₂Li WIS in iron layered vanadate nanocomposite. The synergistic effect of unique properties of iron layered vanadate nanocomposite and bi-WIS resulting high energy density of 53 Wh kg⁻¹ at power density of 672 W kg⁻¹. This environmental friendly electrolyte is very promising for next generation of supercapacitor.

EN03.08.17
Highly Conducting and Robust Laser Irradiated Graphene Film with Healed Defect for Integrated Metal-Free Energy Storage Devices Navpreet Kamboj and Ramendra S. Dey; Institute of Nano Science and Technology, Mohali, India

Small-scale energy resources become basic need for various widespread applications like implantable devices and portable electronics and internet of things (IOTs). Extensive development in supercapacitor technology aims to increase the electrical performance of electrode materials.¹ Interconnected porous graphene have gained a special attention to be use as supercapacitive material as well as current collector in developing metal-free interdigitated microsupercapacitor (IMSC) due to its superior conductivity and porosity.² Herein, Electrochemical followed by laser-irradiation (LI) method gives advancement in prototyping conductive graphene-based robust MSC device. Raman spectra proves that the laser irradiation method is capable of forming fused interconnected graphene sheets within healed structural defects, resulting high conductivity and improved crystallinity of LIG sample.³ An on-chip metal free microsupercapacitor using graphene as current collector as well as electrode material shows advantages of large working voltage of 1.2 V in aqueous solid electrolyte, providing high energy-density and long-term stability. The MSC, without any metal current collector, interestingly shows unique electrical-double layer behavior and unprecedented cycling stability with 100% retention of initial capacitance after 1,00,000 continuous cycle. A large cell voltage of 10.8 V was realized by modularizing the array of devices without much degrading the rectangular shapes of the voltammogram even at higher scan rates (100 V s⁻¹). Based on such high voltage MSCs, a hybrid structure of commercial solar cell and metal free supercapacitor was designed to make a self-charging power system. This study provides an effective strategy to build up metal-free supercapacitor with exceptional life cycle, highly durable and high-voltage flexible MSCs to facilitate progress toward a self-sustainable energy future.

References:

EN03.08.18
Laser Ablation Synthesis in Solution (LASiS) as an Efficient Route for the Rational Design of Hybrid Carbon-Based Nanocomposites for Enhancements in Electrochemical Storage Erick L. Ribeiro, Bamin Khomami and Dibyendu Mukherjee; University of Tennessee, Knoxville, United States

The increasing global demand for clean and sustainable energy sources has given rise to the significant interest in the rational synthesis and design of low-cost and efficient functional nanocomposites and nanomaterials as supercapacitors in advanced electrochemical energy storage systems. Nonetheless, the design of such nanomaterials with tailored interfacial functionality and charge transport properties relies on the systematic and fundamental understanding of the processing-structure-property relations for precise tailoring of architectures and compositions of the active nanomaterials without using any undesired chemicals/surfactants/ligands that can compromise their electrochemical performance and interfacial activities. Herein, we present our most recent findings in using Laser
Ablation Synthesis in Solution (LASiS) as a strategy and pathway for the facile and environment-friendly, yet efficient, synthesis of new classes of carbon-based hybrid nanocomposites (HNCs) decorated with metal-oxide nanoparticles (NPs) that exhibit unique supercapacitive properties. Initially, we report the use of LASiS coupled with two-post treatments for the fabrication of (1) Co3O4 NPs/reduced graphene oxide (rGO), (2) Co3O4 nanorods (NR)/rGO, and (3) Co3O4 NPs/nitrogen-doped graphene oxide (NGO). This methodology allows us to tune the selective functionalities of the HNC by adjusting their structure-property relationships. The Nitrogen doping in the NR/rGO HNCs, for instance, promotes a higher electron conductivity while enhancing the electrochemical activity and preventing the aggregation between NPs. These interfacial energetics and arrangements coupled to the presence of a network of interconnecting 1D nanostructures have indicated to yield an effective charge transport and electrolyte diffusion at the electrode-electrolyte interfaces, resulting in the enhancement of the supercapacitive properties. Secondly, we will present the screening for other potential metal oxides with supercapacitive properties and the use of the same technique for the design of their HNCs for electrical chemical storage systems. Finally, we will present our advances on the development of functional conductive inks with fluidic properties containing the aforementioned HNCs for the fabrication of all-printed solid-state supercapacitors using drop-on-demand (DoD) inkjet printing; our results have shown that by tailoring the ratio of solvent, binder, and HNCs we can obtain an ink with the viscoelastic properties required for an efficient printing, while preserving the electrochemical efficiency of the composites.

EN03.08.19
Catalytic Origin and Universal Descriptors of Heteroatom-Doped Semiconductor Photocatalysts for Solar Fuel Production
Yonghao Zhu1, Lele Gong1, Detao Zheng1, Xiaowei Wang2, Jing Zhang3, Lipeng Zhang1, Liming Dai4 and Zhenhai Xia2; 1Beijing University of Chemical Technology, China; 2Univ of North Texas, United States; 3Northwestern Polytechnical University, China; 4Case Western Reserve University, United States

Solar fuels produced from sunlight via photocatalytic water splitting and artificial photosynthesis represent one of the most promising clean energy sources. Various semiconductors, including graphitic carbon nitride (g-C3N4) and transition metal oxides, have been considered as photocatalysts for the fuel production, but there lacks of the design principles for rapid screening of the best photocatalysts from numerous candidate materials. Here, we demonstrate, for the first time, a universal guiding principle that governs the photocatalytic activities of p-orbital element-doped C3N4-based photocatalysts for photocatalytic water splitting, which is also applicable to other doped semiconductors including ZnO and TiO2. An activity indicator is introduced to determine the efficiency of non-metal-doped semiconductor photocatalysts for the solar fuel production. These predictions are supported by experimental results. This generalized principle could guide a broad photochemical production of solar fuels including hydrogen, hydrocarbon, and other green chemicals.

EN03.08.20
Laser-Induced Graphene Microsupercapacitors from Biomass-Derived Poly(Furfuryl Alcohol) through Salt and Graphene Oxide Doping
Gillian Hawes1, Bruno Noremberg2, Dilara Yilman1, Priyanka Verma1 and Michael Pope1; 1University of Waterloo, Canada; 2Federal University of Pelotas, Brazil

Graphene has been widely investigated for applications in supercapacitors, due to its extremely high theoretical specific surface area, excellent electrical conductivity and lightweight nature. However, most synthesis routes for graphene-based supercapacitors are highly energy-intensive and costly, utilizing harsh chemicals, multiple synthesis steps, high temperatures, and/or specialized instrumentation. In 2014, the Tour group introduced a simple method to prepare high surface area, conductive and porous graphene through the laser-induced carbonization of specific polymers such as polyimide. This one-step approach is rapid, scalable, and cost-effective, utilizing commercial CO2 infrared laser systems commonly employed for laser cutting to combine graphene production and device fabrication in a single step. This approach has been utilized to fabricate polyimide-based laser-induced graphene microsupercapacitors with specific areal capacitances of ~ 9 mF/cm2. However, thus far this approach has been limited to costly synthetic polymers prepared from coal or petroleum-based products. Methods to extend this approach to other green materials such as lignin, paper, and wood employ more costly visible or UV lasers, fabrication in inert atmospheres, or pre-treatment of the substrate materials, limiting the ease and scalability of this approach. In this work, we demonstrate for the first time the laser-induced carbonization of poly(furfuryl alcohol), a green polymer easily prepared from the one-step polymerization of furfuryl alcohol, which is a biomass waste derivative obtained from corn cobs, rice hulls, bagasse, and wood. Notably, we explore the use of graphene oxide as a carbonization catalyst, demonstrating that loadings as low as 1 wt.% facilitate the laser-induced carbonization of
PFA utilizing an inexpensive CO2 laser under ambient conditions. Furthermore, we demonstrate that composites of PFA microspheres and graphene oxide can achieve specific areal capacitances as high as 16.0 mF/cm2 at 0.05 mA/cm2, which both outperforms the most commonly utilized polyimide films, and is among the highest specific capacitances achieved for supercapacitors prepared from this method. We further demonstrate that these devices cycle for over 10,000 cycles with over 97% capacitance retention. Finally, we introduce a novel method to utilize inexpensive and widely abundant salts, such as sodium chloride, as catalysts for the laser-induced carbonization of PFA. We demonstrate that these salts can enable the carbonization of the PFA into a porous, conductive carbon material and present results on the performance of supercapacitors prepared from these eco-friendly composites. Supercapacitors prepared from laser irradiation of PFA/GO and PFA/salt composites indicate the potential of uniting green materials and energy-efficient laser-induced fabrication for high-performance and sustainable next-generation supercapacitors.

References

EN03.08.21
Synthesis of Stable Bio-Based Aqueous Rechargeable Lithiu-Ion Batteries by Atmospheric Plasma Process
Jacopo Profili, Steeve Rousselot, Lida Hadidi, Maxime Nicolas, Luc Stafford and Mickael Dollé; Université de Montréal, Canada

In the last decade, many efforts have been made to develop new thin films by using atmospheric pressure plasma process. In this sense, many authors have developed complex materials such as nanocomposite thin films [1,2], biodegradable coatings [3] and advanced chemical treatments on complex surfaces [4]. In parallel, the use of plasma process has also been recently proposed to improve the electro-chemical characteristic of rechargeable lithium ion batteries (LIB) [5]. In this context, atmospheric pressure dielectric barrier discharges (DBDs) could offer the possibility to strongly improve the material’s surface properties with a limited cost and a little environmental impact in the manufacturing process. Moreover, today these systems can be easily modified to scale up the process in a production line.

Through this work, we aim to present our recent results on plasma-enhance modified composite electrodes employing water soluble Carboxymethylcellulose (CMC) as a binder that are usable in aqueous electrolyte rechargeable LIB (ARLB).

Plasma-deposited coatings were then characterized by SEM-EDX, FTIR and XPS. The electrical analysis of the process shows that the discharge remains stable and homogeneous during the process. This suggests that the substrate slightly affect the physical regime of the discharge. The SEM analysis obtained on the final electro-active material, shows a homogeneous surface and the creation of a specific morphology for the coating. From the FTIR analysis, different chemical groups were observed on the surface depending on the distance from the entrance of the discharge. Finally, the physico chemical properties and electrochemical performance of such electrodes were also investigated.


EN03.08.22
Dopamine-Assisted Au-Coated Polypropylene Micromembrane as a Flexible Porous Electrode
Shih-Cheng Chou, Bo-Han Huang, Tzu-Ling Fan, Wei-An Chung and Pu-Wei Wu; National Chiao Tung University, Taiwan

Porous electrodes exhibit impressive advantages including large surface area and fast electrolyte permeability. In the literatures, noble metals such as Au and Pt are known for electrochemical stability against different reactions and electrolytes, and therefore they are often used as the electrode materials. Unfortunately, due to their excessive cost, it is necessary to reduce their utilization. In this work, we adopt a polymeric membrane which provides a flexible and inexpensive porous substrate on which dopamine is deposited to render it hydrophilic so electroless Au deposition
could be proceeded successfully to fabricate a three-dimensional microporous flexible Au conductive electrode. SEM and EDS analysis are used to characterize the surface structure and composition distribution. Electrochemical and impedance analysis are carried out to identify the electrochemical surface area (ECSA) of Au film and solid-liquid interface resistance. In addition, we measure the resistance after multiple cycles of the bending test to determine the mechanical strength. We envision this Au-coated flexible porous electrode will become rather useful in flexible electronics.

**EN03.08.23**

**Binder-Free Phosphide-Based Nanostructures for High Performance Asymmetric Supercapacitor Devices**

Amina Saleh; The American University in Cairo, Egypt

A simple one-step method was demonstrated for the electrodeposition of phosphide-based nanostructures on nickel foam substrates. The electrodeposited materials were characterized using field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS) techniques. The materials were used as supercapacitor electrodes and showed exceptional high specific capacitance and rate capability. Upon using them to fabricate asymmetric supercapacitor device, high power density and energy density were obtained, indicating the high potential of the fabricated materials for practical energy storage devices.

**EN03.08.24**

**Melting Point Depression—A Simple Tool for Solubility Prediction of Phenothiazine Blends as High-Concentration Redox-Active Materials**

Giorgio Baggi, Darius A. Shariaty, Aman Preet Kaur and Susan A. Odom; University of Kentucky, United States

Non-aqueous redox flow batteries have shown great promise for grid energy storage, due to their independent scaling of power and energy, long operational lifetimes, simple manufacturing, and, when compared to their aqueous counterparts, a wider voltage window and a broader choice of electrochemical couples. Nevertheless, non-aqueous redox flow batteries must operate with high active material concentrations to exhibit high energy densities and simultaneously remain financially viable. In our previous work, we demonstrated that phenothiazine derivatives are valid candidates as posolytes for non-aqueous redox flow batteries, due to the high stability of their radical cations. The systematic chemical modification of the phenothiazine core allowed us to access an array of compounds with varying solubilities, both in neutral and radical cation state. Despite our effort to adopt simple and high-yielding synthetic routes, designing and synthesizing new redox active compounds with improved solubilities is time-demanding, often involving a trial-and-error approach. To overcome the burden of such discovery process, we proposed the study of binary and ternary mixtures of phenothiazines chosen from the active materials library developed in our group as higher-solubility alternatives to the pure constituents of such mixtures. Mixtures of solids are known to undergo the phenomenon of melting point depression – an “impure” solid exhibits a lower melting point than its pure form –, which, in turn, is associated to an overall increase in solubility of the mixture. In light of this, we first screened blends of phenothiazines to identify the ratios where a decrease in melting point is observed by thermal analysis. Subsequently, we determined the solubility of these mixtures in both states of charge – neutral and radical cation – in acetonitrile, with or without a supporting electrolyte, to correlate the extent of melting point depression to the increase in solubility. Preliminary results show significantly enhanced solubility for poorly soluble phenothiazines when present in mixtures. Also, an increase to up to three-fold has been observed for the total achievable concentration of mixtures of radical cation species. The results we report herein introduce an alternative, simpler method to achieve high concentrations of redox active materials and pave the way for a new approach to high-capacity non-aqueous redox flow batteries.

**EN03.08.25**

**Drop-on-Demand 3D Printed Lithium-Ion Batteries**

Ido Ben-Barak, Dan Schneier, Yosef Kamir, Meital Goor, Inna Shekhtman, Diana Golodnitsky and Emanuel Peled; Tel Aviv University, Israel

Innovation in rechargeable energy storage devices has a pivotal role in the green and sustainable energy cycle and in the portable device market. The recent trend of miniaturization of electronic devices in many fields, including remote sensors, personal electronics and medical implants, increased the demand for highly customizable, high energy-density batteries. These new demands provide opportunity for development of novel microbatteries and manufacturing processes that facilitate design of miniaturized electronic devices while maintaining a minimal
ecological footprint and waste production. Such devices have the potential to be designed to be lighter, smaller and more customizable, and use more sustainable chemistries than those of current commercial batteries.

To facilitate production of microbatteries of this type, we use drop-on-demand dispensing, a highly robust printing method already in use for various types of functional materials. This method, based on piezoelectrically actuated mechanical droplet formation, enables high accuracy and repeatability in the printing of active-material inks with different properties and rheological parameters. For a sustainable production process, we use aqueous inks, avoiding the use of organic solvents for the battery printing process, thus eliminating formation of organic fumes and waste. We have used this method to print various types of active materials for lithium-ion batteries, including cathode (lithium iron phosphate, LFP) and anode (silicon-nickel-based nanoparticles). Both yielded repeatable printability at a resolution better than 200µm, which allows customization of the printing process to produce various geometries, including 3D construction of upright electrodes for increased space efficiency and enhanced design possibilities. We found that the electrochemical performance of the printed active materials is highly competitive with traditional manufacturing methods. Cathodes show very high specific capacity, up to 160mAHr/g_{LFP}, close to its theoretical capacity, and good cycleability. Electrochemical impedance spectroscopy of cathodes shows that cathode chemistry and performance are unaffected by the printing process. Hence, direct implementation of well-established equivalent-circuit models is enabled for data analysis.

Anodes also show high capacity – up to 1200mAHr/g_{anode} and their electrochemical behavior is similar to that of anodes prepared by traditional methods. We studied the adhesion of printed anodes to several current collectors and present methods of improving it, both by modification of the current collector and the anode ink itself. The anodes with improved adhesion gave longer cycle life and better performance of microbatteries printed in nonconventional geometries.

As a substitute for typical battery separators, we have developed a self-pore-forming ink to be printed between electrodes. The ink is based on binders similar to those of the cathode and anode, which enable improved adhesion, high uptake of liquid electrolyte, and good mechanical and electrochemical properties.

Our results inspire further studies, development of manufacturing protocols, and designs for highly customizable batteries. Such development is of particular importance for small-scale and flexible production in many fields of applications, such as in-situ 3D printing of embedded batteries during the assembly process of electronic devices.

EN03.08.27
Electrocatalytic CO₂ Hydrogenation to Pure Formic Acid Vapour Using All-Solid-State Devices Lei Fan; Rice University, United States

Liquid electrolyte is inevitable to electrocatalytic transform CO₂ to liquid fuels, which will cause safety issues and energy-consumed downstream separations for pure products. Here we report an all-solid-state electrochemical CO₂ hydrogenation system, which can continuous produce pure formic acid (HCOOH) vapour without the employ of any liquid electrolyte in the full device. CO₂ and H₂ streams were separated into the cathode and anode by solid-state electrolyte (SSE), where generated HCOO⁻ and H⁺ were recombined to produce pure HCOOH vapour. Coupling with high activity (formate partial current densities > 440 mA cm⁻²) and selectivity (Faradaic efficiencies > 97%) grain boundary-enriched bismuth catalyst, we present a record high pure HCOOH vapour (ca. 100 wt.%). A wide range concentrations of pure HCOOH solutions without mixing with other ions were obtained by tuning the flow species (N₂ or water) and flow rates in the SSE layer. A 100-hour constant production of pure HCOOH with negligible degradation in selectivity and activity was demonstrated to verify the operational stability of our all-solid-state electrochemical CO₂ hydrogenation system.

EN03.08.28
Novel Binder-Free MXene/Transition Metal Oxide Hybrid Electrode Material with High Capacitance and Ultra-Long Lifetime Madhu S. Gaire, Kun Liang, Michael Naguib and Douglas B. Chrisey; Tulane University, United States

Transition metal oxide based pseudocapacitors have received significant attention as energy storage devices because of their excellent characteristics such as high power and energy density, long cycling stability etc. Among metal oxides, cobalt oxide (CoOx) is widely used; however, its low energy density compared to batteries, low conductivity along with larger volume change during the redox processes are still the limiting factors for utilizing it. A novel strategy to address these issues is to hybridize cobalt oxides with highly conductive and structurally robust materials that can improve the conductivity and the structural stability of the electrodes. In this regard, MXenes, a family of two-dimensional transition metal carbides and nitrides, are excellent candidates for the fabrication of the
nanocomposite with cobalt oxides due to their high conductivity, high surface area, hydrophilic surfaces and excellent electrochemical properties. As the size and surface morphology of the metal oxides play a crucial role in the electrode’s performance because the pseudocapacitance originates from the surface-based redox reactions, we have successfully synthesized a highly porous MXene-cobalt composite nanostucture, which facilitates the movement of ions/electrons and offers extremely high electrolyte-accessible surface areas, leading to a significant improvement in the electrochemical performance. Firstly, we have spray-coated the composite thin film on a Pt-Si substrate using an air spray. Secondly, we have synthesized the MXene-cobalt oxide composite electrode by using a novel PulseForge photonic curing technique in several seconds as opposed to the traditional methods such as, hydrothermal growth, chemical vapor deposition, chemical reduction etc. which take from minutes to hours for processing. To our knowledge, the processing we are reporting is the easiest, quickest and roll-to-roll amenable, making it a high-throughput and low-cost processing method. Furthermore, because of the extremely short photonic processing time, flexible and inexpensive substrates can also be used, signifying their potential application in modern wearable, flexible and portable electronics.

Through varying processing parameters such as the number of pulses, applied voltage, pulse length etc., we have shown we can easily control the resulting nanostructure of the electrode. The as-synthesized composite electrode exhibits initial specific capacitance of 26 mF/cm² and shows excellent improvements in electrochemical performance over the cobalt oxide electrode by retaining more than 60 % of initial specific capacitance whereas cobalt oxide electrode retains 30 % of initial specific capacitance after 15000 continuous charge-discharge cycles at 0.25 mA/cm² areal current density. These results could be attributed to the excellent electrochemical behavior of MXene along with its synergistic effect with the cobalt oxide material. Moreover, the nanostructures are grown directly on the highly conductive substrate, which improves the conductivity of the electrode and eliminates the need for a binder.

SESSION EN03.09: Green Electrochemical Energy Storage Solutions—Materials, Processes and Devices VII
Session Chair: Min–Kyu Song
Thursday Morning, December 5, 2019
Sheraton, 2nd Floor, Republic A

8:30 AM *EN03.09.01
Organic Molecules as Charge-Storing Materials for Redox Flow Batteries  Susan A. Odom; University of Kentucky, United States

The development of charge-storage materials for use in redox flow batteries (RFBs) requires possession of a diverse property set that will lead to high capacities, voltages, and lifetimes for large-scale stationary storage application. High capacities require high solubilities in all states of charge. High voltages stem from large differences in redox potentials. Long lifetimes require stability far greater than the timescales at which many chemists are used to operating, who rarely have the need to isolate a charged species at high concentration in diverse environments for a decade or more. None of these properties may be compromised in realizing a commercial battery, on top of which low cost and scalability are paramount. Given the demands in materials design, cost, and scale, it’s a small wonder that the variety of redox couples utilized in commercial redox flow batteries are few. While the challenge of meeting these requirements may at first seem daunting, to the right organic chemist, an opportunity is presented. The flexibility in design and tunability of properties of organic materials presents a cornucopia of choices to evaluate as electrolyte candidates. In this presentation, I will focus on the design and characterization of organic molecules as candidates for charge-storage species in non-redox flow batteries with nonaqueous electrolytes.

9:00 AM EN03.09.02
Insertion Mechanisms of the PF6-, TFSI- and FSI- Anions in Carbonaceous Cathodes for All-Carbon Dual-Ion Batteries  Antonia Kotronia, Habtom Desta, Asfaw, Daniel Brandell and Kristina Edström; Uppsala University, Sweden

The possibility to intercalate anions into graphite is a well-known phenomenon, which was initially observed in 1983. However, studies of such compounds in the context of electrochemical energy storage were first reported in 2012, in connection with the coining of the term dual-ion battery (DIB). Dual-ion batteries operate through
simultaneous cation and anion intercalation in the anode and cathode and they could constitute a breakthrough for large-scale, grid energy storage applications. The main benefit of all-carbon DIBs compared to other battery chemistries is their completely metal-oxide free nature. This key characteristic of DIBs would result in cheaper, environment friendly, naturally abundant and more sustainable batteries. Furthermore, the replacement of oxygen-rich cathodes with graphite would be a big leap towards increased operational safety, since electrode decomposition and evolution of flammable gases would become minimized.

The main challenge faced by all-carbon DIBs at the moment is the capacity fading related to the structural changes of the graphite upon anion intercalation; since the anion together with its solvation shell occupies a substantial volume. This will eventually lead to exfoliation of the graphitic sheets and effectively loss of active material and capacity. However, recent research as well as the preliminary results of this study indicate that the exfoliation issue can be partially supressed through careful design of both the electrolyte and carbon host material.

In this study, several carbonaceous materials with different crystallographic and morphological features are explored as potential hosts: (1) a monolithic, graphitic carbon foam which is partially turbostratically disordered (2) a flexible, expanded graphite foil and (3) a composite electrode comprised mostly of highly graphitized KS6 graphite. Additionally, the intercalated anions are varied, with the main focus being on the PF₆⁻, TFSI⁻ and FSI⁻ species, which are inserted from both conventional organic solvents and from more "exotic" alternatives such as ionic liquids. The electronic and structural changes which occur in the graphite as a consequence of the cell cycling are followed through the aid of in-operando Raman spectroscopy and ex-situ X-ray diffraction. These results are thereafter coupled to the electrochemical behavior of the different carbon-salt systems in order to gain a thorough understanding of the related intercalation mechanisms.

9:15 AM EN03.09.03
Visualizing Electron Transfer at the Nanoscale in Printable Conductive Polymer Electrodes for Energy Storage
Zhiting Chen¹, Enrico Daviddi², Brooke Massani¹, Cameron Bentley², Patrick Unwin² and Erin L. Ratcliff¹;
¹University of Arizona, United States; ²University of Warwick, United Kingdom

Green or bio-sourced carbon-based materials offer sustainability in electrochemical energy storage applications. Electron transfer is a fundamental process and as such, understanding the underlying structure-function properties is critical to new technological development. In many cases, polymeric materials are blended together to create an ensemble of collective properties, such as combining redox activity with mechanical or optical properties. This blending results in spatial heterogeneity of electrochemical properties. Inspired by the ability to tune the opto-electronic properties of conductive polymers and the prospect of highly controlled photoelectrochemical processes, this work undertakes a proof-of-principle study to evaluate the charge transport-charge transfer mechanism in conductive polymer/electrolyte interfaces at the micron to nanometer length scale. Both charge transport and charge transfer will follow paths of least resistance, hypothesized to be due to local percolation pathways and intermolecular spacings. The vision to develop a collective characterization tool suite that allows for imaging of distributions in nanoscale properties, which will enable identification of key structure-function relationships leading to higher performance, and finally, leveraging these known nanoscale properties to increase photon-to-electron-to-molecule conversions.

As a model system, amorphous insulating polymethylmethacrylate (PMMA) was blended with conductive poly(3-hexylthiophene) (P3HT). The enthalpy and entropy of mixing are such that the materials phase segregate, creating an ideal spatial heterogeneity to investigate connections between macroscale and nanoscale electrochemistry approaches. Using scanning electrochemical cell microscopy, the spatially-dependent electron-transfer kinetics associated with a rapid outer-sphere electron transfer process (ferrocenedimethanol oxidation) is mapped at the nanoscale. We combine the kinetic insight with complementary conductive AFM to understand the underlying electrical charge transport properties. A new technique - synchrotron infrared nanoscale spectroscopy (SINS) - is used to image local chemical structure and evaluate composition of buried interfaces. Finally, using finite analysis, we demonstrate the limitations of macroscale electrochemical approaches to assess rate constants due to uncompensated resistances.

9:30 AM BREAK

10:00 AM *EN03.09.04
Study on Organic Compounds as Electrode Materials for Na Beta-Alumina Battery  Guosheng Li; Pacific Northwest National Laboratory, United States

Due to its high natural abundance and low material cost, sodium (Na) based battery technology faces tremendous opportunities for electric vehicle and grid scale energy storage applications. Traditional Na Beta-alumina batteries (NBBs), such as Na-S and ZEBRA batteries, have been commercialized to demonstrate a variety of grid services, including power shift, renewable integration, frequency regulation, and standby power, etc. However, it is quite difficult for traditional NBBs to penetrate into larger application market due to its inevitable “barrier”-high operating temperatures (> 300°C). In the past few years, we have been developing intermediate temperature (~190°C) Na-metal halide (Na-MH) batteries, which present several advantages, including simple battery architecture, improved thermal management, lower operating temperature, and lower manufacturing cost over traditional NBBs. Recently, we found that the use of organic compounds as electrode materials in NBBs can provide a new pathway to further reduce the battery operating temperature to near or below 100°C. Here, we will present the preliminary results on investigating the possible application of organic candidates for NBBs applications.

10:30 AM EN03.09.05

Green, Transparent and Flexible Batteries, Supercapacitors and Photovoltaics Based on Multicomponent Thin Films  Aldo J. Zarbin, Samantha Husmann and Lucimara Roman; Federal Univ of Parana, Brazil

Carbon nanostructures (graphene, nanotubes)-based nanocomposite thin films applied in the field of both energy storage devices (batteries and supercapacitors) and renewable energy (photovoltaics) will be presented in this work. We developed a novel and versatile way to prepare thin, transparent and homogeneous films of advanced and multi-component materials, based on immiscible liquid/liquid interfaces (for example, Zarbin et al., Adv. Funct. Mater. 2013; Electrochim. Acta 2016; Sci. Reports 2016; Sci. Reports 2017; J. Power Sources 2017; Electrochim. Acta 2018). Due to the specific preparation route (unique for some classes of materials as the ones discussed here), the films can be deposited over any kind of substrates, plastics included, allowing the preparation of flexible devices. Also, evident material economy is observed in the final process.

We will demonstrate the application of some of those films in green energy. First, carbon nanotubes/Prussian blue analogues developed according a methodology developed by us (Zarbin et al. J. Mater. Chem. 2012; J. Phys. Chem. C 2014; Chem. Eur. J. 2016), were applied as cathodes in ion-based batteries totally operating in aqueous electrolytes. Aqueous electrolytes are safer, cheaper, environmentally friendly and more conductive than organic ones. Results showed huge performances in K- and Na-ions batteries (cheaper than Li-ions ones), achieving impressive high discharge rates (up to 44.4 A g⁻¹), capacities up to 150 mAh g⁻¹ at 0.67 A g⁻¹ rate, and retention of 90% after 2000 cycles. A transparent and flexible device was built using those thin films deposited over plastics as cathode, a C/Co₃O₄ nanocomposite as anode and an aqueous NaCl solution as electrolyte, showing capacity of 85 mA h g⁻¹, energy density of 53.3 Wh kg⁻¹ and retention higher than 90% after 2000 cycles. Flexible and transparent batteries correspond to emerging technology with direct impact on modern flexible and transparent devices. The device operation will be demonstrated showing four charged 1x1 cm devices connected in series and lightening a white LED. Also, flexible and transparent alkaline-batteries based on carbon nanotubes/nickel hydroxide thin films, as well as symmetric supercapacitors based on carbon nanostructures/polyaniline thin films will be demonstrated. Prussian blue was also utilized as an innovative sensitizer in a photoanode for dye-sensitized solar cells – DSSC. An innovative tri-component nanocomposite thin films of carbon nanotubes/TiO₂/Prussian blue was prepared through the liquid/liquid route. In this configuration in a single film we have the sensitizer (Prussian blue, used by the first time for this application), the semiconductor (TiO₂ nanoparticles) and the carbon nanotubes as the anchoring point for both the sensitizer and the semiconductor, as well as an efficient charge-transport material. The photoresponse evaluated in a total aqueous electrolyte was of impressive 600 µA cm⁻².

Summarizing, this work presents the preparation of complexes and multi-component materials, their innovative deposition as thin films using an unique methodology and their application as active components in environmentally friendly batteries and photovoltaics, fully operating in water. Materials and processes for green energy.

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10:45 AM EN03.09.06

PEDOT: PSS-Cellulose Nanocomposite Supercapacitors by Spray Coating and Printing  Mehmet G. Say¹, Calvin J. Brett²,³, Stephan V. Roth³,², L. D. Söderberg²,³, Isak Engqvist¹,² and Magnus Berggren¹,³; ¹Linköping University, Sweden; ²KTH Royal Institute of Technology, Sweden; ³Deutsches Elektronen-Synchrotron (DESY),

Final Program 1/13/2020  527
Conductive polymers have been extensively investigated as part of next-generation green electrochemical energy storage solutions. Organic electrochemical capacitors/supercapacitors are great candidates for flexible, portable power supply due to quick charge delivery and environmentally friendly materials and production. The combination of conductive polymer Poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS) and bio-sourced cellulose nanofibrils (CNF) provides a mechanically robust, ionically and electronically conductive nanonetwork for high energy and power density paper electrodes that can be solution-processed into supercapacitor systems. Spray coating allows large area, roll-to-roll compatible fabrication of nanometer thin up to, macroscopically thick, free-standing electrodes from functional inks. In this work, up to 30 µm thick conductive nanocomposite electrodes made from CNF and PEDOT: PSS were achieved by industrial spray deposition and then combined into supercapacitors. The crystalline structure of these spray coated nanocomposite films with certain additives and different thicknesses was evaluated by grazing incidence wide-angle x-ray scattering (GIWAXS).

The manufacturing strategies introduced in this study are to realize customized supercapacitor architectures for portable printed electronics by combining spray-coated electroactive paper electrodes with stencil printing of gel electrolyte and screen-printed cell components. Excellent electrochemical performance with 1.2 µWh/cm² energy and 20 mW/cm² power densities at 0.1 mA/cm² was demonstrated, and all-printed devices survived extreme bending tests and cycle life up to 3000 charge-discharge cycles. The proposed fabrication methods and architectures enable the integration of thin and flexible energy storage devices with printed solar cells, exemplified in a wristband for applications in low power wearable electronics.

11:00 AM EN03.09.07
Water-Transferable, Inkjet-Printed Supercapacitors towards Conformed Three-Dimensional and Epidermal Energy Storage Pavlos Giannakou, Mehmet Tas, Brice L. Borgne and Maxim Shkunov; University of Surrey, United Kingdom

The rapid development of Internet-of-Things (IoT) requires the use of embedded electronics into physical components and daily objects which stimulates a tremendous and rapidly grown interest for electronic devices and energy storage systems that are flexible, wearable and conformal. Typical fabrication methods, such as photolithography and winding or stacking, that are commonly used in conventional electronics and energy storage systems respectively, are difficult to be applied as fabrication strategies towards devices with advanced form factors (e.g. three-dimensional (3D), stretchable, conformal). In this study, we demonstrate the fabrication of supercapacitors on 3D objects through inkjet and water-transfer printing. To the best of our knowledge, this is the first reported study on water-transfer printing of an active functional device such as energy storage. Planar supercapacitors constituted from nanoparticle-based silver current collector, nanoparticle-based nickel (II) oxide (NiO) active electrode material and an ionic liquid or surfactant-based saturated magnesium perchlorate/ultraviolet-cured triacrylate polymer-based solid-state electrolyte, were chosen as model materials to explore the feasibility of the proposed concept. To further explore the practical potential of the inkjet-printed supercapacitors with a particular focus on wearable applications, we fabricated an epidermal (or tattoo) printable supercapacitor, that was water-transferred on the skin of a human subject, to potentially serve as the power source for wearable health systems. The 3D and epidermal devices showed areal specific capacitances of up to 52 mF cm⁻² and 27 mF cm⁻² respectively. This new class of water transferable, inkjet-printed, all-solid-state supercapacitors with advanced conformality, offer new alternative approach towards monolithically-integrated/object-tailed power sources that are needed for complex-shaped devices for IoT and flexible/wearable electronic applications.

11:15 AM EN03.09.08
New Chemistries and Structural Principles for Li-Containing, Air-Stable and High Voltage Organic Battery Chemistries Louis Sieuw¹, Jiande Wang¹, Philippe Poizot² and Alexandru Vlad¹; ¹Univ Catholique-Louvain, Belgium; ²Universite de Nantes, France

The redox chemistry of organic molecules is increasingly attracting interest as it has the potential to provide battery electrode material candidates combining high capacities, practical redox potentials and allow for transition metal-free chemistries. While many redox chemistries have been extensively explored, achieving high redox potentials has long remained a challenge. What is more important, lithiated organic redox chemistries (akin Li-ion inorganic cathodes) are severely lacking which makes difficult thus far practical implementation of an organic Li-ion battery technology.
This contribution aims at reporting some of our recent advances for the development of true organic Li-ion cathode materials. Design principles for new organic redox chemistries with limited solubility [1], high voltage via structural electrostatic interactions [2], as well as a new organic redox chemistry with intrinsic high voltage and ambient air stability will be detailed [3]. We hope that such findings can pave the way for designing high voltage organic Li-ion batteries in a near future.


11:30 AM EN03.09.09
Surface Modification of Lithium Iron Phosphate Electrode for an Innovative and Efficient Mining of Oceanic Lithium Po-Wei Huang and Nian Liu; Georgia Tech, United States

Clean and renewable energy has become a focal point due to its multiple impacts on our global sustainability. Lithium-ion batteries (LIBs), owing to its unique properties, have dominated the consumer electronics, automotive, medical, and industrial markets since the 1990s. Recently, the rapid development of portable electronic devices and electric vehicles (EVs) has led to an unprecedented demand for LIBs. Therefore, lithium, “the new gold,” become a strategically important commodity and is one of the most valuable resources in the foreseeable future. However, the current lithium production can’t satisfy the spiking demand for lithium and has been reported to cause negative impacts on the environment. Therefore, seeking new lithium sources and developing new lithium mining methods are the overarching issues to reach a sustainable future.

To address this challenge, we proposed to use an electrochemical method to extract lithium from the ocean. Inspired by lithium-ion rechargeable batteries, we applied lithium iron phosphate (LFP) to extract lithium from seawater due to its innate properties of lithium-ion selectivity, appropriate working potential, and fast cycling life. The ocean has been reported as the most potential source of lithium. While lithium is abundant in seawater, its low concentration hinders its practical application. Furthermore, the high concentration of sodium-ions that coexist in the seawater further increase the difficulty of the extracting process. From our experimental result, it showed that the lithium-recovery ability, the number of lithium-ions that can be released back into recovery solution, of LFP decrease 54% after one cycle in artificial seawater (0.1M LiCl + 0.5M NaCl) comparing to pure lithium solution (0.1M LiCl). Consequently, designing an electrode that can selectively extract lithium-ions, meanwhile, hinder the negative impacts causing by sodium-ions is the main challenge when developing electrochemical mining of oceanic lithium. From the electrochemical performance (galvanostatic charge-discharge measurement) of LFP in artificial seawater, we, the first, observed the second platform occurring in the discharge curve, corresponding to sodium-ion co-intercalation. The sodium-ion co-intercalation have been reported to cause phase transformation from LFP (olivine structure) to sodium iron phosphate (maricite structure), which not only cause capacity decay but also lower the reversibility. Surface modification has been used in our work to alleviate the co-intercalation reaction. We design a polymer, containing lithium ionophore, acting as a customized tunnel for lithium-ion to diffuse, but block sodium-ion, to enhance the selectivity. The second platform occurring in the discharge curve can be inhibited by applying our method; besides enhancing the concentration by a factor of 10.77 (Li/Na molar ratio of initial solution = 0.2 and Li/Na molar ratio of recovery solution = 2.15), we improve the selectivity of the LFP electrode by a factor of 3.15, and increase 19% of the “recovery efficiency” (amount of lithium-ions that can be released back into recovery solution/ amount of lithium-ions that have been extracted from the artificial seawater) after 25 cycles.

By utilizing the surface modification, we can greatly block the co-intercalation of sodium-ions, prevent the phase transformation of LFP, and enhance the cycling ability. By applying the electrochemical lithium mining method, we can shorten the manufacturing cycle from years to days and provide new opportunities to harvest the ocean’s resources, and accelerate progress toward a sustainable future.

11:45 AM EN03.09.10
Self-Assembly of 1D Particles and 2D MXenes for Nanocomposite Energy Storage Devices Mahiar M. Hamedi1, Weiqian Tian1, Zhen Wang1, Liangqi Ouyang1, Armin VahidMohammadi2, Majid Beidaghi2 and Lars Wågberg1; 1KTH, Sweden; 2Auburn University, United States

We report two different strategies to achieves nanocomposites with very high precision at the nanoscale:
i) Layer-by-layer (LbL) self-assembly of a small molecule, tris(2-aminoethyl) amine (TAEA), in combination with a colloidal dispersion of the 2D material, Ti3C2Tx MXene, to form self-assembled multilayers. This LbL assembly of MXenes with small molecules is fundamentally different from assembly with polymers and results in highly ordered pillared (MXene/TAEA)n multilayer where the TAEA expands the interlayer spacing of MXene layers by only around 1 Å and reinforces the interconnection between MXene flakes. The TAEA-pillared MXene multilayers show higher electronic conductivity of $7.3 \times 10^4$ S m$^{-1}$ to other MXene multilayers fabricated by LbL self-assembly. These multilayers are also resistant to mechanical deformation. Importantly, the MXene/TAEA multilayers could be used as electrodes for flexible all-solid-state supercapacitors delivering a high volumetric capacitance of 583 F cm$^{-3}$ and an integrated high energy density of 3.0 Wh L$^{-1}$ corresponding to a power density of 4400 W L$^{-1}$. This strategy enables large-scale fabrication of highly conductive pillared MXene multilayers, and potentially fabrication of other types of 2D heterostructures on various substrates.

ii) Aqueous self-assembly of a multifunctional nanocomposite using the combination of a one-dimensional (1D) abundant biomaterial (cellulose nanofibrils, CNFs) with Ti3C2TxMXene. This nanocomposite has one of the best multifunctional integration of strength (341 MPa), conductance (295 S cm$^{-1}$), and capacitance (298 F g$^{-1}$) than any previously reported composite. We rigorously studied and optimized these nanocomposites and concluded that the geometrical match between the 1D and 2D particles are crucial as they define the strength as well as the conductivity of the composite, and that the 1D and 2D phase must have a strong interaction at short range to overcome the colloidal repulsion and lock into a strong composite

References:


SESSION EN03.10: Green Electrochemical Energy Storage Solutions—Materials, Processes and Devices VIII
Session Chair: Min–Kyu Song
Thursday Afternoon, December 5, 2019
Sheraton, 2nd Floor, Republic A

1:30 PM *EN03.10.01
Towards Rechargeable Batteries Made of Abundant Chemical Elements Philippe Poizot1, Alia Jouhara1, Vincent Cadiou1, Thibault Gutel2, Nicolas Dupré1, Eric Quarez1, Michel Armand1 and Franck Dolhem4; 1University of Nantes, France; 2CEA, LITEN, DEHT, STB, France; 3CIC Energigune, Miñano, Spain; 4University of Picardy Jules Verne, France

Routine access to power sources is an essential factor towards the continuing progress of our technology-oriented society, and toward ensuring a better quality of life. In this context, due to the ever-increasing implementation of renewable energy sources, electrical energy storage systems are set to play a central and potentially critical role in the next-generation energy infrastructure. The use of rechargeable (or secondary) batteries, which are already widely used for powering electric vehicles and electronic devices of all kinds, also seems to be particularly relevant with respect to this future scenario [1]. However, being faced with such a high global battery demand, issues concerning the resource availability or the recyclability also have to be further addressed together with the technical requirements in terms of capacity, energy density, cyclability, safety or cost. In this regard, and in parallel to research activities on regular inorganic-based electrode materials, the past decade has seen significant progress with respect to redox-active organic compounds, attracting much interest from the energy storage community. This is evidenced by the rapid increase in the number of studies and recent reviews on the topic [2], although this approach is still in its infancy. Based on the tailoring of naturally abundant chemical elements (C, H, N, O, and S in particular), organic chemistry also provides great opportunities for the discovery of innovative electrode materials able to operate both in aqueous and non-aqueous electrolytes. Additionally, it must be pointed out that two types of electrochemical mechanisms can be used in practice: n-type structures involving a charge transfer between the negatively charged state and the neutral state of the organic moieties (with cation release/uptake) and p-type
structures involving a charge transfer between the neutral state and the positively charged state of the organic moieties (with anion uptake/release). In this communication, we will present our past and recent advances for developing efficient and sustainable organic electrode materials. In particular, we will report on several types of terephthalate derivatives [3] able to reversibly host both cations or anions by electrochemical reactions making different cell configurations possible including anionic “rocking-chair” batteries for which few examples are reported in the literature.

References:

2:00 PM EN03.10.02
Converting Eggs to Flexible, All-Solid Supercapacitors Yunya Zhang and Xiaodong Li; University of Virginia, United States

The rapid expansion of electrochemical energy storage markets has imposed an impending need for low-cost, sustainable materials for high-performance electrodes, separators, and electrolytes. A rational strategy is to derive the electrochemical materials from renewable biomass. Here, we report a feasible approach to fabricate flexible, all-solid supercapacitors from eggs. Egg white/yolk and eggshell acted as the carbon source and sacrificial templates for porous activated carbon, respectively. The egg-derived 2D graphene-like carbon sheets with a thickness of 1.25 nm exhibited an outstanding combination of energy density and power density when being used in supercapacitor electrodes due to their high specific surface area (1527.2 m²/g) and naturally doped functional groups. Egg white/yolk also reacted with KOH, forming gel-like solid electrolyte with competitive ionic conductivity and water preservation. With eggshell membrane as a superb separator, flexible, all-solid supercapacitors were assembled which exhibited superlative electrochemical performance and mechanical flexibility. The proof-of-concept study provides inspirations of comprehensive utilization of biomass materials for energy storage. The egg-derived 2D graphene-like carbon and solid-state electrolytes should find more applications in different fields.

2:15 PM EN03.10.03
Solar Light Enhances Melanin Electrochemical Energy Storage Performance Abdelaziz M. Gouda¹, Francesca Soavi² and Clara Santato¹; ¹Ecole Polytechnique Montreal, Egypt; ²University of Bologna, Italy

We explored the possibility to integrate the conversion and storage functions within the same multi-functional bio-sourced material. We identified the redox-active, quinone-based, melanin pigment, featuring a broad band absorption in the UV-Vis region, as the ideal candidate for such an exploration. Electrodes of melanin on carbon paper were investigated for their morphological, optical and voltammetric characteristics prior being assembled into symmetric supercapacitors operating in aqueous electrolytes. We observed that, under solar light, the capacity and the capacitance of the melanin electrodes significantly increase with respect to the dark conditions (by 22% and 39%, respectively). Once in supercapacitor configuration, besides featuring a Coulombic efficiency close to 100% after 5,000 cycles, the capacitance and capacity of the electrodes, rated by the initial values, improve after prolonged illumination, as it is the case for the energy and power density.

2:30 PM BREAK

3:00 PM *EN03.10.04
A Facile Approach to Identify Lithium Content in Spent Battery Cathode Materials Chunmei Ban; Virginia Tech, United States

Electrochemical or chemical relithiation of end-of-life cathodes has been used to compensate the loss of lithium ion in the lithium-ion battery cathodes and recover their electrochemical reversibility. This method opens a new venue to directly recycle the spent cathode materials in a fast, energy-efficient and nondestructive way, without destroying the original structures happened in the traditional pyrometallurgy and hydrometallurgy processes. However, the
direct relithiation method can effectively restore the electrochemical properties of the spent materials, only if the loss of lithium ion is the primary aging mechanism for the cathodes. The lack of efficiently identifying the degradation mechanism and determination of lithium ion content in the spent cathode materials makes it difficult to sort spent cathode materials suitable for direct relithiation in the battery recycling process. The determination of lithium ion content in the cathode materials, which is currently performed by coupled plasma-mass spectrometry (ICP-MS), involves tedious procedure and error-prone preparation. In this work, a new method has been developed to quickly sort the spent cathode materials—herein, Li(Mn0.35Ni0.4Co0.23)O2—for relithiation recycling. Furthermore, we introduce a new methodology to fast determine the lithium content in spent cathode materials without using ICP-MS. Finally, we have applied these methods developed in this work, to investigate the effectiveness of direct electrochemical-relithiation on recycling the spent cathodes and provide the insights in the future development of direct battery materials recycling.

3:30 PM EN03.10.05
Flexible Fiber-Shaped High Performance Energy Storage Devices Bin Wang; China Academy of Engineering Physics, China

With the development of flexible wearable electronics, fiber-shaped energy storage devices (FSESSs) have attracted considerable interest in recent years. Owing to their large geometric dimension and solid inner structure, the specific surface area and the utilization of the electrodes are limited, which results in low capacities and energy densities of FSESSs. To further improve the energy densities of the FSCs, the nanostructure of the one-dimensional electrodes should be designed to promote the utilization and increase the accessible area for electrolyte and thus improving their specific capacities and energy density.

In this study, polymer or carbon-based fiber electrodes with hierarchical porous structures have been fabricated as electrodes of FSESSs. As electrodes of the all solid-state or quasi-solid-state FSESSs, the fiber electrodes exhibit high flexibility and remarkable electrochemical performances with a high energy density.

3:45 PM EN03.10.06
Stable Cycling of High-Voltage Lithium-Ion Batteries Enabled by Localized High-Concentration Electrolytes Xianhui Zhang1,2, Xia Cao1, Xiaodi Ren1, Haiping Wu1, Ji-Guang Zhang1 and Wu Xu1; 1Pacific Northwest National Laboratory, United States; 2Chinese Academy of Sciences, China

Nickel-rich layered oxide materials (LiNi0.5Mn0.35Co0.15O2, NMC), such as NMC622 and NMC811, have attracted great interest for application as high energy-density cathode materials in lithium-ion batteries (LIBs) because of their high specific capacities at high voltages compared with other commercial cathodes. Pushing cathode materials towards high-voltage operation is an effective way to further increase the energy density of the batteries. However, it is still a big challenge to operate Ni-rich NMC in LIBs under high voltage conditions (e.g. 4.4 V and above) due to the severe capacity fading. This fading is directly related to the instability of the cathode/electrolyte interface, induced by the ongoing chemical and electrochemical decompositions of electrolyte, the structural degradation of the cathode material and the dissolution of transition metals from the cathode; therefore, the commercial application of the Ni-rich NMC is limited so far. Besides the approaches of doping and coating the Ni-rich NMC materials to improve the long-term cycling stability of the batteries, developing new electrolytes is also an effective way to improve the practical application of Ni-rich NMC materials in LIBs. Here, we report new localized high-concentration electrolytes (LHCEs) that can greatly enhance the stability of Ni-rich NMC cathode and full cells with graphite (Gr) anode under 4.4 V comparing to the conventional carbonate electrolyte. This effect, in combination with the superior stability of Gr in these LHCEs, achieves dramatically improved long-term cycling performances of Gr/NMC cells in wide temperature range from -30 to 60 °C. The findings in this work shed light a very promising strategy to develop new electrolytes for practical high-energy LIBs with Ni-rich NMC cathodes.

4:00 PM EN03.10.07
Porous Carbon Fibers for Energy Storage Zhengping Zhou1,2; 1North Dakota State University, United States; 2Virginia Tech, United States

Porous carbon fibers with a high surface area and rich functionality are attracted as electrode materials for electrochemical energy storage devices (for example, supercapacitors and rechargeable batteries). Their widespread use is limited by their low porosity and ion-accessible surface area, and relatively sluggish electron/ion transport.
Here, we present a new strategy of utilizing the microphase separation of block copolymers associated with electrospinning, pyrolysis and chemical activation to synthesize a porous carbon fiber with a well-controlled improved porosity, a highly effective ion-accessible surface area, and a fast electron/ion transport. Two-electrode supercapacitors fabricated from the prepared porous carbon fibers yielded high capacitance values in ionic liquid electrolyte. In addition, this approach is readily scalable to produce porous carbon fibers on industrial levels.

4:15 PM EN03.10.08
Active Materials of Mixed-Phase MnO2/Nitrogen-Containing Graphene for Flexible Asymmetric Solid-State Supercapacitors Hsin-Ya Chiu and Chun-Pei Cho; National Chi Nan University, Taiwan

The MnO2/nitrogen-containing graphene (x-NGM) composites with various Mn contents hydrothermally fabricated were used as electrode active materials for flexible asymmetric solid-state supercapacitors (ASSCs). By SEM, TEM, EDS mappings, XPS, and Raman spectra, the presence of nitrogen-containing graphene (NG) and MnO2 was confirmed. TEM results manifested that the MnO2 in the composites was a two-phase mixture of γ- and α-MnO2. The co-existence of NG and MnO2 enhanced not only the reversible Faraday reactions on the surface but also the charge transfer capability. However, excess MnO2 caused reduced conductivity and a smaller slope of Nyquist plot in the low-frequency region unfavorable for ion diffusion and charge transfer. Better charge transfer efficiency was achieved only when the optimum MnO2 content was contained. Overloaded mass of active materials on the flexible electrode was detrimental to improved conductivity. Thus, both the mass loading of active materials and the MnO2 content were crucial to capacitor performance. The x-NGM composites and graphene (G) were used as the active materials for cathodes and anode, respectively, so the ASSCs were operated simultaneously by two charge storage mechanisms. The synergistic effect enabled better charge storage purposes. Among the supercapacitors, the 3-NGM1/G1 capacitor showed the highest conductivity, more efficient charge transfer, and thereby best capacitive properties. It exhibited a high specific capacitance of 579 F/g, giving rise to the high energy density and power density of 1223.3 Wh/kg and 73153.6 W/kg, respectively. The high retention rate (86.7 %) of specific capacitance after 2000 bending cycles demonstrated good cycle stability of the flexible ASSCs using the x-NGM composites. The best capacitor performance achieved in this work was superior to most literature results, implying that x-NGM composites are indeed promising electrode active materials for flexible ASSCs.

4:30 PM EN03.10.09
Energy Materials from Waste Maria Crespo Ribadeneyra1, Heather Au1, Hande Alptekin1 and Magdalena Titirici1,2; 1Imperial College London, United Kingdom; 2Queen Mary University of London, United Kingdom

Emerging energy technologies rely on materials, at the same time that the production of these materials relies on an energy supply. To keep a balance between the production of new materials we need to minimise the energy we employ to produce them, starting from which precursors we chose for their synthesis. In this context, we want to unlock part of the technological challenge of upgrading compounds generated from anthropogenic pollution, biomass and industrial by-products. We propose to produce highly efficient and low-cost energy components through the catalytic conversion of waste into non-geopolitically compromised rechargeable Na-ion battery electrodes as a sustainable solution to keep such energy/materials balance.

We present preliminary data on the hydrothermal carbonisation and microwave treatment of different biomass/plastic waste precursors in the presence of environmentally friendly catalysts. We study the relationship of carbonisation treatment with the final microstructure and relate this to the Na-ion absorption mechanism during electrochemical charge-discharge cycles between 2.5 and 0 V.

4:45 PM EN03.10.10
Direct Electrosynthesis of Pure Aqueous H2O2 Solutions Up to 20% by Weight Using a Solid Electrolyte Chuan Xia; Rice University, United States

Hydrogen peroxide (H2O2) synthesis generally requires substantial post-reaction purification. Here I will introduce a direct electrosynthesis strategy that delivers separate H2 and O2 streams to an anode and cathode separated by a porous solid electrolyte, wherein the electrochemically generated H+ and HO2- recombine to form pure aqueous H2O2 solutions. By optimizing a functionalized carbon black catalyst for 2-electron oxygen reduction, we achieved >90% selectivity for pure H2O2 at current densities up to 200 mA cm⁻², which represents a H2O2 productivity of 3.4
mmol cm^{-2} \text{h}^{-1} (3660 \text{ mol kg}^{-1} \text{cat} \text{h}^{-1}). A wide range of concentrations of pure H_2O_2 solutions up to 20 wt.% could be obtained by tuning the water flow through the solid electrolyte, and the catalyst retained activity and selectivity for 100 hours. As one representative practice, our device demonstrated a continuous treatment of total organic carbon in Houston rainwater with a processing rate up to 2180 L m^{-2} \text{electrode} \text{h}^{-1} to meet drinking water standards.

**SYMPOSIUM EN04**

Advanced Membranes for Energy-Efficient Molecular Separation and Ion Conduction  
December 2 - December 5, 2019

Symposium Organizers  
Yifu Ding, University of Colorado Boulder  
Yunxia Hu, Tianjin Polytechnic University  
Haiqing Lin, SUNY Buffalo  
Tomonori Saito, Oak Ridge National Laboratory

* Invited Paper

SESSION EN04.01: Advanced Membranes for Energy Storage Applications I  
Session Chairs: Xi Chen and Tomonori Saito  
Monday Morning, December 2, 2019  
Sheraton, 3rd Floor, Fairfax A

8:30 AM *EN04.01.01  
**Ion-Conducting Membranes for Large-Scale Energy Storage**  
Michael Hickner; The Pennsylvania State University, United States

New polymer membranes are needed to advance energy storage and conversion technologies for distributed and grid-scale applications. We have recently demonstrated new ion-conducting polymer membranes that have achieved excellent performance and long-lifetime stability in vanadium redox flow batteries, a leading technology candidate for deployment in renewable power networks and grid-scale energy storage systems with sizes ranging from 10s to 100s of megawatts. By tuning the nanoscopic self-assembly of the ionic domains in the polymers, we are able to increase the cycle life of the device by impeding vanadium ion transport through the membrane while facilitating high conductivity in the electrolyte to maintain the battery current density. For instance, by decreasing the vanadium permeability of the membrane by a factor of two, we have been able to double the lifetime of the device, which provides significant life-cycle cost savings. We have also demonstrated membranes with nearly zero vanadium permeability that show 100% coulombic efficiency in flow battery charge-discharge cycling tests. Currently, we are working on demonstrating these membranes over 100s of charge-discharge cycles. Anion exchange membranes have the potential to rid fuel cell technology of expensive precious-metal catalysts. Acidic fuel cells with NAFION® membranes require platinum, but anionic membranes that operate at high pH open the door for the use of silver and nickel fuel cell catalysts which would greatly decrease the cost of polymer fuel cell technology. We have developed new anion exchange membrane polymer structures that show exceptional stability under fuel cell conditions and have helped to increase the performance and lifetime of anion exchange membrane fuel cells. This talk will show how polymers with new chemical structures can be applied to many different types of batteries and other electrochemical devices. Common design principles and considerations for fabricating new ion exchange membranes for energy processes will be discussed.
9:00 AM EN04.01.02
Electrochemical Properties of Various Oxide Ion Conducting Membranes for Solid Oxide Membrane (SOM) Electrolysis Kuk Jin Hwang1,2, Miyoung Shin1, Myung-Hyun Lee1 and Tae Ho Shin1; 1Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of); 2Pusan National University, Korea (the Republic of)

The solid oxide membrane (SOM) process is an environmentally friendly and innovative technology that can produce valuable metals directly from their oxides by high temperature solid oxide electrolysis. For direct metal-reduction high ionic conductors such as doped zirconia could use as the anode to remove oxide ion in the SOM electrolysis system. Particularly, yttria-stabilized zirconia (YSZ) tube is normally employed as the anode; it is immersed the molten salt containing dissolved metal oxides and oxygen anions that move to the tube where they are reduced without any emission. However, the SOM process for metal production via oxide reduction is limited because of several challenging issues, such as high oxide ion conductivity, YSZ phase stability and yttrium dissolution by the reaction at high temperature electrolysis condition in the harsh corrosive molten salt flux.

In this study, we introduce the layered configuration to improve stability and performance; the thin YSZ dense layer coated on porous Ni-YSZ cermet tube to reduce ohmic resistance of long oxide ion conducting path way in thick membrane, the protection layer coated on YSZ to enhance phase stability of the anode tube, and mixed ionic and electronic conduction (MIEC) materials were employed to reduce polarization of oxygen evolution reaction. When the electrical potential applied between the cathode and anode, it is expected that the ohmic resistance is reduced more than the conventional YSZ tube. It will be discussed that the effect of the functional layered SOM tubes for a current efficiency and the amount of metal reduction.

9:15 AM EN04.01.03
A Crosslinked Polyelectrolyte with Pendant Carbonate Group Demonstrating High Conductivity and Chemical Stability for Lithium Battery Yubin He, Yamin Zhang, Paul Kohl and Nian Liu; Georgia Institute of Technology, United States

Lithium ion batteries (LIBs) are the state of art power source in mobile devices like cellphones and electric vehicles. However, there are huge safety hazard due to the volatility and flammability of conventional liquid electrolytes. In the pursuing of high performance solid polyelectrolytes (sPE), polycarbonate (PC) has emerged as the most promising category due to its distinct advantages like extended electro-chemical stability window, decreased crystallinity and higher Li+ transference number.

Previously, several advanced PC-sPEs have been developed either by adding plasticizer or adopting the “polymer in salt” strategy. Although good conductivity ranging from 0.1 to 0.4 mS/cm was achieved, these method inevitable led to non-free-standing membranes due to weakened mechanical strength. Another problem of PC-sPE remains unsolved is its instability with lithium metal. The hydroxyl terminations of PC chains is readily reactive towards Li metal, leads to “unzipping” degradation.

To address the aforementioned problems of PC-sPE, an ultimate solution is developed to access free standing sPE with simultaneously achieved Li metal stability and high ionic conductivity. Firstly, an acrylate monomer with pendant propylene carbonate (DB-PC) is synthesized. Upon UV irradiation, this monomer is shown to polymerize within several minutes. Unlike the conventional PC-sPE, the UV cured sPE (UVPC-sPE) adopts polyethylene as mainchain and cyclic propylene carbonate as pendant group, thus avoiding thermal triggered main chain random scission and terminal –OH group triggered “unzipping” degradation respectively.

Besides, the abstraction of hydrogen attached to carbonate ring lead to enhanced chain transfer reaction and efficient crosslinking process. As a result, the free standing UVPC-sPE exhibits high room temperature conductivity up to 1 mS/cm, which is a significant upgrade to the conventional PC-sPE. In addition, the assembled Li/UVPC-sPE/LFP full battery shows excellent cycling performance at 0.5 C (25 °C) and 1C (65 °C), demonstrating its promising potential in Li ion battery applications.

9:30 AM EN04.01.04
Discovery of a New Class of Potential Superprotonic Conductors by High-Throughput Computing Pandu Wisesa, Chenyang Li and Tim Mueller; Johns Hopkins University, United States

The development of new proton conducting materials would be beneficial for a variety of applications, including hydrogen separation membranes and fuel cell electrolytes. Much of the work on proton-conducting inorganic
materials has been limited to a few well-known structure types, and many classes of materials remain relatively unexplored for their ability to conduct protons. We present the results of a high-throughput computational search for new classes of proton-conducting oxides. As the use of density functional theory (DFT) to directly screen for proton mobility would be prohibitively expensive, we have developed a potential energy model for rapidly screening candidate materials to identify classes of materials that are most likely to exhibit high proton mobility. We will present the results of our model on thousands of candidate materials, including both well-known proton-conducting oxides and a new class of stable oxide materials that are predicted by both our model and DFT to have exceptionally low activation energies for proton conduction.

9:45 AM EN04.01.05
Structural Designs of Alkaline Durable Imidazolium-Containing Anion Conducting Membranes Prepared by Radiation-Induced Grafting for Pt-Free Fuel Cells Kimio Yoshimura1, Yue Zhao1, Ahmed Mahmoud1, Akihiro Hiroki1, Hideyuki Shishitani2, Susumu Yamaguchi2, Hirohisa Tanaka3 and Yasunari Maekawa1; 1National Institutes for Quantum and Radiological Science and Technology, Japan; 2Daihatsu Motor Co., Ltd., Japan; 3Kwansei Gakuin University, Japan

We have been developing alkaline-durable anion conducting electrolyte membranes (AEMs) for liquid fuel (hydrated hydrazine) type fuel cell (FC) vehicles. Even though the AEM-FC system has been significantly attractive because of non-precious metals used as active catalysts, there is no commercially available AEMs due to the severe damage of the membranes in alkaline operating conditions [1]. Thus, we applied the radiation-induced grafting technique to introduce various anion conducting graft-polymers into a thermally and mechanically tough poly(ethylene-co-tetrafluoroethylene) (ETFE) film to develop new AEMs.

Recently, we investigated a series of imidazolium-type AEMs because of the low basicity of imidazolium hydroxide as an Arrhenius base [2]. Most of the imidazolium-type AEMs exhibited lower water uptake and higher thermal stability than those of the corresponding AEMs containing trimethylammonium hydroxide. Furthermore, AEMs containing weak base imidazolium groups suffered less damage of polymer backbones via self-base catalyzed degradation. Even though N-vinylimidazolium graft-type AEMs are subjected to $\beta$-elimination and hydrolytic ring opening degradation to reduce the anionic conductivity in an alkaline solution at elevated temperature (1M KOH, 80°C), we introduced the graft-copolymers of vinylimidazolium with styrene because the adjacent vinylimazolium cations led very fast elimination due to the double $\beta$-positioned hydrogen. Furthermore, for suppressing hydrolysis, the protecting group is introduced at 2-posion of imidazolium rings, which are subject to hydroxide attack. The alkaline durability of the AEMs having the abovementioned molecular designs showed drastically improved alkaline durability. Namely, a poly(2-methyl-N-vinylimidazolium hydroxide-co-styrene)-grafted ETFE (MIm/St-AEM, MIm/St ratio of 60/40) retained 26% of the initial conductivity (>14 mS cm$^{-1}$) after 1300 h in the actual fuel of 5% hydrated hydrazine in 1 M KOH at 80 °C. The membrane-electrode-assembly (MEA) consisting of MIm/St-AEM with the anion conducting ionomer having a similar polymer structure to the grafts, showed a maximum power density of 230 mW cm$^{-2}$ in a direct hydrazine hydrate FC [3].

Since the electrolyte properties, durabilities, and fuel cell performance of the graft-type AEMs could not be elucidated only by these chemical structures of the graft-type AEMs, we performed the hierarchical structure analysis of the synthesized AEMs. Contrary to the above mentioned MIm/St-AEM, the AEM with higher styrene ratios (MIm/St = 40/60 and 20/80) showed less durability in the alkaline solution. By a SANS contrast variation method, only the AEMs with MIm/St = 40/60 and 20/80 showed water puddle sphere with a diameter of 3-4 nm. Thus, we concluded that the imidazolium groups around the water puddle are subjected to the hydrolytic attack to lead the degradation of the AEMs [4]. We find out that the elucidation of hierarchical structures of the AEMs takes important role to develop alkaline durable AEMs.

Acknowledgement:
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References:

10:00 AM BREAK

10:30 AM *EN04.01.06
An Overview of Composite Polymer Electrolyte Systems Bamdad Bahar; Xergy Incorporated, United States

Among all choices of electrolytes, polymer-based systems have attracted widespread attention due to their utility in cell design and excellent processability. Polymer electrolytes have an intrinsic feature: they lose mechanical properties with increase in ionic conductivity. Thus, in order to make high performance media, they must be mechanically supported (composited). This paper will provide a review on how this problem has been historically addressed including a survey of different composite media including fabrics, microporous media and discrete fibers and fillers and their impact on polymer electrolytes from an industrial point of view, leading to the current state of the art. The paper will discuss other critical features in polymer electrolytes where compositing can make a critical contribution to overall system performance – such as improved processability, cell separation, reduced reactant cross-over, reduced volume of electrolyte use, incorporation of crucial additives within support matrix, improvement of ionic continuity, ionic modification, and improved designs. Each aspect is discussed in detail. Specific polymer electrolyte composite strategies for different applications such as industrial electrolysis (Chlor-alkali), fuel cells, pervaporation and others are reviewed. In-situ measurements and specific features and benefits are discussed.

11:00 AM EN04.01.07
Mechanically Robust Polymer Membranes for Non-Aqueous Flow Battery Michelle Lehmann¹,², Guang Yang², Pengfei Cao², Ethan C. Self², Alexei Sokolov²,¹, Frank Delnick², Jagjit Nanda²,¹ and Tomonori Saito²,¹; ¹The University of Tennessee, Knoxville, United States; ²Oak Ridge National Laboratory, United States

Large scale grid storage is imperative for an efficient use of renewable energies. While aqueous redox flow batteries (RFBs) such as vanadium-based aqueous RFB are relatively mature technologies for a grid storage, non-aqueous RFBs present an attractive alternative strategy for potentially providing much higher energy density. One of the key enablers for non-aqueous RFBs is mechanically robust and highly ion-conductive membranes. In aqueous RFBs, membranes can achieve high proton or anion conductivity due to water mediating their ion conduction, thus there are various high performance membranes for aqueous RFBs. On the other hand, for membranes in non-aqueous RFBs, achieving high ion conductivity while maintaining mechanical and chemical stability is a major challenge. The design principle for such membranes is poorly understood due to the complexity of the system. Our membranes are developed for a non-aqueous RFB with an alkali alloy anode technology that has the potential to achieve high energy density, high safety, low cost and long cycle life. This presentation will discuss the fundamental design principle in polymer membranes for non-aqueous RFBs and our recent efforts on the development of novel plasticized polymer membranes that simultaneously provide high conductivity and tailored mechanical modulus. In one system, mechanically robust crosslinked poly(ethylene oxide) membranes were synthesized and doped with sodium triflate and tetraglyme. The relationships between ion conductivity (reached up to 10⁻⁴-10⁻³ S/cm at r.t.), salt/gel content, glass transition temperature (Tg) and mechanical properties are investigated. The synthesized membranes are mechanically robust with storage modulus maintaining at ~1 MPa from -20 °C to 180 °C even saturated with tetraglyme. In another system, mechanically tailored novel single-ion conducting polymer electrolytes (SICPEs); trifluoromethane sulfonimide (TFSI) functionalized block and graft copolymers are synthesized and investigated. The SICPEs with covalently attaching TFSI moieties to the polymer backbones only allows specific cations, such as lithium (Li) or sodium (Na) ions, to move freely and provide ionic conductivity (i.e. the transference number is close to 1), which is imperative for RFBs. The Li and Na ion conductivity and the mechanical properties with the presence of a plasticizer (non-aqueous solute in RFB) are investigated. RFB performance such as a cross-over behavior is evaluated.

11:15 AM OPEN DISCUSSION

11:30 AM EN04.01.09
Characterization of Mechanical Behavior and Stability of Membranes for Energy Conversion Devices
Claire Arthurs\textsuperscript{1,2}, Douglas Kushner\textsuperscript{2} and Ahmet Kusoglu\textsuperscript{2}; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Lab, United States

Ion-conductive membranes are the core components of electrochemical energy conversion devices (including fuel cells, electrolyzers and flow batteries) which offer a tremendous potential to reshape clean and renewable energy technologies for stationary and transport applications. Key to the sustainable performance of these devices is the concerted improvement in membrane transport and stability, which can be related to their functionality as the polymer solid-electrolyte and separator. Nevertheless, material parameters and operational environment that are optimized for membrane functionality and performance (e.g., ion-exchange capacity and hydration) could undermine mechanical stability. Understanding the interrelation of transport and stability, and how it is affected by structure and environment, is challenging for ion-containing polymers due to the complex polymer-ion-water interactions in a chemically-heterogeneous morphology. While such interactions have been studied for proton-exchange membranes (PEMs) for fuel cells, there is need to extend these investigations to membranes exchanged with various cations and anion-exchanged membranes (AEMs) employed in fuel-cells and electrolyzers. In this talk, the role of structure and hydration in mechanical properties of various ion-containing polymers will be explored to investigate environmental and structural factors governing the membrane’s transport-stability relationship. First, impact of environment on structure-mechanics relationship of cation-exchanged and composite perfluorinated sulfonic acid (PFSA) membrane will be presented, with a focus on the interplay between their mechanical response and hydration behavior. The results will be discussed to elucidate how a membrane’s mechanical properties change due to chemical structure and water-ion interactions. Then, these investigations will be extended to selected AEMs to present a broader picture on ion effects. Lastly, various mechanical properties will be compared and discussed to provide insight into mechanical testing techniques that could best characterize membrane stability relevant to the operation environment in energy conversion devices.

11:45 AM EN04.01.10
Preparation of Anion Exchange Membranes by Friedel-Crafts Bromoalkylation and Crosslinking of Polystyrene Block Copolymers Jong Yeob Jeon and Chulsung Bae; Rensselaer Polytechnic Institute, United States

Anion exchange membrane (AEM) fuel cells have gained significant attention due to the possible use of non-precious metal electrocatalysts which reduce the cost of fuel cells. However, there has been a lack of AEMs simultaneously satisfying high chemical stability, robust mechanical properties and high anion conductivity, under high pH operating conditions. Herein, we suggest a convenient method for the preparation of AEMs by Brønsted acid catalyzed Friedel-Crafts alklylation of aromatic polymers using bromoalkylated tertiary alcohols, followed by amination with trimethylamine. This simple one-step “bromoalkylation” allowed convenient control of both the degree of functionalization and cation tether length, by changing the molar ratio and the structure of the bromoalkylated tertiary alcohol. A series of elastomeric polystyrene-\text{-}b\text{-}poly(ethylene-co-butylene)-b-polystyrene (SEBS) based AEMs with different ion exchange capacities (IEC) and ionic tether lengths were systematically investigated by comparing water uptake and anion conductivity. Since the backbone of the SEBS AEMs are composed of all carbon-carbon bonds, they showed good alkaline stability under 1 M NaOH aq. solution at 80 °C. To enhance the mechanical properties of the AEMs, the hard segment PS units were crosslinked by 1,6-hexanediamine. The crosslinking of SEBS AEMs significantly reduced their water uptake (e.g., 155\% vs. 28\%) preserving IEC and ionic conductivity. Alkaline membrane fuel cell performance was evaluated with the crosslinked SEBS AEM, and a peak power density of 520 mW/cm\textsuperscript{2} was achieved at 60 °C under H\textsubscript{2}/O\textsubscript{2} conditions.
As a promising alternative to proton exchange membrane fuel cells (PEMFCs), anion exchange membrane fuel cells (AEMFCs) based on hydroxide conducting polymers have received great attention in recent years. The high pH operating condition of AEMFCs allows use of non-precious metal catalysts and less expensive metal hardware. Recently, a power density over 1.0 W cm\(^{-2}\) has been achieved for AEMFC approaching close to that of PEMFCs.

One of key requirements for high performance of AEMFCs is anion exchange membranes (AEMs) with high ion conductivity, good chemical stability and mechanical durability. New materials development using novel polymer backbones and side chain ionic functional groups have been extensively investigated over the past decade.

In this presentation, we will present the effects of different structures of polymer backbones and the location of ionic side chains on the membrane properties of AEMs and their device performance in fuel cell and electrolysis. Polymeric made of soft backbone, such as polystyrene-b-poly(ethylene-co-butylene)-b-polystyrene (SEBS), and rigid backbones, such as polyarylenes containing biphenyl and terphenyl core groups (namely BPN and TPN series), have been evolved from my group at RPI over the past years. Because the backbone of those polymers are made of all carbon-carbon bonds, they showed excellent chemical stability under alkaline conditions. The high molecular weights (>100,000 g/mol) of those functionalized polymers also afforded good mechanical strength and high strain when made into film. A perspective of quatern ammonium-functionalized polymers that have been developed from RPI will be presented with emphasis on synthetic strategy and materials performance in AEMFC test condition.

2:00 PM EN04.02.02
Decoupling Mechanical Properties and Ion Conductivity in Supramolecular Stretchable Battery Materials
David Mackanic, Xuzhou Yan, Yi Cui and Zhenan Bao; Stanford University, United States

As soft electronic devices increasingly require stretchable, conformable batteries, safety concerns regarding the use of liquid electrolytes in lithium ion batteries (LIBs) arise. Unfortunately, the canonical tradeoff between mechanical strength and ionic conductivity in polymer electrolytes has forced most reported stretchable batteries to incorporate mechanically weak electrolytes containing flammable liquids within strain engineered structures. Herein, we introduce a supramolecular design as a novel strategy to decouple ionic conductivity from mechanical strength in polymer electrolytes. The supramolecular lithium ion conductor (SLIC) is a block copolymer that includes a hydrogen-bonding domain based on 2-ureido-4-pyrimidone (UPy) and an ion conducting domain based on poly(propylene glycol)-poly(ethylene glycol)-poly(propylene glycol) (PPG-PEG-PPG). By systematically tuning the amount of UPy in the polymer backbone of SLIC, we demonstrate that the UPy domains and the PPG-PEG-PPG domains are orthogonally functional, and that varying the amount of UPy in the backbone has little effect on the ionic conductivity of the polymer. The resulting SLIC polymer containing 23 mol.% UPy in the backbone yields a polymer electrolyte with high resilience (4.9 MJ m\(^{-3}\)) and high ionic conductivity (1.2\times10^{-4} S cm\(^{-1}\) at 25\(^\circ\) C). Implementation of SLIC as a binder material allows for the creation of stretchable Li-ion battery electrodes with strain capability of over 900\% via a conventional slurry process. Impressively, strain capability of 100\% is maintained when the loading of polymer in the electrode film is as low as 20 wt.\%. The supramolecular structure of SLIC allows for intimate bonding at the electrode-electrolyte interface. Good adhesion between the stretchable battery components enables the fabrication of the first intrinsically stretchable LIB. The SLIC battery has a capacity of 1.1 mAh cm\(^{-2}\), an operating voltage of 1.8 V, and functions even when stretched to 70\% of its original length. The method reported here of decoupling ionic conductivity from mechanical properties opens a new route to create highly resilient ion transport materials for energy storage applications.

2:15 PM EN04.02.03
Gel Composite Electrolyte Membrane for Lithium-Metal Batteries
Xi C. Chen\(^{1}\), Yiman Zhang\(^{1}\), Laura C. Merrill\(^{2}\), Michelle Lehmann\(^{3}\), Tomonori Saito\(^{1}\), Jennifer L. Schaefer\(^{2}\), Frank Delnick\(^{1}\) and Nancy J. Dudney\(^{1}\); \(^{1}\)Oak Ridge National Laboratory, United States; \(^{2}\)University of Notre Dame, United States; \(^{3}\)The University of Tennessee, Knoxville, United States

Gel polymer electrolytes consisting of a crosslinked polymer electrolyte swelled with a plasticizer overcome the weakness of low ionic conductivity of typical dry polymer electrolytes. With a large amount of plasticizer, however, the mechanical strength of gel polymer electrolytes is weakened. The poor mechanical properties may render gel polymer electrolytes prone to lithium dendrite growth.
In this work, we fabricate gel composite electrolyte membranes by incorporating lithium-ion-conducting ceramic particles into the gel polymer matrix. The purpose of this work is to test the hypothesis that the high modulus of the ceramic particles helps preventing Li dendrite growth. Our results show that the room temperature ionic conductivity of the gel composite electrolyte is $1 \times 10^{-4}$ S/cm, the same as the gel polymer electrolyte without ceramic. The handleability of the gel composite membrane is significantly improved. Li symmetrical cell cycling performance is evaluated with different ceramic loadings. We also compare the ionic conductivity and Li symmetrical cell cycling performance of gel composite membranes with a single-ion-conducting gel polymer host.

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2:30 PM OPEN DISCUSSION

2:45 PM EN04.02.05
Engineering Scale Simulation of Non-Equilibrium Diblock Copolymer Materials for Battery Electrolytes
Ludwig Schneider and Marcus Müller; Georg-August University, Germany

Diblock copolymer materials exhibit a rich equilibrium phase diagram, qualifying them for applications in fuel cells, filters, and battery materials. Self-assembly of these materials rarely results in the equilibrium structures. Instead, configurations are trapped in long-lived meta-stable states and can be stabilized via cross-linking or cooling below the glass transition temperature of one component. The properties of these structures, such as ion-conductivity and mechanical stability, can deviate from those of the corresponding equilibrium phases.

SOMA, our massively-parallel implementation of the Single-Chain-in-Mean-Field (SCMF) algorithm, enables us to study systems with billions of particles and predict their structure formation, thus unraveling the transport properties of self-assembled diblock-copolymers as a function of volume fraction, $f$. Our investigations show that non-equilibrium morphologies exhibit a large scale fractal-like domain structure that influences the transport properties. The length scale of these structures highlight the necessity of the simulation large system sizes with micrometer scale to obtain bulk properties. We quantify the transport via the tortuosity and the diffusion inside the network phase and show that equilibrium phases overestimate the transport capabilities of random networks.

3:00 PM BREAK

3:30 PM *EN04.02.06
Tuning Self-Assembly and Macromolecular Properties in Ion-Conducting Block Copolymer Systems by Controlling Monomer Segment Distribution
Thomas Epps; University of Delaware, United States

The self-assembly of block polymers (BPs) presents unique opportunities to design materials with attractive chemical and mechanical properties based on the ability of BPs to form periodic structures with nanoscale domain spacings. One area of recent progress in our group focuses on the behavior of tapered BPs in which the segment distribution at the interface between blocks is synthetically varied to tune morphology, domain density profiles, thermal transitions as well as mechanical and transport properties. Two application targets for these materials are lithium-ion conducting membranes for batteries and nanostructured thin films for nanotemplates and barrier membranes. In the first target area, we found that the taper volume fraction and composition allow us to manipulate the self-assembly of salt-doped BPs in a well-defined manner that permits optimization of morphology and ion-content. Additionally, we found that the tapered interfaces influence the glass-transition behavior of the ion-conducting block leading to significant changes in lithium-ion transport (ion conductivity). In the second target area, we found the taper content alters the rate of self-assembly as well as the rate of island/hole formation (and ultimate island/hole size) upon thermal annealing. Additionally, using reflectivity techniques, we probed the domain density profiles as a function of taper composition and linked these profiles to changes in domain spacing and glass transition temperature. Overall, these studies show the versatility of tapering to provide a unique handle for simultaneously optimizing multiple materials properties.
Solid polymer electrolytes (SPEs) have received sustained interest as a potential replacement for liquid electrolytes in lithium ion batteries because they are intrinsically nonflammable, processable, and mechanically robust. In the past decade, polymer networks with dynamic bonds that can undergo associative exchange processes, also known as vitrimers, have been investigated as recyclable and self-healing materials. It is an open question if a dynamic network can provide not only mechanical integrity to suppress dendrites, but also substantial conductivity. Here, we develop a vitrimer for Li ion conduction consisting of triethylene glycol, boric acid, and a lithium salt (LiTFSI). These networks were studied over a range of Li/ethylene oxide ratios and exhibit storage moduli > 1 MPa at room temperature but the ability to flow upon heating. Conductivities up to $10^{-4}$ S/cm were measured in the absence of solvent at 90 °C. The vitrimers also show an interesting phenomena where the network is no longer formed at high LiTFSI concentrations, likely due to anion interactions with boron. We report on conductivity and modulus trends as a function of molecular structure to demonstrate that vitrimer electrolytes are a promising platform for SPEs.

The performance of proton-conducting ionomer membranes is complicated by an intricate interplay between chemistry and morphology that is challenging to characterize and control. Here, we report on a class of perfluoro ionene chain extended (PFICE) ionomers that contain either one (PFICE-2) or two (PFICE-3) bis(sulfonyl)imide groups on the side-chain in addition to a terminal sulfonic acid group. PFICE ionomers are promising new materials, exhibiting greater water uptake and conductivity over a range of relative humidity values compared to prototypical perfluorinated sulfonic acid (PFSA) ionomers. Advanced in situ synchrotron characterization combined with simulations reveals insights into the connections between molecular structure and morphology that dictate performance. Energy-tunable X-rays with sensitivity to sulfur can decipher the unique bonding environment of different protogenic groups on the polymer side-chain. Guided by simulations, X-ray absorption spectroscopy can be sensitive to hydration level and configuration that dictates proton dissociation. In situ resonant X-ray scattering reveals that PFICE ionomers have a phase-separated morphology with enhanced short-range order that persists in both the dry and hydrated state, allowing for improved transport pathways across hydration levels. Furthermore, side-chain chemistry and length can be used as a molecular design parameter to predict phase-separated domain spacing. The enhanced conductivity of PFICE ionomers is attributed to a unique side-chain chemistry and structure promoting hydrogen bonding configurations that facilitate proton dissociation at low water content in combination with a well-ordered morphology that forms transport pathways. Our findings also show how energy-tunable X-rays can reveal additional details on the disordered morphology of well-studied PFSAs. Overall, these results provide guidelines to design new ionomers with improved transport properties and demonstrate the value of in situ characterization methods such as resonant X-ray scattering and spectroscopy for unraveling the structural features in chemically-heterogeneous polymer membranes.

Order-disorder and order-order morphological transitions of block copolymers are important phenomena to consider in mechanical properties and ion transports for various electrochemical devices. Among others, the transitions can often be caused by the addition of ionic liquids (room-temperature “molten” salt), but understanding the role of molecular interactions in the phase stability of the mixture of a block copolymer and an ionic liquid is still limited. To provide a better guiding principle to control phase behaviors, we developed a mean-field theory that accounts for the electrostatic interactions, excluded volume effect, and dielectric response between the species. Our theory compares favorably with observed transitions between the ordered microstructures corresponding to lamellae, hexagonally close-packed cylinders, body-centered cubic lattices, and double-gyroid phases, but it still poses a question about the stability of the gyroid phases. We will also discuss the effect of the dielectric contrast between the species on morphological transitions.
Using Chemical Functionalization to Control the Ion Permeability of 2D Material Based Laminar Membranes
Mark A. Bissett, Wisit Hirunpinyopas, Pawin Iamprasertkun, Jonathan Aze and Robert Dryfe;
University of Manchester, United Kingdom

The popularity of two-dimensional (2D) materials such as graphene and molybdenum disulfide (MoS2) have provided renewed interest in the development of laminar membrane technology. These membranes can be used for a variety of applications including water filtration, desalination, ion exchange, electrodialysis, reverse osmosis, and electrodeionization (EDI). Laminar membranes of two-dimensional materials are excellent candidates for applications in water filtration due to the formation of nanocapillaries that can exhibit a size and charge sieving effect, while allowing high water flux.

Previously we have demonstrated that laminar membranes of MoS2 show outstanding potential for practical applications in energy conversion/storage, sensing, and as nanofluidic devices by tuning their ion permeability by chemical functionalization.1 Chemical modification of these MoS2 membranes has been shown to improve their ionic rejection, however the mechanism behind this improvement is not well understood and further work is needed. To elucidate this mechanism we report the potential dependent ion transport through these functionalized MoS2 membranes.2 The effect of pH, solute concentration, and ionic size/charge on the ionic selectivity of the functionalized MoS2 membranes is also reported. Similarly graphene membranes are produced by simple liquid phase exfoliation possessing a low oxygen content, unlike the GO/rGO material commonly used, and their effectiveness in potential dependent ion sieving applications demonstrated.3 We observe a strong dependence on flake morphology, with decreasing flake size leading to an increase in the number and tortuosity of the nanochannels, resulting in a significant reduction of ion transport. By controlling the number of edge sites and hence surface functional groups this again demonstrates that the surface chemistry of these 2D materials can be used to carefully tune the ion permeability when used to form laminar membranes.

various treatment procedures that lead to an optimized activated product. $^{29}$Si magic-angle spinning nuclear magnetic resonance (MAS NMR) is useful to analyze the local silicate structure (the Q-distribution) in order to monitor the activation process. The Q-distribution is specified by the fraction of resolved Q$n$ resonances where “n” is the number of bridging oxygens (from one to four) in a silicate unit. The silicate composition, deduced from these experiments, provides information about the evolution of HTS’ silicate environment under various activation treatments.

**EN04.03.02**
Removal of Hazardous Dyes from Simulated Wastewater Using Nitro-Oxidized Carboxycellulose Nanofibers Extracted from Coconut Fibers

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Harmful dye compounds found in dyeing industry wastes can have deleterious effects on human health and the environment, especially in developing regions. Also, the accumulation of coconut waste in developing areas poses a need for novel methods for coconut waste utilization. This study transformed waste coconut biomass into a negatively-charged Nitro-Oxidized Carboxycellulose Nanofiber (NOCNF) adsorbent for cationic dye removal in water by using the nitro-oxidation method. Nitro-oxidation has been noted as a simpler and more cost-effective method to extract CNF from raw biomasses compared to conventional methods, such as carboxymethylation and TEMPO Oxidation. In another step, positively-charged NOCNF was synthesized by modification with glycidyltrimethylammonium chloride (GTMAC) for the remediation of anionic dyes. Both the anionic and cationic NOCNF were characterized using FTIR, $^{13}$C CPMAS NMR, WXRD, TEM and SEM. Anionic NOCNF was found to possess carboxylate groups in the range of 0.777 mmol/gram. Moreover, the cationic NOCNF demonstrated 6% nitrogen content, indicating that the cationic charge existed in the form of NH$_3^+$ charge. Adsorption studies were conducted for Basic Red 5 (BR 5) and Malachite green (MG) dyes with anionic NOCNF and cationic NOCNF, respectively. Interestingly, both substrates showed significant removal of their respective dye in the range of 40-75 ppm with a removal efficiency of ~90-75% and ~92-70%. Anionic NOCNF exhibited maximum removal efficiency of BR5 with 100% at pH=4. Moreover, cationic NOCNF presented maximum removal efficiency of Acid Orange (AO) with ~100% at pH=8. The above studies show that coconut waste material is excellent for dye removal after using the simple nitro-oxidation method. Furthermore, this novel approach could be applied to solve the problem of overabundance of coconut waste in developing regions.

**EN04.03.03**
The Use of Sacrificial Graphene Oxide Layer for Inorganic Hollow Fiber Membranes with Superior Permeability

Young Hoon Cho$^1$, Hosik Park$^1$, Ho Bum Park$^2$, Seung-Eun Nam$^1$ and You-In Park$^1$; $^1$Korea Research Institute of Chemical Technology, Korea (the Republic of); $^2$Hanyang University, Korea (the Republic of)

Recently, the ceramic and inorganic membrane materials draw attentions in both conventional and emerging molecular separation applications due to their outstanding mechanical, chemical and thermal stability in various liquid, gas and vapor environment. However, there are several hurdles to compete with conventional polymeric membranes in the market such as high production cost, difficult scale-up, low packing density and productivity. In addition, ceramic membranes for ultrafiltration, nanofiltration and gas separation range need repeated coating, sintering or reaction processes to apply thin separation layers on the surface of porous ceramic substrates to maximize their permeability. Still, the preparation of ceramic composite membranes with both high permeability and nano-size pores is limited for large area production. Here, we newly developed a simple and facile pre-coating method to prepare defect-free, ultrathin film composite ceramic hollow fiber membranes. Prepared composite membranes showed outstanding separation performance compared to membranes prepared by the conventional method. The thin separation layers with the thickness under a few hundreds nanometers were successfully coated on highly porous substrates without any defects and pore-clogging. The results clearly showed superior molecular separation properties of prepared membranes and the potential for the applications in separation processes at harsh conditions such as organic solvents, high feed temperature or concentration.

**EN04.03.04**
Preparation of Cellulose NF Membrane for Selective Separation of Free Fatty Acid and Chlorophyll in Extra Virgin Olive Oil

Yongjun Ahn and Seung-Yeop Kwak; Seoul National University, Korea (the Republic of)
The traditional Mediterranean diet is characterized by the preferential consumption of vegetables, legumes, fruit, nuts, and cereals, and olive oil is the main dietary fat. Extra virgin olive oil (EVOO) is obtained from pressing Olea europea (olive) fruit. The characteristic aroma, taste and color of this oil distinguish it from other edible vegetable oils. The excellent organoleptic and nutritional properties of EVOO and the current tendency of consumers to select minimally processed food, have prompted a re-assessment of its consumption in daily diet. Recently, the consumption of olive oil blended with other refined vegetable oils is increasing for use as frying oil, due to economic reasons and customer desire for taking healthy components. However, as-extracted EVOO is still turbid and opalescent and, contains impurities such as free fatty acid (FFA), chlorophyll and pieces of fruit or stone that can compromise the quality of EVOO since they facilitate hydrolysis, fermentation and can cause the oil to become rancid.

The filtration process is considered to efficiently removes these damaging substances. In particular, nanofiltration (NF) is developed for molecular separation on the basis of size and charge differences. Beyond drinking water production and wastewater treatment, NF technology has also been applied for the separations carried in organic solvents such as in the pharmaceutical, petroleum and food industry. NF membrane can be expected to efficiently separate the damaging substance from EVOO.

Cellulose has emerged as an indispensable membrane material due to its abundant availability, low cost, and environment benignancy. However, this unique molecular architecture also leads to cellulose insolubility in the common organic solvents. Only very few usable solvents are known and those are often highly reactive, toxic or impractical for industrial use. Moreover, cellulose membranes typically have meso- or macro-pores, making them suitable only for ultra- or microfiltration. In previous our research, it was proposed that the morphology of cellulose can be controlled by the cellulose molar mass of the cellulose in an ionic liquid. Comparing to the typical cellulose membranes, cellulose formed from ionic liquid is expected to possess micropores suitable for nanofiltration that can separate from molecular level.

In this study, a simple method is provided to prepare cellulose NF membrane from cellulose hydrolyzed in cellulose, and then it was applied to the selective separation of FFAs and chlorophyll from EVOO. To verify the effects of pore size and surface functionality, a series of cellulose NF membrane with various pore size was prepared, and then they were functionalized by amine group to improve interaction of FFAs. The fatty acid composition and antioxidant content (total phenols and tocopherol) were analyzed to demonstrate the selective separation of the amino-functionalized cellulose NF membrane without a component conversion. To confirm the thermal stability, we observed the smoking point of EVOO filtrated by cellulose NF membrane and compared the smoking point with that of crude and physically refined EVOO. The surface functionalization and pore size of NF membrane significantly influenced the separation efficiency for FFAs and chlorophyll, respectively. It was found that the amine group on the surface of cellulose was necessary to improve the selectivity and adsorption capacity. It also demonstrated that the chlorophyll separation efficiency was optimized when the pore size was smaller than 7 nm. The resulting absorbent selectively removed 90% and 81% of FFAs and chlorophyll, respectively, without the composition change of fatty acids. This study can provide a facile method for enhancing thermal stability of EVOO and thus aid the development of better treatment process for crude oils using cellulose NF membrane.

**EN04.03.05**

**An Insight Investigation towards Aqueously Cathodic Deposition of MOF Membrane**

Heng-Yu Chi, Ruicong Wei and Zhiping Lai; Advanced Membranes and Porous Materials, Saudi Arabia

Electrochemical deposition has been developed and started attracting a number of research attentions in this decade for membrane production. Due to its ease of operation, low cost, and ability for continuous production, it has been widely accepted as a promising approach for large-scale industrial membrane production. Currently, the research in this area is still in its early stage with most efforts being gravitated towards MOF film fabrication. Recently, our group has developed an aqueously cathodic deposition (ACD) approach for ultra-facile membrane production without any post-synthesis treatment. The obtained defect-free membrane exhibits superior performance in C3H6/C3H8 separation. ACD can be extended for other types of MOFs and is considered as an attractive approach for scalable membrane fabrication. As a new approach, the mechanism behind of ACD was not well understood. Here, we conducted a detailed investigation to understand the fundamentals of ACD approach for membrane fabrication. Through this study, we achieved an in-depth understanding of cathodic reactions involved in membrane formation via cyclic voltammetry study. The influence of precursor compositions, current density and counter-electrode were demonstrated. Following these understandings, we are able to ultimately shorten the fabrication time from 60 min to 20 min, tune the thickness of the membrane from 100 nm to 500 nm, and enhance the membrane chemical stability for exceptional performance in gas separations.
Preparation of Perfluorosulfonic Acid Based Composite Membranes for Energy Conversion Devices
Seohhee Lim, Jong-Hyeok Park and Jin-Soo Park; Sangmyung Univ, Korea (the Republic of)

Many of half cell reactions for electrochemically driven energy conversion devices consist of movement of ions and electrons simultaneously during anodic and/or cathodic reactions to complete full electrochemical cells. In addition, ions generated at electrodes move from anode to cathode or vice versa for electron exchanges. Pathway for ions is normally in an aqueous phase. Regardless, the introduction of any aqueous phase in energy conversion devices causes many problems during fabrication, operation, maintenance, and so on. Thus, much efforts have been devoted to develop quasi-solid electrolytes such as gel polymer, ion exchangeable polymers, impregnation of ions in porous matrix and so on. One of major disadvantages to use polymeric electrolytes is significant Ohmic voltage decay due to high areal resistance compared to aqueous phases. An approach to minimize areal resistance of film-type polymeric electrolytes is to make film thickness as thin as possible. Free standing polymeric electrolytes, however, show low mechanical properties. Thus, composite membranes could be used by impregnating polymeric electrolytes into thin porous substrates. In this study, three-layered (electrolyte-skeleton/electrolyte-electrolyte) composite membranes with various thicknesses were prepared. A technique to impregnate polymeric electrolytes into hydrophilic or hydrophobic porous substrates were intensively developed so as to prepare void-free composite membranes. Characterization in terms of ion conductivity, ion exchange capacity, water uptake, dimensional stability, mechanical strength was carried out.

Acknowledgement
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Bacterial Cellulose Based Membrane Electrode Assembly in Microbial Fuel Cells
Mehrdad Mashkour1,2, Federico Poli1, Mostafa Rahimnejad2, Mahdi Mashkour3, Carlo Santoro4, Mohammad Said El Halimi1,5 and Francesca Soavi1; 1University of Bologna, Italy; 2Babol Noshirvani University of Technology, Iran (the Islamic Republic of); 3Gorgan University of Agricultural Sciences and Natural Resources, Iran (the Islamic Republic of); 4UWE, United Kingdom; 5University Abdelmalek Essaadi, Morocco

Microbial fuel cell (MFC) has been nominated as an alternative to nonrenewable sources of energy capable of transforming organic matters directly into electricity by bacterial anaerobic respiration on the anode surface and oxygen reduction reaction on the cathode surface. It is low cost because of exploiting waste matters as fuel. But low electricity generation is a big challenge in this technology [1]. Two pathways are possible for bringing MFC to commercialization: i) increasing electricity generation; ii) using cheaper components like electrode and membrane. In MFCs, membrane play the role of separator for taking anode and cathode apart each other. Anode’s required condition is anaerobic while cathode needs oxygen. Therefore, the membrane should be impermeable to oxygen. On the other hand, the membrane’s capability in transferring hydronium ions or cations from anode to cathode compartment is in high level of importance. Although using membrane results in increase in internal resistance of MFC, but for long-term operation of MFC it can protects cathode against contaminant and microbial biofilm formation on the electrode surface [2].

In single Chamber MFCs the cathode can be used as membrane-less and or membrane assembly electrode (MEA). An MEA is an integrated electrode system resulting in electron and ion transfer to reach cathode surface in presence of oxygen. There are two main positive points in using MEA i) lower internal resistance of MFC in comparison with double chamber MFC; ii) higher durability of SCMFC’s compared to membrane-less ones. Therefore, making a cheap MEA with high performance for MFC is an interesting and vital field of research. Bacterial cellulose (BC) produced by some species of bacteria like *acetobacter xylinum* is a three dimensional network of nano cellulose fibers. The latter can be easily modified by carbon materials and conductive polymers to develop air-breathing cathodes. From this point of view, it has the potential to be used as a cheap substrate for high performance membrane specially compared with Teflon based composite cathodes [3].

Here we report about fabricating a novel cellulose based air-cathode coated with multi-walled carbon nanotubes (CNT) and polyaniline (PANI). Also BC was treated by nano-zycosil (Zyc) to be hydrophobic. The results of the electrochemical test are presented and compared to those obtained with conventional Teflon-based cathodes. Our
work aims at demonstrating new routes to develop a cheap, high performance and green MEA for MFC technology.

Acknowledgments
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References:

EN04.03.08
Magnetically Induced Self–Healing in of Iron Oxide–Poly(ethylene oxide) Nanocomposites Charlotte Teunisse, Sarah Dalakos, Vanessa Swepson, Grace Gionta, Donovan Weiblen, Deniz Rende and Rahmi Ozisik; Rensselaer Polytechnic Institute, United States

Current research aims to quantify self-healing capabilities of iron oxide (Fe3O4) nanoparticle (NP) infused poly(ethylene oxide) (PEO). Iron oxide NPs of varying surface chemistries (bare, aminopropyl triethoxysilane coated, and polyethylene glycol α-, ω–diphosphate coated) are used to prepare nanocomposites of varying concentrations less than 1% by weight. Each sample, in the form of a cylindrical disc, is indented using a LECO M400 Microindenter at five different locations between the center and edge. The indentation site is examined before and after being placed in an alternate magnetic field (AMF) to induce healing. The micrographs of each indent were collected with an Olympus PMEG microscope at the same imaging parameters. Healing efficiency is quantified using visual and software-based image analysis, identifying the percentage of healing as a function nanoparticle concentration and surface chemistry. Multiple methods of software-based image analysis were developed to perform this analysis. Nanoindentation experiments were also carried out to evaluate impact of surface coating and concentration on mechanical properties and viscoelastic behavior of these nanocomposites.

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EN04.03.09
Comb Shaped Hydrocarbon Polymer Electrolyte Membrane for Fuel Cell with Well-Developed Microphase Separation Su Min Ahn1,2 and Tae-ho Kim1; 1Korea Research Institute of Chemical Technology, Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

Comb shaped polymer electrolyte membrane was synthesized by grafting highly sulfonated poly(arylene sulfide sulfone) side chain to poly(arylene ether sulfone) backbone, differing the molecular weight and the density of the side chain. Side chain, synthesized from A-B type monomer, was designed with monofunctional terminus to avoid crosslinking in grafting. Furthermore, side chain is highly sulfonated with one sulfonic acid group per one benzene ring, inducing well-developed microphase separation. Structure-property relationship was investigated by varying the architecture of graft polymer, comparing graft polymer structures with dense, short side chains to those with sparse, long side chains at similar ion exchange capacity. Analyses for proton conductivity, water uptake, dimensional change, and membrane electrode assembly performance have been conducted. Fuel cell performance of graft polymer at 0.6 V resulted in 0.7957 A cm-2 at 100% hydrated condition. Also, graft polymer endured 730 hours before the OCV drop and 17000 wet/dry cycles before reaching 2 mA cm-2, the Department of Energy (DOE) standard of fuel cross over, showing remarkable chemical and physical durability. The synthesized graft polymer may be a promising candidate as a polymer electrolyte membrane for fuel cell application.

EN04.03.10
Tuning Pore Size and Robustness of Membranes Formed by Scalable Self-Assembly of Random Copolymer Micelles Luca Mazzaferrro1, Ilin Sadeghi2 and Ayse Asatekin1; 1Tufts University, United States; 2Massachusetts Institute of Technology, United States
Membrane separations are energy-efficient, simple, and scalable. Yet, their broader use is limited by the separation capabilities of membranes prepared by conventional methods, typically confined to size-based separations. Self-assembly of functional polymeric materials is a powerful method for designing membranes capable of new separations, including the separation of organic compounds of similar size from each other. This can potentially be achieved by membranes that mimic biological pores such as porins, with pores that are only slightly larger than the target solute and functionalized with groups that selectively interact with one compound over another. Our group has developed a method for preparing such membranes by the spontaneous self-assembly of random amphiphilic copolymer in methanol into micelles that are then coated onto a support to form a selective layer of tightly packed micelles. These membranes, produced by a simple manufacturing process, have ~1-4 nm pores lined with carboxylic acid groups that enable charge-based separation of organic solutes. Additionally, the carboxylic acid groups can be converted to a wide range of possible functional groups through coupling reactions. This can provide selectivity towards solutes by affinity. Because of the distinctive geometry and selectivity of these membranes, it is valuable to assess the versatility of this technology. The goal of this study was to tune the pore size by changing the micelle size, and analyze the robustness of these thin film composite membranes. The pore size was tuned by interactions of dissolved metal ions with micelles while the robustness of the system was altered by different crosslinking procedures.

EN04.03.11
Self-Assembling Random Terpolymers Use to Fabricate Membranes with a Tunable Pore Environment
Samuel Lounder and Ayse Asatekin; Tufts University, United States

Water purification is necessary for the well-being of both people and the environment. While membranes are firmly established as the leading water purification technology, they still face a host of challenges that limit their performance. For conventional polyamide nanofiltration membranes, the main challenges are selectivity, fouling, and chlorine sensitivity. In the present work, we created a random terpolymer that can self-assemble into a membrane with a tunable pore environment. We added charge to the pores, which granted the membrane with selectivity comparable to commercial nanofiltration membranes. By virtue of the material, these membranes are also fouling resistant and chlorine tolerant. Self-assembly is defined as the formation of hierarchical structures from simple molecular building blocks. This process is driven by interactions between said building blocks, and can be used to engineer ordered structures ranging from nanometers to micrometers in size. Zwitterions are defined as molecules that contain an equal number of positive and negative charges. This charge disparity grants zwitterions an enormous dipole moment, which leads to powerful electrostatic forces occurring between neighboring zwitterions. These forces drive self-assembly, even in random copolymers with very short zwitterionic segments. In the present work, we show that random terpolymers comprised of zwitterionic, hydrophobic, and zwitterion-philic repeat units self-assemble to form a bicontinuous nanodomain of zwitterionic/zwitterion-philic and hydrophobic sections, each 1-2 nm in size. When these terpolymers are coated onto a porous support to form the selective layer of a thin film composite membrane, the zwitterionic/zwitterion-philic domain acts as a network of nanochannels for the permeation of water and other solutes. Through pragmatic choice of the zwitterionic-philic repeat unit, it is possible to tune the properties of these nanochannels. Here, we show that the random terpolymer poly(trifluoroethyl methacrylyate-r-sulfobetaine methacrylate-r-methacrylic acid) (PTFEMA-r-SBMA-r-MAA) can be used to fabricate nanofiltration membranes that address the challenges faced by conventional polyamide membranes. The presence of charged groups, through dissociated MAA repeat units segregated into these nanochannels, leads to the selective rejection of salts and charged organic compounds. These membranes are also resistant to fouling and exposure to chlorine. Furthermore, we demonstrate that the properties of the nanochannels and the selectivity of the membrane can be further tuned by the functionalization of carboxylic acid groups on MAA repeat units to access additional separations. These features demonstrate the promise and versatility of this new polymer family for a wide range of membrane applications.

EN04.03.12
Study of Structural, Thermal & Electrical Properties of Electrolytes Composites (1-x) CsH2PO4 + xZrO2 For Fuel Cells by Silver Deposition Advanced Electrode
Pawan Kumar1, Deshraj Singh2, Jitendra Singh2, Arvind Kumar3 and Ram S. Katiyar4; 1Gurukul Kangri Vishwavidyalaya, Haridwar, India; 2K.G.K. College, Moradabad, India; 3Kalindi College, India; 4University of Puerto Rico, United States

Composites proton conducting material based on cesium dihydrogen phosphate were prepared and doped with
zirconium oxide and observed the structural, thermal and transport properties of composites proton electrolytes in terms of X-ray diffraction (XRD) analysis, Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Raman spectroscopy and conductivity measurements. We have investigated that the ionic conductivity of undoped CsH$_2$PO$_4$ increases up to three order of magnitude within the transition temperature 230°C to 250°C, which is in small limit range and unstable. We doped ZrO$_2$ with different composition (1-x) CsH$_2$PO$_4$/x ZrO$_2$ (0≤x≤0.4). CsH$_2$PO$_4$ transition temperature range is (230°C -250°C) after doping of ZrO$_2$ its transition temperature range increases from 230°C to 280°C. The stability, ionic conductivity and fuel cell performance were investigated within the temperature range 230°C to 280°C under environments atmospheric humidification. The superprotonic transition of CsH$_2$PO$_4$/ZrO$_2$ Composites was identified with advanced silver electrode by vapor deposition of silver.

EN04.03.13
Design, Fabrication and Characterization of 3D Printed Membrane Structure for Efficient PM Removal
Yejin Kim$^{1,2}$ and SeungBin Park$^2$; $^1$Korea Institute of Energy Research, Korea (the Republic of); $^2$Korea Advanced Institute of Science and Technology, Korea (the Republic of)

3D printing (additive manufacturing) can be applied in various ways because of its infinite versatile approaches in its structure and materials, etc. In addition, the application range can be expanded without restrictions when applied with different material. For this point of view, optimization of printing scheme and printed material property (frame material, structure, pore distribution, shape and particle size etc) with respect to the appropriate purpose could be essential factor for maximizing efficiency of printed output.

In addition, various studies have been carried out on the fine dust (PM 2.5), which is one of the global disasters as an urgent field to understand the generation behavior and occurrence of PM these days. The designed 3d printed structure and defined distribution with the inner flow pattern could be a good tool for understanding the complex action of various factors for removal characteristics with controlled condition.

For this purpose, we have applied various methods to fabricate porous structures of various structures through FDM 3D printing and to obtain basic data for evaluating complex reaction characteristics of precursors for PM secondary particle production.

Here we introduce the relationship between the structural parameters of the reaction kit and adsorption characteristics of the prepared filter were confirmed in two aspects. First, a reaction kit was designed, fabricated and the inner flow characteristics were defined. Second, the 3d printed structures for adsorption/desorption behavior of PM precursor (NH$_3$, SO$_x$) were studied for each physicochemical conditions by using various zeolites with different pore variance as adsorbent, and their reaction characterized through the analysis of adsorption/desorption behavior - breakthrough curve analysis.

We expect that this study on the relationship with the structural parameters of the designed filtration provide important basic knowledge for design efficient membranes for removal of PM.

EN04.03.14
Thermal and Mechanical Analysis of Chemically Stable Aromatic Anion Exchange Membranes
Luke Cherniack, Ding Tian, Jong Yeob Jeon and Chulsung Bae; Rensselaer Polytechnic Institute, United States

Anion exchange membrane (AEM) fuel cells is a promising alternative to proton exchange membrane (PEM) fuel cells through the ability to operate with a non-precious metal catalysis and faster kinetics of the oxygen reduction reaction; however, AEMs are not widely commercialized due to their inferior hydroxide ion conductivity, inadequate mechanical properties, and lack of chemical stability under alkaline conditions. Recently, biphenyl and terphenyl based polymers were synthesized and exhibited favorable electrochemical properties. In this study, the thermal and mechanical properties of these polymers were analyzed by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) to determine their capability of manipulating membrane electrode assembly for fuel cell applications. A two-day annealing process was also performed and studied to evaluate its effects on mechanical properties. Thermal analysis results indicated that these AEMs remained both chemically and mechanically stable within a fuel cell operating temperature range. The glass transition temperature (Tg) of mTPBr and BPBr are 174°C and 188°C respectively. After quaternization, mTPN1 and BPN1 didn’t show a Tg.
Desalination and Nanofiltration through Multilayered Graphene Oxide Membranes on Polymer Substrates
Balgin Zhanibek1, Kurbangali Tnyshtykbaev1 and Zinetula Z. Insepov1,2; 1Nazarbaev University, Kazakhstan; 2Purdue University, United States

In recent years, GO-based filtration membranes have received a lot of attention in the field of filtration technology. In this study, the feature of the multilayered reduced graphene oxide (rGO) membranes on different polymer substrates (Polyvinylidene difluoride (PVDF), Polytetrafluoroethylene (PTFE) and Anodic Aluminum Oxide (AAO) membranes (Millipore) are given. GO powders were prepared from graphite powder by the modified Hummers method. For comparison, GO of Sigma-Aldrich brand was also used. rGO membranes prepared by vacuum filtration and drying of the powders GO in water with the subsequent ultrasonic influence within 30 min. Later GO was deposited on a polymeric PVDF membrane. rGO suspensions and membranes were characterized by Fourier Transformation Infrared Spectroscopy (FTIR) using NicoletiS10 FTIR, Raman spectroscopy, scanning electron, and atomic force microscopy. Filtration abilities were measured by pH meter (Mettler Toledo S20-KS SevenEasy) and desalination rate was measured by Ion Chromatography (Metrohm 930 Compact IC Flex). Experimental salt solution (pH=8.5) was used for desalination experiments. The possibility of efficient rGO/PVDF membranes creating by using GO on the surface in standard polymeric PVDF membranes is shown. rGO/PVDF membranes have the best effectiveness of filtration than standard polymeric PVDF membranes. The increasing of water transportation speed across rGO/PVDF membranes with a decreasing of the sizes of membrane nanochannels are observed. It is experimental fact is explained by a decrease of activation energy of shear viscosity of the liquid in nanochannels.

Water Nanofiltration through 2D Nanomembranes Using Reverse Osmosis Method
Abat Zhuldassov1 and Zinetula Z. Insepov1,2; 1Nazarbayev University, Kazakhstan; 2Purdue University, United States

Fluid flow process in an isolated system at nanometer scale has great fundamental importance in nanofluidics. Nanofiltration process through advanced two-dimensional nanomembranes using reverse osmosis method has a particular interest in water desalination and purification. In this work, computational model was created, in order to simulate a process of water filtration through 2D materials such as graphene, grapheme oxide, MoS2 and BN using molecular dynamics method. All 2D materials had a hexagonal structure, the diameter of pores were between 6 Å and 10 Å. The volume of water containing ions was 28,830 Å³, the volume of water was 15360 Å³. The piston pressure was 3.5 GPa. To assess the structural relationship in the liquid solution, the radial distribution function was calculated. Obtained data have a good agreement with the experimental results. Our computer simulation results clearly indicated that nanomembranes based on two-dimensional materials were able to reject salt ions, providing a high flow of water molecules. The highest water flow rate and lowest salt penetration ratio was observed in MoS2 membranes, due to the low energy barrier and unique pore structure, with alternating hydrophobic and hydrophilic edges. Thus, the computational model of a nanofiltration system using 2D materials and reverse osmosis method was created. Our computer simulation results showed that 2D nanomaterials can be used as new generation desalination membranes. Such membranes are expected to be more energy-efficient in comparison with other modern membranes used today.

Low Temperature Electric Field-Assisted and Conventional Sintering Samaria-Doped Ceria/Alkali Halide Carbonate Ceramic Membranes
Sabrina G. Carvalho1, Eliana N. Muccillo1, Fernando Marques2 and Reginaldo Muccillo1; 1Energy and Nuclear Research Institute, Brazil; 2University of Aveiro, Portugal

Samaria-doped ceria (SDC) oxide ion conductors and mixed alkali salts (e.g., Li, K) were proposed as electrolytes for intermediate temperature (500 °C-700 °C) solid oxide fuel cells and as membranes for high temperature CO2 separation. In this work, dual-phase composite membranes were obtained by two techniques: i) producing a porous GDC pellet using alkali halides as sacrificial pore former, followed by molten carbonate vacuum infiltration, and ii)
electric field-assisted sintering by applying a low voltage at 420 °C to a (75 wt.% GDC+25 wt.% eutectic Li-K carbonate mixture) pressed green pellet. The microstructure of the impregnated porous ceramic and the electrical field assisted sintered pellet were observed by scanning electron microscopy to evaluate the distribution of carbonates. The electrical behavior of the membranes was assessed by electrochemical impedance spectroscopy measurements in the 350 °C-550 °C range, and these data used to draw Arrhenius-type plots. Membranes obtained by electric field-assisted sintering have electrical conductivity higher than those based on impregnated porous ceramics.

EN04.03.19
Neural Network for the Phase Separation of Polymer Mixtures
Issei Nakamura; Michigan Technological University, United States

Polymer-containing liquid mixtures can exhibit macroscopic phase separation and microphase separation. For example, diblock copolymer melts show the phase transition from a homogeneous to a lamellar phase when the temperature is decreased. Molecular simulations such as molecular dynamics and Monte Carlo simulations and thermodynamic theories are conventional approaches to understanding the phase behaviors of polymer mixtures. However, more computationally fast simulation methods that are fairly robust against the choice of force fields and applicable to various phase behaviors are greatly needed because we must analyze the abundant and diverse experimental data obtained concurrently. To address this challenge, we develop deep neural networks (DNNs) as a third approach to assist with the existing theories and simulations and experimental analyses. In this talk, we discuss our new hidden layer that is constructed through coarse-grained mean-field theory and the scaling laws in polymer physics. This characteristic hidden layer enables us to perform the learning process efficiently with relatively small numbers of artificial neurons and provides the DNNs with reasonable predictive power. To demonstrate the efficacy of our DNNs, we will discuss the phase diagrams of polymer solutions, and the salt-free and salt-doped diblock copolymer melts. Moreover, we will show the predictive power of the DNNs by considering some experiments for the lithium salt-doped diblock copolymers such as PEO-b-PS.

EN04.03.20
Anisotropic Proton Conduction in a Coordination Polymer for Fuel Cell Membranes
Ali Javed1, Stephan Wöhlbrandt2, Norbert Stock2 and Michael Tiemann1; 1Paderborn University, Germany; 2Kiel University, Germany

In recent years, fuel cell technology has become an integral part in modern and sustainable concepts of energy storage and conversion. Proton-conducting polymer electrolyte membranes (PEMs) play a key role in this respect. Standard materials such as Nafion tend to be expensive and their proton conductivity is often strongly humidity-dependent. Metal-organic frameworks (MOFs) and other coordination polymers (CPs) have recently attracted attention as potential alternatives [1-3]. Still, profound knowledge of the underlying mechanisms of proton conduction in coordination polymers is scarce. Impedance spectroscopy is a powerful and versatile tool for studying proton conduction in coordination polymers [4]. It is usually applied to powders; we have recently reported on impedance measurements on MOF single crystals [5].

We present impedance spectroscopic studies of proton conductivity in a single-crystalline coordination polymer of composition \([\text{Ba}_2(\text{HSPP})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\) that consists of \(\text{Ba}^{2+}\) ions connected by organic phosphonatosulfonate linker molecules (HSPP\(^4^-\) = \([\text{O}_2\text{PCH}_2\text{N}(\text{H})-\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{]}^4\)). From the crystal structure proton conduction by a proton 'hopping' mechanism could be anticipated [6]. However, the crystal structure also contains non-coordinated water molecules that may affect the proton conductivity. The material forms elongated crystals. We have measured impedance data by varying the temperature, relative humidity, and, especially, the orientation of the single crystal with respect to the contact electrodes. Proton conductivity turns out to dependent on said orientation, which implies anisotropic conduction paths in the crystal structure.

The 73 – 216 µm thick nanostructured membranes based on free two-layer films of nanoporous anodic alumina with pore diameters about 55 nm are discussed to be formed by the two-side anodization in the electrolyte of oxalic acid and further bipolar anodizing. The basic idea of the bipolar anodization is to use a two-chamber electrolytic bath, in which the alumina membrane with Al inclusions was placed as an insulating partition. One of the chamber is filled with the anodization electrolyte (7 % H$_2$C$_2$O$_4$), while the buffer electrolyte (10 % CuSO$_4$) is used in the second chamber. The cathode electrode (−) is placed in the first chamber and the anode electrode (+) is connected to the second one. When the current is switched on (U ~ 55 V), a positive charge appears on one side of the membrane opposite the Al inclusions. The membrane becomes an anode, and anodic oxidation (anodizing) of Al inclusions takes place. The second side of the membrane is charged negatively and becomes a cathode. The recovery of buffer electrolyte cations (Cu$^{2+}$) on the cathode side opposite the Al inclusions was observed with a guaranteed absence of sparks and burn-through of the oxidized layer in these zones. The volume growth coefficient in the conversion of Al to Al$_2$O$_3$ was 1.44 – 1.46. The membranes obtained demonstrated high resistance to cracking and the ability to save the form at high temperature exposures. Highly ordered nanostructured nature of their cellular porous morphology that can be controlled by electrochemical and temperature modes of the electrochemical anodizing process appears to have considerable promise.

The development of advanced hybrid materials based on polymers from biorenewable sources and mineral nanoparticles is currently of high importance. Lignin has a great potential as a sorbent for removal of transmission metals and organic pollutants from wastewater. By combining lignin with inorganic carrier, organic-inorganic hybrid composites with improved sorption properties can be obtained.

Lignin-based composites were synthesized by crosslinking of different amount of lignin on silica. For that, lignin solutions with concentration from 1 to 10 % were adsorbed on mesoporous silica surface. FTIR spectroscopy confirmed the creation of lignin layer on silica surface. Concentration of immobilized lignin was estimated using thermogravimetric analysis. Specific surface area and changes in pore size distribution with increasing of lignin concentration as composites component were estimated.

Synthesized hybrid composites were found to be effective as sorbents for the recovering of cobalt(II) from aqueous solutions.

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In quest of a viable method for low-cost carbon capture and release, the integration of photoswitchable elements into porous materials in order to modulate their CO$_2$ adsorption and release properties on demand is of great interest. Serving as an attractive stimulus, light is naturally abundant, and it could be harnessed to replace conventional energy-intensive regeneration techniques. Among the light-responsive elements, azobenzenes interconvert from the thermodynamically stable form of trans to the cis configuration by rotation of the aromatic rings around the -N=N- bond upon UV and visible light irradiation, respectively. Considering amine functional groups as proven CO$_2$ adsorptive sites, the CO$_2$ capture and release
properties of an adsorbent could be tailored by the interplay between amine sites and photoresponsive azobenzene groups in a porous structure. Simply put, by accommodating amine groups on the far end of azobenzene pendant groups, the exposure of active amine sites to CO$_2$ molecules are regulated by light-driven isomerization. Despite the investigation of several photoresponsive systems for CO$_2$ adsorption, various challenges are yet to be addressed prior to achieving a concrete material design. More precisely, the photoresponsive adsorbents usually suffer from delayed response upon irradiation, largely due to sterically hindered azobenzene isomerization in the relatively small pore structure. Moreover, their cavity is partially occupied by the photoswitchable pendant groups, leading to lower CO$_2$ uptake capacity.

To tackle these constraints, in this work, we first conduct a structural optimization of the porous material hosting azobenzene groups by means of density functional theory (DFT) methods. In the following steps, the *cis*-isomer and *trans*-isomer contents in light-responsive adsorbents are determined by NMR after certain irradiation time to validate the effectiveness of irradiation. The CO$_2$ uptake amount of the as-synthesized adsorbents are subsequently investigated by applying UV and visible light for a range of time and intensity. Further characterizations including XRD, FTIR, BET surface area and UV-vis spectroscopy are also performed to discuss the effect of photoswitching on CO$_2$ adsorption properties of adsorbents.

SESSION EN04.04: Novel Membrane Structure and Chemistry for Controlled Transport I
Session Chairs: Yifu Ding and Haiqing Lin
Tuesday Morning, December 3, 2019
Sheraton, 3rd Floor, Fairfax A

8:30 AM *EN04.04.01
Thin-Film Composite Membranes by Interfacial Polymerisation for Molecular Separations in Aqueous and Organic Liquid Systems Andrew Livingston; Imperial College, United Kingdom

Membranes have had a huge impact in molecular separations in aqueous systems, especially desalination. The workhorse membrane for reverse osmosis is the thin film composite (TFC) membrane formed by interfacial polymerisation. This presentation will focus on research into understanding the formation and function of TFC membranes for both desalination and Organic Solvent Nanofiltration (OSN) [1].

Advanced imaging and tomography has been used to understand the morphology of commercial TFC membranes and the flow paths through them [2]. To better reveal the relationship between fabrication and function, ultra-thin polyamide films (sub-10nm) have been formed by interfacial polymerisation and then used to fabricate composite membranes [3]. These ultra-thin polymer films 6-8nm thick are strong, and can be several centimetres in lateral dimension. Interestingly, the morphology of these films can be manipulated from smooth to highly crumpled, by adjusting the reaction conditions. The films can be applied in liquid filtration, and show unprecedented permeances in organic solvents, and high rejection of all solutes. Because the films can be prepared free-floating at a liquid-liquid interface, they can be used to explore how composite membranes function. This reveals that through matching of rough and smooth films with different supports, it is permeance rather than surface roughness, that determines fouling. Further, we find that the support permeance has a strong effect on the composite membrane permeance, for the same film placed on different supports [4], and that that the support rather than the thin film separating layer of a composite membrane leads to physical aging and flux decline. These insights are counter-intuitive to current thinking.

Intrinsic microporosity can be introduced into the ultra-thin polymer films through selection of contorted monomers for interfacial polymerisation. These intrinsically microporous polymer nanofilms provide higher interconnectivity of pores and greater permeance than films obtained from planar monomer systems [5]. Finally, the potential for ultra-high permeance membranes to impact on actual molecular separation processes will be discussed, including the relative merits of selectivity, permeance and stability [6].

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<p><em>Nanofiltration – A Critical Review</em>, Chemical Reviews, 114, 10735 – 10806 (2014)<br>Klosowski, MM, McGilvery, CM, Li, Y, Abellan, P, Ramasse, Q, Livingston, AG and Porter, AE, “Micro-to nano-scale characterisation of polyamide structures of the SW30HR RO membrane using advanced electron microscopy and stain tracers”, J.Mem.Sci (2016) 520 pp.465-476</p><p>3) Karan S, Jiang Z, Livingston AG, Sub-10 nm polyamide films with ultrafast solvent transport for molecular separation, Science 348 pp 1347-1351 (2015)</p><p>4) Z Jiang, S Karan, AG Livingston “Water transport through ultrathin polyamide nanofilms used for reverse osmosis” Advanced Materials (2018) 30 (15), 1705973</p><p>5) Jimenez-Solomon, MF, Song, Q, Jelis, KE, Munoz-Ibanez, M and Livingston, AG, Polymer nanofilms with enhanced microporosity by interfacial polymerization, Nature Materials Vol 15, Issue 7, pp.760-767 (2016)</p><p>6) Shi B, Marchetti P, Peshev D, Zhang S and Livingston AG Will ultra-high permeance membranes lead to ultra-efficient processes? Challenges for molecular separations in liquid systems J.Mem.Sci (2017) 520 pp.35-47</p><p><strong>9:00 AM EN04.04.02</strong><br>Polystyrene-Based Gyroid Membranes—A Progress Report Paul Meyer⁴, Qingjun Zhu⁴, Xingwen Yu², Nathaniel Lynd¹, Manthiram Arumugam² and C. Grant Willson¹,²; ¹The University of Texas at Austin, United States; ²The University of Texas at Austin, United States</p><p>Block copolymers (BCPs) readily self-assemble into highly ordered morphologies, such as lamella, cylinders and gyroids and are promising materials for applications in microelectronics, catalysis, and membranes. The cylinder morphology has been extensively studied for isoporous membranes with channels on the nanometer length scale, but this morphology suffers from alignment issues: The channels must be oriented perpendicularly to the surface while also extending through the full thickness of the membrane. Gyroids, on the other hand, form networks of isoporous channels that are connected in all three dimensions, thereby avoiding the orientation challenge of cylinders. Thus, the gyroid morphology is of great interest, but the fabrication of such materials presents a challenge with both synthesis and processing.</p><p>The synthesis and characterization of three different gyroid-forming di-block copolymers will be presented. In these materials, one block is made of the easily degradable polylactide (PLA) and the other features a functionalized polystyrene block to offer rigidity. Anionic polymerization in conjunction with organocatalytic ring-opening polymerization was used to provide BCPs with low polydispersity and a high degree of control over the relative volume fraction. These materials can be made reproducibly and on multigram scales.</p><p>Thin films of the materials were studied before and after the removal of the PLA block and processes were developed to overcome wetting layers that close the surface of the gyroid film. Atomic layer deposition was explored as a means of changing both the pore dimension and surface energy. These BCPs have been combined with a polyethersulfone (PES) layer to generate composite membranes composed of a thin, selective gyroid layer and a mechanically strong, porous PES layer. These composite membranes were investigated for applications in batteries, gas separation, and water purification.</p><p><strong>9:15 AM EN04.04.03</strong><br>Selectivities and Permeabilities in Anisotropic Membranes for Gas Separations Juan M. Restrepo-Florez¹,², Martin Maldovan¹ and Katie Dongmei Li-Oakey³; ¹Georgia Institute of Technology, United States; ²University of Wisconsin–Madison, United States; ³University of Wyoming, United States</p><p>The design and synthesis of membranes for gas separations has mainly relied on isotropic materials. Physically, isotropic materials control the magnitude of the flux and separations in isotropic systems occur as a result of different flux magnitudes of the species of interest. We have recently introduced a novel approach for the design of membranes based on anisotropic materials in which flux directional control is induced to perform separations. Remarkably, the use of anisotropic materials provide membranes in which selectivities and permeabilities are spatially dependent. In this talk, we discuss the capabilities of these novel anisotropic membranes for gas separations under planar configurations and provide unprecedented selectivities for separations of binary mixtures. We also discuss how anisotropic materials can be used to improve the separation ability of current isotropic membranes, pushing the limits of existing technologies. Furthermore, we discuss the existence of a unique trade-off relation between selectivity, permeability and collected fraction of permeate. Our findings are applied to the separation of binary mixtures of O₂/N₂ and H₂/CH₄.</p>
Polymer Membranes with Spatially Controlled Gas Permeability
Adrienne Blevins1, Lewis Cox2, Jason Killgore3 and Yifu Ding1; 1University of Colorado Boulder, United States; 2Montana State University, United States; 3National Institute of Standards and Technology, United States

Polymer membranes utilize the difference in permeability between molecules and ions to achieve molecular separation. For both gas separation and desalination processes, the transport of permeates through polymeric barrier layer films occurs through a solution diffusion process. Typically, the transport is modeled as one-dimensional, i.e. along the thickness direction of the barrier layer. However, recent evidences suggest that these films are often heterogeneous in terms of structure and composition. The effect of spatial heterogeneity, both in terms of length scale and spatial arrangement, on the transport behavior (especially permeability) remains unclear. Besides homogeneous membranes, recent developments in mixed matrix membranes aim to use more permeable additives (e.g. metal organic framework or MOF particles) to enhance the permselectivity of the matrix membranes.

In this work, we demonstrate a new type of polymeric membrane with tunable, well-defined, spatially heterogeneous permeability. This is achieved by photopatterning over a two-stage thiol-ene polymer network, which leads to spatially varying rubbery and glassy networks with nearly identical chemistry but different permeability. This talk will discuss the materials formulation; photopatterning with regards to both resolution and spatial arrangements; mechanical, and gas transport properties of these films. Further, the effects of both domain size, interfacial profile, and volume fraction of the glassy regions on the overall gas permeability of the membrane will be compared with composite models. Besides their potential applications in molecular/ion separation, the films are promising in areas of encapsulating nanodevices that require spatially varying permeability.

Ion Partitioning, Mobility, Permeation, Conduction and Association in Polymeric Membranes—A Unified Picture
Viatcheslav Freger1,2; 1Technion- Israel Institute of Technology, Israel; 2Technion–Israel Institute of Technology, Israel

Despite the wide use of ion-rejecting and ion-conducting polymeric membranes in processes such as nanofiltration (NF), reverse osmosis, electrodialysis (ED) separations, membrane electrolysis and fuel cells (FC), understanding ion transport and selectivity still presents a challenge. Mean-field models of charged nanopores (e.g., Donnan or Poisson-Boltzmann) have been the standard for last few decades, yet they fail to reproduce correctly some observed trends, e.g., multi-ion separations in NF or ion specificity in ED. These difficulties can be traced back to inherent flaws of mean-field models in charged low-dielectric media. On the other hand, simple phenomenological models with adjustable ionic permeabilities work well, but require ad hoc composition-dependent parameters and the physics behind this dependence remains obscure.

Here, we abandon the standard mean-field nanopore picture and introduce a simple solution-diffusion model of a homogeneous NF membrane that treats the strong departures from mean-field by adding ion association effects in a manner of classical Bjerrum theory. The model consistently explains our recent elaborate NF data for NaCl-CaCl₂ mixtures [1] and other published data, e.g., a high portion of nominal ion-exchange capacity in FC membranes inactivated by presumable “condensation” (association) of counter-ions on fixed charges [2]. It also addresses the fact that, in a non-mean-field treatment, ion uptake and mobility are no more decoupled (like in the Donnan model) and must be computed in a consistent manner from the same physical picture.

The results emphasize the importance of non-mean-field effects in general and ion association in particular for correct modeling of ion uptake, permeation and conductance in polymeric membranes. Our analysis also highlights the fact that simple continuum electrostatics is unable to supply an accurate quantitative description of effects such as association and solvation, for which the new model offers a simple and approximate yet physically sound and transparent way to treat the problem and define relevant ion-specific parameters.

**11:00 AM EN04.04.06**

**Borosulfate Anhydrous Proton Conducting Electrolyte Membranes** Matthew D. Ward, Brian Chaloux and Albert Epshteyn; U.S. Naval Research Laboratory, United States

Proton exchange membrane fuel cells are a potential zero emission power source to reduce and replace dependency on fossil fuels. While research and development efforts to date have concentrated on materials and systems that either function below the boiling point of water (25-100 C) or systems where the conductive medium is a ceramic or glass requiring very high temperatures (> 500 C), materials and systems that operate at intermediate temperatures (150-300 C) have received considerably less attention. Moving to this temperature regime can provide a number of advantages, including the requirement of a lower catalyst loading, reduced potential for catalyst poisoning, and reduced complexity from removing bulky and costly humidification systems, while also allowing for the use of lower cost non-precious catalysts. One of the key challenges to operating fuel cells at intermediate temperatures is the search for new proton conducting electrolyte materials that show conductivities >10^{-3} S/cm and good chemical stability under these conditions. Here we have explored a new family of solid-acid compounds, the borosulfates, as proton conducting electrolytes. These materials show promise, with measured conductivities on the order of 10^{-4} S/cm at ambient temperatures/humidity with further increases in conductivity to 10^{-3} S/cm above 100 C. TGA measurements show that these materials are stable to temperatures above 300 C, and we also demonstrate that this material can be consolidated into dense pucks at mild temperatures using a standard hydraulic press.

**11:15 AM EN04.04.07**

**Understanding the Correlation between Polymer Structure and Gas Transport Properties Using a Free Volume Model** Haiqing Lin; SUNY Buffalo, United States

Understanding the structure and property relationship is critical to designing high-performance membrane materials for gas separation, particularly for materials with balanced permeability and selectivity above or near the upper bound. Herein, a modified free volume is adapted to describe the upper bound for the separation of several gas pairs, such as O2/N2, He/CH4, CO2/CH4, and H2/CO2. The results are compared with conventional activation energy model reported in the literature. More importantly, this model can be used to predict the structure of polymers with targeted separation properties on demand. I will demonstrate that for the separation of specific gas pairs, polymers with specific free volumes can achieve the best performance. Such an understanding may be useful for the design of membrane materials through data mining or machine learning.

**11:30 AM EN04.04.08**

**Determination of Intrinsic Polymeric Membrane Permeability Using a Combined Experimental–Simulation Approach** Marielle Soniat1,2, Sarah Dischinger1,2, Lien-Chung Weng1,2, Daniel J. Miller1,2, Adam Z. Weber1,2 and Frances Houle1,2; 1Joint Center for Artificial Photosynthesis, United States; 2Lawrence Berkeley National Laboratory, United States

Membrane stability is a crucial determinant of the performance and lifetime of energy storage and conversion devices such as batteries, fuel cells, and photoelectrochemical CO2 reduction (CO2R) devices. In direct methanol fuel cells (DMFC) and CO2R devices, membrane stability is compromised by methanol, which solvates many polymeric membrane materials. Stability can be assessed by evaluating membrane permeability over time, with constant permeability suggesting a stable material and allowing for stable device performance. However, permeabilities obtained from experimental data are often average values and may include the effects of swelling, liquid-membrane boundary layers specific to the device architecture, and changing material properties. This talk reports a combined experimental-simulation study of methanol permeation through Nafion to determine intrinsic permeability, building on our prior modeling work examining time-dependent sorption in this system. Experiments provided independent measurements of swelling, sorption, and time-dependent permeation. Computational fluid dynamics simulations were used to generate an independent estimate of boundary layer thickness in the experimental system. A multiscale reaction-diffusion model was constructed using these data, and stochastic simulations were used to predict the intrinsic membrane permeability as well as apparent permeability for comparison to the experimental data. Deviations of experimental data from theoretical predictions using a standard permeation model as the system approaches equilibrium are explained. The approach we used is general, and is valuable for understanding and predicting the kinetics of structure-property-performance changes for polymeric membranes.
Microporous Polymer Derivatives for Energy-Efficient Gas Separations Katherine Mizrahi Rodriguez, Alexander Liu and Zachary P. Smith; Massachusetts Institute of Technology, United States

Current industrial gas separations, such as CO2 removal from natural gas, rely primarily on energy-intensive and environmentally unfriendly processes. Polymer membranes offer a promising alternative due to their potentially lower energy costs and ease of operation, but they are infrequently deployed because of performance limitations of currently available polymers. In this work, the effect of backbone functionalization and polymer packing structure on transport performance was investigated for a high-performance polymer of intrinsic microporosity, PIM-1. Through post-synthetic modification reactions, the PIM-1 backbone was altered in various ways. First, carboxylic acids (PIM-COOH) and amines (PIM-NH2) were introduced to promote hydrogen bonding and improve the affinity between the polymer and CO2. Second, bulky protecting groups (PIM-PROT), which could subsequently be removed to manipulate packing structure, were also considered. A facile and time-efficient PIM-1 hydrolysis method has been developed, yielding solution-processable PIM-COOH with greater than 90% conversion. Transport measurements reveal that when converted to PIM-COOH, permeability decreases and selectivity increases for CO2-related gas pairs, while, when converted to PIM-NH2, permeability and selectivity for CO2-related gas pairs both decrease. These trends are mechanistically evaluated through a suite of materials characterization tests including surface area measurements and positron annihilation lifetime spectroscopy (PALS). Additionally, a deconvolution of sorption and diffusion up to high pressures (i.e., > 30 bar) is presented to assess how changes in backbone chemistry and packing structure influence transport behavior. Moreover, plasticization behavior is presented. The PIM-COOH sample shows reduced plasticization resistance as compared to PIM-NH2, and these results are likewise assessed from the framework of the solution-diffusion model.

Mechanisms Controlling Molecular and Ion Transport through Polymer Membranes Alexei Sokolov1,2; 1Univ of Tennessee, United States; 2Oak Ridge National Laboratory, United States

We present an overview of mechanisms controlling molecular and ion transport in polymer membranes. Molecular permeability is controlled by solubility and diffusivity. Elastic forces provide the major resistance to molecular diffusion. The polymer shear modulus G, the size of the molecule R, and available free volume define the energy barrier controlling molecular diffusion through a polymer membrane. This leads to the exponential dependence of diffusion on molecular size [1] and provides the basis for the size-sieving selectivity approach used in most of the glassy membranes for gas separation. We show that Anderson-Stuart model [1] provides reasonable description of molecular diffusion in many polymers. However, when molecular size are comparable (e.g. CO2, N2, O2), selectivity in solubility becomes the most important parameter controlling selectivity of molecular permeability through the polymer membrane. It also provides the main selectivity for transport through rubbery membranes where elastic forces have rather low energy barrier due to much lower G. We show examples of some rubbery polymers where by tuning molecular solubility one can significantly improve selectivity for permeability of CO2 vs N2 [2,3].

In the case of ion transport, coulombic interactions provide additional resistance for ion diffusion. The energy barrier in that case varies inversely with the ion size. As the result the energy barrier for ion transport has a non-monotonous dependence on the ion size. Indeed analysis of the energy barrier controlling ion diffusion in polymerized ionic liquids has a minimum, and increases sharply for small ions, such as Li, due to strong coulombic interactions, and then increases with ion size for large ions, such as TFSI, due to elastic forces [4,5]. We demonstrate that Anderson-Stuart model [1] can describe well the energy barrier controlling ion diffusion in polymers. We suggest that this additional coulombic term is the major reason for improved water desalination performance by polymer membranes containing attached ions. We also demonstrate that the ion conductivity in polymers is strongly affected by ion-ion correlations (the so-called Haven ratio) that might reduce the ionic conductivity by more than 10 times [4,5]. At the end we propose polymer structures that might provide significant
ionic conductivity at ambient temperature even in the dry state.


2:00 PM EN04.05.02
Tunable Poly(Ethylene Glycol)-Based Network Polymer Membranes for Simultaneous CO2 and H2S Removal from Natural Gas Daniel Harrigan, Benjamin Sundell and John Lawrence; Aramco, United States

Processing sub-quality natural gas remains an economic and environmental challenge, especially as natural gas demand increases. Toxic and/or corrosive sour gas contaminants, such as hydrogen sulfide (H2S) and carbon dioxide (CO2), must be removed from methane (CH4) to meet pipeline specifications. Gas separation membrane technology offers a low cost alternative to traditionally energy intensive adsorption-based separations. This work describes a series of hydrophilic network polymer membranes synthesized for sour gas applications. Oligomeric poly(ethylene glycol) (PEG) of varying molecular weight was reacted with stoichiometric amounts of a trisiloxane crosslinker to create highly crosslinked amorphous gels cast directly on top of membrane supports. Polymer network structure was confirmed by FTIR, DSC, and DMA. Thermal characterization showed dramatic increases in polymer Tg as PEG chain length between crosslinks decreased from 2000 Da to 200 Da, transitioning from rubbery to glassy around 600 Da. Predictably, gas permeabilities decreased over the same range of PEG molecular weights due to the higher crosslink density and corresponding network rigidity. However, pure gas CO2/CH4 followed a bell-shaped trend with maximum selectivity achieved by the 600 Da PEG membrane, subverting expected tradeoff relationships. High pressure mixed gas permeation tests performed at 800 psi with simulated sour gas feeds containing up to 20% H2S by volume demonstrated superior membrane performance and stability of the PEG-based materials compared to commercial controls. The highest performing PEG membrane exhibited 3.0 times higher H2S permeability and 1.9 times higher H2S/CH4 selectivity than cellulose acetate as well as 1.8 times higher CO2/CH4 selectivity and 1.2 times higher H2S/CH4 selectivity compared to commercially available Pebax. Finally, we explore the amenability of this technology to thin film processing to improve membrane productivity.

2:15 PM EN04.05.03
Understanding the Role of Architecture, Polarity and Charge Spacing in Precise Network Polymerized Ionic Liquids on Aggregation and Ionic Conductivity Christopher Evans, Qiujie Zhao and Chengtian Shen; University of Illinois at Urbana-Champaign, United States

We have investigated nearly identical linear and network PILs containing precise linker lengths between ammonium cations. Two different linker chemistries, either an 11 atom hydrocarbon (HC) or 11 atom ethylene oxide (EO) chain, to vary the polarity. Wide-angle X-ray scattering measurements revealed that the ionic aggregation peaks were less intense in the EO systems, consistent with a more polar chemistry providing better ion solvation. Network PILs of both HC and EO linkers had a more pronounced ionic aggregation peak intensity than their linear counterparts, indicating that polymer architecture impacts ion clustering. In addition to a more pronounced aggregation peak, the EO network showed a two order of magnitude increase in conductivity relative to the linear analogue at Tg + 10 °C. Conversely, linear and network PILs with HC linkers show identical Tg normalized conductivities. In the HC networks, we systematically increased the length from 4 to 12 carbons and observed pronounced odd-even effects on Tg and conductivity which shifted as much as 50 K and 2 orders of magnitude, respectively, by adding one carbon between ionic sites. This systematic study provides a new insight on how polymer architecture, polarity, and precision can influence aggregation and transport of ions in PILs.

2:30 PM EN04.05.04
Molecular Design of Polymerized Ionic Liquid Membranes for the Separation of Toluene/Heptane Grant S. Sheridan and Christopher M. Evans; University of Illinois at Urbana-Champaign, United States

Precise network polymerized ionic liquid membranes (PILMs) with tethered imidazolium cations, variable anion, and controlled crosslink density were developed to understand how molecular structure impacts solubility and diffusion in the context of toluene/heptane separations. Switching the anion from tetrafluoroborate (BF4) to
bis(trifluoromethane)sulfonimide (TFSI) led to a 25 K drop in the glass transition temperature, concomitant increase in penetrant diffusion coefficients, and increased solubility of toluene relative to heptane. Reducing crosslink density led to an increase in toluene swelling, while heptane uptake remained relatively low and constant. Differences in toluene and heptane diffusion coefficients exhibited a maximum selectivity at intermediate crosslink density. It is hypothesized that a fully crosslinked network has a mesh size small enough to impede transport while lower crosslink densities allow toluene to swell the system to a greater extent in contrast to heptane. The interplay of diffusion and solubility effects lead to a non-monotonic trend in selectivity, which will inform the design of membranes as effective organic liquid separations media.

2:45 PM EN04.05.05
Supported Ionic Liquid Membranes Using π Electron Cloud Interactions for Specific Separation

Sumith R. Wickramasinghe, Ronald Vogler, Mahmood Jebur, Mohanad Kamaz and Arijit Sengupta; University of Arkansas, United States

Development of membranes for highly specific separations is challenging and will depend on specific surface interactions. Here we have investigated the feasibility of using ionic liquids and polyionic liquids containing imidazolium groups trapped within the pores of a membrane (supported ionic liquid membrane) to separate compounds with differing p-electron cloud densities due to their interactions with pi-electron clouds. In this study, these supported ionic liquid membranes are used for the separation of stereoisomers, amino acids as well as similar heterocyclic compounds. A 0.45 micron pore size polypropylene microfiltration membrane is used to trap 1-hexyl-3-vinylimidazolium bromide within the membrane pores. The separation of furan and thiophene in hexane (organic solvent) and cytosine, guanine, and thymine in water (aqueous solvent) has been investigated. The specificity for separation was found to be related to the affinity of the ionic liquid towards the p electron cloud density and extent of conjugation in the solute. Polyionic liquids that are formed from 2-vinyl pyridine or 4-vinyl pyridine are used to separate stereoisomers. The ability of the polyionic liquids to separate stereoisomers at ambient temperature indicates their potential for energy-efficient separations of similarly structured compounds with varying pi-electron clouds. The incorporation of ionic liquids and polyionic liquids into the membrane is verified using infrared spectroscopy and/or imaging with scanning-electron microscopy. The results obtained here indicate that membranes for highly specific separations could be developed based on p electron cloud interactions.

3:00 PM BREAK

3:30 PM *EN04.05.06
Advanced Membrane Characterization Enabled by Molecular Layer-By-Layer Deposition of Polyamides

William D. Mulhearn, Peter A. Beaucage, Velencia J. Witherspoon, Ryan C. Nieuwendaal and Christopher M. Stafford; National Institute of Standards and Technology, United States

The state-of-the-art membranes for desalination are comprised of thin film composites where the permselective layer is a thin, interfacially polymerized polyamide. Although effective, the rapid polymerization rate and reaction conditions produce films with rough surface structures and chemical heterogeneity, which precludes some exquisite characterization techniques for probing thin and ultrathin films. In 2011, we proposed a paradigm shift in how these types of membranes are fabricated, where the selective layer is created layer-by-layer through a reactive deposition process. Even so, there are still many challenges yet to overcome, from membrane support design to membrane characterization. In this talk, I will describe our efforts to meet these challenges through judicious experimental design and materials selection. Specifically, I will describe efforts to measure the internal structure of these membranes using resonant and non-resonant x-ray scattering, as well as measure the dynamics of water and salt in these membranes using quasi-elastic neutron scattering and electrochemical impedance spectroscopy, respectively. Then, I will discuss how these measurements have challenged our thinking in how these materials selectively pass water while rejecting salt.

4:00 PM EN04.05.07
Highly Permeable MOF-Based Mixed Matrix Membranes for Energy-Efficient CO2 Capture

Shouliang Yi1,2 and David Hopkinson1; 1U.S. Department of Energy – National Energy Technology Laboratory, United States; 2Leidos Research Support Team, United States

Membrane-based separation processes have been considered as one of the most promising technologies for post-

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combustion carbon capture due to lower energy consumption, smaller environmental footprint, and the potential to be installed in an existing power plant as a true bolt-on technology. However, polymeric membranes, currently considered the most promising candidate for industrial application, are limited by a trade-off upper bound between the productivity and separation efficiency. Metal–organic frameworks (MOFs) are promising candidates to overcome the limitations of polymer membranes, by fabricating mixed matrix membranes (MMMs) due to their high surface area and porosity, diverse functionalities and tunable pore structures.

In this presentation, several MOF-based mixed matrix membranes were developed by incorporating different types of MOF crystals (e.g., surface functionalized Uio-66 and nano-sized zeolitic imidazolate framework-8) into a variety of polymers (e.g., polymers of intrinsic microporosity, poly(ether-block-amide) copolymers, polymer blends composed of PIM-1 and MEEP80 polyphosphazene) for highly energy-efficient carbon capture. The mixed gas permeation results showed that these MOF-based mixed matrix membranes have displayed superior separation performance (the CO2 permeability of up to 6000 Barrers with a CO2/N2 selectivity of higher than 22), surpassing the 2008 Robeson upper bound. Testing these membranes using real flue gas streams at the National Carbon Capture Center (Wilsonville, Alabama) will also be presented. We demonstrated that the excellent CO2/N2 separation performance makes MOF-based mixed matrix membrane a very promising platform for practical CO2 separations.

4:15 PM EN04.05.08
Separation Performance of Modified Novel Poly(ether-b-amide) Membranes for Acid Gas Removal from Natural Gas John Yang1, Daniel Harrigan1, Milind M. Vaidya2, Sebastien A. Duval2 and Michelel Ostraat1;
1Aramco Services Company, United States; 2Saudi Aramco, Saudi Arabia

Natural gas use as a primary energy source has expanded rapidly over the past several decades. A 69% increase in worldwide consumption for natural gas over the 2012 level is anticipated by 2040. However, raw natural gas from some wells can contain significant amounts of other gas components, including H2S, CO2, N2, water, and other hydrocarbons (C2+). Among these contaminants, the acid gases (H2S & CO2) must be treated to avoid corrosion of transportation pipeline and to meet the standard pipeline specifications of sales gas. Polymeric membrane-based technologies have gained great industrial attention for natural gas upgrading and treatment due to their relatively energy-efficient and environment-friendly footprint. Current commercial rubbery polymer membranes for acid gas removal from natural gas, such as poly(ether-b-amide) copolymer (PEBAX), show a decline separation performance under industrially relevant feed streams and testing conditions. In this talk, we describe a modification of the polymer backbone by blending and crosslinking to develop novel PEBAX membrane materials for simultaneous CO2 and H2S removal from natural gas. Modified PEBAX membrane materials comprised of crosslinked polyethylene glycol as a CO2-pohilic additive were produced via either UV crosslinking of diacrylated-terminated polyethylene glycol or chemical crosslinking of a diisocyanated-terminated polyethylene glycol by controlling crosslinking moieties and crosslinked networks in the membrane matrix. High-pressure pure and mixed sour gas transport properties of these modified PEBAX membranes were investigated as a function of loading, feed pressure, temperature, and gas composition at moderate to high H2S% concentration. The modified PEBAX membranes demonstrate improvements in gas separation performance (16% and 12% increase in H2S/C1 and CO2/C1 selectivities) and enhanced membrane stability (64% and 100% increase in mechanical strength and swelling resistance) compared to neat PEBAX membrane under industrially relevant feed streams and testing conditions (e.g. feed pressure of 800 psi and 20% H2S). Based upon the enhanced membrane performance, this modified PEBAX membrane material can be a potential candidate in combination with amine absorption system for acid gas separations from natural gas.

4:30 PM EN04.05.09
Spatially Directed Immobilization of Kinetically Matched Enzyme Cascades in Membrane Flow Nanoreactors Deniz T. Yucesoy1,1, Susrut Akkineni1, Candan Tamerler1,1,2, Bruce Hinds1 and Mehmet Sarikaya1,1,1;
1University of Washington, United States; 2University of Kansas, United States

Enzymatic pathways that perform multi-step biochemical reactions in biological cells constitute a crucial part of life. Biomimetic reconstruction of these metabolic pathways by incorporating multiple enzymes and relevant cofactors in a confined environment holds tremendous promise for sustainable green synthesis of fine chemicals e.g., pharmaceuticals, biofuels, and consumer products, as well as developing efficient biomolecular devices. Controlled localization of enzyme immobilization onto support platforms, however, remains a major challenge. In metabolic pathways, enzymes are spatially coupled to prevent unfavorable side-reactions, eradicate inhibitory products and channel metabolites sequentially from one enzyme to another. Biomolecular assemblies mimicking natural cascades
can be reconstructed using monolithic mesoporous anodized aluminum oxide (AAO) membranes that allow sequential mass transport of catalytic products between spatially immobilized enzymes under convective flow. Here, we developed a peptide-guided approach for spatially controlled immobilization of a bi-enzyme model, L-Lactate dehydrogenase and Formate Dehydrogenase, with high precision for cascadic biosynthesis. Each enzyme is fused with a solid-binding peptide to direct self-directed immobilization across the membrane that facilitates sequential production of L-lactate with the concomitant regeneration of nicotinamide adenine dinucleotide (NADH). Catalytic turn-over rates of immobilized enzymes are found to be consistent with homogeneous solution rates. The 85% overall sequential reaction efficiency is achieved at a flow rate that kinetically matches the residence time of the slowest enzyme. Furthermore, 84% of initial catalytic activity is preserved after 10 days of continuous operation. Peptide-guided immobilization described herein is an effective strategy to build robust bioreactors and diagnostic devices involving cascadic systems. The study was supported by NSF-DMREF program through the grant DMR-1629071 and NSF-CBET Program through the grant 1460922.

SESSION EN04.06: Novel Membranes for Enhanced Water Treatment
Session Chairs: Yifu Ding and Haiqing Lin
Wednesday Morning, December 4, 2019
Sheraton, 3rd Floor, Fairfax A

8:45 AM *EN04.06.01
Modifying Ion Transport in Nanoporous, Ionic Lyotropic Liquid Crystal Polymer Membranes via Situ Polymerization of Reactive Counterions in the Pores
Michael McGrath, Samantha Hardy, Andrew Basalla, Gregory Dwulet, Bryce Manubay, Zhangxing Shi, Hans Funke, Doug Gin and Richard Noble; University of Colorado, United States

Cross-linked, ionic lyotropic (i.e., surfactant) liquid crystal (LLC) assemblies have periodic, uniform-size, charged pores in the 0.7–1.0 nm range that allow them to be used as new type of polymer membrane material for molecular size separations in water. Ordered, 3D-nanoporous LLC networks with a type I bicontinuous cubic (Q) phase can be prepared from an imidazolium bromide-based gemini LLC monomer blended with glycerol. These Q assemblies can be readily processed and polymerized into supported thin-film composite (TFC) membranes that have 0.96-nm-wide annular pores with fixed cationic imidazolium sites in the walls and mobile bromide counterions in the pore interior. After exchange of water for glycerol in the pores, the resulting TFC Q membranes can exclude dissolved molecular solutes and small salt ions from water via a combination of size sieving and charge repulsion effects in the pores. In addition to water purification, these charged, nanoporous membranes may be useful for selective ion conduction applications, such as separator membranes for aqueous flow batteries. However, one of the liabilities of this ionic membrane material is that the mobile counterions can be easily exchanged with other anions from external salt solutions, thereby resulting in unwanted changes in effective pore size and water/salt transport properties during application. Herein, we show that the cationic pores of this cross-linked Q LLC material can be modified by exchange of the original Br– ions in the pores with polymerizable organosulfonate anions, followed by in-situ polymerization of the reactive counterions inside the Q pores. The resulting ordered ‘snake-in-cage’ nanocomposite was found to be highly resistant to ion-exchange: the formed anionic polymer was found to remain inside the nanopores even when the bulk material is exposed to concentrated (i.e., 1 M) aq. salt solutions for long periods of time. After polyanion formation inside the pores, the LLC material loses its overall ion-exchange capacity, presumably due to ionic cross-linking between the cationic pore walls and the anionic groups on the confined polymer chains. However, the pore environment remains ionic, as confirmed by water and salt sorption measurements. Aqueous ion transport tests on TFC membranes made from the modified Q material with polyanion chains in the pores show that salts such as MgCl2 and K2SO4 permeate through at significantly different rates than unmodified TFC Q membranes with mobile counterions in the pores. This relatively simple modification procedure provides a new way to modify and stabilize the transport properties of nanoporous ionic LLC networks for use in selective ion transport applications. The relative merits and avenues for control of this approach will be discussed.

9:15 AM EN04.06.02
Facile Grafting of Zwitterions on Membrane Surface Using Bio-Inspired Polydopamine
Haiqing Lin and Nima

Final Program 1/13/2020 560
Shahkaramipour; SUNY Buffalo, United States

Water purification membranes usually suffer from surface fouling, which dramatically decreases water permeance. The fouling is often mitigated by hydrophilizing the membrane surface, such as coating by hydrophilic zwitterions (ZW) and poly(ethylene glycols) (PEGs). We demonstrate a facile method to graft the ZWs and PEGs onto the membrane surface by co-depositing with dopamine. Dopamine can be easily polymerized to polydopamine (PDA), which can covalently bind ZWs or PEGs containing acrylate or amine functional groups through Michael Addition. Specifically, acrylate-terminated compounds include sulfobetaine methacrylate (SBMA) and PEG-diacrylate (PEGDA), and amine-terminated SB-amine and PEG-diamine were co-deposited with dopamine onto the silicon wafers and ultrafiltration (UF) membranes. The effect of the composition of coating solutions and coating time on the coating layer thickness, compositions, and hydrophilicity are investigated. The coating can deposit a layer of 10 – 50 nm containing 30 – 72% ZW or PEG. The effect of coating and surface chemistry on the membrane properties (including molecular weight cut-off and water permeance) will be systematically investigated to derive the structure/property relationship.

9:30 AM EN04.06.03
Zwitterionic-Containing Ultrathin Hydrogel Selective Layer for Fouling-Resistant Ultrafiltration Membranes
Alice O. Aguiar¹, Timothy M. Gronet¹, Ilin Sadeghi² and Ayse Asatekin¹; ¹Tufts University, United States; ²Massachusetts Institute of Technology, United States

Membrane fouling by organic compounds is still one of the main challenges faced by membrane separation processes. Advanced fouling-resistant membranes can be obtained by increasing the hydrophilicity of the membrane surface. Hydrogels are materials that can absorb large quantities of water and swell, which makes them inherently fouling resistant. Zwitterions, defined as neutrally charged molecules with equal numbers of cationic and anionic groups, and very high dipole moments, exhibit strong hydration layers and, accordingly, excellent fouling resistance. These properties make hydrogels, especially those incorporating zwitterionic groups, promising membrane materials. However, the applicability of hydrogels as fouling-resistant selective layers of thin film composite membranes has been hindered by the lack of a fabrication process that allowed for the formation of a thin, defect-free hydrogel layer on a porous support. We have recently demonstrated a new method, namely Interfacially Initiated Free Radical Polymerization (IIFRP), to address this challenge. In IIFRP, the monomer and photoinitiator are separated into two immiscible phases. The aqueous phase is impregnated into a porous support. Its surface is then covered with an organic phase containing a photoinitiator and exposed to UV light. The ultrathin hydrogel selective layer, as thin as ~80 nm, is then formed at the interface of the two phases, at the membrane surface. The goal of the present study was to explore the incorporation of zwitterionic (ZI) groups into hydrogel selective layers obtained by IIFRP. We have shown that the incorporation of ZI moieties can further increase membrane fouling resistance and improve membrane properties such as hydrophilicity and permeability. The partial substitution of poly(ethylene glycol) diacrylate (PEGDA) units in the hydrogel layer with the zwitterionic monomer sulfobetaine methacrylate (SBMA) led to an increase in permeance of almost an order of magnitude (from 3.9±0.4 L/h.m².bar to 34.7±0.8 L/h.m².bar). Moreover, although this substitution for SBMA also decreased the crosslinking density of the hydrogel, the rejection properties of these membranes remained essentially constant (99.2±0.6% and 98.7±0.6% myoglobin rejection, respectively). Furthermore, the zwitterionic-hydrogel membranes exhibited higher fouling resistance to oil emulsions compared to both commercial membranes and the zwitterion-free hydrogel membranes. Consequently, zwitterionic-containing ultrathin hydrogel selective layers obtained by IIFRP are very promising materials for fouling-resistant ultrafiltration membranes.

9:45 AM EN04.06.04
Development of Novel Scheme for Molecular Modeling of Membrane Separation with Multi-Component Feed Solution
Hayato Higuchi and Hiromitsu Takaba; Kogakuin University, Japan

Membrane has been applied to various separation systems, in particular, for the separation of aqueous or organic solvents. membrane separation is considered promising for reducing CO₂ emission in terms of energy efficiency. For a development of more efficient membrane process, better understanding of separation mechanism of solvent including multicomponent species is of fundamental. Molecular modeling becomes a powerful tool for prediction of membrane performance and design of membrane materials for particular separation systems. Our group has reported a novel simulation scheme of molecular dynamics for the permeation of feed solution through nano porous membranes. Molecular dynamics of multi component species in the feed, however, is still difficult to be simulated.
because a feed concentration of multicomponent such as ions cannot keep at a constant in our simulation techniques as well as other conventional non-equilibrium molecular dynamics scheme. In this paper, to model multicomponent solutions through nanofiltration or reverse osmosis membranes, we will present a novel molecular dynamics technique that can control the feed concentration including multicomponent species at constant. This simulation technique is completely new and first methodology that could model multicomponent solution systems in membrane separation from atomistic level, as long as our knowledge. We will report that this simulation technique works well and can produce the permeation of multicomponent feed solution. The flux and solute moleculars selectivity were calculated and compared to the theoretical values to examine the validity of our proposed scheme.

10:00 AM BREAK

10:30 AM *EN04.06.05
Controlling Water and Ion Transport in Hydrated Polymer Membranes via Chemical Functionality
Yuanyuan Ji, Hongxi Luo, Kevin Chang and Geoffrey M. Geise; University of Virginia, United States

Providing sustainable supplies of purified water and energy is a critical global challenge for the future, and polymer membranes will play a key role in addressing these clear and pressing global needs for water and energy. Controlling rates of water and/or ion transport in these membranes is critical for efficient separation processes (e.g., water purification or dialysis) and energy technologies (e.g., flow batteries or reverse electrodialysis). Much remains unknown about the influence of polymer structure on intrinsic water and ion transport properties, and these relationships must be developed to design next-generation polymer membrane materials. Here, we report and discuss measurements and modeling related to the influence of chemical functionality on rates of water and ion transport in hydrated polymers. Our results demonstrate how polymer properties (e.g., backbone rigidity, functional group type, and/or polarizability) can be engineered to enhance selective transport via thermodynamic and kinetic contributions to the transport process.

11:00 AM EN04.06.06
Nanostructured Thin Metallic Films on Polymeric Membrane Support for Reactions and Separation
Michael J. Detisch, John Balk and Dibakar Bhattacharyya; University of Kentucky, United States

Metallic thin films were deposited onto commercial ultrafiltration (UF) membranes to produce composite structures which show promise both for separations and for catalysis applications. Magnetron sputtering was used to deposit thin films of tantalum and MgPd alloy on top of polysulfone (PSf) membranes. The thin Ta films were found to have significant effects on flux and separation properties of the membranes. The composite membranes with MgPd films were subsequently dealloyed to produce nanoporous Pd, which performs well as a catalyst for wastewater remediation applications. Both types of composites will be presented here.

The addition of just a thin (10 nm) layer of Ta to the surface of the UF membrane was found to dramatically alter its properties as a membrane. Membrane flux dropped from 180 LMH/bar for the base UF PSf to 10 LMH/bar for the Ta composite system. Dye tagged dextran used as a model compound for the determination of molecular weight cutoff (MWCO). The UF PSf was found to have a MWCO above 70 kDa while the Ta composite membrane showed a MWCO below 5 kDa. Modifying the rejection characteristics of a membrane with only a 10 nm added layer is a valuable technique, especially as tantalum is a corrosion resistant metal. This makes this composite membrane applicable to both solvent based separations and separations in corrosive environments.

For the membranes with the MgPd film, a subsequent dealloying step in water was performed to remove the Mg component of the film and create a nanoporous film of Pd. This generates a high surface area, sponge-like structure of interconnected nanowires known as ligaments with characteristic size of <10 nm. The nanoporous palladium film was used as a catalyst with hydrogen gas for the degradation of pollutant compounds in wastewater. Specifically, PCB’s were dechlorinated while permeated in a water solution under pressurization with 5% hydrogen gas (remainder argon). In permeation testing over 60% of PCB-1 was degraded in solution with a single pass through the composite membrane at 40 LMH. Adding a high surface area nanostructure like a nanoporous metal to the surface of a membrane in this way produces a composite structure that can drive reactions as solutions are permeated through the membrane, giving favorable reaction rates. Furthermore, since this nanostructure is produced spontaneously as the MgPd alloy is dealloyed in water, production is straightforward and reproducible.

11:15 AM EN04.06.07
Direct Contact Membrane Distillation (DCMD) Using a Composite Electrospun Nanofiber Membrane for
Water Desalination Application Mahmoud Baniasadi, Momena Monwar and Francisco Cubas; Georgia Southern University, United States

Every year more than three million people die from water-related diseases. Having access to clean and good quality drinking water is a continuous challenge in our world. Increasing the world’s population together with the declining the water tables and increasing the salinity of water resources, resulting in a crisis that is already a major concern, while the situation getting worse every year.

Among various water desalination membrane technologies, Membrane Distillation (MD) is an emerging thermally-driven, membrane-based desalination technology highly suitable to treat hypersaline solutions. MD is a thermally driven process involving a nano/microporous, hydrophobic membrane through which only water vapor can diffuse. Compare to other membrane technologies, MD is a compact and low energy separation technology (the temperature requirement for MD is ~70°C). Although MD has been investigated by researchers, still it cannot compete with other technologies such as reverse osmosis (RO), mainly due to lower production rate, energy efficiency, consistency performance, energy efficiency, and fouling resistance to be named.

In the present study, modified PVDF electrospun nanofiber membrane composites with various support structures were studied for DCMD application. Hydrophobicity of the nanofiber membranes was investigated and different filler and parameter setting of the electrospinning process has been optimized in order to optimize the performance of the nanofiber membrane in the water desalination process. Surface modification of the nanofibers has been investigated using atomic force microscopy (AFM), in order to correlate the nanostructure of nanofibers, with the performance of the nanofiber membrane in DCMD. In order to enhance the performance of the system, nanofibers decorated with different nanoparticles were used to increase the hydrophobicity of the membrane. surface treatments were considered as another approach to enhance the performance of the desalination system using electrospun nanofiber membrane.

11:30 AM EN04.06.08
Water Filtration through Nanomembranes Actuated by Surface Acoustic Waves Zamart Ramazanova1, Zinetula Z. Insepov2,1,3 and Kurbangali Tnyshykbaev1; 1Nazarbayev University, Kazakhstan; 2Purdue University, United States; 3National Research Nuclear University MEPhI, Russian Federation

Nanofiltration technology for water desalination and other fluids purification from salts, germs, bacteria and viruses are based on the so called Nanopumping (NP) effect, when a fluid flow through nanomembranes and nanochannels is actuated using surface acoustic waves (SAW) is presented.

The paper considers processes of water nanofiltration through a carbon nanomembrane using SAWs under different RF powers and frequencies. A prototype device was build using LiNbO3 piezoelectric substrate and carbon nanomembranes on the substrate. The process of nanofiltration consisted of filtration of droplet volume of 3, 5 µl and in using SAW transducers with different frequencies from 34 to 58.2 MHz, with power range 0.1-1.23 W. The process of nanofiltration of water includes the processes of droplet moving, atomization and passage through nanopores.

We analyzed optimization of the basic characteristics of a SAW device, selection the optimum operating parameters of the SAW device and fabrication working prototype of the SAW device. This work is devoted to the development of an active model of the SAW device that demonstrates the work on water filtration using nanomembranes, in which liquid motion is driven with the help of sufficiently powered SAW. The dependences of the travel time of droplet moving and atomization of water on the power, the frequency vs. time, frequency vs. volume of the droplet are established.

It is shown that with increasing of power and frequency of SAW, the filtration process proceeds rapidly and has a power-law character. We investigated this problem both experimentally and numerically in 3D using COMSOL Multiphysics software.
Bunching and Immobilization of Ionic Liquids in Nanoporous Metal–Organic Framework

Anemar Bruno Kanj, Rupal Verma, Modan Liu, Julian Helfferich, Wolfgang Wenzel and Lars Heinke; Karlsruhe Institute of Technology, Germany

Room-temperature ionic liquids (ILs) are a novel class of designer organic solvents with unique properties of great interest in energy storage, supercapacitors and ion-based sensors and electronics. Metal-organic Frameworks (MOFs) are a unique class of designer nanoporous functional-material platforms compound of metal ions and organic linkers.

In our investigation of dynamic properties of IL embedded in porous hosts of MOF, specifically [BMIM][NTf2] in HKUST-1, we observe a drastic change in ion mobility from combined analysis of molecular dynamics simulation and experiment.

We found at low loading of ILs in MOF, ions drift in MOF pores along external electric field, forming a homogeneous flow; whereas at increased IL loadings, collective field-induced interactions of cations and anions lead to transient blockage of ion transport, suppressing ion mobility and tremendously decreasing the conductivity. At extreme loading as IL fills MOF pores, cations and anions travelling in opposite directions bunch-up to form a dense, inhomogeneous, and immobilized IL layer.

Novel molecular-level dynamics insights into IL in nanoconfinement provide guide lines in tuning of quantitative structure-property relationships of IL materials.

Our work is published as:
Bunching and Immobilization of Ionic Liquids in Nanoporous Metal–Organic Framework
Anemar Bruno Kanj, Rupal Verma, Modan Liu, Julian Helfferich, Wolfgang Wenzel, and Lars Heinke
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Polybenzimidazole-Derived Carbon Molecular Sieves with Microcavities and Ultra-Microporous Channels
Achieving Superior Membrane H2/CO2 Separation Properties

Hien Nguyen1, Maryam Omidvar1, Liang Huang1, Cara Doherty2, Anita J. Hill2 and Haiqing Lin1; 1University at Buffalo, United States; 2CSIRO, Australia

Membrane technology is highly attractive for H2/CO2 separation for pre-combustion CO2 capture, which requires membrane materials with both high H2 permeability and H2/CO2 selectivity at 100 – 300 °C. Herein, we present carbon molecular sieve (CMS) membranes with superior H2/CO2 separation properties via the pyrolysis of polybenzimidazole (PBI, a leading polymer for H2/CO2 separation). We thoroughly investigated the effect of the pyrolysis temperature on physical properties (pore size, d-spacing, density, solubility, diffusivity) and H2/CO2 separation properties of the CMS films. PBI exhibits H2 permeability of 27 Barrers and H2/CO2 selectivity of 14 at 150 °C, while the CMS films pyrolyzed at 600 °C, 850 °C, and 900 °C exhibit H2 permeability of 370 Barrers, 190 Barrers, and 54 Barrers at 150 °C, respectively, and their corresponding H2/CO2 selectivity of 8.9, 16, and 80, respectively. The pyrolysis forms micro-cavities leading to high gas permeability and ultra-microporous channels leading to strong size-sieving ability, which is also confirmed by the Positron Annihilation Lifetime Spectroscopy (PALS). As the pyrolysis temperature increases from 600 °C to 850 °C and then 900 °C, the free volume element size increases from 5.08 Å to 5.46 Å first and then decreases to 4.90 Å. When tested with a mixture containing 50% H2 and 50% CO2 at 150°C, CMS pyrolyzed at 900 °C show H2 permeability of 39 Barrers and H2/CO2 selectivity of 53, which surpasses the Robeson’s upper bound for H2/CO2 separation at 150 °C. The film shows stable mixed-gas separation performance for 40 h. When water vapor of 0.31 mol% is introduced, the H2 permeability slightly decreases to 37 Barrers while the H2/CO2 selectivity remains the same. The mixed-gas H2 permeability increases to 39 after the water vapor is removed. The stability and robust H2/CO2 separation properties demonstrate the potential of PBI-derived CMS for practical H2 purification and CO2 capture.
Design of Enhanced CO₂ Selective Inorganic Membranes

Fumiya Hirosawa and Hiromitsu Takaba; Kogakuin University, Japan

In this study, we investigate the separation properties of several type zeolite membranes by NEMD for CO₂/CH₄ separation, and suggest the ultra-selective membrane structure for CO₂ by utilizing the effect of grain boundary on ternary separation systems. In the non-equilibrium molecular dynamics (NEMD) simulation, a single crystal membrane model and two types of polycrystalline membrane models were considered. In the polycrystalline membrane models, two patterns were examined, one in which grain boundary is present inside the zeolite crystal and the other in which the grain boundary is exposed on the surface of the zeolite crystal. In the upper part of the membrane models, the gas molecules were made to appear at regular intervals to keep the partial pressure constant, and the gas molecules which permeated through the membrane were deleted at the lower part of the membrane. Our NEMD results indicates that the presence of grain boundary could increase the selectivity, which means that a control of grain boundary is a key factor to enhance the selectivity.

On the other hand, conventional natural gas is multi-component gas including trace components e.g. hydrocarbon, and there is a concern about the effect of the trace components for membrane performance. In addition to that, grain boundaries in inorganic porous membranes are known to degrade membrane performance, however, the detailed information of effect on selectivity for multicomponent gas systems still difficult to predict prior to the permeation test. The NEMD simulation is an atomistic-scale modeling, thus this can easily apply to the prediction of permeability and selectivity in multicomponent gas systems. The effect of trace components for membrane performance can be also investigated using NEMD. Since the structure of the membrane can be arbitrarily modeled in the NEMD simulation, it is possible to investigate the behavior of the multicomponent gas in the zeolite membrane having grain boundaries by using the NEMD method. In the conference, we will suggest an ultra-selective zeolite membrane based on the interesting phenomenon that the selectivity is enhanced by the structure of grain boundaries.

2:15 PM EN04.07.04
Propylene/Propane Separation by Advanced Mixed Matrix Membranes

Yang Liu¹, William Koros¹, Mohamed Eddaoudi², Zhijie Chen², Youssef Belmabkhout², Chen Zhang¹ and Gongping Liu¹; ¹Georgia Tech, United States; ²KAUST, Saudi Arabia

Membrane-based propylene/propane separation can reduce the operation cost in petroleum refining and petrochemical industries; however, developing advanced membranes with promising performance is still challenging due to the close size (~0.15 Å difference) between these two components. We hereby address such a critical scientific question by a novel strategy: first, attention to detailed conformational differences accessible to propylene and propane; next, identification of a suitable MOF pore-aperture to exploit the accessible conformational differences; thirdly, matching polymer properties with the MOF to achieve promising performance.

Specifically, with both C-C single bonds rotated (double eclipsed conformation), the C₃H₈ molecule exhibits its minimum end-on essentially triangular shape but with a rotation energy barrier. Our strategy is to design/screen a “triangular” pore-aperture to allow only the double eclipsed C₃H₈ conformer to pass through, effectively preventing all other C₃H₈ conformers from diffusion jumps. This combination of factors leads to a very low C₃H₈ diffusivity. On the other hand, the more compact C₃H₆ molecule can pass through the pore-aperture with relative ease. According to our theoretical calculations based on transition state theory, a membrane with such desired pore-aperture can offer a C₃H₈/C₃H₆ diffusion selectivity over a thousand. We further identified a MOF, Zr-fum-fcu-MOF, possessing the desired contracted triangular pore-aperture and fabricated mixed-matrix membranes using this MOF as an efficient filler. The fabricated hybrid membranes display very attractive C₃H₆/C₃H₈ separation performance, far beyond the current trade-off limit of polymer membranes. Back-calculations using composite theory suggests the MOF displays a diffusion selectivity, like the ideally targeted, above 1000. This is the highest value reported for the C₃ pair to date, and we refer to this phenomenon as “conformation-controlled molecular sieving effect”. Furthermore, we optimized the membrane performance by matching the polymer properties with the MOF to (i) achieve higher C₃H₆/C₃H₈ separation efficiency, and (ii) overcome the plasticization effect. The developed membranes show record performance on C₃H₆/C₃H₈ separation at high pressures (~ 900 kPa), surpassing all mixed matrix membranes reported by far. Our work establishes a novel bottom-to-up strategy to develop membranes for gas separation.

2:30 PM BREAK
3:30 PM EN04.07.05
Correlation of Hydrogen Diffusion in Pd Membrane—A First-Principles Calculation Chaoping Liang1, Haoran Gong1 and Dingying Dang2; 1Central South University, China; 2University of Kentucky, United States

Pd membranes are widely used for hydrogen separation and purification attributed to their excellent combination of H selectivity and permeability. During (de)hydrogenation process, a large number of vacancies forms in the α Pd-H solid-solution phase and β-Pd hydride phase, so-called superabundant vacancies (SAV).1 The H atoms will be trapped near the vacant sites, which leads to a complexed H diffusion behavior.2 Recently, many researchers found the (de)hydrogenation process can also promote the multiplication of dislocations and nanotwins.3 However, the transport properties of H in the defected Pd membranes have yet to be well understood.

In present work, we use Pd vacancy as a typical example to study the correlation effect of a defected zone on the H diffusion in Pd membranes. The results show a strong biased interstitial diffusion around the Pd vacancy. The H is prone to sink into the first nearest neighbor shell of Pd vacancy. The second nearest neighbor shell, which has a very low jump rate, prevents the reverse diffusion of the H atoms. Using Koiwa’s matrix method,4 we have derived an analytical formula for the H diffusion around the vacancy. The correlation effect is then estimated for H diffusion as a function of Pd vacancy concentration. Our findings could possibly clarify the uncertainty on the H diffusion coefficient in pure Pd and also shield lights on the interstitial diffusion in other defected systems or alloyed cases.


3:45 PM EN04.07.06
An Ultra-Facile Aqueously Cathodic Deposition Approach for MOF Membrane Fabrication Ruicong Wei, Heng-Yu Chi and Zhiping Lai; King Abdullah University of Science and Technology, Saudi Arabia

Electrochemical deposition has emerged as a novel approach to fabricate MOF films. This approach requires relatively minor or none pre-treatment of the substrate, shorter synthesis time, and milder synthesis condition. It also allows for continuous production which acts as a major advantage compared with other methods for industrial scale-up. As a promising approach, research on electrochemical deposition of MOF is still at its infant stage with most of the efforts being focused on thin film production, only a few works have been published for membrane fabrication. The deposition procedure and set-up are mostly delicately controlled such as careful selection of electrolyte and reference electrode, using double electrolyte cell to eliminate the disturbance of the reactions occurred on the counter electrode, and prolonged post-synthesis treatment, which makes this approach challenging to be used for scale-up production. In addition, little publication has used this approach to achieve satisfactory performance in gas separation with both high permeance and selectivity.

Here, we developed an aqueously cathodic deposition (ACD) approach to fabricate ZIF-8 membrane without addition of any supporting electrolyte or modulator. The fabrication process used 100% water as solvent and a defect free membrane was obtained in only 60 min without any pre- or post-synthesis treatment. The membrane exhibited superior performance in C3H6/C3H8 separation with 180 GPU C3H6 permeance and 142 selectivity, making it sit at the upper bound of permeance vs selectivity graph, outperforming majority of the published data up to 2019. Notably, this approach uses water as the sole solvent, adopts an extremely low current density (0.13mA/cm²), and employs an ultra-facile apparatus set-up, enabling an attractive way for environmentally friendly, energy efficient and easily scalable MOF membrane fabrications. This approach also opens a door for aqueously electrochemical deposition of MOF membrane in the future research.

4:00 PM EN04.07.07
Structure Tailoring of Hierarchical Fibrous Composite Hydrophobic Membranes for State-of-the-Art Desalination Performance in Membrane Distillation Yunxia Hu, Xiaochan An and Baolei Xie; Tianjin Polytechnic University, China

Membrane distillation (MD) displays superiorities to alleviate the ever-increasing freshwater crisis through seawater desalination and/or wastewater recycling. However, MD faces critical challenges of fabricating high-performance membranes. Our study introduced a novel hierarchical fibrous composite (HFC) hydrophobic membrane with great
achievements in elevating the MD performance. This HFC membrane comprises of a thin active dense layer with nanofibers for the maximum mass transfer and a thick support layer with microfibers for the minimum heat transfer. By tailoring the structures of both active and support layers to solve the trade-off between mass transfer and heat transfer during the MD process, the optimized HFC membrane could obtain the reported highest water flux of as high as 79.21±4.17 L m⁻² h⁻¹ and salt rejection higher than 99.9% using 3.5 wt% NaCl as a feed under the temperature difference of 40°C in the direct contact membrane distillation (DCMD).

4:15 PM EN04.07.08

Fabrication of Novel Janus Membrane for High Temperature Oxygen Separation and Water Thermochemical Reduction

Yudong Chen, Xiao-Yu Wu, Georgios Dimitrakopoulos and Ahmed F. Ghoniem; Massachusetts Institute of Technology, United States

Mixed ionic and electronic conducting (MIEC) membranes have been applied to increase the efficiency of oxygen separation, and water and carbon dioxide thermochemical reduction [1, 2]. Both surface reactions and bulk diffusion can impact the oxygen flux depending on the operating conditions. Efforts have been focused on developing new membrane materials, i.e., doped perovskites and dual-phase materials, and catalysts to accelerate the oxygen permeation fluxes.

Herein, we present a novel Janus membrane [3] concept for MIEC oxygen permeable membranes, which have different properties on the two surfaces to favor the respective surface reactions based on thermodynamic considerations. The high oxygen chemical potential side consists of a material with high oxygen vacancy formation energy which favors oxygen incorporation or water reduction, while the material on the low oxygen chemical potential side favors oxygen evolution and reaction with fuel. As a result, this Janus membrane can achieve higher performance compared to membranes of uniform chemical compounds when surface reactions are the rate-limiting step. To demonstrate the concept, this study investigates the co-production of hydrogen (H₂) and syngas (a mixture of H₂ and CO) from H₂O-splitting and methane (CH₄) partial oxidation, respectively, using La₀.₈Sr₀.₂Cr₀.₉₅Co₀.₀₅O₃₋δ (LSCrCo) at the H₂O-splitting side and La₀.₈Sr₀.₂CoO₃₋δ (LSCO) at the CH₄ partial oxidation side.

One major challenge related to the feasibility of the concept is the fabrication of two intact layers with high mechanical and chemical stability. We have explored several ways, such as co-sintering and screen-printing. In the co-sintering approach, the two different materials in the Janus membrane may lead to different shrinkage during sintering due to the factors such as particle sizes and applied pressure. We optimized the parameters such as calcination temperature of the oxide powders, uniaxial applied pressure and heat treatment to avoid the shrinkage mismatch when sintering the Janus membrane. In the second approach, LSCO ink was screen printed on LSCrCo membrane. The viscosity of the ceramic paste was adjusted by adding terpineol based ink vehicle to the ceramic powder. The ink printed layer was heat treated at 1350°C for 3 hours to ensure adhesion.

Experiments showed that the single-layer LSCrCo membrane has high H₂ production rate equal to 0.45 μmol/cm² s when operating at 1000°C with 50% steam concentration diluted by nitrogen at the feed side and 20% CH₄ concentration diluted by argon at the sweep side. The performance of this material remained stable for more than 100 hours. With the second layer of LSCO added on the CH₄ side, the Janus membrane is expected to have enhanced performance due to the faster CH₄ oxidation kinetic on the side.

*Xiao-Yu Wu and Georgios Dimitrakopoulos contributed equally to this work

References:

4:30 PM EN04.07.09
An Investigation into Chemical Stability of Dual-Phase Lanthanum Chromite-Based Perovskite and Stabilized Zirconia Fluorite Phases

Hooman Sabarou and Yu Zhong; Worcester Polytechnic Institute, United States

Dual-Phase ceramic membranes are a promising candidate for mixed ionic-electronic ceramic conductors. These composites have inherited good traits of both perovskite and fluorite phases in order to separate oxygen from air under harsh working conditions. While they are capable of working around 1000°C and under both oxidizing and reducing atmospheres (p(O2)=0.21 to 10^-22 atm), the long term compatibility between these two phases are still challenging. The current research investigates the chemical and structural stabilities of dual-phase membranes of perovskite and fluorite phases with changes in composition, temperature (T), and oxygen partial pressure p(O2).

Lanthanum chromite-based perovskite has been doped with Sr and Fe as A- and B-site dopants, respectively. Different compositions of the perovskite phase with change in A-site and B-site dopants and A-site deficiency have been considered. There different stabilized zirconia as the fluorite phase have been examined with the perovskite phase: ScYSZ, ScCeSZ, and YSZ. The interaction between these two phases under fabrication and processing conditions have been studied through experimental and computational thermodynamics. The results reveal the correlation between Cr:Fe ratio and the formation of secondary phases. XRD results with thermodynamics calculations show that valance stabilities of Fe and Cr ion species regarding applied T and p(O2) and defect chemistry of the perovskite phase are responsible to maintain structural integrity of composites. The formation mechanism of secondary phases and their effects have been discussed in the purpose of minimizing and controlling their formation. It is offered how to tune initial compositions of the perovskite phase to control the formation of most detrimental phases of SrZrO3 and La2Zr2O7. Owing to use of computational thermodynamics, it is discussed how applied T and p(O2) during either fabrication or processing leave effects on chemical/structural stabilities of dual-phase membranes. In fact, computational thermodynamics provides practical guidelines about controlling composition, T, and p(O2) to maintain structures and control desired stoichiometries. Structural stability of fluorite phases has been also examined via X-ray diffraction methods.

SESSION EN04.08: Transport and Applications of 2D Membranes

Session Chairs: Yifu Ding and Sui Zhang

Thursday Morning, December 5, 2019
Sheraton, 3rd Floor, Fairfax A

8:00 AM EN04.08.01
Surface Engineered 2D Hexagonal Boron Nitrides as Bidirectional Superionic Conductors

Jasneet Kaur1, Adel Malekhhoyan2, Gurpreet Singh Selopan3, Zhiming Wang1, Federico Rosei2 and Hadis Zarrin3; 1Ryerson University, Canada; 2Institut National de La Recherche Scientifique, Canada; 3Institute of Fundamental and Frontier Science, University of Electronic Science and Technology of China, China

In the era of smart wearable electronics and compact electric transportation system, there is an urge for the development of flexible, lightweight, solid-state and efficient energy storage devices. For realizing high performance energy devices, novel electrolyte materials with high energy density at enhanced power and longer life cycle are demanding. The recent development in the field of two-dimensional (2D) materials, including graphene, hexagonal boron nitride (hBN) and transition metal dichalcogenides, have exhibited promising applications in various areas, such as electrochemistry and clean energy storage devices. In particular, 2D hBN, also known as “white graphene” is an isomorph of graphene with similar layered structure in a hexagonal lattice, which is uniquely featured by its outstanding physicochemical properties along with mechanical robustness and thermal stability. Due to its remarkable electrochemical properties, it is considered as a promising candidate that can be integrated with other 2D materials for the next generation electrochemical energy storage and conversion applications including fuel cells, batteries and supercapacitors. Moreover, hBN possess electrically insulating behavior at wide range of humidity and temperatures, which makes it more versatile to be manipulated and used as an electrolyte membrane in electrochemical energy systems.

Herein, we have developed functionalized hexagonal boron nitride (FhBN) polymer electrolyte membranes (PEMs) and presented as a potential proton exchange membrane for electrochemical energy storage and conversion devices.
The dispersions and functionalization of FhBN nanosheets are produced by direct in-situ liquid phase exfoliation and functionalization. FhBN dispersions possess excellent dispersibility and stability over several months of few-layered FhBN nanosheets in the solution, which is indicated by highly positive zeta potential values of $+42.5 \pm 3.2$ mV of the dispersion. Physicochemical properties of FhBN nanoflakes are investigated by various spectroscopic and microscopic characterisation tests, confirming strong covalent interactions/attachment in the FhBN nanoflakes between the hBN lattice and sulfonic acid groups. Further to fabricate proton conductive FhBN PEMs, high concentration of FhBN nanoflakes are blended with Nafion solution to form a stable dispersion, which are thermally and chemically treated to form the membranes. The addition of FhBN nanoflakes with sulfonic groups provides additional proton conduction sites and enhances the ion exchange capacity of the nanocomposite FhBN-Nafion PEMs with lower swelling ratio compared to that of bare Nafion. The in- and through-plane proton conductivity of the FhBN-Nafion PEMs is significantly increased under various conditions relative to that of re-casted Nafion membrane. The maximum value of in-plane conductivity of FhBN75%-Nafion PEM is observed at 80°C - 80% relative humidity (RH) condition, which is 0.41 S/cm, i.e., 7 times higher than that of the recast Nafion, under the same conditions. Moreover, at 80°C - 80% RH, the through-plane conductivity of FhBN75%-Nafion PEM is 0.1 S/cm i.e., 14 times higher than that of the recast Nafion under the same conditions. The superionic transport characteristic of highly concentrated 2D FhBN PEMs provide promising solutions for various applications in electrochemistry and clean energy devices, including supercapacitors, polymer electrolyte membrane for fuel cells and water electrolysis.

8:15 AM EN04.08.02
Stable Functionalized Graphene Oxide—Cellulose Nanofiber Solid Electrolytes with Long-Range 1D/2D Ionic Nanochannels Wei Jia and Peiyi Wu; Fudan University, China

Solid electrolytes which could transport cations are widely used in energy-related and environmental applications. Herein, functionalized graphene oxide-cellulose nanofiber solid proton electrolytes (NPGOM-CN1F) were successfully prepared. Based on 1D CNF and 2D dopamine-functionalized GO (NPGO), long-range 1D and 2D ionic nanochannels are constructed in the membranes with perfluorinated sulfonic acid resin (PFSA). The proton conductivity of NPGOM-10-CN1F is as high as 0.4 S cm$^{-1}$ at 80°C-95 %RH, two times higher than that of commercialized Nafion117. The single-cell performance of NPGOM-10-CN1F-based MEA is 31% higher than that of Nafion117-based MEA at 60°C-100 %RH on account of higher proton conductivities and better H$_2$ impedance ability. Besides, NPGOM-CN1F membranes also possess outstanding stability in water and high methanol barrier performance, demonstrating great practical application potential in both proton-exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC) areas.

8:30 AM *EN04.08.03
Diffusion and Partitioning of Organic Micropollutants in Graphene Oxide Membranes Baoxia Mi and Sunxiant Zheng; University of California, Berkeley, United States

Pharmaceuticals and personal care products (PPCPs) have recently been recognized as emerging contaminants that pose potential hazards to environment and human health. Conventional nanofiltration membranes relies heavily on the size exclusion and charge repulsion for the separation of contaminant from water and herein are less effective in rejecting neutral micropollutants. In this research, graphene oxide (GO) nanosheets were stacked into 50 nm thin film as a tight nanofiltration membrane to remove pharmaceuticals and PPCPs in water. The layer-stacked GO membranes has sub-nanometer-sized channels that enhance the interactions between GO and the targeting contaminants which lead to hindered diffusion of neutral micropollutants. The diffusion and partitioning coefficient of three representative PPCPs were for the first time characterized based on their adsorption kinetics into the GO thin films using quartz crystal microbalance with dissipation (QCM-D). The results suggest that the diffusion coefficient of caffeine, acetaminophen and carbamazepine in the confined GO nanochannels are more than four magnitudes slower than that in the bulk water. By comparing the solute flux measured experimentally using a nanofiltration system and the theoretical values calculated from the diffusion and partitioning coefficient, we can confirm the transport of neutral micropollutants in the GO membranes are dominated by the diffusion process.

9:00 AM EN04.08.04
Graphene-Polymer Thin-Film Composite Membranes as Energy Efficient and Anti-Fouling Membranes for Water Purification Sanju Gupta; Western Kentucky University, United States
Water is our planet’s most precious resources and life’s most basic indispensable component. Reverse osmosis (RO) filtration is highly adopted, growing technologies to produce clean water by removing undesired (charged or uncharged) solute species. However, polymer and ceramic membranes suffer from low permeability, structural breakdown and fouling. Graphene, a form of carbon, provides the foundation for the production of highly permeable membranes as an emerging technology for RO desalination. Adding oxygen to few-layer graphene nanosheets, i.e. graphene oxide (GO), opens allows efficient adsorption of charged ionic species (selectivity) and augmented flow of water molecules (ultrafast permeability). This works reports on the development of novel graphene oxide thin film nanocomposite (G-TFNC) membranes embedded with a thinner active polymer layer via interfacial polymerization to tackle the trade-offs among water flux transport and salt ionic species rejection, robustness and anti-fouling characteristics. This study overcomes the gap between drinkable freshwater demand and supply through nanotechnology-enabled high performance graphene composite membranes.

9:15 AM EN04.08.05
Spray-Coated Graphene Oxide Membranes for Water Filtration Aaron Morelos-Gomez1, Rodolfo Cruz-Silva1, Josue Ortiz-Medina2, Takumi Araki3, Ayaka Yamanaka3, Syogo Tejima3, Mauricio Terrones4 and Morinobu Endo1; 1Shinshu University, Japan; 2Universidad Panamericana, Mexico; 3Research Organization for Information Science & Technology, Japan; 4The Pennsylvania State University, United States

The demand of water is increasing along with population growth, where fresh water sources are decreasing and improved methods for water reclamation are needed. This is fundamental in order to create self-sustaining societies. Graphene oxide (GO) membranes have been widely studied for water desalination, pigment filtration and solvent separation, however there are few scalable methods to produce large membranes for water filtration. In addition, chemical stability and antifouling properties are needed in order to be promising candidates for real applications. In this work, we present a spray-coated GO membrane for water filtration. Its desalination performance was measured for a mixture of GO/few-layered graphene and only GO, where salt rejection can reach between 80% and 90% and a permeate flux of 0.1 - 0.4 m3m-2day-1. The membranes were kept in a solution of sodium hypochlorite (200 pm), a typical agent for industrial cleaning of filtration membranes. Here, the membranes with few-layered graphene exhibited an increased chemical resistance. Furthermore, protein fouling against negative and positive charged proteins bovine serum albumin and lysozyme, respectively, was carried out by monitoring variations in permeate flux and microscopy. The GO membranes demonstrated excellent anti-fouling against both membranes due to electrostatic interactions, hydrophilicity and surface smoothness. The present membranes have excellent scalable fabrication method, chemical resistance and anti-organic fouling necessary for real-world applications in water reclamation, desalination, food industry, etc.

9:30 AM EN04.08.06
Covalently Modified MoS2 Nanochannels for Water Purification Ries Lucie1,2, Philippe Miele1,2,3 and Damien Voiry1,4; 1European Institute of Membranes (IEM), United States; 2ENCSM, France; 3Institut Universitaire de France, France; 4CNRS, France

Membrane separation technology plays an important role in various fields including water treatment, chemicals and gas separation in many industrial processes, and food processing. There has been a renewed focus on 2D material for membrane application since their atomic thickness and confined interlayer spacing could theoretically lead to enhanced separation performance. Indeed, multilayer assembly of single nanosheets – forming nanolaminate membranes – creates 2D capillaries that can efficiently sieve chemical species depending on their size. Selectivity and size controlled diffusion of these nanochannels can be modified to tune the transport mechanism within the structure. For instance, chemical modifications of the surface of 2D nanosheets via functionalization have opened new avenues for tuning the membrane properties in both fields of molecular3 and gas sieving. Among the different building blocks of the nanolaminate membranes made of two-dimensional materials (2D), graphene oxide (GO) has been studied as a candidate for molecular sieving via size-limited diffusion in the 2D capillaries1. Unfortunately the high hydrophilicity of GO nanosheets make GO membranes unstable in water, while the poor control of the capillary width between the nanosheets limits the water permeance of membranes. Exfoliated nanosheets of transition metal dichalcogenides (TMDs) constitute attractive platforms for the realization of nanolaminate membranes. Recent works carried out on nanolaminate membranes made of molybdenum disulfide (MoS2) have demonstrated improved stability. Here, we report a novel type of nanolaminate membranes with well-controlled surface chemistry of the nanosheets. We will notably present our recent investigations on the performance of lamellar membranes based on chemically functionalized MoS2 nanosheets toward water desalination and
micropollutant removal. Our results open novel directions for fine tuning the sieving behavior of membranes based on 2D materials.


9:45 AM EN04.08.07
Two-Dimensional Molybdenum Disulphide Membranes for Organic Solvent Nanofiltration—Stability, Structural Manipulation and Separation Performances Sui Zhang; National University of Singapore, Singapore

Two-dimensional (2D) materials such as molybdenum disulfide (MoS2) present tremendous opportunities in membrane-based molecular separation. Compared to graphene oxide, MXene and other 2D inorganic materials, MoS2 show exceptional stability in organic solvents. A few studies have reported the preparation of MoS2 membranes for separation in aqueous solutions. However, there have been no investigations on the application of MoS2 membranes for organic solvent separation. In addition, multi-layer and mono-layer MoS2 nanosheets may be prepared by different approaches and have both been used for membrane preparation. Though studies have revealed that monolayer MoS2 structure is unstable in the ambient conditions, there have been no reports on the stability of MoS2 membranes.

This presentation covers our recent progress in 2D MoS2 membranes for organic solvent separation. In the first part, we prepared both multi-layer and mono-layer MoS2 nanosheets using different methods, and compared their structure, stability and performances after made into membranes. It’s found that multi-layer MoS2 membranes are looser in structure, and hence result in higher permeability to isopropanol and lower rejection to dyes. On the other hand, though mono-layer MoS2 membranes show better rejection to dyes in the short tests (within 3 hours), the rejection keeps decreasing over a 5-day tests, which is attributed to the limited stability of such nanosheets that lead to aggregation and breakage. To achieve high rejection and good stability, a ‘bridging’ agent is employed to regulate the interlayer spacing and nanosheet alignment of multi-layer MoS2 membranes, leading to improved rejection and stable performances over one week.

In the second part, mixed matrix membranes containing MoS2 nanosheets based on a 3-step layer-by-layer (LbL) method have been prepared, which provides a more cost-effective and scalable way to fabricate 2D membranes. Very interestingly, while the original LbL polyelectrolyte layer is impermeable to organic solvents, mixed matric membranes containing MoS2 nanosheets open the pathways to solvents while rejecting solutes whose molecular weight is around 300 Dalton. The phenomenon is attributed to the lower of surface energy by MoS2 and its bridging effects. With a thin layer of < 50 nm, the mixed matrix membrane can achieve ethanol permeance –selectivity that surpasses the hypothetical upper bound, e.g., 92.9 % rejection for Victoria blue B (VBB, MW 506.08) with an ethanol flux of 11.4 L m⁻² h⁻¹ bar⁻¹.

10:00 AM BREAK

10:30 AM *EN04.08.08
Graphene Oxide Membranes in Extreme Operating Environments—Concentration of Black Liquor and Water Recycling in Biomass Pretreatment Processes Sankar Nair; Georgia Institute of Technology, United States

Kraft black liquor (BL) is a corrosive (pH >12), high total solids (> 15 wt%), and high-volume byproduct (~500 million tons/yr worldwide) of biomass pretreatment for pulp and paper production [1]. BL contains lignin, hemicellulose, organic acids, inorganic salts, and water. Dewatering of BL is currently performed by multi-effect evaporators, which is highly energy-intensive (about 0.2 Quads/year in the US alone). Membrane-based concentration of black liquor [1,2] is attractive as an energy-efficient alternative, but challenging due to the harsh operating conditions, complex feed composition, and high fouling potential of BL. This talk will discuss our pursuit of chemically and mechanically robust, low-cost, and scalable GO membranes for black liquor concentration. We will discuss in detail the development and properties of graphene oxide (GO) nanofiltration and reverse osmosis membranes for rejection of lignin, other dissolved organics, and inorganic salts; including their operation in long-term testing under real BL conditions. We will overview our efforts for scale-up of GO membranes, and the development of an overall process for membrane-based concentration of BL streams with simultaneous production.
of usable process-quality water. A brief summary of the technoeconomic analysis for membrane-based BL concentration will also be presented.

References:


11:00 AM EN04.08.09
Analytical Prediction of Gas Permeation through Graphene Nanopores of Varying Sizes—Understanding Transitions across Multiple Transport Regimes Zhe Yuan1, Rahul Prasanna Misra1, Ananth Govind Rajan2, Michael Strano1 and Daniel Blankschtein1; 1Massachusetts Institute of Technology, United States; 2Princeton University, United States

Nanoporous graphene is a promising candidate material for gas separation membranes, due to its atomic thickness and low cross-membrane transport resistance. The mechanisms of gas permeation through graphene nanopores, in both the large and small pore size limits, have been reported in the literature. However, mechanistic insights into the crossover from the small pore size limit to the large pore size limit are still lacking. In this study, we develop a comprehensive theoretical framework to predict gas permeance through graphene nanopores having a wide range of diameters using analytical equations. We formulate the transport kinetics associated with the direct impingement from the bulk and with the surface diffusion from the adsorption layer on graphene, and then combine them to predict the overall gas permeation rate using a reaction network model. We also utilize molecular dynamics simulations to validate and calibrate our theoretical model. We show that the rates of both the direct impingement and the surface diffusion pathways need to be corrected using different multiplicative factors, which are functions of temperature, gas kinetic diameter, and pore diameter. Finally, we utilize our newly developed model to predict the permeances of CO2, CH4, and Ar through graphene nanopores. We show that as the pore diameter increases, gas transport through graphene nanopores can transition from being translocation dominated (pore diameter < 0.7 nm), to surface pathway dominated (pore diameter 1–2 nm), and finally to direct pathway dominated (pore diameter > 4 nm). The various gas permeation mechanisms outlined in this study will be particularly useful for the rational design of membranes made out of two-dimensional materials like graphene for gas separation applications.

11:15 AM EN04.08.10
Ultra-Permeable Wafer-Scale SWCNT-Membranes for Efficient Dye/Salt Fractionation Melinda L. Jue, Steven F. Buchsbaum, Chiatai Chen, Eric R. Meshot, Sei Jin L. Park, Kuang Jen Wu and Francesco Fornasiero; Lawrence Livermore National Laboratory, United States

Enhanced fluid transport in single-walled carbon nanotubes (SWCNT) promises to enable major advancements in several membrane applications, from efficient water purification1 and low-cost recovery of high-value components, to advanced protective garments. Realization of the SWCNT-membrane potential in practical applications has been hampered so far by the challenge of fabricating large-area membranes with a high density of open, small-diameter, SWCNT pores. A high tube density is required to achieve flow rates outperforming those of commercial membranes, whereas small diameters enhance both size and charge based selectivity.

To demonstrate ultra-permeable large-area SWCNT membranes, we optimized the growth of vertically aligned SWCNTs to maximize number density (up to 2x10^{12} tubes/cm^2) and minimize average diameter (down to <2-nm) while simultaneously scaling up growth area (up to 4-in diameter). By filling the intertube gaps with a chemically resistant polymer and then opening the SWCNT caps with dedicated etching steps, we demonstrated wafer-scale SWCNT membranes with water permeances up to 250 LMH/bar, which greatly surpass those of commercial loose nanofiltration / tight ultrafiltration membranes. These SWCNT membranes display high rejection of nm-sized dyes (e.g., Rose Bengal) while permitting complete passage of salts like NaCl or Na2SO4. Contrary to conventional membranes for water treatment, aggressive cleaning methods did not affect detrimentally SWCNT membrane performances. This efficient fractionation and recovery of dyes/salts at modest applied pressures (far below the salt osmotic pressure) suggests that SWCNT membranes hold great promises for sustainable textile-water treatment.
Together with their ultrahigh permeance, the demonstrated chemical resistance of these membranes offers opportunities for energy-efficient nanofiltration/ultrafiltration processes in chemically demanding environments.

References

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11:30 AM EN04.08.11
**Laser-Induced Graphene Enabled by Atomic Layer Deposition for Charged Membrane Applications** David S. Bergsman, Bezawit Getachew and Jeffrey C. Grossman; Massachusetts Institute of Technology, United States

Membrane-based processes are becoming increasingly popular for water treatment due to their relatively high energy efficiency and low cost compared to other treatment methods. However, the advantages of membranes are mitigated by the need for additional pre-treatment steps that are required to maintain their effective operation. The treatment and prevention of membrane fouling, in particular, constitutes a large fraction of typical membrane operational costs. One potential approach to combat fouling is to design conductive membrane coatings that can prevent the attachment and growth of biofoulants both electrostatically and via electrochemical generation of reactive oxygen species. Despite their potential, these conductive membrane coatings are often expensive, requiring additional chemicals and non-scalable methods to produce, e.g. carbon nanotube mats or other graphitic coatings deposited by vacuum filtration. In this work, we explore the use of laser-induced graphene (LIG) for the creation of conductive ultrafiltration membranes. Porous polyethersulfone (PES) membranes are first coated in a thin layer of alumina using atomic layer deposition (ALD) before being irradiated with an infrared laser. We show that this alumina film, which can be scalably produced using spacial ALD, can localize LIG formation to the surface of the membrane, preventing the buried, un-lased areas of PES from melting and losing their porosity during the lasing process. This allows the top-most layer of the PES to be a conductive coating that can be used to charge the membrane surface and used to improve membrane performance (e.g. fouling mitigation). The formation of LIG is verified by scanning electron microscopy and Raman spectroscopy. The conductive layer is also shown to possesses relatively high conductivity, which is important for reducing power consumption in devices. Insight into the mechanism behind the improved stability to melting provided by ALD is provided by thermogravimetric analysis, differential scanning calorimetry, and Fourier-transform infrared spectroscopy. The effect of ALD film thickness and the use of sequential infiltration synthesis will also be explored. These insights are used to discuss the potential application of this approach to creating conductive coatings on other polymers using ALD-based approaches.

11:45 AM EN04.08.12
**Filtering of Sarin Gas by Nanoporous Graphene** Marco A. Maria¹,² and Alexandre F. Fonseca²; ¹Universidade Federal de Sao Carlos/ Sorocaba, Brazil; ²State University of Campinas, Brazil

One of the major worldwide concerns nowadays is the use of chemical warfare agents (CWAs) in events of terrorism or war. One of the compounds used as CWA is the sarin gas. Sarin is a nerve agent capable of bringing a person to death in about 15 minutes. This and other CWA gases are so toxic and lethal that their use is very limited even in research. In view of the need to find out safety protocols both for the handling and storage of this gas and for its detection, filtering and chemical transformation, it is important to develop new and effective methods of researching CWA properties. In particular, theoretical methods are very welcome to study the chemical and physical properties of CWAs at different physical conditions. In this work, we present the results of a computational study of the interaction of sarin molecules and graphene, towards the characterization of sarin-filtering properties of nanoporous graphene. Classical molecular dynamics (MD) are employed here in order to study relatively large system sizes and number of molecules as well as some conditions of concentration and temperature that are prohibitive in *ab initio* studies. A graphene structure of about 32 by 34 Å of lateral sizes with a relatively large hole of about 15 Å is placed in the middle of an 80 Å length environment separating two regions, one with the presence of gas molecules and the other with vacuum, so creating a pressure difference between the two regions. Two sets of
gas molecules are considered, one which has only sarin molecules and the other which has sarin and air (a mixture of 1% of Ar, 78% of N₂ and 21% of O₂) molecules. The aim of the study is to find out at which combinations of sarin concentration and temperature, the sarin molecule remains on one side or pass through the hole, as compared to the passage of air molecules. The MD simulations were carried out at four values of temperatures, 300 K, 500 K, 700 K, and 900 K, and two concentrations of sarin, 5% and 10% with respect to the total number of gas molecules. After 10 ns of simulation time, the results show that not a single sarin molecule went through the porous graphene for T = 300 K, regardless of sarin concentration. This is a remarkable result because the size of the hole is about three times the length of the sarin molecule. For the other values of temperature, the number of sarin molecules that crossed the hole was shown to depend on both temperature and concentration. In all MD simulations, the air molecules passed easily through the hole in graphene, and an interesting accumulation of sarin molecules around graphene structure was observed. We discuss these results on possible applications of porous graphene as a nanofilter of sarin gas.

SESSION EN04.09: Novel Membrane Materials, Metrologies and Applications
Session Chairs: Yunxia Hu and Haiqing Lin
Thursday Afternoon, December 5, 2019
Sheraton, 3rd Floor, Fairfax A

1:30 PM EN04.09.01
Carbon Dioxide and Methane Selectivity of a Smectite Clay with Different Intercalated Cations Kristoffer W. Hunvik¹, Leide P. Cavalcantí², Martin Riess³, Patrick Loch³, Konstanze K. Seljelid¹, Vegard Josvanger¹, Roosevelt Droppa⁴, Dirk Wallacher⁵, Barbara Pacakova⁶, Paulo H. Michels Brito⁷, Kenneth Knudsen¹,¹, Josef Breu⁸ and Jon O. Fossum¹; ¹NTNU, Norway; ²Institute for Energy Technology, Norway; ³University of Bayreuth, Germany; ⁴Universidade Federal do ABC, Brazil; ⁵Helmholtz-Zentrum Berlin, Germany

Carbon dioxide and methane are the main greenhouse gases and their accumulation is responsible for worldwide environmental repercussions. In addition to the efforts to reduce their emissions, it is imperative to establish effective ways of capturing these compounds. The first step in this respect is to develop an understanding of what mechanisms are important for the interaction with potential sorption materials, with a goal of developing suitable capture materials with particularly high selectivity for CO₂ or CH₄.¹,² A possible solution to reduce anthropogenic CO₂ emissions is through enhanced gas recovery (EGR) operations, by releasing trapped CH₄ through an exchange process with CO₂. By employing such a process, some estimates suggest that additional gas recovery through CO₂ injection may have an indirect value of nearly 1 T$³. The presently unrecoverable methane in shale reservoirs is retained through interactions with organic content and clay minerals. To employ such strategies, the fundamental interactions between clay, methane and carbon dioxide needs to be investigated.

We have studied (Li, Na, Cs, Ca, Ba, Ni)-fluorohectorite⁴ with a capillary based high-pressure cell with synchrotron X-ray powder diffraction and by volumetric adsorption. Here we show how the kinetics of the adsorption depends on the specific cation, clay layer charge, temperatures and pressure. Our studies show crystalline swelling of Ni-Fh within seconds in response to CO₂ exposure. We have investigated CO₂ capture for three different layer charges, 0.3, 0.5, 0.7 per formula unit (Si₄O₁₀F₂), where we observe crystalline swelling for 5-10 bar, 10-15 bar and 30 bar respectively at room temperature. In our experiments Cs-Fh, Ca-Fh and Ba-Fh does not show any sign of crystalline swelling when exposed CO₂. However, when Ni-fluorohectorite is exposed to methane up to a pressure of 60 bar at -20°C we observe no intercalation. Our results show the selectivity of CO₂ over CH₄ in fluorohectorite clay.

1:45 PM EN04.09.02
Water Treatment Membranes Embedded with a Stable and Bactericidal Nano Diamond Material

Abelardo Colon1, Gerardo Morell1, Brad Weiner1, Dariel Ortiz2, Javier Avalos2, and Rafael Rios3; 1University of Puerto Rico at Rio Piedras, United States; 2University of Puerto Rico at Bayamón, United States

Water treatment using membranes have emerged as a critical technology in solving societally important problems such as waterborne diseases caused by poor water quality and sanitation issues. This high energy consumption technology confronts key challenges for the technology to drive such as membrane selectivity and permeability, fouling and membrane lifetime. Functional nanomaterials can be a solution to these challenges by changing the membranes’ mechanical and bactericidal properties by enhancing these properties in a synergistic way. The ultra-dispersed diamond (UDD) is a versatile carbon allotrope with a small particle size range (4-5 nm), with easy surface functionality and biocompatibility properties, ideal for use in water treatment processes. This research studies UDD’s bactericidal and functionality properties embedded in membranes for water purification systems. Scanning and electron transmission microscopy (SEM) and Fourier Transmission IR (FTIR) techniques were performed to study the membrane surface and identify functional groups present in the nanoparticle. Tensile strength test was done to measure the nano composite membrane mechanical properties. Coliscan Membrane characterization was performed to obtain fecal coliforms forming units CFU on filtered samples and microorganism reduction significance was obtained using T-test analysis at a 95% level of confidence. This research aims to demonstrate how current water purification membranes can be enhanced by adding nano diamond particles to reduce bio-fouling problems, strengthen its mechanical stability, and increase its lifetime for water purification.

2:00 PM EN04.09.03
Increasing Water Flow Rate via Membranes by Applying High-Frequency Acoustic Pressure

Nurkhat K. Zhakiyev1, Zamart Ramazanova1, K.B. Tynshytkbayev1 and Zinetula Z. Insepov1,2,3; 1Nazarbayev University, Kazakhstan; 2Purdue University, United States; 3National Nuclear Research University (MEPhl), Russian Federation

Ion-exchange membrane technologies used for water purification, in flow batteries for energy storage. To improve the transmission characteristics of the membranes, various methods are used, such as passivation of dangling bonds, increase inlet pressure, use of reverse osmosis, the design of optimal geometry, taking into account natural convection conditions and etc. We have investigated the impact of high-frequency acoustic pressure on the convection rate capacity of the membranes. This study is a continuation of previous works [1, 2]. Typically, vortex shedding takes place in the vicinity of the slit region. At medium to high sound pressure levels, the local particle velocity in the narrow region of the perforate or slit can be so large that the linear assumptions of acoustics break down. Thus, non-linear characteristics of acoustic waves interacting with the membrane simulated using advanced approached of finite-element modelling (FEM). FEM packages used to solve equations for unsteady state two-dimensional fluid flow coupled with acoustic pressure, species transport. In this work, we present our findings relating to increasing the convection rate using acoustic waves. Experimental test for flow rate increasing and simulating performance of the process done by using FEM. Acoustic waves Influencing approach offers interesting solutions for low cost increasing performance of water filters or Vanadium Redox Flow Battery energy storages.

1) Z. Insepov, D. Wolf, A.Hassanein, Nanopumping using carbon nanotubes, 2006 Nano Letters 6(9), 1893-1895

2:15 PM EN04.09.04
Monolithic Janus Membrane via Pulsed Laser Heating for High-Performance Solar Steam Generation

Minsu Kim1, Kwansoo Yang1, Pilgyu Kang2, Yun Ho Kim1 and Byoung Gak Kim1; 1Korea Research Institute of Chemical Technology, Korea (the Republic of); 2George Mason University, United States

Utilization of abundant source of solar energy to generate steam has a broad range of applications such as power generation, desalination, water purification, and sterilization. Micro/nanostructured Janus photothermal materials with asymmetric surfaces and thermal properties have been widely sought for use in high-performance solar steam generators. Many approaches to constructing Janus structures that incorporate graphene based light absorbing materials fulfill the requirements of self-floating solar steam systems, such as light absorption, thermal insulation, and capillary action. However, achieving multiscale-structured materials remains a challenge due to processing requirements of high thermal/chemical energy, and lengthy period of time consumption. Herein, we demonstrate a simple and scalable laser-based photothermal method for directly producing monolithic Janus membranes of
hierarchically porous graphitic carbon and polyimide foam for use in floating solar steam generators. Our monolithic Janus membrane performs not only outstanding solar steam generation, with an energy conversion efficiency of 84%, but high salt rejection ratios of 99.9% in the solar desalination systems. The laser photothermal method to obtain monolithic bilayer membrane has future potential to substantially reduce the cost of high-efficiency solar-thermal systems for scalable solar steam generations.

2:30 PM EN04.09.05
Electrochemical Impedance Spectroscopy as a Performance Indicator of Water Dissociation in Bipolar Membranes
Marijn Blommaert, David Vermaas, Boaz Izelael, Ben ‗t Veen and Wilson Smith; *T*U Delft, Netherlands; ‡Aquabattery B.V., Netherlands; §Shell Global Solutions International B.V., Netherlands

A bipolar membrane (BPM) can be used to maintain a pH difference in an electrolysis cell, which provides freedom to independently optimize the environments and catalysts used for paired redox reactions. A BPM consists of two physical layers, of which one is selective for the exchange of cations and the other for anions. The water dissociation reaction (WDR) splits water into protons and hydroxide ions under an electric field that concentrates at the interface of the two membrane layers. However, salt ions in commonly used electrolytes influence this WDR when they are present at the interface. Using electrochemical impedance spectroscopy (EIS), we observed the rate of water dissociation decrease in the presence of salt ions while also observing the diffusion and migration of these salt ions, showing a clear link between the peaks observed in EIS and ion crossover.

Our work comprises the first detailed impedance study using modern, commercial BPM’s in different electrolytes while varying the current density. This unique series of experiments allows the ability to obtain important fundamental knowledge of a BPM, i.e. insights on the voltage behavior around the plateau current density. This information shows a direct correlation between ion crossover and electrolyte composition, which is a highly debated and controversial topic in the BPM field. In addition, we have found that using electrochemical impedance spectroscopy, it is possible to observe the degradation of individual components of a BPM, which has immense implications for industrial applications.

References

2:45 PM BREAK

3:15 PM EN04.09.06
Covalently-Functionalized Three-Dimensional Graphene Nanosheets as a Stationary Phase Material for Chiral Liquid Chromatography
Lindsay Candelaria, Liliya Frolova, Brian Kowalski, Kateryna Artyushkova, Alexey Serov and Nikolai Kalugin; *New Mexico Tech, United States; ‡The University of New Mexico, United States; §Pajarito Powder LLC, United States

Carbon-based stationary phases for chromatographic separation are known to be highly resistant to aggressive mobile phases and extreme pH values of solvents and eluents, a significant advantage compared to commercial silica-based alternatives. We report on a new variant of carbon-based stationary phases for liquid chromatography, specifically developed for chiral separation.

The recent interest in carbon-based chiral separators is related to the implementation of new forms of carbon: graphene, graphene oxide (GO) and reduced graphene oxide (rGO). Recent papers report on the attempts of chiral separation and sensing, where GO or rGO was used as one of components of modified electrodes or as a part of (quasi)stationary phases for capillary electrochromatography. We have to mention recent suggestions of separation membranes made out of chemically functionalized graphene-based materials. including the idea of using holes in planar graphene for transport of chiral compounds across graphene layers, reports about the usage of L-glutamic acid-functionalized GO membranes for the separation of phenylalanines, and attempts of making intrinsically chiral mesoporous carbon synthesized via carbonization of chiral ionic liquids. Despite the achieved progress, no previous reports have so far demonstrated carbon nanotubes- or graphene-based CSPs for use in high performance liquid chromatography that are fully competitive with commercial silica-based immobilized CSPs. In our work, mesoporous three-dimensional graphene nanosheets (3D GNS), functionalized with tetracyanoethylene oxide (TCNEO) and (S)-(−)-2-pyrrolidinemethanol, used as Chiral Stationary Phases (CSPs),
demonstrate separation performance parameters competitive to currently commercially available CSPs. The modification of graphene with tetracyanoethylene oxide (TCNEO) introduces reactive cyano groups to the material, opening a wide spectrum of possible secondary modifications and uses. Demonstrated graphene-based CSPs are chemically stable, and up to an order of magnitude less expensive comparing to commercial silica-based analogues.

References

3:30 PM EN04.09.08
Studying the Impact of Ink and Process Parameters on Electrospun Fibers for Electrocatalytic Applications
Nisha Sharma, Sunil Kumar, Sadia Kabir, Scott Mauger, Kenneth Neyerlin and Michael Ulsh; Chemistry & Nanoscience Center National Renewable Energy Laboratory, United States

The world is facing several challenges related to climate and environmental issues. Current research is focused on solutions such as CO₂ reduction and polymer electrolyte membrane fuel cells (PEMFC), which have the potential to address such issues. These technologies can enable clean and affordable energy. Among the latest innovations, PEMFCs are quite promising, due to their low operating temperature and high-power output. Commercialization is one of the major challenges due to high cost. One potential cost reduction method under research is using the electrospinning technique to fabricate nanofibers which are rich in catalytic material. Nanofibers fabricated with intra-fiber porosity result in well distributed catalyst and ionomer, which has high surface area for electrochemical reaction and catalyst mass activity (1). Such electrospun cathodes are highly durable (2) and promising for cost reduction. However, to achieve our goal of fabricating nanofibers with high electrochemical surface area and high catalyst mass activity we are studying the impact of polymer solution properties and electrospinning process parameters on spinnability. The presence of carboxylic acid groups in poly (acrylic acid) (PAA), enhances polymer chain entanglement and is known for adding viscosity to the polymer solvent solution (3). We have studied the fabrication of PAA by itself and with a blend of Nafion ionomer and catalyst, such as Pt-Vulcan, in this work. These experiments improve our understanding of the morphology and diameter of these different blends of polymer solvent solutions with respect to their viscosity at different polymer concentration, and different processing and ambient parameters of electrospinning.

This study was conducted to better understand the morphology and diameter of fibers with different concentration of PAA, ranging from 5 – 20 wt.%, with and without Nafion and the catalyst (Pt-Vulcan). The PAA polymer was dissolved in a 2:1 ratio of isopropanol and water solvent. This work will be conducted at different processing conditions (ranging from needle-to-drum distance of 8-12 cm, voltage of 10-20 KV, and flow rates of 0.75ml/hr. and 1 ml/hr.). Further, these conditions will be then tested at different humidity condition ranging from (25-45 % RH). The polymer solvent solution with and without Nafion and catalyst were mixed for approximately 72 hours. Fiber size and morphology were measured using scanning electron microscopy, and the Image J software (NIH, Bethesda, MD, USA) was used for automated fiber diameter determination and statistics.

This work demonstrates the effect of ink (e.g. viscosity) and process parameters with respect to spinnability of the fibers at different weight percent (ranging from 5-20 wt.%) of poly (acrylic acid) (PAA) polymer solvent solution with and without blend of Nafion and catalyst.

Reference:
Dendrolytes – A New Generation of Free-Standing Ion Selective Membrane Materials Based on Hyperbranched Polyglycerol for Bioelectronics Tobias F. Abrahamsson¹, David J. Poxson¹, Erik O. Gabrielsson¹, Mikhail Vagin¹, Mats Sandberg², Magnus Berggren¹ and Daniel T. Simon¹; ¹Department of Science and Technology, Linköping University, Sweden; ²RISE Acreo AB, Sweden

Hyperbranched polymers constitute a category which fundamentally outlines as polymers with multiple covalent branching points of structural arrangement, rendering an intrinsically spherical-like conformation. We present hyperbranched polyglycerols multi-functionalized with tuneable degrees of unsaturated groups utilized for click cross-linking and ionic groups for electrolytic properties. The resulting ‘dendrolyte’ polymers have been applied in organic electronic devices in a one-step process to achieve free-standing monolithic ion-selective membranes for controlled electrophoretic ion delivery¹. This new generation of organic ion-conductive materials showcase the capability of performing selective electrophoretic transport of large charged aromatic compounds, coupled with the opportunity for miniaturized manufacturing² and processing for applications in organic (bio)electronic devices, broadening the possibilities for communication with biological systems³ with specificity and high spatiotemporal resolution.


“All Electric” Ion Pumps for Small Scale Water Desalination Gideon Segev¹,¹,², Shane Ardo³,³, Rylan J. Kautz³, David M. Larson¹,¹, Joel Ager¹,¹,⁴ and Francesca Maria Toma¹,¹; ¹Lawrence Berkeley National Laboratory, United States; ²Tel Aviv University, Israel; ³University of California, Irvine, United States; ⁴University of California, Berkeley, United States

The high capital and energetic costs of reverse osmosis based water desalination technology limits its adoption in remote communities. Furthermore, the immense capital costs associated with constructing and maintaining a national scale water distribution make this technology practically irrelevant to considerable parts of the world. For this reason, a small scale, energy efficient water desalination technology is called for. Electrodialysis and capacitive deionization technologies were suggested as technologies that can fill this gap. However, the need for energy intensive chemical reactions in electrodialysis and the capacitance limitations in capacitive deionization technologies impose significant barriers to these technologies. Hence, an ion pumping technology that can operate in steady state without requiring lossy chemical reactions can provide a significant step forward towards a viable, small scale water desalination technology. We have demonstrated a first of its kind ratchet based, all electric ion pump. Electronic ratchets are devices that utilize modulation in a spatially varying electric field to drive steady state current. Similar to peristaltic pumps, where the pump mechanism is not in direct contact with the pumped fluid, electronic ratchets induce net current with no direct charge transport between the power source and the pumped charge carriers. Thus, electronic ratchets can be used to pump ions in steady state with no electrochemical reactions between the power source and the pumped ions resulting in an “all electric” ion pump. In this contribution we analyze the applicability of this technology, its challenges and its advantages for small scale water desalination. The pumping efficiency is shown to be limited by series resistance and is heavily affected by the pore size.

Sustainable Nanocellulose Membranes for PEM Fuel Cells George Cai¹, Songze Wu², Songtao Li³, Aniket M. Raut⁴, Likun Wang⁴, Sunil K. Sharma⁴, Priyanka Sharma⁴ and Miriam Rafailovich⁴; ¹Wayzata High School, United States; ²High school affiliated to Remin University, China; ³Princeton International School of Mathematics and Science, United States; ⁴Stony Brook University, The State University of New York, United States

Carboxycellulose nanofibers (CNFs) promise to be a sustainable and inexpensive alternative material for polymer electrolyte membranes compared to the expensive commercial Nafion membrane. However, its practical applications have been limited by its relatively low performance and reduced mechanical properties under typical operating conditions. In this study, citric acid cross-linked carboxycellulose nanofiber (CA/CNF) membranes were
prepared by solvent casting method. Carboxycellulose nanofibers were derived from wood pulp by using chemical oxidation of hydroxy group present on C6 position of the cellulose chain. Results from FT-IR spectroscopy, $^{13}$C NMR spectroscopy, and XRD reveal a chemical crosslink between the citric acid and CNF, and the optimal fuel cell performance was obtained crosslinking 70 mL CNF suspension with 0.3 mL of 1.0 M citric acid solution. The membrane electrode assemblies (MEAs), operated in oxygen atmosphere, exhibit maximum power density of 27.7 mW/cm$^2$ and maximum current density of 111.8 mA/cm$^2$ at 80 °C and 100% relative humidity for the CA/CNF membrane with 0.1 mg/cm$^2$ Pt loading on anode and cathode, which is approximately 30 times and 22 times better respectively than the uncrosslinked CNF film. The surface morphology of Carboxycellulose nanofibers and corresponding membranes were characterized SEM, EDX, TEM, and AFM techniques.

Acknowledgments: We gratefully acknowledge support from the Louis Morin Charitable Trust and NYS Department of Economic Development.

References:

4:30 PM EN04.09.12
Investigation of In-Situ Iron Oxide Nano-Particles Produced with Air-Diffusion Cathode in Iron-Electrocoagulation
Arkadeep Kumar$^1$, Siva Bandaru$^2$, J. Nathan Hoehman$^3$ and Ashok Gadgil$^1$; $^1$Lawrence Berkeley National Lab, United States; $^2$University of California, Berkeley, United States; $^3$University of Connecticut, United States

Iron-electrocoagulation (Fe-EC) is a method producing in-situ iron (oxyhydr)oxide nano-particles which attach with contaminants such as Arsenic and other heavy metals, coagulate and settle down- thus making water safe for use. Fe-EC is rate limited by amount of dissolved oxygen which is key in oxidizing Fe(II) dissolving from sacrificial anode to Fe(III). We present an improved process using gas-diffusion cathode or air-cathode, which generates in-situ hydrogen peroxide, a stronger oxidant than dissolved oxygen. We investigate the iron-oxides in conventional Fe-EC and air-diffusion cathode enabled Fe-EC. The findings from this research will guide future development of the Fe-EC process.
Chemistries and Architecture for Stable Lithium Metal Anode Ping Liu; University of California, San Diego, United States

Rechargeable lithium metal batteries can reduce the cost of energy storage for both transportation and grid applications. In order to combat issues of infinite volume change, dendrite growth, and parasitic reactions with electrolytes, we have employed several approaches. We have designed a multifunctional 3D host structure with built-in electrolyte additives which promotes dendrite free deposition by reducing effective current densities while improving current efficiency. In terms of electrolyte chemistry, our guiding principle has been the minimization of reactivity with lithium. In this regard, new multicomponent ether-based electrolytes have shown promise. In addition, we emphasize the importance of the chosen electrolyte to be compatible with leading cathode chemistries such as sulfur and transition metal oxides. Performance of lithium metal cells utilizing different cathodes based on the ether electrolytes will be discussed. Finally, we have pursued the formation of surface coatings that can promote uniform lithium ion flux on the electrode surface to enable dendrite free lithium deposition. Our approach favored the use of in-situ chemical reactions in the electrolyte to form protective coatings, which range from lithium organic carbonates to polymeric lithium ion conductors.

Acknowledgements: This work was supported by the Office of Vehicle Technologies of the U.S. Department of Energy through the Advanced Battery Materials Research Program (Battery 500 Consortium) under Contract DE-EE0007764. Part of the work used the UCSD-MTI Battery Fabrication Facility and the UCSD-Arbin Battery Testing Facility.

Lithium Metal Protection Layer for High Performance Lithium Metal Batteries Taeseup Song1, Seho Sun1, HyukSu Han2 and Ungyu Paik1; 1Hanyang University, Korea (the Republic of); 2Hangik University, Korea (the Republic of)

Lithium metal has been considered as an ultimate anode material due to the advantages of the high specific theoretical capacity (3860 mAh g⁻¹) and the lowest electrochemical potential (-3.04V vs the standard hydrogen electrode) for the next generation lithium ion batteries (LIBs). However, its practical use has been hindered by the Li dendrite growth, large volume changes and the low Coulombic efficiency during cycling, which finally leads the cell failure and safety issues. Various approaches have been suggested; i) Physical suppression of the Li dendrite growth. ii) Regulating Li deposition with dense and planar structures. iii) SEI layer reinforcement iv) Composite electrode engineering. We have focused on the Li protection layer for the control of the Li-ion flux on the Li/electrolyte interphase and the increase of Sand’s time. Herein, we report the novel Li metal protection layer and its application for the stable and high performance of Li metal batteries (LMBs). The mechanical property, electronic conductivity and ionic conductivity have been considered for the design of Li metal protection layer. The designed protection layer could effectively retard the Li dendrite growth with the uniform Li-ion flux and the prevent of the repeated electrolyte decomposition during cycling.

Rethinking How External Pressure Can Suppress Li Dendrites Stephen J. Harris1, Q. Jane Wang2, Xin Zhang2, Katherine Harrison2, Katherine J. Jungjohann2 and Peter Attia4; 1Lawrence Berkeley National Laboratory, United States; 2Northwestern University, United States; 3Sandia National Laboratories, United States; 4Stanford University, United States

Lithium metal anodes are critical enablers for high energy density next generation batteries, but they suffer from
poor morphology control and parasitic reactions. Recent experiments have shown that an external packing force on Li metal batteries with liquid electrolytes extends their lifetimes by inhibiting the growth of dendritic structures during Li deposition. However, the mechanisms by which pressure affects dendrite formation and growth have not been fully elucidated. For example, beneficial pressure effects have been observed even for thin polymer separators whose mechanical properties are not expected to be able to hinder dendrite growth. In this paper we offer an explanation for how dendrite growth can be inhibited when the cell is subjected to an external load, even with a relatively soft separator. We carried out a three-dimensional contact mechanics model based on the semi-analytical method for tracking Li surface and sub-surface stresses for a pouch cell architecture with realistically (micron-scale) rough electrode surfaces subjected to a packing force. Our work shows that the picture normally used to understand dendrite penetration, where micron-scale Li metal protrusions under a fixed local current density press conformally against a separator, is oversimplified. At the larger, sub-mm scales studied here, contact between the Li metal and the separator is highly heterogeneous and far from conformal for surfaces with realistic roughness: the load is carried at a relatively small number of the tallest asperities, while the rest of the Li surface feels no force at all. Yet, dendrite growth is suppressed over the entire Li surface. To explain this observation, we suggest that (1) local contact stresses can be high enough (tens of MPa) at the peaks of Li protrusions (incipient dendrites) so that incremental Li⁺ ions plate instead in regions of low or zero stress; and (2) creep ensures that Li protrusions are gradually flattened. These mechanisms cannot be captured in micron-scale analyses of dendrite growth.

9:45 AM EN05.01.04
Compression Mechanics of Lithium Metal Alvaro Masias¹², Nando Felten¹ and Jeff Sakamoto¹; ¹University of Michigan, United States; ²Ford Motor Company, United States

Recent technological advances such as modern electric vehicles and portable personal electronics have enabled by advances in lithium ion batteries. This technology has improved at a relatively steady 8% per year (in terms of specific energy, Wh/kg) since introduction in 1991. To grow the rate of electrified vehicle adoption, larger improvements in battery technology are needed. While there is a range of competing chemistries for next generation batteries, most would benefit from the use of lithium metal anodes as one of the primary means of improving energy density.

Despite the considerable interest and dependence on lithium anodes in future generation batteries, its mechanical properties are poorly understood. Recently our group investigated the elastic, plastic and creep behavior of lithium metal [1]. This presentation will extend the scope from our previous study to battery specific mechanical environments, specifically aspect ratio, temperature and strain speed.

REFERENCES

10:00 AM BREAK

10:30 AM *EN05.01.05
Measuring Mechanical Deformation of Energy Storage Materials at Small Length Scales with Nanoindentation Kurt Johanns¹ and Erik G. Herbert²; ¹KLA, United States; ²Michigan Technological University, United States

The lifetime, efficiency and reliability of energy storage devices depends strongly on the complex relationships between chemistry and mechanical properties of the materials within the device. As defined by this symposium, there is a need to characterize the mechanical properties of energy storage materials to provide relevant information for chemo-mechanical simulations and models. Here, we cover the measurement of mechanical properties and deformation using nanoindentation techniques. Specifically, elastic modulus, hardness, and creep deformation will be discussed with reference to the relationship between strength, defects, and length scale. The importance of incorporating as-processed material properties with respect to “bulk” property measurements into simulations will be highlighted. Nanoindentation measurements of elastic modulus, hardness, and creep of lithium, ceramic separators, and thin films will be provided to show current capabilities and the experimental challenges of understanding material deformation at the nanoscale. Challenges include film thickness, surface roughness, and large time dependent deformation at room temperature. Because of these challenges, we have performed
Nanoindentation experiments that allow for elastic modulus measurements below 10nm of indentation depth, statistically significant hardness measurements on rough surfaces, and creep deformation measurements at fractions of the time required for standard creep testing. To summarize, nanoindentation can be used as a method for examining mechanical behavior of the materials in energy storage devices, but it is important to understand experimental challenges and what can be done today and, in the future, to overcome those challenges.

11:00 AM EN05.01.06
How the Intersection of Thermo-Mechano-Electrochemical Behaviors Affects Battery Safety and Performance  
Corey T. Love¹, Rachel Carter¹,², Robert W. Atkinson³, Emily J. Klein¹, Conner Fear⁴ and Partha Mukherjee⁵; ¹U.S. Naval Research Laboratory, United States; ²National Research Council, United States; ³EXCET, Inc., United States; ⁴Purdue University, United States

Interfaces in Li-ion batteries play a crucial role in the reversibility of intercalation or plating behaviors. These interfaces are influenced by the coupling of electrochemical reactions, thermal conditions and mechanical changes. As batteries are exposed to a varying environments (low temperature or aggressive charging rates) performance and safety are altered. These variations can enable undesired side reactions like SEI growth or lithium plating. Herein, plating prone conditions, specifically low temperature and thermal shock) are characterized in experimental and commercial Li-ion batteries. Electrochemical behavior is carefully analyzed with (impedance spectroscopy and incremental capacity) and the physical implications on the system are assessed with non-destructive µ X-ray CT (computed tomography). This combined analysis identifies lithium plating and jellyroll collapse as dominate capacity loss mechanisms in abuse scenarios. An accelerated rate calorimeter (ARC) modified with high temperature borescope is used to assess the implications of these conditions (lithium plating or jellyroll collapse) on thermal runaway behaviors. The careful analysis of failure modes identifies thermal gradients as a high risk condition for lithium plating. Coin cell assemblies were utilized to probe this behavior further. These studies reveal the ability to modulate lithium plating behavior in Li-ion and Li-metal systems with external thermal gradients. This observation emphasizes the importance of temperature uniformity in commercial systems and provides an avenue for design of high performance lithium metal anodes.


11:30 AM EN05.01.07
Mechanical Property Measurements of Electroplated Mossy Lithium at Room Temperature  
Dingying Dang¹, Yikai Wang¹, Ming Wang¹, Xingcheng Xiao² and Yang-Tse Cheng¹; ¹University of Kentucky, United States; ²General Motors Global Research and Development Center, United States

Lithium (Li) dendrites and mossy Li remain the major obstacle for the application of Li metal electrodes in liquid electrolyte-based batteries because they excessively consume the electrolyte, can penetrate through the separator, and form dead Li. While new electrolytes and artificial solid electrolyte interphases (SEIs) are being developed, mechanical suppression by, for example, applying proper external pressure, functional separators, and surface coatings, is emerging as an effective approach to improve the cycling stability of Li metal electrodes (even with mossy Li) in liquid electrolyte-based batteries. To better design mechanical suppression approaches, it is indispensable to gain a fundamental understanding of the mechanical behavior of bulk Li as well as mossy Li. Although recent progress has been made in measuring the mechanical properties of bulk Li, the mechanical behavior of electroplated mossy Li is unknown. To fill this knowledge gap, we investigated the mechanical behavior of electroplated mossy Li at room temperature using flat punch indentation inside an argon-filled glovebox. It is found that the Young’s modulus of mossy Li depends on the porosity and is smaller than that of bulk Li. Both the mossy and bulk Li show clearly indentation creep behavior. Despite the highly porous microstructure, the impression creep velocity of the mossy Li is far less than that of bulk Li under the same compressive stress. We proposed possible mechanisms for the significantly higher creep resistance of the mossy Li over bulk Li. These findings may be helpful for developing mechanical suppression approaches to improve the cycling stability of Li metal electrodes.
Stress Evolution in Lithium Metal Electrodes and the Impact of Artificial Passivating Layers Jung Hwi Cho¹,
Xingcheng Xiao², Kai Guo¹, Huajian Gao¹ and Brian W. Sheldon¹; ¹Brown University, United States; ²General
Motors Global R&D Center, United States

The potential advantages of lithium (Li) metal anodes have been widely touted (lowest reduction potential, etc.). However, the poor stability of Li metal / liquid electrolyte interfaces leads to chronic problems, such as dendrite formation and capacity loss. The possible impact of mechanical effects on interface stability and dendrite formation leads to critical questions that are difficult to probe directly. An important part of this are the stresses that arise during battery cycling. These were measured with in-situ wafer curvature. Using this technique during Li plating and examining film thickness effects, it was possible to separate contributions from the bulk lithium metal and the solid electrolyte interphase (SEI). These investigations show that significant stresses are created in the SEI films. Similar stress evolution measurements were also performed during lithium plating and stripping using both soft (PEO) and hard (LiF) artificial surface layers. The results indicate that stresses in surface films can be tuned to improve performance when artificial SEI layers are employed. A basic chemo-mechanical model indicates that hybridizing the two layers may benefit interface stability and performance in Li metal anodes.

SESSION EN05.02: Anode II
Session Chair: Corey Love
Monday Afternoon, December 2, 2019
Sheraton, 2nd Floor, Republic B

1:30 PM *EN05.02.01
Morphological Changes of Alkali Metal Anode in SO₂-Based Inorganic Liquid Electrolyte Juhye Song¹, Goojin Jeong² and Hansu Kim¹; ¹Hanyang University, Korea (the Republic of); ²Korea Electronics Technology Institute, Korea (the Republic of)

Dendritic growth of alkali metal anode during cycling is one of major issues to be addressed for practical application of alkali metal based rechargeable batteries. In this work, morphological changes of Na and Li metal anode were investigated using SO₂ solvated inorganic liquid electrolyte. We found that Na metal anode showed highly stable cycle performance without dendritic formation during cycling in non-flammable and highly Na⁺-conductive NaAlCl₄-2SO₂ inorganic electrolyte, as a result, showing superior electrochemical performances to those in conventional organic electrolytes, which was possible by inducing polygonal growth of Na deposit using a highly concentrated Na⁺-conducting inorganic electrolyte and also creating highly dense passivation film mainly composed of NaCl on the surface of Na-metal electrode. We also found that surface modification of Li metal with Na-containing SO₂ electrolyte can be an effective way to prevent dendritic Li growth during cell operation. The surface-modified Li metal anode exhibited no dendritic deposits even under a high areal capacity (5 mA h cm⁻²) and a high current density (3 mA cm⁻²), while the unmodified anode showed typical filamentary Li deposition. The surface-modified Li metal anode also demonstrated significantly enhanced electrochemical performance, which could be attributed to the newly-formed Na-containing inorganic surface layer that exhibits uniform and dense properties.

Keywords: Li metal, dendrite, battery

2:00 PM EN05.02.02
Stress-Composition Coupling in Li-Alloys and Their Applications Sangtae Kim¹ and Jong Min Yuk²; ¹Korea Institute of Science and Technology, Korea (the Republic of); ²Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The stress inevitably imposed during electrochemical reactions is expected to fundamentally affect the electrochemistry, phase behavior and morphology. Using graphene liquid cell electron microscopy, we recently unveiled the strong stress-composition coupling in lithium binary alloys in the nanoscale. During lithiation of core-shell nanoparticles, the generation of non-uniform composition field is directly visualized with in situ graphene liquid cell electron microscopy imaging. Based on this coupling, we demonstrate that we can directionally control the lithium distribution by applying different stresses to lithium alloy materials. We show a few device concepts of
stress-composition coupling, including electrochemically driven mechanical energy harvesters and non-volatile electrochemical actuators.

2:15 PM EN05.02.03
Operando Quantification of Gas Evolution During Lithium Plating-Stripping in Carbonate Electrolytes
Gustavo M. Hobold and Betar M. Gallant; Massachusetts Institute of Technology, United States

Despite possessing physical properties that justify their use in high voltage, high power aprotic battery chemistries, carbonate-based electrolytes and their resulting solid electrolyte interphases (SEI) do not generally enable morphologically homogeneous plating and stripping to and from metal electrodes. Instead, due to interphase breakdown, freshly plated metal is continuously exposed to the electrolyte. High electrode-electrolyte reactivity causes loss of coulombic efficiency and promotes dendrite growth, ultimately leading to catastrophic cell failure. Efforts to circumvent this issue have often focused on the ex-situ design of an artificial inert SEI or on engineering customized electrolyte systems that are hypothesized to form stable interphases in-situ. Still, due to the difficulty in probing the SEI at the molecular scale, little is known about the dynamics of its formation and breakdown during plating and stripping, and the products thereof. Here we investigate the gas phase products resulting from lithium plating and stripping under operando conditions using a custom electrochemical cell coupled to a gas chromatograph. Under electrochemical activity, we quantify the evolution of several C1-C2 species, as well as CO, CO2 and H2, that are dynamically formed due to electrolyte decomposition and SEI formation and breakdown. The operando nature of our experiments enables the identification of gases evolved through pathways that have rate-limiting electron-transfer steps, as well as gases that have chemical reactions as rate-limiting steps. Moreover, we show that SEI transformations, such as the chemical conversion of interfacial Li2CO3 into Li2O, release detectable gas signatures, which are then correlated with interfacial composition measured by X-ray photoelectron spectroscopy. Because some species are formed exclusively by pathways involving electron transfer, we correlate gas evolution with plating-stripping coulombic efficiency, and hence capacity loss. By varying galvanostatic conditions, we observe rate-dependent gas evolution, which we link to surface morphology using ex-situ scanning electron microscopy. We then investigate electrolyte systems that are known to enable morphologically homogeneous plating-stripping, in which gas evolution is expected to be suppressed due to the formation of a likely stable SEI. Finally, we suggest that operando gas analysis can be effective in identifying species and their formation mechanisms that result from parasitic electrode-electrolyte reactions, the evolution of which needs to be suppressed to achieve high cycling stability.

2:30 PM EN05.02.04
Atomistic Conversion Reaction Mechanism of WO3 in Secondary Ion Batteries of Li, Na and Ca
Yang He1, Meng Gu2, Haiyan Xiao3, Langli Luo4, Yuyan Shao1, Fei Gao5, Yingge Du1, Scott X. Mao6, Chongmin N. Wang1 and Linze Li1; 1Pacific Northwest National Laboratory, United States; 2Southern University of Science and Technology, China; 3University of Electronic Science and Technology of China, China; 4Tianjin University, China; 5University of Michigan, United States; 6University of Pittsburgh, United States

Intercalation and conversion are two fundamental chemical processes for battery materials in response to ion insertion. The interplay between these two chemical processes has never been directly seen and understood at atomic scale. Here, using in situ HRTEM, we captured the atomistic conversion reaction processes during Li, Na, Ca insertion into a WO3 single crystal model electrode. An intercalation step prior to conversion is explicitly revealed at atomic scale for the first time for Li, Na, Ca. Nanoscale diffraction and ab initio molecular dynamic simulations revealed that after intercalation, the inserted ion-oxygen bond formation destabilizes the transition-metal framework which gradually shrinks, distorts, and finally collapses to an amorphous W and M2O (M=Li, Na, Ca) composite structure. This study provides a full atomistic picture of the transition from intercalation to conversion, which is of essential importance for both secondary ion batteries and electrochromic devices.

2:45 PM EN05.02.05
Controlling Electrochemical Lithium Deposition and Sulfur Reduction Mechanism through Liquid Electrolytes
Heng-Liang Wu; National Taiwan University, Taiwan

Lithium metal anode has been regarded as the "Holy Grail" of next-generation battery technologies. In order to stabilize the electrodeposited Li metal for safe and high energy batteries, highly concentrated electrolytes (solvate electrolytes) have been proposed to suppress the formation of Li dendritic structure and polysulfide dissolution in
lithium-sulfur (Li-S) batteries. (1-5) In this talk, we use in situ transmission X-ray microscopy (TXM) to study the effect of solvate electrolyte on Li plating/stripping process. In situ TXM images show that electrodeposited Li particles with uniform density are formed in solvate electrolyte during initial plating process. The effect of solvate electrolyte on the mechanism of Li growth is studied in detail. Additionally, in situ spectroscopy including Raman and X-ray spectroscopy (X-ray diffraction and X-ray absorption spectroscopy) are used to investigate sulfur reaction mechanism and the interaction between polysulfide and solvate electrolyte. We found that the sulfur species formed in the solvate electrolyte are different from the sulfur species formed in conventional DOL/DME electrolyte. These results suggest that solvate electrolyte changes both polysulfide solubility and sulfur reaction mechanism. We next propose different solvate electrolytes with low polysulfide solubility and high stability toward Li metal to enhance the capacity retention of Li-S batteries.

References:

3:00 PM BREAK

3:30 PM EN05.02.06
Si Anodes for Li-Ion Batteries from Electrospray/Spin Particle-Polymer Nanofibers Abhishek N. Mondal¹, Ryszard Wycisk¹, Peter Pintauro¹, Ethan C. Self² and Jagjit Nanda¹; ¹Vanderbilt University, United States; ²Oak Ridge National Laboratory, United States

Presently, there is a high demand for rechargeable batteries which provide high energy and power densities. Generally, the usage of portable electronic devices is limited by the short lifetime and charge capacity of batteries. Therefore, to cope with the increasing demand of consumers, novel battery electrodes with enhanced volumetric, gravimetric and areal capacities under fast charging rates need to be developed. This demand has prompted intensive research efforts for developing next generation Li-ion battery electrodes, e.g., to replace conventional slurry cast carbon anodes. Electrospinning is considered to be a convenient and promising approach for the fabrication of porous mats with tailored micron/sub-micron diameter fibers containing nanoparticles and polymer binder.¹,² Electrospun anodes for Li-ion batteries have superior characteristics including: (i) high electrode/electrolyte interfacial area, (ii) flexible interfiber void space of an electrode mat to facilitate electrolyte infiltration, and (iii) micron/sub-micron sized fibers with a high nanoparticle content (short Li⁺ ion transport pathways in the radial fiber direction). Pintauro and co-workers have examined and reported on several different types of electrospun anodes for Li-ion batteries with TiO₂/C³, Si/C⁴ or PVDF/C⁵ nanoparticles with either poly(acrylic acid) (PAA) or poly(vinylidene fluoride) (PVDF) as the polymeric binder. In our current work we are focusing on an electrospun/electrosprayed system where a Si/binder ink was electrosprayed into fiber with the simultaneous electrospinning of a C/binder ink. Preliminary half-cell charge/discharge data are very promising. For example, an anode containing 61 wt.% Si-PAA fibers (40 wt.% PAA) and 39 wt.% C-PVDF droplets (37 wt.% PVDF) exhibited a terminal discharge gravimetric capacity of 1100 mAh/g (based on the total anode weight) at 0.1C and 600 mAh/g at 1C, with remained constant for 50 charge/discharge cycles. For this anode, the areal capacity was 1.2 mAh/cm² and the coulombic efficiency was ~99%. During this presentation, details will be given on the fabrication method and structure of the fiber/sprayed anodes, along with charge/discharge data at different C rates. The effects of binder type and Si/C weight ratio on anode performance (gravimetric, volumetric, and areal capacities) at different C-rates will be discussed.

References:
3:45 PM EN05.02.07
The Impact of Oxide Content on Cycle Life and Stress Evolution in Silicon-Based Composite Electrodes
Mok Yun Jin¹, Elizabeth Healy¹, Xingcheng Xiao² and Brian W. Sheldon¹; ¹Brown University, United States; ²General Motors Global R&D Center, United States
Silicon has received much attention as a promising negative electrode material, however, it undergoes extremely large volume changes during lithiation/delithiation. This leads to substantial stresses inside of particle-based electrodes, which are believed to cause poor cycling performance. Composite electrodes that also incorporate oxidized silicon are a cost-effective way to accommodate these stresses and extend cycle life. To obtain fundamental information about chemomechanical phenomena in these composite structures, several different types of materials are being investigated: (1) Si nanoparticles with oxide shells, (2) Si thin films with oxidized surface layers, and (3) composite SiOx particles. The evolution of internal stresses in all of these structures was monitored with precise in-situ curvature in conjunction with parallel electrochemical measurements. Ex situ characterization with electron microscopy, x-ray diffraction, and XPS provide important complementary information about changes in the materials. The different types of materials used for this work make it possible to systematically investigate key length scales, by independently varying oxide layer thicknesses and particle sizes. Analysis of these results requires assessments and models of both the chemical and mechanical effects oxide surface layers and silicon encapsulation. The implications for optimizing these composite electrode structures will also be presented.

4:00 PM EN05.02.08
Long Cycle-Life and High-Rate Magnesium-Ion Battery Anode Enabled by Self-Healing through Near-Room-Temperature Solid-Liquid Phase Transition
Lin Wang, Samuel S. Welborn, Hemant Kumar Kumar, Vivek Shenoy and Eric Detsi; Univ of Pennsylvania, United States
Resources used in lithium-ion batteries are becoming more expensive due to demand, and the global cobalt market heavily depends on supplies from countries with high geopolitical risks. Alternative battery technologies including magnesium-ion batteries are therefore desirable. Progress toward practical magnesium-ion batteries have been impeded by an absence of suitable anodes that can operate with conventional electrolyte solvents. Although alloy-type magnesium-ion battery anodes are compatible with common electrolyte solvents, they suffer from severe failure associated with huge volume changes during cycling. Consequently, achieving more than 200 cycles in alloy-type magnesium-ion battery anodes remains a challenge [1]. In this talk I will an unprecedented long-cycle life of 1000 cycles, achieved at a relatively high (dis)charge rate of 3C (current density: 922.5 mA/g) in Mg2Ga5 alloy-type anode, taking advantage of near-room-temperatures solid-liquid phase transformations between Ga(liquid) and Mg2Ga5(solid)[2]. A combination of Finite-Element Modelling (FEM), electrochemical characterization, and operando wide-angle X-ray scattering (WAXS) is used to investigate this remarkable cycling performance[2]. This concept should open the way to the development of practical anodes for the next generation magnesium-ion batteries.

Keywords: Beyond lithium, Magnesium-ion battery anode, self-healing, solid-liquid phase transformation, operando X-ray scattering.


[2] L. Wang, S.S. Welborn, H. Kumar, Z. Wang, M. Li, V. Shenoy, and E. Detsi: High-Rate and Long Cycle-Life Alloy-Type Magnesium-Ion Battery Anode Enabled through (De)magnesiation-
A 0.7 mAh LiFePO4/graphite Li-ion pouch cell with a 1.0 M LiPF6 1:1 Ethylene Carbonate:Ethyl Methyl Carbonate v/v electrolyte was overdischarged by a fixed 35.7 kOhm resistive load applied continuously for 2 weeks. The resistive load was applied after the 5th conditioning cycle discharge by constant 0.07 mA current to 2.5 V cell voltage. 3-electrode measurements show that the anode increases to 3.4 V vs. Li/Li+, which is greater than the copper oxidation potential, after about an hour after application of the fixed resistive load as the cell voltage decreases to ~200 mV. At about the 6th hour of the fixed resistive load overdischarge step, the cell voltage rapidly (~5 minutes) increases from 200 mV to about 1.5 V, plateaus for about 4 hours then decreases during the next ~4 hours to 0.0 V. The 3-electrode results show that the cell voltage increase is driven by the anode potential rapidly decreasing from 3.4 V vs. Li/Li+ to about 1.5 V vs. Li/Li+ at the 6th hour for about 4 hours. The cathode potential rapidly decreases from 3.5 to ~3.0 V vs. Li/Li+ at the 6th hour and plateaus for about 4 hours. The cathode and anode potentials then decrease to ~1.0 and ~0.5 V vs. Li/Li+, respectively, during hours 10-14 of the fixed resistive load step until the electrode potentials asymptote together and increase to about 2.6 V vs. Li/Li+ during the remaining ~322 hours of the fixed resistive load step. When the cell was recharged after the 2 week fixed resistive load overdischarge step the cell charge/discharge capacity increased by about 0.08 mAh. The electrode potential characteristics also changed consistent with an increase in the reversible lithium available in the cell compared to before the fixed resistive load overdischarge.

Visual inspection of the anode shows darkening in some areas of the composite surface. Scanning electron microscopy (SEM)/energy dispersive x-ray (EDX) and x-ray photoelectron spectroscopy (XPS) results show a significant, non-uniform change to the interfacial chemistry of the anode with an increase in the presence of fluorine, phosphorous, copper and lithium on the surface compared to a control cell that was not overdischarged. The increased presence of the phosphorous, lithium and fluorine was more substantial in the visually darkened areas. High resolution XPS scans of the Phosphorous 2p, Fluorine 1s, and Oxygen 1s show the 2 week fixed resistive load overdischarge increases the presence of LiPFy, LiF, LiPOyFz and P4O10 compounds on the surface of the anode, particularly in the visually darkened areas of the anode. Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) of dried electrolyte samples shows an increase in copper content of the electrolyte in an overdischarged cell compared to a cell that was not overdischarged.

The next generation high-energy batteries comprise light element metals for the cathode, electrolyte, and anode (Li-S, Li-O, and solid electrolytes, respectively) and will be replacing its non-transition metals counterpart. The former materials, however, are known to be highly reactive – the materials are very sensitive to air and electron beam. Sample preparation and experimentation are challenging because it is necessary to transfer samples between milling
systems and microscopes while simultaneously maintaining the material’s integrity. A critical requirement in developing these materials for tangible applications is the ability to characterize the materials in a pristine state, without environmental modifications or contamination. Furthermore, transmission electron microscopy (TEM) is a critical analytical technique for battery research and development. Following the advancement of cryo-electron microscopy (cryo-EM) in life sciences, cryo-EM has been adapted for Li battery research, which allows for the preservation of the Li battery materials’ native state during imaging at the atomic scale. This study presents robust controlled environments that protect the material during the sample preparation phase (bulk to focused ion beam [FIB] preparation) and through the multi-length scale electron microscopy characterization phase. At the micrometer scale, scanning electron microscopy (SEM) characterization will show the morphology of the solid electrolyte while the sub-angstrom scale using the TEM providing interfacial chemistry and morphology. High quality, Li ion battery TEM specimens that are free from amorphous and Ga damage will be prepared and imaged under cryo-EM conditions.

The controlled environments workflow for SEM and TEM sample preparation and microscopy characterization involved the preparation of the bulk sample using broad ion beam (BIB) Ar⁺ milling to remove surface oxides. A vacuum/inert gas transfer capsule protected the sample post-BIB milling. A glove box with a positive pressure environment was used to transfer the bulk sample from the vacuum/inert gas transfer capsule to a FIB transfer system, and thereafter, to a FIB system for morphology and elemental characterization and subsequently TEM specimen preparation. A TEM half grid was secured in the cartridge of a vacuum transfer specimen holder. This cartridge was inserted into the FIB by means of the FIB transfer system. A TEM specimen was prepared using standard lift-out methods and polishing steps (30 and 5 kV) in the FIB. The cartridge with the TEM specimen was moved into the FIB transfer system and then to the glove box. Subsequently, the cartridge was mounted on the vacuum transfer specimen holder within the glove box. The TEM specimen holder was then moved to a concentrated Ar⁺ beam milling system. Ar⁺ milling was performed by rastering the beam within a defined area of the TEM specimen at decreasing milling energies. Subsequently, the TEM specimen was loaded on a cryo TEM holder inside the glove box; a glove bag with inert gas protected the TEM specimen during insertion of the cryo holder in the TEM. The cryo holder was then cooled in the TEM.

Cryo-EM imaging and analysis using energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) before and after ion milling to quantify the removal of FIB-induced damage and the workflow’s ability to prevent specimen oxidation and contamination will be presented.

4:45 PM EN05.02.11
Maintaining the Contact between Solid Polymer Electrolyte and Lithium Metal Anode Using an Adaptive Buffer Layer Nian Liu and Haochen Yang; Georgia Institute of Technology, United States

Solid polymer electrolytes (SPEs) have the potential to enhance the safety and energy density of lithium batteries. However, poor interfacial contact between the lithium metal anode and SPE leads to high interfacial resistance and low specific capacity of the battery. In this presentation, I will show a novel strategy to improve this solid–solid interface problem and maintain good interfacial contact during battery cycling by introducing an adaptive buffer layer (ABL) between the Li metal anode and SPE. The ABL consists of low molecular-weight polypropylene carbonate, poly(ethylene oxide) (PEO), and lithium salt. Rheological experiments indicate that ABL is viscoelastic and that it flows with a higher viscosity compared to PEO-only SPE. ABL also has higher ionic conductivity than PEO-only SPE. In the presence of ABL, the interface resistance of the Li/ABL/SPE/LiFePO4 battery only increased 20% after 150 cycles, whereas that of the battery without ABL increased by 117%. In addition, because ABL makes a good solid–solid interface contact between the Li metal anode and SPE, the battery with ABL delivered an initial discharge specific capacity of >110 mAh/g, which is nearly twice that of the battery without ABL, which is 60 mAh/g. Moreover, ABL is able to maintain electrode–electrolyte interfacial contact during battery cycling, which stabilizes the battery Coulombic efficiency.

This presentation is based on our recent publication: *ACS Appl. Mater. Interfaces*, 2019, 11 (31), 27906-27912 https://doi.org/10.1021/acsami.9b08285
Battery cathode materials that could host both cationic and anionic redox activities have demonstrated an impressive capacity and, therefore, are the subject of intense research. The interplay among the co-existing redox centers is critical to battery performance. While tremendous efforts have been devoted to investigating the electrochemically-driven redox evolution on the surface and in the bulk of the high-energy-density cathodes at room temperature, their behavior under elevated temperature is an area that lacks in-depth investigation.

In this presentation, I will show our recent systematic investigation of the thermally-driven redox coupling effect in lithium- and manganese-rich (LMR) materials using Li$_{1.2}$Ni$_{0.15}$Co$_{0.1}$Mn$_{0.55}$O$_2$ as an example. Under thermal abuse conditions, we report the structural degradation from the atomic scale up to the particle level. In particular, under mildly elevated temperature (~100 C), we observed long-range charge transfer between the oxygen anions in the bulk and the transition metal cations on the surface. Our results suggest that the thermally-activated ionic mobility in the hosting LMR lattice could lead to the redistribution of lithium-ions, which facilitate the long-range redox coupling effect and maximizes the entropy of the system as it settles to a new equilibrium.

These findings highlight the dynamic nature of redox couples in LMR material at even slightly elevated temperature. Such temperature sensitivity can have profound impacts on both the battery safety and electrochemical performance.

We assess the heterogeneous electrochemistry and mechanics in a composite electrode of commercial batteries using synchrotron X-ray tomography analysis and microstructure-resolved computational modeling. We visualize the morphological defects at multi-scales ranging from the macroscopic composite, particle ensembles, to individual single particles. Particle fracture and interfacial debonding are identified in a large set of tomographic data of active particles. Mechanical failure in the regime near the separator is more severe than toward the current collector. The active particles close to the separator experience deeper charge and discharge over cycles and thus are more mechanically loaded. The difference in the Li activity originates from the polarization of the electrolyte potential and the non-uniform distribution of the activation energy for the charge transfer reaction. We model the kinetics of intergranular fracture and interfacial degradation to confirm that the various Li activities are the major cause of the heterogeneous damage. The interfacial failure may reconstruct the conductive network and redistribute the electrochemical activities that render a dynamic nature of electrochemistry and mechanics evolving over time in the composite electrodes. We further quantify the influence of the mechanical damage on the metrics of battery performance. We simulate the electrochemical impedance profile to build a relationship between the interfacial debonding and the impedance of electron transport and surface charge transfer. The mechanical failure disrupts the conduction path of electrons and results in significant polarization and capacity loss in batteries.

We have devised an approach to fabricate dense textured V$_2$O$_5$ thin films, which allows us to scrutinize the root cause of capacity fade in V$_2$O$_5$ cathodes of Li-ion batteries. Specifically, we performed in-situ measurements of stress of V$_2$O$_5$ thin films during 50 electrochemical cycles. Surprisingly, electrochemical cycling appears to induce elastic and rate-independent deformation over a voltage range relevant to battery operation (4 - 2.8 V). However, the
compressive stresses gradually increase with cycle number during the first few cycles, likely due to side reactions and/or residual Li left in the V$_2$O$_5$, even after delithiation (to 4 V). Further cycling leads to accumulated mechanical (e.g., fracture, delamination) and structural changes which ultimately result in severe capacity fade.

9:30 AM EN05.03.04
Transition Metal Dissolution from LiNi$_{0.8}$Mn$_{1.5}$O$_4$ Cathode Investigated by Ab Initio Free Energy Simulations
Vitaly Alexandrov$^1$, Nadia Intan$^1$ and Konstantin Klyukin$^2$; $^1$University of Nebraska-Lincoln, United States; $^2$Massachusetts Institute of Technology, United States

Dissolution of transition metals (TMs) from the cathode and their subsequent accumulation on the anode contributes to the capacity fading of lithium ion batteries (LIBs) regardless of the chemical nature of the cathode. In recent years this stability aspect of LIBs has received growing attention in the community, however, mechanistic understanding of the associated processes is hampered by the complexity of electrochemical interfaces under study. Here, we present the results of our first-principles molecular dynamics based investigation of TM dissolution from the high-voltage spinel-structured LiNi$_{0.8}$Mn$_{1.5}$O$_4$ cathode into the liquid organic electrolyte. By employing accelerated free-energy simulations with explicit treatment of the organic electrolyte, we analyze a number of factors affecting the kinetics of TM dissolution including the nature of TM (Ni, Mn) and electrolyte species, the presence of surface protons and oxygen vacancies. The obtained results also suggest a clear correlation between the adsorption strength of electrolyte species and TM dissolution barriers enabling materials screening toward systems less prone to TM dissolution.

9:45 AM BREAK

10:30 AM *EN05.03.06
A Resistor-Network Method for the Investigation of Structure-Transportproperty Relations in Granular Cathodes of Lithium-Ion-Batteries
Oleg Birkholz and Marc Kamlah; Karlsruhe Institute of Technology, Germany

The properties of lithium ion batteries (LIB) depend critically on the transport properties in the electrodes. In this work, we focus on the effective transport properties of the granular cathode consisting of active material particles, liquid electrolyte, and additives, i.e. a mixture of binder and carbon black. To study the impact of the granular structure through the effective transport parameters on the cell performance is our objective in this work. The classical Newman cell model requires effective transport parameters, electronic and ionic, in the solid and liquid phases. Typically, they are obtained by empirical theoretical models such as the well-known Bruggeman relation. In our approach, we compute all needed effective transport properties by resistor network methods, as well as the structural data such as porosity and specific surface area. To this end, either tomographic real data or statistically equivalent virtual structures are imported from project partners. To study the structure property relations of the cathode, we simulate half cells with a lithium foil and a separator of which the effective transport parameters are obtained from Bruggeman relations, for simplicity. The active material in the cathode is represented as an assembly of spherical particles of a given size and at a given packing factor. A resistor network method will be presented to model the effective transport through this phase. In this approach, each particle corresponds to a node with a certain potential and the edge to a connected neighbor defines a resistor as a function of the bottleneck geometry. This computationally efficient and simplifying approach was validated by comparison to spatially resolved finite element models. Furthermore, a resistor network method will be introduced for the effective transport property in the space surrounding the particles. In this case, the so-called Voronoi tessellation is used where the corners of the resulting cells are the nodes and resistors are assigned to the edges based on the throat geometry in the space between particles. This method was validated by comparison to finite element simulations as well.

In the next step we account for the fact that the space between active material particles is filled by an additive, consisting of a binder-carbon black mixture, on the one side and liquid electrolyte, on the other. A method is presented how to calculate the effective electronic conductivity of the additive phase and verified by comparison to experiments in literature. Depending on the volume fraction of liquid electrolyte in the remaining space between active material particles, the effective ionic conductivity and diffusivity are is determined. In this way, all effective transport properties needed for cell modeling, are obtained from structural data of cathodes. We present and discuss values of structural and transport properties for some real electrodes. Furthermore, cell simulation shows the C-rate dependence of specific capacity. A characteristic drop at a certain C-rate is found which depends on the electrode thickness. These trends are in good agreement with experimental results by project.
partners. Finally, we will present a parameter study concerning electrode thickness, particle size, porosity, and specific surface area in view of the effect of these parameters through the related effective transport properties on the cell performance.

11:00 AM EN05.03.07
Electrochemical-Shock Resistant Single-Crystal Ni-Rich Layered Cathode Materials Linsen Li, Guannan Qian and Zi-Feng Ma; Shanghai Jiao Tong University, China

Ni-rich layered oxides LiNi$_x$M$_{1-x}$O$_2$ (x>0.6, M = Co, Mn and/or Al) are technologically important cathode materials for lithium-ion batteries due to their high energy density and good power capability. These materials are usually prepared by a co-precipitation and post-calcination method that produces micron-sized polycrystalline (PC) particles consisting of nanoscale grains. The unique microstructure and anisotropic Vegard coefficient make them vulnerable to grain-boundary fracture (“electrochemical shock”), a major cause for impedance growth and performance degradation. We have recently developed a scalable method to prepare a variety of single-crystal (SC) Ni-rich cathode materials. SC-NMC622 outperforms the commercial PC-NMC622 in cycling stability, rate performance, and thermal stability. Post-cycling structural characterizations reveal that the SC-NMC622 do not crack and its surface undergoes less phase transformation than PC-NMC622. The fracture mechanism of PC and SC layered oxide cathode materials will be discussed and compared. SC Ni-rich cathode materials are critical to fabricating mechanically reliable solid-state batteries and provide a unique platform for studying doping and surface modification methods.

11:15 AM EN05.03.08
Observation and Elucidation of Stress-Induced Non-Uniform Reaction Behavior in LiFePO$_4$ Secondary Particles Fan Wang, Kaiqi Yang and Ming Tang; Rice University, United States

Particle-level reaction heterogeneity in lithium ion batteries can lead to formation of microcracks, local over-charge/discharge, and thus loss of capacity and shortened cycle life. The origin of this phenomenon is still not well understood, with many factors in play including particle morphology, thermodynamic properties, nonuniform electronic connections as well as the applied cycling conditions. In this work, operando measurements using synchrotron-based transmission X-ray microscopy (TXM) are conducted for LiFePO4 (LFP) secondary particles upon slow charging. We show that persistent nonuniform distribution of state-of-charge (SOC) exist during the entire charge process. Unlike the core-shell structure often observed in the cycling of single-crystalline electrode particles, the delithiated phase nucleates at a small number of “hotspots” and grows outwards in a highly anisotropic, finger-like pattern. Our phase-field simulation well captures the experimental phase morphology and explains the observed phase evolution behavior. We propose the incompatibility of lattice expansion among randomly oriented primary particles as the source of the reaction heterogeneity. It induces non-uniform Li-insertion stress among primary particles, which results in spatially varied nucleation and growth energy barriers. As a result, new phase preferentially nucleates at grains where adjacent grains can expand coordinately and follows a growth pathway with the least elastic energy penalty. As many battery compounds exhibit anisotropy in lattice expansion and elasticity, our observation may represent a general phenomenon for secondary electrode particles.

11:30 AM EN05.03.09
Structural Inclusions-Induced High-Rate and Long Cycle-Life in Bulk Na$_{2/3}$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ Sodium-Ion Battery Cathodes Jintao Fu$^{1}$, John Corsi$^{1,2}$ and Eric Detsi$^{1,2}$; $^{1}$University of Pennsylvania, United States; $^{2}$Vagelos Institute for Energy Science and Technology (VIEST), United States

Recently, sodium-ion batteries (SIB) have been considered as a promising alternative to lithium-ion batteries due to the abundance of sodium resources (Na is the Earth’s 6th most abundant element, while Li is 33th) and its low extraction costs. Among various SIB candidate cathode materials, the layered oxides Na$_x$Ti$_3$O$_7$ (Ti=3d transition metal elements and their mixture) made of earth-abundant elements can reversibly store sodium by intercalation at relatively high voltages (up to ~3.8 V vs Na/Na$^+$). However, these cathode materials suffer from a poor rate capability and short cycle life. In this talk, I will present a novel bulk Na$_{2/3}$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ structure containing void-type inclusions, which we have developed using ultrafine three-dimensional (3D) bicontinuous nanoporous nickel (NP-Ni) scaffold as template. During the conversion of this 3D NP-Ni scaffold into Na$_{2/3}$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ through solid-state reaction, the void space in the NP-Ni gives rise to structural inclusions in the bulk of the Na$_{2/3}$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$. The as-synthesized cathode materials exhibit outstanding cycling stability with ~94% capacity
retention at 5C after 1000 cycles. When cycled at ultra-fast rates of 50C, the material still shows an unprecedented rate capability with roughly 50% capacity retention. Kinetic analysis at a scan rate of 1 mV/s reveals that ~86% of the overall capacity originates from the capacitive contribution, suggesting that sodium storage between the layers is not diffusion-limited. Therefore, High-resolution Transmission Electron Microscopy (HRTEM) analysis was performed to understand the origin of the ultra-fast Na-ion migration in and out of the material. It was found that the Na-intercalation layer spacing increased by ~16% due to inclusions, compared to pristine material counterparts without inclusions. These structural inclusions were further studied using Small/Wide-angle X-ray Scattering (SAXS/WAXS). Such void inclusion-induced structure can be applied to a wide range of material systems, and will shed new light on the design of high-performance cathode materials.

11:45 AM EN05.03.10
Effect of Sn Doping on the Enhanced Charge Transport Properties of V_2O_5 Cathode of Li-Ion Batteries—A First-Principles Study
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Vanadium pentoxide (V_2O_5) is one of the most promising cathode materials used in metal-ion batteries due to its high theoretical capacity. However, it still suffers from several limitations such as slow electrochemical kinetics. Although the introduction of Sn impurities in V_2O_5 has been proposed to alleviate the kinetic drawback of the cathode, the origin of the enhancement is still vague. To find fundamental explanations and better understand the role of Sn dopants, we carried out the density functional theory (DFT+U) calculations to identify the most thermodynamically stable defects in the presence of Sn dopants. Specifically, we computed the defect formation energies of various point defects, charge carriers, and defect complexes to determine their relative stabilities in the lattice. We find that Sn could be inserted in the lattice or substituted at a V site. Sn insertion exhibits mixed ionic/covalent interaction with the lattice and donates two electrons which are localized at the two nearby V centers. Alternatively, Sn is found to be more stable to replace at the V lattice site when an oxygen vacancy (V_O) is created at the nearest neighbor position. The Sn-V_O defect complex generates one extra electron localized at the nearby V center. These extra electrons created upon the defect formations are trapped at the V sites which in turn induce distortion of local structure and form small polarons. Small polarons can undergo thermally activated hopping from one V site to the nearby site throughout the lattice where their transport properties could affect the diffusion of Li^+ ions. In order to study the transport properties of ions and polarons, we employed nudged elastic band (NEB) method to calculate their migration barriers. Overall, computations show that Sn doping increases number of charge carriers in the V_2O_5 cathode. Structural distortion upon doping increases stabilities of Li insertion while does not diminish migration properties of charge carriers. The obtained fundamental understanding of the defect formation in the V_2O_5 based cathode materials could be one way to promote the improvement of the battery technologies.
densities of states near the Fermi level and reduce the work function, hence efficiently enhancing its oxygen reduction activity. In addition, we demonstrated the critical role of structural H2O. The results suggest that the H2O-solvated Zn2+ possesses largely reduced effective charge and thus reduced electrostatic interactions with the V2O5 framework, effectively promoting its diffusion. We also identified the exciting electrochemical properties (including high electric conductivity, small volume change and self-preserving effect) and superior sodium storage performance of alkaline earth metal vanadates through preparing CaV4O9 nanowires. Furthermore, a novel assembled nanoarchitecture was also presented, which consists of V2O5 nanoparticles embedded in amorphous carbon nanotubes that are then coassembled within a reduced graphene oxide network. The naturally integrated advantages of each subunit exhibit highly stable and ultrafast sodium-ion storage. Our work presented here can inspire new thought in constructing novel one-dimensional structures and accelerate the development of energy storage applications.

2:00 PM *EN05.04.02
Material-Gene and Structure Chemistry of Li-Ion Battery Feng Pan and Tongchao Liu; Peking University Shenzhen Graduate School, China

Insight into relationship between Crystal/Interface structure and properties of capacity, stability and rate capability by methods of material-Gene and structure chemistry are important for developing advanced Li-ion batteries. (Ref. 1) Using theoretical calculations combined with experimental in-situ tests, we did extensive studies on the kinetic of Li-ion diffusion for two representative cathode materials: layered Li(NixMnyCoz)O2 (NMC) (x + y + z = 1) and LiFePO4. We not only focus on the bulk kinetics, but also the kinetics across electrode/electrolyte solid-liquid interface and in the electrolytes.(Ref. 2) Using ab initio calculations combined with experiments, we clarified how the thermal stability of NMC materials can be tuned by the most unstable oxygen. In NMC, insight of Ni/Li disorder has be investigated by theory and experimental e.g. neutron powder diffraction experiments and magnetization measurements. Thus, the variation of Li/Ni exchange ratio vs. TM mole fraction in NMC with different compositions can be well understood and predicted in terms of magnetic frustration and superexchange interactions. (Ref. 3) The formation of the SEI between a graphite anode and a carbonate electrolyte are investigated through combined atomic-scale microscopy and in situ and operando techniques. The insight of “H2O in Salt” and related structure vs. electrochemical window are revealed . (Ref. 4)

Ref.
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2:30 PM EN05.04.03
Design and Operation of Electro-Chemo-Mechanical Actuators Evgeniy Makagon, Eran Mishuk, Sidney R. Cohen, Ellen Wachtel and Igor Lubomirsky; Weizmann Inst of Science, Israel

The electro-chemo-mechanical (ECM) effect causes dimensional change in a solid due to change in chemical composition induced by a Faradaic electric current. The ECM effect seriously impairs the functioning of batteries or
fuel cells, limiting their lifetime and degrading their performance. However, it is was recently suggested that the electro-chemo-mechanical coupling has the potential for use in actuation\cite{1}. To explore this idea, we propose the following scheme as a basic design for an ECM actuator: electrode1\WB1\solid-electrolyte(SE)\WB2\electrode2, where WB denotes a working-body comprising a mixed ionic-electronic conductor with a large chemical expansion coefficient.

Theoretical analysis of this actuator design indicates: 1. The speed of actuation is limited by the ionic diffusion coefficient in WBs but not in SE. 2. ECM actuation has several potential advantages: (a) ECM actuators can simultaneously deliver large strain and large stress, which is difficult to achieve with other actuation mechanisms; (b) ECM actuators maintain their state after external voltage is removed; (c) displacement and force generated by an ECM actuator are determined by the amount of charge transferred, which is more readily controlled than electric field-driven devices. 3. The only major shortcoming of ECM actuation is that its energy conversion efficiency cannot exceed a few percent.

To demonstrate the concept, we have constructed a room temperature, nanocrystalline ECM membrane actuator (2mm diameter and »2µm thick) with Gd-doped ceria as SE. We tested two alternative compositions for WB’s: (1) metal/(metal oxide) or (2) nanocrystalline ceria/metal composite. Electrical and electromechanical measurements demonstrated that the actuator response with metal/metal oxide WB’s is limited by the rate of oxygen diffusion from the solid electrolyte to the metal surface. Actuators with ceria/metal composite WB’s provide shorter response time (»20sec) and larger vertical displacement (>3.5µm). These findings suggest that the ECM effect may indeed become a valuable actuation mechanism for MEMS applications.

References

2:45 PM EN05.04.04
Explicit Consideration of Carbon Binder Domains in 3D-Resolved Model to Optimize Fabrication Process
Mehdi Chouchane1,2, Alexis Rucci1,2 and Alejandro A. Franco1,2,3; 1Laboratoire de Réactivité et Chimie des Solides, France; 2RS2E, France; 3ALISTORE-ERI (CNRS), France

In the literature, reported 3D-resolved battery models rely on oversimplifications, such as an implicit representation of the carbon-binder domains (CBD) through the use of effective parameters for porosity and tortuosity or by merging CBD with the Active Material (AM) as a single solid phase.

This work’s novelty relies on the explicit representation of CBD, leading to a new level of accuracy in terms of electrochemical modeling. This achievement is made possible thanks to an in-house algorithm, INfinite Number Of phases meshing through Voxelization (INNOV)\cite{1}. INNOV can generate a volumetric mesh from data of different types due to its flexible input format. INNOV takes as input binary stack of images to reconstruct the 3D structure. Such an input can arose from tomography imaging, from slicing a 3D object or from Coarse Grained Molecular Dynamics(CGMD) simulations\cite{2}. For the latter a function has been developed to convert its output (coordinates of the centers and radii of the particles) into a binary stack of images. This algorithm is designed in the scope of the ARTISTIC Project\cite{3} to import a multi-phase volumetric mesh of an electrode (from a CGMD simulation) into COMSOL Multiphysics to simulate the performances of the cell.

The segmentation method of Nielson and Franke\cite{4} has been translated and optimized for MATLAB language and modified to suit the COMSOL Multiphysics meshing importation process. To tackle the computational cost of a 3 phases mesh, a “precision” parameter is introduced to downsample the number of nodes, faces and elements. Time-efficient meshing is achieved thanks to the simplicity of the operations and to an optimization through a matrix formalism in MATLAB.

The core of this work is to increase the current level of precision of the modeling of batteries by separating active and inactive materials. In doing so, one must not sacrifice the integrity of the mesostructure geometry. To ensure this, INNOV provides a number of observables, which can be compared to experimental numbers (e.g. arising from tomography characterizations). Among them, two distinct values of porosity are displayed by INNOV: the porosity of the mesh and the porosity of the stack of images. Furthermore, the volume ratio of each phase in the mesh is compared to its value in the stack of images. This can render proof of the overall volume conservation of each phase; however, these are average values and cannot highlight local deformations within the mesh. Another useful
insight is the surface coverage between different phases.

Once the integrity of the mesh is ensured, electrochemical simulations can be done to characterize the two structures along different hypotheses for the CBD behavior. The first approach is to consider the CBD as blocking, i.e. there is no diffusion nor intercalation of Li inside the CBD. The second one is transparent CBD, the Li diffuse inside the CBD with the same diffusion coefficient as in the electrolyte but there is still no intercalation. Such study can highlight the importance of the CBD morphology in a 3D-resolved battery model beyond its role as an electronic conductor.

In conclusion, INNOV offers a time-efficient tool to perform meshing without requiring substantial computational resources. Simulations can later be performed to characterize these meshes with the CBD explicitly considered. It can lead to new approaches to characterize battery microstructures and the impact of each components.

REFERENCES

3:00 PM BREAK

3:30 PM *EN05.04.05
Designing the Additives to Prevent Spontaneous Structural Degradations of the Ni-Rich Cathode Yongwoo Shin1, Yoon-Sok Kang2 and Dong Young Kim2; 1Samsung Research America, United States; 2Samsung Advanced Institute of Technology, Korea (the Republic of)

Ni-rich layered oxides have been attracting the research interests due to their low price and high discharge capacities comparing the commercial Co-based Li-ion battery (LIB). However, one of the critical obstacles to commercialize the Ni-rich cathode is the capacity fade during early cycles which has been widely observed in Ni-rich layered oxide systems (i.e., LiNiO2, LiNi1−xMxO2, LiNi1−x−yMxMy′O2, and Li[Ni1−x−yCoxMny]O2: M, M′=metal). Indeed, the capacity loss is directly associated with the structural degradation of the cathode, which has been attributed to the cation mixing from the partial reduction of the Ni-ions. In other words, the production of inactive Ni is the main factor of the capacity fade, which is strongly related to oxygen loss. Convincingly, preventing the spontaneous oxygen evolution from the cathode surface could be a critical breakthrough for commercializing the Ni-rich layered oxide.

In this research, we studied the degradation mechanisms of the Ni-rich layered oxide and their protective procedures by introducing the new additives; which has been investigated using the Ni-rich LiNi0.8Co0.1Mn0.1O2 (NCM)/graphite 18650 cylindrical-type cells as well as the first principles Density Functional Theory (DFT) computations. First of all, we comprehended the structural degradations of NCM via the Electron Energy Loss Spectroscopy (EELS), Scanning Transmission Electron Microscope (STEM) High Angular Annular Dark Field (HAADF) and DFT calculations. Here, we confirmed that the reduced Ni-ions on the surface has been penetrated to the bulk by cycling along with the spontaneous oxygen evolutions from the cathode surface. Besides, we proposed the novel functional electrolyte additives to stabilize the surface Ni via ab initio computations. We found the generic trends of COx, SOx, and POx compounds in the local atomic environments of Ni-rich cathode surface through computing the intrinsic oxidation/reduction energies, protonation energies, dehydrogenation energies, Li+ interactions, and Ni2+ interactions. Finally, we studied the additives effect on the cathode surface by close collaboration with the computations and experiments. The cathode surface interacts with the electrolyte and additive molecules which can enhance or prevent the structural degradations. Consequently, incorporating the surface protecting substances on the electrolyte would be an efficient procedure to preserve the cathode surface. Therefore, we investigated the electronic structure, adhesive energy, and surface oxygen protection potentials for the candidate additives, which are phosphorus-based, carbon-based, sulfur-based, and phenyl-based molecules. Our computations and experiments illustrated the spontaneous oxygen evolutions on the surface and sub-surface layers for the charged cathode system, which oxygen evolutions were prevented with the functional additives. In the candidate list, four molecules have been shown strong adhesive tendency on the charged cathode surface, and that molecules successfully prevent the spontaneous oxygen evolutions. Therefore, our proposed functional additives instruct the designing aspect of additives to protect the Ni-rich cathodes. Consequently, we provided an effective procedure to overcome the most significant obstacle
The energy generators for human activities, which converts human-induced energies into electricity, is emerging as a next-generation energy harvester for various applications, such as wireless sensors and Internet of Things (IoT) consisting of small-scale elements that are difficult to be integrated with the battery. Previous studies have primarily focused on improving energy generation efficiency of devices through simply merging various energy harvesters with different mechanisms. However, optimizing energy harvesting performance that are diversified depending on the time scale of external stimuli has not been much explored, although it is one of the most important task for practical applications. In this study, the dual energy generator consisting of the tiled arrangement of PDMS and Bismuth telluride is proposed as the efficient energy harvester using thermoelectric–triboelectric mechanisms, induced by the mechanical contact of human skin, and design optimization strategies are suggested according to the input stimuli frequency (0.5–2.5 Hz) and temperature gradient, which is determined by the input variables in operating environment.

To fabricate the dual energy generator, Ag electrode for triboelectricity is deposited on a poly(ethyleneterephthalate) (PET) substrate by a sputtering method, while bismuth telluride tiles involving P-N junctions are attached for thermoelectricity. The empty spaces between tiles are filled with PDMS which acts as a separating and guiding layer for thermoelectric components and transaction of charge carries, respectively.

Depending on the frequency at which human skin contacts the device surface, complex heat transfer of convection and conduction occurs by body temperature, and it leads to various patterns of thermal saturation and temperature distribution. PDMS layer serves both as a triboelectric layer in single electrode mode and an insulation layer that maintains the thermal gradient among bismuth telluride. Interfacing thermoelectric materials with PDMS also increases the amount of generated triboelectricity due to their dielectric properties, leading to feature-size dependent triboelectric energies. The hybrid energy harvester exhibits dominantly triboelectric energy when the touch motion exhibits high frequency. In the opposite case, thermoelectric power dominates the average power due to its continuous power generation.

We establish balanced design guidelines based on this simple rationale, providing detailed analyses of the heat transport properties upon human touch and the optimization strategies for the hybrid energy harvesters. These results outperform the simple merge of hybrid energy harvesters and can be widely applicable to wireless sensors and IoT technologies where human touch occurs environmentally.

Polymeric binder has turned out to be very critical for stable operation of high capacity battery electrodes including silicon (Si) anodes, as the binder could stabilize the electrode films even during the large volume change of active materials. In this talk, I will present novel binder designs focusing on supramolecular chemistries targeting high capacity battery materials represented by silicon. Such binder designs include 1) the use of mussel-inspired catechol functional group, 2) multi-dimensional cross-linkable hydrogen bonding network, 3) self-healing polymer network, 4) host-guest interaction network, and finally 5) elastic binder network incorporating molecular machines. The series of these investigations suggest the usefulness of noncovalent polymer interactions and the future role of supramolecular chemistry in the binder development. The same design principles were also applied to Li metal electrodes, with high elasticity being proved as a unique functionality.

The development of solid-state batteries has encountered a number of problems due to the complex interfacial
contact conditions between Li metal and solid electrolytes (SE), where high interface resistance can limit Li ion transport and where dendrite penetration can lead to cell failure. Recent experiments have shown that applying a stack pressure can ameliorate these problems. To understand quantitatively the relationship between pressure, Li microstructure, and the Li-SE interface resistance, we have developed a 3D, time-dependent, and multi-scale contact model for describing the Li-SE interface evolution under a stack pressure. Our simulation considers the surface roughness of the Li and the SE, Li elastoplasticity, Li creep, and the Li metal plating/stripping process. Our results show that the Li-SE projected contact area does not depend only on the stack pressure; instead, it depends primarily on the ratio between stack pressure and Li yield strength, which has been reported to depend on the scale of the Li microstructure and on the presence of Li impurities. Contact elastoplasticity is related to the ratio between the Li yield strength and surface roughness, which is revealed to play a key role in the evolution of Li dendrites and voids. During charge/discharge, there is a competition between Li plating/stripping and creep, where the latter gradually results in a more conformal Li-SE contact and a more homogeneous contact stress field. However, the surfaces do not become conformal as long as there is any charging or discharging, since newly-deposited and newly-stripped Li occurs only at contact points. Simultaneous fitting to very recent experiments from two different research groups requires an effective yield strength of the Li used in those experiments of 16 ± 2 MPa. We suggest that the preferred stack pressure is between 20 and 50 MPa, in order to maintain a relatively small interface resistance and stable stripping without void formation, while limiting material damage and fracture.

SESSION EN05.05: Poster Session I: Chemomechanical and Interfacial Challenges in Energy Storage and Conversion—Batteries and Fuel Cells
Session Chairs: Jianguo Yu and Kejie Zhao
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EN05.05.01
Demonstration of the Nanosize Effect of Carbon Nanomaterials on the Dehydrogenation Temperature of Ammonia Borane
Soon Hyeong So; Seoul National University, Korea (the Republic of)

Ammonia borane (AB, NH₃BH₃) is a highly promising hydrogen storage material, but, its high dehydrogenation temperature hinders its wider use in practice. The infiltration of AB into the pores of porous materials can lower the dehydrogenation temperature by what is known as the nanoconfinement effect. Nonetheless, it is unclear as to whether this phenomenon stems from a catalytic effect or the nanosize effect. In this work, carbon nanomaterials with an uniform pore size and with inertness to AB were chosen as nanoscaffolds without catalytic sites to control the particle size of AB. It is proved experimentally that the dehydrogenation temperature from AB is inversely proportional to the reciprocal of the particle size, which means that the nanoconfinement effect can be caused solely by the nanosize effect without a catalytic effect.

EN05.05.02
Unusual Trends in the Enhanced Ce³⁺ Surface Concentration in Ceria-Zirconia Catalyst Materials and Its Relation with the Catalytic Activity
Weizi Yuan¹, Qing Ma², Yangang Liang³, Hao Yong⁴, Michael J. Bedzyk¹, Ichiro Takeuchi³ and Sossina M. Haile¹; ¹Northwestern University, United States; ²DND-CAT, Northwestern Synchrotron Research Center at the Advanced Photon Source, United States; ³University of Maryland, United States; ⁴Chinese Academy of Sciences, China

Ceria and ceria-zirconia solid solutions are important catalytic materials, either serving directly as catalysts themselves or serving as supports for metal nanoparticle catalysts. On the basis of extensive studies of these materials, there is a growing consensus that the catalytic activity correlates with the concentration of reduced Ce³⁺ species. However, the extent of reduction at the surfaces of these oxides, where catalysis occurs, is largely unknown. To address this gap, we employ angle-resolved X-ray Absorption Near Edge Spectroscopy (XANES) to quantify, under technologically relevant conditions, the Ce³⁺ concentration in the surface (2-3 nm) and bulk regions of well-defined ceria-zirconia films. Under all measurement conditions, we find an extraordinary level of surface enhancement of the Ce³⁺ concentration in the surface regions of the films, relative to that in the bulk. Moreover,
although the Ce$^{3+}$ concentration generally increases in the bulk with increasing Zr concentration, the opposite is true in the surface regions, although the surface enhancement remains substantial. Such behavior is entirely unexpected. On the other hand, we measured the relevant surface reaction constant of Zr doped and undoped ceria using electrical conductivity relaxation method (ECR), the result of which shows that adding Zr slows down the reaction by more than one order of magnitude. This suggests that high Zr concentration, which is desirable for increasing thermal stability and bulk oxygen storage capacity, may be detrimental in terms of area-specific catalytic reaction rates.

EN05.05.03
Electric Field Dependent Ionic Transport in Passive Corundum Al$_2$O$_3$ from DFT—Application to Localized Corrosion
Aditya Sundar and Liang Qi; University of Michigan, United States

Thin passive oxides (5-10 nm) such as corundum play crucial roles in several technologies including corrosion inhibition in metals, solid electrolyte interfaces in batteries, gate oxides in microelectronics etc. While these oxides are chemically and electronically inert under normal operational conditions, exposure to high anisotropic electric fields can significantly accelerate ionic transport in such oxide films. One particular example is localized corrosion of metallic Al, Cr surfaces, where passive oxides Al$_2$O$_3$, Cr$_2$O$_3$ are known to locally disintegrate in the presence of corroding agents such as halide electrolytes. According to the well-known point defect model, the diffusion flux of ionic species play important roles in determining the rates of localized corrosion, but the underlying mechanisms of ionic diffusion under electrochemical conditions are not clearly understood at the atomic level. In this work, we compute the effect of electric fields (0-10 MV/cm) on the migration barrier of Al$^{3+}$ and O$^{2-}$ ions in hexagonal Al$_2$O$_3$. The migration barriers are then integrated with a lattice kinetic Monte Carlo simulation to compute average diffusion fluxes at different temperatures. Calculations of Al$^{3+}$ migration barriers in the absence of electric field reveal the diffusivity of Al$^{3+}$ to be 10$^{-26}$ cm$^2$/s at 300 K. This value is too small to contribute to localized corrosion behavior at room temperature. These zero field barriers are computed using the climbing image nudged elastic band method. Further calculations are performed by computing the ground state of the previously generated replicas (for CI-NEB) under homogeneous potential gradients.
An electric field with magnitude up to 10 MV/cm (measured in corrosive environments) is applied perpendicular to the basal plane in Al$_2$O$_3$. The energy barriers are found to be asymmetric; favouring Al$^{3+}$ hopping in the direction of the electric field.

EN05.05.04
A Core-Shell Structured Nanocarbon as an Anode Material for Sustainable Microbial Fuel Cells
Yu-Chen Liu1, Yu-Hsuan Hung1, Tzu-Yin Liu1, Chia-Liang Sun2 and Han-Yi Chen1; 1National Tsing Hua University, Taiwan; 2Chang Gung University, Taiwan

In recent years, energy crisis has become one of the most urgent issues that people try to deal with. Microbial fuel cell (MFC) is an environmentally friendly, sustainable technology that converts chemical energy to electricity directly. Biofilms attached on the anode oxidize organic matters during metabolism and produce electrons and protons. Since MFCs can generate electricity and achieve wastewater treatment simultaneously, this novel technology is regarded as a promising solution for increasing energy needs. Although MFCs have high potential for power generation, low power density is the major problem that limits MFCs’ application. Anode materials of MFCs are generally recognized as a key factor for electricity generation, which can directly affect biofilm formation and charge transfer efficiency. Therefore, modifications on anode materials have been widely investigated to improve MFCs’ performances.

In our work, a core-shell structured carbon nanotube (CNT)@graphene oxide nanoribbon (GONR) prepared through a simple unzipping process was proposed as the anode material for MFCs. First of all, the microstructures of CNT@GONR anodes are characterized by scanning electron microscopy, transmission electron microscope, Brunauer–Emmett–Teller method. Secondly, X-ray photoelectron spectroscopy, X-ray diffraction, and Raman spectroscopy are used to analyze elemental composition. Furthermore, the electrochemical properties of the MFCs have been investigated by linear sweep voltammetry, cyclic voltammetry, and electrochemical impedance spectroscopy in our study. CNT@GONR provides large specific surface area, high conductivity, and high electron transfer ability that can improve the power output of MFCs significantly. With comparison to the pure CNT anode, the devices with CNT@GONR anodes performed higher power density (more than 3 times), demonstrating its great
potential for enhancing the performances of MFCs.

EN05.05.05
High Catalytic Activity towards ORR on Iron/Carbon Nanostructures in Fuel Cells for Space Applications
Armando Pena-Duarte1, S.H. Vijapur2, T.D. Hall2, S. Snyder2, E.J. Taylor2, Jeffrey Sweterlitsch1 and Carlos R. Cabrera2; 1University of Puerto Rico, United States; 2Faraday Technology Inc, United States; 3NASA/Johnson Space Center, United States

Fuel cells are promising candidates for clean energy conversion for terrestrial and space applications such as human space travels, which require several technological developments that support the energy-efficient production and preservation of closed systems in microgravity spacecraft environments [1]. The overpotential required for the Oxygen Reduction Reaction (ORR) is the main electrochemical factor that diminish practical application of fuel cells [2]. ORR in aqueous solutions occurs mainly by two pathways: the direct four-electron reduction pathway from O2 to H2O, and the two-electron reduction pathway from O2 to hydrogen peroxide (H2O2). In fuel cell processes, the four-electron direct reaction is highly preferred. The two-electron reduction pathway is used in industry for H2O2 production [3]. Carbon nanostructures (Nanocarbons), such as Vulcan and carbon nano-onions (CNOs), have been previously used as catalyst due to high stability and surface area, high electrical conductivity, and mesoporous structure. Studies have revealed that carbon nanostructures and metal-carbon structures show catalytic activity in ORR [5,6]. Rotating disk slurry electrodeposition technique (RoDSE), as electrodeposition process without high temperatures, hazardous compounds, and nor energetic procedures, has been used to deposit metal nanoparticles on carbon to prepare a hybrid catalyst in powder form, [7]. Accordingly, in order to evaluate the ORR essential role in fuel cells in microgravity conditions and space applications, iron nanoparticles supported on Nanocarbons (FeNanocarbons) were synthesized and characterized by RoDSE. The structural properties of the FeNanocarbons were investigated using X-ray diffraction, Raman spectroscopy, scanning electron microscopy, induced coupled plasma, and X-ray photoelectron spectroscopy. FeNanocarbons electrochemical characterization revealed higher performance than Nanocarbons, due to Fe nanoparticle enhances the electronic conductivity and specific capacitance. An analysis of the rotating disk electrode (RDE) technique data was done to evaluate the ORR kinetics, including n-values which are related to the mechanism of oxidation, at the FeNanocarbons, using the Koutechy-Levich (K-L) equation. ORR over FeNanocarbons and Nanocarbons was evaluated in O2 saturated 0.1 M KOH, by a scan rate of 10 mV/s at different rotation rates: 800, 1200, 1600, 2000, and 2400 rpm. Initial fuel cell tests at 6V utilizing oxygen and RO water, showed that Fe/Nanocarbons and Nanocarbons can generate 0.055 and 0.025 w/w% peroxide concentration, respectively. The system output current was 0.38 amps for Fe/Nanocarbons and 0.25 amps for Nanocarbons. These results suggested that Nanocarbons performs high selectivity toward a two-electron pathway reduction process, whereas Fe/Nanocarbons catalyzes a four-electron route. Therefore, our approach would be promising to control of four- or two-electrons route kinetics of ORR in fuel cells for space technologies, by the nanocarbon source and metal-nanocarbon configurations. References: [1] NASA Strategic Plan, 2018, at: https://www.nasa.gov/sites/default/files/atoms/files/nasa_2018_strategic_plan.pdf. [2] J. K. Nørskov, J. Rossmeisl, A. Logadottir and L. Lindqvist. J. Phys. Chem. B, 108 (46), 17886–17892, 2004. [3] Song, C., Zhang, J. Electrocatalytic ORR in PEM fuel cell electrocatalysts and catalyst layers. Springer; 2008, 89-134. [4] F. Henrich, C. Chan, V. Moore, M. Rolandi, and M. O’Connell, “The element carbon,” in Carbon Nanotubes Properties and Applications, M. J. O’Connell, Ed., Taylor & Francis, Boca Raton, Fla, USA, 2006. [5] Xing W, Qiao SZ, Ding RG, Li F, Lu GQ, Yan ZF..Carbon, 44(2):216–24, 2006. [6] Frédéric Haschéa, Mehtap Oezaslan, Peter Strasser, Tim-Patrick Fellinger. Journal of Energy Chemistry 25, 251-257, 2016. [7] D. Santiago, G. G. Rodriguez-Calero, H. Rivera, D. A. Tryk, M. A. Scibioh, and C. R. Cabrera, J. Electrochem. Soc., 157(12), F189 (2010).

EN05.05.06
Activation of Solid-Oxide Fuel Cell Cathode by Reversing Dopant Segregation with Anodic Polarization
Dongha Kim and Bilge Yildiz; Massachusetts Institute of Technology, United States

Perovskite oxides (ABO3) are considered key players in clean energy conversion applications, including solid oxide fuel/electrolysis cells (SOFC/EC) and solar-to-fuel conversion. However, most of the state-of-the-art SOFC materials, such as (La,Sr)MnO3 (LSM) and (La,Sr)CoO3 (LSC), suffer from degradation of surface chemistry and oxygen exchange kinetics at elevated temperatures, which limit their long-term application. This degradation is primarily because of Sr segregation and concomitant formation of SrO-like insulating phases at the surface which block the electron transfer and oxygen exchange pathways[1,2]. The formation of inactive surface oxide phase therefore leads to a severe drop in oxygen reduction reaction (ORR) kinetics.
Numerous previous studies observed that applying cathodic polarization induced significant increase in oxygen exchange kinetics at the LSM surface by up to 50-fold. In virtue of in-situ X-ray techniques, it was shown that cathodic polarization actually suppressed Sr segregation and removed the SrO-like secondary phases at the surface[3]. However, several previous studies go against or obscure this observation. For example, a number of previous studies observed that cathodic polarization rather promoted Sr segregation instead of suppressing it, which contradict the observed increase in cathode performance during the activation process[4]. Also, other possible origins of activation process that are also induced under cathodic polarization cannot be simply excluded, such as the formation of oxygen vacancies or extension of the active area by spreading of Mn(II) onto the electrolyte surface. To elucidate if dopant segregation indeed contributes significantly to the activation process, it is important to first understand how polarization affects the dopant segregation behavior of perovskite oxides. Recent study by our group revealed that the segregation behavior of La0.8D0.2MnO3 (D=dopant) can be explained by the sum of two driving forces; electrostatic (E_{elec}) and elastic energy (E_{ela})[5]. We observed that these two driving forces change with electrical polarization oppositely to each other; E_{elec} decreased with polarization while E_{ela} increased with polarization. The convolution of these two driving forces therefore makes a valley-shaped segregation graph. In case of La0.8Ca0.2MnO3 (LCM), however, the contribution from E_{ela} is negligible due to the negligible size misfit between Ca and La, thus showing monotonically decreasing segregation graph; the higher anodic polarization, the less segregation.

Inspired by the segregation graph of LCM, we studied if applying anodic polarization could remove the dopant oxides at the surface of LCM and if this could consequently activate the surface oxygen exchange kinetics of LCM. By using X-ray photoelectron spectroscopy (XPS), we show that insulating dopant oxide at LCM thin film can actually be removed with anodic polarization and this process is high controllable by following its segregation graph. In-situ electrochemical impedance spectroscopy (EIS) shows that applying anodic polarization for a short time reactivates the initially degraded surface of LCM by removing dopant oxide at the surface. This activation process is distinguished from the previous reports on the activation of LSM in that the process is induced under anodic polarization instead of cathodic one, thus confirming the bipolarity of the activation process. By investigating the kinetics of activation process in combination with X-ray absorption spectroscopy (XAS), we propose a new mechanism behind this exotic activation process under anodic polarization.


EN05.05.07
Surface Modification of Ce(Mn, Fe)O2 / La(Sr)Fe(Mn)O3 Ceramic Anode for Propane Fueled Solid Oxide Fuel Cells Minkyu Kim, Young Wook Lee and Tae Ho Shin; Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of)

Propane, which is the main component of Liquified Petroleum Gas (LPG), is commonly used as a fuel for internal combustion engines (ICEs), portable stoves and residential heaters because of its high volumetric energy density and simplicity for storage and transportation in a liquid state. Thus, propane could be a superior candidate fuel for portable fuel cells and remote power generation applications such as an unmanned aerial vehicle (UAV). Direct utilization of this propane is one of the attractive projects in Solid Oxide Fuel Cells (SOFCs) as well application due to its high energy conversion efficiencies and the possibility for simplification of the systems. However, the use of propane directly has been limited due to several challenging issues such as low anode activity and carbon coke. We previously reported Ce(Mn, Fe)O2 (CMF) and La(Sr)Fe(Mn)O3 (LSFM), oxidation-tolerant oxide anode for SOFC with reasonably high performance and good tolerance to coking, even when using dry propane as a fuel.

In this study, to enhance catalytic performance and electron conductivity of previous oxide anodes, two ways of surface modification of these oxide anodes were investigated. First, a composite oxide of CMF-LSFM (LSFM@CMF) with a nano-composite particle structure was prepared by a wet process. Nano-sized CMF successfully deposited on LSFM backbones and it was found that surface activity of this composite oxide was much improved compared to simply mixed one. Remarkably high maximum power density of 0.76 Wcm⁻² and 1.24 Wcm⁻² was achieved at 800 °C for hydrogen and propane as a fuel. Secondly, we evaluated the surface modification of previous ceramic anode with various transition metal (Ni, Co, Fe, Cu, Ru, Pd), prepared by infiltration method. In particular, Co infiltrated CMF (CMF-Co) and LSFM (LSFM-Co) shows fairly good maximum power density of
EN05.05.08
Activity and Selectivity of Electrochemical CO2 Reduction at High Temperature—A First-Principles Study
Jianguo Yu, Yipeng Gao, Hanping Ding, Lucun Wang, Wei Wu, Wenjuan Bian and Dong Ding; Idaho National Laboratory, United States

It has maintained an extensive interest in developing advanced direct electrochemical reduction of CO2 into value-added fuels and specialty chemicals using renewable energy as an input. However, its application is still constrained partly due to chemomechanical and interfacial challenges related to activity and selectivity toward the particular product of interest. Detailed ab initio molecular dynamics simulations are invaluable in complementing the experimental investigations to unravelling important aspects of the electrochemical reduction reaction mechanisms for various type of catalysts. Here, we present advances in the understanding of reactivity and selectivity in the electrocatalysis of converting CO2 into methanol using density functional theory and thermodynamics. We will also discuss the role of protons and electrons transfer, the effect of doping and oxidation, and possible processes through different surface-bound reaction intermediates in order to steer catalyst selectivity among the vast number of possible carbon-based products.

EN05.05.09
A Unique Encapsulation of Insoluble Powders into Nanofibers for Electrode Composites
Hiep Pham and Jonghyun Park; Missouri University of Science and Technology, United States

Lead (Pb)-embedded polyacrylonitrile-based carbon nanofiber (PAN-CNF) anodes for lithium-ion batteries were prepared via the electrospinning method. PAN is a well-known polymer precursor to prepare CNF that has demonstrated high electrical conductivity and cycling stability over numerous cycles. The use of lead-based anodes with high amounts of carbon has been shown to improve the cycling performance of batteries through increased capacity retention and cycling stability. Despite this, encapsulation of Pb directly into a PAN-based electrospinning solution is not feasible due to the incompatibility of Pb solutions with PAN. In this work, we report the first demonstration of Pb encapsulated in PAN-CNF as anode materials and elucidate the mechanism which allows Pb to be indirectly embedded into PAN-CNF to yield significant enhancement to the specific capacity and cyclability of lithium-ion batteries.

SESSION EN05.06: Electrolytes and Interfaces I
Session Chairs: William C. Chueh and Yoon Seok Jung
Wednesday Morning, December 4, 2019
Sheraton, 2nd Floor, Republic B

8:30 AM *EN05.06.01
All-Solid-State Batteries Based on Closo-Borate Electrolytes
Léo Duchêne, Ryo Asakura, Seyedhosein Payandeh, Ruben-Simon Kühnel, Arndt Remhof and Corsin Battaglia; Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Closo-borates represent a promising but yet under-explored alternative class of electrolytes for all-solid-state batteries. We recently reported ionic conductivities of 1 mS/cm and an electrochemical stability window of 3 V at room temperature for Na4(B12H12)(B10H10).[1] The mixed-anion configuration stabilizes the ion-conducting high-temperature phase at room temperature.[2] We further demonstrated stable cycling for a 3 V class all-solid-state battery based on this electrolyte consisting of a sodium metal anode and a NaCrO2 cathode.[3] The cathode composite can be assembled by simple cold pressing, but cycling performance is enhanced through a preliminary solvent-based impregnation step of the cathode particles by a thin electrolyte coating. This coating guarantees intimate contact between cathode particles and electrolyte resulting in reversible and stable cycling with 85%
capacity retention after 250 cycles at C/5. We recently extended this approach by demonstrating that closo-borates can also be infiltrated into porous electrodes, where they crystallize into their highly conductive phase.[4] I will further discuss routes to translate these results to lithium analogues and our efforts to establish low-cost synthesis routes for these non-toxic materials.[5] Our results demonstrate that owing to their physical properties and processability, closo-borate-based electrolytes could play a significant role in the development of a competitive all-solid-state battery technology.


9:00 AM *EN05.06.02
Lithium Thiophosphate Based Solid Electrolytes and Cathode Interfaces Jagjit Nanda; Oak Ridge National Laboratory, United States

Advances in solid electrolytes (SEs) with superionic conductivity and stabilized electrode-electrolyte interfaces are key enablers for all solid-state batteries (SSBs) to meet the energy density and cost targets for next generation batteries for electric vehicles. Compared to their oxide counterparts, sulfide- and thiophosphate-based electrolytes offer several key advantages, including (i) exceptionally high ionic conductivities up to 10⁻² S/cm (comparable to nonaqueous liquid electrolytes) as recently reported for Li₁₀GeP₂S₁₂ and Li₉.₅₄Si₁.₇₄P₁.₄₄S₁₇Cl₀.₃ (2), (ii) availability of low temperature and inexpensive synthesis routes to produce glass, glass-ceramic, and crystalline structures, and (iii) soft mechanical properties, which facilitates material processing. Among their drawbacks, sulfides have a narrow electrochemical stability window and hence limited stability against lithium metal and cathodes. They also suffer from poor chemical stability and are highly sensitive to moisture. Despite rapid progress in achieving higher bulk ionic conductivities of SEs the rate capability of SSB’s is affected by interfacial side reactions that increase the cell resistance during electrochemical cycling. Computational modeling based on density functional theory (DFT) predicts narrow electrochemical stability windows (typically 1.6-2.5 V vs. Li/Li⁺) for most thiophosphate-based compositions. Due to their narrow thermodynamic stability range, most SEs rely on formation of kinetically stabilized interfacial layers with reasonable ionic conductivity and very low electronic conductivity. In addition to the thermodynamical instability, significant mechanical stresses develop in SE due to (i) volume changes of the electrode material during repeated lithiation (delithiation) and (ii) interface roughening from side reactions upon extended cycling. This “chemo-mechanical effect” results in poor interfacial contact between the SE and cathode. The talk will review recent progress on synthesis and characterization of new thiophosphate based cathodes for SSB based on catenation reaction with sulfur to the ionically conductive Li₃PS₄ framework. In addition various approaches to address the high interfacial resistance between the thiophosphate SE and cathode interfaces will be presented.

Acknowledgement
Research supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy through the Advanced Battery Materials Research (BMR) Program

9:30 AM EN05.06.03
Developing All-Solid-State Batteries with Organic Electrode Materials Yan Yao; University of Houston, United States

Attaining stable cathode-solid electrolyte interfaces is a great challenge in sulfide-based all-solid-state sodium batteries (ASSSBs). Currently, these ASSSBs experience low specific energy and poor cycling performance due to the interfacial incompatibility between cathode materials and sulfide electrolytes. A resistive layer forms at the interface when cathode is charged above the anodic stability potential of sulfide electrolyte. We have demonstrated some of the longest-cycling cathode materials and Na anodes through the control of interfacial structure and electrolyte decomposition. For instance, we demonstrated an organic cathode material, pyrene-4,5,9,10-tetraone (PTO), that induces reversible cathode-electrolyte interfacial resistance evolution during cycling as the result of the
reversible conversion between the superionic conductor \( \text{Na}_3\text{PS}_4 \) and the resistive oxidation products \( \text{Na}_4\text{P}_2\text{S}_{10}/\text{Na}_2\text{P}_2\text{S}_6 \). Structural and mechanical analyses further showed that a low-modulus cathode material like PTO (Young’s modulus = 4.2 ± 0.2 GPa) can effectively accommodate interfacial stress and maintain intimate interfacial contact with solid electrolytes. The reversible electrolyte decomposition, revealed by time-of-flight secondary ion mass spectrometry (ToF-SIMS), the consistently intimate interfacial contact, visualized by focused ion beam-scanning electron microscopy (FIB-SEM), and the soft nature of cathode material, characterized by nanoindentation, are all first-time reports in the field of solid-state batteries, and they have collectively led to a high specific energy (587 Wh kg\(^{-1}\)) at the active-material level and an 89% capacity retention over 500 cycles, a record cycling stability among all-solid-state Na batteries.

9:45 AM EN05.06.04

Universal Chemomechanical Design Rules for Solid-Ion Conductors to Prevent Dendrite Formation in Lithium Metal Batteries Victor Venturi\(^1\), Zeeshan Ahmad\(^1\), Venkatasubramanian Viswanathan\(^1\), Brett A. Helms\(^2\) and Chengyin Fu\(^3\); \(^1\)Carnegie Mellon University, United States; \(^2\)Lawrence Berkeley National Laboratory, United States; \(^3\)Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Lithium metal anodes could enable the next generation of high energy density lithium ion batteries required for increased adoption of electric vehicles. The formation of dendrites on charge/discharge cycles, however, is a safety hazard that hinders their commercialization. The use of solid-ion conductors (SICs) as electrolytes may allow for stable, dendrite-free, lithium electrodeposition, provided the properties of the electrode-electrolyte interface obey certain criteria related to the mechanical and chemical properties [1, 2]. Optimal SIC candidates must have properties that are either pressure-driven dendrite-blocking, or density-driven dendrite-suppressing, but not both. This division between two regimes of stable electrodeposition stems from the opposite influences of the SIC shear modulus and those of the partial molar volume of Li\(^+\) relative to those of the lithium anode. In this work, we use density functional theory (DFT) simulations to investigate a SIC soft polymer composite – LiF@PIM hybrid – in the dendrite-suppressing regime. Lithium ion motion through this material was studied using the nudged elastic band (NEB) method on a LiF surface. The activation energy for lithium movement computed in this manner shows good agreement with experimental results. The molar volume of Li\(^+\) in the composite, which is experimentally challenging to obtain, was determined using Bader charge analysis. The effects that functional groups representative of the PIM polymer matrix have on our calculated values were also investigated. Our results confirm the electrodeposition stability of this composite, which has been demonstrated to extend cell cycle-life (>300 cycles against ~100 cycles for control cells) [3]. Such nanostructured composites may be integrated into the battery manufacturing and provide a path forward for commercialization of metal anode batteries.


10:00 AM BREAK

10:30 AM *EN05.06.05

Interfacial Chemistry of Carbonaceous Anodes in Alkali Metal Ion Batteries Yaxiang Lu, Hong Li and Yong-Sheng Hu; Chinese Academy of Sciences, China

Alkali metal ion batteries (AMIBs), which employ alkali metal ions (AMIs) as charge carries, have been intensively investigated for storing the electricity from renewable energy due to the simple working principle and high energy efficiency. Among all available anode candidates, carbonaceous materials show the superior overall performance and low production cost, where the formed solid electrolyte interface (SEI) on the carbonaceous anode is essential to the long-term cycling life of AMIBs. Even though the presence of the anode SEI is critical, its formation and growth together with the influence on the battery performance are less understanding, in particular, when different AMIs are stored. In this work we investigated the interfacial chemistry by choosing different parameters including various AMIs, type of carbonaceous anode, electrolyte composition and concentration as well as electrochemical condition, attempting to understand the formation and functionality of SEI on the initial capacity loss, rate capability and cycling stability of AMIBs. The understanding gained potentially provides reference for the optimization of electrode/electrolyte interface and artificial design of SEI on the carbon anode for AMIBs.
11:00 AM EN05.06.06
Resolving Local Dynamics and Grain Boundary Resistance in Glass-Ceramic Solid-State Electrolyte Jiangyu Li; Shenzhen Institutes of Advanced Technology, China

Glass-ceramic electrolytes are promising for all-solid-state batteries, yet their enhanced ionic conductivity is not well understood. We investigate the structural difference between ceramic and glass-ceramic Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ tuned by boron, which is found to enhance conductivities of glass-ceramic by one order of magnitude, yet reduces that of ceramics. Raman and Magic Angle Spinning Nuclear Magnetic Resonance spectra indicate boron are primarily contained in glass phase, while electron energy-loss spectroscopy and high-resolution transmission electron microscopy reveal inhomogeneous distribution of boron, glassifying and relaxing its grain boundaries. This substantially reduces interfacial resistance at grain boundaries with little effect on bulk resistance, which is further supported by spatial and spectrscopic electrochemical strain microscopy that resolves the local dynamics. The grain boundary resistance of ceramics, on the hand, is increased by boron. We thus establish lower interfacial resistance at glassified grain boundaries is responsible for higher conductivity in glass-ceramics, while boron can relax their grain boundaries even further.

11:30 AM EN05.06.07
Sulfide Solid Electrolyte—Core-Shell Structure and Interfacial Coatings Luhan Ye, William Fitzhugh, Fan Wu and Xin Li; Harvard University, United States

Solid electrolyte is the key component for solid-state batteries. Among different electrolytes, ceramic sulfide electrolyte shows the highest ionic conductivity. However, narrow intrinsic electrochemical stability window of the electrolyte and interfacial reactions between electrolytes and electrodes remain a problem for the application in solid state batteries. Here we show our unique understanding and strategies to improve electrochemical window and interfacial stability of sulfide electrolyte. A core-shell structured Li$_{9.54}$Si$_{1.74}$P$_{1.44}$S$_{11.7}$Cl$_{0.3}$ (LSPS-Cl) and Li$_{10}$GeP$_2$S$_{12}$ (LGPS) were designed, synthesized and tested. The sulfide electrolytes with core-shell structure show improved stability windows in both electrochemical test and theoretical simulation. The interfacial reaction was alleviated by applying coating materials to separate the sulfide electrolyte from the electrode materials. A high-throughput screening from computational simulation helps find functional coating materials, and the stability between coating materials and electrolyte/electrode materials were demonstrated by experiments. All-solid-state batteries with LiCoO$_2$ or LiNi$_{0.5}$Mn$_{1.5}$O$_2$ high voltage cathode and Li$_{1.3}$Ti$_3$O$_{12}$ or lithium metal anode were demonstrated with good cycling performance based on our sulfide electrolytes.

Reference:

11:45 AM EN05.06.08
Experimental Assessment of the Practical Electrochemical Stability of Lithium Thiophosphate Solid Electrolytes in Li-S Cells Georg F. Dewald, Saneyuki Ohno, Juergen Janek and Wolfgang Zeier; Justus-Liebig-Universität Giessen, Germany

Lithium sulfur (Li-S) cells are promising candidates for high energy density battery systems. However, employing conventional liquid electrolytes leads to continuous degradation in Li-S batteries because of soluble reaction intermediates.[1] Today, ongoing developments in the field of solid electrolytes are drawing attention to all-solid-
state Li-S cells in which the so-called polysulfide shuttle is physically prevented by a solid separator.[2] Although modern thiophosphate electrolytes provide promising ionic conductivities, degradation reactions at the electrode interfaces due to their limited thermodynamic stability represent a major bottleneck for application. Experimentally, stabilities of thiophosphates up to 5 V vs. Li/Li⁺ are often claimed from cyclic voltammetry (CV) using planar working electrodes. Contradictorily, redox activity of electrolytes was observed at lower potentials in solid-state batteries.[4,5]

In this presentation, we will report how employing a high surface area carbon-electrolyte composite working electrode in a CV setup helps to visualize the practical stability limit of state-of-the-art solid electrolytes.[6] As carbon is a widely used additive in electrodes for solid-state batteries, this approach allows information on the practical stability of the electrolyte of interest. Furthermore, by combining CV and X-ray photoelectron spectroscopy, an insight into the underlying chemistry, i.e. the oxidation of thiophosphate building units, is given. Hereafter, we show the decomposition products to be redox active. Due to the partial reversible cyclability of the oxidized species, the decomposed electrolyte acts as pseudo-active material adding additional cell capacity while degrading the long term cell performance due to its highly resistive nature.

In a solid-state battery, the overall performance is governed by the evolving interphase between carbon and thiophosphate. By restricting the cycling window, the capacity retention can be increased significantly.

References
This electrochemo-mechanical model could be used for predicting whether and where the fractures would be produced in order to guide the architecture design of 3D ASSB with balanced energy density and mechanical integrity.

2:00 PM EN05.07.02
**Operando X-Ray Tomography of the Li/β-Li3PS4 Solid-State Electrolyte Interface at the Micro- and Nano-Scale**
Natalie Seitzman¹, Johanna N. Weker², Mowafak Al-Jassim³ and Svitlana Pylypenko¹; ¹Colorado School of Mines, United States; ²SLAC National Accelerator Laboratory, United States; ³National Renewable Energy Laboratory, United States

An optimally engineered lithium metal/solid electrolyte interface promises all-solid battery technologies that reap the capacitive benefits of Li metal anodes while mechanically resisting the Li interface evolution and thus prolonging lifetime. Additionally, such systems offer greater safety than chemistries that include flammable liquid electrolytes. However, detrimental interface evolution and short-circuit inducing Li protrusions are observed in solid state batteries despite theoretical mechanical resistance.¹,² There is debate as to whether these protrusions nucleate at the Li anode or within the ceramic electrolyte as well as the most crucial factors that affect these protrusions. These factors include electrolyte density, pre-existing defects, anode/electrolyte interfacial contact, and imperfect electronic insulation within the electrolyte.³ Understanding the influence of these variables is greatly enhanced by directly imaging the interior of the ceramic material at multiple scales in conjunction with electrochemical experiments and complementary chemical analyses.

In this talk, *operando* X-ray micro-tomography addresses the contribution of electrolyte density and defects, interfacial contact, and conductivity to structural changes at the interface between Li metal and β-Li3PS4 (LPS) ceramic electrolyte with sub-micron resolution. Cells of Li, LPS, and a blocking contact are constructed and studied during cycling at 200 psi and 70°C. Because electrolyte density and initial defects depend on the composition and synthesis of the ceramic conductor, two syntheses of LPS with different particle sizes are compared. Including pressure and temperature as variables addresses the remaining factors of interest as pressure is a key parameter in the quality and stability of interfacial contact while temperature affects both the ionic and electronic conductivity of the ceramic.

In our previous work, image analysis of micro-tomography data has identified sites of Li microstructure growth⁴ while the present work now isolates variable-dependent trends such as pressure-dependent void formation in the Li anode. Additionally, X-ray absorption spectroscopy at the phosphorus and sulfur K-edges tracks chemical changes in the LPS at the anode/electrolyte interface between pristine and cycled cells. Progress toward combining these data with *operando* transmission x-ray microscopy, which offers spatial resolution in the tens of nanometers, is also presented. Linking structural and chemical changes observed during cycling to the factors that contribute to Li evolution will guide the design of robust ceramic electrolytes with improved performance and safety.


2:15 PM EN05.07.03
**In Situ/Operando X-Ray Spectroscopy (XAS and RIXS) Characterization of the Interfacial Charge Transfer in Energy-Storage Materials**
Yi-Sheng Liu, Xuefei Feng and Jinghua Guo; Lawrence Berkeley National Lab, United States

X-ray spectroscopic techniques with operando capabilities offer the unique characterization in energy materials and catalysis in regards to the functionality, complexity of material architecture, chemical interactions. A particularly powerful soft x-ray technique is the resonant inelastic x-ray scattering (RIXS), which provides access to elementary excitations, such as d-d (f-f) excitations, vibrational excitations, and charge transfer effects that are critical for energy-related materials and chemical functions. Current in situ x-ray spectroscopy techniques (XAS and RIXS) have provided element-specific access to local chemical states in liquids and at solid/liquid interfaces during electrochemical reactions. The presentation will give a brief introduction on the XAS and RIXS and overview a number of the experimental studies that successfully revealed the electrochemical reactions at solid/liquid interfaces.
in real time, e.g. electrochemical interface of photocatalysis and batteries. The experimental results demonstrate that the operando soft x-ray characterization provides the unique information for understanding the real reaction mechanism. Also, an extension of this method toward simultaneous spatial- (100 nm) and time-dependent (ns and longer) RIXS probing of electronic and chemical dynamics is envisioned.

2:30 PM BREAK

3:00 PM *EN05.07.04
Electrochemical and Chemomechanical Effects of Charged Interfaces KSN Vikrant and Edwin Garcia; Purdue University, United States

Experimental studies aimed to understand the bottlenecks that control the transport and microstructural evolution in ionic ceramics indicate that grain boundary properties impact (positively or negatively) its macroscopic behavior. Scientific arguments to explain the ambiguous behavior in interfaces span a wide range of explanations that include the description of phenomena such as interfacial structural disorder, electrostatic phenomena, segregation of impurities and dopants, and even the appearance of glassy pockets. In this presentation, a thermodynamically consistent variational theory is presented to naturally include the effects of non-diluted segregation, dipolar and self-induced electric field effects, as well as long range, chemically induced (chemomechanical) elastic energy density contributions to the total free energy of the system. The developed model provides a rational basis to understand the stability of charge point defect distributions away from the interface and its effect on the properties and microstructural evolution of ionic polycrystalline ceramics. The theory is demonstrated on chemistries such as GDC, YSZ, and STO and validated against experimentally measured properties.

4:00 PM *EN05.07.05
Multimodal X-Ray Characterization of Interfacial Chemistry in Li-Ion and Multi-Valent Batteries Johanna N. Weker1, Jesse Ko1 and Yang Ren1 2; 1SLAC National Accelerator Laboratory, United States; 2Weifang University, China

Solid-liquid interfaces play key roles in the degradation mechanisms of rechargeable batteries, yet they are notoriously difficult to study because they are buried and require in situ probes. Multimodal X-ray characterization spanning many relevant length scales during typical battery operation is vital in understand and overcoming the failure mechanisms of these complex and heterogenous interfaces. We will discuss our multimodal in situ approach combining information from high resolution X-ray microscopy and spectra-microscopy, micro- and nano-tomography, high resolution X-ray diffraction, and X-ray absorption spectroscopy to probe and ultimately understand the dynamics across buried interfaces in energy storage systems. Specifically, we will present our recent results in designing anode architectures to stabilize solid electrolyte interphase. We will also present recent work studying the interfacial and chemomechanical properties in multivalent ion systems.

4:30 PM EN05.07.06
Time-Dependent Interface Resistance between a Solid Electrolyte and an Electrode Ryo Nakayama1, Kazunori Nishio1, Daisuke Imazeki1, Naoto Nakamura1, Ryota Shimizu1 2 and Taro Hitosugi1; 1Tokyo Institute of Technology, Japan; 2PRESTO, Japan Science and Technology Agency, Japan

Solid-state lithium batteries (LBs) are promising next-generation energy storage devices due to high energy density, and long lifetime. However, in solid-state LBs, the high interface resistance (charge-transfer resistance $R_t$) between electrolyte and positive electrode hinders fast charging and discharging. Although the origin of the interface resistance is still controversial, considerable effects of the structural disorder and the space-charge layer near the interface have been pointed out.[1,2] Notably such structural disorder and space-charge layer are considered to be static factors, therefore the time-dependence of the interface resistance has never been discussed. In this study, we report time-dependent interface resistance between the solid electrolyte Li$_3$PO$_4$ (LPO) and 5 V-class positive electrode LiCo$_{0.5}$Mn$_{1.5}$O$_4$ (LCMO). To quantitatively evaluate $R_t$ of the electrolyte and electrode interface, model electrodes using (001)-oriented LCMO epitaxial thin films were fabricated, in which the electrode area, crystal structures and orientations are well-defined. The (001)-oriented LCMO epitaxial thin film on a LaNiO$_3$ epitaxial film was prepared on a Nb: SrTiO$_3$ (001) substrate by using pulsed laser deposition. Using this model electrode, we fabricated solid-state thin film LBs consisting of Li (negative electrode) on an LPO (solid electrolyte)/LCMO (positive electrode)/LaNiO$_3$ (current

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collector) layered structure. All the processes including thin-film fabrication and electrochemical characterization were performed under high vacuum (In-vacuo process).[3]

In cyclic voltammetry, observed redox peaks at around 4.0 V and 5.3 V correspond to the Mn$^{3+}/4+$ and Co$^{3+}/4+$ redox reactions of spinel-structure LCMO. The interface resistance of the fabricated battery was quantitatively evaluated by electrochemical impedance spectroscopy, and the interface resistance at 4.0 V (13 $\Omega\text{cm}^2$) was comparable to that of the previously reported solid electrolyte electrode interface.[4] However, the interface resistance at 5.3 V was three orders of magnitude larger than that at 4.0 V, indicating that the interface resistance was rapidly increased with increase in voltage. Although the interface resistance showed hysteresis behavior during charge and discharge process, the interface resistance at 4.0 V was almost recovered from $7.4 \times 10^2 \Omega\text{cm}^2$ to its original value (12 $\Omega\text{cm}^2$) about 9.5 hours after discharge process (from 5.5 V to 3.5 V). Thus, the reversibility and time-dependence of the interfacial resistance at 4.0 V was observed after exposure to high voltage above 5 V. These results suggested that the origin of the interfacial resistance at high potential (> 5 V vs Li+/Li) was the formation of a Li depletion layer at the Li$_3$PO$_4$/LCMO interface and/or a reversible structural change at the interface.

4:45 PM EN05.07.07

*In Situ* Tracking of Chemo-Mechanical Transformations at Solid Electrolyte-Electrode Interfaces Using Advanced Synchrotron Techniques Marm Dixit and Kelsey B. Hatzell; Vanderbilt University, United States

While solid|liquid interfaces are the origin for degradation and transformation in liquid batteries, solid|solid interfaces govern transformations pathways in solid state batteries. The nature of anode|electrolyte and cathode|electrolyte effective interfacial properties (elastic, electrochemical, and morphological) govern transport, durability, and lifetime. Furthermore, the underlying electro-chemo-mechanical coupling that occurs during operation affect stability. During discharge, lithium metal is oxidized to Li$^+$ which transports through the electrolyte to the cathode. A vacancy forms at the anode surface and when the discharge rate exceeds the diffusion rate for lithium to fill this vacancy, interface morphology instabilities can occur and pores can form at the surface. Pores can lead ultimately to delamination of the anode, formation of dead lithium, and contribute to poor rate performance. At the cathode, there is a volume expansion upon discharge (i.e. intercalation). The active material in a lithium ion battery electrode undergoes volume changes during electrochemical cycling (i.e. charge and discharge) that can lead to local stress formation. This stress remains localized at the active material because the plastic binder and liquid electrolyte do not transfer stress. Herein, we demonstrate a technique that can probe both interfaces at the same time in-situ. By combining real and reciprocal space imaging and characterization techniques we can track strain at both interfaces and start to describe degradation pathways.

SESSION EN05.08: Poster Session II: Electrolytes and Interfaces I
Session Chairs: Hailong Chen and Bilge Yildiz
Wednesday Afternoon, December 4, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EN05.08.02

DFT Study on Mechanism of Oxygen Reduction Reaction on Hg-Au(111) in Acidic and Alkaline Solution **Ji Liu** and Michael Nolan; Tyndall National Institute, Ireland

Oxygen reduction reaction (ORR) is a topic of significant interest for the design of efficient and affordable catalysts for fuel cells. However, the sluggish kinetics of ORR has hindered the large-scale application of fuel cells. Platinum (Pt) is regarded as the best metal catalyst for ORR and Pt-based cathodic devices have been developed and researched for years to achieve high efficiency, long durability and stability. In recent years, Pt-free cathode materials such as palladium (Pd) have also attracted much attention and it is worth examining other metals that can promote ORR. In this contribution, we have investigated the mechanism of ORR on Hg doped Au(111) by first principles calculations and experimental work. We have considered the ORR reactions in both acid and alkaline solutions and calculated the adsorption energies of key intermediates including atomic O, O$_2$, OOH, OH. The possible reaction mechanisms are investigated by plotting the minimum energy pathway and computing the energy barriers for each elementary step. Both the associative mechanism and dissociative mechanism are considered. The
associative mechanism includes formation of OOH; and the dissociative mechanism includes the direct dissociation of O$_2$ into two atomic O. Along the pathway, the reactant and the product differ in acidic media and alkaline solution.

In addition to the bare surface, a H$_2$O-covered Hg-Au(111) surface is adopted to accurately simulate the mechanism of ORR. With the consideration of water interaction, a new mechanism called H$_2$O-mediated mechanism has been recently proposed by Liu and co-workers.\textsuperscript{1,2} Previous studies of ORR on Pt(111) in alkaline solution has proposed that the H$_2$O-mediated mechanism is more competitive than the dissociative and associative mechanisms. Here, based on previous experimental observation and DFT studies, one layer of ice-like bilayer structure of water layer is placed on top of Hg-Au(111) surface. This water layer is constructed by a honeycomb ($\sqrt{3}\times\sqrt{3}$) R30 pattern with 2/3ML of water coverage, where half of the water molecules are H$_2$O and the other half have an O-H bond pointing down (H-down). The H$_2$O-mediated mechanism is investigated by plotting the reaction pathway and calculating the energy barriers in each elementary step. Finally, the potential energy diagrams of the ORR via different mechanisms are plotted and the ORR activities of pure Au and Hg-Au are compared. This work sheds light on the ORR mechanism on gold and Hg modified gold.

References

EN05.08.03
WO$_3$ Hybrids Promoting Electrocatalytic Oxygen Reduction Reaction Jun-Hyeong Lee, DaBin Yim, Jung-Hyun Park, Jong-Min Ju, Chanhee Choi and Jong-Ho Kim; Hanyang University, Korea (the Republic of)

The growing global energy demand continues to derive the search for sustainable energy storage and conversion techniques such as metal-air batteries and fuel cells. In these next-generation energy storage and conversion systems, the electrocatalytic oxygen redox reactions are significantly sluggish in kinetics, limiting their performance. Hence, it is of great significance to develop electrocatalysts that can effectively promote the oxygen redox reactions. Here, we report a simple solution approach for the synthesis of thin WO$_3$ nanosheets bearing Pd nanoparticles as an electrocatalyst to promote the oxygen reduction reaction (ORR) effectively. Exfoliated WS$_2$ nanosheets were oxidized to WO$_3$ in H$_2$O along with deposition of Pd nanoparticles on the nanosheet surface. The coverage of Pd nanoparticles on the WO$_3$ surface was adjusted and found to influence the ORR kinetics. As-prepared WO$_3$/Pd hybrids exhibited excellent catalytic activity and durability in ORR at basic conditions.

EN05.08.04
Atomic Structure Variation at the Surface of Cathode-Oxide for Aqueous Lithium-Ion Batteries Pilgyu Byeon\textsuperscript{1}, Hyung Bin Bae\textsuperscript{2} and Sung-Yoon Chung\textsuperscript{1}; \textsuperscript{1}Korea Advanced Institute of Science and Technology, Korea (the Republic of); \textsuperscript{2}KAIST Analysis Center, Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Understanding the surface change of electrode materials in contact with an electrolyte, at the atomic-level, is a fundamental step toward achieving better electrochemical performance of rechargeable cells. Various type of water-based aqueous solutions have been proposed as alternative electrolytes to the currently used flammable organic solvents in Li-ion batteries. However, most research on aqueous rechargeable Li-ion cells has mainly focused on the synthetic processing of materials and resulting electrochemical properties rather than in-depth atomic-scale observation at the electrode surface where the initial charge transfer and the (de)intercalation reaction take place. By using LiCoO$_2$ single crystals with a (001) surface, in this article, we demonstrate the severe Co dissolution from LiCoO$_2$ surface into an aqueous solution under an O$_2$-flow environment without any electrochemical cycling. In addition, it is directly identified via atomic-scale scanning transmission electron microscopy that Co can occupy the tetrahedral interstices. Ab initio density functional theory calculations also reveal that this tetrahedral-site occupation is stabilized when cation vacancies are simultaneously present in both Li and Co sites. In addition to demonstrating the importance of controlling of oxygen content in an electrolyte to suppress Co dissolution, the findings in this study emphasize the significant role of vacancies in atomic structure variation and its local stability in Li-intercalation oxides.
Energy crisis has become one of the world's most serious challenges, as the rapid growth of the total energy consumption. The renewable energies have been intensively explored and converted into electricity to ensure the sustainable development. The inexhaustible blue energy from the ocean is independent of season, circadian rhythm and weather.\cite{1} At the same time, triboelectric nanogenerators (TENGs) are considered as one of the most promising approaches for harvesting blue energy.\cite{2,3} Previously, most of the blue-energy-harvesting TENGs are based on the friction between solids, but the contact/friction area is only a tiny portion of the total surface due to the roughness of the surface and the inefficient contact condition.\cite{4,5} In this work, a network of liquid-solid-contact triboelectric nanogenerator (LS TENG) is fabricated to efficiently harvest the huge quantities of blue energy from ocean. Due to the sufficient contact condition of the liquid-solid interface, the energy output per cycle of LS TENG is about 48.7 times bigger than that of the solid-solid-contact triboelectric nanogenerator (SS TENG) with the same area. The buoy LS TENG can generate several sequential damping signals just by one pulse of triggering, demonstrating the maximum utilization of the vibration energy. This characteristic merit renders it available for the buoy LS TENG to collect the low-frequency energy sufficiently. The output current, transferred charge and the output voltage of the network of 18 LS TENGs are 290 μA, 16725 nC and 300 V. Additionally, the buoy LS TENG can acquire energy from different types of movements, including the up-down, shaking and rotation movements. The last but not the least, the network of buoy LS TENGs could harvest large quantities of energy, including surface wave energy and submarine current energy, to power portable electric devices or navigation systems. In this work, the electricity energy generated from the LS TENGs is stored in the capacitor to drive a wireless SOS radio frequency (RF) transmitter for ocean emergencies. This work provides a more efficient method of capturing the blue energy and expands its applications.

Reference:
\cite{2} X. Y. Li, J. Tao, J. Zhu, C. F. Pan, APL Mater. 2017, 5, 074104.

Achieving widespread adoption of EVs requires higher energy density and safer, cheaper batteries. The development of solid-state electrolytes to enable Li metal solid-state batteries is one approach to achieve > 350 Wh/kg and > 1200 Wh/L. However, the underpinning mechanisms that control Li metal initiation and propagation in ceramic electrolytes remain unsolved. Most of the research has focused on solid Li-solid LLZO interfaces where researchers have demonstrated > 1 mA/cm² before Li penetration occurs. However, based on our recent study we have observed that the critical current density (CCD) of a molten Li-LLZTO-Li cell is significantly higher (hundreds of mA/cm²). Current densities of this magnitude may have applications for grid storage, but more importantly it elucidates the point that the CCD can increase over a hundred-fold simply by operating at higher temperatures. While the bulk properties of LLZO, such as electronic and ionic conductivity, increase with temperature along with an increasing CCD, there is still a large step increase in CCD across the melting point of Lithium at 180°C. Thus, it is possible to dramatically increase the CCD of a solid electrolyte without changing its intrinsic properties simply by making the interface liquid-solid rather than solid-solid. We coupled our CCD data with Operando cell cycling videos showing lithium dendrite propagation observable macroscopically. We believe the results of this study can help elucidate the vexing phenomenon that allows for a molten metal to penetrate a hard and dense ceramic electrolyte. These findings can establish deeper mechanistic insight into the factors that control the maximum Li plating density in Li metal batteries using ceramic electrolytes.
EN05.08.07
Synthesis and Evaluation of Zwitterion/Oligoether Copolymers (II)—Influence of Zwitterion on Thermal Properties and Conductivity Ryoma Ota, Yuko Takeoka, Masahiro Rikukawa and Masahiro Fujita; Sophia University, Japan

Mg-ion secondary batteries have been attracting attention as a next-generation rechargeable battery. Since Mg is a divalent ion and is abundant natural resource, Mg-ion secondary batteries can be expected to realize high capacity and low cost. Research on poly(ethylene oxide) (PEO) as a solid polymer electrolyte has been energetically conducted, but it is necessary to further improve their ionic conductivity. Therefore, we focus on zwitterions. Zwitterions are substances that have cation and anion fixed in the parent molecule. Zwitterions have a high polarity. Because of its high polarity, it can be expected to enhance Mg-salt dissociation and the ionic conductivity. In this study, diblock copolymers (PEGAm-b-SPBn) (m and n denote the unit numbers) were synthesized by RAFT polymerization of an oligoether monomer (PEGMA) and a zwitterionic monomer (SPB). The introduction of SPB block is expected to improve the electrochemical properties of PEGMA-based electrolytes. A given amount of Mg-salt (magnesium (II) bis(trifluoromethylsulfonyl)amide (Mg(TFSA)2) was added to the copolymers to prepare composites. Thermal and electrochemical measurements were performed. PEGMA44-b-SPB75/Mg(TFSA)2 exhibited an ionic conductivity value of 2.3 × 10⁻⁵ S cm⁻¹ at room temperature. On the other hand, the composites of the homopolymer PEGMA22 and Mg(TFSA)2 exhibited an ion conductivity value of 6.4 × 10⁻⁸ S cm⁻¹ at room temperature. The copolymerization of zwitterion improved the ionic conductivity. In phase AFM measurements, PEGMA44-b-SPB75, which showed the highest ionic conductivity, showed gyroid structure. It is suggested that there is a correlation between the microphase separation structure and the ion conductivity. When the unit ratio of PEGMA : SPB was 1: 1.7, a higher ionic conductivity was obtained as compared with those of other unit ratios. Raman spectroscopy was performed, and the results indicated that the dissociation of the Mg-salt was enhanced in PEGMA-b-SPB/Mg(TFSA)2 compared with PEGMA/Mg(TFSA)2.

EN05.08.08
Facile Synthesis of Palladium-Core@Carbon-Shell Catalysts for Proton Exchange Membrane Fuel Cells Hyo Eun Bae1, Youngkwang Kim2, Dohyeon Lee1, Mohanraj Karuppannan3 and Oh Joong Kwon1; 1Incheon National University, Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

Proton exchange membrane fuel cell (PEMFC) has been attracting great attention as an alternative energy system to the energy conversion devices based on fossil fuels due to its high efficiency, high energy density, low operating temperature, and fast start-up and shut down. However, there is an obstacle in commercializing PEMFCization due to because it uses the high price of platinum (Pt) as a catalyst for boosting electrochemical reactions such as hydrogen oxidation and oxygen reduction. Therefore, huge studies have been conducted to develop cheaper catalysts such as non-precious metal catalyst and alloy catalyst. Palladium (Pd) is one of them. In this study, we investigated the Pd nanoparticles encapsulated by carbon shell (Pd@CS) and its electrochemical properties especially durability which is needed to be improved for Pd to be applied in PEMFC instead of Pt. Pd catalyst having a nitrogen doped carbon shell was synthesized by delicately controlling the synthesis order in this study. It is well known that Pd procures are reduced without a reducing agent when it is mixed with aniline monomers. Pd forms Pd nanoparticles while aniline monomers turn into polyaniline (PANI) through oxidative polymerization. The PANI becomes a nitrogen doped carbon shell when it is carbonized with Pd nanoparticles under specific condition. Actually, we optimized the specific condition. The structure of Pd@CS was characterized through XRD, HR-TEM, and TGA and it was revealed that Pd nanoparticle has well defined carbon shell. To demonstrate the electrochemical properties of Pd@CS, typical half cell and unit cell tests were conducted. Cyclic voltammetry and linear sweep voltammetry were studied for half cell, and current-potential and current-power curves were compared with those of Pt/C in the unit cell test. For durability, we have adopted the test protocol suggested by Department of Energy (DOE) in 2016. From the durability test, it was figured out that the carbon shell supplements the weakness of Pd.

EN05.08.09
Inversely Polarized Ferroelectric Polymer Contact Electrodes for Triboelectric Generators from Identical Materials Artis Linarts, Kaspars Malnieks, Linards Lapčinskis, Māris Knite, Juris Blums and Andris Šutka; Riga Technical University, Latvia
Triboelectric nanogenerators (TENG) are intriguing energy harvesting devices that convert mechanical energy into electricity and could power small portable devices, sensor networks or charge batteries [1;2]. Although it is known that (TENG) based on polarized ferroelectric polymer films show better performance, the origin of this enhancement is not fully clear. To date, it has been accepted that enhancement is observed due to shift of the effective work function of ferroelectric polymer insulator which in turn enhance electron transfer between TENG electrodes. The present study based on measurements in TENG and in piezo-regime reveals that the enhancement is observed due to induction driven by piezoelectric charges. Furthermore, a novel piezoelectric-electrostatic generator has been constructed from inversely polarized polyvinylidene films, which exhibit higher performance than TENG for mechanical energy conversion to electricity uncovering a promising avenue for further development of mechanical energy harvesting nanogenerators.


In Situ Visualization of Ion and Thermal Transport Behavior in Electrolytes During Battery Operation by Phase-Contrast X-Ray Imaging

Daiko Takamatsu, Akio Yoneyama, Shin Yabuuchi and Jun Hayakawa; Hitachi, Ltd., Japan

Optimal operation and design of batteries, particularly lithium-ion batteries (LIBs), in high-power applications such as electric vehicles, requires knowledge of transport properties (e.g., ion transport, thermal transport, etc.) in electrolytes during battery operation. As the electrolytes used in commercial LIBs exhibit large concentration polarization due to comparatively low lithium-ion transference number and salt diffusivity, the polarization is largely related to the transport properties. It is known that internal resistance of the LIBs temporarily rises by repeating high-rate charge/discharge cycles and that it decreases by stopping the battery operation and rest. Because such a reversible resistance rise occurs only during the battery operation, this phenomenon is speculated to be related to the ion concentration distributions in the electrolyte. However, there are few techniques that can be used to quantitatively characterize ion transport behavior in the electrolytes during the battery operation. Phase-contrast X-ray imaging is a technique that can be used to visualize density differences by detecting the X-ray phase shift caused by an X-ray passing through a sample. The sensitivity of the phase-contrast X-ray imaging is about 1000 times higher than that of conventional X-ray absorption imaging in a hard X-ray region for light elements. Since the electrolytes of batteries are also composed of light elements, the phase-contrast X-ray imaging is expected to be effective in visualizing small density differences in an electrolyte during battery operation. We demonstrated that in situ phase-contrast X-ray imaging technique can quantitatively visualize the salt concentration distributions that arise in electrolytes during battery operation [1].

Another crucial concern about batteries used in high-power applications is the thermal management of batteries. It is known that temperature of the batteries temporarily rises by repeating high-rate charge/discharge cycles and such a temperature distribution causes inhomogeneous reaction distribution of batteries. Therefore, a fundamental understanding of thermal transport properties in battery electrolytes during battery operation is also important. Although there are several conventional temperature measurement methods, such as thermistors, resistive temperature detectors, thermocouples, infrared thermography, etc., these methods detect the temperature directory through physical contact or using infrared and visible light from the object, and therefore, the detectable depth is limited to a few mm from its surface. So, its inner temperature distribution cannot be measured in principle. We have successfully demonstrated that nondestructive observations of inner temperature and thermal flow in heated water by using phase-contrast X-ray imaging [2].

In this presentation, we will show the quantitative evaluation of ion concentration distribution and thermal distribution (inner temperature gradient) in the electrolyte simultaneously during battery operation with high temporal (a few seconds) and spatial (a few microns) resolutions. We envisage that the phase-contrast X-ray imaging will become a versatile tool for evaluating electrolytes, both aqueous and non-aqueous, of many electrochemical systems, which will further our understanding of the dynamic behavior of electrolytes in actual applications.

EN05.08.11
Formation of Ion Conduction Pathway in Porous Electrodes for Proton Exchange Membrane Fuel Cells Jong-Hyeok Park, Seohhee Lim and Jin-Soo Park; Sangmyung Univ, Korea (the Republic of)

Pathway for ions is normally in an aqueous phase. Regardless, the introduction of any aqueous phase in energy conversion devices causes many problems during fabrication, operation, maintenance, and so on. Thus, much efforts have been devoted to develop quasi-solid electrolytes such as gel polymer, ion exchangeable polymers, impregnation of ions in porous matrix and so on. Among the candidates, ion exchangeable polymers are quite often chosen as ion conducting media for energy conversion devices. The technique to introduce ion exchangeable polymers within electrodes for oxidation and reduction reactions is to solidify catalyst inks consisting of electrocatalyst, dispersion of ion exchangeable polymers, controlling solvents and additives by evaporation of all solvents in catalyst inks. Ion exchangeable polymers could be dispersed in various solvents. It causes different shapes of ion exchangeable polymers in solvents, for instance, cylindrical rods, a less-defined large particles, coils and so on. Such different types of ion exchangeable polymers form distinguished structure catalyst layers. In this study, the effect of solvents dispersing ion exchangeable polymers on the performance and durability of catalyst layers was investigated. Electrochemical characterization such as I-V polarization, cyclic voltammetry, impedance and so on and microscopic characterization such as SEM and TEM were carried out to evaluate the performance and durability of catalyst layers.

Acknowledgement
This work was supported by the New and Renewable Energy of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (No. 20173010032100).

EN05.08.12
Direct Measurement of Nano-Sized Li Dendrite Growth Stress by In Situ TEM Megan Aubin; University of Central Florida, United States

The all-solid-state Li-ion battery is attracting attention because it enables the use of a high capacity Li metal anode while easing safety concerns by employing a stable solid electrolyte. It is expected that the use of a solid electrolyte with a high shear modulus would prevent the growth and propagation of destructive lithium dendrites. However, there are several studies showing that dendrites can still penetrate solid electrolytes, causing the cell to short. The exact mechanism of the dendrite penetrations is still under debate. Additionally, a large compressive stress is generally applied to the cell to maintain good contact between the electrode and the solid electrolyte. This can affect the lithium deposition process. Therefore, understanding the relationship between the mechanical stress and lithium dendrite growth is a key factor in decoding the dendrite penetration process.

We developed a new in-situ transmission electron microscopy (TEM) technique to directly observe the lithium dendrite growth process and obtain the force on a Li dendrite to gain insight into the early stages of this destructive phenomenon. The in-situ TEM observation showed a nano-sized lithium pillar growing vertically causing increasing stress. It continued its vertical growth until the force reached a critical value of 13.5 nN, resulting in a maximum stress of 15.8 MPa. The pillar then changed its growth direction and started to expand horizontally. The measured critical stress is much higher than the yield stress of bulk lithium, which indicates that lithium can locally introduce high stresses on solid electrolytes without yielding. The information obtained in this work is useful for constructing a constitutive model of a lithium plating process in an all-solid-state system and understanding the mechanical stability of solid electrolytes particularly at the early stage of lithium deposition.

EN05.08.13
Durability Analysis of Size-Controlled Platinum Nanoparticle Synthesized Continuous Flow Method for Fuel Cells by Whole Powder Peak Fitting of Powder XRD Keiko Miyabayashi and Ankit Singh; Shizuoka University, Japan

Researches about the improvement of durability of fuel cell electrocatalysts have addressed for proliferate the fuel cell vehicle [1]. Electrochemical active surface area (ECSA) is one of characteristic parameters to measure durability of platinum based catalysts and is strongly correlated with the size of nanoparticles. Change of nanoparticle size during the potential cycle test is commonly evaluated by TEM observations [2]. The size and distribution of nanoparticles estimated by TEM, however, are originated from limited area of catalyst. To acquire the
size and size distribution from whole catalyst, powder X-ray diffraction (XRD) is a potential technique but only the crystal size is estimated from Scherrer equation in most cases.

In the present study, we prepared the size-controlled platinum nanoparticles by batch and continuous flow synthesis for catalyst coated glassy carbon GC electrode and MEA fabrication, respectively. After accelerated durability test, the crystal size and size distribution of nanoparticles were evaluated by whole powder peak fitting (WPPF) of powder XRD spectra.

As a model electrocatalyst, size-controlled platinum nanoparticles were prepared by batch and continuous flow synthesis. For batch synthesis, platinum nanoparticles were prepared using a previously reported method [3]. For continuous flow synthesis, platinum precursor (H₂PtCl₆) was dissolved in mixed solvent of water and ethylene glycol. Sodium hydroxide was added as additive to the solution. The precursor solution was then placed in an oven at 180 °C. The flow rate was controlled by micropump at 3ml min⁻¹. The synthesized nanoparticle solution was mixed with carbon black (Vulcan XC 72R) and stirred overnight. The platinum loading of catalyst was 30–35 wt% determined by ICP. Preparation of the catalyst coated GC electrodes and MEAs followed procedures reported in the literature [3, 4]. Electrochemical analyses were tested under start-stop potential cycling by the Fuel Cell Commercialization Conference of Japan’s (FCCJ) [4].

The average diameter of platinum nanoparticles (arithmetic mean) estimated by TEM observation was 2.3±0.4 nm. The nanoparticles dispersed well on the carbon support without aggregation irrespective of synthesis method. The distribution of arithmetic diameter was converted to that of volume mean diameter (2.4±0.4 nm) for comparison with XRD results. The WPPF of powder XRD analysis shows similar crystal size and distribution (2.3±0.6 nm) to those estimated by TEM. The result indicates that the WPPF analysis is useful for evaluation of size of nanoparticles from whole catalyst. After 2000 potential cycle test of GC electrode at 60 °C, the size of nanoparticle increased to 4.6±1.1 nm (TEM) and 5.1±1.1 nm (XRD). Evaluation of platinum nanoparticle size in degraded catalysts by TEM has some difficulty since the catalysts contains irregular shape nanoparticles and the contour of nanoparticle is unclear. This difficulty may cause underestimation of average size of nanoparticles. WPPF of powder XRD spectra is more or less structure independent analysis. We believe that WPPF of powder XRD provide more practical crystal size for degraded electrocatalyst.


This work has been financially supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan.

EN05.08.14
Understanding Degradation Mechanism behind Degradation of the Garnet Solid Electrolyte Li₇La₃Zr₂O₁₂ and LiNi₀.₆Mn₀.₂Co₀.₂O₂ Cathode During Sintering Younggyu Kim and Bilge Yildiz; Massachusetts Institute of Technology, United States

Li-ion batteries which we use every day suffer from inherent safety issues due to low ignition point of liquid electrolytes. This problem can be solved by using solid electrolytes since they are non-flammable. LLZO (Li₇La₃Zr₂O₁₂) has been considered as a major candidate among the solid electrolytes because of its high conductivity and wide electrochemical window. Therefore, we can potentially develop all solid batteries with high stability and energy density using LLZO.

However, interfacial resistance of solid-state batteries remains too high for commercialization. The major problem comes from the sintering process which is necessary to gain good contact between electrodes and solid electrolyte. During the sintering, detrimental secondary phases form at the interface. These ruins the cell performance by blocking Li transport. There have been many works on the anode|electrolyte interface to improve the stability. However, works on the cathode side are relatively scarce. Considering the importance of cathode|electrolyte interface that has been recently demonstrated by our group (Vardar et al. 2018), we believe that unraveling the degradation mechanism at the cathode|electrolyte interface can be a major milestone in the development of successful solid Li-batteries.

We chose NMC622 (LiNi₀.₆Mn₀.₂Co₀.₂O₂) as the cathode and Al-doped LLZO (Al₀.₂₄-Li₆.₂₈La₃Zr₂O₁₂) as the solid electrolyte. We deposited thin film cathode (<100nm) on top of pre-prepared solid electrolyte pellets. Afterward, we annealed the samples in the air with different temperature conditions to simulate the sintering process.
process. In the samples with conventional geometry, it is difficult to characterize the cathode|electrolyte interface since they are buried deep inside the samples. In contrast, since we used thin film cathodes, we could characterize interfacial regions by using surface sensitive techniques such as XAS. By combining findings from those techniques with conventional characterization techniques such as XRD and EIS, we could clarify the degradation mechanism at the interface.

We could see major decomposition products at the interface of the sample which was annealed at 700°C. With XRD, we could see the formation of La2Zr2O7, Li2CO3 and a perovskite phase with La on A-site. The exact identification of the perovskite phase could be done by XANES analysis. We could detect drastic shape change of Co L-edge indicating the formation of Co4+(High Spin) (Merz et al. 2010) Based on this finding, we suggest that La(Ni,Co)O3 has formed at the interface. Due to the electronegativity difference between Ni and Co, Co4+(High Spin) could form in La(Ni,Co)O3. (Pérez et al. 1998) Effect of the secondary phase at the interface on the electrochemical property of the cell could be clearly seen in EIS analysis. We could identify additional arc which does not exist in the sample without further annealing. We attribute this feature to the interfacial resistance due to the detrimental secondary phase.

In conclusion, we claim that temperature for typical sintering condition(700°C) is too high for solid Li-batteries. This has been proven by multiple characterization techniques clarifying the formation of secondary phases and their detrimental effect on cell performance. As an alternative, we suggest a low-temperature annealing process(300°C) in order to inhibit degradation at the interface.

We acknowledge U.S. Army Research Office for funding the research through the Institute for Soldier Nanotechnologies. (Cooperative Agreement Number W911NF-18-2-0048)

EN05.08.15
Highly Active and Durable PtCo Nanocatalysts with Surface Structure Modification for Enhanced Oxygen Reduction Reaction Daeil Choi1, Docheon Ahn2, Kug-Seung Lee2, Namgee Jung2 and SungJong Yoo1; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Pohang Accelerator Laboratory, Korea (the Republic of); 3Chungnam National University, Korea (the Republic of)

Polymer electrolyte membrane fuel cells (PEMFCs) have gained attention as future power devices due to their high energy density and no pollutants such as carbonaceous materials during operation. However, the commercialization of PEMFCs is interrupted by several issues since their electrocatalysts should satisfy not only activity but also durability. Commonly, carbon-supported Pt nanoparticles are utilized as catalysts for PEMFCs owing to their excellent oxygen reduction reaction (ORR) activity at the cathode. However, the expensive cost of Pt according to low reserves impedes the commercialization of PEMFCs. In order to solve this practical problem, a great deal of effort has focused on the development of cost-effective and highly active electrocatalysts, as demonstrated by the widely investigated alloys of Pt with relatively cheap transition metals such as Ni, Co, and Fe. The above alloying optimizes d-band structure of Pt, which binding energy between Pt and oxygen species is more favorable than that of the pure Pt as well as decreases the cost of the catalyst thanks to the usage of inexpensive materials. However, it easily is dissolved under electrochemically stressful condition during PEMFC operation even though the alloyed electrocatalysts exhibit high enhanced ORR activity, which requires the development of durable bimetallic catalysts. A number of researches to improve the electrochemical durability have been introduced, for instance, core-shell structures, intermetallic structure, dealloyed surface structure, and additional surface functionalization with organic or inorganic materials. In spite of these efforts, the development of active, durable, and cost-effective ORR electrocatalysts has not been achieved yet. Herein, we propose several types of Pt skin structure PtCo nanocatalysts toward through various post-treatments such as acid treatment, thermal treatment, and additional Pt reduction. The physical and electrochemical properties were investigated and compared to commercial Pt/C. The Pt skin structure nanocatalysts showed enhanced catalytic activity approximately 2-fold compared with commercial Pt/C because of the tuning of d-band structure of Pt by alloying with Co. Furthermore, the Pt skin structure nanocatalysts exhibited the better ORR activity than initial performance of commercial Pt/C despite low loading amount of Pt even after accelerated degradation test (ADT) under harsh condition. Subsequently, the reason for improvement in long-term durability were analyzed via physical characterizations. Based on these results, the supplementary Pt-skin structure formation on the surface of PtCo nanocatalysts diminishes the amount of defect sites of Pt and prevents metal dissolution during electrochemical test. We expect that this study suggests a novel solution for designing active and
durable nanocatalysts for ORR and promotes the commercialization of PEMFCs.

SESSION EN05.09: Electrolytes and Interfaces III
Session Chair: Corsin Battaglia
Thursday Morning, December 5, 2019
Sheraton, 2nd Floor, Republic B

8:30 AM *EN05.09.01
Interfaces for Electrochemical Energy Conversion and Storage Vojislav Stamenkovic, Dusan Strmcnik, Pietro Papa Lopes, Nenad Markovic and Nigel Becknell; Argonne National Laboratory, United States

The development of new multi-functional electrochemical interfaces that can solve challenging problems of clean energy production, storage, and conversion is of paramount importance in the quest to find alternatives to fossil fuel use. Electrocatalysis – the study of electrode processes where the rate of reaction has a strong dependence on the nature of electrochemical interfaces – lies at the heart of the spectrum of electrochemical transformations relevant for resolving these challenges. Ability to tune physicochemical properties of electrochemical interfaces has evolved towards ability to define the nature, arrangement, and transformations of electrode surface atoms along with hydrated ions in the double layer, including the kinetics of electron transfer. Implementation of this approach will be presented for the development of non-precious and platinum-based nanoscale catalysts for the hydrogen evolution reaction, oxygen reduction and evolution reactions. The role of molecular species at the interface such as water, counter cations and anions, for both two and three phase interfaces, will be discussed in terms of ability to identify and understand their influence on reaction kinetics.

9:00 AM *EN05.09.02
Modeling Chemo-Mechanical Coupling in Ceramic Ion-Conducting and Phase-Transformation Electrolytes and Electrodes Robert J. Kee, Kasra Taghikhani, Huayang Zhu, Sandrine Ricote and John Berger; Colorado School of Mines, United States

Polycrystalline ceramic materials play central roles as electrolytes and electrodes within a wide range of electrochemical technologies, including fuel cells and batteries. Heterovalent doping within ceramic electrolytes (e.g., perovskites) produces mobile oxygen vacancies as well as facilitating the transport of other charged defects, including protons and small polarons. The lattice strain associated with lattice-scale defect concentrations induces mechanical stress. This paper is concerned with modeling thermo- and chemo-mechanical coupling, which can lead to potentially damaging stresses. The primary emphasis is on membrane-electrode assemblies (MEA) fabricated from proton-conducting ceramics. However, the paper will also incorporate recent efforts to extend the models to Li-ion battery electrodes.

9:30 AM EN05.09.03
Spontaneous Formation of Lithium Ion Conductor in Ultrathin Al2O3 Layer at the Interface of Solid Electrolyte and Anatase TiO2 Electrode Using Solid-State Li Thin-Film Batteries Daisuke Imazeki1, Kazunori Nishio1, Ryo Nakayama1, Ryota Shimizu1,2 and Taro Hitosugi1; 1Tokyo Institute of Technology, Japan; 2JST-PRESTO, Japan

All-solid-state lithium batteries are one of the candidates for next-generation energy storage devices due to high energy density and long cyclability. It is well known that the insertion of a thin electrical insulator, such as Al2O3, MgO, and ZrO2, between a solid electrolyte and an electrode is effective on improving battery performances.[1] However, the insulators do not contain lithium ions, and thus, the function of insulators remains unclear. Accordingly, it is crucial to understand the interfacial ionic transport properties across the solid electrolytes and electrodes through thin insulators.

Here, we present quantitative studies of the ionic transport through the thin insulators using thin-film batteries consisting of epitaxial films. This approach provides well-defined crystal orientations and interface structures. To verify the influence of the inserted thin insulator, we fabricated thin film lithium batteries using a very flat model electrode and covered the surface with a thin Al2O3 layer.
We prepared anatase Ti_{0.996}Nb_{0.004}O_2 (TNO) epitaxial thin films as a very flat model electrode (25 nm thickness, average surface roughness: \( R_a = 0.28 \) nm) on a (LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7} (LSAT) (100) substrate by employing pulsed laser deposition. Using this model electrode, we fabricated all-solid-state thin-film lithium batteries through \textit{in-vacuo} process that provides clean interfaces.[2] The thin film batteries consist of Li anode (800 nm), Li_3PO_4 solid electrolyte (450 nm), TNO thin film on LSAT substrate. Al_2O_3 thin layers with a variety of thicknesses ranging from 1 to 50 nm were inserted at the interface of a Li_3PO_4 and a TNO.

Cyclic voltammetry (CV) of the thin film battery without Al_2O_3 insertion showed redox peaks (Ti^{4+}/Ti^{3+}) in good agreement with those reported earlier using organic electrolytes.[3] As the thickness of the inserted Al_2O_3 layer was increased, the difference in the redox peak voltages was enlarged, indicating an increased overpotential. It is surprising to observe the battery redox cycling even though a Al_2O_3 layer completely covered the surface of a TNO electrode. In addition, we found that the overpotential decreased as the cycle number of CV was increased. These results suggest that a lithium ionic conductor has formed electrochemically in the Al_2O_3 layers.


9:45 AM EN05.09.04
\textbf{New Strategy for Fast Ionic Conduction in Nanostructured Ceria-Based Electrolytes} Mehmet E. Kilic\(^1\), Junsung Ahn\(^1,2\), Ho-II Ji\(^1\), Jong-Ho Lee\(^1\) and Kwang-Ryeol Lee\(^1\); \(^1\)Korea Institute of Science and Technology, Korea (the Republic of); \(^2\)Seoul National University, Korea (the Republic of)

Cerium oxide (CeO_2) or ceria is a known fast oxide ion conductor with an oxygen vacancy-mediated transport mechanism. The highest ionic conductivities are observed when it is doped with Gd_2O_3 and Sm_2O_3. For this reason, ceria-based materials are widely used electrolyte for solid oxide fuel cells (SOFCs). Over the past decade, many attempts have been made on the development of fast oxygen-ion conductors in SOFC. Strain engineering has been one of the most effective ways to enhance ionic conductivity. Many researchers have observed various strain-induced enhancements of ion conductivity in nanostructures such as ultrathin, multicoated, and free-standing layers.

In this study, using an atomistic model, we investigate the effects of biaxial extrinsic and local intrinsic lattice strain on oxygen-ion transport in doped ceria via performing molecular dynamics (MD) simulations with well tested interatomic potentials.

We have performed three main analyses to examine the structural integrity of doped ceria: (1) radial distribution function (RDF) analysis for the phase and bond informations, (2) the coordination number (CN) analysis for the vacancies, and (3) mean square displacement (MSD) analysis for the cations and anions.

We have focused on the oxygen ion diffusion of doped ceria by considering five main mechanisms contributing to accelerate oxygen-ion transport: (1) the influence of type of cations with respect to the ionic size, (2) the influence of cation concentration, (3) the influence of cation distribution, (4) the influence of local lattice intrinsic strain induced by co-doping and, (5) the influence of biaxial extrinsic strain.

References:

10:00 AM BREAK

10:30 AM *EN05.09.05
\textbf{Garnet-Type Solid Electrolyte with Superior Electrochemical/Chemical Properties for Operating All-Solid-State Battery} Byoungwoo Kang; Pohang University of Science and Technology (POSTECH), Korea (the Republic of)

The demand for rechargeable Li batteries having more safety and higher energy density has been increased to meet the strong demand of novel applications such as electric vehicles and energy storage system. In this aspect, lithium ion batteries containing typical liquid electrolytes have fundamental limitations because liquid electrolytes can act as fuels in thermal runaway behavior leading to a fire or an explosion of battery and can be decomposed at high potential (> 4.5V) leading to the restricted use of high potential cathodes. Also, liquid electrolytes cause severe
safety problems with Li metal, which is the best anode material for high energy density with low potential and high capacity, because Li metal in liquid electrolytes easily leads to the formation of dendrite that can produce a short-circuit between cathode and anode. To address these problems, there are several approaches. One of promising approaches is to apply proper oxide-based solid electrolytes (SEs) instead of liquid electrolyte. Among oxide-based SEs, garnet-type SEs has been a lot of attraction because they can have several advantages over liquid electrolytes in terms of electrochemical window, chemical stability with Li metal, and safety.

In this talk, I will discuss about the newly developed garnet-type SE that has superior electrochemical/chemical properties with respect to the wettability with Li metal, ionic conductivity, and chemical stability with air. Also, I will talk about the efforts in our group to build up all solid-state battery by using the developed garnet-type SE.

11:00 AM  *EN05.09.06  
Structure, Chemistry and Charge Transfer Resistance of the Interface between Garnet Solid Electrolyte and Oxide Cathodes  
Bilge Yildiz; Massachusetts Institute of Technology, United States

All-solid-state batteries promise significant safety and energy density advantages over liquid-electrolyte batteries. The interface between the cathode and the solid electrolyte is an important contributor to charge transfer resistance. Strong bonding of solid oxide electrolytes and cathodes requires sintering at elevated temperatures. Knowledge of the temperature dependence of the composition and charge transfer properties of this interface is important for determining the ideal sintering conditions. To understand the interfacial decomposition processes and their onset temperatures, model cathode systems of LiCoO$_2$ (LCO) and LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (NMC622) thin films deposited on cubic Al-doped Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) pellets were studied as a function of temperature, gas composition and electrochemical conditions. The methods combine interface-sensitive techniques, including X-ray photoelectron spectroscopy (XPS), synchrotron X-ray absorption spectroscopy, hard X-ray photoemission (HAXPES), and synchrotron X-ray diffraction. In this talk, we will present the found precipitation products at the interface as a function of synthesis and electrochemical conditions, their role in altering the interface resistance to Li transfer, and compare the LCO and NMC related cathodes in terms of their instability onset conditions. We will also present the role of protective coatings such as LiNbO$_3$ in interfering with the detrimental interface reactions.

11:30 AM  EN05.09.07  
Yaqian Zhang$^{1,2}$, Yaosen Tian$^{1,2}$, Yihan Xiao$^{1,2}$, Lincoln J. Miara$^1$, Tan Shi$^{1,2}$, Mary Scott$^{1,2}$ and Gerbrand Ceder$^{1,2}$; $^1$University of California Berkeley, United States; $^2$Lawrence Berkeley National Laboratory, United States; $^3$Advanced Materials Lab, Samsung Research America, United States

Solid-state batteries (SSB) have been considered as promising next-generation energy storage device with improved safety and potentially increased energy density. Among all the inorganic solid electrolytes (SE), thiophosphates offer competitive advantages in terms of the low cost, high ionic conductivity, low Young’s modulus and yield strength, which makes them a strong candidate for room temperature application in SSB.$^1$

Despite providing high bulk conductivity and good processability, both theoretical calculations and experimental results suggest that thiophosphates will experience oxidation/decomposition upon charging when being in direct contact with commonly used oxide cathode materials.$^{2,3}$ This interfacial instability results in increased interfacial resistance during cycling and highlights the necessity of interfacial protection at the cathode/SE interface. Searching for promising cathode coatings and understand the mechanism of the coating functionality and validity is critical for improving the SSB cycle life. In this work, we predict potential coatings materials for thiophosphate Li$_3$PS$_4$ (LPS) system through ab-initio computational calculation, and we experimentally verify the performances of the selected coating materials through direct observation using advanced (scanning) transmission electron microscopy ((S)TEM) analysis with air-free sample preparation. By combining different modes of microscopy techniques (image, diffraction, and spectroscopy), we were able to probe the chemical composition and interface structure in SSB at a resolution of nanoscale. Our work elucidates the correlation between calculated chemical /electrochemical stability and the observed coating integrity during cycling, and provides a powerful method for predicting and probing the interfacial stability issue of the cathode/SE.

Strain Effect on Li-Ion Migration in $\beta$-Li$_3$PS$_4$

Pjotrs Zguns and Bilge Yildiz; Massachusetts Institute of Technology, United States

$\beta$-Li$_3$PS$_4$ is a promising Li-ion conductor (0.2 mS/cm at room temperature). Recently, its air-stability and ionic conductivity were improved by a small amount of ZnO doping (1 mS/cm), making it even more appealing study case. Here, we investigate the influence of interfacial cathode/electrolyte strain on $\beta$-Li$_3$PS$_4$ ionic conductivity by studying the effect of uniaxial and biaxial strains on Li-ion migrations by means of DFT calculations. Interestingly, migration energies show non-linear response to strain indicating that strain accommodation in lithium-phosphorus-sulfide family is different from that in conventional oxide-ion conductors, and, overall, the effect of strain is smaller. The structural response to strain and atomistic mechanisms behind migration barrier reduction are discussed.

SESSION EN05.10: Electrolytes and Interfaces IV
Session Chair: Johanna Weker
Thursday Afternoon, December 5, 2019
Sheraton, 2nd Floor, Republic B

Computation Accelerated Design of Materials and Interfaces for Solid-State Batteries

Yifei Mo; University of Maryland, United States

All-solid-state Li-ion battery based on solid electrolytes is a promising next-generation battery technology with high energy density, intrinsic safety, long cycle life, and wide operational temperatures. However, multiple materials challenges, such as low ionic conductivity of solid electrolytes and poor interfacial compatibility at the solid electrolyte-electrode interfaces, are impeding the development of this new battery technology. To resolve these materials challenges, we develop and leverage an array of ab initio computation techniques to provide unique insights into the fundamental materials limitations and to establish general design principles of materials and solid interfaces. Our first-principles atomistic modeling studies reveal the origin of ultra-fast Li-ion diffusion in lithium super-ionic conductors. Based on the newly gained understanding, we establish design principles for fast ion-conductor materials, and demonstrate these design principles for the computation discovery and design of new lithium super-ionic conductors. In addition, we develop thermodynamic calculations based on the materials-genome database for investigating the compatibility of heterogeneous interfaces between solid electrolytes and electrodes. Key factors affecting the compatibility of the solid electrolyte-electrode interfaces are identified, and interfacial design strategies are proposed from our thermodynamic computation. The demonstrated computation capabilities represent a transferable model in designing new materials and interfaces for emerging technologies.

Accelerated Materials Design for Solid-State Batteries with In Situ Characterizations

Shan Xiong, Zhantao Liu, Lufeng Yang and Hailong Chen; Georgia Institute of Technology, United States

In the past, advanced characterization methods, no matter in situ or ex situ, are majorly considered as means for understanding the functioning mechanisms of materials. However, they can also be powerful tools for accelerating the materials design loops, especially in the cases where computational designs nowadays can quickly provide dozens and hundreds of promising candidate materials for synthesis trials. High-throughput synthesis is a straightforward approach to accelerate the synthesis trials. However, in the cases where high-throughput synthesis is difficult or too expensive, in situ characterizations on the synthesis process represent a more economical and even more information-rich route for the quick synthesis of target materials.

Here we report multiple case studies where in situ characterizations for a variety of synthesis methods were used to advance our understanding on the thermodynamics and phase diagrams of novel battery materials, including
electrodes and solid electrolytes. The discovery of a sodium cathode P2-Na0.66Li0.12Fe0.18Mn0.70O2 with very high capacity and outstanding capacity retention will be discussed. In situ XRD and solid state NMR characterizations were used to understand the formation and functioning mechanisms. Novel sulfide based Li+ and Na+ ionic conductors identified with using in situ XRD will also be presented with their structure resolution, ionic conductivity measurement and full-cell battery tests.

2:30 PM EN05.10.03
Computational Screening of Cathode Coatings for Solid-State Batteries Yihan Xiao1,2, Lincoln J. Miara3, Yan Wang4 and Gerbrand Ceder1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3Samsung Research America, United States

Solid-state batteries (SSBs) are considered as the next-generation batteries due to their potential for improved safety, power density, and energy density compared with conventional Li-ion batteries. However, the interfacial reactivity and resulting resistance increase between the cathode and solid-state electrolyte (SSE) can significantly deteriorate the cell performance. Since virtually none of the SSEs are intrinsically stable against both electrodes, coatings are needed that are chemically and electrochemically stable with the SSE and the electrode.

We employ a high-throughput (HT) computational framework to screen Li-containing materials for cathode coating application, focusing on their phase stability, electrochemical and chemical stability, and ionic conductivity. The HT results show that there are clear chemical rules to explain reactivity between electrodes and SSEs and that the optimal coating materials need to be selected for each specific SSE/cathode combination.

We identified polyanionic oxides as promising cathode coating candidates to protect sulfide electrolytes against oxide cathodes, with LiH2PO4, LiTi2(PO4)3, and LiPO3 being particularly appealing choices. Some lithium borates exhibiting excellent (electro)chemical stability at various interfaces are also highlighted. Lastly, factors affecting the stability of coating materials such as Li content and oxygen bonding covalency are also discussed.

2:45 PM EN05.10.04
Characterizing Chemo-Mechanical Degradation at Solid-State Battery Interfaces John Lewis, Jared Tippens, Francisco J. Cortes and Matthew T. McDowell; Georgia Institute of Technology, United States

The solid-state lithium metal battery is a promising next-generation technology due to the high energy density of the lithium metal anode and the potential for solid-state electrolytes (SSEs) to prevent failure modes seen in liquid electrolyte lithium metal batteries. However, the interfaces between many SSEs and lithium metal are (electro)chemically unstable, and we lack a detailed understanding of how interfacial transformations relate to electrochemical degradation. Using the NASICON-type Li1.4Al0.4Ge1.6(PO4)3 (LAGP) as a reactive SSE, we study the reaction processes that occur at the lithium metal/SSE interface and develop a chemo-mechanical understanding of degradation in LAGP. In situ transmission electron microscopy reveals that lithium insertion into LAGP at the interface drives the transformation to form an amorphous phase with expanded volume [1]. In symmetric Li/LAGP/Li cells, the evolution of mechanical stress due to this transformation ultimately causes fracture of the SSE and complete cell failure. Ex situ characterization of LAGP after cycling shows that the morphology of the interphase layer is highly dependent on the applied current density, and the interphase morphology significantly influences mechanical stability. In situ X-ray tomography during electrochemical cycling of symmetric cells reveals the onset of fracture and growth of the crack network throughout cycling [2]. Our results show that the impedance begins to increase when fracture first initiates, indicating that the ionic conductivity of the interphase is comparable to pristine LAGP and is not responsible for the significant increase in impedance. This work highlights that the nature of the reaction at the Li/SSE interface plays a crucial role in determining chemo-mechanical degradation mechanisms, with implications for understanding degradation in a wide range of practical SSEs.

References:
Formation and migration of point defects underlie nearly all materials for energy transformation, such as electrodes and solid electrolytes for lithium-ion batteries and solid oxide fuel cells. The distribution of point defects such as lithium and oxygen vacancies reflect electro-chemo-mechanical equilibria. In this talk, I will present two such examples. First, we show that anisotropic and polycrystalline lithium layered oxide can exhibit extremely non-uniform lithium concentration due to mechanical effect due to orientation distribution of crystallites. Second, we present a general theory framework for understanding how mechanical contribution plays a key role in determining the space-charge effect at interfaces.

Na-ion batteries (SIB) as one of the battery technologies for grid-scale energy storage has attracted great attention recently. SIBs, like Li-ion counterparts, usually have solid electrolyte interphase (SEI) at the anode side and cathode electrolyte interphase (CEI) on cathode surface, which determine the reversibility and rate of the cell reactions for the rest of the cell life. The electrode/electrolyte interphases have not been thoroughly investigated despite the progress in SIB development. Here, we reported our work on the development of advanced electrolyte systems for 1) controlled SEI on hard carbon anodes and hence fast Na-ion transfer; and 2) mitigated cathode surface phase transition and significantly improved cyclability. Hard carbon anodes demonstrated high rate and good low temperature performance in TEGDME based electrolyte. The specific capacity of hard carbon anode is ~180 mAh/g at the current density of ~250 mA/g at room temperature. The specific capacity is ~200 mAh/g at -20oC/ discharge at the current density of ~25 mA/g. The O3-type metal oxide cathode in localized high concentration electrolyte delivers a high specific capacity of ~190 mAh/g between 2-4.2V. The capacity retention is >80% over 1000 cycles between 2-4V with a specific capacity of ~150 mAh/g.

The solid-electrolyte-interphase (SEI) is probably the least understood component in Li-ion batteries. Considerable effort has been put in the understanding of its formation and electrochemistry under realistic battery conditions, but mechanistic insights have been inferred mostly indirectly. Here we show the formation of the SEI between a graphite anode and a carbonate electrolyte using combined atomic scale microscopy and in-situ and operando techniques. In particular, we weigh the graphic anode during its initial lithiation process with electrochemical quartz crystal microbalance, which unequivocally identifies lithium fluoride (LiF) and lithium alkylcarbonates as the main chemical components at different potentials. In-situ gas analysis confirmed the preferential reduction of cyclic over acyclic carbonate molecules, making its reduction product the major component in SEI. We find that SEI formation starts at graphite edge-sites with dimerization of solvated Li+-intercalation between graphite-layers. We also show that this lithium salt, at least in its nascent form, is re-oxidizable, despite the general belief that an SEI is electrochemically inert and its formation irreversible.
Degradation of Nominally Ionic Solid Electrolytes—A Thermodynamic Perspective Yanhao Dong¹, I-Wei Chen² and Ju Li¹; ¹MIT, United States; ²University of Pennsylvania, United States

Electrochemical devices such as solid oxide fuel/electrolyzer cells (SOFC/SOEC) and all-solid-state batteries employ an ion-conducting and electron-blocking solid electrolyte and can be operated reversibly between charge and discharge. Yet reversing operation modes from SOFC to SOEC, or from battery discharge to charge often lead to more severe degradations, as evidenced by oxygen bubble formation at the grain boundaries in the zirconia electrolyte, Na metal islands in the Na-beta-alumina solid electrolytes of Na-S batteries and similar Li metal islands inside the Li/La₃Zr₂O₁₂ electrolyte in lithium ion batteries. While conventional wisdoms rationalized such observations by electrode overpotential and thought internal phase formation can be kinetically suppressed by sluggish electron transport through electron-blocking electrolytes, our thermodynamic analysis show (i) possible overpotential at transport bottlenecks inside solid electrolytes, leading to (ii) potential overshoot/undershoot beyond two boundary values at electrode/electrolyte interfaces, thus setting (iii) largest chemical driving forces to precipitate damaging internal phases, and (iv) electrons/holes can be readily transported to form such phases with ionic transference number >0.999 under typical operation conditions of such electrochemical devices. To the end, our work calls for better understanding of materials theory and better characterizations of transport properties for solid electrolytes, in order to achieve higher-energy-density and safer electrochemical devices.

References

An Artificial Solid Interface for Dendrite-Free Lithium Deposition Rajesh Pathak, Ke Chen, Jyotshna Pokharel, Wei He, Abiral Baniya, Qiquan Qiao and Yue Zhou; South Dakota State University, United States

Lithium (Li)-metal based anode is of particular interest owing to their high energy density, and specific capacity more than ten times to that of LiC₆ anodes. However, the highly reactive Li-metal inhibit further practical applications due to the growth of undesired Li dendrites and the formation of unstable solid electrolyte interphase (SEI) formation. This Li dendrites growth and continuous formation of SEI consume much electrolyte leading to low CE and capacity fading. In addition, the notorious Li dendrites can pierce the separator causing the short circuit and fire explosion. To improve the cycling performances and safety concerns, herein, we consider a rational approach for designing an artificial Li-metal/electrolyte interface. Facile and cost-effective mechanism of engineering ex situ artificial SEI layer was introduced by using WS₂. The chemical and mechanical stable artificial layer provides both high Li-ion conductivity that facilitates fast Li-ion diffusion and high Young’s modulus enough to suppress the Li dendrite growth. The ability to store Li by the conversion reaction and plating underneath the SEI layer induces a homogenous Li deposition. Such an artificial protected Li symmetrical cell showed significantly long hours plating/stripping cycles and reduced overpotential compared to the bare Li. The full cell configuration with high-loading (11.88 mg.cm⁻²) of NMC111 showed astonishing results such as longer stable cycling, higher capacity at higher rates and higher rate capability compared to the bare Li anode. This approach could lead to the development of high energy density and safe Li-metal based batteries.

Engineering Solid Electrolyte Interphase Composition by Assessing Decomposition Pathways of Fluorinated Organic Solvents for Lithium Metal Batteries Yumin Zhang, Dilip Krishnamurthy and Venkatasubramanian Viswanathan; Carnegie Mellon University, United States

The development of lithium metal batteries (LMB) is hauled by uncontrollable dendrite growth and short cycling life, which restrained its potential to replace lithium ion batteries (LIB) or bring revolutionary advances to energy storage systems. Engineering solid electrolyte interphase (SEI) by modifying electrolyte recipe is considered the most effective way to improve the performance of LMB. Despite the general acceptance of potential improvements by substituting more Fluorine to organic electrolytes, it is still unclear what differences in decomposition mechanisms or derived SEI components between Fluoroethylene Carbonate (FEC) and Difluoroethylene Carbonate
(DFEC) can lead to contradictory results with respect to the general expectation. In this study, using Density Functional Theory (DFT) and the developed "two lithiums" method, we have observed distinctive spontaneous initial bond-breaking mechanisms for FEC and DFEC. FEC breaks by forming CO and LiF, or Li$_2$CO$_3$ and CHFCH$_2$; while DFEC breaks by forming CO, 2LiF and C$_2$H$_2$O$_2$, or Vinylene Carbonate (VC) and 2LiF. DFT confidence measurement C-value indicates absolute energetic favorability of CO forming mechanism for FEC, while approximately equal competence of both mechanisms for DFEC. On the basis of initial bond breaking mechanisms, we provide and discuss the detailed step-by-step energetic pathways and identify the full sets of FEC and DFEC decomposition products. The final SEI components from our analysis are carefully compared to X-ray photoelectron spectroscopy (XPS) results from literature and found good agreements. The results from this study provide the evidence of contrasts in bond breaking mechanisms and final decomposition products between FEC and DFEC, which offer sound explanation of the variations in cell performances and enhanced fundamental understanding of SEI formation. At last, we suggest electrolyte additive with more Fluorine substitution does not necessarily contribute to cell performance upgrade, and a rigorous study using the demonstrated methodology in this work should be performed beforehand to assist electrolyte selection and SEI engineering.

EN05.11.04
Simulation of Depositional and Morphological Stability at Li Metal/Solid Electrolyte Interface in Solid-State Batteries Qingsong Tu, Luis Barroso-Luque and Gerbrand Ceder; University of California, Berkeley, United States

Theoretical investigations are important for understanding the depositional and morphological evolutions at the interface of Li metal and solid electrolyte (SE) in Li-metal solid state batteries (LMSSBs), especially when direct experimental measurements are hard because of the buried nature of the interface between two solids. In this work, we provide theoretical illustrations of the evolution of the Li metal/SE interface under the relevant boundary conditions (BCs) of LMSSBs. We first prove that the effect of mechanical pressure on the interfacial electrochemistry is negligible compared with other factors, such as the charge-transfer and the mass-transfer of Li-ions. We then investigate the Li electrodeposition and Li plastic deformation for a wide range of BCs, including the initial surface irregularity, kinetics of charge transfer and mass transfer of Li-ions, yield strength of Li metal, and applied stack pressure at boundaries. We conclude that the interfacial contact loss and surface overpotential at Li metal/SE can be well controlled by optimizing the electrochemical and mechanical conditions, such as the applied stack pressure and applied current density.

EN05.11.05
High Active Material Loading in All-Solid-State Battery Electrode via Particle Size Optimization Tan Shi$^1$, Qingsong Tu$^1$, Yaosen Tian$^1$, Yihan Xiao$^1$, Lincoln J. Miara$^2$, Olga Kononova$^1$ and Gerbrand Ceder$^1$; $^1$University of California, Berkeley, United States; $^2$Samsung Research America, United States

The rapid expansion of electrical vehicle market raises the demand for batteries with improved safety and higher energy density. All-solid-state batteries (SSBs) are widely considered as the next-generation energy storage device that can meet both requirements. They improve safety by removing organic carbonate-based liquid electrolytes and can potentially increase energy density by utilizing a Li-metal anode. However, because of the large solid-electrolyte fraction (30 wt%–50 wt%) typically required in cathode composites to provide sufficient ionic diffusion, the volume fraction of cathode (cathode loading) of current SSBs is low, resulting in low energy density. Using experiments and modeling, we demonstrate in this work that very high volume fractions of cathode can be fully utilized in a composite cathode as long as the ratio of the solid electrolyte to cathode particle size is controlled in a cold-pressed composite cathode. This conclusion is experimentally verified, and a composite cathode with > 50 vol% cathode loading is demonstrated using Li$_2$O–ZrO$_2$ (LZO)-coated LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$ (NMC) as the active material and amorphous 75Li$_2$S–25P$_2$S$_5$ (LPS) as the solid electrolyte. Our model is applicable to various active materials and solid conductors and provides a generalized guideline for increasing active material loading via particle size optimization.

EN05.11.06
Design of Double-Layer Coatings in All-Solid-State Lithium-Ion Batteries for Enhanced Mobility and Stability Chuhong Wang, Koutarou Aoyagi and Tim Mueller; Johns Hopkins University, United States

All-solid-state lithium-ion batteries have attracted significant interest as candidates for the next generation of
rechargeable batteries. However, commonly observed interfacial reactions between sulfide electrolytes and oxide electrode materials can increase interfacial impedance, thus degrading the battery performance. Interposing an ionic conductor as an interface coating can suppress any unanticipated reactions while maintaining lithium ion diffusion through the battery. However, known lithium-ion-conducting sulfides are usually unstable against cathode materials while the stable oxides are typically poor lithium ion conductors. To increase the space of potential interfacial coatings, we propose that a double-layer coating design could potentially stabilize the electrolyte-electrode interfaces and facilitate the lithium ion transfer. We present the results of a search for stable double-layer coatings with high ionic conductivity. Mobility of lithium ions in the double layer coatings is characterized with a recently developed class of machine learning interatomic potentials, which accesses nanosecond-long molecular dynamics with nearly \textit{ab initio} accuracy. The identified coating strategies highlight opportunities for creating stable solid-state lithium-ion batteries with fast charge and discharge rates.

\textbf{EN05.11.07}

\textit{In Operando} KPFM—Interfacial Potentials in a Thin-Film All-Solid-State Li-Ion Battery Evgeni Sirek1,2, Elliot J. Fuller2, Michael Swift4, William McGreevey1, Nikolay Zhitelev3, Yue Qi3, Jabez McClelland1 and Alec Talin2; 1NIST, United States; 2University of Maryland, United States; 3Sandia National Laboratories, United States; 4Michigan State University, United States

The continuing search for methods to engineer safer, smaller, lighter, cheaper, and more stable batteries requires comprehensive understanding of the processes governing their operation at multiple length scales. All-solid-state power sources do not contain flammable organic electrolytes, and therefore, are safer. However, they suffer from high internal impedances, arising at the interfaces between the solid electrolyte and electrodes. The nanoscopic thickness of these interfaces calls for microscopic tools to study their behavior. Here, using in operando Kelvin Probe Force Microscopy (KPFM), we measure the potential distribution in a solid-state Li-ion battery as a function of its state of charge. The battery was fabricated by sequentially depositing thin layers of Pt (110-130 nm), LiCoO2 (280-420 nm), LIPON (1100-1200 nm), Si (50-240 nm) Cu or Pt (150-200 nm) onto a Si/SiO2 wafer (oxide thickness 100 nm). The fabricated battery was cleaved in an Ar atmosphere to expose the stacked layers, mounted on a holder, wired, and safely transferred without exposing to air into a dual-beam instrument that combines a scanning electron microscope (SEM), a Ga-ion focused ion beam (FIB) and an atomic force microscope (AFM) in one vacuum chamber (residual pressure of 10^{-4} Pa). The stacked battery was milled to expose a cross-section of the layers, and imaged using SEM and KPFM, while cycling the battery. The acquired potential maps reveal a highly non-uniform interelectrode potential distribution, with most of the potential drop occurring at the electrolyte-Si anode interface in the pristine battery. During the first charge, the potential distribution gradually changes, revealing complex polarization within the LIPON layer due to Li-ion redistribution. Cycling the battery at high rate significantly decreased its capacity, although the capacity loss can be recovered. KPFM imaging allowed the detection of the interface responsible for this capacity loss. The acquired data was compared to first principles calculations shedding light onto the interfacial Li-ion transport in the battery and its reversibility.

\textbf{EN05.11.08}

Insight into the Compatibility of Lithium Lanthanum Zirconium Oxide (LLZO) and Conventional Liquid Electrolytes Arushi Gupta1, Michael Wang2 and Jeff Sakamoto2,1; 1University of Michigan-Ann Arbor, United States; 2University of Michigan–Ann Arbor, United States

Lithium lanthanum zirconium oxide (LLZO), a ceramic oxide is a promising solid electrolyte candidate to enable Li metal anodes due to its high ionic conductivity (1 mS/cm), stability and low interfacial impedance against Li. However, in a full cell configuration, how LLZO is integrated into cathode constructs requires further development. Recently, bilaminar cell configurations consisting of discrete LLZO membranes to protect Li metal anodes, coupled with conventional liquid electrolyte permeated cathodes, has been suggested as a viable approach. In this electrolyte configuration, LLZO would act to stabilize the Li anode and the liquid electrolyte provides facile transport between LLZO and the cathode. However, we have shown that there may be an incompatibility between typical liquid electrolyte (1M LiPF6 in Ethylene carbonate/Dimethyl carbonate) and LLZO. For example, in hybrid cell configurations, the interfacial impedance increases with time. This work was focused on first developing a mechanistic understanding of the interactions between LLZO and carbonate-based liquid electrolytes. Understanding the reaction pathways between LLZO and liquid electrolytes provided us insight to develop approaches to enable a stable interface between LLZO and the catholyte. In this work, we propose a candidate for the catholyte which is compatible with LLZO and would enable a low interfacial impedance and stable cycling in a
full cell configuration. The results of this work provide an insight into the limitations of using liquid electrolytes with LLZO. We also provide a solution which would help in enabling Li metal anodes using a bilaminar electrolyte configuration.

EN05.11.09
New Insights into How Ultra-Thin Coatings Improve Battery Performance Yaqi Zhu, Yufang He, Hiep Pham and Jonghyun Park; Missouri University of Science and Technology, United States

Atomic layer deposition (ALD) coating technique is proved to be an effective and efficient strategy to improve the capacity and cycle capability of lithium-ion batteries. One of the key roles of the ALD coating layer is to facilitate the species transfer and diffusion in electrode particles. It has been generally believed that this enhancement has resulted from the higher conductivity of the coating layer itself. However, there is a concern about this idea because the proportion of ALD coating layer is very small. Here, we propose a new hypothesis about the role of ALD coating layer in ion transportation. Due to the agglomeration of particles, the surfaces of electrode particles are partially blocked, and, as a result, Li-ion intercalation is not uniform over the surfaces. On the other hand, ALD coating could provide a path to quickly distribute Li-ions over the whole particle surface, leading to enhanced diffusivity of Li-ions through the particles. This hypothesis is validated by both continuum simulation and experiment in this work. In addition, an investigation is conducted to study the ALD coating thickness impact on Li-ion diffusivity via first-principles calculations, which shows that the Li-ion diffusion increases to the maximum value and then decrease as the coating thickness increases. We find that this is related to the higher diffusivity of the ALD coating than that of the active material, and higher diffusivity through the surface than through the bulk. This combined work reveals the influence of ALD coating layer on Li-ion diffusion and provides us a clue why there is an optimal ALD coating thickness for the best battery performance.

EN05.11.10
Features of Mechanical Behavior of LiPON Sergiy Kalnaus, Andrew S. Westover and Nancy J. Dudney; Oak Ridge National Laboratory, United States

Ability to resist penetration of metallic lithium is the major requirement for the electrolyte membrane in an all solid-state lithium cell. In this regard, the lithium phosphorus oxynitride (LiPON) electrolyte has been demonstrated to successfully block Li metal propagation (often termed lithium dendrites) in thin-film cell configuration. It is therefore important to understand which properties of LiPON are critical for such stable performance with Li metal so that other electrolytes could be designed following similar metric. Here we concentrate on mechanical properties of LiPON, specifically its resistance to cracking, i.e. fracture toughness. This property appears to be rather important, since metallic lithium penetration has been demonstrated from artificially introduced defects even in the absence of grain boundaries.

By using instrumented nano-indentation we observed unusually high resistance of LiPON to crack initiation and propagation. We compare this behavior to fracture in typical glass materials and other Li-ion conducting glass-ceramic electrolytes. In addition to resistance to cracking LiPON apparently exhibits time-dependent behavior and is capable of partial recovery upon unloading. We discuss these features in relation to LiPON functionality in all solid state cell with metallic lithium anode.

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EN05.11.11
Improving the Durability of Pt-Alloy Nanoparticles for the Oxygen Reduction Reaction in Acidic Media via
Encapsulation Qiang Sun, Sanjeev Mukerjee and Qingying Jia; Northeastern University, United States

The Oxygen Reduction Reaction (ORR) is the desired cathode reaction in Proton Exchange Membrane Fuel Cells (PEMFCs). Carbon-supported platinum alloy (PtM/C) nanoparticles are by far the most effective ORR catalysts in PEMFCs. However, the durability of PtM/C is not satisfying. Efforts to improve their durability have been impeded by the poor understandings of their degradation mechanisms. In this study, by conducting accelerated stress tests (ASTs) on a commercial PtCo/C catalyst in both a rotating disk electrode and a PEMFC, we identified that a significant fraction of the electrochemical surface area (ECSA) loss of the PtCo/C upon the AST was recoverable. This recoverable ECSA loss was tentatively ascribed to the poisoning of the Pt surface by the sulfate ions either from the H2SO4 electrolyte in a RDE or the Nafion in a PEMFC. We further demonstrated that this poisoning effect can be largely suppressed without compromising the activity by encapsulating PtCo/C into thin functionalized carbon overlayers that were tuned to be permeable to H+, O2, and H2O, but not to sulfate ions.

EN05.11.12
Nanomechanical Studies of Ultrathin ALD and MLD Films Applied as Protective Layers for Metallic Li Anodes Using AFM Maedeh D. Amirmaleki1, Yang Zhao2, Teng Cui1, Xueliang A. Sun2 and Tobin Filleter1; 1University of Toronto, Canada; 2University of Western Ontario, Canada

Solid-state batteries (SSBs) have been considered as one of the most promising next-generation energy storage systems. However, interfacial issues such as mechanical instability between electrodes and solid-electrolytes are critical factors affecting the cyclic performances of SSBs. Ultrathin Al2O3 and polyurea thin film prepared by atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques have been used as a coating layer for Li metal anode and solid-electrolyte materials in SSBs, which helped to boost the cycling performance and mechanical stability by protecting the interface of electrode/electrolyte. However, the static and dynamic mechanical response of ALD and MLD films is still unclear. We studied the elastic, fracture, and fatigue behavior of ALD Al2O3 and MLD aglucone as well as hybrid MLD/ALD films on a thickness range of 2 nm to 20nm. The static and dynamic mechanical behavior of suspended ALD and MLD films over supporting monolayer graphene was studied using atomic force microscope (AFM) film deflection technique. All ALD films at all thicknesses failed by brittle failure and showed higher stiffness than MLD films. The overall stiffness of ALD and MLD films affected by graphene to a greater extent below the critical thickness of 2 nm and 9 nm, respectively. Remarkable fatigue life was obtained for all Al2O3 films from million to several billion cycles under force range of 50% to 80% of static failure forces, while the fatigue cycle numbers increased by decreasing the thickness. Higher stiffness and failure forces of “15nmMLD/5nmALD” hybrid film in compare to “5nmALD/15nmMLD” films were shown to be the reason behind their better electrochemical performances in contact with Li metal anodes.


EN05.11.13
Understanding Organic Electrolyte Interactions in Calcium Ion Batteries from First Principles Joshua Young1, Peter Kulick2, Taylor Juran3 and Manuel Smeu2; 1New Jersey Institute of Technology, United States; 2Binghamton University, United States

Batteries utilizing multivalent species (e.g., Mg, Ca, Zn, or Al) as the working ion are gaining increasing attention for use in applications where large numbers of inexpensive cells are needed, such as grid storage. Ca in particular offers several advantages, including a reduction potential close to that of Li, high volumetric capacity, and fast solid state diffusion. However, the breakdown of commonly used organic electrolytes causes an ionically insulating passivating layer (the solid electrolyte interphase, or SEI) to form on the electrode surface, preventing reversible plating and stripping of the Ca metal anode. In this work we use density functional theory (DFT) and ab initio molecular dynamics (AIMD) calculations to study the interaction of Ca ions with various organic solvents used in typical electrolytes and investigate their breakdown on Ca metal surfaces. We find that Ca2+ forms a large first solvation shell in ethylene carbonate (EC) and propylene carbonate (PC) and a slightly smaller one in tetrahydrofuran (THF). We then use AIMD to compute the diffusion coefficient of Ca in each solvent using ClO4 as...
a counterion, and find that it diffuses fastest in THF, and slower in EC and PC. Finally, we used AIMD to identify the principle components of the SEI by studying the decomposition of EC on Li, Ca, and Al surfaces. We believe that these results have generated an increased understanding of Ca-based electrolytes and can help in the design of new ones in the future.


EN05.11.14
Revealing Electrolyte Oxidation via Carbonate Dehydrogenation on Ni-Based Oxides in Li-Ion Batteries by In Situ Fourier Transform Infrared Spectroscopy
Yirui Zhang, Yu Katayama and Yang Shao-Horn; Massachusetts Institute of Technology, United States

Understanding (electro-)chemical reactions at the electrode-electrolyte interface (EEI) is crucial to promote the cycle life of lithium-ion batteries. In this study, we developed an in situ Fourier-transform infrared spectroscopy (FT-IR) method, which provided unprecedented information on the oxidation of carbonate solvents via dehydrogenation on LiNi0.5Mn0.2Co0.3O2 (NMC). While ethylene carbonate (EC) was stable against oxidation on Pt up to 4.8 VLi, unique evidence for dehydrogenation of EC on LiNi0.8Co0.1Mn0.1O2 (NMC811) at voltages as low as 3.8 VLi was revealed by in situ FT-IR measurements, which was supported by density functional theory (DFT) results. Unique dehydrogenated species from EC were observed on NMC811 surface, including dehydrogenated EC anchored on oxides, vinylene carbonate (VC) and dehydrogenated oligomers which could diffuse away from the surface. Similar dehydrogenation on NMC811 was noted for EMC-based and LP57 (1 M LiPF6 in 3:7 EC/EMC) electrolytes. In contrast, no dehydrogenation was found for NMC111 or surface-modified NMC by coatings such as Al2O3. In addition, while the dehydrogenation of solvents was observed in 1 M electrolytes with different anions, they were not observed on NMC811 in the concentrated electrolyte (EC/EMC with 3.1 M LiPF6), indicating lithium coordination could suppress dehydrogenation. Dehydrogenation of carbonates on NMC811 accompanied with rapid growth of interfacial impedance with increasing voltage revealed by electrochemical impedance spectroscopy (EIS), while the electrode-electrolyte combinations without dehydrogenation did not show significant impedance growth. Therefore, minimizing carbonate dehydrogenation on the NMC surface by tuning electrode reactivity and electrolyte reactivity is critical to develop high-energy Li-ion batteries with long cycle life.

EN05.11.15
Oxide Ion Vacancies and Covalency Difference to Understand Chemical Expansion by Hydration Reaction between Yttrium-Doped SrCeO3 and SrZrO3
Takaya Fujisaki1, Aleksandar T. Stayko1, Kwati Leonard1, Yuhang Jing2,3, Narayana R. Aluru2,3 and Hiroshige Matsumoto1; 1Kyushu University, Japan; 2Beckman Institute, United States; 3University of Illinois at Urbana-Champaign, United States

It is necessary to reduce operating temperature below 600 °C for solid oxide fuel cell (SOFC) and solid oxide electrolysis cell (SOEC) toward cost reduction. High temperature proton conducting oxides have gained widespread interest as an electrolyte materials which are alternative to oxygen ion conductors. For typical high temperature proton conducting oxides, aliovalent cation-doped perovskite-type oxides (ABO3) exhibit proton conductivity originating from the hydration of oxide ion vacancies [1]. The hydration reaction is accompanied by structural deformation, i.e. chemical expansion. The chemical expansion lead to mechanical failure in electrochemical devices, and thus it is necessary to understand the causes of this process at the atomic scale. In this study, the chemical expansion behaviors of Y-doped strontium cerate (SCY) and Y-doped strontium zirconate (SZY) were comparatively investigated. High temperature X-ray diffraction and thermogravimetric analysis revealed that the cerate exhibits higher chemical expansion. To understand the reason why cerate has experimentally higher chemical expansion than zirconate, density functional theory (DFT) calculations revealed that size of oxide ion vacancies, and covalency between B-site and oxygen played important roles to understand the chemical expansion difference [2]. DFT shows the chemical expansion of SZY is larger than that of SCY when two dopant Y atoms are close each other. However, the reverse is also true for the case in which two dopant Y atoms are distant from each other. The former Y clustering case is energetically more stable in comparison with the latter of Y distant case. When it comes to sintering process of SZY and SCY, it seems that Y atoms are not experimentally diffused on the most stable atomic positions. Moreover, DFT revealed that the size of oxide ion vacancies in SZY is much smaller than that in
SCY in the case of Y-clustering; this is the reason why the chemical expansion of SZY is large than that of SCY. However, in case of the Y atoms are distant, oxide ion vacancies’ size is similar between SZY and SCY. Ionic and covalent bonding nature support the trend that SCY experimentally shows larger chemical expansion than SZY.

Acknowledgements
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References

SESSION EN05.12: Fuel Cells
Session Chairs: Veronica Augustyn and Feng Lin
Friday Morning, December 6, 2019
Hynes, Level 2, Room 201

8:30 AM *EN05.12.01
Rigidity of Interlayer Structural Water in Tungsten Oxide Leads to High-Rate, Pseudocapacitive Electrochemical Proton Intercalation
Veronica Augustyn; North Carolina State University, United States

In order to understand proton transport during a faradaic reaction in an oxide whose structural water content and structure was well-known, we have been investigating the electrochemical de/intercalation of protons in hydrated tungsten oxides, WO₃●nH₂O (n = 1, 2). Recently, we found that the presence of structural water leads to a transition in the energy storage mechanism from solid-state diffusion limited in WO₃ to surface-limited (or pseudocapacitive) in WO₃●2H₂O. We also found that WO₃●2H₂O exhibits much smaller and more reversible mechanical deformation during proton intercalation than WO₃, suggesting that the presence of structural water minimized the electrochemically-driven structural transformations (electrochemomechanics). Surface-limited energy storage in WO₃●2H₂O would suggest that a facile solid-state proton diffusion mechanism, such as Grotthuss transport, was present in this material. However, the fact that the energy storage process was closely related to the mechanical deformation of the material led us to consider an alternate explanation for the observed kinetic behavior. We investigated the role of structural water on the observed kinetic and electrochemomechanical differences between WO₃●nH₂O and WO₃ by coupling electrochemical characterization with fundamental studies of the structure and dynamics of both the solid state structure and confined water network. Operando X-ray diffraction (XRD), ex situ quasielastic and inelastic neutron scattering (QENS and INS, respectively), and density functional theory (DFT) calculations as a function of potential and proton content reveal that structural water in WO₃●nH₂O is extremely stable, which allows for rapid and facile structural transformation during electrochemical proton intercalation. We demonstrate that the facile electrochemomechanics of WO₃●nH₂O allow for reversible proton intercalation at a scan rate of 2 V s⁻¹, corresponding to a charge/discharge time of only ~ 500 ms. We hypothesize that it is the structural rigidity of the water network and not the presence of a Grotthuss mechanism, that leads to pseudocapacitive proton storage in the WO₃●nH₂O. This leads us to propose a new materials design strategy for high power, high energy density storage via the presence of structurally rigid fluids confined in the interlayer of 2D materials that stabilize the solid state structure at high rates.

9:00 AM EN05.12.02
In Situ GISAXS Investigation of Asymmetric Ostwald Ripening into PtNi Bimetallic Alloy under Operational Conditions of PEM Fuel Cells
Marco Bogar1,2, Ivan Khalakhan3, Josef Mysliveček3, Vladimir Matolin3 and Heinz Amenitsch2; 1CERIC-ERIC, Italy; 2Technical University of Graz, Austria; 3Charles University, Czechia
In the last years, several Platinum-based bimetallic alloys have been studied as possible substituents of pure Platinum catalysts in Proton Exchange Membrane Fuel Cells (PEMFCs) to strongly reduce production cost. In particular, PtNi alloy was found to be a promising alternative to pure Pt due to its very good mass activity and its competitive catalytic activity. The main drawback is related to the acid-based environment in which catalyst has to operate, which causes the dissolution of the less noble metal and the consequent degradation of the whole catalyst layer. In this framework, in situ Grazing Incidence Small Angle X-ray Scattering combined with electrochemistry is used to investigate the real-time kinetics of the surface degradation of PtNi alloy during electrochemical cycling voltammetry. In order to simulate the realistic fuel cell operation conditions, the study has been performed by applying different upper potentials and using different alloy compositions. Obtained results, have been complemented with in situ Electro-Chemical AFM and with Inductively Coupled Plasma Mass Spectrometry. Data revealed in depth the degradation of the aforementioned catalyst, the structural / compositional changes during fuel cell operation, and the asymmetric Ostwald ripening process, here described in electrochemistry the first time.

The authors acknowledge the financial support from project CEROP, which is a CERIC-ERIC internal research project.

9:15 AM EN05.12.03
Nitro Oxidized Cellulose Nano Paper for Proton Exchange Membrane Fuel Cells Sunil K. Sharma, Priyanka Sharma, Miriam Rafailovich, Benjamin S. Hsiao and Likun Wang; Stony Brook University, The State University of New York, United States

Nanocellulose is a renewable, inexpensive and biocompatible nanomaterial with high strength and tunable surface chemistry. Due to high global energy demand and environmental concerns it is vital to find alternative of fossil fuel; in this aspect Polymer electrolyte membrane fuel cells are highly effective and environmental friendly energy source. But higher cost for fabrication of proton exchange membrane in the fuel cell is major factor which makes it expensive. In this regards we have used novel, simple, cost effective and less chemical oriented Nitro-oxidation method to prepare high strength Cellulose nanopore having -COONa and -COOH functionalities with high proton conductivity at (80 °C with various RH%), good gas barrier properties and efficient fuel cell performance (37 mS2). Further we have characterized NO-CNF Nanopaper with morphological, spectroscopic and analytical techniques which includes IR, elemental anlysis, SEM, TEM, WXRD, 13CPNMR, BET surface area analysis, DMA etc.

9:30 AM EN05.12.04
Development of Nanocrystalline/Amorphous (La,Sr)CoO3-(La,Sr)2CoO4 Composite Cathodes for IT-SOFCs D. Sari1,2, B. Yasar1,2, F. Piskin1,2,3, Y.E. Kalay1,2 and Tayfur Ozturk1,2; 1Middle East Technical University, Turkey; 2Middle Eastern Technical University, Turkey; 3Mugla Sitki Kocman University, Turkey

A new class of amorphous/nanocrystalline (La,Sr)CoO3-(La,Sr)2CoO4 composite cathodes were developed for IT-SOFCs via co-sputtering of the respective oxides. The cathodes as deposited were amorphous at mid-compositions and could remain so when used at reduced temperatures. They could crystallize into two phase structures at temperatures close to 700 °C, with grains no more than 10 nm in size yielding a structure with extremely high density of hetero-interfaces[1]. EIS responses measured on symmetric cells imply satisfactory ORR performance at temperatures as low as 575°C especially when the volume fractions are in the range 0.40 < (La,Sr)2CoO4 < 0.60. Moreover it was found that co-sputtered (La,Sr)CoO3-(La,Sr)2CoO4 cathodes, followed in terms of area specific resistance (ASR), had highly stable cathode performance in prolonged testing. Cathodes were resistant to Sr segregation due probably to the high stability of extremely fine two-phase structure.

9:45 AM EN05.12.05
Flexible and Wearable All-Solid-State Al-Air Battery Based on Iron Carbide Encapsulated in Electrospun Porous Carbon Nanofibers Yuanyuan Ma1,2, Afriyanti Sumboja3, Xu Li3 and John Wang1; 1National University of Singapore, Singapore; 2Institute of Materials Research and Engineering, A*STAR, Singapore; 3Institut Teknologi Bandung, Indonesia

The growing demand for wearable and flexible energy storage devices requires batteries with high capacity and low cost. A rationally designed air cathode with high catalytic activity and robust mechanical properties is the key
requirement to realize flexible metal-air batteries for wearable applications. In this work, electrospinning N-doped carbon nanofibers containing iron carbide (Fe$_3$C@N-CFs) are synthesized and employed as the cathode in the flexible Al-air battery. Benefiting from the excellent catalytic activity of the iron carbide which are uniformly encapsulated in the N-doped carbon matrix, as well as the large specific surface area of the cross-linked network nanostructure, the as-prepared Fe$_3$C@N-CFs show outstanding catalytic activity and stability during oxygen reduction reaction. The as-fabricated all-solid-state Al-air batteries with Fe$_3$C@N-CFs catalyst show a stable discharge voltage (≈1.7 V) for 8 hours, giving a capacity of 1287.3 mAh g$^{-1}$. They are also demonstrated to power a LED watch continuously for over 22 hours, indicating their promising application as energy storage device for flexible electronics.

10:00 AM BREAK

10:30 AM EN05.12.06  
**In Situ X-Ray Absorption Spectroscopy of Synergistic Co–Mn Spinel Oxides as ORR Electrocatalysts in Alkaline Fuel Cells**  
Yao Yang, Yin Xiong, Rui Zeng, Francis J. DiSalvo and Héctor Abreuña; Cornell University, United States

As high-efficiency energy conversion devices, proton exchange membrane fuel cells (PEMFCs) have been recognized as crucial technologies for electric vehicles. However, PEMFCs still rely on expensive platinum-based electrocatalysts for the sluggish oxygen reduction reaction (ORR). As an emerging alternative, alkaline polymer electrolyte fuel cells (APEFCs) have drawn increasing attention because they can enable the use of non-precious metal electrocatalysts, in particular 3d metals, due to their low cost and high activity. Here, we report on a novel family of Co-Mn spinel oxide nanoparticle catalysts, that exhibit significantly enhanced ORR activity when compared to both Co$_3$O$_4$/C and Mn$_3$O$_4$/C and which rival Pt/C catalysts in alkaline fuel cells. Co-Mn spinels achieved a benchmark peak power density of 1.2 W/cm$^2$ at 2.6 A/cm$^2$ in membrane electrode assembly (MEA) tests at an optimal loading of 80 wt.% metal oxide on carbon supports. However, the origin of such electrocatalytic activity remains elusive, and necessitates the use of *in situ* techniques to identify the catalytically active (and relevant) sites under real-time electrochemical conditions.

Synchrotron-based *in situ* X-ray absorption spectroscopy (XAS) is a powerful nondestructive technique to study electrocatalytic mechanisms because it can provide atomic-level information on electrochemical reactions under operating conditions. The high penetration depth of high-energy X-rays, combined with a home-made electrochemical cell, have enabled the operando study of Co-Mn oxide catalysts. *In situ* X-ray absorption near-edge structure (XANES) was employed to track/monitor the oxidation state changes of Co and Mn, not only under steady state (constant applied potential), but also under non-steady state (potentiodynamic cyclic voltammetry) conditions. The periodic conversion between Mn(III, IV), Co(III) and Mn(II, III), Co(II) during the CV scans suggested that Co and Mn redox couples serve as co-active sites (co-catalyst) for the ORR. Rapid X-ray data acquisition, combined with a slow sweep rate in CV, enabled a 3 mV resolution in the applied potential and X-ray measurements, approaching a non-steady (potentiodynamic) state. Changes in the Co and Mn valence states were simultaneous and exhibited periodic patterns that tracked the cyclic potential sweeps. These observations strongly suggest a potential (and very likely) synergistic effect between Co and Mn, which may explain the superior activity of the Co$_{1.5}$Mn$_{1.5}$O$_4$/C electrocatalyst over the monometallic oxide counterparts. Aiming for a practical Pt-free cathode for AEMFCs for automotive applications, non-precious ORR electrocatalysts need to not only fulfill the requirements of high initial ORR activity, but also address durability concerns. We designed a family of Mn-Co-Fe trimetallic oxides to effectively improve the durability of our first-generation Mn-Co catalysts. The periodic conversion between Mn(III, IV)/Co(III) and Mn(II, III)/Co(II) as well as the essentially constant oxidation state of Fe during the CV suggested collaborative efforts among Mn, Co, and Fe. Mn and Co served as the synergistic coactive sites to catalyze the oxygen reduction, resulting in the observed high activity, while Fe worked to maintain the integrity of the spinel structure, likely contributing to the remarkable durability of the catalyst.

In summary, *in situ* XAS studies of electrocatalytic systems for the ORR in alkaline media have dramatically advanced our understanding of catalytic systems with various-valence multi-metallic active sites, in general, and for fuel cells, in particular.

**References:**
10:45 AM EN05.12.07
Extremely Stable Platinum Core/Carbon Shell Electrocatalyst for Oxygen Reduction Reaction Youngkwang Kim1, Sujin Gok2, Mohanraju Karuppannan2, Eunjik Lee3, Jee Youn Hwang3, Ji-Hoon Jang3 and Oh Joong Kwon3; 1Seoul National University, Korea (the Republic of); 2Incheon National University, Korea (the Republic of); 3Hyundai Motor Group, Korea (the Republic of)

Polymer electrolyte membrane fuel cell (PEMFC) is considered as a promising energy source due to high energy efficiency and environment friendly characteristics. However, its commercialization is hampered by platinum catalysts requiring high cost and having low stability originating from an aggregation and a dissolution. To prevent particle agglomeration and dissolution, some researchers have introduced shells on platinum particles. For example, Chung et al. [“Highly Durable and Active PtFe Nanocatalyst for Electrochemical Oxygen Reduction Reaction” J. Am. Chem. Soc. 2015, 137, 15478−15485] reported PtFe electro-catalysts coated by carbon shell by adopting polydopamine layer and a carbonization. The carbon shell hinders the aggregation of alloy particles during the pyrolysis step carried out to transform the crystal structure of PtFe from fcc to fct. In addition, this shell protects platinum from dissolution during electrochemical reaction, thus enhances the durability at both half cell and unit cell tests. Chen et al. [“Nanostructured Polyaniline-Decorated Pt/C@PANI Core−Shell Catalyst with Enhanced Durability and Activity” J. Am. Chem. Soc. 2012, 134, 13252−13255] reported that the polymer coated commercial Pt / C had better durability than the uncoated Pt/C. They coated Pt/C with polyaniline and confirmed the carbon shell using a transmission electron microscope. PANI coated Pt/C exhibits improved activity and stability in half-cell test.

In this study, we are going to propose a new method for synthesizing platinum electro-catalyst encapsulated with a carbon shell and prove its improved durability in unit cell performance test. Typically, the carbon shell can be prepared by heating the polymer or carbon source coated on metal particle. However, this method requires extra processes which are generally difficult and tricky. Typical methods for synthesizing platinum core/carbon shell catalyst are comprised of 1) platinum reduction (electrochemical catalyst synthesis), 2) polymer or carbon source coating and 3) pyrolysis (carbon shell formation). In contrast, we have simplified the process to two steps of 1) synthesis of platinum and carbon source complexes and 2) pyrolysis (platinum reduction + carbon shell formation). Platinum-aniline complex made the reduction of synthesis step possible. The structural characteristics were investigated through XRD and HR-TEM and it was revealed that the Pt particles are encapsulated by 2~3 layers of graphitic carbon shells. From the Pt particle size of 5 nm, it could be inferred that aniline prevents the aggregation of Pt while it is decomposing to carbon.

In order to verify that carbon shell is perfectly covering Pt particle and this could contribute to the enhancement of durability of Pt catalyst, as-synthesized catalysts were electrochemically studied following the AST protocol suggested by DOE in 2016. The catalyst showed a similar activity but an enhanced stability in half cell test compared to the result obtained with a commercial Pt/C. Unit cell test had proved the real value of carbon shell. No loss in current density at 0.6 V was observed after 30 K AST cycles carried out following DOE 2016. The analysis of MEA performed after AST revealed that carbon shell still encapsulates the Pt particle and no aggregation and dissolution happen.

11:00 AM EN05.12.08
Reducing Degradation of PEM Fuel Cells Using HOR-Selective Anode Catalysts Leiming Hu1, Bharothy Parimalam1, Bo Ki Hong2, Jong-Gil Oh2 and Shawn Litster1; 1Carnegie Mellon University, United States; 2Hyundai Motor Company, Korea (the Republic of)

Polymer electrolyte membrane (PEM) fuel cells are promising power systems for future automotive applications, due to their low emissions and high efficiency. However, the lifetime of PEM fuel cells can be strongly affected by their various operation modes and transitional states. One such case is start-up/shutdown cycles, during which the air/hydrogen gas boundary will form in the anode gas flow channel and elevate the catalyst-electrolyte interfacial potential difference in the cathode. This increased interfacial potential causes carbon corrosion and Pt dissolution inside the cathode catalyst layer, leading to a loss of active catalyst area and performance degradation. One mitigation strategy is to use a selective catalyst at the anode that inhibits the anode half-cell reaction, which in turn reduces the corresponding corrosion current at the cathode. In this case, the selective anode uses a catalyst with high hydrogen oxidation reaction (HOR) activity and low oxygen reduction reaction (ORR) activity.
In this current work, we investigate the effectiveness of different selective anode catalysts, including iridium (Ir) and platinum (Pt) alloys of alloy composition on the PEM fuel cell’s start-up/shutdown durability. Results show that the anode with Ir on carbon (Ir/C) catalyst has the highest start-up/shutdown durability, with less than 20% of electrochemically active surface area (ECSA) lost after 1100 start-up/shutdown gas purging cycles. In comparison, conventional Pt/C anode causes more than 60% of ECSA loss after the same amount of cycles. Among Pt_xIr_y alloy catalysts, the Ir_3Pt_1/C shows the highest improvement on the start-up/shutdown durability, but not comparable with the Ir/C catalyst. Differences in the HOR and ORR activity of these anode catalysts are compared, and the degradation patterns are analyzed for better understanding of cause of the differences in start-up/shutdown durability.

11:15 AM EN05.12.09
Chemomechanical Response of Defective MnO_2 Nanosheet Pseudocapacitor Electrodes Scott T. Misture, Madeleine N. Flint, Peter Metz, Robert Koch, Peng Gao and Alec Ladonis; Alfred University, United States

X-ray total scattering was teamed with Raman and X-ray spectroscopy and related tools to probe the atomic-scale defects and chemomechanical response of MnO_2 nanosheet assemblies. The data reveal a direct link between surface Mn_3+ defects and charge storage, where intentionally introducing ~25% Mn_3+ defects increases the gravimetric capacitance by a factor of 3. An operando measurement cell was developed for X-ray PDF and XAS studies, and new PDF modeling approaches were developed that yield accurate quantification of the interatomic spacings and defect content vs. charge state. The data demonstrate that the nanosheets breathe in 2-D; in other words, the interlayer spacing between nanosheets remains invariant while the nanosheets expand and contract in the plane of the nanosheets by as much as 1% during charging. X-ray spectroscopy provides the Mn oxidation state which completes the picture of Mn redox. Overall, the study demonstrates that adding ~25% Mn_3+ defects increases charge storage by 3X with improvement in charge transfer resistance and dramatically improved cycle stability.

11:30 AM EN05.12.10
Modeling of PEM Fuel Cell Aging Due to Platinum Catalyst Degradation Giovanna Bucci1,2, Nathan Craig1 and W. Craig Carter2; 1Bosch Research Center, United States; 2Massachusetts Institute of Technology, United States

Ongoing development of proton exchange membrane (PEM) fuel cells focuses around the durability and the precious metal content of the membrane electrode assembly (MEA) of the fuel cell stack [1, 2]. The loss of the electrochemical surface area (ECSA) of the platinum (Pt) catalyst in the cathode electrode, particularly induced by voltage cycling, is a very important factor governing the performance degradation of the MEA [3, 4]. Thus, understanding the performance loss mechanism of voltage cycling is crucial for the successful commercialization of the PEM fuel cell for automotive applications.

We present a physics-based Pt catalyst degradation model that predicts ECSA loss via Pt particle coarsening and the formation of electronically disconnected Pt particles in the ionomer phase. The continuum electrochemical model includes: dissolution of Pt and subsequent electrochemical deposition on Pt nanoparticles; platinum-oxide coverage that forms a passivating layer, decreasing dissolution of the metal underneath; diffusion of Pt ions in the membrane electrode assembly; and Pt ion chemical reduction in membrane by hydrogen permeating through the membrane from the anode electrode [5-8]. Coarsening of Pt nanoparticles follows the mechanism of source-limited Oswald ripening, and it is investigated by tracking the evolution of the particle size distribution upon cycling. In the model, the Gibbs-Thompson effect drives the redistribution of mass from small to large particles, therefore decreasing the Pt active surface area. Diffusion of dissolved Pt at the micrometer scale leads to permanent mass loss and the formation of Pt bands in the membrane.

Comparing with literature experimental data [3, 4], the analysis provides further understanding of catalyst degradation mechanisms under voltage cycling and accelerated stress test conditions.

References:
SESSION EN06.01: Single Atom Catalysis I
Session Chairs: Wen Ju and Hailiang Wang
Monday Morning, December 2, 2019
Sheraton, 2nd Floor, Independence West

8:45 AM OPENING REMARKS

9:00 AM EN06.01.01
Role of Buffering Anions and Proton Donors in Carbon Dioxide Reduction at Immobilized Cobalt Phthalocyanine
Joy Zeng, Nathan S. Corbin, Kindle S. Williams and Karthish Manthiram; Massachusetts Institute of Technology, United States

Immobilized molecular complexes are an atomically precise platform on which to systematically interrogate and design electrocatalysts. This is a particularly exciting prospect because in electrocatalysis, the interplay between electrode, solvent, electrolyte, and reactants is often complex, and well-defined active sites could be leveraged to clarify some of that complexity. Cobalt tetrapyroles, such as cobalt phthalocyanine (CoPc), are well known to be active and selective for the reduction of carbon dioxide (CO₂) into carbon monoxide (CO) when immobilized on carbonaceous supports. To date, many studies of CoPc have focused on achieving performance, and indeed, current densities upward of 100 mA/cm² with near unity Faradaic efficiencies to CO have been reported. However, in order to take deeper lessons from this successful catalyst, and use them to guide rational design of future catalysts, it is important to understand intrinsic catalytic properties of CoPc. Towards this more fundamental goal, we measured the influence of bicarbonate buffer concentration on CO₂ reduction to CO at well-dispersed, immobilized CoPc. We found that the apparent bicarbonate order dependence shifted from negative to positive as the applied potential became more reductive. Tafel slopes were also found to vary depending on bicarbonate concentration. Coupled reaction-diffusion models suggested that transport limitations do not account for these observations. We propose a
mechanism in which CoPc is deactivated either via coordination to bicarbonate anions or partial reduction, which is able to explain the measured bicarbonate order dependencies and Tafel data. This work provides evidence that the rate determining step in the CoPc catalytic cycle is in fact an initial proton coupled electron transfer and that the presence of various “spectating” ionic species affect intrinsic activity. Such a complete set of mechanistic measurements on immobilized CoPc has not been reported before, and these surprising results have important fundamental implications for elucidating reaction mechanism and practical implications for designing and evaluating high-performance devices.

9:15 AM  EN06.01.02
Haber–Bosch Reaction Mechanism and Kinetics on Highly Reactive Iron Surface and Hierarchical High-Throughput In Silico Screening Catalyst Design Qi An1, Alessandro Fortunelli2 and William A. Goddard3; 1University of Nevada, Reno, United States; 2Consiglio Nazionale delle Ricerche, Italy; 3Caltech, United States

To discover new alloy catalysts that might dramatically improve the efficiency of the Haber–Bosch (HB) process for ammonia synthesis from hydrogen and nitrogen, we employed quantum mechanics (QM) to determine the reaction mechanism and free energy reaction barriers for the two most highly reactive Fe surfaces (Fe(211)R and Fe(111)) under experimental single crystal reaction conditions (400°C and 20 atm). We determined the rates for all 10 important surface reactions on both surfaces. Then we used this information in a full kinetic Monte Carlo (kMC) simulation (60 minutes) to determine the kinetics. We predict that the Turn Over Frequency (TOF) for Fe(111) surface is TOF =18.7 s⁻¹ per 2 x 2 surface site for 1.5 Torr NH₃ pressure in excellent agreement with experiment (9.7 NH₃/sec for (111) and 7.3 NH₃/sec for (211)R) which is consistent with experiment (~1:0.75). The excellent agreement between theory and experiment on two very different surfaces and reaction mechanisms is a testament to the completeness and accuracy of our QM and kMC modelling. To dramatically improve the efficiency of HB reactions on these highly reactive surfaces, we applied hierarchical high throughput screening approach to sift the promising doping elements on these two highly reactive surfaces. We found several promising dopants that can significantly improve the TOF.

9:30 AM  EN06.01.03
Unraveling Mechanistic Reaction Pathways of the Electrochemical CO₂ Reduction on Fe-N-C Single Site Catalysts Wen Ju1, Peter Strasser1, Alexander Bagger2, Jan Rossmeisl2 and Ana Sofia Varela3; 1Technische Universität Berlin, Germany; 2University of Copenhagen, Denmark; 3National Autonomous University of Mexico, Mexico

We report an experimental-computational study of mechanistic reaction pathways during the electrochemical reduction of CO₂ to CH₄, catalyzed by solid-state, single-site Fe-N-C catalysts. Fe-N-C catalysts feature molecularly dispersed catalytically active Fe-N motifs and represent a type of non-Cu-based catalysts that yield “beyond CO” hydrocarbon products. The various multi-step mechanistic pathways toward hydrocarbons with these catalysts has never been studied before and is the focus of this study. A number of different reactant molecules with varying formal carbon redox states, more specifically CO₂, CO, CH₂O, CH₃OH and formate were electrochemically converted at the Fe-N sites, yet only CO₂, CO and CH₂O could be protonated into methane. Also, we observed a distinctly different pH dependence of the catalytic CH₄ evolution from CO and CH₂O, suggesting differences in the proton participation of rate determining steps. In comparing the experimental observations with Density Functional Theory (DFT) -derived Free Energy Diagrams of reactive intermediates along the reaction coordinates, we unraveled the distinctly different dominant mechanistic pathways and roles of CO and CH₂O along the catalytic CO₂-to-CH₄ cascade and their rate-determine-steps (RDS). We close with the first comprehensive reaction network of the CO₂ electroreduction on a M-N-C catalyst. Our findings offer valuable insights in the catalysis of the CO₂RR on single site Fe-N-C catalysts that may prove useful in developing efficient, non-Cu-based catalysts for direct electrochemical hydrocarbons production.

9:45 AM  BREAK

10:15 AM  EN06.01.04
Cooperative and Reversible Photoactivation of Single-Atom Cu/TiO₂ Photocatalysts Taeghwan Hyeon1,2 and Byoung-Hoon Lee1, 2; 1Seoul National University, Korea (the Republic of); 2Institute for Basic Science (IBS), Korea (the Republic of)
I present the design and synthesis of highly active TiO₂ photocatalysts incorporated with site-specific single copper atoms (Cu/TiO₂) that exhibit reversible and cooperative photoactivation process.¹ I believe that this study represents one of the important breakthroughs in atomically defined photocatalysts that share the similar mechanism with metalloenzymes. The reversible and cooperative activation process is one of the most important characteristics of biological enzymes, and has been frequently used in designing homogeneous catalysts. However, there is nearly no report on industrially important heterogeneous catalysts with these enzyme-like characteristics. Herein we designed single atom catalysts (SACs) with well-dispersed copper atoms exclusively occupied in the most stable Ti vacancies in the hollow TiO₂ nanoparticles, and identified atomic-level reversible and cooperative photoactivation process during dynamic photocatalysis. Furthermore, we demonstrate that in single-atom Cu/TiO₂, the dynamic cooperation between site-exclusive Cu atoms and TiO₂ can trigger the unprecedented reversible photo-activation process that includes valence state change of Cu atom and reversible modulation of surface electronic structure of the local TiO₂ environment. This unique photo-activation process has led to the extremely strong light absorption in the whole visible range and resulting highly enhanced H₂ generation activity that far exceeds state-of-the-art TiO₂-based photocatalysts incorporated with earth-abundant transition metal-based cocatalysts. This first demonstration of heterogeneous catalysts with the enzyme-like characteristics is a monumental discovery in realizing the reversible electronic structure modulation in heterogeneous catalysts. I will also report various catalytic applications of SACs based on nanomaterials of CeO₂, TiO₂, and graphene oxide.


10:45 AM OPEN DISCUSSION

11:00 AM EN06.01.06
Ultrafast, Controllable Synthesis of Sub-Nano Metallic Clusters and Single Atoms through Defect Engineering Yonggang Yao and Liangbing Hu; Univ of Maryland, United States

Supported metallic nanoclusters (NCs, < 2 nm) are of great interests in various catalytic reactions with enhanced activities and selectivity, yet it is still challenging to efficiently and controllably synthesize ultra-small NCs with a high-dispersal density. Herein, we report the in situ synthesis of surfactant-free, ultra-small, and uniform NCs via a rapid thermal shock on defective substrates. This is achieved by using high temperature synthesis with extremely fast kinetics while limiting the synthesis time down to milliseconds (e.g. ~1800 K for 55 ms) to avoid aggregation. Through defect engineering and optimized loading, the particle size can be robustly tuned from > 50 nm particles to < 1 nm uniform NCs with a high-dispersal density. We can also achieve high-density single atom dispersion using a similar high-temperature method. We demonstrate that the ultra-small NCs exhibit drastically improved activities for catalytic CO oxidation as compared to their nanoparticulated counterparts. In addition, the reported method shows generality in synthesizing most metallic NCs (e.g. Pt, Ru, Ir, Ni) in an extremely facile and efficient manner. The ultrafast and robust synthesis of uniform, high-density, and size-controllable NCs paves the way for the utilization and nanomanufacturing of NCs for a range of catalytic reactions.

11:15 AM EN06.01.07
Stabilization of Dinuclear Rhodium Clusters on a Layered Titanate Support Ritesh Uppuluri, Jennifer Gray and Thomas E. Mallouk; The Pennsylvania State University, United States

Atomically dispersed clusters comprising single and pairs of atoms are gaining increasing attention for heterogeneous catalysis as they are structurally different from bulk metal and metal nanoparticles. The different catalytic activity stems from both surface effects, where the number of unsaturated bonds increase with decreasing cluster size, and electronic effects that result in discrete energy levels of the electrons thus enabling greater orbital overlap with substrate molecules. In recent years, the structure and catalytic activity of single atom catalysts has been extended to selectively investigate the stability of dimers on different supports by wet chemical deposition.¹,² In this study, we present that dinuclear rhodium complexes could be well-dispersed on layered titanate supports (H₀.₁₃Ti₀.₈₇O₂ and H₂TiO₃ nanosheets). Nanosheets derived from layered metal oxides represent a unique class of catalyst supports as they can be imaged by electron microscopy and were previously shown to resist sintering of late transition metal oxide nanoparticles.³ The stability of dinuclear clusters on layered titanate supports are elucidated by a combination of aberration-corrected transmission electron microscopy, DRIFT spectroscopy, and X-ray absorption (EXAFS and XANES) spectroscopy.

References


**11:30 AM OPEN DISCUSSION**

**11:45 AM EN06.01.09**

*Elucidate Atomistic Mechanisms of Single Atom Catalysis on Graphene for CO2 Reduction* Yuanyue Liu; The University of Texas at Austin, United States

Single metal atoms anchored on N doped graphene (M-N4-G) have attracted extensive interest as catalysts for carbon dioxide reduction. Although DFT calculations based on computational hydrogen electrode mode have been performed to understand the atomistic mechanisms, several important questions remain unexplained. For example, the DFT calculations show that the formation free energy of *COOH, a critical intermediate during CO2R, is rather high (> 1 eV), contradicting with the experimental report of high activity. Here, using ab initio molecular dynamics (AIMD) simulations with explicit water molecules and surface charge (which are neglected in conventional DFT calculations), we are able to elucidate the atomistic mechanisms, and explain the difference in catalytic activity of different metal atoms.

**SESSION EN06.02: Single Atom Catalysis II**

*Session Chairs: Michelle Lee and Karen Mulfort*

*Monday Afternoon, December 2, 2019*

Sheraton, 2nd Floor, Independence West

**EN06.02.01**

*Electrochemical Reduction of Carbon Dioxide on Copper MOFs—Effect of Ligand Functional Groups on Efficiency and Selectivity* Nusrat Rashid and Pravin P. Ingole; Indian Institute of Technology Delhi, India

The current rate of energy consumption has shifted the balance of environment especially owing to the exponentially increasing concentration of carbon dioxide. Reduction of carbon dioxide into fuels or useful chemicals is probed as a new way to clean the air, lessen the release of carbon dioxide in the atmosphere (especially from point sources) and store renewable energy like electricity as chemical energy. Different approaches have been used to reduce carbon dioxide, like electrochemical, photochemical, thermochemical, biological or combination of any of these approaches. The electrochemical route is attractive given many renewable energies are stored in electric form and hence are readily available. Copper metal has been found unique pertaining to its ability to reduce carbon dioxide into hydrocarbons which can be used as fuels or industrial feedstock. Given the affinity of MOFs to absorb gases like carbon dioxide many groups developed different MOFs to study ERC (electrochemical reduction of carbon dioxide). Copper variants of MOFs have shown promising activity for ERC. Taking cues from the gas absorbing capability of MOFs and promising performance of copper towards ERC, we synthesized different copper MOFs like CuBDC (copper benzyl-di-carboxylic acid) and CuBTC (copper benzyl-tri-carboxylic acid) to study ERC. The materials were characterized by XRD, FESEM, TEM, IR, Raman, XPS and TGA. All analysis confirmed the formation of impurity-free successful synthesis of CuMOFs. We found that both MOFs are active for ERC but CuBDC is more selective for hydrocarbons than CuBTC. Further, it was found and thoroughly analyzed that the active site for ERC is actually *in situ* formed metastable copper and copper (I) oxides which are formed over negative potentials applied. Structural changes were also found on the application of negative potentials, metal and metal oxides were embossed in the carbon backbone. Earlier reports suggest that MOFs are proven to convert CO2 into alcohols while we found they convert CO2 considerably into ethylene and some methane. Recent studies have proved that associated organic groups with metal catalysts as ligands or stabilizers are also
involved in the alteration of catalytic activity of the materials, especially in nano-domain. We altered the free -COOH groups in terephthalate groups of an organic framework with amine groups to check the effect of functional groups on ERC associated with the metal centers. It was found that -NH2 groups aid in catalyzing the ERC with greater selectivity towards hydrocarbons and higher cumulative faradaic efficiencies towards ERC. Also, the stability of the catalyst increased with keeping hydrogen evolution limited under 30%.

Use of Functionalization on Bimetallic MOFs for Enhanced ORR and OER Performance Simranjit K. Grewal and Min-Hwan Lee; University of California, Merced, United States

Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is the most studied reactions for clean energy devices for energy conversion devices such as fuel cells as result of slow kinetics. Transmission metal oxides (TMO) such as Co3O4, Fe3O4, and MnOx [1] have been extensively researched as way to replace platinum and its alloys for both sustainability and cost effectiveness. To combat the intrinsic low conductivity of TMOs, they are often incorporated into a highly conductive carbon nanostructure such as metal organic frameworks (MOFs). MOFs have garnered wide attention for their ability to efficiently and effectively improve adsorption of reactants, stability, and conductivity.

In this study a bimetallic MOF was synthesized via a solvothermal method and pyrolysis using both cerium and cobalt nitrate salts with a ligand called 1,3,5-Benezenetricarboxylic acid to create MOF-Co-Ce with extreme surface area and excellent electronic conductivity. Though this structure is conductive, this can be enhanced with the functionalization of cerium particles. Specifically, the Ce(IV) complexes has shown superior rates of phosphonate ester bond cleavage compared to other metal oxides. This unprecedented activity of the Ce(IV) complex has been attributed to it’s 4f orbital being able to “mix” with the orbitals of the P=O bond to form hybrid orbitals[2]. To functionalize cerium, phosphoric acid is employed to induce the binding of phosphate groups onto cerium oxide. This gives rise to the pentacoordinate intermediate being susceptible to a nucleophilic attack [2]. The functionalized MOF-Co-Ce is subjected to the solvothermal method at 160°C for 24 h with the precursor P25, thus creating MOF-Co-Ce with TiO2 attached (MOF-Co-Ce-Ti).

Results have shown an enhanced performance in terms of current density and onset/halfwave potential for both CV and LSV data as result of phosphate groups absorbing cerium nanoparticles. FTIR data indicates the absorption of 1040 cm⁻¹ (phosphate group peak) appeared after MOF-Ce-Co treatment of phosphoric acid. X-ray analysis indicated that both samples (MOF-Co-Ce and MOF-Co-Ce-Ti) had cerium and cobalt particles, with MOF-Co-Ce-Ti having an additional peak at 56°. Thus, indicating the presence of TiO2 (anatase). Therefore, the improved performance of the treated MOF is the result of its functionalization.

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References:


Tuning Catalytic Activity by Confinement: Aluminum Metal Organic Framework Triggers Selectivity for Carbon Dioxide Reduction Michelle Lee1,2, Alberto De Riccardis1, Roman Kazantsev1, Jason K. Cooper1, Aya K. Buckley1, Paul Burroughs1, David M. Larson1, Giuseppe Mele3 and Francesca Maria Toma1; 1Lawrence Berkeley National Laboratory, United States; 2Cornell University, United States; 3Università del Santo, Italy

Confinement of metal centres is a powerful tool to manipulate reactivity of catalytic centres and tune selectivity in chemical transformations. While aluminum as a foil is inactive for CO2 reduction and shows high selectivity for hydrogen evolution reaction, here we show that aluminum centres confined in a metal organic framework, MIL-53(Al), suppress hydrogen evolution reaction activity and interestingly enhance carbon dioxide reduction.
Aluminum confined in MIL-53 can electrochemically reduce CO₂ to both carbon monoxide and formic acid, as valuable carbon-based products. Control experiments support that the catalytic activity is related to the presence of aluminum and that the confinement effect promoted by the organic ligands is key to obtaining carbon dioxide reduction behaviour. The observation of Al⁰ after electrochemical CO₂ reduction supports that the active form of the catalyst may involve the presence of aluminium in this oxidation state. This aluminum MOFs can produce up to 40% faradaic efficiency for carbon monoxide and formic acid, and with a turnover frequency of 174 h⁻¹. This study demonstrates that the confined reaction space enables changes in reaction selectivity and can impart atypical catalytic capabilities to metals.

2:15 PM *EN06.02.04
AIM-ing for Single Atom Precision for High-Density Supported Arrays of Hetroegeneous Catalysts Joseph T. Hupp, Jian Liu, Hyunho Noh and Subhadip Goswami; Northwestern University, United States

A frontier challenge in the materials chemistry of heterogeneous catalysis is to obtain designed, stable arrays of desired catalysts that are uniform in structure and composition. Catalyst organization in high-density, yet reactant accessible, form enables catalysts to out-perform lower density structures simply because rates of chemical transformations generally scale as the quantity of accessible catalyst employed. Thus, heterogeneous electrocatalysts that are perhaps marginal in sub-monolayer amounts can yield kinetic overpotentials that are hundreds of millivolts smaller when the same catalysts are presented as hundreds or thousands of redox-addressable, and reactant- and product-permeable monolayers at electrode/solution interfaces.¹,² Related arguments are relevant to heterogeneous catalysis of gas phase chemical reactions.

Uniformity of catalyst structure and composition, while standard for molecular catalysts, can be difficult to achieve - or, once achieved, difficult to sustain -- for non-molecular, heterogeneous catalysts. To the extent that uniformity can be achieved, however, hypothesis-driven approaches to advancing Catalysis Science can be pursued. For heterogeneous catalysis, pertinent hypotheses may include the dependence of catalyst activity, selectivity, and long-term stability on, for example: a) catalyst-catalyst site-isolation versus reactant accessibility, b) the nature of the environment beyond the catalyst active-site,³ c) cluster-type-catalyst metal nuclearity, d) the nature and extent of catalyst/support interactions, e) the chemical basis for conversion of synthesized precatalysts to functional catalysts, and f) the ability of the surrounding infrastructure, for example the porous MOF, to supply or sustain essential ancillary properties or components such as local pH, reaction-space confinement, suitably reactive oxidizing or reducing equivalents, charge-compensating ions, or reactive photo-generated molecular excitons.

This presentation will focus on synthesis, characterization, and chemical/photochemical/electrochemical application of cluster-based catalysts that are constructed in automated, atom-by-atom fashion and supported on crystallographically well-defined metal-oxide nodes within high porosity, metal-organic frameworks.⁴,⁵ By way of illustration, two or three case studies will be presented.

2) “Fe-Porphyrin Based MOF Films as High-Surface-Concentration, Heterogeneous Catalysts for Electrochemical Reduction of CO₂,” Hod, et al., ACS Catal. 2015, 5 (11), 6302-6309

2:45 PM BREAK

3:15 PM *EN06.02.05
Single Atom Alloys—Novel Catalysts for Selective Catalytic Reactions Georgios Giannakis, Ryan T. Hannagan, Mengyao Ouyang, Charles H. Sykes and Maria Flytzani-Stephanopoulos; Tufts University, United States
Novel catalyst designs aiming at the development of energy-efficient, low-cost and sustainable processes are of great interest for applications to fuels and chemicals production, and to environmental pollution abatement. Identification of the active catalytic site and design of catalysts with 100% atom efficiency has been a long-standing goal in heterogeneous catalysis. For catalytic metals, atomic dispersion affords better utilization, different (often better) selectivity than the extended metal, and new prospects for low-cost and green process development. It is crucial to understand the mechanisms behind catalysis by supported single metal atoms, as this will guide new, improved catalyst designs.

A new class of single-atom heterogeneous catalysts will be presented, namely Single-Atom Alloys that comprises catalytically active elements like Pt, Pd and Ni alloyed in a more inert host metal like Cu, Au or Ag at the single-atom limit. Single-atom alloys offer a unique approach towards rational catalyst design, one that combines surface science, catalysis and theory in a most efficient way. Model surfaces and nanoparticles that can host isolated atoms in the surface layers behave similarly in escaping the linear scaling relationships and allowing for the rational fine-tuning of activity and selectivity. Good stability is imparted by the strong metal-metal bonds between the host and the minority metal, and atomic dispersion can be maintained at high temperatures. Resistance to CO poisoning and to coking are additional advantages of these promising materials, as will be shown in the presentation drawing examples from alkyne and alkadiene hydrogenation and alkane dehydrogenation. Novel synthesis methods and the stability of single-atom metal catalysts in various supports and reaction environments will be discussed.

3:45 PM EN06.02.06
Diverse Effects of Metal-Oxide Interfaces in Catalysis Sergey Kozlov; National University of Singapore, Singapore

Numerous global challenges, such as the development of environmentally friendly energy and fuel technologies, can be addressed by the development of advanced heterogeneous catalysts. Increasingly often, such catalysts are developed by designing metal-oxide interactions that can boost the catalytic activity by several orders of magnitude. However, such interactions are notoriously challenging to characterize experimentally, which puts electronic structure simulations to the forefront of research on complex nanostructured catalysts.

In this contribution, first I will discuss pioneering density functional simulations of Pd and/or Pt nanocrystallites up to 1.5 nm in size supported on MgO(100), cubic ZrO2(111) and/or CeO2(111) supports. The electron transfer from Pt nanoparticles to reducible CeO2(111) support was quantified by experiments and simulations, which showed that it can reach up to 0.1 electrons per Pt atom and significantly change the reactivity of Pt particles.[1] In turn, the effect of irreducible oxide supports on the nanoparticle reactivity is more complicated. On the one hand, MgO(100) support was calculated to insignificantly affect H adsorption and absorption in supported Pd and Pt nanoparticles.[2] On the other hand, perimeters sites on MgO(100) and ZrO2(111) interfaces with Pd particles were calculated to have increased resistance to CO poisoning, which was observed to significantly increase overall CO tolerance of μm-large Pd aggregates in societally important CO oxidation reaction.[3]

At the same time, interactions with metallic supports also affect the structure and the catalytic properties of the oxides. For example, indium oxide films on Co supports are calculated to contain more O vacancies, which are active sites for CO2 reduction, and have higher methanol selectivity compared to pristine indium oxide surfaces, which is also shown experimentally.[4] In another study, we show how MoOxHy clusters interacting with Ni support adopt the structure and the degree of oxidation that makes them highly active in electrochemical hydrogen evolution reaction (HER) at neutral pH, which is in line with the experimental characterization of Ni-Mo catalysts.[5]

The discussed studies shed light on the electronic aspects of metal-oxide interactions and offer strategies for using such interactions to improve the activity and the selectivity of catalysts.

Enhanced Ethylene Yields in the Electroreduction of CO2/CO Co-Feeds on Cu and Cu-Tandem Electro catalysts Xingli Wang1, Jorge Ferreira de Araújo1, Jan Rossmeisl2 and Peter Strasser1; 1Technical University Berlin, Germany; 2University of Copenhagen, Denmark

The electrochemical CO2 reduction reaction (CO2RR) valorizes CO2 directly into chemicals and fuels. In addition to energy efficiency and selectivity challenges, the supply of CO2 in sufficiently high purity is of great concern. Industrial CO2 feeds are often contaminated with CO, which calls for an investigation of the catalytic CO2RR under CO2/CO co-feed (“dirty CO2”) conditions. In this talk, we present new mechanistic insights into the electroreduction of external (mixed) CO2/CO co-feeds on Cu-based nanocatalysts, which exhibits significantly promoted ethylene production rate over a wide range of electrode potentials and co-feeding ratios. Kinetic isotope labelling experiments using 12CO2 and 13CO – performed in a novel operando differential electrochemical mass spectrometry (DEMS) capillary flow cell with milli-second time-resolution – showed that in both cathodic and anodic scan direction the enhanced C2H4 production originated to almost 50% from the C-C coupling of a 12CO with a 13CO molecule, that is from a cross-coupled “12CO2-13CO” reactive pathway, and to a lower degree from the 12CO2-12CO2 or 13CO -13CO pathways. These transit results with DEMS setup identify the stationary results with gas chromatography and further evidence the absence of a kinetic competition between CO2 and CO molecules for surface adsorption sites, implying distinct surface sites for CO2 and CO adsorption/reduction and suppressed surface adsorbate scrambling. Based on these fundamental mechanistic insights, the practical significance of sustained local interfacial CO partial pressures under local CO2 depletion is then demonstrated using the family of non-metallic/metallic and metallic/metallic tandem CO2RR catalysts with improved and stable ethylene yields. Together, our findings uncover the mechanistic origin of improved C-C product selectivities under co-feeding, but also highlight technological opportunities of impure CO2/CO process feeds for use in the electrochemical CO2 reduction process.

Impact of the Metal Support on the Catalytic Activity of Nanoclusters Mira Todorova, Su-Hyun Yoo and Jörg Neugebauer; Max-Planck-Institut fuer Eisenforschung, Germany

Strategies to enhance catalytic activity are manifold and often rely on exploiting features of seemingly disjoint system. Examples are electrochemistry based catalytic approaches (e.g. electro-catalysis or photo-catalytic electrochemistry processes), nano-catalyst, supported catalyst and others. We will discuss two examples, in which density-theory calculations provide insight into features relevant for catalysis, thereby suggesting routes to tailor catalytic activities. The first example is concerned with ZnO surfaces, where the contact with an aqueous environment leads to the stabilization of catalytically active step and kink sites [1]. The second example, focuses on gold nanocatalysts supported on reduced TiO2 surfaces, for which we discuss the alignment of the respective band structures and its consequences for the catalytic activity of the overall system [2].


Rational Design of Alloy Catalysts by Simultaneously Addressing Strain and Ensemble Effects Tim Mueller and Liang Cao; Johns Hopkins University, United States

The activity, selectivity, and stability of alloy catalysts can be optimized by tailoring their bulk lattice parameters (the strain effect) and near-surface atomic order (the ensemble effect). However this same compositional and structural flexibility makes it difficult to predict the structure and catalytic properties of alloys from first principles. We will present an approach for simultaneously accounting for the strain and ensemble effects in alloy surfaces that enables the rapid prediction of the surface structure and catalytic properties of stable and metastable alloy materials.
We use our approach to introduce complete maps of catalytic activity for thermodynamically stable phases across compositions and temperatures, making it possible to identify the synthesis conditions likely to produce the most active catalysts. By analyzing these maps, we will discuss in particular the roles of intermetallic phases, nanoparticle sizes, and atomic ensembles in determining the catalytic activity of alloy surfaces. We will present examples from Pt-based alloys for the oxygen reduction reaction, but the approach we present is applicable to a wide range of reactions on alloy surfaces.

**4:45 PM EN06.02.10**

**Automated Detection and Characterization of Surface Restructuring Events in Bimetallic Catalysts** Jin Soo Lim¹, Nicola Molinari¹, Kaining Duanmu², Philippe Sautet²,³ and Boris Kozinsky¹; ¹Harvard University, United States; ²University of California, Los Angeles, United States

Surface segregation in bimetallic systems plays a crucial role in heterogeneous catalysis. However, mechanistic studies of such restructuring phenomena remain scarce due to the large configurational space that makes it challenging to establish the most relevant set of mechanisms. To this end, we develop an automated method to discover elementary surface restructuring processes in an unbiased fashion, and apply it to Pd/Ag single-atom alloy as an example.

We employ high-temperature classical molecular dynamics (MD) to rapidly detect restructuring events, isolate them, and optimize using density functional theory (DFT). Our approach, combining MD and ab initio calculations, has two main advantages over conventional static transition state modeling methods. First, our approach is unbiased and does not rely on human intuition, instead discovering the relevant transition state pathways from the real-time surface dynamics. Second, the process is streamlined, quickly and automatically detecting restructuring events from MD and optimizing every event with DFT.

In addition to finding the previously proposed mechanism of exchange descent, our approach has revealed three new general classes of concerted restructuring events, dominant at step edges of close-packed surfaces: (1) vacancy insertion; (2) direct exchange; (3) interlayer exchange. Our results highlight the importance of vacancies at steps and kinks in facilitating Pd-Ag exchange processes, an insight that could not be established from previous DFT calculations on model terraces. The restructuring events discovered through our automated scheme enable us to go beyond thermodynamics and construct a complete set of mechanisms by which Pd is incorporated into the Ag host in vacuum at the single-atom limit. Furthermore, the approach establishes an important foundation to investigate more complex restructuring phenomena, such as Pd/Ag heteroepitaxy and adsorbate-induced reverse segregation. Our automated method is transferable to other alloy systems of interest and allows the dynamic nature of surfaces to be studied at the microscopic level with ab initio level of accuracy. The atomistic insights presented in our work provide a step toward systematic understanding and engineering of surface segregation dynamics in bimetallic catalysts.

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**EN06.03.01**

**Paving the Way to Greener Chemistry with Nanocatalyst Control—Stable AuPd for On-Site Hydrogen Production and Use** Michelle Muzzio and Shouheng Sun; Brown University, United States

Catalysis is one of the main tenants of green chemistry and the optimization of catalytic processes to improve the stability and reusability of the catalyst is an important research endeavor. Nanocatalysts in particular have been widely used and can uniquely catalyze more than one reaction on their large amounts of surface area – potentially minimizing solvent, substrate, and catalyst waste if reactions are engineered properly. In this work, we report the synthesis of a series of AuPd alloy nanoparticles with careful control of nanoparticle size and composition. We
highlight AuPd’s high activity for ammonia borane (a green alternative hydrogen source) dehydrogenation. With a TOF of 160 min\(^{-1}\) for AB methanolysis, Au\(_{66}\)Pd\(_{34}\) has the highest activity of all Pd-based catalysts reported for H\(_2\) production with a very low activation energy, 22.4 kJ/mol. Not only is the AuPd active for the formation of hydrogen (H\(_2\)), but, we can then use this generated H\(_2\) in-situ for the dehalogenation of polychlorinated phenols (tough to degrade chemicals that have been used as pesticides in the past). Beyond this, ambient pressure H\(_2\) formed can also be used for the mild reductive amination of levulinic acid/ethyl levulinate, biomass derivatives, to value-added pyrrolidones, over the same AuPd catalyst, simply recycled and used for both reactions, over ten times with no change in catalyst activity.

EN06.03.02
Solar-Driven Asymmetric Reduction of C=C Bonds via Light-Harvesting Alginate Hydrogel for Sustainable Photobiocatalysis
Yoon Jaeho\(^1\), Sahng Ha Lee\(^1\), Tieves Florian\(^2\), Rauch Marine\(^2\), Hollmann Frank\(^3\) and Chan Beum Park\(^4\); \(^1\)Korea Advanced Institute of Science and Technology, Korea (the Republic of); \(^2\)Delft University of Technology, Netherlands

Here, we report a robust platform for sustainable photobiocatalysis using an ene-reductase from *Thermus scotoductus* SA-01 (*TsOYE*) and a light-harvesting dye (rose bengal, RB) co-immobilized alginate hydrogel. *TsOYE*-encapsulated alginate hydrogel was prepared by simple mixing and gelling with high efficiency. Highly efficient encapsulation of RB in alginate hydrogel was followed using the intrinsic affinity between *TsOYE* and RB, which allowed for the construction of robust RB-*TsOYE*-loaded alginate capsules. A series of spectroscopic and electrochemical assays verified spontaneous binding of RB molecules to the flavin prosthetic group of *TsOYE* with a higher affinity than NADH, and direct electron transfer and co-reduction of *TsOYE* and RB in alginate hydrogel. In the absence of NADH, the photobiocatalytic system facilitated asymmetric hydrogenation of 2-methylcyclohexenone to an enantiopure (R)-2-methylcyclohexanone (max. conversion: 70.4%, turnover number: 300.2, turnover frequency: 1.54 min\(^{-1}\)) under illumination of a white light-emitting diode (LED) (power: 5.22 mW/cm\(^2\)). While the limited mobility of immobilized *TsOYE* and substrate accessibility reduced the overall catalytic performances, we revealed a significant enhancement of *TsOYE*'s robustness against heat and chemical denaturants and reusability while immobilized in alginate hydrogel. This study provides insight into a greener and sustainable approach of cofactor-free OYE biocatalysis for solar-driven synthesis of value-added chemicals.

EN06.03.03
Selective Oxidation of Methane to Methanol Using Bioinspired Metal–Organic Framework Catalysts
Jayeon Baek\(^1\), Bunyarat Rungtaweeworani\(^2\), Gabor A. Somorjai\(^3\) and Omar M. Yaghi\(^3\); \(^1\)Korea Institute of Industrial Technology, Korea (the Republic of); \(^2\)National Science and Technology Development Agency, Thailand; \(^3\)University of California, Berkeley, United States

Selective methane oxidation to methanol represents an important challenge in catalysis due to the difficulty in activating the strong C–H bond of methane (bond dissociation energy = 104 kcal mol\(^{-1}\)), giving rise to selectivity and activity problems. Finding a solution to this impediment is a key toward the direct synthesis of methanol from methane.

In nature, particulate methane monooxygenase (pMMO) is known as an effective catalyst for the oxidation of methane to methanol. Inspired by pMMO, molecular complexes have been developed utilizing the tunability of ligand design in pursuit of duplicating the structure and reactivity in a synthetic system. However, it has been a challenge to incorporate copper active sites bound to imidazole units in the pore of heterogeneous catalysts for methane oxidation.

We envisaged that metal–organic framework (MOF) can serve as a scaffold akin to the polypeptide chains in enzymes whose arrangement of secondary and tertiary structures can be achieved by judicious choice of structure and topology of MOFs. From structural analysis of various MOFs, MOF-808 was used to postsynthetically install ligands bearing imidazole units for subsequent metalation with Cu(I) in the presence of dioxygen. The catalysts show high selectivity for methane oxidation to methanol under isothermal conditions at 150 °C. We identified the structure of the active sites using solid-state UV–vis, resonance Raman, and X-ray absorption spectroscopies complemented by density functional theory (DFT) calculations. The results led us to conclude the most probable active site as bis(μ-oxo) dicopper species. We also demonstrated the modularity of our system by incorporating three different ligands bearing imidazole groups with different levels of rigidity and studied their effects on the catalytic
EN06.03.04
Interfacial Study of First Row Transitional Metal Ferrites as Oxygen Reduction Reaction (ORR) Electrocatalysts
Joselyn C. Del Pilar; Universidad de Puerto Rico-Rio Pied, Puerto Rico

Proton exchange membrane fuel cells (PEMFC) are a promising power technology for vehicles. However, their commercialization has been hindered due to high-cost platinum and platinum-based electrocatalyst which accounts for approximately 20% of the PEMFC total cost. Alkaline membrane fuel cells (AMFC) have emerged as an alternative to PEMFC as ORR kinetics are greatly improved in alkaline conditions. Alkaline media also enables the use of first row transition metal thus allowing for more cost-effective catalysts to be develop. Here we present the use of first row transition metal ferrites as ORR electrocatalyst in alkaline media and study their electrocatalytic mechanism using synchrotron-based X-ray absorption (XAS) techniques. We use a facile co-precipitation method to prepare zinc, cobalt and manganese ferrites. X-ray diffraction patterns suggest a spinel crystal phase is formed for cobalt and manganese ferrites. However, when zinc is used, two crystal phases are observed; zinc oxide and zinc ferrite. Electrocatalytic activity toward ORR was performed in 1.0 M NaOH using a glassy carbon rotary disk electrode (RDE). The highest onset potential was observed for MnFe2O4 followed by CoFe2O4 and ZnFe2O4. Beyond just evaluating the ORR activity of the materials, our work seeks to gain an understanding of the in situ electrocatalytic reactions taking place during ORR. To this end, efforts to conduct in situ XAS electrochemical characterization at are underway. ACKNOWLEDGMENTS: This work was supported by the National Science Foundation NSF-PREM: Center for Interfacial Electrochemistry of Energy Materials (CiE²M) grant number DMR-1827622.

EN06.03.05
Pt-Au Solid-Solution Alloy Nanoparticles with Remarkable Catalytic Performances for H2O2 Direct Synthesis
Hong Woo Lee1,2, Kwan-Young Lee2 and Sang Soo Han1; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Korea University, Korea (the Republic of)

Hydrogen peroxide (H2O2) has been mainly produced by the sequential hydrogenation and oxidation process of anthraquinone molecules, which is called as an indirect synthesis method. However, this process requires large volume facilities and a large quantity of energy. So, a direct synthesis method from H2 and O2 molecules in the presence of Pd catalyst has been considered for small-scale and on-site H2O2 production. However, the disadvantages of the prototypical Pd is that water is easily generated during the synthesis process. In order to improve the catalytic performance, many researchers have focused on Pd-based bimetallic alloys that can be easily formed thermodynamically such as Pd-Pt, Pd-Au, and Pd-Sn. In other words, the combinations of immiscible elements have been thoroughly ignored so far. Therefore, it has been a big challenge to broaden the scope of catalyst research into a wider area.

In this study, we report solid-solution alloy nanoparticles (NPs) of Pt and Au with a face-centered cubic (fcc) structure, although they are completely immiscible in the bulk phase. X-ray diffraction, transmission electron microscopy (TEM), energy-dispersive X-ray measurements, and density functional theory (DFT) calculations revealed that Pt and Au atoms were homogeneously distributed in a wide composition range of the Pt$_x$Au$_{100-x}$ NPs (7≤x≤82). Out of all tested compositions, Pt$_7$Au$_{93}$ NPs exhibited superior catalytic performances both in productivity (2,327 mmol /gcat h) and H2O2 selectivity (99.2%) and even under ambient conditions (20 °C, 1 atm) and without halide-ion additives. This exceptional catalytic property of the solid-solution Pt-Au alloys was clearly proved with the reaction mechanism obtained from the DFT calculation. In addition, we have checked that the introduction of inactive Au atoms likely suppresses dissociations of O$_2^*$ and OOH*, which leads to enhance the H2O2 selectivity. To our knowledge, this study is the first demonstration of stabilizing non-equilibrium solid-solution NPs as H2O2 direct synthesis catalysts. In addition, this work suggests that active utilization of other bulk-immiscible elements is highly desirable for catalyst development.

EN06.03.06
Facile Norbornadiene—Quadricyclane Interconversion Mediated by a Magnetic Catalyst
Patrick Lorenz, Tobias Luchs and Andreas Hirsch; University of Erlangen-Nuremberg, Germany

One problem that most solar based devices have in common is the discontinuous energy production and the concomitant mismatch between energy production and energy demand. This problem can be circumvented by using
molecular solar thermal (MOST) energy storage and release systems. These systems are capable of harvesting the energy and transforming it into a storable form on a molecular level. When needed the stored energy can then be released as thermal energy.[1] The valence isomerization of norbornadiene (NBD) to its metastable and energy rich isomer quadricyclane (QC) is regarded a promising candidate for MOST applications.[2]

Within the scope of this project, we designed and synthesized NBD and QC interconversion couples with red-shifted absorption profiles. These NBD derivatives can undergo photoisomerization to their metastable QC isomers upon direct irradiation without the need for a triplet photosensitizer. We investigated each interconversion couple regarding their photophysical properties, stability of the energy rich isomer (t₁/₂ ranging from hours to over a year at room temperature) and their potential energy storage capacity. Finally, the most promising derivatives were treated with a magnetic nanoparticle catalyst, designed in our group, to facilitate strain energy release via back-conversion of QC to NBD followed by straightforward purification by the action of an external magnetic field.


Role of Oxygen Vacancies in CuO/In₂O₃ Nanocomposite for Selective Electrochemical Reduction of CO₂ to CO

Pinki Devi, Karan Malik, Ekta Arora, Saswata Bhattacharya, Anil Verma and Jitendra P. Singh; Indian Institute of Technology Delhi, India

Abstract: Sequestration of carbon dioxide (CO₂) through electrocatalytic reduction to produce high-value industrial precursors, such as, CO is a promising avenue for sustainable development. However, the choice of an energy efficient and stable electrocatalysts for the selective reduction of CO₂ is a major challenge. Here, we prepare highly active, stable and cost effective CuO/In₂O₃ nanocomposites. We demonstrate a novel approach that utilizes oxygen vacancy (Vₒ), in CuO/In₂O₃ nanocomposites for the reduction of CO₂ to CO. Here, we control the concentration of Vₒ by varying the calcination environment during synthesis of the CuO/In₂O₃ nanocomposites. Photoluminescence, X-ray photoelectron and electron paramagnetic resonance spectroscopy measurements indicate that CuO/In₂O₃ nanocomposites prepared in an argon environment exhibit higher concentrations of Vₒ defects in comparison with samples that are prepared in air ambient. Moreover, CuO/In₂O₃ nanocomposites with less Vₒ defects exhibit 63% faradaic efficiency at -0.645V, while, CuO/In₂O₃ nanocomposites that are rich in Vₒ defects yield CO with 85% faradaic efficiency at -0.895V w.r.t. RHE suggesting that Vₒ serves as the active site for CO₂ adsorption. Through a combination of electrochemical measurements, physical characterization and density functional theory (DFT) calculations, we establish that the enhancement in CO yield is directly correlated to the concentration of Vₒ defects in the CuO/In₂O₃ nanocomposites and propose a plausible mechanism for electrocatalytic CO₂ reduction.

References:

Photocatalytic Stereoselective C-C Oxidative Coupling Reactions with Semiconductor Quantum Dots

Yucheng Yuan, Hua Zhu and Ou Chen; Brown University, United States

Semiconductor quantum dots have emerged in diverse practical applications including bioimaging and labeling, solar energy harvesting, light-emitting diodes, and next-generation displays. Most recently semiconductor quantum dots have attracted more and more attention in the field of photocatalysis, owing to their suitable optoelectronic properties for photocatalytic reactions, including high absorption coefficient and long carrier lifetime. Herein, we report the visible-light-mediated stereoselective C-C oxidative coupling reactions photocatalyzed by semiconductor quantum dots. High quality of halide perovskite and CdSe-based quantum dots have been synthesized and characterized, and then been applied to the model reaction to afford optimized reaction conditions. The desired product can be generated exhibiting high yield with high stereoselectivity. The reaction can be generalized to...
different starting materials with various substituents on the phenyl ring and varied functional moieties. Furthermore, we study the reaction pathway by using radical trapping agent and electron paramagnetic resonance (EPR) spectroscopy. We propose our stereoselectivity is caused by steric hindered radical reactions. Our study shows semiconductor quantum dots are expected to bring new insights in photochemical synthesis.

EN06.03.10
Efficient Electrochemical Nitrogen Reduction Reaction on Nickel Single Atom Catalyst Yeeji Baek, Ying Chuan Tan and Jihun Oh; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Ammonia is used in various industries as an essential chemical in the modern industrial economy. Haber-Bosch process has been widely used to produce ammonia, which involves extremely high temperature and pressure, and hydrogen gas produced from steam reforming. As a result, this process emits more than 1.9 ton CO₂ per ton NH₃. Due to the high global demand of ammonia, 2% of the world’s total energy supply is used for ammonia production, and thus is responsible for more than 400 Mt of emitted CO₂, which is 1.6 % of total CO₂ emissions. Therefore, electrochemical nitrogen reduction reaction (NRR) is attracting attention as an alternative to this process, because electrochemical NRR could serve as an environmentally friendly approach to synthesize ammonia with lower or potentially zero CO₂ emission depending on the electrical source. However, it has many drawbacks. One of them is the low activity for NRR, because nitrogen is a very stable compound due to its triple bond. Catalysts are critical to achieve better activity and selectivity. Single atom catalyst is one of the attractive materials not only for electrochemical ammonia production, but also for various electrocatalysis where high product selectivity could be achieved.

Here, we present the use of nickel single atom catalyst (Ni-SAC) as an efficient electrocatalyst for NRR. Ni-SAC is derived from Ni²⁺-exchanged ZIF-8 (Ni-ZIF), which involved the ionic exchange between Zn²⁺ and Ni²⁺. Pyrolysis of Ni-ZIF at 950°C yielded Ni-SAC, in which the Ni-atom in this material bonds with 3 nitrogen atoms and 1 carbon atom. The as-prepared Ni-SAC shows high ammonia production rate (3.9 µg h⁻¹ mg⁻¹) and faradaic efficiency (0.27 %) at -1.2 vs. RHE in a flow cell. These values are independent on ambient ammonia which are obtained by subtracting the amount of ammonia present during NRR in Ar atmosphere. The high performance can be attributed to the ensemble effect and electronic effect of the isolated Ni²⁺ ion in Ni-SAC. Also, it has high surface area and porosity, which translates to more catalytic sites being accessible for NRR. In this conference, we will present a more holistic evaluation of the high performance observed for NRR and discuss the differences of NRR performances using Ni-SAC in H-cell and in flow cell.

EN06.03.11
Fe-Doped Lanthanum Nickelate Deposited on Pyrolytic Graphite Sheet as Potential Electrode for Oxygen Evolution Reaction Cipriano B. Gozzo¹, Mario R. Soares¹,², Júlio C. Sczancoski¹, Fabricio B. Destro¹ and Edson R. Leite²,¹; ¹Federal University of São Carlos, Brazil; ²Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), Brazil

In recent years, there is an unprecedented interest of worldwide organizations in replacing fossil fuel-based energies with other renewable energy sources to reduce the emissions of greenhouse gases released into the atmosphere and to overcome the serious problem of climate change. A viable alternative for this purpose is the use of electrocatalysts for the production of hydrogen (Hydrogen Evolution Reaction - HER) and oxygen (Oxygen Evolution Reaction - OER). In general, the main attributes of efficient electrocatalysts for practical applications include use of low cost and non-toxic materials, high chemical and mechanical stability, durability and low overpotential. Particularly, the lanthanum nickelate (LaNiO₃) is a promising candidate as electrocatalyst because of its high conductivity, low charge transfer resistance, and interesting electrocatalytic properties for OER. The intrinsic OER activity of LaNiO₃ has been attributed to the existence of a single electron in the eg orbital belonging to Ni³⁺. However, Ni³⁺ is easily reduced to Ni²⁺, leading the eg orbital to exhibit more than a single electron. The commonly employed strategy to solve this, it’s the partial replacement of crystallographic sites occupied by Ni³⁺ with other transition metals. Therefore, the main aim of our study was to investigate the electrocatalytic properties of LaNiₓ₋ₓFeₓO₃ (x = 0.0, 0.3, 0.6, and 0.9 mol%) for OER, mainly analyzing the influences provoked by Fe³⁺ ions in the lattice and the use of pyrolytic graphite sheet (PGS) as a potential substrate for electrocatalysis. LaNiₓ₋ₓFeₓO₃ powders were synthesized by the co-precipitation method followed by post-heats treatment (900 °C for 4 h). The thin film electrodes were prepared depositing the obtained powders on PGS substrates via drop-casting. In relation to the powders, X-ray diffraction patterns revealed that the Fe³⁺ level was responsible for a structural phase transition from
rhombohedral \((x = 0.0 \text{ to } x = 0.3 \text{ mol%})\) to orthorhombic \((x = 0.6 \text{ to } x = 0.9 \text{ mol%})\). The substitution of \(\text{Ni}^{2+}\) by \(\text{Fe}^{3+}\) in the crystalline structure favored a morphological change from irregular cube- to spherical-like microparticles. A superior electrocatalytic activity for OER was detected for Fe-doped electrodes in relation to phase pure \((\text{LaNiO}_3)\), so that the \(\text{LaNi}_{0.4}\text{Fe}_{0.6}\text{O}_3\) was the most efficient for this purpose. Besides the low charge transfer resistance, \(\text{LaNi}_{0.4}\text{Fe}_{0.6}\text{O}_3\) demonstrated a lower overpotential (439 mV) and a smaller Tafel slope (52 mV dec\(^{-1}\)) than the \(\text{LaNiO}_3\) (465 mV and 76 mV dec\(^{-1}\)). In addition, a current density above 10 mA cm\(^{-2}\) was registered for this electrocatalyst in chronoamperometry tests, confirming its effectiveness over long times. The potentiality of PGS substrate for our electrocatalysts was confirmed by comparing with other electrocatalytic tests performed on glassy carbon substrate.

**EN06.03.12**

**Understanding the Heterogeneous Nucleation of Pt Single-Atoms and sub-Nanometer Clusters** Pavithra B\(^1\), Dipanwita Chatterjee\(^2\) and Ravishankar Narayanan\(^1\); \(^1\)Indian Institute of Science, India; \(^2\)Norwegian University of Science and Technology, Norway

Supported precious metal catalysts are extensively employed in industries for several chemical processes. Size of the metal species is a decisive factor in controlling the performance of such catalysts. Smaller the size, higher is the activity. So, huge interest has been directed towards the formation, stabilization and characterization of single atom catalysts and sub-nanometer clusters in the past few years. However, Supersaturation controlled, wet chemical methods have been hardly explored to synthesize such catalysts on various supports. We describe a robust wet chemical method to synthesize catalyst that consists of stable, isolated single atoms and sub-nanometer clusters of Pt anchored to the surfaces of \(\text{ZnO}\) nanorods. The thermodynamic and kinetic aspects of reduction of Pt salt under microwave heating conditions and heterogeneous nucleation of Pt atoms/clusters on \(\text{ZnO}\) have been understood. Driving force of the reaction has been optimized to obtain as small nuclei as possible with no post-nucleation growth and to have only heterogeneously nucleated ones. Heterogeneous nucleation also helps in further reduction of the cluster size by truncating the clusters. Facets on the \(\text{ZnO}\) rods having highest surface energy possess the lowest kinetic barrier for nucleation and thus such sites are always the most favored for nucleation. Having a very low driving force for nucleation, all the observed Pt clusters sit preferentially on the basal planes of the nanorods. Also, it is desired to produce catalysts that are resistant to sintering. These Pt clusters are stable under elevated temperatures both in air and CO atmosphere at least till 220°C. So, these can be efficiently utilized for CO oxidation which happens below 200°C. Electron microscopy HAADF-STEM technique, which is the only viable tool to visualize atomically distributed species, has been exploited extensively to characterize the \(\text{ZnO}/\text{Pt}\) hybrid structures. Having the finer size of Pt nucleated on \(\text{ZnO}\), we expect to achieve higher catalytic activity as compared to Pt nanoparticles on \(\text{ZnO}\).

**EN06.03.13**

**Synthesis of Fibers with Zeolite/Lignin by Electrospinning for the Deoxygenation of Bio-Oil from Soybean Hulls** Jose L. Toro Trochez, Eileen S. Carrillo Pedraza, Héctor M. Leija Gutierrez, Diana Bustos Matínez and Eduardo Soto Regalado; Universidad Autónoma de Nuevo León, Mexico

Catalytic upgrading of biomass derived pyrolysis vapors, by passing them over a zeolite catalyst has been explore in the last years. In the fibers incorporated zeolite HZSM-5 as a catalyst, have shown that the Zeolite HZSM-5 has the best yields in the deoxygenation of pyrolytic oil. The synthesis of a catalyst using fibers could increase the accessibility to the active sites and improving the deoxygenation of the pyrolytic oil and to promote green chemistry practice using biopolymers instead of traditional polymers derived from fuel. The use of fibers with zeolite/lignin is proposed in this work to promote de-oxygenation reactions, improving the characteristics of pyrolytic oil such as pH, calorific value, among other properties in the soybean hulls pyrolytic bio-oils. The aim is the fabrication of fibers using lignin as polymer, reducing the use of traditional polymers such as polyvinylpyrrolidone (PVP) and polyacrylonitrile (bread), polymers of high economic value and harmful to environment, compared to lignin. The fibers and zeolite will be characterized by the techniques of XRD, SEM, and ATP. Pyrolytic oils are characterized by GC/MS. This research will contribute to the synthesis of a new catalyst, as well as to use in obtaining biofuels.

The characterization of HZSM zeolite and the thermal characterization of the polymers has been carried out. the XRD Analysis is obtained the crystalline phases of the HZSM-5 zeolite, with sharp reflections corresponding to the MFI structure, the results of nitrogen physisorption Analysis was obtained TYPE IV isotherm and hysteresis characteristic from Mesopores, according to the IUPAC. The analysis BET obtained a surface area of 289.2 m\(^2\)/g,
was obtained with a promised pore diameter of 36.1 nm, characteristic of structures mesoporous, these structures promote the obtaining of bio-oil and the reduction of biochar. The obtained the different signals from the acid sites, the desorption signals of ammonia less than 200 °C correspond to sites with weak superficial acidity, while desorption signals exhibited between 200-400 °C are associated with medium-strength acid sites, and the signals found to temperatures higher than 400 °C, correspond to sites with strong acidity, weak acid sites are in greater proportion, the results are similar to those obtained by Jia Lui et al. 2015 (Liu et al. 2015). The next step is to manufacture fibers with zeolite HZSM-5 to favor accessibility to acid sites and to increase the deoxygenation of pyrolytic oil, which until now was obtained 18% of deoxygenation using a zeolite catalyst.


EN06.03.14
Pd and Cu Single-atom Doped Two-Dimensional Ti3C2Tx Nanosheets as Efficient Catalysts for Electrochemical CO2 Reduction Essraa A. Hussein, Yasseen S. Ibrahim, Samah Dib, Zainab Abdul-Rahman, Kamel Eid, Aboubakr M. Abdullah and Ahmed Elzatahry; Qatar University, Qatar

Recently, single atom catalysts (SACs) have gained a great deal of attention as heterogeneous electro-catalysts, owing to their high surface area, abundant active sites, stability, and selectivity. Here, we report the fabrication of Pd and Cu single atom co-doped two-dimensional 2D Ti3C2Tx, MXene nanosheets (Pd/Cu/Ti3C2Tx). This is achieved by the selective chemical etching of Ti3AlC2 (MAX phase) followed by ultrasonic irradiation at room temperature and then co-doping with Pd and Cu. This drove the formation of well-defined, ordered, and exfoliated Ti3C2Tx nanosheets with average dimensions of 300nm in length and 150nm in width as well as homogeneously co-doped with Pd and Cu as single atom (nearly 1 wt. % each). The catalytic activity and durability of the typically prepared Pd/Cu/Ti3C2Tx were investigated relative to metal-free Ti3C2Tx nanosheets. The results displayed the significant activity of Pd/Cu/Ti3C2Tx as reflected in its earlier onset potential, lower reduction potential, and higher reduction current density. This is in addition to the high tolerance to the intermediate poisonings owing to the combination between the unique properties of MXene and impressive electro-catalytic properties of Pd/Cu single atom. Intriguingly, Pd-Cu/Ti3C2Tx nanosheets showed a high propensity to reduce CO2 into formic acid with a great faradaic efficiency. We believe that the results obtained from this work may open the door for new efficient and well-designated SACs/MXenes catalysts for further electrochemical applications.

EN06.03.15
Tailored the Fabrication of Cu and Zn Single Atom Doped Two-Dimensional MXene Nanosheets for the Efficient Electrochemical Reduction of CO2 at Room Temperature Ghada G. Abdo, Yasseen S. Ibrahim, Samah Dib, Zainab Abdul-Rahman, Kamel Eid, Aboubakr M. Abdullah and Ahmed Elzatahry; Qatar University, Qatar

Accumulation and excessive release of CO2 into the atmosphere resulting from the consumption of fossil fuels are considered as serious debate on harmful environmental changes, such as global warming, desertification, and ocean acidification. To tackle these problems, electrochemical reduction of CO2 has been regarded as a paramount demand in order to enable the recycling and conversion of CO2 to useful fuels. Herein, we controlled fabrication of Cu and Zn single atom doped MXene denoted as (Cu/Zn/Ti3C2Tx). The typically prepared Cu/Zn/Ti3C2Tx were obtained in a high yield of uniform and exfoliated two-dimensional nanosheets with average diameters of (400 nm) in the length and (200 nm) in the width and coherently doped with Cu (1 Wt. %) and Zn (1 Wt. %) in the form of single atom. Cu/Zn/Ti3C2Tx showed a significant higher electrochemical CO2 reduction activity and stability compared to Ti3C2Tx at room temperature. The obtained current density on Cu/Zn/Ti3C2Tx was around 3 times higher than that of Ti3C2Tx as well as faster reduction kinetics. Intestinally enough, Cu/Zn/Ti3C2Tx revealed higher selectivity and tendency to reduce CO2 into ethanol. The insights gained from this work would shed the light on designing novel bimetallic systems with MXene support for the electrochemical reduction of CO2.

EN06.03.16
Utilization of Nb2O5/g-C3N4 heterostructure as Catalyst to CO2 Heterogeneous Photoelectroreduction Eduardo H. Dias; USP, Brazil

Pollution caused by CO2 emissions in the atmosphere causes a number of environmental damages, such as the so-
called greenhouse effect. Thus, in recent years the search for technologies capable of bringing environmental and economic benefits has been intensified, converting CO2 into value-added molecules, such as ethanol, ethane and formic acid. Among the efficient ways of promoting this conversion of CO2, we highlight the electrocatalytic and photocatalytic processes, mainly using semiconductors. Niobium pentoxide (Nb2O5) and graphite carbon nitride (g-C3N4) demonstrate good catalytic performances for degradation of organic pollutants and water splitting. However, these catalysts have as limitation their high recombination of the photogenerated charge carriers. One way to overcome this negative effect in photocatalytic processes is the formation of heterojunctions between the two materials (Nb2O5 and g-C3N4). Therefore, in this work the photo and electrocatalytic efficiency of the Nb2O5/g-C3N4 heterostructures was verified for conversion of CO2 into CH4. In addition, we investigated the electrical properties of the synthesized materials, such as flatband values. Thus, this properties change the selectivity of the formed products, obtaining highly efficient processes. In the electrochemical and photoelectrochemical tests, the Nafion and PEDOT: PSS5 was used with binder to increase the contact between the synthesized samples (Nb2O5, g-C3N4, and Nb2O5/g-C3N4) and de substrate (Fluorine doped Tin Oxide Glass). The photoelectrocatalytic tests shown that the electrode with the heterostructure Nb2O5/g-C3N4 and PEDOT:PSS has 10 times higher current values than the value obtained to the electrode without PEDOT: PSS (12 μA cm2 and 1.5 μA cm2) to 0.4V under irradiation. However, both samples showed increase of current in the presence of light, double for samples with nafion and triple for samples with PEDOT. The flatband values obtained were -0.55V and -0.77V, for the Nb2O5/g-C3N4 samples with and without PEDOT through the Motty-Schottky analyzes using the frequency of 100 Hz, showing that PEDOT decreased the flat band value. It was possible to verify that the synthesized samples are photoactive and that they have great chances of being possible catalysts for photoelectroreduction of CO2 and will be tested later with quantification of the products through GC and HPLC measurements, and the studies in different potential will be performed to analyse the effect of the potential in the selectivity.

Gelson T.S.T.da Silva; André E.Nogueira; Jéssica A.Oliveira; Juliana A.Torres; Osmando F.Lopes; Caue Ribeiro.
Applied Catalysis B: Environmental, v. 242, p. 349-357, march 2019

EN06.03.17
Electrochemical Reduction of CO2 over O3-Pretreated Ag Cathode Masaatsu Ishida, Soichi Kikkawa, Kentaro Teramura, Hiroyuki Asakura, Saburo Hosokawa and Tsunehiro Tanaka; Kyoto University, Japan

In electrochemical reduction of CO2 in aqueous media, it is well-known that CO is generated as a main product over Ag cathodes. Several research groups reported that anodic oxidation (anodization) improves the current density and faradaic efficiency toward CO evolution due to the crystal orientation and the valence of Ag cathode. On the other hand, ozone (O3) is generally used for chemical oxidation. In this study, we investigated the current density and faradaic efficiency toward CO evolution for the electrochemical reduction of CO2 by using the O3-pretreated Ag cathode.

Ag foil (Nilaco Co., 99.98%, 6 cm2) electrodes were sonicated in hexane, ethanol, and Milli-Q water, prior to the electrochemical measurements. The O3 pretreatment of Ag electrodes were performed in an O3 generator (ASM401N, Asumi Giken Ltd.). Front and back sides of Ag foil were exposed to O3 atmosphere for 10 hours each. The electrochemical CO2 reduction experiments were conducted in a H-type two-glass chamber with using Pt wire and Ag/AgCl as a counter electrode and a reference electrode, respectively. The electrolyte was 0.1 M KHCO3 aqueous solution under flowing of CO2 gas (99.999 %) at a flow rate of 20 mL min-1. The CO2 reduction activity was evaluated at constant potential (~1.6 V vs. Ag/AgCl). The electrochemical surface area (ECSA) of Ag electrodes were determined by using underpotentially deposition of lead (Pb UPD) in an aqueous solution containing 0.1 M HClO4, 0.1 M NaClO4, 1 mM Pb(ClO4)2. The crystal structure was confirmed by X-ray diffraction (XRD) analysis.

The XRD patterns of O3-pretreated Ag electrode were assigned to the typical diffraction pattern of AgO. This electrode exhibited the current density of 3.9 mA cm-2 and faradaic efficiency of 95%, although these were 1.2 mA cm-2 and 68% over Ag foil, respectively. After the electrochemical reduction of CO2 only the diffraction patterns of fcc structure of Ag metal were observed, suggesting that AgO species on O3-pretreated Ag electrode were reduced to Ag metal during the reaction. The amount of underpotentially deposited Pb atoms on O3-pretreated Ag electrode
(13 nmol) was almost two times larger than that on Ag foil (6.2 nmol). The current density and faradaic efficiency toward CO evolution were not dependent on only ECSA. After the reaction, the ratio of (111) to (200) facets of O$_3$-pretreated Ag electrode was much higher than that of Ag foil in the XRD pattern. We concluded that the high current density and faradaic efficiency toward CO evolution were attributed to not only the high ECSA but also the face orientation of O$_3$-pretreated Ag electrode.

**EN06.03.18**

**Nanostructured Amalgams with Tuneable Silver-Mercury Bonding Sites for Selective Electroreduction of Carbon Dioxide into Formate and Carbon Monoxide** Wanfeng Yang, Sheng Chen, Wenhao Ren, Yong Zhao, Xianjue Chen, Chen Jia, Junnan Liu and Chuan Zhao; UNSW Sydney, Australia

Realizing highly efficient and selective electrochemical CO$_2$ reduction by using cost-effective catalysts is key to large-scale commercialization of this technology. In this work, a nanoporous amalgam catalyst with tuneable amount of Ag-Hg bonding sites has been developed for selective CO$_2$ electroreduction to formate or CO via a one-step wet-chemistry method. This catalyst is composed of Ag(Hg) solid solution phase and Ag-Hg intermetallic compound, exhibiting a loosened nanorod-channel networks morphology. Ag$_{70}$Hg$_{30}$ alloy drives efficient formate generation with a high Faradaic efficiency of 85% at a moderate overpotential of 790 mV while Ag$_{91}$Hg$_9$ alloy promotes CO$_2$ reduction to CO with a Faradaic efficiency of 58% at a low overpotential of 590 mV. The switchable product selectivity has been correlated to a preferable formation of HCOO* or *COOH intermediates at Ag-Hg and Ag-Ag bonding sites. This work highlights amalgams as novel electrocatalysts for CO$_2$ reduction to valuable products on demand.

**EN06.03.19**

**Active Site Engineering by Surface Sulfurization for a Highly Efficient Oxygen Evolution Reaction—A Case Study of Co$_3$O$_4$ Electrocatalysts** Ying Pan$^1$, Hangjuan Ren$^1$, Haiwei Du$^2$, Fuyang Cao$^1$, Yifeng Jiang$^1$, Haojin Du$^1$ and Dewei Chu$^1$; $^1$University of New South Wales, Australia; $^2$Anhui University, China

Surface sulfurization strategy is utilized to construct Co$_3$O$_4$@CoS$_x$ heterogeneous catalysts with a highly efficient activity towards the oxygen evolution reaction (OER), and the enhanced catalytic activity is dependent on the degree of surface sulfurization. It is found that forming amorphous CoS$_x$ on the Co$_3$O$_4$ surface through surface anion exchange can effectively generate more Co$^{2+}$ ions and oxygen vacancies in the lattice structure, not only inducing the production of more CoOOH but also facilitating water adsorption during the water oxidation process.

**EN06.03.20**

**Controllable Local Electronic Migration Induced Charge Separation and Red-Shift Emission in Carbon Nitride for Enhanced Photocatalysis and Potential Phototherapy** Zongzhao Sun and Limin Huang; Southern University of Science and Technology, China

Since the performance is highly dependent on the electronic structure of the material, it is crucial to adjust electron distribution to achieve various improved properties for the utilization of the material in cross-functional applications. Here, precise control of the local electronic migration of carbon nitride via molecular grafting has been successfully developed. The electronic structure could be carefully tailored by the incorporation of π-conjugated molecules and electronwithdrawing groups. Experimental results and theoretical calculation reveal the possible electronic migration path to reset the local electronic configuration, leading to charge separation and red-shift emission. As a result, H$_2$ evolution of 5 mmol h$^{-1}$ g$^{-1}$ with a high AQY of 20.98 % at 420 nm and in vitro phototherapy for the anti-cancer effect can be realized. These findings provide a new opportunity for modifying the properties of emerging materials for extended applications through careful control of the electronic structure process.

**EN06.03.21**

**Bioinspired Fabrication of ZnS/Polydopamine Nanorods for Solar-Light-Driven Photocatalytic Hydrogen Production** Yeonho Kim and Hae Jin Kim; Korea Basic Science Inst, Korea (the Republic of)

Photocatalytic hydrogen (H$_2$) production of ZnS catalysts still remains unsatisfactory because of the fast charge carrier recombination originated from the inherent characteristics of the direct-bandgap semiconductor as well as the photocorrosion by the oxidative holes in the valence band. In this study, we developed the strongly coupled
ZnS/polydopamine (ZnS/PDA) photocatalysts via a facile in-situ polymerization method with the precisely controlled thickness of PDA layer onto the ZnS nanorods. The introducing of thin PDA shell on the surface of ZnS nanorods exhibits enhanced photocatalytic H₂ production activity and stability than a single component of pristine ZnS or PDA itself. The synergistic effect responsible for the enhancement of catalytic performance can be attributed to the favored effective charge separation/transport at the ZnS/PDA heterojunction interface as well as extended light absorption of photocatalysts due to the origin of partially formed ZnO. Moreover, the higher surface wettability of ZnS/PDA nanocomposites could be desired properties for photocatalytic water splitting H₂ production than that of the pristine one. The density functional theory (DFT) calculation reveals advantageous type-II band alignment of ZnS/PDA, hole accepter levels of PDA can facilitate the charge-carrier separation and long-periods stability of ZnS via lowering the oxidative capacity of holes in the valence band state. The optimized catalyst of ZnS/PDA hybrid nanorods with PDA shell thickness of 1.2 nm, exhibits excellent photocatalytic H₂ production rate of 2162.5 mmol h⁻¹ g⁻¹ (10 mg catalysts) without using a Pt cocatalyst as well as enhanced photostability over long periods.

EN06.03.22
Cobalt-Iron-Phosphorus Catalysts for an Efficient Hydrogen Generation from the Hydrolysis of Ammonia Borane Solution
SeKwon Oh; Korea Institute of Industrial Technology, Korea (the Republic of)

Co-Fe-P catalysts for fast hydrogen generation from hydrolysis of NH₃BH₃ were fabricated by an electro-deposition. Effects of cathodic current density and plating time on the microstructures of the Co-Fe-P catalysts and their catalytic activities for hydrolysis of NH₃BH₃ were explored. The microstructure, surface morphologies, and composition of the Co-Fe-P catalysts were analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), respectively. Their hydrogen generation kinetics were measured using mass flow meter (MFM). The particle sizes and composition of Co-Fe-P catalysts were depended significantly on the current densities and deposition times during an electro-deposition. As a current density increase, the particle sizes of the Co-Fe-P catalysts increased. With an increase in deposition time, the particles of the Co-Fe-P catalyst get agglomerated densely. The hydrogen generation kinetics of the catalysts was depended largely on their microstructures, which was affected by the electro-deposition conditions such as current density and deposition time. In particular, the Co-Fe-P catalysts, which was deposited at 50 mA for 5min, exhibits the best hydrogen generation rate of 2858. min⁻¹ g⁻¹-catalyst in 1 wt% NH₃BH₃ solution at 30 °C. With an increase in a solution temperature from 10 to 60 °C, the hydrogen generation rate increases dramatically. Specially, at 60 °C, which is the optimal temperature for the best PEMFC operation, the hydrogen generation rate was 8915 ml min⁻¹ g⁻¹-catalyst in 1 wt% NH₃BH₃ solution at 60 °C. With increasing the concentration of NH₃BH₃ from 0.5wt% to 3wt%, the hydrogen generation rate of the Co-Fe-P catalyst increased gradually from 1900 ml min⁻¹ g⁻¹-catalyst to 8105 ml min⁻¹ g⁻¹-catalyst. This behavior of the Co-Fe-P catalyst was in contrast with that of noble metals such as Ru and Pt. Since it is necessary to increase the concentration of NH₃BH₃ in the solution for high hydrogen storage density, it is considered that the Co-Fe-P catalyst is more suitable than noble metal catalysts for a practical use.

EN06.03.23
Electrochemical CO₂ Reduction to C₂ or C₃ Alcohols over Cu-Supported N-Doped Porous Carbon Catalysts
Hyunsu Han, Seongmin Park, Wongeun Yoon, Junil Choi, Dahee Jang, Hyunwoo Ahn and Won Bae Kim; Pohang University of Science and Technology (POSTECH), Korea (the Republic of)

Electrocatalytic conversion of carbon dioxide (CO₂) to multicrocarbon alcohols (C₂H₅OH and C₃H₇OH) in a selective and efficient manner remains a great challenge in renewable and sustainable energy research. Herein, we report a series of hybrid catalysts of Cu nanoparticles supported on N-doped porous carbon with different contents of pyridinic N and demonstrate that the selectivity to the multicarbon alcohols could be tuned by introducing the cocatalyst of N-doped porous carbon materials. By varying the contents of pyridinic N in hybrid catalysts, the highly selective production of multicarbon alcohols is achieved with notable total Faradaic efficiencies of multicarbon alcohols up to the value of 73.3 % at – 1.05 V (vs RHE) for both C₂H₅OH and C₃H₇OH products. We hypothesize in this work that pyridinic N as a CO-producing site together with Cu catalytic sites can act cooperatively to produce C₂H₅OH and C₃H₇OH. Furthermore, a two-site mechanism to rationalize the efficient CO₂ reduction to multicarbon alcohols on the hybrid catalysts is proposed and discussed. These findings provide a new guideline for the rational design of electrocatalysts for tuning catalytic activity and selectivity toward multicarbon alcohols.

EN06.03.24
Z-Scheme Electron Transfer of ZnS/ZnIn₂S₄ Heterostructure as a High Efficiency Photocatalyst for CO₂
Utilization of carbon dioxide conversion to chemical fuels using an artificial photocatalyst under solar irradiation is an ideal goal in renewable energy studies. To date, a variety of strategies have been demonstrated to boost the quantum efficiency of CO₂ photoreduction. Coupling of semiconductors considered one of the key challenges to designing a good photocatalyst that can activate the CO₂ molecule with smallest possible activation energy and produce selective fuels. Since the activity and selectivity are mainly determined by the suitable band structures and surface states of photocatalysts as well as the photoreaction conditions. In this study, we fabricate ZnS/ZnIn₂S₄ composite for CO₂ reduction under visible light irradiation. When the mass ratio between Zinc and Indium is varied, the composite catalyst shows dramatically increasing of acetaldehyde and methanol formation as major products of CO₂ conversion. The optimum ratio exhibits a 200 times enhancement over a single phase of ZnS. The as synthesized samples were characterized by XRD, SEM, TEM, Photoluminescence, UV-Visible diffuse reflectance spectroscopy, XPS, UPS, surface area and CO₂ adsorption measurements. Based on the experimental evidence, the interface between both phases is the crucial role of interfacial charge transfer and subsequent enhancing of catalytic activity. In-situ FTIR study has been done to get a deeper insight into the product formation and gain a detailed comprehension of the fundamental reaction steps during the photocatalysis. In conclusion, my presentation will focus on how to efficiently manage the photo-generated charge carriers and surface reactions of semiconductor photocatalysts to boost the photoreduction activity.

**EN06.03.25**

**Determining Rate Dominant Steps and Synergistic Effects in Heterogeneous Catalytic Reactions Using Nano-Porous Supports**

Hongyu Li, Anatoly Frenkel and Dilip Gersappe; State University of New York at Stony Brook, United States

Catalysts embedded in porous structures are widely used in materials research and industry. Understanding the dominant step of catalytic chemical reaction rate is crucial for the development of such catalysts. However, the coupling of mass transport and kinetic effects with reactions presents a significant computational challenge. Here, we show that by using a Lattice Boltzmann approach we can develop a model that will allow us to include kinetic effects such as adsorption and desorption of reactants/products, mass transport bottlenecks in the support, and possible pore blocking effects. Further, we show that our model can be used to determine possible synergistic interactions when bi-metallic catalysts are used. We use a model system composed of Ni-Pt bimetallic catalysts, that are used to catalyze the reverse water gas shift reaction and methanation through a nanostructured support as an case study for our approach. We compare our results to experimental results and show that our model can be used to explain synergistic effects in this system.

**EN06.03.26**

**Interfacial Electron Transfer of Metal/Nitrogen Carbon Composite Prompts Efficient Green Chemical Transformation**

Hui Su; Shanghai Jiao Tong University, China

The transition-metal/nitrogen carbon hybrids with the features of low-cost and high-stability are emerging candidates to homogeneous catalysts used to efficiently catalyse novel sustainable chemical transformation process. The relatively low activity of active metal sites has been an insurmountable dilemma to inhibit development of heterogeneous metal/nitrogen carbon catalyst for their practical application. Attractively, the electron transfer effect of metal/nitrogen carbon interface was wide available to enhance reactivity towards thermal and electrochemical conversions. However, the exact relationship between electron population of metal/carbonic support boundary and specific catalytic performance still remains elusive. We initially used nanoscale assembly of metal-organic complexes to realize the construction of high-loading Co/carbon interfaces. The as-obtained Co nanoparticles embedded into carbon nanofibers with high conductivity exhibited superior activity for electrochemical hydrogen evolution reaction (Nano Energy, 2016, 16, 79). To further enhance the catalytic activity of Co nanoparticles, the Mott-Schottky catalyst of nitrogen-rich carbon-coated cobalt nanoparticles (Co@NC) was prepared through direct polycondensation of simple organic molecules and inorganic metal salts in the presence of polymeric carbon nitride powder. The presented electron-deficiency Co particles induced Mott-Schottky effect can trigger the synthesis of a series of alkyl esters and even diesters in high yields via base-free aerobic of alcohol (J. Am. Chem. Soc., 2017, 139, 811). More importantly, high electron density of single Ni-N₄ sites anchored into nitrogen-doped carbon was
fabricated via ligand-stabilized polycondensation method. The experiment and theoretical calculation results elucidates that the enhanced electron density at each single Ni-N4 site by a collective grouping effect substantially decreases the binding energy of H radicals to Ni, promoting a highly efficient hydrogen transfer coupling of benzyl alcohol and aniline into N-benzyl aniline (*Angew. Chem. Int. Ed.* 2018, 57, 15194).

**EN06.03.28**

**Facile Underwater Plasma Discharge Process for the Synthesis of the Nitrogen-Functionalized Onion-Like Carbons and Their Enhanced Electrocatalytic Activities** SangYul Lee1, Jung-Wan Kim2 and Hoe-Kun Kim1; 1Korea Aerospace University, Korea (the Republic of); 2InCheon National University, Korea (the Republic of)

Nitrogen-functionalized onion-like carbon (N-OLC) was synthesized using an arc discharge in a liquid phase (a so-called Solution Plasma Process) in the presence of different ammonia concentrations. The N-OLC was investigated as a catalyst support material for a catalytic oxygen reduction reaction (ORR). With increasing ammonia concentrations up to 5 M, the nitrogen doping degree increased to 1.7 at.%, which created a highly defective onion-like structure. The edge and defective sites induced from nitrogen atoms effectively facilitated the nucleation of Pt clusters, which led to the stable dispersion and size-reduction of Pt nanoparticles (PtNPs), as revealed via XPS, XRD, Raman spectroscopy and electron microscopy. From the results of the electrochemical characterization, the PtNPs supported on the N-OLC with a nitrogen content of 1.7 at.% exhibited the highest electrochemically active surface area (ECSA), specific current density and half-wave potential. The enhanced (ORR) could be ascribed to the defective outermost layers and the electronic modification. Moreover, even after an accelerated durability test (ADT) with 5,000 cycles, the N-OLC with a nitrogen of 1.7 at.% exhibited less degradation, indicating the excellent ORR durability.

**Acknowledgement**

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**EN06.03.30**

**Mesoporous CuOx-Derived Nanostructured Copper Catalysts for CO2 Reduction** Giorgio Giuffredi1,2, Federica Arena1,2 and Fabio Di Fonzo1; 1Istituto Italiano di Tecnologia, Italy; 2Politecnico di Milano, Italy

Electrochemical reduction of emitted CO2 to fuels and complex hydrocarbons represents a promising solution to efficiently store intermittent, renewable energies-generated electricity in the form of chemical energy of carbon-based fuels. Copper is one of the most interesting CO2 reduction electrocatalysts, thanks to its ability to reduce carbon dioxide to complex hydrocarbons with good efficiency, however when in bulk polycrystalline form it has low activity and requires a high overpotential for the reduction reaction. Obtaining Cu catalysts by the in-situ reduction of a copper oxide precursor at CO2 reduction potentials - with the so-called Oxide-derived Cu catalysts - is considered one of the most efficient way to increase the intrinsic activity of Cu: this class of materials have higher selectivity for complex hydrocarbons and longer stability. Moreover, their CO2 reduction activity and selectivity are strongly affected by the morphology, which controls the mass transport of the reactants to the active sites and the residence time of the reaction intermediates near the CO2 reduction active sites.

In this contribution, the CO2 reduction activity and selectivity of Cu catalysts derived from the reduction of Copper Oxide (CuOx) hierarchical nanostructures with different structural features are investigated. We firstly employ a nanocrystalline CuOx material, which presents a higher availability of undercoordinated surface sites which, coupled with the high surface area, increases the activity. We synthesize nanostructures for this highly-active material by Pulsed Laser Deposition (PLD), a synthesis method that allows us to control the morphology of the deposited nanostructures down to the nanoscale: this technique, in fact, allows for a fine control over the deposit morphology by finely tuning the deposition parameters. In this way, the chemical composition and thickness of the hierarchical quasi-1D nanostructures are kept constant and it is possible to modify their aspect ratios, their nanostructuring and their micro- and nanopores diameters. Characterization of the PLD-synthesized nanostructures shows an amorphous matrix with embedded crystalline seeds of CuO and Cu2O, differently from other reported oxide-derived Cu catalysts. CO2 reduction performance of the oxide-derived Cu nanostructures is assessed through chronocoulometric measurements in aqueous electrolyte, showing good current densities and a good stability for at least one hour of prolonged operation. Liquid products
analysis, performed via 1H NMR spectroscopy, shows a high productivity of ethanol at limited potentials applied (V = -0.4 VRHE). Overall, the CuOx-derived nanostructures show a good faradaic efficiency at low overpotentials applied, with an FE for CH4 of 40% and an FE for liquids of 55% at -0.4 VRHE.

This contribution shows how coupling an amorphous, oxide-derived Cu catalyst with a fine control over morphology can be an efficient way to increase the activity of CO2 reduction catalysts.

**EN06.03.31**

**In Situ Characterization of MOx/CeO2 (M=Fe, Co, Ni and Cu) Catalysts for the Methane Activation and Methane Dry Reforming Reaction**

Feng Zhang¹, Zongyuan Liu², Sanjaya D. Senanayake³ and Jose A. Rodriguez²,³; ¹Stony Brook University, The State University of New York, United States; ²Brookhaven National Lab, United States

Based on the concept of electronic effect used in the development of homogeneous catalysts, we have prepared the heterogeneous systems, in which metal-support interaction leads to methane activation at room temperature, enabling the conversion of this hydrocarbon into value-added chemicals. *In-situ* characterization techniques, such as Time-Resolved X-ray Diffraction (TR-XRD), X-ray Absorption Fine Structure(XAFS) and Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) were employed to investigate changes in chemical state and structural transformations occurring in a series of MOx/CeO2 (M = Fe, Co, Ni and Cu) powder catalysts upon reaction with methane and under the methane dry reforming condition. XPS shows the presence of adsorbed CHx and COx species after exposing the powder catalysts to methane at room temperature. Temperature-programmed reduction (TPR) measurements point to the reaction of the samples with methane and formation of CO, CO2, and H2O gas at temperatures as low as 100 °C. The TR-XRD results show that all of the transition-metal oxides in the as-prepared catalysts can be reduced to their metallic phase during the CH4-TPR process with the ceria support undergoing significant reduction from the surface to bulk, yet the reduction temperature varies for different MOx/CeO2 samples. Among these samples, CuOx/CeO2 shows the lowest reduction temperature (below 260 °C) for both the oxide overlayer and the ceria support. The NiOx/CeO2 and CoOx/CeO2 powder catalysts also activate CH4 at relatively low temperatures (below 350 °C), and the oxide overlayers undergo NiO → Ni and Co3O4 → CoO → Co transformations. In the case of FeOx/CeO2, a series of complex changes in the chemical state is observed for the oxide overlayer, Fe2O3 → Fe3O4 → FeO → Fe → Fe3C. The ceria support of all of the three MOx/CeO2 (M = Cu, Ni, and Fe) samples undergoes severe reduction and form Ce2O3 at high temperature (> 650 °C) during the CH4-TPR reaction. The *in-situ* TR-XRD results highlight rich and complex chemistry for methane on these MOx/CeO2 mixed oxide systems. The strong metal-support interactions seen in the Ni and Co/CeO2(111) model catalysts also determine the good performance of the MOx/CeO2 (M = Ni, Co) powders for the methane dry reforming reaction.

**EN06.03.32**

**Catalyst-Free Coproduction of Hydrogen and Activated Alumina as Value-Added Byproduct from Hydrolysis of Nanoporous Aluminum with Pure Water**

Timothy Lee¹, Jintao Fu¹, Victoria Basile², John Corsi¹ and Eric Detsi¹,¹; ¹University of Pennsylvania, United States; ²University of California Los Angeles, United States

The sale of value-added byproducts from hydrogen-generating reactions is a strategic approach to lower the costs of hydrogen fuel in realizing a truly-sustainable hydrogen economy. Metal hydrolysis is a chemical process that produces hydrogen together with a metal hydroxide species; however, this reaction is rarely observed without addition of chemical catalysts or extreme reaction conditions. In this talk, I will demonstrate the use ultra-fine nanoporous aluminum to create hydrogen at standard conditions for temperature and pressure via hydrolysis without any catalyst additives.[1] The advantage of this method is the co-production of pure aluminum hydroxide (Al(OH)3) during the process. I will demonstrate the transformation of this hydrolysis byproduct into valuable materials to elucidate measures in reducing the overall cost of hydrogen. Our results show that (i) the synthesis of nanoporous aluminum is scalable to meet the needs of large scale production for a hydrogen gas economy, and (ii) the transformation of the hydrolysis byproduct Al(OH)3 to create high surface-area “activated alumina” (Al2O3) as a commercially viable product.

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**EN06.03.33**
Optimal nanodesign of catalysts can surely be obtained benefitting from the functionalization of carbon based materials. By this approach various functionalities can be strategically anchored on the backbone of these materials, aiming at specific applications such as catalytic. In the context of catalysis, the development of heterogeneous nanocatalysts allies not only the interesting intrinsic properties of nanomaterials but also the facile separation and reuse of the catalysts. The main challenges involve how to design the desired functionalities on heterogeneous surfaces, which many times is inspired on homogenous reactions. Herein, we pursued various functionalization of graphene oxide (GO) and carbon nanotube (NTC) with functional groups and metallic nanoparticles (NPs) towards several application, highlighting the efficient production of hydrogen. In this sense, we obtained nanocatalysts derived from GO, NTC filled with Co, Ag NPs and Ni NPs obtained as thin films, which were employed in the hydrogen production from the hydrolysis reaction of NaBH₄. The maximum rate of hydrogen production reached over 50 x10³ mL⁻¹ min⁻¹ g⁻¹, among the highest reported. Hence, high volumes of hydrogen could be produced using low amounts of catalysts (~0.1–0.8 mg) and could be reused for 10 consecutive cycles without losing activity. The facile use of the nanocatalyst thin film is the most promising aspect towards such an important field: sustainable energy. We can produce high amounts of hydrogen, in a controlled system (ceasing the production is easy) and easily remove the thin film (deposited on glass substrate), wash and reuse it again. Furthermore, another catalytic application is regarding the monitoring and destruction of toxic agrochemical in the field or our food and also chemical warfare in terrorist attacks or war zones, mainly concerned in promoting worldwide chemical security. We have been using the functionalization GO and NTC with various moieties covalently (imidazole, thiol, hydroxamate) and non-covalently (Ni and Ag NPs) linked, obtained as powder and thin film. An innovative interfacial functionalization method is proposed for obtaining the thin films. Bifunctionalization has also been carried out by anchoring two different neighbouring groups. Expressive rate enhancements up to 10⁸-fold were obtained in the presence of the nanocatalysts compared to the spontaneous reaction. The nanocatalysts also showed a dual function: could be used as sensors for detecting these toxic agents. These results can be further extended for alerting pesticide contamination and chemical attacks. In summary, indeed the nanodesign of heterogeneous catalysts opens a myriad of possibilities for achieving prominent catalysis.

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EN06.03.34
Adsorption/Oxidation Performance of Hybrid Co3O4/ZSM-5 Monolithic Catalysts under Low Temperature Combustion of Diesel Condition Junfei Weng and Pu-Xian Gao; University of Connecticut, United States

Abstract

Cobalt oxide nano-arrays structured catalysts had been demonstrated to exhibit high NO oxidation performance with porous nature of nanowires and relative amount of Co³⁺ on the surface ¹, and ZSM-5 was studied as a porous catalytic material for trapping hydrocarbon during the cold-start process ². In this work, hybrid Co₃O₄/ZSM-5 monolithic catalysts were synthesized on honeycomb cordierite substrate by hydrothermal methods. Two configurations were adopted: Co₃O₄ nanoarray was grown on substrate first followed by the growth of ZSM-5 (CZ), and ZSM-5 layer was grown first followed by the growth of Co₃O₄ nanoarray (ZC). The adsorption/oxidation performance was evaluated under low temperature combustion of diesel (LTC-D) condition with feed gas of CO, C₂H₄, C₃H₆, C₃H₈, and NO. The results showed that within the tested temperature range (up to 300 °C), although the adsorption/oxidation behavior for CO, C₂H₄ and C₃H₈ were similar, ZC configuration exhibited higher adsorption capacity for C₃H₈ and NO than those of CZ. In ZC, C₃H₈ was not released and oxidized directly below 300 °C while NO was desorbed at 280 °C, which was higher than that in CZ.

References
1. Zheng Ren, Y. G., Zhonghua Zhang, Caihong Liu and Pu-Xian Gao, Nonprecious catalytic honeycombs


**EN06.03.35**

**Preparation of Gold-Platinum Bimetallic Nanoparticles via Pulsed Laser Dewetting** Stephanie Bonvicini, Annie Hoang, Viola Birss and Yujun Shi; University of Calgary, Canada

Platinum is an important catalyst for many fuel cell applications. Due to the high cost of platinum, there is continuing research interest in developing nanostructures to reduce the amount of platinum used while maintaining performance. Bimetallic nanoparticles containing platinum are a promising approach to improve the efficiency of fuel cells at a reduced cost. In this work, we report on the formation of gold-platinum nanoparticles through pulsed laser dewetting of metal thin films. Important parameters in laser dewetting, such as laser fluence and irradiation time, were explored. The sputtering order and thickness of the gold and platinum thin films were also investigated. Elemental analysis confirms that both gold and platinum are found within the nanoparticles after dewetting. The results from cyclic voltammetry of the produced bimetallic gold-platinum nanoparticles will also be presented.

**EN06.03.36**

**Electrochemical Desulfurization of Molybdenum Disulfide Nanocatalysts Supported on Reduced Graphene Oxide for Efficient Hydrogen Evolution Reaction** Sanju Gupta, Taylor Robinson and Jacob Dobler; Western Kentucky University, United States

Recent development of two-dimensional layered materials including graphene-family and related nanomaterials have arisen as potential game changer for energy, water and sensing applications. While graphene is a form of carbon arranged hexagonally within atomic thin sheet, MoS2 is becoming a popular, efficient, and cost-effective catalyst for electrochemical energy devices, in contrast to expensive platinum and palladium catalysts. In this work, we electrochemically desulfurize few-layer molybdenum disulfide (MoS2) and aerogels with reduced graphene oxide (rGO) prepared under hydrothermal conditions ((P< 20 bar, T< 200 oC), for improving hydrogen evolution reaction (HER) activity via point defects (S-vacancy). Moreover, the interactions between rGO and MoS2 components create emergent heterostructures with desirable physicochemical properties (specific surface area, mechanical strength, faster diffusion, facile electron and ion transport) enabled by chemically bridged (covalently) tailored interfaces. We demonstrate that with an optimized number defect density, particularly by exposing the edges of MoS2 layers and nanowalls in graphene-MoS2 hybrid aerogels, interfacial processes during catalytic reactions are accelerated. To understand the effects of defects on HER activity, we varied the applied potential and operating duration for optimized defect density. This study offers a unique method for tuning the properties of layered MoS2 and hybrids as promising, cost-effective and efficient nanocatalysts. In addition, it establishes the structure–catalytic activity relationships via scanning electrochemical microscopy at electrode/electrolyte interface besides mapping electrochemical (re)activity and electro-active site distribution.

**SESSION EN06.04: Catalysis of and with Oxygen I**

Session Chairs: Jehad Abed and Yongye Liang

Tuesday Morning, December 3, 2019
Sheraton, 2nd Floor, Independence West

**8:15 AM EN06.04.01**

**Self-Assembled Iridium Cobalt Hollow Structure on Activated MXene for Efficient Overall Water Splitting** Thi Anh Le1,2, Ngoc Quang Tran1,2, Ye sul Hong2, Meeree Kim1,2 and Hyo young Lee1,2, 1Centre for Integrated Nanostructure Physics Institute for Basic Science (IBS), Korea (the Republic of); 2Sungkyunkwan University, Korea (the Republic of)

Electrochemical water splitting has been recognized as a promising route for hydrogen fuel generation at the
industrial scale. However, due to the sluggish kinetics of both half cathodic and anodic reactions of the electrolyzer (hydrogen/oxygen evolution reactions-HER/OER), the water electrolysis usually requires large input energy that strongly inhibits its application in practice. Therefore, facile and scalable construction of catalytic active, durable and low-cost electrocatalysts to largely boost the sluggish kinetics during electrocatalytic process remains a huge challenge.

Hybridization of a catalytic active material with a large surface area and good electrical conductivity with a hydrophilic substrate is a wise strategy to enhance the electrocatalytic performance by achieving the synergistic effects. Recently, two-dimensional (2D) titanium carbide MXene-based composites applied for energy conversion applications have widely attracted researches due to their unique electronic structure and surface properties over other carbonaceous materials such as reduced graphene oxide (rGO), carbon nanotubes (CNTs), etc. However, MXenes suffer from sluggish ionic accessibility and mass transport due to the strong van der Waals attraction and hydrogen bonding between inter-sheets, which seriously inhibits the realization of the full potential for these materials.

In this work, we develop an advanced electrocatalyst system composed of iridium cobalt (IrCo) hollow structure homogeneously distributed on the highly porous activated titanium carbide MXene (ac-Ti₃C₂) matrix via a wet chemical method at room temperature. We exploit the OER performance of the as-prepared catalyst (IrCo@ac-Ti₃C₂), which shows significantly enhanced catalytic activity with a low overpotential of 220 mV at a current density of 10 mA cm⁻², surpassing the benchmark IrO₂ and stability for 30 h of continuous testing in alkaline media. We also demonstrate the effectiveness of the electrode architecture through the rapid charge/mass transport in the internal electrode by tripling the mass loading on the rotating disk electrode. As expected, the novel catalyst displays a negligible dependence of the current density on the mass loading. Finally, when employed as a bifunctional catalyst in overall water splitting reaction, the optimal IrCo@ac-Ti₃C₂ also shows superior activity with the low voltage cell and excellent long-term durability, standing among the best catalytic activity of the reported electrocatalysts.

The outstanding performance can be attributed to the synergistic effects below: (1) the excellent electrical conductivity of the substrate and the smooth metal-support electronic interaction can ensure fast electron conductance; and (2) the hierarchically porous nanoarchitecture of the obtained compound with abundant of macro/meso/micropores and edges/defects sites not only benefits the ionic accessibility, increases the electrode wettability, boosts the migration of reactant-related species, and fastens gas evolution/evacuation by shortened mass-transport pathways, but also assures uniform distribution and maximization of the number of active sites exposed to the electrolyte, preventing the aggregation of active materials during electrochemical process.

8:30 AM EN06.04.02
Promoting the Oxygen Evolution Reaction through the Incorporation of V and Se in Amorphous Nickel-Cobalt Based Electro catalysts Jehad Abed, Aoni Xu, Edward H. Sargent and Steven Thorpe; University of Toronto, Canada

Stable and affordable electrocatalysts are urgently needed to accelerate the transition from conventional fossil fuels to sustainable energy resources such as hydrogen derived from renewable energy sources such as solar and wind. Converting said harvested energy electrochemically into chemical fuels and feed stocks is also highly desirable. Over the last two decades, the electrocatalytic splitting of water, and carbon dioxide reduction to hydrocarbons have received great attention, however approximately 90% of the electricity input is consumed in the anodic oxygen evolution reaction (OER) due to poor reaction kinetics. Precious metal based catalysts (Pt, Ir, Ru) are commonly used as OER catalysts, but prove uneconomic for large scale industrial deployment. New low cost, stable, earth-abundant catalysts such as those based on transition-metal alloys (Ni,Co) offer great promise to overcome these kinetic limitations.

In this work, we used a two-step novel milling process to produce NiCo-based amorphous nano-electrocatalysts. Cryo-milling (mechanical milling of precursors at cryogenic temperatures to achieve alloying) followed by surfactant-assisted ball milling (SABM for particle size reduction) create stable amorphous alloys with high surface areas and coordinatively unsaturated active sites for the reaction of OER intermediates. The improved stability of the amorphous alloys is yet another exciting feature that can significantly enhance the overall catalytic performance of the catalyst.

Using density functional theory (DFT) calculations, two potential elements V and Se were predicted to reduce the overpotential of the catalyst when incorporated in these structure. Alloys of NiCoV and NiCoSe were milled under
various conditions and the structural evolution of the system monitored using x-ray diffraction (XRD) and electron microscopy. Our results confirm the production of two fully alloyed ternary systems after 6 hours of milling time. Furthermore, a wide composition range could be investigated using this synthesis technique to accordingly tailor the activity of the catalyst. The electrocatalytic activity and stability of the catalysts was evaluated by Tafel measurements obtained from linear sweep voltammetry (LSV) and cyclic voltammetry (CV) experiments. We found that V in NiCo-based alloys helped the amorphous structures to stabilize by forming non-transitional clusters\(^2\) while Se significantly reduced the size of the produced particles. Operando X-ray Absorption Spectroscopy (XAS) was conducted to reveal the role of adding V and Se on the chemical-structural transformation and bonding environment of surface species during the reaction. This work suggests that milling can potentially be used to produce OER catalysts for industrial applications.


**8:45 AM EN06.04.03**

**Guiding Principles for Designing Metal-Coordinated Frameworks as Electrocatalysts for Clean Energy Conversion**

Chun-Yu Lin and Zhenhai Xia; University of North Texas, United States

We are facing energy crisis because of the limitation of the fossil fuel and the pollution caused by burning it. Clean energy technologies, such as fuel cells and metal-air batteries, are studied extensively because of their high efficiency and less pollution. Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are essential in the process of energy storage and conversion, and noble metals (e.g. Pt) are needed to catalyze the critical chemical reactions in these devices. Functionalized metal coordinated frameworks such as metal organic frameworks, covalent organic frameworks, and zeolitic imidazolate frameworks can be used as efficient catalysts to replace expensive and scarce platinum-based catalysts for energy storage and conversion. Traditionally, experimental studies on the catalytic performance of metal coordinated frameworks have been conducted extensively, however, there is lack of computational studies to guide the experiments for rapid search for the best catalysts. In addition, catalytic mechanism and rational design principles towards ORR and OER also needed to be fully understood.

Density functional theory calculations are performed to calculate the thermodynamic and electrochemical properties of metal coordinated frameworks for ORR and OER. Gibb’s free energy, overpotential, charge transfer and ligands effect are evaluated. The charge transfer analysis shows the positive charges on the metal coordinated frameworks play an essential role in improving the electrochemical properties of the metal coordinated frameworks. Based on the calculations, design principles are introduced to rationally design and predict the electrochemical properties of metal coordinated frameworks as efficient catalysts for ORR and OER. An intrinsic descriptor is discovered for the first time, which can be used as a materials parameter for rational design of the metal coordinated frameworks for energy storage and conversion. The success of the design principles provides a better understanding of the mechanism behind ORR and OER and a screening approach for the best catalyst for energy storage and conversion.

**9:00 AM EN06.04.04**

**Nonradical Activation of Peroxydisulfate Promoted by Oxygen Vacancy-Laden NiO for Catalytic Phenol Oxidative Polymerization**

Nian Liu; Georgia Institute of Technology, United States

Engineering the electronic properties of catalysts to facilitate electron transfer and activation of dynamically stable peroxydisulfate (PDS) offers a promising strategy for efficient remediation of recalcitrant organic pollutants through heterogeneous Fenton-like processes, but it also presents challenges due to a lack of facile methods. In this presentation, we report a simple defect engineering strategy that significantly increases the efficiency of PDS adsorption and activation by introducing oxygen vacancies (VO) into NiO to produce an electron-rich surface. Experimental studies and density functional theory (DFT) calculations confirmed that VO confined in NiO could successfully cause synergetic effects of lower adsorption energy and more exposed active sites, thus facilitating the bonding with PDS molecules and promoting the reactivity of PDS-NiO complex, giving rise to dramatic enhancement of catalytic performance with removal rate as high as 3.978 mmol(phenol) min\(^{-1}\) g(NiO)\(^{-1}\). Mechanistic studies further reveal that the surface-activated PDS-NiO complex mediate oxidative polymerization of phenol (a model pollutant) involved in the generation of phenoxy radicals and subsequent coupling reactions,
providing the potential to convert recalcitrant organic pollutants into value-added products. We believe this work pave the way toward practical fabrication of highly efficient “defect-type” Fenton-like catalysts, and the present method also provides new opportunities to achieve sustainable wastewater treatment through reuse of organic pollutants.

This presentation is based on our recent publication:  
*Applied Catalysis B: Environmental*, 2019, 254, 166-173  
https://doi.org/10.1016/j.apcatb.2019.04.094
evolution, thus validating the applicability of single crystal surfaces to understand the OER mechanism on polycrystalline surfaces.

In order to understand the kinetic behavior of oxygen evolution of RuO$_2$ surfaces, electrochemical activity measurements were combined with highly sensitive electrochemical mass spectrometry to quantify the amount of evolved oxygen at low overpotentials. The combined electrochemical and mass spectrometry results indicate that the current-potential dependence goes through three distinct Tafel regimes, where the Tafel slope increases with electrochemical potential from 30 mV/decade at low potentials to 120 mV/decade at high potentials. We rationalize this kinetic behavior by modeling the coverage of the reaction intermediates as a function of potential, based on their energetics proposed on the (110) surface. Finally, using oriented RuO$_2$ surfaces, which have different binding energetics for oxygenated species, we highlight differences in Tafel behavior as a function of potential. Thus, by using different experimental and theoretical techniques as well as model surfaces, this study identifies the active sites and reaction mechanism for oxygen electrocatalysis. We also highlight the importance of understanding and controlling kinetics of OER on highly active catalysts, in order to achieve higher current densities at low overpotentials.

References:

10:45 AM OPEN DISCUSSION

11:00 AM EN06.04.09
Symmetry Breaking of Atom Configurations as an Efficient Tool for Oxygen Evolution Electro catalysis in Perovskite Oxides Sung-Yoon Chung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

As metal-oxygen octahedra in $ABO_3$-type perovskite oxides are regarded as active sites for notable oxygen electrocatalysis, many studies have been carried out seeking higher catalytic activity by experimenting with various transition metals and their combinations on the $B$ site, as well as the influence of oxygen vacancies. In contrast to the substantial amount of research on different compositions and their impact on overall catalytic performance, the correlation between the structure of the oxygen octahedra in perovskites and electrocatalysis performance has been overlooked, resulting in a limited understanding of the effect of structural variation. From a structural viewpoint, the $ABO_3$ perovskite framework consists of corner-shared $[BO_6]$ octahedral units, which are catalytically active sites, together with $A$-centered dodecahedra. Consequently, identifying variations in the shape of the $[BO_6]$ octahedra and understanding under what circumstances structural change takes place remain as key issues for the accurate prediction of electronic structure and subsequent oxygen evolution reaction (OER) activity. In particular, since the shape of the $[BO_6]$ octahedra is determined largely by the location of oxygen anions in the lattice, visualization of the oxygen positions is an essential part of that direct observation of structure (J. Bak et al., Nano Lett. 17, 3126 (2017)), despite being very challenging.

In the first part, by using both sintered polycrystals with various grain sizes and thin films on bicrystal substrates, we directly verify that surface-terminating grain boundaries in LaCoO$_3$ and LaMnO$_3$ are exceptional in oxygen evolution electrocatalysis, showing more than an order of magnitude higher activity. A combination of atomic-scale structure observation and density functional theory calculations demonstrates that the displacement of atoms in metal-oxygen octahedra correlates with significant splitting of the degenerate transition-metal $3d$ orbitals, and subsequently higher covalency for rapid charge transfer between metals and oxygen is attained (Y. Heo et al., Adv. Energy Mater. 8, 1802481 (2018)). In the second part, by utilizing epitaxial LnNiO$_3$ ($Ln =$ La, Pr, Nd) thin films, we also demonstrate that order-of magnitude higher catalytic activity for the OER can be achieved by selective electrochemical exchange of Fe in the surface region. In addition, we directly establish that strong distortion of oxygen octahedra is induced during the Fe exchange, and that this structural perturbation correlates with the high density of Ni/Fe $3d$ and O $2p$ states near the Fermi level, permitting easier charge transfer (J. Bak et al., Nature Commun. (in press)). By demonstrating the remarkable structure-property relationship in oxygen electrocatalysis, our findings suggest that symmetry breaking by atom displacements in metal-oxygen octahedra can be a new and
Combining Theory and Experiment to Engineer \( \text{Ba(Fe, Co, Zr)}O_{3-d} \) (BFCZ) as a Family of Stable, Highly Active Oxygen Reduction Catalysts

Ryan Jacobs\(^1\), Jian Liu\(^2\), Boem-tak Na\(^2\), Shiwoo Lee\(^2\), Gregory Hackett\(^2\), Harry Abernathy\(^2\) and Dane Morgan\(^1\); \(^1\)University of Wisconsin–Madison, United States; \(^2\)National Energy Technology Lab (NETL), United States

The discovery of new materials with high oxygen reduction reaction (ORR) catalytic activity and high thermodynamic stability under typical cathode operating conditions are crucial for the development of improved solid oxide fuel cell (SOFC) and related technologies. To aid in this discovery we have performed high-throughput Density Functional Theory (DFT) calculations of \( \sim 2150 \) perovskite materials,\(^1\) assessed bulk thermodynamic stability via multicomponent phase stability analysis using the Python Materials Genomics (Pymatgen) package\(^2\), and predicted oxygen reduction reaction (ORR) catalytic activity with the \( O_p \)-band center. We found that \( \text{BaCo}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-d} \) (BFCZ) \((x+y+z=1)\) was a promising family of highly active and stable ORR cathode materials.\(^1\)

Here, perovskite-type oxides with compositions \( \text{BaCo}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-d} \) (BFCZ) \((x+y+z=1, z=0.2, 0.4, 0.6 \text{ and } 0.75 \text{ Zr fraction})\) were synthesized and characterized via X-ray diffraction (XRD) analysis and electrical conductivity relaxation (ECR) measurements. The bulk stability of BFCZ was analyzed with XRD and atomic force microscopy (AFM) after accelerated high temperature testing. The performance of BFCZ as an electrode was characterized by monitoring the impedance over time of dense spin-coated BFCZ films on a Sm-doped ceria (SDC) protected YSZ electrolyte.

All of the synthesized BFCZ compositions exhibit the cubic perovskite structure. ECR measurements indicate exceptionally high oxygen surface exchange rates and bulk oxygen diffusivity values, on par or better than other state-of-the-art high surface exchange materials like \( \text{Ba}_0.5\text{Sr}_0.5\text{Co}_0.8\text{Fe}_0.2\text{O}_3 \) (BSCF).\(^3,4\) Comparisons between the experimentally measured activities and the model predicted activity results in good qualitative agreement. Chemical trends of activity and stability as a function of Zr content are also in agreement between the computational model and the experimental results. These results collectively demonstrate (1) the power of the developed modeling scheme in predicting and rationalizing the stability and activity of BFCZ and perovskite catalysts more broadly and (2) experimental confirmation of the promise of BFCZ with high Zr content as both a highly active and stable ORR catalyst material.

References:


Parallelization of Multi-Step Electrocatalytic Reactions

Heechae Choi and Minyeong Je; University of Cologne, Germany

In general, ‘Task Parallelization’ is the simplest and ultimate solution for bottle-neck problems of serial multi-step tasks. Catalytic reactions for energy conversion and storage are in many cases, serial multi-step reactions having bottle-neck steps. In this work, we first suggest the concept of ‘Task Parallelization’ in multi-step catalytic reactions. As the prototype study, we applied this concept to oxygen evolution reaction (OER) on electrocatalytic materials. Since the catalytic activity of a material is the result of moderate adsorption energies of reactants and intermediates, mixture of multiple phases having different bottle-neck reaction steps can lead to excellent catalytic material composite, even though each phase is not much good. In this study, we used first-principles calculations and thermodynamic modeling to predict reaction pathways and facile synthesis of multiphase nanostructure. Our well-designed experiments prove this concept very well for OER electrocatalysis.
SESSION EN06.05: Catalysis of and with Oxygen II
Session Chair: Jun Chen
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Independence West

1:30 PM EN06.05.01
Surface Restructuring of Phosphides Catalyzing Water Electrolysis Zishan Wu1,2, Ling Huang1,3, Huan Liu1,4 and Hailiang Wang1,2; 1Yale Energy Science Institute, United States; 2Yale University, United States; 3Sichuan University, China; 4Harbin Institute of Technology, China

Transition metal phosphides (TMPs) are a well-known category of catalysts with good activity and durability for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Most TMPs are found to possess a naturally oxidized surface under ambient condition. However, how the oxidized surface adapts to the electrochemical conditions and leads to the observed catalytic properties are poorly understood. To gain insights into their structure-properties correlations, quasi-in-situ X-ray Photoelectron Spectroscopy (XPS) is employed to study the surface restructuring of TMPs under electrochemical conditions. It is found that the naturally oxidized and phosphorus-rich surface of cobalt phosphide (CoP) will be removed in acidic electrolyte under HER conditions, exposing a fresh CoP surface. Under HER conditions in alkaline electrolyte, electrochemical reduction of the oxidized species and dissolution of the oxidized P species will together render a Co-rich phosphide surface. Under OER conditions in alkaline electrolyte, a cobalt hydroxide/oxide surface will be formed as a result of combined oxidation and anion substitution. In order to explore the dependence of catalytic reactivity on substitutional doping, cation- and anion- substituted CoP nanoparticles are also investigated. For Fe0.5Co0.5P, the Fe substituents are more easily oxidized than Co in the air; they are also more difficult to be reduced under HER conditions in alkaline electrolyte and the remaining Fe-OH species on the surface hampers the activity for HER. For CoP0.5S0.5, the S substituents are less oxidized than P in the air; they are also more difficult to be oxidized under OER conditions in alkaline electrolyte, and the remaining sulfate like species enhance the activity for OER.

1:45 PM EN06.05.02
Oxygen Evolution Activity and Stability of Amorphous Ni-Based Nanoparticles Produced through Surfactant-Assisted Ball Milling Kevin Cole, Donald Kirk and Steven Thorpe; University of Toronto, Canada

The use of novel anion exchange membranes (AEM) in alkaline water electrolysers is now of particular interest since it eliminates the aqueous KOH electrolyte and can provide improved form factors and much higher current densities that rival proton exchange membrane (PEM) electrolysers.1 The use of AEM water electrolysis also enables the use of less expensive, earth-abundant, non-platinum group metals (PGM) materials such as nickel-based alloys as electrocatalysts.1 Conventional Ni electrocatalysts for the oxygen evolution reaction (OER) still display large overpotentials and slow reaction kinetics. The addition of Co to Ni-based alloys has been noted to increase the activity by stabilizing the β-NiOOH phase over γ-NiOOH, but this often leads to an increase in the oxygen overpotential.2,3 The issue of increased overpotential can be mitigated with the use of amorphous structures to reduce oxygen overpotentials with the addition of Co.3,4 This prior research has been limited to structures not ideal for catalysts in AEM water electrolysis.4

In this work, amorphous Ni79.2-xCoxNb12.5Y8.3 (x = 0 and 5 at.% Co) nanoparticles were synthesized using cryogenic mechanical alloying followed by surfactant-assisted high energy ball milling (SA-HEBM).5 This two-stage ball milling process provided a novel processing route for the production of nanostructured / amorphous materials with a wide range of possible compositions not achievable through rapid solidification, electrodeposition, or chemical reduction techniques. The effect of milling temperature and time on the resulting powder microstructure was characterized using a combination of x-ray diffraction and electron microscopy. The electrocatalytic activity and stability of amorphous nanoparticles on the alkaline oxygen evolution reaction were investigated through cyclic voltammetry and Tafel measurements. Cyclic voltammograms demonstrated stable and reproducible curves for amorphous alloys up to 10000 cycles while crystalline Ni and Ni50Co50 showed signs of deactivation with cycling. Initially the addition of Co to crystalline Ni resulted in enhanced OER catalytic performance, but the performance drastically reduced beyond 500 cycles. A similar increase in performance was observed when adding Co to amorphous Ni79.2Nb12.5Y8.3, except the activity and stability was maintained throughout the 10000 cycles. The presence of Co in Ni-based materials is shown to enhance the OER activity with amorphous
structure providing excellent long-term cycling stability. These features, along with the high surface area achieved through SA-HEBM, provide a cost-effective and simple method for producing stable and active amorphous electrocatalysts for the oxygen evolution reaction in AEM water electrolysis.


2:00 PM EN06.05.03
Boron Decorated Nickel Electrodes for Efficient Oxygen Evolution Reaction
Viridiana L. Perez, Audrey K. Taylor, Michael T. Paul, Jeffrey Ovens, Alexi Pauls, Mehrtoos Eslamibidgoli, Michael Eikerling and Byron D. Gates; Simon Fraser University, Canada

Clean energy sources such as hydro, wind and solar energy represent some of the alternatives to diminish our dependency on fossil fuels. Fluctuations in their availability due to geographical features and seasonal weather limit their use. Finding reliable ways to store the energy produced by these clean energy sources will help mitigate these issues.

Chemical energy storage and energy conversion are two ways to approach this problematic. Hydrogen is a clean fuel source, but currently it is mostly obtained from fossil fuels. Water splitting for the production of hydrogen in alkaline water electrolyzers arise as a viable option. However, commercial electrolysers perform at efficiencies of 60 to 70%, which is insufficient to supply for the demand of the fast-growing hydrogen economy. Hydrogen production by electrochemical water splitting is limited by the oxygen evolution reaction (OER). This reaction takes place at the anode, sluggish kinetics and accumulation of oxygen bubbles can block active sites on the surface of the electrode. Electrodes are typically made of expensive precious metals, however nickel-based metal oxides are a promising and robust alternative. Nickel electrodes have shown high activity and reduced activation energies for alkaline OER. However, the surface wettability and the accumulation of oxygen bubbles blocking active sites remain as an issue.

Our work explored the inclusion of boron containing species that are conductive, improve wettability, are stable under alkaline conditions and are inert at OER potentials. The decorated nickel surfaces showed improved OER activity. The electrodes were characterized using electron microscopy, electrochemical testing and X-ray diffraction measurements. The study was complemented with theoretical calculations of the electronic effects of the boron species and reaction intermediaries at the interface of the electrode and the electrolyte.

2:15 PM EN06.05.04
Tracking Structures in Solar Fuels Catalysis—In Situ X-Ray Structure Characterization of Heterogenized Molecular and Thin-Film Metal-Oxide Water-Splitting Catalysts
David M. Tiede1, Gihan Kwon2, Emily Sprague-Klein1, Tae Wu Kim1, Karen Mulfort1 and Alex B. Martinson1; 1Argonne National Laboratory, United States; 2Brookhaven National Laboratory, United States

A key challenge for the design of efficient photoelectrochemical devices that employ nanoscaled interfacial designs for solar energy-to-fuels conversion lies in resolving atomic structures and dynamics at the active interfaces, and relating these to the complex cascade of events which includes excited-state charge separation, charge-accumulation, and multi-step energy conversion and catalysis. Our research programs have been developing in-situ, time-resolved X-ray techniques aimed at the resolution of atomic-scale structures that underlie interfacial charge transfer and photo-driven water-splitting catalysis under conditions relevant to photoelectrochemical function for both interfacial thin-films and molecular photosensitizers and catalysts bound to semiconductor surfaces.

This presentation will show how high energy (>50 keV) X-ray scattering and pair distribution function (PDF) analysis provides atomic structure characterization that usefully complements electronic structure characterization derived from a combination of soft X-ray absorption (XAS), resonant X-ray emission (RXES), resonant inelastic X-ray scattering (RIXS) techniques for structure-function analysis of transition metal semi-conductor and catalyst thin films. Microporous high surface area electrodes were designed that allowed PDF analysis to be accomplished 0.2 Å spatial resolution for amorphous transition metal oxide thin films having thickness of down to 60 nm. The combined
electronic and structural analyses demonstrate that hole transfer to catalytic sites in amorphous cobalt oxide thin films is the rate-limiting step for electrochemical water-splitting rather than the multi-step catalytic events themselves. The macroscopic catalytic properties of the thin films were found to be correlated to the electronic structures measured at the atomic scale for the metal-oxo cluster domains. These results show the interplay between intrinsic catalytic activity and charge transport properties of semiconductor thin-film catalysts.

We have extended this approach by the development of nanoporous electrode architectures which enable the use of combined PDF and X-ray spectroscopy analyses to resolve differences in coordination structures for molecular photosensitizers and catalysts in solution and when bound to semiconductor oxide surfaces. Measurements on ruthenium photosensitizer complexes bound to the TiO₂ surface resolve distortions in the surface-coordinating ligand structures. On-going work is investigating the correlation between ligand structural distortion and the metal-to-ligand charge-transfer (MLCT) states with ultrafast interfacial charge injection function.

2:45 PM BREAK

3:15 PM *EN06.05.05
Tracking Structural Transformations by Operando X-Ray Scattering for the Oxygen/Water Electrocatalysis
Fabio Dionigi and Peter Strasser; Technische Universität Berlin, Germany

The intermittent nature of renewable energy sources, i.e. wind and solar radiation, requires storage solutions to match the energy demand of human activities. Among the chemical fuels, hydrogen is an interesting energy vector due to its high gravimetric energy density. Energy can be stored in the chemical bonds of hydrogen by water electrolysis and electric energy can be obtained with the related back reaction by using a fuel cell. The oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR), involved respectively in the forward and backward reaction, are associated with higher conversion efficiency losses in comparison with their half-reaction counterparts. Therefore, catalysts with superior activity for these reactions are of high interest. Understanding the reaction mechanism and identifying the catalytically active sites is important in order to improve the performance of the state-of-the-art catalysts. However, the atomic structure under reaction condition can be different than in the as synthesized phase. In this contribution, we will present operando wide angle X-ray scattering (WAXS) results providing insights into important structural changes leading to formation of catalytic active phases or associated to degradation mechanisms.

For the OER, NiFe layered double hydroxides (LDHs) are recognized among the most active catalysts in alkaline electrolytes [1]. Their crystal structure is known and is composed of layers of edge sharing metal oxygen octahedra that are intercalated with water molecules and charge balancing anions. Despite their structure is well characterized, there are evidences that the OER active structure of LDH catalysts during OER is different than the one of the as prepared materials [1]. Using operando WAXS we identified the structure of the catalytically active catalyst state and observed that both the interlayer and in-plane distances contract under operating conditions [2]. We further proved that this structure is also exhibited by other Fe containing LDHs under OER conditions. These results are important to validate the structures used in theoretical models to predict the OER mechanism and ultimately to develop strategies to improve the OER activity of NiFe LDH catalysts.

In a second study, we show that operando WAXS can also be applied to study degradation mechanisms. For ORR, octahedral PtNi alloy based nanoparticles shows very high activities in thin film rotating disk electrode measurements in acid [3]. However, the prevention of Ni loss and morphological stability under operation are still challenging. Using a combination of operando WAXS and ex situ X-ray fluorescence spectroscopy (XRF) we found that a structural transformation is involved in the degradation mechanism occurring while cycling the applied potential. The catalyst crystalline structure was modeled using multiple metal phases and the dealloying of the Ni richer phase with associated Ni loss is proposed as the main degradation mechanism [4]. The sensitivity of this process to operating conditions such as the upper potential limit of the cycling protocol was investigated. The binary PtNi alloy based nanoparticles were also compared with surface doped ternary compositions as potential method to prevent structural changes.

Fundamental Understanding of Activity-Stability Issues on Electrocatalysis for Oxygen Evolution Reaction

Dong Young Chung, Pietro Papa Lopes, Dusan Strmcnik, Vojislav Stamenkovic and Nenad Markovic; Argonne National Laboratory, United States

Water electrolysis has been accentuated important building blocks for energy conversion and storage concepts in aqueous system. In particular, oxygen evolution reaction (OER) is important counter reaction for not only hydrogen evolution reaction but also various electrochemical synthetic reaction including CO2 and N2 process. Durable electrocatalyst designs are an urgent problem in both acid and alkaline media because even noble metal based Ru and Ir materials suffer significant activity loss due to the highly corrosive thermodynamic potential window. In order to obtain highly durable electrocatalyst with high activity, it is urgent to link the activity-stability relationship during reaction. Here, we will discuss activity-stability relationship in water electrolysis reaction using our well-defined model system from simple monometallic system to bimetallic and complicated system. In the model system approach, we will discuss the general relationship between activity and stability what we observed and suggest which concept appeal to the future direction for achieving high activity and stability in OER electrocatalysis.

Engineering Dopant Position in Core-Shell CeO2-ZrO2 Nanoparticles to Control Catalytic Activity

Behnam Safavinia1, Pragathi Darapaneni1, Orhan Kizilkaya1, David Cullen2, Kerry M. Dooley1 and James A. Dorman1; 1Louisiana State University, United States; 2Oak Ridge National Laboratory, United States

Tailoring active sites position and concentration on the catalyst surface has been shown to effect activity and stability of a catalyst. Specifically, the surface coverage of transition metals on CeO2-ZrO2 (CZO) nanoparticles (NPs) is known to directly affect the redox property and ability to utilize lattice oxygens. Recently, Ni incorporation in the core of a CZO NPs has caused a two-fold increase in catalytic activity per surface area due an increased oxygen storage capacity. However, the activity of the particle is dependent on the Ni surface concentration and is traditionally deposited via the insipid wetness impregnation technique, forming Ni on the surface of the particle. In this work, the role of Ni position on catalytic activity is probed to develop a two-step synthesis process which allows for spatially controlled dopant distribution for improved catalytic activity.

A two-step process, co-precipitation/molten salt synthesis (MSS), has been explored for the catalyst core, and urea deposition synthesis for the shell of CZO:Ni NPs. The concentration of oxygen vacancies in these NPs was studied using Raman spectroscopy, which shows an order of magnitude increase in oxygen vacancies based on the change in intensity of defect-induced (D) band at 600 cm⁻¹ as the position of the active site is modified. High resolution transmission electron microscopy (HRTEM) and energy dispersive x-ray spectroscopy (EDX) identify that a core-shell structure is obtained with spatially controlled Ni concentrations To further correlate the dopant position and oxygen vacancies, local bond structure and geometry of the active site (Ni) were studied by performing L edge X-ray Absorption Spectroscopy (XAS) measurements. Geometric distortions due to the eg and t2g orbitals is dependent on the distribution of Ni within the NPs. The change in the geometric structure of Ni was observed via in situ CO chemisorption XAS measurements and correlated to the orbital structures. These preliminary results on the spatially controlled CZO core-shell NPs demonstrate that controlling the position of the active site (Ni) modifies the oxygen vacancies of the NPs which is the first step to understand the diffusion of the active site during a reaction and deactivation pattern of the catalyst.

Engineer Metal Oxide–Metal–Carbon Interface for Highly Efficient Oxygen Reduction

Jun Chen; University of California, Los Angeles, United States

Engineer Metal Oxide–Metal–Carbon Interface for Highly Efficient Oxygen Reduction

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Abstract:
Oxygen is the most abundant element in the Earth’s crust. The oxygen reduction reaction (ORR) is also the most
important reaction in life processes and energy converting/storage systems. Developing techniques toward high-
efficiency ORR remains highly desired and a challenge. Here, we report a N-doped carbon (NC) encapsulated
CeO2/Co interfacial hollow structure (CeO2–Co–NC) via a generalized strategy for largely increased oxygen
species adsorption and improved ORR activities. First, the metallic Co nanoparticles not only provide high
conductivity but also serve as electron donors to largely create oxygen vacancies in CeO2. Second, the outer carbon
layer can effectively protect cobalt from oxidation and dissociation in alkaline media and as well imparts its higher
ORR activity. In the meanwhile, the electronic interactions between CeO2 and Co in the CeO2/Co interface are
unveiled theoretically by density functional theory calculations to justify the increased oxygen absorption for ORR
activity improvement. The reported CeO2–Co–NC hollow nanospheres not only exhibit decent ORR performance
with a high onset potential (922 mV vs RHE), half-wave potential (797 mV vs RHE), and small Tafel slope (60 mV
dec–1) comparable to those of the state-of-the-art Pt/C catalysts but also possess long-term stability with a negative
shift of only 7 mV of the half-wave potential after 2000 cycles and strong tolerance against methanol. This work
represents a solid step toward high-efficient oxygen reduction.

References (# Equal contribution author; * Corresponding author)
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4:30 PM EN06.05.09
Exploring the Low-Temperature Carbon Monoxide Oxidation and Thermochemical Water Splitting
Capabilities of High Entropy Oxides James E. Park1, Elizabeth Paisley1, Eric N. Coker1, Abhaya Datye2 and
Stanley S. Chou1; 1Sandia National Laboratories, United States; 2The University of New Mexico, United States

High entropy oxides (HEOs) have been a recently emerging class of materials with promising catalytic activities
and electrochemical energy storage capabilities.1 By incorporating five or more cations, an entropy-stabilized single-
phase crystal structure can be formed with various combinations of atomic elements. However, there have been a
limited number of reports of HEOs being utilized for catalytic reactions. Here, HEOs with fluorite and rock-salt
structures were synthesized via solid state synthesis, and their catalytic activities for low-temperature carbon
monoxide (CO) oxidation and thermochemical water splitting (TWS) were explored. HEOs allow incorporation of
different elements while maintaining the same crystal structure. Thus, unprecedented chemical combinations can be
synthesized to engineer chemical and defect structure of oxides for improved catalysis. Moreover, the phase stability
at different temperatures and atmospheres will be investigated to provide insight into the extent of entropy
stabilization in HEOs. Current research focuses on HEOs with fluorite-type and rock-salt-type structures but will
expand to perovskite-type and spinel-type structures with multiple cation sites.


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4:45 PM EN06.05.10
Comparison between Thermochemical and Electrochemical Exsolution of Catalysts from Perovskite Oxides
for Efficient Hydrogen Production through Steam Electrolysis Georgios Dimitrakopoulos1, Jia Yue Wang1,
Rachael Rothman2 and Bilge Yildiz1; 1Massachusetts Institute of Technology, United States; 2The University of
Sheffield, United Kingdom
Increasing the performance of Solid Oxide Electrolysis Cells for the production of hydrogen (H₂) from water (H₂O) splitting requires the use of electrodes with low polarization resistance. To effectively enhance their splitting rate, catalysts are infiltrated into the porous electrodes. Traditional catalyst deposition methods such as wet impregnation or atomic layer deposition are expensive and the resulting catalysts suffer from agglomeration due to operation at high temperature that reduces the long-term performance. To improve upon the aforementioned methods and reduce the catalyst deposition cost, the in-situ growth of catalysts from perovskite oxides (termed catalyst exsolution) has been proposed as a means to decorate the porous electrode with highly dispersed, nanometer-sized catalytic particles [1-3]. These particles are highly active towards reactions of interest and show increased resistance to agglomeration due to their socketed nature [4].

Exsolution occurs when the oxygen chemical potential is reduced significantly and hence can be triggered either thermochemically (i.e. reduction of a perovskite oxide at elevated temperatures in the presence of fuel, usually H₂) or electrochemically (i.e. application of a voltage/current at elevated temperatures with/without the presence of fuel) [5]. In this work, we study the dependency of the exsolution mode (thermochemical vs. electrochemical) on the particle morphology, distribution, dispersion and activity towards H₂O-splitting to H₂. To investigate this dependency, exsolution of metallic Iron (Fe⁰) from an A-site deficient La₀.₇₅Sr₀.₂Cr₀.₉₅Fe₀.⁰₅O₃₋δ (LSCF) electrode was examined. Exsolution was triggered at different temperatures (in the 700C-900C temperature range) either thermochemically using 3%H₂-N₂ or electrochemically under an applied bias ranging between 0-2V in a 3% H₂O – 3% H₂ – N₂ environment. The polarization resistance before and after exsolution is measured using Electrochemical Impedance Spectroscopy (EIS) on asymmetric cells employing La₀.₈Sr₀.₂CrO₃₋δ as the counter electrode. Electrode polarization resistances under Open Circuit Voltage (OCV) in 3% H₂O – 3% H₂ – N₂ show that the exsolution mode plays a significant role in the particle growth and electrode activity. We demonstrate that, under the same environment, applying a bias to trigger exsolution generates more particles on the surface of the electrode compared to thermochemical exsolution. Characterization of the samples using X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) confirm the presence of Fe⁰ nanoparticles on the surface of the LSCF electrode and their existence decreases the polarization resistance as observed from EIS data.

References:

SESSION EN06.06: Light-Driven Catalysis I
Session Chairs: Virgil Andrei and Hailiang Wang
Wednesday Morning, December 4, 2019
Sheraton, 2nd Floor, Independence West

8:30 AM EN06.06.01
Scalable Photoelectrochemical Perovskite-BiVO₄ Tandem Devices for Solar Fuel Synthesis Virgil Andrei,
Haijiao Lu, Sebastian D. Pike, Robert L. Hoye, Bertrand Reuillard, Shahab Ahmad, Dominic S. Wright, Michael De
Volder, Richard H. Friend and Erwin Reisner; University of Cambridge, United Kingdom

As the energetic demands of our society keep rising, any emerging technology faces the challenge of matching the commercial benefits presented by fossil fuels in terms of energy storage and mobility. Since a vast part of the modern energetic infrastructure already relies on fuels, their production in a sustainable manner stands out as an obvious solution. Therefore, the light-driven conversion of small molecules such as water and CO₂ into so-called solar fuels (e.g. H₂, CO) represents an attractive alternative for simultaneous energy harvesting and storage.[1,2] While great progress has been made in the development of light absorbers maximizing the solar spectrum coverage, their integration with catalysts into photoelectrochemical (PEC) devices for fuel production still poses challenges. Beside the performance and stability of common PEC prototypes, their scalability and choice of catalyst are also
major factors which must be considered for commercial applications. In this work, we address those issues by developing approaches to synthesize and characterize up-scaled PEC devices, which are able to produce fuels autonomously in the absence of external bias. To overcome the overpotential losses of electroreduction, we introduce state-of-the-art photocathodes obtained by protecting triple cation mixed halide perovskite solar cells with a Field’s metal encapsulant. Their PEC performance is benchmarked using a platinum nanoparticle catalyst for proton reduction, reaching photocurrents as high as -14 mA cm\(^{-2}\) at 0 V against the reversible hydrogen electrode (RHE) under 1 Sun irradiation.\[^{[3,4,5]}\] By combining the perovskite photocathodes with robust BiVO\(_4\) photoanodes, tandem PEC devices can be obtained which sustain unassisted water splitting at a solar-to-hydrogen conversion of approximately 0.3%. The PEC devices present remarkable stabilities of up to 20 h under operation in an aqueous medium,\[^{[4,5]}\] revealing key general insights for the encapsulation of perovskite optoelectronic devices.

To investigate the scalability of our “artificial leaves”, we prepare devices of sizes up to 10 cm\(^2\) which reveal a similar performance to their 0.25 cm\(^2\) counterparts. The PEC tandems are characterized in a versatile 3D-printed PEC cell, which can accommodate a wide array of samples due to its modular design.\[^{[5]}\] The potential for further device up-scaling is revealed by fabricating 25 and 300 cm\(^2\) doped BiVO\(_4\) panels from bismuth (transition metal) polyoxovanadate single-source precursors.\[^{[6]}\] The overall findings are applicable to a wide range of photoelectrochemical systems employing various photoabsorbers.\[^{[7]}\] Looking beyond water splitting, we will also discuss our recent progress on the development of PEC devices that can couple the more challenging CO\(_2\) reduction to water oxidation, with the ultimate goal of contributing towards a circular carbon economy via photoelectrocatalysis.

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8:45 AM EN06.06.02
Nanosurface Engineering of Oxide Based Semiconductor towards Full Solar Spectrum Harvesting—A Combined Experimental and Theoretical Investigation Tuhin K. Maji\(^1\), Debjani Karmakar\(^2\) and Samir Kumar Pal\(^2\); \(^1\)SN Bose National Centre for Basic Sciences, India; \(^2\)Bhabha Atomic Research Centre, India

That there is an environmental and energy crisis due to civilization is beyond question. Utilization of full solar light spectrum to harvest energy is considered to be one of the most efficient techniques to overcome the energy crisis. The photothermal effect and photocatalytic effect are considered to be two of the most suitable strategies for solar light energy conversion. Metal oxide semiconductors are extensively used in photocatalysis because of their ability to absorb light from different part of the solar spectrum (depends on their band gap). Besides they also have other beneficial properties like high surface area, morphology, stability, non-toxic nature etc. We have tailored the surface defect state of ZnO nanoparticle (NP) using halide ion to enhance the charge separation property of ZnO. Particular halide ion (namely chloride) shows enhance photocatalytic activity in presence of UV light as well as room temperature magnetic activity. In our other work, we have prepared a new nanohybrid heterojunction using one low band gap semiconductor (CuS) with a wide bandgap semiconductor (ZnO) to form an efficient NIR harvesting photocatalyst. This newly prepared nanohybrid exhibit efficient photocatalytic performance using the NIR fraction of the solar light spectrum. An increment of significant charge separation from the conduction bands of CuS to those of ZnO is the key mechanism behind the enhanced photocatalysis. To utilize visible light for photocatalytic activity, we have prepared porphyrin dye sensitized metal oxide nanohybrid. Porphyrin dye is very much advantageous for visible light based photocatalytic activity due to their additional absorption band that resembles with the visible range of the solar spectrum. Here we have functionalized protoporphyrin IX with copper (II) ion and sensitized a
porous metal oxide microsphere TiO$_2$ (~1.5 µm diameter) in order to prepare a unique functional nanohybrid for visible light photocatalysis application. We have applied the nanohybrid for an efficient reduction of a toxic metal ion Cr (VI) to non-toxic Cr (III) in water under visible light illumination. For a prototype application, we have developed an active filter (having physical and chemical filtering capability) by depositing the nanohybrid on an extended surface of a stainless-steel metal mesh. The prototype active filter exhibits significant potential for chemical filtering of toxic Cr (VI) ions along with physical cleaning of suspended particulates present in water. Various microscopic and spectroscopic characterizations have been carried out to confirm the heterojunction formation. We have utilized first principles investigations to understand the modulation of electronic properties and obtain the insight to the photocatalytic process.

9:00 AM EN06.06.03
Photobase Effect in Photocatalytic Activity of Carbon Dots Jiawen Fang, Jacek K. Stolarczyk and Jochen Feldmann; Ludwig-Maximilians-Universität München, Germany

Carbon dots (CDs) are a versatile nanomaterial with attractive photoluminescent and photocatalytic properties. Their complex internal structure, considered to comprise sp$^2$-hybridized domains embedded in an amorphous sp$^3$-hybridized matrix, results in an intricate interplay between the constituent parts with multiple charge and energy transfer pathways determining the photocatalytic properties.[1,2] In effect, the mechanism of the photocatalytic hydrogen generation with CDs remains the subject of a debate. Here we demonstrate that the mode of nitrogen inclusion in the CDs within the aromatic domains controls the charge transfer and separation and thereby the photocatalytic activity for water reduction. [3,4] Furthermore, we propose that the photobasic effect, that is the abstraction of a proton from water upon excitation of CDs by light, facilitates the photoexcited electron transfer to the proton. In this context, we studied the effect of controlled inclusion in CDs of photobasic molecules which resemble the molecular moieties found in photocatalytically active CDs. We show that such addition strongly increases the hydrogen generation. Ultrafast spectroscopy measurements corroborated these findings, revealing the dynamics of the relevant electron and excited state proton transfer processes. The study demonstrates the critical role of understanding the structure and dynamics of the CDs in designing the materials with improved photocatalytic efficiency.


9:15 AM *EN06.06.04
Heterogenized Molecular Catalysts for Water Oxidation Gary Brudvig; Yale University, United States

Devising cost effective methods for efficiently capturing and storing solar energy is among the grand challenges of science. We are using insights from studies of natural photosynthetic systems to develop bioinspired molecular catalysts for photo- and electrochemical water oxidation necessary for solar fuel production. Molecular catalysts are known for their high activity and tunability, but their solubility and limited stability often restrict their use in practical applications. We are developing anchoring chemistry to attach molecular water-oxidation catalysts to metal oxide surfaces, which not only greatly increases the stability of the molecular catalyst but also improves the catalytic performance of the oxide material. Our progress on the development and characterization of molecular iridium, copper and manganese water-oxidation catalysts, along with their application for photoelectrochemical water oxidation and solar fuel production, will be discussed.

9:45 AM BREAK

10:15 AM *EN06.06.05
Solar-Driven Synthesis of Fuels and Chemicals with Semiconductor Powders Erwin Reisner; University of
The synthesis of solar fuels and chemicals through artificial photosynthesis allows the direct pairing of light absorption to drive chemical redox processes. This approach is a one-step and versatile alternative to the more indirect coupling of a photovoltaic cell with electrolysis and enables potentially the synthesis of a wide range of fuels and feedstock chemicals. A common drawback in most artificial photosynthetic systems and organic photocatalysis is their reliance on expensive materials and device architectures, which challenges the development of ultimately scalable devices. Another limitation in many approaches is their inefficiency and reliance on sacrificial redox reagents, which may be system damaging and often prevent truly energy-storing chemistry to proceed. This presentation will give an overview about our recent progress in developing molecular-semiconductor hybrid systems to perform efficient full redox cycle solar fuel catalysis with inexpensive components, and our steps in extending this approach for sustainable waste polymer photoreforming and fine chemical synthesis.

Representative recent publications
(1) “Electro- and solar-driven fuel synthesis with first row transition metal complexes”
(2) “Photoreforming of lignocellulose into H₂ using nanoengineered carbon nitride under benign conditions”
(3) “Plastic waste as a feedstock for solar-driven H₂ generation”
(4) “Solar Hydrogen Generation from Lignocellulose”
(5) “Solar-driven reforming of lignocellulose to H₂ with a CdS/CdOₓ photocatalyst”
(6) “Carbon dots as photosensitisers for solar-driven catalysis”
(7) “Solar-driven Reduction of Protons Coupled to Alcohol Oxidation with a Carbon Nitride-Catalyst System”
CuSnO nanoclusters was explored. Characteristic infrared absorptions of CO probe molecules confirmed the formation of bimetallic clusters (2142, 2135 cm⁻¹), with the surface metal centers reduced to Cu(I) and Sn(II) (2128, 2111 cm⁻¹) by illumination of ZrOCo – cluster units in the presence of adsorbed diethylamine electron donor. Formate was detected by FT-IR as sole photo-reduction product of vapor phase CO₂ upon excitation with 405 nm light. Photocatalytic units consisting of bimetallic nanocatalyst cluster of Cu with Pd coupled to ZrOCo have been prepared and characterized for exploring CO₂ photoreduction to more energy dense products beyond 2-electron species. Photocatalytic results will be discussed.

11:15 AM EN06.06.08
Plasmonic Ruthenium (II) Nanopigments for Field-Enhanced Photocatalysis of Urea Oxidation and Visible Light Fuel Cells Xingda An and Björn M. Reinhard; Boston University, United States

The localized surface plasmon resonance (LSPR) of noble metal nanostructures provides appealing strategies to enhance photoinduced charge transfer in photocatalysis. While the plasmonic hot charge carrier production mechanism is well-characterized for initiating direct catalysis by plasmonic metals or heterostructures, the intense but evanescent Electric (E-) field generated by the nanoantennas provides a powerful alternative pathway to magnify resonant intramolecular transition processes in plasmonic catalysis. Harnessing plasmonic E-fields for photocatalysis, however, is fundamentally challenged by the trade-off between distance-dependent local field intensity enhancement and excited state quenching through the metal. Here, we explore quantitative optimization of photocatalysis mediated by an E-field enhanced metal-to-ligand charge transfer (MLCT) process. We present a hierarchical nanopigment architecture that localizes a transition metal photocatalyst, [Ru(bpy)₃]²⁺, in an electromagnetic “sweet spot” for efficient plasmonic enhancement of photocatalysis. A phospholipid membrane self-assembled around a Ag nanoparticle (NP) binds [Ru(bpy)₃]²⁺ as well as serves as a spacer between the transition metal complex and the NP, whose LSPR overlaps with the [Ru(bpy)₃]²⁺ MLCT. The nanopigments allow for substantial absorption enhancement but avoid quenching of photoexcited Ru*(II). We demonstrate direct photocatalytic urea oxidation with the nanopigments, and implement a visible light-driven Direct Urea Fuel Cell (LDUFC) to achieve simultaneous solar energy harvesting and waste water treatment. Our approach provides great promise as an effective and broadly applicable strategy to enhance intramolecular charge or energy transfer processes with metal plasmon resonances, and it depicts a blueprint for designs of bio-mimetic efficient and specific nanoreactors.

11:30 AM EN06.06.09
Magnetic Nanoparticles for the Facile Release of Photochemically Stored Energy Tobias Luchs, Patrick Lorenz and Andreas Hirsch; University of Erlangen-Nuremberg, Germany

With record high emissions of greenhouse gases, the global demand for renewable energies increases. Therefore, also the need for efficient and flexible energy storage systems arises. On the molecular level photoswitches that can undergo reversible transformation to a high energy isomer display a promising class of storage systems. We report on a novel, inexpensive and effective process for the repeatable photoisomerization of norbornadiene (NBD) to its metastable isomer quadricyclane (QC), followed by catalytically induced strain energy release via back-conversion of QC to NBD. By implementing a quasi homogeneous catalyst system based on magnetic iron oxide (Fe₃O₄) nanoparticles that were covalently functionalized with a Cobalt (II) complex, tedious purification steps can be avoided. These core-shell nanoparticles combine a high active surface area with the intrinsic magnetic properties of the iron oxide core to enable facile separation by the action of an external magnetic field. Together with the interconversion couple NBD1-QC1 that provides an extraordinary stability of the high energy isomer QC1 (t₁/₂ = 450 days at room temperature), as well as a high energy storage capacity (88.3 kJ/mol) these core-shell nanoparticles present a promising system for photochemical energy storage.


11:45 AM EN06.06.10
BiFeO Thin Films as a New Visible-Light Active Photoanode Material for Solar Water Splitting Joe Briscoe¹, Yaqiong Wang², Matyas Dabóczi³, Camilo Mesa³, Sinclair R. Ratnasingham³, Ji-Seon Kim³, James R. Durrant², Steve Dunn³ and Haixue Yan¹; ¹Queen Mary University of London, United Kingdom; ²Imperial College London, United Kingdom; ³London South Bank University, United Kingdom
BiFeO$_3$ is a material that is of interest for many applications due to its combination of visible bandgap (2.3-2.7 eV) with multiferalic properties (ferroelectricity combined with antiferromagnetism). Bi$_2$Fe$_4$O$_9$ is normally considered as an unwanted secondary phase in the synthesis of BiFeO$_3$ and therefore has received little attention. However, modelling has shown that it should also possess a bandgap in the visible range [1], and one report has shown that powders of the material are active for photocatalysis, showing degradation of organic pollutants [2].

Here we report the synthesis of Bi$_2$Fe$_4$O$_9$ thin films via simple sol-gel deposition with, for the first time, photoelectrochemical (PEC) properties of the films demonstrating their suitability for use as photoanodes for solar water splitting. UV-Vis absorption show a highly suitable bandgap (2.05 eV) with strong absorption from 600 nm. Phase and composition are also confirmed using XRD and XPS. Furthermore, measurement of the energetics of the material show that this band gap straddles the water reduction and oxidation potentials, with the material displaying slightly n-type behavior.

PEC measurements in the 0 V to 1.5 V range (vs Ag/AgCl) show almost twice the photocurrent compared to BiFeO$_3$. Further insight is achieved by testing using a hole scavenger (H$_2$O$_2$), which leads to an increased photocurrent from 0.05 mA/cm$^2$ to 0.1 mA/cm$^2$ at 1.2 V (vs NHE), a shift in onset potential from 0.5 V to 0 V (vs Ag/AgCl), and the disappearance of positive/negative photocurrent transients upon light chopping. These results indicate that hole injection barriers leading to slow kinetics and surface recombination limit the photocatalytic performance of this material, thus combination with appropriate water oxidation catalysts may lead to further improved performance. To test this, Co-Pi was deposited on the surface of the thin-film photocatalyst, leading to a 5-fold increase in photocurrent. To confirm water splitting was taking place, oxygen evolution was successfully measured from the photocatalyst, and by comparing to the measured photocurrent a Faradaic efficiency of 82.1% was calculated – over 10% higher than BiFeO$_3$ photocatalysts.

Overall these results indicate that Bi$_2$Fe$_4$O$_9$ may be a promising new material for PEC water oxidation, with the potential for significant improvements to be made in the future through routes such as nanostructuring and reduction of surface defects. Also, the measured band positions indicate that PEC water reduction may also be possible with this visible-bandgap oxide material via suitable p-type doping and stabilization at cathodic potentials.

Solar Driven CO₂ Reduction to CO with 19 % Efficiency in a PV-GDE Flow Cell under Outdoor Solar Illumination

Wen-Hui Cheng¹, Matthias H. Richter¹, Ian Sullivan¹, David M. Larson², Bruce S. Brunschwig¹, Chengxiang Xiang¹ and Harry A. Atwater¹; ¹California Institute of Technology, United States; ²Lawrence Berkeley National Laboratory, United States

Producing sustainable fuels from sunlight is an important objective for mitigating climate changes. We report here results for a solar-driven CO₂ reduction device for CO generation using a flow-by type gas diffusion electrode (GDE), employing a Ag nanoparticle catalyst layer and a GaInP/GaInAs/Ge triple junction solar cell. The GDE is designed to utilize high CO₂ concentration and low overpotential catalysts for the CO₂ reduction reaction. Near-unity Faradic efficiency is obtained for CO₂-to-CO conversion and a solar-to-CO efficiency of 19.5 % can be realized with AM 1.5G illumination at 3.25 Suns. The device was shown to be stable for >20 h with no loss in efficiency, suggesting that high efficiency GDEs are a promising path to producing a chemical fuel from CO₂. Outdoor measurements were performed under ambient solar illumination in Pasadena, CA, resulting in a solar-to-CO conversion efficiency of 18.9 % during noontime, a diurnal-averaged solar-to-CO conversion efficiency of 6.1 %, and yielded a CO production rate of 50 mg/cm² per day. This work gives an outlook for the potential of solar driven carbon dioxide reduction. Pathways to further improvements beyond this record efficiency will be discussed, including the optimization of band gaps and further catalyst engineering. The system opens a new avenue for research into very high efficiency and stable devices for solar CO₂ conversion.

2:00 PM OPEN DISCUSSION

2:30 PM BREAK

Developing Nanostructured Photoelectrochemical Electrodes and Electrocatalysts for Efficient Solar Energy Conversion

Shihe Yang; Peking University Shenzhen Graduate School, China

Photoelectrochemical (PEC) water splitting is a promising technique to directly convert solar energy into hydrogen energy for storage and transportation. PEC devices need to efficiently absorb sunlight and separate and collect the photocarriers. Herein we will present our recent work on the development of photonic structures for light trapping, PEC electrodes and electrocatalysts for water splitting. The importance of understanding both the light harvesting and the charge collection characteristics will be highlighted for the light trapping structural design. For electrocatalysts, we will focus on two-dimensional (2D) materials, and combine experimental and theoretical techniques to reveal the importance of the specific nanostructures for hydrogen evolution reaction and oxygen evolution reaction in electrolytes of different pH values. Our overall goal is to develop cost-efficient and robust photocatalysts and electrocatalyst to efficiently convert the abundant solar energy to clean, storable and transportable chemical fuels.

4:00 PM Enhanced Catalytic Activity of Dye-Sensitized Photoelectrosynthesis Cells by Characterizing and Passivating NiO Surface Defect Sites

Aaron Taggart, Jake Evans and James Cahoon; University of North Carolina at Chapel Hill, United States

Tandem water splitting with wide-bandgap metal oxides functionalized with chromophore-catalyst assemblies is a potential low-cost solution to synthesize solar fuels. In recent years, high performing molecular catalysts have been developed for reducing protons to H₂ and reducing CO₂ to CO, CH₄, and other useful carbon derivatives. However, many of these dye-sensitized photocathodes are based on NiO scaffolds which exhibit poor performance and limit the catalytic efficiency in aqueous conditions and at potentials needed for tandem water splitting. Here, we elucidate that in the presence of water, intra-bandgap surface states exist that are associated with hydroxyl and oxygen moieties adjacent to Ni vacancies. Through a combination of electrochemical measurements and First-principles calculations, we show that these trap states give rise to a surface capacitance which can be almost completely eliminated by targeted atomic deposition (TAD) of Al treatment. TAD-treated electrodes functionalized with chromophore-catalyst assemblies sustain cathodic photocurrent at positive electrochemical potentials and yield a champion Faradaic efficiency of 46.0 ± 5.9% for H₂ evolution compared to 3.1 ± 0.4% for untreated films at +0.83
V vs. RHE. To the best of our knowledge, these results are the most positive potentials at which H₂ evolution has been observed for a dye-sensitized photoelectrosynthesis cell to date, and they represent an important step toward designing tandem water splitting devices with high efficiencies. This work demonstrates the utility of TAD passivation in suppressing recombination and side reactions that impede aqueous photocatalytic performance, especially at the positive electrochemical potentials needed for wireless operation of tandem solar fuel devices.

4:15 PM EN06.07.06
Energy Level Alignment and Charge Transport at the Semiconductor-Protoporphyrin IX-Interface Felix Eckmann, Jennifer Padberg and Martin Stutzmann; Technische Universität München, Germany

Efficient photocatalytic conversion of carbon dioxide to solar fuels presents an attractive option to reduce the problem of energy storage present in today’s renewable energy technology. Until today, most effort has been put into either homogeneous or heterogeneous approaches, working separately on molecular catalysts in solution or metal and semiconductor surfaces, respectively. By anchoring molecular catalysts on semiconductor surfaces and therefore combining approaches of heterogeneous and homogeneous catalysis, one might be able to profit from advantages of both, leading to enhanced efficiency and stability. A major challenge of this idea is the lack of fundamental knowledge about the interaction of the molecular catalyst with the semiconductor.

In order to gain more information specifically on the energy level alignment and charge transport between catalytically active molecules and semiconductor surfaces, a simple model system containing a protoporphyrin IX (PPIX) monolayer deposited on different semiconductor substrates via Langmuir-Blodgett deposition is investigated. Monolayer morphology as well as molecular packing density are studied using atomic force microscopy and surface pressure isotherms, indicating a closely packed monolayer with a slightly tilted orientation on Silicon and Gallium Nitride surfaces. The potential landscape at the interfaces of Silicon and Aluminum Gallium Nitride surfaces with varying Aluminum to Gallium ratio and PPIX are investigated by surface photovoltage analysis, showing indications of a surface potential shift due to an interface dipole. Photoluminescence (PL) studies of these PPIX monolayers reveal a strong dependence of the PL intensity on the band gap of the underlying substrate and excitation wavelength. Shorter excitation wavelengths and higher electron affinities of AlGaN substrates yield lower PL intensity, giving rise to the assumption that electrons in excited molecular states are transferred to the substrate’s conduction band, if the excited electron has sufficient energy compared to the conduction band minimum. This leads to a quenching of the luminescence in this model system and would lead to a decrease in efficiency for a photocatalytically reducing device, highlighting the necessity of matching the choice of the semiconductor support to the specific catalytic molecule in order to ensure beneficial interaction.

4:30 PM EN06.07.07
Bimetallic Plasmonic Catalysts—Effect of Nanostructure on Thermal and Non-Thermal Light Enhancement Peter Novello¹, Siyuan Zhu¹, Leah Zachary¹, Pani Varanasi²¹ and Jie Liu¹; ¹Duke University, United States; ²U.S. Army Research Office—Materials Science Division, United States

Plasmonic catalysts where a single material combines plasmonic and catalytic functionalities can improve reaction rates, improve catalyst lifetimes, and alter product selectivity. These catalytic processes are largely affected by energy transfer between a plasmonically excited active-site and reactants. To access a broader range of reactions, catalysts with weak or no plasmonic properties have been utilized and coupled to a plasmonic absorber. This work addresses the more complex nature of the interaction between a plasmonic absorber, a catalyst, and reactant molecules. Specifically, though alteration of the nanostructure of bimetallic plasmonic-catalytic particles, we analyze the light enhanced reaction rates and separate out thermal and hot-electron transfer effects. Alloy, co-impregnated, and core-frame Pt-Rh catalysts were examined with findings suggest a guiding set of nanostructure design principles which can be used to maximize the efficiency of bimetallic plasmonic catalysts.

4:45 PM EN06.07.08
Balancing Light Absorption and Charge Transport in Vertical SnS₂ Nanoflake Photoanodes with Stepped Layers and Large Intrinsic Mobility Binod Giri¹, Maryam Masroor Shalmani¹, Tao Yan¹, Kateryna Kushnir¹, Alexander D. Carl¹, Curtis W. Doiron¹, Haochuan Zhang², Yanyan Zhao², Arthur McClelland³, Geoffrey A. Tompsett², Dunwei Wang², Ronald L. Grimm¹, Lyubov V. Titova¹ and Pratap M. Rao¹; ¹Worcester Polytechnic Institute, United States; ²Boston College, United States; ³Harvard University, United States

Significant optical absorption in the blue-green spectral range, high intralayer carrier mobility, and band alignment
suitable for water splitting suggest tin disulfide (SnS\textsubscript{2}) as a candidate material for photoelectrochemical applications. In this work, vertically aligned SnS\textsubscript{2} nanoflakes are synthesized directly on transparent conductive substrates using a scalable close space sublimation (CSS) method. Detailed characterization by time-resolved terahertz and time-resolved photoluminescence spectroscopies reveals high intrinsic carrier mobility of 330 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} and photoexcited carrier lifetimes of 1.3 ns in these nanoflakes, resulting in a long vertical diffusion length of \(~1\) \textmu m. The highest photoelectrochemical performance is achieved by growing SnS\textsubscript{2} nanoflakes with heights that are between this diffusion length and the optical absorption depth of \(~2\) \textmu m, which balances the competing requirements of charge transport and light absorption. Moreover, the unique stepped morphology of these CSS-grown nanoflakes improves photocurrent by exposing multiple edge sites in every nanoflake. The optimized vertical SnS\textsubscript{2} nanoflake photoanodes produce record photocurrents of 4.5 mAcm\textsuperscript{-2} for oxidation of a sulfite hole scavenger and 2.6 mAcm\textsuperscript{-2} for water oxidation without any hole scavenger, both at 1.23 V\textsubscript{RHE} in neutral electrolyte under simulated AM1.5G sunlight, and stable photocurrents for iodide oxidation in acidic electrolyte.

EN06.08.02
Soft-Template Synthesis of Mesoporous Metal Sulfide Nanoparticle Networks for Efficient Photocatalytic Hydrogen Evolution
Ioannis Vamvasakis and Gerasimos S. Armatas; University of Crete, Greece

Photocatalytic hydrogen production through water splitting has recently gained significant attention for efficient solar-to-chemical energy conversion.\(^1\) However, despite immense research efforts on semiconductor materials, key challenges of obtaining catalysts with high activity and long-term stability still remain. Recently, the synthesis of highly crystalline mesoporous semiconductors has been the focus in the field of electro- and photocatalysis. These materials combine the high reactivity of semiconductor nanoparticles with mesoporosity, offering new perspectives in designing novel catalysts with improved efficiency and reliability. Unlike to bulk-like microstructures and individual nanoparticles, 3D mesoporous networks of connected nanoparticles can benefit from the large and accessible surface area within the assembled structure and enhanced light-harvesting efficiency arising from multiple scattering of light inside the pores.

Herein, we present the synthesis of chemically stable and robust mesoporous networks of β-Ni(OH)\textsubscript{2} and ZnS decorated CdS nanoparticles (ca. 4–5 nm) that show high photocatalytic activity for hydrogen evolution under visible light irradiation.\(^2\) We utilize polymer-assisted self-assembly of colloidal nanoparticles to assemble mesoporous CdS nanoparticle-linked frameworks with high interstitial porosity. This method utilizes the nanoparticles as building block units and based on the coassembly of these nanoscopic units with organic structure-directing agents to construct 3D structures with open-pore morphology.\(^3\) The resulting materials feature a nanometer-sized framework perforated by uniform pores, which allows rapid mass transport and provides plenty of exposed surface-active sites available for reaction. In addition, using a combination of photocatalytic experiments and optical absorption, luminescence and electrochemical impedance spectroscopy studies, we highlight the effect of β-Ni(OH)\textsubscript{2} and ZnS additives on the electronic structure and photochemical performance of CdS. For instance, our results indicate that the p-type β-Ni(OH)\textsubscript{2} acts as hole collector, favoring efficient charge transfer and separation across the β-Ni(OH)\textsubscript{2}/CdS nano-heterojunctions. As thus, the β-Ni(OH)\textsubscript{2}/CdS catalyst containing 10 wt% Ni reached a photocatalytic H\textsubscript{2}-evolution rate of 1.4 mmol/h with an apparent QY of 72% at 420 nm, while demonstrating excellent stability in alkaline (5M NaOH) ethanol solution (10% v/v). The results of these studies can offer new insights into the design and development of efficient photocatalysts for energy conversion and environmental remediation applications.

References
Electrocatalytic carbon dioxide (CO$_2$) reduction is an attractive approach to provide renewable energy from atmospheric CO$_2$. For achieving efficient CO$_2$ reduction reaction, electrocatalysts are required to have high selectivity to target gas product, and their enormous conversion rate. The developments of nanostructures achieved high energy efficiency and selectivity for reusable carbon-containing chemicals. However, the complicated nanostructures have restricted the CO$_2$ conversion rates because of poor mass transport of reactants. Herein, we propose a three-dimensional (3D) hierarchically porous Au consisting of continuous macroporous channels (200-300 nm) and nanopores (<10 nm) fabricated by Proximity-field nanoPatterning (PnP). This hierarchically porous nanostructures could be fabricated involving three sequential processes: i) fabrication of 3D epoxy-based periodic nanostructures using PnP technique on an electrically-conductive substrate, ii) electroplating the Au-Ag alloy into the 3D nanostructured template, and iii) selective removal of Ag components and 3D epoxy template using dealloying and plasma etching machine, respectively. The fabricated macroporous channels have well-ordered pores with the periodicity is approximately 600 nm along the x, y-axis and 1 µm along the z-axis. The roles of each pore network are investigated using reliable 3D nanostructures possessing controlled pore distribution and size: nanoporous Au (N-Au), macroporous Au (M-Au), and hierarchically porous Au (N/M-Au). The continuous, perfectly periodic macropores and nanopores enable efficient mass transport and large active areas, respectively. Numerous nanopores in N/M-Au produce a large electrochemical surface area that is 66.1 times larger than that of electroplated Au film, and high index facet results in high CO selectivity of 85.5 % at a low overpotential of 264 mV. For analysis of the structural effect on CO$_2$ conversion rates, the specific $j_{CO}$ is measured using nanostructured electrodes with various thickness at a different applied potential of -0.274 VRHE and -0.574 VRHE. The Au nanostructures having macroporous channels show a noteworthy tendency that has higher specific $j_{CO}$ at the relatively high applied potential of -0.574 VRHE. The 3D hierarchically porous electrodes consequent allow efficient mass transport during vigorous electrolysis resulting in maximum 3.96 times higher $j_{CO}$ per mass than that of dealloyed nanoporous Au film. Thus, the systematic model study shows the proposed hierarchical nanostructured electrodes have critical value in increasing the efficiency of expensive Au. These investigations are also useful for other electrochemical applications in an aqueous base solution including batteries, flow cell, and electrocatalysts.
Then, using the low-dimensional model developed by Joshi et al., we quantified the relative contributions of the chemical kinetics, internal mass transfer and external mass transfer as functions of various catalyst design and operating parameters. The analysis indicates that the nanoarray-based monolithic catalysts show decreased internal mass transfer resistance compared to the washcoat-based catalysts, which originates from the ordered nanoarray configuration and decreased catalyst layer thickness, which facilitate the diffusion of the reactant gas molecules through the nanoarray layers. Furthermore, the mesoporous TiO₂ nanoarrays provide sufficient specific surface area and catalytically active sites for reactions, and the adherent interface between the in-situ grown nanoarrays and substrate channel surfaces promoted the mechanical robustness of the monolithic catalysts. This study sheds light on the design of novel monolithic catalysts for various gas phase reactions.


**EN06.08.06**

**ZnS Nanoparticle Embedded N, S-Codoped Mesoporous Carbon for Efficient Oxygen Reduction Reaction**

Dongjun Kim¹, Geonho Kim¹, Seoyeob Oh¹, Jiheyon Park¹, Seokhee Lee¹, Wonsik Lee¹, Seoyoung Yoon¹, Eunkyoung Cho², Kwonnam Sohn², Doo-kyung Yang² and Jiwon Kim¹,¹; ¹Yonsei University, Korea (the Republic of); ²LG Chem., Korea (the Republic of)

As demand for energy increases, it is inevitable to develop more efficient, stable, and long-life energy conversion/storage systems. Accordingly, devising highly active and stable electrodes for oxygen reduction reaction (ORR) has attracted a great attention. Heteroatom doped mesoporous carbon is one of the most promising substitutes for Pt-based ORR electrocatalysts with outstanding stability, activity, and electric conductivity. Furthermore, hybridization with transition metal is known to be one of the most efficient ways to improve ORR catalytic activity of mesoporous carbon (MC). Herein, we demonstrate a novel synthetic method of ZnS nanoparticle embedded N, S-codoped mesoporous carbon (NSMC) and its enhanced electrochemical property compared to the commercial Pt/C catalyst. NSMC was synthesized by one-step pyrolysis of a novel metal-organic framework (MOF), S-modified Zn-MOF-74, which was additionally doped with thiourea. The as-prepared NSMC exhibited high catalytic activity (limiting current density \( J_L = -5.19 \) mA cm\(^{-2}\)), superior stability (91.7% of \( J_L \) retention after 25000 s), and a great methanol tolerance in ORR. The enhanced ORR properties might be attributed to the ZnS nanoparticles as catalytic active sites and well-defined structure of N, S-codoped mesoporous carbon. Our results suggest that the introduction of ZnS nanoparticle and N, S-codoping could be a promising strategy for enhancing ORR in basic medium.

**EN06.08.07**

**A Duable, Inexpensive Oxygen Reduction Reaction Electrocatalyst**

Sung Beom Cho¹,², Cheng He¹, Arashdeep S. Thind¹, Shrihari Sankarasubramanian¹, Jordan Hachtel¹, Albina Borisiević³, Juan-Carlos Idrobo², Vijay Ramani¹ and Rohan Mishra¹; ¹Washington University in St. Louis, United States; ²Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of); ³Oak Ridge National Laboratory, United States

The current proton exchange fuel cells (PEFC) employ platinum group metal (PGM) catalysts in their electrode for oxygen reduction reaction (ORR). However, the excessive cost of PGM catalysts is a major hurdle for realizing the potential of PEFCs, thus necessitating the development of inexpensive non-PGM catalysts. Amongst the different PGM-free catalysts, a complex mixture of carbon (C), nitrogen (N), and transition metals (M) forming M-N-C clusters (M=Co, Fe, Ni, Mn, etc.) are currently the leading candidates due to their comparable activity to PGM catalysts and cost-effectiveness [1]. This complex is generally synthesized by the pyrolysis of carbon-based support
with metal and nitrogen precursors [2]; however, the carbon-based support suffers from catastrophic failure during repeated start-up/shut-down events wherein the high cathode interfacial potential results in the irreversible corrosion of carbon and hence to the loss of active centers [3]. More distressingly, the reactions typically yield a complex structure, where the active site and reaction mechanism is still under the debate.

To overcome this issue, we employed an approach based on first-principles calculations to rapidly screen through a large set of TMN clusters (TM = Mn, Fe, Co, Ni, Zn, Zr, and Mo) on corrosion-resistant TiC supports that have a good combination of stability, surface area and conductivity. We predict FeN₄ clusters on TiC support to be an inexpensive and durable catalyst having better performance than TMN clusters on carbon (graphene) supports. This catalyst formulation was obtained by developing a scaling relation based on the electrostatic interactions between the TiC support and the TMN clusters. To validate our theoretical predictions, we synthesized various TMN catalysts on TiC supports. We characterized their structure and composition using a suite of techniques including XPS, SEM, STEM-EELS to show successful incorporation of the catalytically active clusters onto the TiC support. The measured ORR activity of these catalysts precisely confirmed our electrostatics-based scaling relation.

Moreover, upon comparing an electrocatalyst comprising FeN₄ clusters on TiC with a baseline carbon-supported FeN₄ cluster electrocatalyst synthesized using the same method, we found that FeN₄/TiC exhibited an ORR activity (2.3mA.cm⁻² at the half-wave potential E₁/₂) that was 20% greater than FeN₄/C (1.85mA.cm⁻² at E₁/₂) and comparable to the state-of-the-art [4, 5]. Furthermore, it showed high stability under 1000 cycles of the stringent accelerated start-up/shut-down stability protocol [6] adopted by the US Department of Energy and most major automotive companies.


EN06.08.08
Understanding the Origin of Products Selectivity on Copper Catalysts During Electrochemical CO₂ Reduction Tsu-Chin Chou¹, Chiao-Chun Chang²,¹ and Heng-Liang Wu¹; ¹National Taiwan Univ, Taiwan; ²National Taiwan Normal University, Taiwan

Electrochemical CO₂ reduction has been considered as a potential route to convert harmful CO₂ to valuable hydrocarbons for sustainable carbon cycles. Since late 1980s, copper catalyst has been recognized as one and the only catalyst which produced hydrocarbons as primary products;¹ however, the poor selectivity obstructs the applications. According to DFT calculations, surface CO is the most common and important intermediate during CO₂ reduction reaction,² but further reaction mechanisms are still unclear, e.g. protonation and dimerization of CO. Cu(I) oxide was correlated to the formation of C₂ products during reactions,³ yet there is lack of solid intermediate evidence to distinguish different reaction routes.

In this talk, we used in situ surface enhanced infrared absorption spectroscopy, in situ X-ray absorption spectroscopy (Cu L-edge) and on-line GC to study the electrochemical CO₂ reduction mechanism occurred in different copper catalysts. We observed various CO intermediates such as CO₅ atop and CO₅ bridge on copper surface during electrochemical CO₂ reduction and the formation of CO₅ atop/CO₅ bridge can be correlated to the existence of surface Cu(I) and Cu(0) sites, respectively. Our results suggested that the existence of CO₅ atop can result in the formation of methane during further reduction. In addition, ethylene can be produced in the presence of CO₅ atop and CO₅ bridge. Our results both prove theoretical predictions ⁴ and meet the gap to illustrate the detail reaction mechanisms from CO₂ to hydrocarbons. We next propose a method to create Cu(I) sites efficiently on copper catalysts.

References
The Magnetic Field Tunability of the Photocatalytic System Based on Spintronic Materials  
Jie He; Tianjin University of Technology, China

In recent years, many achievements have been made in improving photocatalytic activity, but the solar conversion efficiency of photocatalysts is still far below the expected value. According to the reaction mechanism of photocatalysis, the factors affecting the conversion efficiency of photocatalyst can be summarized as follows: the band gap, the position of conduction band and valence band, the efficiency of carrier separation and transfer. The magnetic field can be introduced into the photocatalytic process and enhance the solar conversion efficiency: on the one hand, in some molecular catalytic reactions, the ferromagnetic arrangement of catalyst materials will align the spin orientation of the electrons accumulated on the surface, effectively promoting the occurrence of oxygen evolution reaction, on the other hand, magnetic field can change the conductivity of some materials with specific properties, and increase the carrier transport and separation. In addition, the external magnetic field does not require direct contact with the reactor vessel, and does not affect the morphology and own characteristics of photocatalysts, therefore the magnetic field will not cause secondary pollution.

In this work, the composite photocatalysts ZnFe₂O₄/Ag and ZnFe₂O₄/AgBr based on spintronic material ZnFe₂O₄ are constructed. The interface between ZnFe₂O₄ and Ag or AgBr can induce the magnetic moments in Ag or AgBr due to the magnetic proximity effect, emerging negative magnetoresistance (MR) effect in composite photocatalysts. Under the magnetic field, the organic dyes can be removed more efficiently compared to that without magnetic field. The measurement results demonstrate that the magnetic field plays two kinds of roles during the photocatalytic process, firstly, the magnetic field promote the transfer and separation of electrons and holes to enhance the photocatalytic activity because of the negative MR of the composite photocatalysts. Secondly, the magnetic field can replace the function of electron transmission medium in Z-scheme structure, which can simply the structure of the Z-scheme photocatalyst ZnFe₂O₄/AgBr. The combination of spintronics and photocatalysis is of great scientific significance in understanding charge transfer, physical mechanism of photocatalysis, mutual promotion between spin characteristics and photocatalytic performance, meanwhile, this combination provides an important reference for the development of multifunctional electronic devices.
EN06.08.11

**Shaped Controlled Synthesis of Core Shell Ir-Ni Nanostructures toward Efficient Oxygen Evolution Electrocatalysis**

Seongeun Park¹, Meital Shviro¹, Marcelo Carmo¹ and Detlef Stolten¹,²; ¹Forschungszentrum Jülich GmbH, Germany; ²RWTH Aachen University, Germany

Electrocatalytic water splitting is a highly efficient and sustainable way for hydrogen production.¹ For the development of electrocatalysts there have been countless studies, however, the choice of electrocatalysts for oxygen evolution reaction (OER) in acidic condition is quite limited by harsh working condition given by the low pH and high overvoltage.² Iridium oxide is by far the most durable and active performance anode catalyst, but its restricted reserves and increasing price requires a decrease in the usage of Iridium. Many approaches have been done, for example, synthesis of multi-metallic catalysts,³ designing of hollow structures, and more. Herein, we developed a facile, in one-pot preparation core-shell Ir-Ni nanoparticles which further etched to form a defined nanoframe structure.

The Ir-Ni nanostructures growth mechanism was studied to control the Ir layer. The as prepared Ir-Ni, and the nanoframe structure were tested as electrocatalysts for OER in acidic conditions. The nanoframe structure showed better activity than the pristine structure with lower onset potential compared with commercial IrO₂.

This work provides a deep insight into the design of bimetallic electrocatalysts with controlled shape and shape dependent catalytic performance.

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EN06.08.12

**Size Effect of Pt Decorations on Oxygen Reduction Reaction Performance for Co@Pd Core-Shell Nanocatalyst—A First-Principles Study**

Haolin Li¹,²², Jyh-Pin Chou¹, Alice Hu¹,¹ and Tsan-Yao Chen²,²; ¹City University of Hong Kong, Hong Kong; ²National Tsing Hua University, Taiwan

The sluggish kinetics of the oxygen reduction reaction (ORR), insufficient durability and the use of high-cost Pt-based catalyst restrict the comprehensive performance as well as the widespread commercialization of fuel cells (FC). For the development of cost-effective catalyst possessing low noble-metal loading, outstanding ORR activity and long-term stability, we propose novel model nanocatalysts with size-variable Pt clusters decorated Co@Pd core-shell configurations use for the fuel cells cathode. In this work, the effects of Pt-cluster size on ORR catalytic activity for Co@Pd core-shell structure were studied via tuning the number of Pt atoms from 3 to 9 (in size of 0.3-1 nm), 16 and 32 (regard as 1 cover layer and 2 cover layers), based on density functional theory (DFT) calculations. Our results show that the size of Ptn (n=3-9, 16 and 32) decoration significantly effects the ORR catalytic activity, the active sites selectivity and the stability of Co@Pd model nanocatalyst, which are attributed to their modified electronic structures giving rise to the strong electronic coupling and unique charge transfer process. The moderate ORR-species (O, O₂, H₂O and OH) adsorption energies on different stable active sites and moderate O₂ dissociation barriers corresponding to the Ptn-cluster model catalysts exhibit the better ORR activity compare to the pure Pt and Pd models. The influence of d-band center shift, strain and ligand effects on the adsorption energies on different surfaces are also discussed. In particular, small platinum-trimer (Pt₃) decorated Co@Pd model nanocatalyst exhibits the most significant enhancement in the ORR kinetics and the predicted structural stability, due to the electron transfer from Pd shell to Pt₃ cluster and then to the adsorbates giving the Pt-trimer a role as ‘charge transfer station’ during the whole ORR process. As a consequence, the ‘charge transfer station’ avoids the valence electrons transfer of adsorption-site Pt atoms to the direct-contact ORR-species, but proceeding the indirect charge transfer between the Pt-neighboring Pd atoms and ORR-species atoms instead, so that reducing the risks of the noble metals oxidation and poisoning. Therefore, the Pt-associated sites are selected spontaneously as the preferred stable active sites, and meanwhile the atomic scale Pt-trimer provides the most number of the optimal active sites. These results are consistent with our latest experimental results.[1] The effect on the ORR performance of our size-tunable clusters from atomic scale to thin film scale decorated on the core-shell models, can be further extented to other ternary or multi-metallic systems with most types of 3d-5d transition metals in the three (core-shell-cluster) regions. This conclusion can be applied to guide the selection of candidate systems and predict the performance of the ORR in studies for the catalyst development toward low cost, excellent activity, high durability and environment-friendly designs.

**Reference:**


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Final Program 1/13/2020 679
Development of New Solid-Solution Alloy Nanoparticles for Three-Way Catalytic Applications Kohei Kusada\textsuperscript{1} and Hiroshi Kitagawa\textsuperscript{2}; \textsuperscript{1}Kyushu University, Japan; \textsuperscript{2}Kyoto University, Japan

The properties of elements are correlated directly with their electronic states. If we can realize a concept of “density-of-states (DOS) engineering”\textsuperscript{1} for the design of materials having the most suitable electronic structure for the target properties, we will be able to make full use of available elements and relieve the resource problems. To freely control an electronic state of a material, the solid-solution alloy is advantageous because its electronic state can be continuously controlled by tuning the compositions and/or combinations of the constituent elements. However, the majority of bulk alloy systems are the phase-separated type under ambient conditions. Recently, we demonstrated that the nanosize effect offers a chance to find a way out of this metallurgical difficulty; that is, we can obtain metal nanoparticles (NPs) having new phases that do not exist in bulk states\textsuperscript{2-9}. As one of the examples, we found that Pd\textsubscript{0.5}Ru\textsubscript{0.5} NPs having a similar electronic structure to Rh exhibit comparable NO\textsubscript{x} reduction activity, even though monometallic Ru or Pd NPs do not show high activity.\textsuperscript{5, 10} However, this alloy structure is destroyed after the reaction due to the nature of the alloy system, resulting in the degradation of catalytic activity. In this work, we designed and synthesized ternary PdRuM alloy systems to develop a stable and highly active NO\textsubscript{x} reduction property. DFT calculations predicted suitable third metal candidates to improve PdRu systems. The designed ternary solid-solution alloy NPs were successfully synthesized and characterized structures by synchrotron X-ray powder diffraction technique and scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy. The designed ternary PdRuM exhibited higher NO\textsubscript{x} reduction than Rh or PdRu NPs and maintained its structure after the reaction.


Distinctive Functionality of Carbon Shells Coated on Metal Nanoparticles for Fuel Cell Applications Namgee Jung\textsuperscript{1}, SungJong Yoo\textsuperscript{2}, Monika Sharma\textsuperscript{1}, Hukwang Sung\textsuperscript{1}, Jeonghee Jang\textsuperscript{1}, Jiho Min\textsuperscript{1} and Youngjin Kim\textsuperscript{1}; \textsuperscript{1}Chungnam National University, Korea (the Republic of); \textsuperscript{2}Korea Institute of Science and Technology, Korea (the Republic of)

Recently, carbon shell-encapsulated metal nanoparticles have been widely studied to enhance the durability of metal catalysts in proton exchange membrane fuel cells (PEMFCs) and anion exchange membrane fuel cells (AEMFCs). However, through the interfacial interaction between the carbon shells and the core metal nanoparticles, the carbon shells can also serve as the main and exclusive active sites to boost electrochemical catalytic activity instead of the core metal nanoparticles. Therefore, we propose the distinctive functionality of carbon shells coated on metal nanoparticles for oxygen reduction reaction (ORR) in AEMFCs. As a model study to prove the application feasibility of the ideal carbon-coated metal system for the ORR, the physical and electrochemical properties of Pd nanoparticles encapsulated with carbon shells are investigated. Furthermore, to practically apply the carbon shell-encapsulated metal nanoparticles to the AEMFC system, less expensive Co nanoparticles coated with carbon shells are intensively studied. From the experimental results, it is concluded that the transition metal core materials can boost the ORR activity of carbon shells and the catalyst durability can be also enhanced due to the protection of the core metal nanoparticles. The present work will provide an interesting strategy for designing new types of carbon-based catalysts for the ORR in AEMFCs.

Mechanochemical Synthesis of Copper Sulfide (Cu\textsubscript{2}S) Impregnated Bi-Functional Organic Polymer and Its Integration with the Flow Reactor for the Production of Dimethylcarbonate from Carbon Dioxide Subodh Kumar; Regional Centre of Advanced Technologies and Materials, Palacky University, Czechia

Continuous accumulation of carbon dioxide in the atmosphere is a threat to the environment and its symptoms are increasingly visible every passing year in the form of impulsive whether changes. Therefore, converting carbon dioxide has turned out to be promising to produce fuel and chemicals. Among the various chemicals synthesized...
from CO₂, dimethylcarbonate (DMC), a simplest organic carbonate, has attracted considerable attention due to its applications as green solvent, fuel additive for octane booster, electrolyte in lithium-ion batteries, and monomer for polycarbonate synthesis etc. Conventionally, DMC is produced either by the reaction of phosgene with methanol or oxidative carbonylation of methanol using CO. The use of phosgene and Co, which are highly toxic and corrosive in nature; makes these processes undesirable. Therefore, much importance has been given to the DMC synthesis from CO₂. In this context, various catalytic systems (homogeneous and heterogeneous) have been reported. However, most of the catalyst afford lower yield of the DMC because of the water generation during the reaction as side product, which shifts reaction equilibrium backwards providing lower yield of DMC. Therefore, the use of dehydrating agent is needed for better conversion. However, these dehydrating agents are difficult to separate from the reaction mixture after the reaction and further increase the cost of the process. Moreover, most of the methods are batch process, which restricts their direct application in industries.

Hence, it is desirable to synthesize DMC directly from the methanol and carbon dioxide in a continuous flow without using any external dehydrating agent. In the present paper, we have synthesized copper sulfide (Cu₂S) impregnated two-dimensional organic polymer (Cu-OP) by simple mechanical mixing of CuCl₂·H₂O, 1, 3, 5-trybenzenecarboxydehyde and 2, 5-diaminobenzene sulfonic acid. Synthesized catalyst was then used to perform the reaction of methanol and carbon dioxide on the high-pressure fixed bed flow reactor without using any dehydrating agent and exhibited excellent catalytic activity, selectivity reusability affording up to 43% yield of DMC. Moreover, we also investigated the effect of various reaction parameters including flow rate, pressure, temperature and catalyst amount on the DMC yield. It was observed that the high pressure and lower flow rate facilitates the reaction at desired temperature. In addition, the presence of -SO₃H and -C=N functional groups on the catalyst surface was found to be crucial, which not only helps in trapping the water formed during the reaction, shifting reaction equilibrium forward direction, but also activate the carbon dioxide, respectively.

EN06.08.16 Coverage, Size and Stability Phenomena of Well-Defined Nanoparticle Model Catalysts Synthesized by Mass-Selected Magnetron Sputtering Niklas Secher, Jakob Kibsgaard and I.B. Chorkendorff; Technical University of Denmark, Denmark

Clusters and nanoparticles of late transition group metals have shown promising catalytic properties for reactions for sustainable fuels and chemicals (Seh et al., “Combining Theory and Experiment in Electrocatalysis: Insights into Materials Design”, Science 2017). Entities in this size range (<10 nm) display an increased number of under-coordinated sites and yield a higher surface area per volume. This is advantageous since under-coordinated sites of these materials have been shown to be highly active towards certain reactions e.g. Au for CO oxidation (Janssens et al., “Insights into the Reactivity of Supported Au Nanoparticles: Combining Theory and Experiments”. Topics in Catalysis, 2007). Furthermore, the increase in surface area allows for a lower volumetric loading of these expensive elements. Altogether, this decreases the cost of using non-abundant materials as catalysts in industrial processes.

However, these small entities are prone to deactivation due to their high surface energy and increased reactivity. Deactivation can be due to particle agglomeration via sintering or due to particle oxidation via the reactive sites (Wallace et al., “The Stabilization of Gold Particles by Surface Defects”, Journal of Molecular Catalysis A, 2005). These deactivation phenomena are known to depend on several catalyst properties such as particle size, coverage and the support material. Therefore, it is vital to control these parameters when studying deactivation phenomena of small entities. However, it is worth considering other factors that might influence catalyst deactivation, recently the edge-edge interparticle distance has received growing attention (Nesselberger et al., “The Effect of Particle Proximity on the Oxygen Reduction Rate of Size-Selected Platinum Clusters”, Nature Materials, 2013). Additionally, one might consider new design strategies to counteract deactivation; it is well known that some supports have anchoring sites that stabilize small entities, but perhaps it is possible to design self-anchoring particles with increased stability.

Using a mass-selected magnetron sputter source it is possible to create well-defined model systems of clusters and nanoparticles, where particle size and coverage are controlled in detail (Roy et al., “Impact of Nanoparticle Size and Lattice Oxygen on Water Oxidation in NiFeOxHy”, Nature Catalysis 2018). Furthermore, a suitable substrate can be chosen to allow a variety of characterization techniques including ISS, XPS and electron microscopy followed by catalytic testing either electrochemically or using micro-reactors for gas phase catalysis.

I will present the results of studying how catalyst design, size, coverage or even the edge-edge inter-particle distance
affects relevant catalytic properties of small entities of Au or Pt for different reactions such as CO oxidation or the Oxygen Reduction Reaction. The well-defined model systems are thoroughly characterized before probing their activity/stability leading to a novel insight into the deactivation that typically occurs when using these materials in commercial catalysts.

EN06.08.17
**Hydrogen Evolution Reaction Electrocatalysis—Electrodeposited Electrodes Based on MoS<sub>2</sub>:** Ramunas Levinas<sup>1</sup>, Natalia Tsyntsaru<sup>1,2</sup> and Henrikas Cesulis<sup>1</sup>; <sup>1</sup>Vilnius University, Faculty of Chemistry and Geosciences, Lithuania; <sup>2</sup>Institute of Applied Physics of ASM, Moldova (the Republic of)

Platinum exhibits the best currently known HER catalytic properties, but its sparsity and price prevent widespread use. Transition metal chalcogenides, especially MoS<sub>2</sub>, have been shown also to catalyze the hydrogen evolution reaction. Sulfur vacancies in the crystal lattice have a low free hydrogen adsorption energy and therefore easily bind to H<sup>+</sup> in the solution. This results in the catalysis of the adsorption (Volmer) step of the hydrogen evolution reaction, and these materials generally exhibit Tafel slopes similar to those of platinum (~ 40 mV/dec). Therefore, transitional metal chalcogenides are currently an area of active research.

Although there are several different methods to obtain MoS<sub>2</sub> materials of various crystallographic structures, in this study, we focused on electrodeposition, which results in amorphous MoS<sub>2</sub>. Previous research has shown that amorphous MoS<sub>2</sub> has excellent HER catalytic activity due to the number of defect sites, which act as active sites for cathodic hydrogen evolution. MoS<sub>2</sub> films were electrodeposited cathodically onto copper wire substrates from a solution of tetrathiomolybdate (MoS<sub>4</sub><sup>2-</sup>) which acts as a common Mo and S ion precursor. EDX compositional measurements have shown that the films have a varying stoichiometry, but are deficient in sulfur – MoS<sub>2-x</sub>. Polarization experiments in acidic media (0.5 M H<sub>2</sub>SO<sub>4</sub>) showed that the deposited films have excellent HER activity, and could reach 10 mA/cm<sup>2</sup> at -0.18 V overpotential.

As a further modification of the process, we attempted to incorporate W (as a substitute to Mo) and Se (as a substitute to S) into the films during electrodeposition. Due to the difference in their atomic radii and electronegativity, this could have an effect on the electrodes’ electrocatalytic properties. This was realized by mixing a small amount of the respective material into the precursor solution during synthesis. Subsequent electrodepositions were carried out in the same way. Compositional analysis showed that a small amount of the heteroatoms were incorporated into the material; stoichiometry, such as MoS<sub>1.91</sub>Se<sub>0.03</sub>, or Mo<sub>0.97</sub>W<sub>0.03</sub>S<sub>1.74</sub>, were obtained. The modified electrodes have Tafel slopes of ~ 40 mV/dec, which shows good HER catalytic activity. Electrochemical impedance spectroscopy was also used to characterize the catalyst-solution interface.

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EN06.08.18
**Controlled Modification of Pt-Ni Nanoalloy Surfaces through a Facile Thermal Annealing Process with Carbon Monoxide** Yiliang Luan<sup>1</sup>, Amar Kumbhar<sup>2</sup>, Can Li<sup>1</sup>, Shaohui Yan<sup>1</sup>, Lihua Zhang<sup>2</sup>, Xiaobo Chen<sup>1</sup>, Bo Zhao<sup>1</sup>, Fan Zhang<sup>1</sup>, Guangwen Zhou<sup>1</sup> and Jiye Fang<sup>1</sup>; <sup>1</sup>SUNY Binghamton, United States; <sup>2</sup>University of North Carolina at Chapel Hill, United States; <sup>3</sup>Brookhaven National Laboratory, United States; <sup>4</sup>Texas Tech University, United States

Heterogeneous catalysts have been used in all fields of chemical processes, such as the petrochemical industry, pharmaceutical fabrication, energy conversion, etc. Among these catalysts, Pt and its alloys play important roles due to their unique electronic structures and resultant special catalytic properties. However, the low abundance of Pt poses a grand challenge on the scalability of Pt-based catalysts. As a catalytic process only occurs on the surface of a catalyst, the surface and sub-surface atomic structures greatly impact the catalytic activity and stability. As a result, surface structure modification is expected as one of the significant routes that can improve the catalytic performance. Herein, we report a facile method of Pt-Ni catalyst surface modification through a thermal annealing process with carbon monoxide (CO). Literally, the Ni atoms on the catalyst surface can be etched with CO by forming a gaseous intermediate, Ni(CO)<sub>4</sub>, at an elevated temperature. This method is utilized to modify the Pt-Ni octahedral and plane-tetrahexahedral (p-THH) catalysts towards oxygen reduction reaction (ORR). EDS mapping and ICP elemental analysis are used to identify the structure evolution. Catalytic results indicate that the ORR activity of Pt-Ni octahedra is improved (E<sub>1/2</sub> increased from 0.8 V to 0.88 V vs. RHE) due to a d-band center shift when Ni is removed from the surface lattice. Simultaneously, it is further determined that the electrocatalytic stability is enhanced (only a 10% decrease in mass activity after 3000 electrochemical potential cycles in HClO<sub>4</sub>)
since most of the vacancy defects formed after removing the Ni atoms are diminished due to the thermal annealing effect. In addition, it is observed that this gaseous manipulation can alter the reaction environments from Ni-dominated ORR to Pt-dominated ORR on the Pt-Ni p-THH catalyst, resulting in a change of onset potential from 0.86 V to 1.0 V vs. RHE.

EN06.08.19
Facet-Dependent Enhanced Catalytic Performance Toward 4-Nitrophenol Reduction Reaction by Shape-Controlled CuNi Octahedral and Cubic Nanocatalysts Can Li1, Bo Zhao2, Yiliang Luan1, Amar Kumbhar3 and Jiye Fang1; 1SUNY Binghamton, United States; 2Texas Tech University, United States; 3University of North Carolina at Chapel Hill, United States

Compared with noble metals, the transition metal nanocatalysts including Cu, Fe, Co, and Ni have received considerable attention in a number of catalytic reactions such as hydrogenation and organic reductions, due to their low cost and high earth-abundance. Like the behavior of noble metals, it is believed that their surface structure heavily governs the catalytic process. However, only a few studies reported the crystal facet-dependent catalytic performance of these transition metal nanocatalysts. In this work, we report a facile colloidal method to fabricate shape-controlled CuNi nanocatalysts. The {111}-terminated CuNi nano-octahedra and {100}-bounded CuNi nanocubes were prepared using a group of synergetic capping ligands in a hot organic solvent system. Borane morpholine was adopted as a reducing agent in both syntheses. It was determined that the {100} surfaces of CuNi nanocrystals could be stabilized by chloride ions released from the precursors, leading to the formation of nanocubes; whereas the CuNi nano-octahedra could be achieved through a thermodynamic control. The resultant CuNi nano-octahedra and nanocubes were further loaded on carbon black, respectively, and reduction of 4-nitrophenol (4-NP) using sodium borohydride (NaBH4) as a reducing reagent on these nanocatalysts at room temperature was investigated. Both the CuNi nano-octahedra and nanocubes exhibited remarkable catalytic activities with high rate constants over mass (k/m). Specifically, the CuNi nanocubes (k/m = 235 s⁻¹●g⁻¹) showed better catalytic performance than CuNi nano-octahedra (k/m = 160 s⁻¹●g⁻¹). Results suggest that 4-NP molecules are adsorbed on the {100} facets of CuNi much easier than on the {111}, indicating a strong facet-dependence due to different surface energies.

EN06.08.20
Ab Initio Mechanism Study and Material Screening of Transition-Metal Dichalcogenides for CO2 Reduction Catalysis Sungwoo Kang1, Suyeon Ju1, Youngho Kang2 and Seungwu Han1; 1Seoul National University, Korea (the Republic of); 2Korea Institute of Materials Science, Korea (the Republic of)

The electrochemical CO2 reduction (CO2R) has received great attention in converting CO2 into valuable chemical products. Recently, it was found experimentally that MoS2 converts CO2 to 1-propanol as a major product. It is also reported that the current density decreases when increasing the portion of edge sites, which indicates that the active sites locate on the basal plane rather than the edges. However, the practical utilization of MoS2 is limited because Faradaic efficiency of CO2R is only about 5% because of the poor selectivity compared to hydrogen evolution reaction (HER).

In this study, we first investigate the mechanism of CO2R at sulfur vacancy (VS) of MoS2 by calculating free energies through ab initio calculations and computational hydrogen electrode model.[1] We identify favorable C1, C2, C3, and C4 pathways starting from *OCHO. HCHO is found to be a key intermediate for CN pathways by coupling of sp² carbons. The predicted products and corresponding onset potentials are in good agreement with the experiment. To discover novel materials with better selectivity than MoS2, we perform computational screening of the catalytic activity of CO2R at atomic defects of various transition-metal dichalcogenides (TMDs). As a result of screening, several TMDs are suggested as promising candidates for CO2R catalysts with good selectivity.


EN06.08.21
Calculation of Catalytic Activity for Alloy Nanoparticles with Experimentally Relevant Sizes by Explicitly Predicting Adsorbate Binding Energy Liang Cao and Tim Mueller; Johns Hopkins University, United States

We present the use of ab-initio calculations to calculate the catalytic activity of alloy nanoparticles with
experimentally relevant sizes (5 nm-10 nm) by explicitly predicting atomic-scale structures and adsorbrates binding energies. We demonstrate our approach using PtNi nanoparticles as catalysts for the oxygen reduction reaction (ORR). We achieve our results by constructing a quaternary Pt-Ni-OH-Vacancy cluster expansion model to explicitly predict OH adsorption energies on nanoparticles of varying shape, size, and atomic structure. These adsorption energies are then used to predict ORR activity through a volcano plot. This model enables us to accurately investigate the catalytic activity of various surface sites with different coordination numbers and local atomic environments. Using this model, we evaluate how different parameters affect the ORR activity of Pt-Ni nanoparticles, including size (2 nm-10 nm), Pt composition (50%-100%), and shape. Through the use of kinetic Monte Carlo simulations we evaluate how the activities of the particles change due to Ni dissolution. Our approach provides theoretical insights into how to tune the structures of alloy nanoparticles to optimize catalytic activity.

EN06.08.22
The Reaction Mechanism for Electrooxidation of CH₄ at the β-NiOOH Surface Hyoseok Kim, Seungjae Kwak and Won Bo Lee; Seoul National University, Korea (the Republic of)

The direct conversion of methane at room temperature is a great challenge to replace the existing Fisher-Tropsch process. However, thermodynamic and kinetic mechanisms have hardly been proposed for the electrochemical reactions of methane. In this study, first-principles calculations were performed on the electrochemical oxidation of methane at β-NiOOH electrode surface. An active oxygen species on the surface play an important role in the CH₄ activation reaction. The effect of the implicit solvation model at constant potential was considered in this calculation. The partial charge of the active oxygen is calculated at each onset potential, and how this change influences on the reaction pathways was investigated. Possible reaction paths were suggested and the reaction rates of the anticipated products were calculated based on the microkinetic models.

EN06.08.23
Rapid and Scalable Synthesis of Cuprous Halide-Derived Copper Nano-Architectures for Selective Electrochemical Reduction of Carbon Dioxide Huan Wang, Edward Matios, Chuanlong Wang and Weiyang Li; Dartmouth College, United States

Electrochemical reduction of carbon dioxide (CO₂) into value-added chemicals and fuels provides a promising pathway for environmental and energy sustainability. Copper (Cu) demonstrates a unique ability to catalyze the electrochemical conversion of CO₂ into valuable multicarbon products. However, developing a rapid, scalable and cost-effective method to synthesize efficient and stable Cu catalysts with high selectivity towards multicarbon products at a low overpotential is still hard to achieve and highly desirable. In this work, we present a facile wet chemistry approach to yield well-defined cuprous halide (CuX, X=Cl, Br or I) microcrystals with different degrees of truncations at edges/vertices, which can be ascribed to the oxidative etching mechanism of halide ions. More importantly, the as-obtained cuprous halides can be electrochemically transformed into varied Cu nano-architectures, thus exhibiting distinct CO₂ reduction behaviors. The Cul-derived Cu nanofibers composed of self-assembled nanoparticles are reported for the first time, which favor the formation of C₂+₃ products at a low overpotential with a particular selectivity towards ethane. In comparison, the Cu nanocubes evolved from CuCl are highly selective towards C₁ products. For CuBr-derived Cu nanodendrites, C₁ products are subject to form at a low overpotential, while C₂+₃ products gradually become dominant with a favorable formation of ethylene when the potential turns more negative. This work explicitly reveals the critical morphology effect of halide-derived Cu nanostructures on the CO₂ product selectivity, and also provides an ideal platform to investigate the structure-property relationship for CO₂ electroreduction.

EN06.08.24
Surface Functionalized Graphene Monolayers—Fabrication, Properties and Chemical Catalysis Devika Mudusu, Koteeswara Reddy Nandanapalli, Han Hee Jung, Jiwon Yoon, Sungwon Lee and Kyung-In Jang; Daegu Gyeongbuk Institute of Science & Technology (DGIST), Korea (the Republic of)

Today, one of the focusing issues in graphene technology is the development of functionalized (doped) graphene monolayers since the pristine graphene is chemically inert, hydrophobic and zero band gap material [1]. As a result, the potential applications of graphene are limited to a few fields of science and technology. Recently, functionalization of graphene layers with different materials has received great attention as an alternative route to tailor the physical properties of graphene layers [2, 3]. The surface functionalized graphene layers find applications
in various fields including the development of paints, corrosion resistive tools, plastics, electronics, flexible devices, LEDs, sensors, energy harvesting devices, wearable devices, bio-imaging, drug-delivery systems [4]. In order to adopt these unique 2-dimensional structures for energy harvesting applications, we have developed surface functionalized graphene monolayers, transferred on to SiO2/Si substrates, by covalent attachment of metal-oxide particles. Influence of covalently attached metal-oxide particles on the surface morphology, carbon hybridization, and electrical properties of graphene monolayers was investigated. Further, the surface functionalized structures were adopted for the development of electrocatalytic devices and then, their water-splitting performance in different electrolyte solutions was studied.

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**EN06.08.25**
**Solution-Based Synthesis of Nanostructured Barium Titanate Thin Films for Enhancement of Photocatalytic Activity**
Adriana Augurio, Qian Guo, Ana Belen Jorge Sobrido and Joe Briscoe; Queen Mary University of London, United Kingdom

Today, the study of novel photocatalyst and photo-electrocatalysts (PEC) for solar energy has gained great attention, aiming to use solar energy to directly split water into hydrogen and oxygen to produce solar fuels. To achieve unassisted water splitting, there is a need for low-cost, stable and high-efficiency PEC systems. Therefore, recent research works have focused on a wide range of materials such as Fe2O3, BiVO4, CuWO4, with bandgaps in the range of 2-2.5 eV, which allow visible light absorption compared to the traditional photocatalyst, TiO2. However, these materials generally present high level of surface or bulk recombination and low carrier mobility. Recently, polarization has emerged as novel strategy in photocatalysis to facilitate charge migration towards different sites, promoting selective redox reactions in the respective locations. Thus, in the present work, we develop and investigate a nanostructured, composite thin film, obtained by combining ferroelectric BaTiO3 with the photocatalyst Fe2O3 in parallel at the nanoscale to improve the photocatalytic performance. The polarization of ferroelectrics can aid effective charge separation while narrow bandgaps and good charge transport properties of the photocatalyst are needed for light absorption and carrier extraction. The BaTiO3 thin films are synthesized by solution-based synthesis, which has been optimized in order to obtain suitable thin films for photocatalyst integration. The morphology of BaTiO3 is investigated by SEM, which confirms the successfully preparation of nanostructured thin films. The crystalline properties of BaTiO3 thin films are analysed by X-ray diffraction (XRD) and Raman spectroscopy, in order to verify the transition to the tetragonal phase, which is responsible to the ferroelectric polarization. In addition, the switching of spontaneous polarization of BaTiO3 thin films by an electric field is investigated by piezoresponse force microscopy (PFM). The optical properties of BaTiO3 thin film, Fe2O3 thin film and BaTiO3/Fe2O3 composite photocatalyst thin film are analysed by UV-vis spectroscopy, which allow the estimation of the optical bandgap. The PEC water splitting performance was measured by using the BaTiO3/Fe2O3 composite photocatalyst thin film as working electrode in a 3-electrode half cell configuration and illuminating with AM 1.5 simulated solar light. The BaTiO3/Fe2O3 composite photocatalyst thin film shows an enhancement of the photocurrent density compared to either the bare BaTiO3 or Fe2O3 thin films, which indicates a promising performance of the ferroelectric/photocatalyst composite thin film in solar energy conversion systems.

**EN06.08.26**
**Electrocatalytic Reduction of Gaseous CO2 to CO on Sn/Cu-Nanofiber-Based Gas Diffusion Electrodes**
Wenbo Jun and Corsin Battaglia; Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Earth-abundant Sn/Cu catalysts are highly selective for the electrocatalytic reduction of CO2 to CO in aqueous electrolyte. However, CO2 mass transport limitations, resulting from the low solubility of CO2 in water, so far limit
the CO partial current density to about 10 mA cm\(^{-2}\).[1-2] To enhance CO\(_2\) mass transport, we developed a process to fabricate Sn/Cu-coated polymer nanofiber networks, and demonstrate the materials as gas diffusion electrodes (GDEs) for electrochemically converting gaseous CO\(_2\) to CO.[3] The Sn/Cu-coated PVDF (Sn/Cu-PVDF) nanofiber GDEs achieve CO faradaic efficiencies (FEs) above 80%, and maintain high CO partial current densities of up to 104 mA cm\(^{-2}\). The Sn/Cu-PVDF GDE remains highly stable during extended operation at -1.0 V for 135 hours, with an average FE for CO of > 85%. These results represent an important step towards an economically viable pathway to CO\(_2\)RR.


**EN06.08.27**
Role of CuFeO\(_2\) Surface Oxygen Vacancies in the Catalytic Activation of CO\(_2\)—A First-Principles Study
Eduardo Schiavo\(^1\), Carmen Baiano\(^1,2\), Ana B. Munoz-Garcia\(^1\) and Michele Pavone\(^1\); \(^1\)University of Naples "Federico II", Italy; \(^2\)Scuola Normale Superiore, Italy

Carbon dioxide is the most abundant greenhouse gas produced as byproduct of fossil fuels exploitation and it is the main responsible for the global climate crisis of current days. The recycling of CO\(_2\) back into chemicals via photo-electrochemical cells represents a viable route to mitigate such problem and great research efforts have been focusing on finding and optimizing functional materials able to catalyze the CO\(_2\) reduction reaction [1, 2]. Here we focus on the copper-iron delafossite oxide, CuFeO\(_2\), which has been proven to have suitable physico-chemical properties to photo-catalyze the carbon dioxide reduction to formic acid [3]. We address the specific electronic and structural features that allow activating the highly stable CO\(_2\) molecule. In particular, by exploiting state-of-the art first principles methods, we dissect the effects of surface oxygen vacancies as well as the different roles of copper and iron on the adsorption and the activation of carbon dioxide at the CuFeO\(_2\) most stable surface. Our results highlight the key role of oxygen defects to allow the CO\(_2\) adsorption and to promote the formation of a radical anion or a carbonate-like adsorbate. While the formation of both intermediates is found to be a downhill process, our data show the second one to be the most probable, paving the route to further mechanistic and kinetic studies on the full pathway for the CO\(_2\) reduction reaction.

**References**


**EN06.08.28**
Direct Evidence of Isolated Single Metal Atoms Incorporated on Laser Ablated Defective Graphene Support for Electrocatalysis
Kishwar Khan and Zhengtang Luo; Hong Kong University of Science & Technology, Hong Kong

2D nanomaterials decorated with single atom catalyst (SACs) are efficient and low-cost electrocatalyst candidate for clean energy technologies. The 2D supports and coordination environments play an important role in optimizing the catalytic activity and reaction mechanism of single atom centers. Here we summarize the suitable synthetic strategies of single atom on graphene supports. We used recently different methods that facilitate the formation of homogeneous structure and enabled the regulation of surrounding atomic of environment center. We recently used new laser ablation techniques for making defects in 2D nanomaterials, and then used it as supporting material to grow SAC for catalytic applications. Here, we elucidate our latest results about SAC on laser ablated 2D defective nanomaterials for different electrochemical reactions, including HER, ORR and OER. Uniting advanced experimental and theoretical approaches including aberration-corrected scanning transmission electron microscopy
EN06.08.29
Unraveling the Mechanistic Link between the Carburization Process and Catalytic Active Sites in the Performance of Mo/HZSM-5 Catalysts for Methane Dehydroaromatization
Sonit Balyan, Manish Kumar, Tuhin S. Khan, Saswata Bhattacharya, Kamal K. Pant and M. Ali Haider; Indian Institute of Technology Delhi, India

Structural evolution of catalytic active sites in methane dehydroaromatization (MDA) reaction in non-oxidative conditions over the Mo/HZSM-5 catalyst is a critical factor in deciding the reactivity and stability of the catalyst as discussed by Khan et al. [J. Phys. Chem. C 2018, 122, 11754-11764]. Molybdenum oxide species, which are anchored on the zeolite framework are transformed into oxycarbide and carbide clusters during the carburization process. The molybdenum carbide clusters anchored on the zeolite framework are considered to be the active sites for MDA. On prolong operation, the clusters tend to migrate and agglomerate at the external zeolite surface, leading to catalyst deactivation. Therefore, a diligent and realistic choice of carburization conditions to control the formation and anchoring of the carbide cluster on the zeolite framework essentially holds the key for obtaining high stability and activity of the catalyst in the MDA process. This thoughtful pretreatment of as-synthesized Mo/HZSM-5 catalyst is demonstrated in two different carburization conditions; using pure methane and a mixture of hydrocarbons representing the natural gas. The effect of carburization process under the two different carburization conditions is monitored with catalyst characterization using the X-ray photoelectron spectroscopy (XPS), which is specifically pointing towards the formation of active molybdenum carbide species under natural gas. In contrast, under pure methane, molybdenum species are observed to transform into an oxycarbide phase. This significant change in the structural evolution of active molybdenum species in the two different carburization conditions reflected into a significant change in the reactivity and deactivation behavior of the Mo/HZSM-5 catalyst. The catalyst treated in natural gas showed a higher benzene formation rate of 3199 nmol/gcat.s as compared to the one treated in pure methane (2280 nmol/gcat.s) after 2 hours time-on-stream. This is correlated with high level of BrØnsted acidity measured for natural gas carburized Mo/HZSM-5 catalyst (1.22 mmol/gcat) as compared to the methane-carburized Mo/HZSM-5 catalyst (0.37 mmol/gcat). TPO, TGA, XPS and Raman analysis of the carburized and spent catalysts further pointed towards lesser coke formation for the catalyst pretreated under natural gas environments as compared to pure methane environment. Experimental results are correlated with ab-initio thermodynamic phase diagrams constructed under reaction conditions to understand the stability of different phases of molybdenum in different hydrocarbon environments. Overall the results are elucidating a microscopic level control on active sites in the MDA reaction by macroscopic process conditions.

EN06.08.30
Oxidation Catalysis with LaFe\(_{x}\)Co\(_{1-x}\)O\(_3\) Perovskites Made by Spray Flame Synthesis
Steven Angel\(^1\), Baris Alkan\(^1\), Chakrapani Kalapu\(^1\), Malte Behrens\(^1,2\), Christof Schulz\(^1,2\) and Hartmut Wiggers\(^1,2\); \(^1\)University of Duisburg-Essen, Germany; \(^2\)CENIDE, Germany

The versatile properties of cobalt based perovskites such as chemical stability in alkaline media and high electron mobility have led to detailed investigations of LaFe\(_{x}\)Co\(_{1-x}\)O\(_3\) concerning their utilization as potential catalysts for replacing costly and low-abundant materials (e.g. RuO\(_2\), IrO\(_2\) and Pt). A specific interest is in electrochemical water splitting / anodic oxygen evolution reaction (OER) in alkaline electrolytes. Typically, the synthesis of the perovskite materials is done in time-consuming wet-chemical batch processes followed by a calcination step. Thus, the particle size of the raw materials increases, affecting the effective number of active sites and hence, the catalytic performance.

We utilized the scalable spray-flame synthesis (SFS) method to directly synthesize high surface area LaFe\(_{x}\)Co\(_{1-x}\)O\(_3\) perovskites. Typically, high surface area nanoparticles with sizes below 10 nm could be produced. Their catalytic activity can be tuned by adjusting the Fe-to-Co ratio. Materials containing 20% Fe performed best for the oxygen evolution reaction (OER) than the samples with lower (10%) and higher (30%) iron substitution concentrations. A potential of 1.53 V vs. RHE was achieved for the OER in alkaline at 10 mA/cm\(^2\), which is lower than the commercial IrO\(_2\) reference material (1.59 V vs. RHE at 10 mA/cm\(^2\)). To the best of our knowledge, our high surface area spray-flame made LaFe\(_{0.2}\)Co\(_{0.8}\)O\(_3\) perovskites belong to the best materials for OER and are comparable to the top reported materials for this reaction (e.g. Ba\(_{0.5}\)Sr\(_{0.5}\)Co\(_{0.8}\)Fe\(_{0.2}\)O\(_{3-q}\)).
EN06.08.31
Atomic Structure of Isolated Single Pt Atoms Anchored on Nanographene Kenji Yamazaki, Yosuke Maehara and Kazutoshi Gohara; Hokkaido University, Japan

In single-atom catalysis, the atomic structure of single metal atoms on a supporting material is one of fundamental questions[1]. We experimentally solved these problems for single Pt atoms dispersed on free-standing graphene using aberration-corrected transmission electron microscopy (TEM) [2]. Graphene was synthesized by the chemical vapor deposition (CVD) method on a copper substrate (purity 99.8%; thickness 25 μm; Alfa Aesar #46365)[3]. We dipped the H₂SO₄ and H₂O₂ mixed solution (H₂SO₄ : H₂O₂ = 3 : 1) to remove the misplaced graphene grown on the back of the Cu substrate. After etching the Cu substrate with 100-mM ammonium peroxodisulfate solution for 4 h, the specimen was rinsed thoroughly with distilled water, and then transferred onto a carbon-supported Cu TEM grid. The graphene was verified as a single layer by electron diffraction. Single Pt atoms were uniformly dispersed on graphene by plasma sputtering method. Sputtering in plasma is well established to form thin films, but this method has also been used to synthesize nanoparticles. Several studies have also attempted to downsize the resulting nanoparticles. In this study, we used this method to disperse single atoms on a substrate. We used an aberration-corrected TEM/STEM (Titan Cubed 60-300, FEI) to verify that the graphene was a single layer and to clarify the atomic arrangements of single Pt atoms. Dispersed single atoms with a size less than 2 Å are clearly discernible in the image of a sputtering time of 1 s. The atom was identified as Pt by energy-dispersive X-ray spectroscopy (EDX), and separation of Pt atoms of 99% was confirmed by measuring the nearest-neighbor distance between Pt atoms. High-resolution imaging using TEM was performed in order to clarify the atomic arrangement of Pt atoms adsorbed on graphene. Although the atomic arrangement above the third layers was hardly realized due to the complicated contrast and atomic migration, typical examples could be clarified. Single Pt atom anchored at the step edge of graphene. The first layer showed a pristine hexagonal lattice, whereas the second layer had a polycrystalline structure, e.g., five- and seven-membered rings. Although this polycrystalline graphene has previously been considered to represent amorphous-like hydrocarbons or contaminations, we revealed the contamination was identified as the aggregation of small islands consisting of several layers of nanographene flakes stacked on a single layer of graphene[4]. The nanographene has a rich area of step edges that serve as anchors and active sites for chemical reactions such as adsorption and catalysis. We reported dense and highly selective formation of single Pt atoms on graphene using nitrogen gas atmosphere during plasma sputtering[5]. We also conducted XPS measurements using the same sample, and observed a large core-level shift for single Pt atoms.

References

EN06.08.32
Modulating the Catalytic Efficiency of Pt-Ni Alloy Nanoparticles and Their Role in Mediating the Oxime Reaction Sarah S. Albalawi¹, Sher Bahadar Khan², Esraa M. Bakhsh² and Sherine O. Obare³; ¹Western Michigan University, United States; ²King Abdulaziz University, Saudi Arabia; ³University of North Carolina at Greensboro, United States

Well-defined catalytic nanoparticles consisting of bimetallic Pt-Ni alloys were prepared with homogeneity and characterized by high-resolution transmission electron microscopy (HRTEM), x-ray photoelectron spectroscopy (XPS), and energy dispersive x-ray spectroscopy (EDS). The effect of the support material on the catalytic activity of the nanoparticles was investigated with the aim of optimizing the catalyst activity. Nickel and platinum supported on silica (SiO₂), graphene oxide (GO), and molybdenum sulfide (MoS₂) with the ratio of the Pt:Ni being 1:1, 1:2, and 2:1 were prepared and their catalytic efficiency was evaluated using a model oxime reaction. The catalysts were optimized to allow the reaction to proceed at ambient temperature and in the aqueous phase. The concentration of each metal ion was determined by employing inductively coupled plasma–optical emission spectroscopy (ICP-OES). The turnover frequency (TOF) was calculated to evaluate the catalytic performance of Pt/Ni@SiO₂, Pt/Ni@GO, and Pt/Ni@MoS₂ toward oximation reactions at 50% and 90% conversion. The TOF of Pt/Ni@MoS₂ was found to be higher than that of Pt@SiO₂ and Pt/Ni@GO.

EN06.08.34
Comparing the Electrochemical Performance of Au and Sn Catalysts on Gas Diffusion Electrodes and Aqueous H-Cells
Sanjana Chandrashekar and Wilson Smith; TU Delft, Netherlands

Carbon dioxide can be electrochemically converted into feedstocks for many industrial processes such as the manufacturing of synthetic fuels and chemicals. In order for this technology to be capable of matching and ultimately supplanting any industrial process, it needs the capability to convert CO₂ at an industrial scale. This means the reaction needs to happen at a fast rate for long periods of time and make products with high selectivity and high energy efficiency. In order to achieve these objectives, the electrocatalysts and electrochemical systems need to be studied while operating at high current densities.
This talk will focus on the structure-functionality relationship between Au, Sn, and bimetallic AuSn catalysts, and their CO₂ reduction performance at high current densities.
X-Ray diffraction (XRD), X-ray photoemission spectroscopy (XPS), and atomic force microscopy (AFM) were used to determine the crystal structure, surface topography and composition of compositionally variant alloy thin films of Au-Sn before and after electrolysis. The electrochemical activity for each bimetallic film was measured in terms of electrode potential/current and product selectivity as a function of applied current density/potential and catalyst composition. To achieve high current density operation (>100mA/cm²), gas diffusion electrode’s (GDE’s) were used as the working electrode in a gas-fed electrolyser.
Finally, the reaction’s activity and selectivity were examined in an aqueous H-cell reactor to compare the performance of the bimetallic catalyst’s with liquid and gas-phase feedstock.
The results of this work provide fundamental insights to reaction mechanisms in aqueous and gas-fed CO₂ electrolyser’s, while also providing a template for assessing electrochemical performance across these two reactor configurations. Electrochemical trends at low current density were found to not always translate to high current density operation, and therefore future work is needed to understand the differences in these two architectures.

EN06.08.35
Structural study on the chemical reactivity of GO regarding oxidative amine coupling reaction
Kazuyuki Takai, Ryutaro Suzuki, Takuya Isaka, Kentaro Tajima and Tomoki Yamashina; Hosei University, Japan

Graphene oxide (GO) having oxygen-containing groups is expected as metal-free and environment-compatible catalyst. The research on GO catalyst progressed [1 - 3], although the detail mechanism for GO catalytic activity is not clear yet. Investigating Graphene Oxide (GO) properties before / after the catalytic reaction is a promising strategy for clarification of the mechanism for GO catalytic activity. Additionally, it is known that removing oxidative debris on GO by base-treatment is important factor to get the higher yield for the following catalytic reaction [1]. In this study, the principle for reactivity of GO is investigated by conducting the oxidative amine coupling reaction of benzylamine (1) to N-benzylidenebenzylamine (2) using baGO and thermally reduced one (rbaGO) as catalysts. baGO-Pristine was obtained by washing GO, synthesized by Hummers method, with NaOH. rbaGO was prepared by reducing baGO at 450°C under Ar gas flow. After the reaction, the reaction media filtered for removing the catalyst was characterized by GC-MS. After the 1st cycle reaction, the recovered catalyst was used as that for the 2nd cycle (baGO-1st cycle, rbaGO-1st cycle). The chemical structure of each catalyst after the reaction was evaluated by XPS (Al Ka), where it was washed with ethanol after the reaction. The atomic ratio O/C of catalyst much decreases after the reduction or 1st cycle reaction and rbaGO shows poor yield, suggesting roles of baGO / rbaGO not as catalyst but as oxidant. However, baGO-1st cycle exhibits the highest yield in spite of C1s spectrum and O/C similar to that of rbaGO and rbaGO-1st cycle, which also indicates no more reduction for rbaGO in the 1st cycle reaction. Taking these results and appearance of nitrogen content after the 1st cycle reaction into consideration, a different mechanism in the 2nd cycle reaction is suggested, where nitrogen incorporated into rbaGO / baGO in the 1st cycle reaction plays an important role for the reactivity. To clarify the most responsible functional groups in rbaGO / baGO for the higher catalytic reactivity in the 2nd cycle reaction, we have derived the amount of nitrogen-containing functional group per 100 mg in each GO sample for the 2nd cycle reaction. By plotting the amount of nitrogen-containing functional group and the GC-yield of the product, the correlation coefficient r is calculated for each functional groups. In particular, the GC-yield tends to increase as Graphitic N (correlation coefficient r = 0.94) and Oxidized N (correlation coefficient r = 0.87) increase. The important roles of those functional groups in the oxidation amine coupling reaction could be explained by the enhancement in the oxygen adsorption ability, which is important to produce O2*- species from ambient oxygen molecules for proceeding the oxidative coupling reaction.

References
EN06.08.37
Meatl Phthalocyanine Precursors to Construct Single Metal Site Electrocatalysts Yang Wang and Yongye Liang; Southern University of Science and Technology, China

Single metal sites embedded in nitrogen doped carbon materials have recently demonstrated superior performance as electrocatalysts for oxygen reduction reaction (ORR), carbon dioxide reduction reaction (CO2RR) and so on. However, it's still a challenge to construct abundant single metal atoms during the high temperature processing due to easy aggregation of metal species. Herein, we present a facile method to construct N-doped carbon with prevalent single metal sites by employing metal phthalocyanine derivatives as metal precursors. First, iron phthalocyanine (FePc) molecules are encapsulated during the synthesis of zeolitic imidazolate frameworks (ZIFs), and the subsequent pyrolysis yields the Fe-N/C materials. Cyano substitution on FePc can facilitate the introduction of phthalocyanine molecules into ZIFs and formation of more active sites in the carbene network, thus affording higher activity for oxygen reduction reaction (ORR) than the FePc counterpart. It is also found that the ORR activities in acidic conditions are closely correlated with the surface Fe-Nx contents. Adding iron salt with cyano substituted FePc can afford a better catalyst with enhanced surface Fe-Nx content, which exhibits high activities with a half-wave potential of 0.910 and 0.811 V versus reversible hydrogen electrode in alkaline and acidic conditions, respectively. Moreover, the catalyst derived from cyano substituted FePc exhibits good activities with a reduction current density of 5.0 mA/cm^2 and a turnover frequency of 0.13 s^-1 and high selectivities with Faradaic efficiency for CO production of around 94% at -0.46 V for carbon dioxide reduction (CO2RR). DFT calculations are conducted that the bulk Fe-Nx sites are superior to the surface Fe-Nx sites with better catalytic stability in CO2RR.

EN06.08.38
Hybridization with Carbon Nanotubes to Enhance CO2 Electroreduction Performance of Metal Phthalocyanines Zhan Jiang and Yongye Liang; Southern University of Science and Technology of China, China

Metal phthalocyanines (MePcs) are interesting molecular catalysts for CO2 electroreduction due to well-defined structural and high turnover frequency (TOF). However, MePcs are semiconducting and have strong intramolecular interactions due to the large \( \pi \) system, which often lead to molecular aggregation on electrodes. As a result, their catalytic performance of MePcs reported in literature could vary significantly and often limited by low current density. Here, we report a carbon nanotube (CNT) hybridization approach and prepare MePcs(Me = Co, Fe and Mn)/CNT hybrids to study the CO2 reduce electrocatalytic performance of MePcs molecular catalyst. MePc/CNT hybrids are synthesized with MePc molecules anchored on the surface of CNTs without noticeable molecular aggregations. Both activities and stabilities of MePc are significantly enhanced by hybridization with carbon nanotubes. The activity of FePc/CNT is slightly less than CoPc/CNT, but it could deliver higher Faradaic efficiencies for CO production over 98% at low overpotentials. In contrast, among the neat molecules, only CoPc shows appreciable activities for CO2 electroreduction. Further, the TOF results indicate that CNTs hybridization is helpful to reveal the intrinsic activities of MePc molecules and deliver higher current densities.

EN06.08.39
Operando Atomic Force Microscopy of Gas Diffusion Electrodes to Understand the Gas/Liquid/Electrode Interface Nathan T. Nesbitt, Thomas Burdyny, Divya Bohra, Sanjana Chandrashekar, Recep Kas and Wilson Smith; Delft University of Technology, Netherlands

Electrochemical conversion of carbon dioxide (CO2) to renewable chemical feedstocks and fuels could play an important role for ending the use of fossil fuels. To amortize equipment costs over large product volumes, commercial applications will require high current density devices. Due to solubility and diffusion limitations of CO2 in liquid electrolytes, this requires electrodes to be near the liquid/gas interface, which is accomplished by the gas diffusion electrode (GDE) cell architecture. In designing such electrodes, the question of where the gas/liquid layer is positioned within the GDE becomes important. For example, it has been suggested that the CO2 reduction reaction occurs at a triple-phase-point, where the gaseous CO2, aqueous protons, and electrons from a solid metal
Electrocatalyst can interact. However, from various literature, it seems more likely that the metal is fully wetted and a two-phase reaction occurs with the CO₂ dissolved in the electrolyte. Likewise, it is unclear whether product gas forms nanobubbles on the electrocatalyst surface, or dissolves into the electrolyte.

Here, we use an electrochemical atomic force microscope (EC-AFM) to make operando measurements of the electrocatalyst surface in a GDE CO₂ reduction cell, while operating at 1, 10, and 100 mA/cm². Using peak-force tapping, we map the topography and nanomechanical information. No nanobubbles or macroscopic bubbles are observed. Comparison with a solid metal foil shows bubble formation on only the macroscopic scale, supporting the idea that gaseous reactants and products interacting with the electrocatalyst are primarily, dissolved in the electrolyte.

SESSION EN06.09: Electrocatalysis I
Session Chairs: Peter Strasser and Maureen Tang
Thursday Morning, December 5, 2019
Sheraton, 2nd Floor, Independence West

8:30 AM EN06.09.02
Understanding the Role of Electrolyte in Electrochemical CO₂ Reduction Reactions Qi Dong, Da He, Chaochao Lang and Dunwei Wang; Boston College, United States

Electrochemical CO₂ reduction has attracted significant attention not only for its technological implications but also for the scientific knowledge it holds. One critical challenge is to suppress the kinetically favored hydrogen evolution reaction in an aqueous electrolyte while achieving high selectivities toward carbonaceous products. Here we report a new way to realize such a goal. Our strategy involves a unique system where the hydrogen formation can be controlled. Such a platform offers the opportunity to study the role of electrolyte component in electrochemical CO₂ reduction, which is critical to the understanding of the reaction mechanisms and the performance matrix. Using Au as a prototypical catalyst, we revealed that the selectivity toward CO can be greatly improved by manipulating the electrolyte properties. It was also found that the overall performance can be significantly influenced by mass transport. The results shed new light on the mechanistic understanding of electrochemical CO₂ reduction, and offered a new way to achieve high selectivities for practical applications.

8:45 AM EN06.09.03
Host-Guest Chemistry Meets Electrocatalysis—Cucurbit[6]uril on a Au Surface as Hybrid System in CO₂ Reduction Andreas Wagner¹, Khoa Ly¹,², Nina Heidary¹,³, István Szabó⁴, Tamás Földes⁴, Khaleel Assaf⁵, Steven Barrow¹,⁶, Kamil Sokolowski¹,⁻, Nikolay Kornienko¹,⁻, Moritz Kuehnel¹,⁶, Edina Rosta¹, Ingo Zebger¹, Werner Nau⁵, Oren A. Scherman¹ and Erwin Reisner¹; ¹University of Cambridge, Department of Chemistry, United Kingdom; ²Technische Universität Dresden, Germany; ³Université de Montréal, Canada; ⁴King's College London, United Kingdom; ⁵Jacobs University Bremen, Germany; ⁶RMIT University, Australia; ⁷Polish Academy of Sciences, Poland; ⁸Swansea University, United Kingdom; ⁹Technische Universität Berlin, Germany

A major challenge in electrocatalysis is the rational control of forming and stabilizing reaction intermediates to guide specific reaction pathways. In this work, we present a model system introducing the concept of surface-bound host-guest chemistry in CO₂ electrocatalysis. The functionalization of pristine gold (Au) with cucurbit[6]uril (CB[6]) nanocavities was studied as a hybrid organic-inorganic model system that utilizes host-guest chemistry to influence heterogeneous electrocatalytic reactions.

The combination of surface-enhanced infrared absorption (SEIRA) spectroscopy and electrocatalytic experiments in conjunction with theoretical calculations support capture and reduction of CO₂ inside the hydrophobic cavity of CB[6] on the gold surface in aqueous KHCO₃ at negative potentials. SEIRA spectroscopic experiments show that the decoration of gold with the supramolecular host CB[6] leads to an increased local CO₂ concentration close to the gold interface. Electrocatalytic CO₂ reduction on a CB[6]-coated gold electrode indicates differences in the specific interactions between CO₂ reduction intermediates within and outside the CB[6] molecular cavity, illustrated by a decrease in CO current density, but almost invariant H₂ production.
Based on the obtained results, design criteria of molecular cavities that allow to overcome current limitations in heterogeneous CO\textsubscript{2} electrocatalysis are discussed. We believe that the methodology and molecular insights in the presented work will provide fruitful basis for future design concepts of molecularly engineered catalytic environments through interfacial host-guest chemistry.

9:00 AM EN06.09.04
Beyond Adsorption in Heterogeneous Electrocatalytic Water Splitting Maureen Tang; Drexel University, United States

It has long been recognized that the reaction rates of the hydrogen oxidation and hydrogen evolution reactions (HOR /HER) are up to 200 times slower in basic than acidic electrolytes, even though the surface intermediate of adsorbed hydrogen is independent of solution pH [1]. One explanation for this difference is a proposed `bifunctional mechanism’, in which slow water dissociation is overcome by mediation of adsorbed hydroxide [2]. We have completed detailed microkinetic models of this pathway for single- and two-site catalysts, and compared these models to single-crystal voltammetry on Pt(110) and transition-metal-doped Pt(111) [3-4]. We find that any chemical dissociation steps result in anomalous trends with potential, and that oxophilicity has no effect on hydrogen coverage or HER/HOR rates. Comparison with experiment strongly indicates that the observed bifunctional mechanism is unrelated to hydroxide binding strength [4].

Our work resolves a long-standing paradox in electrocatalysis and surface science by determining that oxophilicity is not an accurate descriptor for alkaline hydrogen electrocatalysts. Other parameters, such as water orientation and non-covalent interactions, must play a greater role in overall activity. In efforts to identify and measure these parameters, we combine a series of techniques from catalysis, classical electrochemistry, and colloid science. These experiments yield new understanding how the solution-phase double-layer interacts with solid-phase surface structure to govern electrocatalytic activity, thus enabling rational design of next-generation catalytic interfaces [5].


9:15 AM *EN06.09.05
Activity and Selectivity Control in CO\textsubscript{2} Electroreduction—Catalyst Structure, Composition and Electrolyte Effect Beatriz Roldan Cuenya; Fritz Haber Institute of Max Planck Society, Germany

The utilization of fossil fuels as the main energy source gives rise to serious environmental issues, including global warming caused by the continuously increasing level of atmospheric CO\textsubscript{2}. Recently, the electrochemical conversion of CO\textsubscript{2} (CO\textsubscript{2}RR) to chemicals and fuels driven by electricity derived from renewable energy has been recognized as a promising strategy towards sustainable energy.

I will provide examples of recent advances in the development of highly active plasma-modified single crystals, nanostructured thin films and nanoparticle (NP) electrocatalysts (Cu, Ag, Zn, Ag-Sn and Cu-M with M = Co, Zn, Ag, Pd) and how their structure, oxidation state and composition influence their selectivity in CO\textsubscript{2}RR. Additionally, the determining role of the electrolyte in the reaction activity and selectivity will be illustrated by considering the role of different cations and anions (Cs\textsuperscript{+}, Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, I\textsuperscript{−}, Br\textsuperscript{−}, Cl\textsuperscript{−}) in aqueous electrolytes. Finally, the importance of in situ and operando characterization methods (e.g. EC-AFM, Liquid-TEM, XAS, XPS) to gain in depth understanding on the structure- and electrolyte-sensitivity of real CO\textsubscript{2}RR catalysts under working conditions will be demonstrated. Our results are expected to open up new routes for the reutilization of CO\textsubscript{2} through its direct selective conversion into higher value products.

9:45 AM BREAK

10:15 AM *EN06.09.06
CO\textsubscript{2} Reduction Electrocatalysis Edward H. Sargent; University of Toronto, Canada

I will discuss advances in increasing the selectivity, improving the energetic efficiency, and improve the rate (current density) of heterogeneous CO\textsubscript{2} electrocatalysts and systems.
A key challenge in heterogeneous catalysis has been developing technologies that can selectively convert CO$_2$ or CO into short-chain multi-carbon oxygenates. Here, I will show how to improve selectivity to multi-carbon oxygenates by rationally controlling a variety of properties that are intrinsic and extrinsic to the catalyst. First, I will discuss how extrinsic properties such as the electrochemical potential and electrolyte pH impact reactivity on polycrystalline Cu electrodes. By comparing CO and CO$_2$ reduction from similar reactors, we demonstrate that alkaline reaction conditions increase the energy efficiency towards multi-carbon products. Furthermore, we reveal selectivity trends that are common to both CO and CO$_2$ reduction, indicating both the production of oxygenates and the growth of longer carbon chains are favored at lower overpotentials. Next, I will show how proper control of these extrinsic properties combined with increasing the electrode surface area of polycrystalline Cu leads to high selectivity for multi-carbon oxygenates. We demonstrate that by increasing the electrode surface area, nearly 100% selectivity for CO electroreduction to multi-carbon oxygenates is achieved at a very low overpotential of ~200 mV, from a concomitant suppression of the competing hydrogen evolution reaction. Furthermore, we reveal the generalizability of this surface area effect by using a variety of methods to synthesize polycrystalline Cu electrodes of many different morphologies and roughness factors, and comparing their electrocatalytic performance. Finally, I will show how combining all of these design principles with controlling the surface composition, an intrinsic property of the catalyst, leads to improved selectivity for a single multi-carbon oxygenate. Under alkaline reaction conditions, we observed high selectivity for CO reduction to acetaldehyde on CuAg bimetallic electrodes at low overpotentials, reaching a maximum total Faradaic efficiency of >70% and selectivity of >90% on a carbon basis.

It is of both scientific and societal importance to advance the sustainable energy technology that enables the conversion of CO$_2$ into fuels and value-added chemicals *via* cost-effective electrocatalysis. At present, precious metals (*e.g.* Au, Ag, and Pd) exhibit the best catalytic activity for the electrochemical reduction reaction of CO$_2$ (CO$_2$RR) to fuels. However, their high cost and lack of selectivity hamper the wide implementation of the technology. Development of alternative catalysts based on earth-abundant elements (*i.e.*, free of precious group metals (PGM-free)) is therefore highly demanded. In recent years, transition metal (TM=Fe, Co, or Ni) and/or nitrogen (N) doped carbon (denoted as TM-N-C) catalysts have been demonstrated to be capable of catalyzing CO$_2$ reduction to CO with a reasonable activity and amazingly high selectivity. However, knowledge about how the activity and selectivity of TM-N-C electrocatalysts for CO$_2$RR are dependent on their chemical composition, structure, morphology, and synthetic chemistry is seriously lacking. For a rational design of these TM-N-C catalysts, we have performed density functional theory (DFT) calculations to investigate CO$_2$RR on various TM-N$_4$ active sites (TM = Fe, Co, Ni) with different moieties. Specifically, three different TM-N$_4$ moieties are studied, such as the TM-N$_4$ moiety embedded in the graphene basal plane, the porphyrin-like moiety and/or the TM-N$_4$ moiety bridging the edges of two adjacent graphene layers. We calculated the adsorption energies of all the possible chemical species and the activation energies for C-O bond dissociation reactions involved in CO$_2$RR on the active sites. Our DFT calculations predicted that the CO$_2$RR could happen at the proposed active sites under an electrode potential more positive than that for competing hydrogen evolution reaction (HER). Consequently, these TM-N-C catalysts exhibit good selectivity by diminishing parasitic HER. Moreover, the TM-N$_4$ moiety bridging the edges of two adjacent graphene layers was predicted to be capable of breaking the C-O bond efficiently. These theoretical results are in agreement with experimental observations. Furthermore, we investigated how the doping of S would affect the CO$_2$RR on Fe-N-C catalysts. Our DFT calculation reveals that the adjacent S atoms engineering increases the charge density of centered Fe in a Fe-N$_4$ site, and thus predicts that endowing S-modified Fe$^{~}$N$_4$ with lower formation energy barriers for the key COOH* intermediate in CO$_2$RR. These results suggest that adding S into the TM-N-C catalysts is an effective approach to enhance their catalytic activity for CO$_2$RR.
The quest for the design of active and stable (electro)catalysts hinges on the ability to unequivocally identify the reaction mechanism under realistic operating conditions. The past few decades of research have focused on developing a range of spectroscopic and imagining tools to enable the study of the chemical and structural changes at the solid/liquid interface.

In this talk, we will bring the most recent understanding of the surface (electro)chemistry of CO2 on Pt surface. The molecular-level understanding of the interfacial (electro)chemical processes on Pt surfaces under CO2-contained aqueous system by *in situ* surface enhanced infrared spectroscopy (SEIRAS) will be particularly discussed. We will also show the integration of those experimental approaches and density functional theory (DFT) calculation further strengthen the understanding of the reaction mechanism. It will be also demonstrated that the holistic information about the nature of the adsorbed species can provide additional knobs to tune the kinetics of electrochemical reaction, leading further improvements in performance for energy conversion and storage devices.

**11:30 AM EN06.09.10**

*Elucidating the Effects of N-Arylpyridiniums on CO2 Reduction at the Cu/Electrolyte Interface*  
*Vincent J. Ovalle* and *Matthias Waegele,* Boston College, United States

Increasing the selectivity of the electroreduction of carbon dioxide on Cu electrodes for valuable hydrocarbons is a great challenge. A promising approach for improving the product selectivity is through modification of the Cu/electrolyte interface with organic additives. For example, it has been shown that the decoration of the Cu electrode surface with amino acids or polyamide films can enhance the selectivity of ethylene by approximately a factor of two. Recently, it has been reported that addition of N-substituted arylpyridinium salts can greatly alter the product selectivity of the electroreduction of CO2 on Cu electrodes [Han *et al.* *ACS Cent. Sci.* (2017) **3**, 853-859]. Han *et al.* found that the product spectrum sensitively depends on the structure of the added pyridinium cation. For example, 1-(4-tolyl)pyridinium (T-Pyr) increases the Faradaic efficiency of C≥2 products to ≈80% (compared to ≈25% observed for unmodified Cu/electrolyte interface). By contrast, in the presence of 1-(4-pyridyl)pyridinium (P-Pyr), hydrogen is the major product. Although it has been shown that thin films derived from the reduced cation species form on the surface of Cu electrode, the mechanisms of how product selectivity is altered remain poorly understood. To further improve the selectivity of CO2 reduction, mechanistic insights are essential. Herein, using surface enhanced infrared spectroscopy (SEIRS) during the electroreduction of CO2, we reveal the differential impact of T-Pyr and P-Pyr on the properties of the Cu/electrolyte contact. We find that under reduction conditions both cations form thin films that are composed of the reduced dimers of the respective cation. In the presence of T-Pyr, we observe a substantial build-up of solution-phase carbonate at the interface. By contrast, no such increase is observed at the bare Cu and P-Pyr-modified interfaces. These observations demonstrate that, in the presence of T-Pyr, the local pH in the vicinity of the electrode measurably increases. Because a high local pH is known to change the selectivity towards C≥2 products, our measurements suggest that the higher local pH in the presence of T-Pyr is the underlying mechanism of the selectivity changes (compared to bare Cu). We propose that the T-Pyr films impose mass transport limitations that give rise to the observed high local pH. In addition, we find that in the presence of P-Pyr, the CO stretch frequency of surface adsorbed CO is significantly red-shifted by several tens of wavenumbers (with respect to the frequencies observed at the unmodified and T-Pyr-modified electrodes). This observation suggests that that the CO adsorption on Cu is negatively impacted by the presence of this additive, explaining the poor selectivity for hydrocarbons in its presence. We will discuss the implications of these findings for the design of catalytic interfaces with organic thin films.

**11:45 AM EN06.09.11**

*Continuous Production of Pure Liquid Fuel Solutions via Electrocatalytic CO2 Reduction Using Solid-Electrolyte Devices*  
*Haotian Wang,* Rice University, United States

Electrocatalytic CO2 reduction is often carried out in a solution electrolyte such as KHCO3 (aq) for ion conduction. Therefore, liquid products that form are in a mixture with the dissolved salts, requiring energy-intensive downstream separation. Here we report continuous electrocatalytic conversion of CO2 to pure liquid fuel solutions in cells that utilize solid electrolytes, where electrochemically generated cations and anions are combined to form pure product solutions without mixing with other ions. Using a HCOOH-selective (Faradaic efficiencies > 90%) and easily-scaled catalyst at the cathode, we demonstrate production of pure HCOOH solutions with concentrations up to 12 M. We
also show 100-hour continuous and stable generation of 0.1 M HCOOH with negligible degradation in selectivity and activity.

**SESSION EN06.10: Electrocatalysis II**
Session Chairs: Courtney Downes and Yongye Liang
Thursday Afternoon, December 5, 2019
Sheraton, 2nd Floor, Independence West

**1:30 PM EN06.10.01**
**PdPt Alloys for Synergistic CO2 Reduction with Microorganisms—Lessons for Catalyst Development and Integration of Electrochemical and Biological Catalysts**
Andrew B. Wong1,2, Frauke Kracke1, Joseph Gauthier3, Alan Landers1,2, Drew Higgins1,2, Antaeres Antoniuk-Pablant1, Christopher Hahn2, Karen Chan1, Alfred Spormann1,1 and Thomas F. Jaramillo1,2; 1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States; 3Technical University of Denmark, Denmark

The development of the next generation technologies for CO2 reductions benefits from investigating a wide range of approaches in order to move catalytic CO2 reduction towards a path to commercialization. This presentation focuses on lessons learned from the development of a novel PdPt bimetallic catalyst with a ‘nanoclam’ morphology for electrocatalytic CO2 reduction. This presentation will be divided into two parts: study of the electrochemical properties of this catalysts and efforts to use this catalyst synergistically with microorganisms to achieve high selectivity to a single multi-electron reduction product.

In terms of catalyst development, the PdPt nanoclams have a unique tapered morphology that combines high surface area with exposure of numerous undercoordinated sites for CO2 reduction with activity exceeding that of either Pd or Pt for CO2 reduction to formate at - 0.2 V vs RHE. In comparison with bulk Pd, PdPt, and Pt systems, we find that the interplay of multiple trends affects the activity:

1. The PdPt alloy composition offers improved activity by disfavoring hydride intercalation into the lattice
2. The incorporation of Pt affects increases the faradaic efficiency for HER over formate production
3. The nanostructured morphology appears to increase the faradaic efficiency for formate production over HER

This PdPt nanoclam catalyst is uniquely suited to integration with microorganisms owing to its high activity for the formation of 2-electron products from CO2 reduction at a mild overpotential of ~ 0.2 V vs RHE as well as reduced deactivation from CO poisoning. Thus, we have developed a hybrid electrochemical-biological CO2 reduction system in which formate and hydrogen are produced through electrochemical CO2 reduction by PdPt nanoclams. These products are metabolized by methanogens in combination with CO2 to yield ~100% faradaic efficiency to methane. The integration of microbial communities with these nanostructured PdPt catalysts has the potential to combine the best-of-both-worlds from electrochemical and biological systems to achieve a regenerative catalytic system with high-selectivity, high activity, and low overpotential.

**1:45 PM EN06.10.02**
**Single-Source Molecular Precursor Route to Metal Phosphide Nanoparticles and Their Evaluation as Electrocatalysts for Energy Conversion Reactions**
Courtney A. Downes, Kurt M. Van Allsburg, Anne E. Harman-Ware, Renee Happs, Frederick G. Baddour, Daniel A. Ruddy, Susan E. Habas, Jack R. Ferrell and Joshua A. Schaidle; National Renewable Energy Laboratory, United States

The utilization of renewable energy sources to drive electrochemical transformations that allow for the storage of energy in chemical bonds is important for the realization of a more sustainable energy infrastructure. The conversion of abundant small molecules into fuels and/or high-value chemicals driven by renewable electrons is a promising strategy to reduce the reliance on traditional fossil fuels in the transportation and industrial sectors, provide liquid energy carriers for energy storage, and improve grid management. To selectively promote these difficult conversions, electrocatalysts that operate at high rates and efficiencies and low overpotentials are needed. Nanoparticle metal phosphides have emerged as a promising class of electrocatalysts for a variety of energy
conversion reactions. Significant advances in the solution phase synthesis of nanomaterials for energy conversion applications have enabled a high level of control over the size, shape, and composition of nanostructured catalysts, which has revealed the importance of these properties on the observed electrocatalytic performance. In this work, we present a novel and facile approach utilizing air-stable and inexpensive metal triphenylphosphine complexes as single-source molecular precursors to access phase-pure metal phosphide nanoparticles that have controlled stoichiometry, size, and shape. The metal phosphide nanoparticles are evaluated as electrocatalysts for several energy converting reactions and important performance metrics, i.e. faradaic efficiency, overpotential, and product selectivity, are discussed.

2:00 PM EN06.10.03
Multi-Component Electrocatalysts for CO₂ Valorization beyond Conventional Reactivity Yueshen Wu¹,¹, Xu Lu¹,¹, Xiaolei Yuan² and Hailiang Wang¹,¹; ¹Yale University, United States; ²Soochow University, China

Electrochemical CO₂ reduction reactions promise the interconversion of carbon emissions to fuels and value-added chemicals with renewable electricity. Exploration of multi-component electrocatalysts with unconventional reactivity (e.g. uncommon mechanistic pathway, bifunctionality or new product) is not only scientifically interesting, but could also lead to new device-level functionality. As a case in point, we report a new Pb-Pd alloy system for CO₂-to-formate interconversion that enables controllable utilization of alternative energy by integrating the functions of a CO₂ electrolyzer, a liquid fuel container and a fuel cell in one device. The alloy system reversibly restructures its phase, composition, and morphology and thus alters its catalytic properties under controlled electrochemical conditions. Under cathodic conditions, the catalyst is relatively Pb-rich and is active for CO₂-to-formate conversion over a wide potential range; under anodic conditions, it becomes relatively Pd-rich and gains stable catalytic activity for formate-to-CO₂ conversion. The bifunctional activity and superior durability of our Pb-Pd catalyst leads to the first proof-of-concept demonstration of an electrochemical cell that can switch between the CO₂ electrolyzer/formate fuel cell modes with stable operation for twelve days.

2:15 PM *EN06.10.04
Design Considerations for Applied Electrochemical Carbon Dioxide Conversion Catalysts Stafford W. Sheehan; The Air Company, United States

Approaches to make fuel and fine chemicals from carbon dioxide, water, and renewable electricity are being widely researched. One advantage of technologies that can produce chemicals in this manner is their potential for on-site production. This is a key value proposition currently being realized by companies that sell on-site electrochemical hydrogen generators. Translating this value proposition and design feature of water electrolyzers for on-site production of chemicals such as carbon monoxide, formic acid, ethylene, and ethanol requires understanding the unit economics and early-stage markets for small-scale carbon dioxide conversion systems. With an understanding of what an integrated electrochemical carbon dioxide conversion system looks like, specifically capital requirements and balance of plant, the metrics required for carbon dioxide conversion catalysts can be determined. Starting with outlining the real-world requirements for carbon dioxide conversion systems, we will discuss the important design considerations, metrics, and cost factors to define targets for heterogeneous and homogeneous catalysts for carbon dioxide conversion.

2:45 PM BREAK

3:15 PM *EN06.10.05
Towards the Efficient Electrosynthesis of Hydrogen Peroxide and Ammonia on Solid Surfaces Ifan E. Stephens; Imperial College London, United Kingdom

Electrochemical synthesis methods can provide sustainable routes to our most coveted chemicals. In this contribution, I will discuss our recent progress in the heterogeneous electrocatalysis of H₂O₂ and NH₃ production. Both chemicals are currently synthesised in enormous quantities, in large centralised reactors, far from the point-of-consumption. The logistical and safety challenges intrinsic to the transportation of these chemicals set them beyond the reach of many end users. In contrast, their electrochemical synthesis is far more attractive.

Efficient electrochemical H₂O₂ production requires a catalyst that can steer the reaction away from the formation of the most thermodynamically stable product, H₂O. To this end, porphyrin like structures offer advantages over pure
metal structures by lieu of their isolated reactive sites. We emulated the reactivity of porphyrins by producing mercury-based alloys, which demonstrated unprecedented selectivity, activity and stability.1,2 I will provide an overview of the factors controlling H2O2 production, focussing on the role of (i) catalyst structure at the atomic scale (ii) electrode mesostructure and (iii) electrolyte pH. I will also compare results from model rotating ring disk electrode to tests in real electrolytic devices.3

Current ammonia production via the Haber Bosch process requires high pressures, high temperatures and consumes >1% of our current fossil fuel production. To the contrary, nitrogenase in nature catalyses N2 reduction at room temperature and atmospheric pressures. At present, sold electrodes are rather inactive and unselective. The translation of the activity and selectivity of nitrogenase to a solid inorganic surface would enable the efficient on-site on demand synthesis of ammonia, powered by renewable electricity.

While we have made huge progress in the electrocatalysis of H2O2 production, there remains much to be learnt about N2 electroreduction. We recently used quantitative isotopic labelling experiments to provide unequivocal proof that Li-based electrodes are able to reduce N2 to NH3 in non-aqueous electrolytes. Our work provides a solid foundation for further progress, and enables scientists to distinguish false positives from true breakthroughs. Nonetheless, the efficiency we reported is rather low, i.e. there is still ample room for improvement. Drawing insight from the nitrogenase enzyme, I will discuss different avenues towards more efficient N2 reduction.


3:45 PM EN06.10.06
**Lithium-Mediated Nitrogen Reduction to Ammonia at Ambient Conditions** Karthish Manthiram; Massachusetts Institute of Technology, United States

The Haber Bosch process has provided a large-scale method of synthesizing ammonia for a century. The large carbon footprint and process conditions which limit modularity have led to new efforts to uncover routes through which ammonia can be produced at ambient conditions using potential. Lithium-mediated routes have emerged as a set of methods which can lead to high selectivities for ammonia synthesis. We are particularly interested in molecular-level understanding of the kinetics of the cathodic reaction through which the nitrogen triple bond is broken and subsequent nitrogen-hydrogen bonds are formed. We have uncovered the reaction network through which ammonia is produced in competition with hydrogen. Our work has shown the importance of transport in controlling this reaction, providing critical insights that have led to high rates of ammonia synthesis and a path towards future increases in both rates and selectivities.

4:00 PM EN06.10.07
**Bioelectrochemical TiN|FDH Catalyst for CO2 Reduction to HCOOH** Federica Arena1,2, Giorgio Giuffredi1,2, Stefano Donini1, Emilio Parisini1 and Fabio Di Fonzo1; 1Istituto Italiano di Tecnologia, Italy; 2Politecnico di Milano, Italy

Among the many strategies proposed to convert generated CO2 into value-added chemicals and energy carriers, its electrochemical conversion using bioelectrochemical systems (BES)1 is extremely promising. The advantage of this new technology lies in the possibility of exploiting the enzyme properties catalysing the reduction reaction with a high selectivity and specificity toward products with a low overpotential applied, overcoming the limited selectivity problem that affects the usually-employed metallic electrocatalysts for CO2 reduction.
In this work, we present a novel BES, where the NAD-dependent enzyme Formate Dehydrogenase (FDH) from Thiobacillus sp. KNK65MA [2] is expressed by heterologous production in E. coli BL21 (DE3) and deposited on a nanostructured mesoporous support of Titanium Nitride (TiN) realized by Pulsed Laser Deposition. Thanks to PLD, we can realize a nanostructured support with high surface area and tree-like morphology. By optimizing the synthesis parameters, it is possible to obtain a nanostructured, hierarchical support that maximizes the available surface area for catalyst absorption, thanks to its BET area of 169 m² g⁻¹, and enhances the bio-interface between enzyme and inorganic electrode by exposing a high density of binding sites for the FDH. We quantify the amount of immobilized enzymatic catalyst on the nanostructure through standard enzymatic assays, demonstrating that the nanostructuration of the TiN support increases the surface area available for enzyme immobilization, achieving a maximum enzyme adsorption of 59 µg cm⁻² for the BES. The TiN support is firstly characterized electrochemically, to verify its mechanical and chemical stability in the electrolyte solution. Subsequently, the enzymatic electrosynthesis of formic acid from CO₂ is investigated at different applied potentials, showing a productivity for formic acid that ranges from 1.5 to 3.7 mmol mg⁻¹enzyme h⁻¹ according to the applied overpotentials. Finally, post-catalysis characterization of the hybrid system shows that the amorphous nanostructure does not undergo any important modifications in its morphology and composition, thus demonstrating the mechanical stability of the TiN scaffold.

This performance, which is unparalleled in previous studies involving enzymes of the FDH family immobilized on inorganic supports, stems from a combination of are the best for inorganic support-immobilized enzymes of the FDH family, achieved thanks to the high reducing activity of TsFDH and the high contact area offered by the nanostructured TiN support, and demonstrates the feasibility and as well as the potential for a biotechnological device in terms of featuring product specificity and stability.

References


4:15 PM EN06.10.08
Electrochemical Ambient Functionalization of Light Alkanes with Transition Metal Catalysts Chong Liu;
University of California, Los Angeles, United States

The abundant yet widely distributed natural gas resources require efficient conversion of methane into liquid chemicals at ambient conditions with minimal infrastructure support. Here we report an electrochemical catalytic system that is capable to functionalize natural gas at room temperature and ambient pressure. This electricity-driven system is capable to liquifies natural gas under ambient conditions with 90% selectivity and turnover numbers beyond 100,000.

4:30 PM EN06.10.09
Creating Renewable Fuels—Spectroscopy and Energetics of CO₂ Electrolysis Xueli Zheng and Yi Cui; Stanford University, United States

CO₂ electrolysis into value-added fuels represents a renewable-electricity-powered strategy to reduce today’s dependence on conventional fossil fuels, mitigating net CO₂ emissions. However, the sluggish electroreduction of CO₂ (CO₂RR) and water oxidation reaction (WOR) limit the performance for CO₂ electrolysis. In this talk, I will describe my research efforts to develop, understand, and eventually design new catalysts for CO₂RR and WOR using computational materials science, in situ/ex situ synchrotron X-ray spectroscopies, and advances in materials chemistry. First, I will report a concept to modulate electronic structures of active sites for CO₂RR by incorporating the third element in an intimately integrated fashion. Specifically, guided by theoretical predications, we synthesized the designed CuSn₃ alloy and sulfur-modulated-Sn catalysts, and found they selectively produced formate from CO₂RR at low overpotentials. Next, I will describe the development of a room temperature sol-gel technology to produce atomically dispersed metal oxy-hydroxides with high WOR activity. Herein, we showed the gelled FeCoW and NiCoFeP oxy-hydroxide materials has potential industrial applications. In situ/Ex situ X-ray absorption and computational studies, taken together, reveal that the enhanced energetics for CO₂RR and WOR resulted from the ready promotion of favorable local coordination environments and electronic structures.
4:45 PM CLOSING REMARKS

SYMPOSIUM EN07

Materials Science for Efficient Water Splitting
December 2 - December 6, 2019

Symposium Organizers
Maytal Caspary Toroker, Technion-Israel Institute of Technology
Francesc Illas, University of Barcelona
Michele Pavone, University of Napoli Federico II
Guofeng Wang, University of Pittsburgh

* Invited Paper

SESSION EN07.01: Nanocatalysts for Water Splitting
Session Chairs: Maytal Caspary Toroker and Michel Dupuis
Monday Morning, December 2, 2019
Sheraton, 2nd Floor, Liberty BC

8:30 AM *EN07.01.01
HydroGEN—A Consortium Working on Efficient and Advance Water Splitting Materials (AWSM) Huven N. Dinh1, Katie Randolph2, Adam Z. Weber1, Tadashi Ogitsu4, Anthony H. McDaniel5, Richard Boardman6, Elise Fox7, James Vickers2, David Peterson2, Eric L. Miller2 and Ned Stetson2; 1National Renewable Energy Laboratory, United States; 2Department of Energy, United States; 3Lawrence Berkeley National Laboratory, United States; 4Lawrence Livermore National Laboratory, United States; 5Sandia National Laboratories, United States; 6Idaho National Laboratory, United States; 7Savanah River National Laboratory, United States

HydroGEN (https://www.h2awsm.org/) Energy Materials Network (EMN) is an U.S. Department of Energy (DOE) EERE Fuel Cell Technologies Office (FCTO)-funded consortium that aims to accelerate the discovery and development of advanced water splitting materials (AWSM) for sustainable, large-scale hydrogen production, and to more effectively enable the widespread commercialization of hydrogen and fuel cell technologies. This is in line with the H2@Scale initiative (https://www.energy.gov/eere/fuelcells/h2-scale), with the goal to meet U.S. DOE’s ultimate production cost target of $2/kg H2. HydroGEN EMN is a six national laboratories consortium comprises National Renewable Energy Laboratory (NREL) - lead, Lawrence Berkeley National Laboratory (LBNL), Sandia National Laboratory (SNL), Lawrence Livermore National Laboratory (LLNL), Idaho National Laboratory (INL), and Savannah River National Laboratory (SRNL).

The HydroGEN Consortium offers more than 80 materials capabilities nodes to help address RD&D challenges in efficiency, durability and cost. The capabilities span computational tools and modeling, materials synthesis, characterization, process manufacturing and scale-up, and analysis. Detailed descriptions of all the HydroGEN nodes are available in a searchable format on the HydroGEN website (https://www.h2awsm.org/capabilities), including information such as the host National Lab, the capability experts, and a synopsis of the node’s unique aspects and capability bounds. By design, the nodes are cross-cutting, and any given node may be useful for one or several advanced water splitting (AWS) technologies. Leveraging the HydroGEN Consortium’s leading technical experts and extensive collection of unique capabilities is expected to help advance all the advance water splitting technologies, including advanced electrolysis (low and high temperature), photoelectrochemical (PEC) and solar thermochemical (STCH) routes which includes hybridized thermochemical and electrolysis approaches to water...
This presentation will provide an overview of the HydroGEN EMN consortium and highlight some water splitting materials projects. These highlights will include theory and experimental approaches for understanding and characterizing water splitting materials. HydroGEN looks forward to growing its community of industry, university and laboratory collaborators that can partner with member-laboratory experts by way of CRADAs and potential future FOAs.

9:00 AM EN07.01.02
Monolayer MoS2 with Better Hydrogen Evolution Catalysis Than Pt
Guoqing Li; North Carolina State University, United States

The development of low-cost high-performance catalysts for hydrogen production via water splitting stands as a key step towards addressing modern energy and environment challenges. We demonstrate a strategy to enable earth-abundant MoS2—a better catalyst than Pt, the best catalyst to date but too precious to be practically useful, for the hydrogen evolution reaction (HER) of water. The strategy is developed by leveraging on new fundamental understanding for the HER catalysis of MoS2. We find that substrates can affect the catalytic activity of MoS2 by forming an interfacial tunneling barrier with MoS2 and also modifying the chemical nature of MoS2 through charge transfer. As a result, we achieve excellent catalytic performance at the monolayer MoS2 films with optimal densities (7-10%) of sulfur vacancy by using substrates that are able to form low interfacial tunneling barriers and transfer electrons to MoS2, such as Ti. The catalytic performance of monolayer MoS2 films may be further improved by crumpling the films on Ti-coated flexible substrates because the crumpling gives rise to compressive strain in MoS2 that may lower the Tafel slope although generates no obvious effect on the exchange current density. The better-than-Pt performance of MoS2 is remarkably stable with no degradation after continuous reaction for more than two months. This work provides a viable solution for the challenge of hydrogen evolution from water and paves the way towards the utilization of hydrogen energy.

9:15 AM EN07.01.03
Highly Efficient Overall Water Splitting in Acid with Metal Nanosheets
Dongshuang Wu, Kohei Kusada and Hiroshi Kitagawa; Kyoto University, Japan

Water is the only available fossil-free source of hydrogen. Splitting water electrochemically is among the most commonly used techniques, however, it accounts for only 4% of global hydrogen production, predominately because of the high cost and low performance of catalysts promoting the oxygen evolution reaction (OER) [1]. Currently, only Ir oxides show moderate stability for OER in acid but still require high overpotentials. In contrast, Ru is the most active OER catalyst and is nearly 5–16 times cheaper than Ir these five years, however, Ru has a serious degradation problem [2]. Here, we report a highly efficient catalyst in acid, that is, solid-solution RuIr nanosized-coral (RuIr-NC) consisting of 3 nm-thick sheets with only 6 at% Ir. Among OER catalysts, RuIr-NC shows the highest mass/intrinsic activity and unprecedented stability (Figure 1). An electrolyzer using RuIr-NC as both electrodes can reach 10 mA cm\(^{-2}\) at 1.485 V for 120 h without noticeable degradation, which outperforms known systems. This electrolyzer is also significantly less expensive than the commercial IrOx and Pt system. Operando spectroscopy and atomic-resolution electron spectroscopy indicate the high-performance results from the ability of the unique facets of RuIr-NC to resist the formation of dissolvable metal oxides and to transform ephemeral Ru into a long-lived catalyst.

9:30 AM EN07.01.04
Importance of Interfacial Band Structure between the Substrate and Mn3O4 Nanocatalysts During Electrochemical Water Oxidation
Moo Young Lee, Heonjin Ha and Ki Tae Nam; Seoul National University, Korea (the Republic of)

Inspired from the Mn4CaO5 cluster in natural Photosystem II, attempts to replace conventional precious metal based electrocatalysts for oxygen evolution reaction (OER) with Mn-based ones have been intensively conducted. Recently, we successfully synthesized uniform and assembled Mn3O4 nanoparticles (NPs) with superior OER activity to conventional bulk Mn oxides, and revealed highly stabilized Mn(III) species on the surface and different OER mechanism from the conventional ones. Using our unique NPs as a structural platform, we have been now conducting the detailed mechanistic investigations such as how the surface of our NPs changes and how the electrons transfer throughout our NPs during OER.
In this regard, we strongly believe that understanding and controlling the charge transfer during OER is not only helpful in comprehending the reaction mechanism but also important in establishing rational strategies of catalysts design. From the previous literature, we think that the overall charge transfer processes in the film-type OER catalysts can be categorized into three transfer pathways: the electrons should transfer through (i) electrolyte-catalysts interface, (ii) inner catalysts, and (iii) catalysts-substrate interface. Among the three pathways, the importance of the charge transfer at the catalysts-substrate interface has not been investigated, that is, there is a lack of interpretation on the interfacial effects between the catalysts and the substrate.

In this study, we discovered the importance of interfacial band structure between the substrate and Mn$_3$O$_4$ NPs for OER, which has not considered in electrocatalytic systems so far. We designed the band structure model of the catalysts-substrate interface and explained the substrate dependent OER activity of Mn$_3$O$_4$ NPs. Moreover, we improved the OER activity of Mn$_3$O$_4$ NPs by introducing the metal interlayer with a proper band structure. We further investigated substrate dependent impedance analysis, resulting in the same tendency to the expectation from our interfacial band structure model.

9:45 AM BREAK

10:15 AM *EN07.01.05
Quantum-Mechanical Embedding Methods for Surface Catalysis Florian Libisch; Technische Universität Wien, Austria

The charge transfer reactions upon dissociative absorption of O2 on metal surfaces is critical for many catalytic processes, yet poses a challenging problem for state-of-the-art ab-initio theoretical modeling. For example, the experimentally observed activation barrier for O2 dissociation on Al (111) is not captured by conventional density functional theory. However, accurate wavefunction-based methods that are well suited to handle the multireference character of the charge transfer state are ill suited to describe extended metal surfaces. Embedding methods offer a way forward, by combining highly accurate wave-function based approaches at the absorption site with an environment described by density functional theory. In the case of O2 on Al(111), such an approach naturally yields an adiabatic barrier [1]. I review our recent advances and challenges in solving catalytic problems using embedding methods, including the build-up of six-dimensional potential energy surface (PES) suited for quasi-classical trajectory calculations [2], projection-based approaches that enable freeze-thaw cycles, and the extension to high-level methods such as Quantum Monte Carlo or Coupled Cluster that can treat periodic boundary conditions.


10:45 AM EN07.01.06
Stacks of Highly-Ordered Nanowire Arrays Achieve Ultra-High Mass Activity for Oxygen Evolution Reaction and Efficient Transportation of Evolved Oxygen Ye Ji Kim and Yeon Sik Jung; KAIST, Korea (the Republic of)

Although hydrogen is the most abundant element in the universe and can be used as a fuel with zero carbon emissions, its economic and stable production still remain as an important issue. One of the promising routes of H$_2$ production is polymer electrolyte membrane water electrolysis (PEMWE), which require noble metal electrocatalysts (e.g., Pt, Ir, Ru) for efficient oxygen evolution reaction (OER). However, to reduce the high capital expense resulting from the high loading of noble metal electrocatalysts, their electrochemically active surface area (ECSA) and specific activity need to be maximized. Here, we suggest woodpile-structured Ir electrocatalysts, consisting of 3-dimensional (3D) stacks of highly-ordered nanowire building blocks, as a novel catalyst structure to markedly improve mass activity compared to conventional nanoparticle-based catalysts. We show that the 3D Ir nanowire stack can be controllably fabricated via solvent-assisted nanotransfer printing (S-nTP). The woodpile-structured Ir electrocatalysts fulfill simultaneously (1) a large electrochemically active surface area, (2) long-range connectivity of building blocks for high electronic conductivity, (3) well-defined pore structures for highly efficient transport of evolved gas species, and (4) extensive geometric controllability for maximization of catalytic performances. With these aspects, Woodpile-structured Ir thin film achieves a high mass activity of 3.7 A/mg (at 1.5 V vs RHE) in half cell and 140 A/mg (at 1.8 V) in single cell, which is ~36 times higher than that of the state-of-the-art commercial Ir nanoparticle catalyst. Based on the advantages from structural engineering, OER mass activity over 80% of its initial values was
achieved during more than 500 repeating chronoamperometry cycles. Furthermore, in order to clarify the substantially improved surface specific activity and mass activity of OER electrode, we performed systematic analysis on the effect of a facile escape of evolved O2 gas bubbles with a systematic control of the 3D geometry. Although there is no experimental demonstration, previous studies suggested possibility for increase in the specific activity due to the facilitated mass transport. Our S-nTP technology enables extensive control of the 3D geometry (e.g. parallel vs. perpendicular stacks) without changing other factors related to catalytic activities such as physiochemical characteristics and ECSA. Systematic tuning of 3D geometry and nanowire building blocks revealed that O2 bubble transport is the key limiting step in the OER catalysts, providing practical design rules for more efficient OER electrode in PEMWE.

11:00 AM EN07.01.07
Zipping Up Ni-Fe Hydroxide-Coated Hematite Nanowires—A Citrate-Chelating Strategy Promotes Photoelectrochemical Water Splitting
Tianyu Liu1, Mingyang Li2, Yexiang Tong2 and Yat Li1; 1University of California, Santa Cruz, United States; 2Sun Yat-sen University, China

Oxygen evolution reaction (OER) catalyst coatings improve the photoelectrochemical (PEC) water splitting performance of photoanodes via facilitating charge transfer across electrode/electrolyte interfaces and passivating surface hole-trap states. Unfortunately, the occurrence of interface segregation between photoanodes and their OER coatings often impedes fast charge transport and therefore, hinders the performance enhancement. This presentation will introduce a citrate-assisted strategy to mitigate the challenge on the interface quality. We discover that sodium citrate, a molecular linker chelating both hematite (α-Fe2O3) nanowires and Ni-Fe hydroxide [NiFe(OH)x] OER catalyst overlayers, results in seamless, conformal, and pinhole-free coatings. Such the high-quality photoanode/OER catalyst interfaces enable the hematite nanowire photoanode to achieve an early turn-on potential of 0.53 V vs. reversible hydrogen electrode, corresponding to an ultralow OER overpotential of 0.13 V. The turn-on potential is approximately 50% lower than those of the state-of-the-art hematite photoanodes encapsulated in transition-metal-oxide OER catalysts. The overall characterization results on morphologies and photoelectrochemical activities presented in this presentation will not only provide guidelines to experimentally design and prepare high-performance photoelectrodes, but also inspire theoretical multiscale models to fully reveal the benefits of molecule-zipped electrode/catalyst interfaces towards efficient and cost-effective water splitting.

11:15 AM EN07.01.08
Solution-Based Growth of ZnO@ZIF-8 Core-Shell Nanowires-MOF for Efficient Photoelectrochemical Water Splitting
Alejandro G. Galan, Andrew Gallant, Del Atkinson and Dagou Zeze; Durham University, United Kingdom

The search for new materials functionalities has led to development of many different types of composite materials that bring enhanced benefits from the synthetic combination of different materials properties arising from their chemical and structural characteristics.

The evolution of nanomaterials over the last few decades has prompted widespread research on their integration into a range of applications resulting from their outstanding physical, optical and electric properties. Nanowires (NWs) have been at forefront of these developments due to the variety of NW materials, especially semiconductors, highly controllable growth coupled with the large surface to volume ratio and the high aspect ratio. ZnO in particular is highly researched due to its wide band gap (3.37 eV) and high exciton binding energy (60 meV) that confers interesting piezoelectric and optoelectronic properties. In recent years, research interest in metal-organic frameworks (MOFs) has developed rapidly. MOFs are a zeolite-like nanomaterial that have been extensively studied due to their remarkably high surface area, enabling catalytic and gas storage properties. MOFs are reticular nanomaterials formed by transition metal cations coordinated by multidentate organic linkers. This combination results in a crystalline material with a flexible structure that can be tuned accordingly to the organic linker chosen. Among the many existent MOF families, the zeolitic imidazolate frameworks (ZIF) are one of the most researched because of their exceptional thermal and chemical stability. ZIF-8 is a standout MOF comprised of zinc as transition metal nuclei and imidazolate linkers as the coordinating agent.

Here, these different forms of nanoscale materials prompted the idea for synergetic combination to create novel nanocomposite materials that exploit the individual outstanding properties, in this case for ultimate application in hydrogen production. In this work, the idea is the realisation of the integration of ZnO NWs and ZIF-8 to form a
core-shell structure in which ZnO is the core and ZIF-8 is the shell around it (ZnO@ZIF-8) via a low-cost and fast production processes. The ZnO NWs are grown through a typically used chemical bath deposition method while the ZIF-8 shell is grown by surface conversion of the NWs using spin coating of a methanol solution containing the imidazole linker. The cheap and easy route to grow the core-shell structure through this process is remarkable, especially considering that the most commonly used alternative is a hydrothermal growth that requires the use of a pressure vessel, water/dimethylformamide mixtures and long reaction times. In our case, only few droplets of a methanol solution are required to obtain comparable results.

This work presents the structural analysis and the optoelectronic characterisation of these nanocomposite materials and aims to show the first results using ZnO@ZIF-8 structures as a photoanode for the photoelectrocatalytic (PEC) water splitting of water. Electron microscopy and x-ray analysis are used to study the structure and voltammetry and optical methods are sued to study the electronic properties. The effect of different coating conditions are compared to demonstrate the control over the growth of the MOF shell in relation to thickness and the long-range homogeneity. It is shown that the shell thickness is a critical factor that can directly influence the performance of the photoanode by controlling the electrolyte diffusion time to the ZnO NW core. The effectiveness of the core-shell structure as photoanode is compared to as-grown ZnO NWs. The PEC tests also show that the presence of the shell in the core-shell structure passivates the surface states of the ZnO core, improving its stability over time, and protecting it from photocorrosion. This in turn results in an improved photocurrent density and better durability, meaning that the shell improves both the performance and lifetime of the photoanode.

11:30 AM EN07.01.09
Coupling Interface Constructions of 2D Nanosheet Arrays/FeNi Heterostructures for Efficient Electrochemical Water Splitting Qian Xiang, Yi Wu, Wenlong Chen, Fan Li, Tao Deng and Jianbo Wu; Shanghai Jiao Tong University, China

Water splitting is considered as a pollution-free and efficient solution to produce hydrogen energy. Low-cost and efficient electrocatalysts for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) are needed. Recently, chemical vapor deposition is used as an effective approach to gain high-quality MoS2 nanosheets (NSs), which possess excellent performance for water splitting comparable to platinum. Herein, MoS2 NSs grown vertically on FeNi substrates are obtained with in situ growth of Fe5Ni4S8 (FNS) at the interface during the synthesis of MoS2. The synthesized MoS2/FNS/FeNi foam exhibits only 120 mV at 10 mA cm−2 for HER and exceptionally low overpotential of 204 mV to attain the same current density for OER. Density functional theory calculations further reveal that the constructed coupling interface between MoS2 and FNS facilitates the absorption of H atoms and OH groups, consequently enhancing the performances of HER and OER. Layered double hydroxide (LDH) has also been widely applied to electrocatalysis for water splitting, especially toward the OER, owing to its flexible layered structure and multifunctionality. Herein, FeNi LDH nanosheet arrays are directly synthesized on various metal foils by a facile hydrothermal method. Compared with single Fe or Ni substrates, the obtained FeNi LDH/FeNi foil exhibited an ultrasmall onset overpotential of ~90 mV, high catalytic activity (overpotential of 130 mV @ 10 mA/cm²), and durable stability in 0.1 M KOH electrolyte. We also demonstrate, by utilizing density functional theory calculations, that the growth of the hydroxide interfacial layer between LDH and FeNi foil makes the LDH possess more favorable adsorption to the OH intermediate during OER than the pure LDH. This reveals that the vertical FeNi LDH arrays on the FeNi alloy substrate are prone to be an efficient catalyst toward water splitting. These newly developed synthesis of vertical grown nanosheets arrays on the FeNi substrates with low overpotentials and high performance strongly demonstrated the potential applications of 2D nanosheet arrays electrode for electrocatalysis, especially for high access of ion or gas molecule as well as excellent electron and ion conductivity. The findings in this work could impact the design and fabrication of 2D nanosheet arrays heterostructures electrodes for the application of catalysis, environmental science, and surface reaction.

References:
1:30 PM *EN07.02.01
Identifying the Limiting Processes at Electrochemical Interfaces—From Experimental Data to Multiscale Modeling
Kiran George, Matthijs van Berkel, Xueqing Zhang, Vivek Sinha, Rochan Sinha, Yihui Zhao, Aafke Bronneberg and Anja Bieberle-Hütter; DIFFER, Netherlands

Electrochemical interfaces are the heart of many alternative, sustainable energy applications. They determine the efficiency and the overall performance. However, in most cases we do not know which processes take place at the interface and which processes are limiting the performance. Experimental electrochemical measurement methods cannot measure mechanisms directly; measuring intermediate species is rather challenging [1,2]. Analysis methods, such as equivalent circuit fitting for electrochemical impedance data, do not allow to link the electrochemistry directly to the measured data. Modeling of these interfaces is a multiscale challenge as discussed in [3] and is still in its infancy.

In this talk, we introduce the audience to this dilemma with a case study on water oxidation in photo-electrochemical water splitting. We will discuss our recent experimental results on metal oxide (Fe₂O₃, WO₃) – electrolyte interfaces [4-7]; in particular, we will discuss electrochemical and operando infrared spectroscopy data in the field of water splitting. Based on these studies, we will show the limitations of experimental studies in analyzing the limiting processes at the interface. We then introduce our new multiscale modeling approach that allows simulating electrochemical data directly from an electrochemical model [8,9]. We use a combination of atomistic and microkinetic modeling. We will show our approach step by step and will present simulated, electrochemical data, such as current-voltage curves and electrochemical impedance spectra. In addition, we will show surface coverage plots which are experimentally not available and will compare the simulated, electrochemical data to the experimental data. Furthermore, we will introduce kinetic Monte Carlo simulations to complement and extend the current multi-scale modeling approach. Our new multiscale modeling approach is generic and can be used for other electrochemical interfaces, such as those in fuel cells, electrolyzers, or batteries.


2:00 PM EN07.02.02
The Role of Overlayers on Water Splitting Catalysis
Maytal Caspary Toroker; Technion-Israel Institute of Technology, Israel

Understanding the role of an overlayer material on a catalyst is crucial for improving catalytic activity. hematite (α-Fe₂O₃) is a widely studied catalyst commonly used for solar water splitting. It was found experimentally that the water splitting efficiency with α-Fe₂O₃ was enhanced by deposition of an α-Al₂O₃ overlayer. In order to understand the origin of this improvement, we perform first-principles calculations with density functional theory + U on the α-Fe₂O₃(0001) surface with an α-Al₂O₃surface overlayer. In agreement with experiment, we find that α-Al₂O₃ coverage decreases the overpotential required for water oxidation on α-Fe₂O₃. We explain this improvement through the decrease in the work function of α-Fe₂O₃ upon α-Al₂O₃ coverage that aids in extracting electrons during the water oxidation reaction. We suggest that selecting an overlayer with a smaller work function than that of the catalyst as a strategy for future development of better catalysts.
Anodic Instability of the SrIrO3 Water Splitting Catalyst—In Situ Microscopy and Electrolyte Variation Studies

Andrew Akbashev1,2 and William C. Chueh1,2; 1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States

Structural instability of highly active oxide catalysts during electrochemical water splitting poses a significant challenge on the way to their implementation. The structural, morphological and electronic changes in materials under oxidizing conditions largely determine the resulting catalyst’s integrity at the solid-electrolyte interface. In some cases, the structural evolution of materials can be driven or accompanied by the dissolution and/or precipitation processes that are controlled by the electrolyte formulation and pH. Providing insight into the degradation mechanisms is crucial for distinguishing and classifying possible pathways and factors affecting the degradation kinetics.

In our work we study strontium iridate (SrIrO3) that, while being among the most active catalysts reported so far, exhibits structural instability during the oxygen evolution reaction. For quantitative analysis of degradation, we use SrIrO3 epitaxial thin films that have an easily characterizable surface with well-defined step terraces. We perform microscopic studies of the degradation process of SrIrO3 via a combination of in situatomic force microscopy (AFM), ex situcharacterization techniques (XPS, XRD, TEM) and variation in the electrolyte composition. In our in situAFM experiments we built a three-electrode flow cell that enables a high flux and efficient replenishing of the electrolyte, which allow us to reach high anodic potentials and reaction currents above those typically used to assess materials stability (over 10 mA/cm²). By enabling a reference height during in situelectrochemical AFM, we track morphological evolution and quantify the dissolution rate of SrIrO3. We demonstrate that the degradation of SrIrO3 catalyst follows different pathways in acidic and basic electrolytes. Furthermore, we found specific electrolyte formulations that can suppress the degradation of SrIrO3 and impede the kinetics of its anodic dissolution.

Structure Predictions in Wet Environments for Ethanol and Water Adsorption on Anatase TiO2 (101) Surfaces

Giuseppe Fisicaro1, Simona Filice1, Silvia Scalese1, Giuseppe Compagnini2, Riccardo Reitano2, Ioannis Deretzis1, Luigi Genovese3, Stefan Goedecker4 and Antonino La Magna1; 1CNR Institute for Microelectronics and Microsystems, Italy; 2Dipartimento di Scienze Chimiche, Università di Catania, Italy; 3Dipartimento di Fisica e Astronomia, Università di Catania, Italy; 4Laboratoire de simulation atomistique (L_Sim), France; 5Department of Physics, University of Basel, Switzerland

Titanium dioxide exhibits superior photocatalytic properties, mainly occurring in liquid environments through molecular adsorptions and dissociations at the solid/liquid interface. The presence of these wet environments is often neglected when performing ab-initio calculations for the interaction between the adsorbed molecules and the TiO2 surface. In this study we consider two solvents, i.e. water and ethanol, and show that the proper inclusion of the wet environment in the methodological scheme is fundamental for obtaining reliable results. Our calculations are based on structure predictions at a density functional theory level for molecules interacting with the anatase TiO2 (101) surface under both vacuum and wet conditions. A soft-sphere implicit solvation model is used to describe the polar character of the two solvents. The integration of ab-initio structure predictions and continuum modelling for the solvent allows to tackle the various scales of a solid/liquid interface with a reduced computational cost. As a result, we find that surface oxygen vacancies become energetically favorable with respect to subsurface vacancies at the solid/liquid interface. Ethanol molecules are able to strongly passivate these vacancies, whereas water molecules only weakly interact with the (101) surface, allowing the coexistence of surface vacancy defects and adsorbed species. Infrared and photoluminescence spectra of anatase nanoparticles exposing predominantly (101) surfaces dispersed in water and ethanol support the predicted molecular-surface interactions, validating the whole computational paradigm. The combined analysis allows for a better interpretation of TiO2 processes in wet environments based on improved computational models with implicit solvation features.

Formation of Polarons—Their Electronic Structures and Effects in Metal-Oxide-Photoelectrocatalysts: α-Fe2O3 and BiVO4

Hori Pada Sarker1, Wolfram Jaegermann2 and Muhammad N. Huda1; 1The University of Texas at Arlington, United States; 2TU Darmstadt, Germany
Production of H₂ from water splitting via photo-electrochemical process is one of the most talked about potential green technologies. The key material for this technology is photo-electro-catalyst. These materials are required to absorb sunlight, excite and transport charge carriers efficiently, and thereby split water molecule at the liquid-semiconductor interface. Metal-oxides are thought to be the most stable materials under the intense interfacial reactive conditions. Despite some of the metal-oxides have near-suitable bandgap, the overall solar to hydrogen generation efficiencies by water splitting are not as high as expected. One of the reasons for this deficient efficiency is attributed to the poor transport properties in metal-oxides, especially in the 3d transition metal-oxides. In this presentation, two representative metal-oxides photo-catalysts will be considered, α-Fe₂O₃ and BiVO₄. Despite being efficient solar absorber materials, these have poor charge transport properties. From detail electronic structure calculations, polaronic states of these oxides will be depicted. In addition, it will be shown that how these polaronic states affect not only the transport properties but also the open circuit voltages, Vₜ. We will also discuss how well these computational results compares with the recent experimental outcome. The work of MNH is supported by National Science Foundation, grant #1609811. Computations were performed on Texas Advanced Computing Center.

3:00 PM BREAK

3:30 PM *EN07.02.06

Recent Method and Application Advances in Multiscale Characterization of Carrier Transport in Materials for Water Splitting, Such as Cation- and Anion-Doped Bismuth Vanadate: Michel Dupuis¹, Vinawan Pasumarthi¹, Pavan Kumar Behara¹, Tai Feng Liu¹,³ and Can Li¹,³; ¹University at Buffalo, The State University of New York, United States; ²Henan University, China; ³Dalian Institute of Chemical Physics, China

The holy-grail in efficient and cost-effective conversion of solar energy into electrical and chemical energy is solar energy-driven water splitting using semi-conductor-based photo-catalysts. Overall conversion efficiencies of best systems so far are however far from the level needed for practical applications. Viable materials must exhibit good visible light absorption and carrier generation, good carrier transport, and good carrier redox reactivity. This presentation will focus on multiscale modeling of carrier transport in semi-conductors, combining quantum chemical calculations of polaron hopping by Marcus/Holstein theory and kinetic Monte Carlo (KMC) modeling of mesoscale transport. We will highlight recent method developments for cation- and anion-doped BiVO₄.

4:00 PM EN07.02.07

Relationship between the Photocatalytic Hydrogen Ion Reduction and Charge Carrier Dynamics of Pt/Cd₁₋ₓNxS catalysts: Tayirjan T. Isimjan¹, Partha Maity², Omar A. Mohammed² and Hicham Idriss³; ¹SABIC-CRD at KAUST, Saudi Arabia; ²KAUST, Saudi Arabia; ³SABIC-CRD-KAUST/University College London, Saudi Arabia

The doping induced local impurity brings a significant modification to photocatalytic performance of the semiconductor. Finding the correlation between charge carrier dynamics and catalytic performance of the semiconductors offers useful information both for the fundamental understanding of the catalytic mechanism and the catalyst optimization. Here, the electron transfer during the hydrogen ion reduction reaction in the presence of Pt/CdS doped with Ni²⁺ (Cd₀.₉₈Ni₀.₀₂S) was studied using fs-pump probe transient absorption spectroscopy (TAS) complemented by photocatalytic tests. Cd₀.₉₈Ni₀.₀₂S is composed of both hexagonal and cubic phases with average particles of 7 nm in size; determined from TEM. TAS of Cd₀.₉₈Ni₀.₀₂S in the presence and absence of the hole scavenger (benzyl alcohol) and in the presence and absence of Pt helped to further probe into the origin of the two most pronounced signals in the 400-800 nm range: the ground state bleaching (GSB) at ca. 480 nm and the photo-induced absorption (PIA) at ca. 600 nm. The first is largely linked to electron de-excitation lifetime and the latter to hole lifetime. From the decay kinetics, it was possible to compute for the charge transfer yields (f) from the semiconductor to the Pt metal particles (electron sink) and for hole trapping lifetime in the presence of benzyl alcohol. The rate of the photocatalytic hydrogen production shows a positive relationship with the decay kinetics obtained by fs-pump probe measurements.

4:15 PM EN07.02.08

Highly Efficient Membrane Electrode Assembly with Less than 10 nm NiFe-Layered Double Hydroxides for Anion Exchange Membrane Water Electrolysis: Hiroyuki Koshikawa, Hideaki Murase, Takao Hayashi, Kosuke Nakajima, Hisanori Mashiko, Seigo Shiraiishi and Yoichiro Tsuji; Panasonic Corporation, Japan
Anion exchange membrane (AEM) water electrolysis is expected to offer a way of converting and storing electrical power generated from renewable energy into hydrogen. However, the development of a membrane electrode assembly (MEA) that are free of noble metals in the catalyst layer and capable of outperforming conventional Pt and Ir-based catalysts, remains a major challenge. Layered double hydroxides (LDHs) are known to exhibit high activity toward oxygen evolution reaction (OER) proceeding at the anode, and increasing the effective surface area by the miniaturization of LDH is a useful strategy to improve OER activity. In the present study, we report a one-pot synthesis of nanometer-sized NiFe-LDH through the application of a spontaneous gelation-deflocculation method and evaluated its electrochemical properties.

Nanometer-sized NiFe-LDH was synthesized by liquid phase reaction in the presence of a chelating agent. The distribution of the LDH particle size was measured by small angle x-ray scattering and the average diameter was calculated to be 7.2 nm, which is less than one tenth of the diameter of conventional LDHs. The chelating agent introduced into the media was thought to increase the concentration of metal hydroxide nuclei and suppress excessive growth of the LDH crystal, resulting in the synthesis of nanometer-sized LDH. NiFe-LDH showed superior OER activity compared to conventional iridium dioxide (IrOx) catalyst in terms of the overpotential required for flowing 10 mA cm\(^{-2}\) (254 mV for NiFe-LDH and 261 mV for IrOx). This overpotential for NiFe-LDH is one of the lowest reported for non-noble metal-based OER electrocatalysts. Notably, an MEA for AEM water electrolysis using NiFe-LDH as an anode catalyst exhibited an energy conversion efficiency of 74.7% in 1 M KOH for flowing 1 A cm\(^{-2}\) at 80 °C. This efficiency is the highest among MEAs implemented with LDH reported to date, and offers a viable replacement for IrOx anode catalyst. Further optimization of the synthesis conditions of our NiFe-LDH and the formation processes of the catalyst layer of the MEA will substantially increase the efficiency.

4:30 PM EN07.02.09
Semiconductor Photocathodes Modified with Transparent Reduced Graphene Oxide Films Loaded with Molecular Sensitizers and Electrocatalysts for Hydrogen Evolution Molly M. MacInnes, Nicolai Lehnert and Stephen Maldonado; University of Michigan, United States

This presentation will describe thin, smooth reduced graphene oxide (RGO) films that also contain either a dissolved hydrogen evolution reaction (HER) molecular catalyst (cobalt (III) bis[benzenedithiolate]) and/or a molecular chromophore on p-type gallium phosphide (GaP) photocathodes. Molecular electrocatalysts and dyes can be employed heterogeneously by immobilization onto an electrode surface but the mode of attachment is typically specific to the particular electrode type. We have developed a method of depositing thin (~10 nm), adherent graphene oxide films that can physisorb molecular species through π-π interactions. These thin films are deposited on a variety of electrode materials by spin coating graphene oxide suspensions. Immersion of these films in non-aqueous solutions of cobaltocene followed by drying produces flat, highly conductive reduced graphene oxide films that are platforms for the physisorption of molecular species. Electrochemical, photoelectrochemical, and spectroscopic data will be presented that demonstrates the robustness of these films and their ability to be modified with a molecular HER electrocatalyst or with a molecular dye. Additionally, finite-element modelling data will be presented that investigates activities of molecular catalysts immobilized on the outer-most surface as well as intercalated within the RGO film. The utility of these films for sensitization and protection against corrosion processes will be featured.

4:45 PM EN07.02.10
Highly Flexible and Efficient Photoanodes Using Surface Functionalized Metal-Oxide Nanostructures for PEC Applications Koteeswara Reddy Nandanapalli, Devika Mudusu, Jinkyu Song, Kyung-In Jang and Sungwon Lee; Daegu Gyeongbuk Institute of Science & Technology (DGIST), Korea (the Republic of)

Recent years, the development of flexible devices for various day-to-day applications including energy harvesting devices, medical devices, wearable electronics, energy storage, communications, sensors, has received great attentiveness owing to their affordability, applicability & wearability, light-weight, and conformality [1]. In this direction, we have developed highly flexible and light-weight heterostructures with an overall thickness of ~50 µm by using low-temperature techniques [2]. Surface passivated vertically aligned zinc oxide (ZnO, ~1 µm length) nanostructures with amorphous cobalt-oxide (CoO\(_2\), < 2 nm thickness) have been developed on different electron-collecting layers deposited flexible sheets. The impact of the electron-collecting layer on the morphology and structure of ZnO nanostructures along with their electrical properties has been investigated. Then, the photoelectrochemical water-oxidation performance of the heterostructures along with their chemical stability and durability were studied. Besides these, the influence of multiple bendings on the device performance of the
Acknowledgments:
We acknowledge the financial support of the National Research Foundation of Korea (NRF-2017R1D1A1B03035194, 2018R1A5A1025511, and 2017R1A2B4012119).


SESSION EN07.03: Photo- and Electro-Catalysts II
Session Chairs: Florian Libisch and Michele Pavone
Tuesday Morning, December 3, 2019
Sheraton, 2nd Floor, Liberty BC

8:30 AM *EN07.03.01
Integrating Supramolecular Photocatalysts into Photoelectrocatalytic Devices Elizabeth A. Gibson; Newcastle Univ, United Kingdom

Efficient dye-sensitized photocathodes offer new opportunities for converting sunlight into storable energy cheaply and sustainably,[1] We are developing dye-sensitized NiO cathodes for the photo-reduction of carbon dioxide or water to high energy products (solar fuels) using the lessons we have learnt from solar cells.[2] The potential advantage of this strategy is it exploits the selectivity of a molecular catalyst in a robust device. Assembling two photoelectrodes in a tandem configuration (see figure) enables water oxidation at the photoanode to supply electrons to the photocathode to be consumed in the reduction of e.g. H⁺ to H₂. Generating hydrogen on one electrode and oxygen on another enables the two gases to be collected separately. Additionally, by separating the functions of light absorption, charge transport and catalysis between the colloidal semiconductor and molecular components, the activity of each can be optimised, rather than relying on one material to have all the necessary credentials. The electron-transfer dynamics are key to the performance and a major challenge is slowing down charge recombination between the photoreduced dye and the oxidised NiO so that chemistry can take place.[3] Highlights from recent work examining charge-transfer at the interface between NiO and new supramolecular photocatalysts using transient absorption spectroscopy and time-resolved infrared spectroscopy will be presented. The effect of the environment on the kinetics will be discussed. The relationship between the structure, dynamics and performance of the photoelectrocatalytic devices will be summarized.

REFERENCES

9:00 AM EN07.03.02
Artificial Photosynthesis Using Perovskite Materials: A SrSnO₃ Case Study Conor J. Price, Ned T. Taylor, Francis H. Davies, Shane G. Davies and Steven P. Hepplestone; University of Exeter, United Kingdom

Photoelectrolysis offers a mechanism for long term, clean energy storage via hydrogen production. Recently, several perovskites have shown promise for this application [1,2]. Perovskites, ABX₃, are highly customisable, with several options for the A, B and X ions. This results in a large range of tailorable properties, such as the band gap and the relative stability, making them highly suitable for photoelectrolysis. The bulk properties of many perovskites have been explored [2,3]. However, their potential for photoelectrolysis is mainly governed by surfaces, making their study critical.

Using techniques such as density functional theory, we develop a large scale theoretical screening process to tackle
the large range of A, B and X combinations. We can further tailor the surface band structure with aggregates/surface coatings. Here we present the results of this method for a group of stannate perovskites, highlighting a case study perovskite, SrSnO\(_3\). We examine the effect of forming surfaces and the introduction of adsorbants (hydrogen, oxygen and OH groups) onto the surface, taking note of the band alignment with respect to the evolution potentials. These adsorptions allow us to investigate the intermediate energetics of the hydrogen evolution and oxygen evolution, and the overpotentials associated with these reactions. We then conclude with a discussion of how aggregates/surface coatings can be used to tailor the surface properties for more efficient water splitting.

1. Int. J. Hydrogen En., 2002, 27, 991-1022

9:15 AM EN07.03.03
Understanding the Complex of 3d Transition Metal Dopants and Sulfur Vacancies in the Activation of MoS\(_2\) Basal Plane for HER—From Structures to Intrinsic Descriptors Mingjie Liu and Qin Wu; Brookhaven National Laboratory, United States

MoS\(_2\) based materials as promising alternative electrocatalysts for hydrogen evolution reaction (HER) have been studied extensively. The activation of MoS\(_2\) basal plane for HER can be achieved by introducing transition metal dopants or sulfur vacancies. The activation is known as strengthening the hydrogen atom binding on “active” sites compared with on pristine MoS\(_2\) basal plane. The intrinsic descriptors for hydrogen binding, however, are still ambiguous in contrast to the d-band center for transition metals. In this work, we systematically studied 3d metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) doped in MoS\(_2\) from their local structures to the intrinsic descriptors for hydrogen binding. We found that the metal dopants prefer to form clusters, and the sulfur vacancy formation is strongly affected by the local dopants configuration. Two mechanisms for hydrogen adsorption on MoS\(_2\) based materials with dopant/vacancy complex are clarified. The intrinsic descriptors for both mechanisms are proposed respectively. Our results illustrate the dopant and vacancy can synergistically form and catalyze HER effectively. The intrinsic descriptors would be beneficial to understand this system and provide guidelines for other transition metal dichalcogenides HER catalysts design.

9:30 AM EN07.03.04
Fundamental Energetics of n-Si/SiO\(_x\)/p-NiO Photoanode for Water Oxidation and Sulfur Doping Effect on PEC Performance Jemee Joe, Thi Anh Ho, Changdeuck Bae and Hyunjung Shin; Sungkyunkwan University, Korea (the Republic of)

n-Si/metal oxide heterojunction structures have been intensively investigated for application in photoelectrochemical (PEC) water splitting obtaining high voltages and preventing surface photocorrosion. Thanks to the relatively high conduction band offset compared to the valence band offset with Si, p-NiO has been studied as both hole-selective and photocatalytic layers on Si surfaces. However, most of the Si/NiO heterojunctions focused on NiO\(_x\) to date, and the studies on relevant energetic are lacking due to the properties of the materials of NiO\(_x\) with unknown phases and the related surface reactions. Here, we describe the energetic study of simple stoichiometric NiO on n-Si and its relation to the water oxidation reactions. Atomic layer deposition (ALD) technique was used for fabricating NiO films for it could offer pin-hole-free, and compact layers in an ultraprecise manner, and systematic study. Moreover, doping sulfur in NiO further tuned the surface energetics by modifying the resulting conductivity. Our optimized n-Si/SiO\(_x\)/p-NiO(S) photoanodes showed well over 24 h of stability under 1 sun illumination with 27 mAcm\(^{-2}\), suggesting a great potential for efficient PEC water splitting.

9:45 AM EN07.03.05
Concurrent Photocatalytic Hydrogen Generation and Dye Degradation Using MIL-125-NH\(_2\) under Visible Light Irradiation Stavroula Kampouri\(^1\), Tú Nguyên\(^1\), Mariana Spodaryk\(^1,2\), Robert Palgrave\(^1\), Andreas Züttel\(^1,2\), Berend Smi\(^1\) and Kyriakos Stylianou\(^1\); \(^1\)Ecole Polytechnique Federale de Lausanne, Switzerland; \(^2\)EMPA Materials Science and Technology, Switzerland; \(^3\)University College London, United Kingdom

Solar to hydrogen (H\(_2\)) energy conversion represents the Holy Grail of energy science and technology. For decades, numerous materials have been developed and used as photocatalysts for this purpose. However, their inadequate visible light absorbance, poor stability and fast charge recombination have prevented their wide, industrial-scale
deployment. Additionally, the use of noble metal-based co-catalysts and the toxicity of the majority of electron donors employed in these photocatalytic systems limit the profitability of this technology. This study aims to tackle these issues using a two-fold strategy. Firstly, we systematically studied the impact of different transition metal-based co-catalysts towards the photocatalytic water reduction, when they are physically mixed with the visible-light active MIL-125-NH₂. All co-catalyst/MIL-125-NH₂ photocatalytic systems were found to be highly stable after photocatalysis, with the NiO/MIL-125-NH₂ and Ni₂P/MIL-125-NH₂ systems exhibiting high hydrogen (H₂) evolution rates of 1084 and 1230 μmol h⁻¹ g⁻¹, respectively. Secondly, we investigated how different electron donors affected the stability and H₂ generation rate of the best Ni₂P/MIL-125-NH₂ system and found that triethylamine fulfills both requirements. By understanding the impact of these components, we then replaced the electron donor with rhodamine B (RhB), a dye that is commonly used as a simulant organic pollutant, with the aim of integrating the visible-light driven H₂ evolution with water remediation in a single process. This is the first study where a metal-organic framework (MOF) system is used for this dual-photocatalytic activity under visible light illumination and our proof-of-concept approach envisions a sustainable wastewater remediation process driven by the abundant solar energy, while H₂ is produced, captured and further utilized. The discovery of such photocatalytic systems paves the way for the development of processes using wastewater to produce clean H₂ and our approach could be extended to other applications where the concurrent oxidation and reduction of species could be of great importance.

10:00 AM BREAK

10:30 AM *EN07.03.06
Defective But Effective—The Role of Defects in Oxide-Based Electrocatalysis Ana B. Munoz-Garcia; Univ of Naples Federico II, Italy

Ab initio simulations play an increasingly important role in materials sciences. In the energy conversion scenario, computational modeling can elucidate, with atomic resolution, the subtle composition-structure-property relationships behind the performance of functional materials and complex interfaces. In heterogeneous electrocatalysis, the underlying bulk and surface charge/mass transport events are often strongly dependent on the presence/absence of structural defects. Thus, a deep knowledge of defect chemistry is key for understanding, tuning and optimizing the properties of different catalysts.

In particular, this contribution will report recent advances in the DFT-based characterization of the role of defects in strongly correlated oxides as electrodes in (photo)electrocatalytic devices. Three case studies will be presented: (i) a new triple-conducting oxide based on Sr₂Fe₁.₅Mo₀.₅O₆ perovskite with promising bifunctional catalytic activity towards oxygen reduction and evolution reactions [1-3] (ii) Fe-doped ZrO₂ for low temperature SOFCs [4] and (iii) CuFeO₂delafossite for CO₂photoreduction [5]. In all cases, we will discuss how surface oxygen vacancies -boosted by aliovalent doping- enable better performances and change product selectivity.

REFERENCES

11:00 AM EN07.03.07
Design and High-Throughput Discovery of Conjugated Polymer Photocatalysts for Photocatalytic Hydrogen Evolution from Water Reiner S. Sprick¹, Yang Bai¹, Christian Meier¹, Liam Wilbraham², Martijn Zwijsenborg³ and Andrew Cooper¹; ¹University of Liverpool, United Kingdom; ²University College London, United Kingdom

Photocatalytic hydrogen production from water is a research area of immense interest as hydrogen has been identified as a potential energy carrier of the future. We have previously shown that conjugated polymers can be
Exciton Delocalization vs Charge Separation in Biomimetic PBI-Based Supramolecules for Artificial Photosynthesis

Maurizio Prato, Marcella Bonchio and Giulio Cerrulo; 1Politecnico di Milano, Italy; 2University of Padova and CNR-ITM, Italy; 3University of Trieste, Italy

Converting solar energy into chemical energy with the aid of a photocatalyst is a promising strategy to solve long-term energy problems. Specifically, engineering a synthetic analogue of a photosynthetic unit which absorbs sunlight and uses it to split water, is an ambitious challenge towards the achievement of an artificial photosynthesis. Towards this goal, major synthetic efforts have been focused on the design of dyads based on a light-absorber (usually a Ru–based complex) and a water oxidation catalyst (WOC). Upon dyad photoexcitation an electron transfer event occurs, however it is usually strongly quenched by possible ultrafast intra-dyad recombination, thus limiting the dyad efficiency.

Recently, some of us proposed a new synthetic strategy inspired by the concept of the ‘quantasome’, defined as the minimal photosynthetic unit responsible for the solar-energy conversion. A quantasome uses a self-assembled light-harvesting antenna in combination with one catalytic cofactor. The artificial quantasome reported here is specifically designed for oxygen evolution. It exploits the self-assembly of multiple perylene bisimides (PBI) chromophores which interact with a Ru-polynoxometalate WOC (Ru4POM). The resulting [PBI]5Ru4POM complex shows an amphiphilic structure and dynamic aggregation into large two-dimensional domains, forming cylindrical units where five PBIs surround one Ru4POM. The PBI self-assembly induces a clear red-shift of the optical absorption, suggesting strong excitonic delocalization. The interplay between the creation of excitonic states, the formation of charge transfer states and the deactivation of the excitons dictates the efficiency of the quantasome.

Femtosecond transient absorption shows that upon excitation of the PBI moieties, the [PBI]5Ru4POM singlet excited state undergoes an ultrafast (ca. 1ps) decay to a charge transfer (CT) state, followed by a formation of a stable charge-separated state1. The ultrafast CT formation is taken as signature of a good quantum efficiency. Nevertheless, a clear understanding of the formation of a favorable PBI-based excitonic manifold is still lacking. Here we apply two-dimensional electronic spectroscopy (2DES) to study the interplay between exciton delocalization and CT formation in the [PBI]5Ru4POM quantasome. 2DES represents a suitable tool to study exciton delocalization in multi-chromophores systems, providing a series of excitation/detection correlation energy maps at different probe delays T. Exploiting sub 20-fs broadband visible pulses, we report a 2DES measurement obtained on the quantasome and we compare it with the ones obtained from an isolated PBI in solution and a self-assembled PBI aggregate.

In 2DES maps, we distinguish two contributions: the signals on the diagonal and the ones observed out of the diagonal (cross-peaks). For the quantasome, at early times (T<20fs), we observe instantaneous positive diagonal peaks appearing in the blue/green spectral region (500-550 nm), reflecting the bleaching of the PBIs excitonic transitions, as well as one negative cross-peaks in the red-shifted detection window at 550/700nm excitation/detection wavelength, assigned to a photoinduced absorption from individual PBI excited states (as confirmed by a reference 2DES map on isolated PBI). At later times (T=100fs) we notice the formation of a second negative cross peak at the 550/600nm wavelengths, completed in about 1ps. Interestingly, similar signal is also
observed in the PBI aggregate and we ascribe it to an excited state absorption band from the PBI exciton manifold. By comparing the spectral shapes and the timescales of the two crosspeaks in the PBI aggregate and in the quantasome we distinguish excitonic effects from electron transfer events. Our results will contribute in understanding the design principles underlying the PBI-based supramolecular systems for efficient artificial photosynthesis.


11:30 AM EN07.03.09
Oxygen Evolution Reaction of Epitaxially Stabilized Columbite IrO$_2$
Kyuho Lee$^1$, Raul A. Flores$^{1,2}$, Yunzhi Liu$^1$, Michal Bajdich$^1$, Yasuyuki Hikita$^2$, Robert Sinclair$^1$ and Harold Y. Hwang$^{2,1}$; $^1$Stanford University, United States; $^2$SLAC National Accelerator Laboratory, United States

The conversion of electrical energy into hydrogen gas via water electrolysis is widely considered to be a promising energy storage mechanism to compensate the intermittent nature of the leading sources of renewable energy.$^{1,2}$ The key to enhancing the overall efficiency of polymer electrolyte membrane (PEM) electrolyzers lies in the development of acid-stable catalysts for the oxygen evolution reaction (OER), the rate-limiting half-reaction of water electrolysis.$^2$ Recently, ternary iridium oxides have been reported to show high catalytic activity and stability in acid, often associated with the formation of distinct IrO$_x$ structures at the surface by the leaching of the second cation.$^{3,4}$ Various Ir-O structures, including polymorphs of IrO$_2$, are identified as possible candidates for these highly active IrO$_x$ structures.$^3$ In parallel, theoretical calculations predict that some polymorphs of IrO$_2$, including columbite IrO$_2$, could be more active OER catalysts than the conventional rutile IrO$_2$.$^5$ These studies strongly motivate the synthesis of new polymorphs of IrO$_2$, but their stabilization has been limited due to the outstanding stability of rutile IrO$_2$.$^{5-7}$ An effective approach to overcome this challenge is to employ heteroepitaxy, in which the metastable polymorph is preferentially stabilized by growing on a well lattice-matched substrate due to enhanced interfacial energy.$^8$ We have successfully stabilized columbite IrO$_2$ (100) in epitaxial thin films for the first time using pulsed laser deposition. X-ray diffraction and transmission electron microscopy measurements are used to identify and characterize the structure of these films. Measurements of the OER catalytic activity of columbite IrO$_2$ (100) thin films reveal clear differences from their rutile counterpart. Details of the activity and comparison with theoretical calculations will be discussed.


11:45 AM EN07.03.10
Effect of Dissolved O$_2$ on Band Alignment at n-GaN/NaOH Interface
Yuki Imazeki$^1$, Supawan Ngamprapawat$^1$, Masahiro Sato$^1$, Katsushi Fujii$^2$, Tsutomu Minegishi$^1$, Masakazu Sugiyama$^1$ and Yoshiaki Nakano$^1$; $^1$The University of Tokyo, Japan; $^2$RIKEN Center for Advanced Photonics, Japan

For efficient solar-to-hydrogen conversion via photoelectrochemical water splitting, semiconductor electrodes such as Fe$_2$O$_3$ and BiVO$_4$ have been developed. On such n-type semiconductors, O$_2$ gas is generated by photoelectrochemical water oxidation. Therefore, amount of dissolved O$_2$ increases with the progress of water splitting in the vicinity of semiconductor/electrolyte interface. Band alignment around the interface has an essential impact on the carrier transport which dominates the progress of photoelectrochemical reactions, and the dissolved O$_2$ will certainly affect the band alignment. We therefore investigated the band alignment under illumination at the interface with and without dissolved O$_2$ using n-GaN/NaOH as a model system. The band alignment at the semiconductor/electrolyte interface is characterized by the flat band potential and the (quasi-) Fermi level of a semiconductor. The former can be obtained via Mott-Schottky analysis and the latter can be measured as open-circuit-potential (OCP). These measurements were performed with the three electrodes system.
which consists of a single crystalline n-GaN (0001) photoanode, a platinum wire as a counter electrode and a Hg/HgO/1M NaOH (+0.113 V vs. SHE) as a reference electrode. Before a measurement, the surface of the n-GaN electrode was conditioned by electrochemical reduction using cyclic voltammetry from -0.25 to +0.45 V vs. RHE in a 1M NaOH degassed by evacuation. To characterize the band alignment under illumination, a He-Cd laser (325 nm) was used for excitation of carriers in n-GaN. To evaluate the drift of Fermi level under illumination, OCP was measured as a function of photon flux ranging from 1.1×10⁹ to 7.5×10¹⁶ s⁻¹cm⁻² either in degassed 1M NaOH or in the same electrolyte bubbled with O₂ at 1 atm.

Without illumination, the flat band potential was -0.53 and -0.60 V vs. RHE for the degassed and the O₂-bubbled NaOH, respectively. The negative shift in the flat band potential with dissolved O₂ would be due to the potential difference at the electric double layer, since adsorbed oxygen on the surface of n-GaN may alter the structure of the double layer. Fermi level was evaluated as +0.70 and +0.73 V for the degassed and the O₂-bubbled NaOH, respectively. As a result, band bending was increased from 1.23 to 1.33 V with O₂ bubbling. OCP, i.e., Fermi level, is the potential at which anodic current is balanced with cathodic current. Therefore, its positive shift would be due to the increased cathodic current by oxygen reduction reaction.

Under illumination, OCP approached the flat band potential with increasing photon flux, assuming that the flat band potential was never changed by illumination. Between photon flux of 1.1×10⁹ and 1.2×10¹¹ s⁻¹cm⁻², O₂ bubbling resulted in larger band bending by 0.09 - 0.14 V compared to the values at each photon flux for the degassed NaOH. In contrast, between photon flux of 1.2×10¹² and 1.9×10¹⁴ s⁻¹cm⁻², band bending was 0.01 – 0.03 V smaller with O₂ bubbling. When OCP exceeded the redox potential of H₂ evolution, the behavior of OCP versus photon flux was affected by the existence of dissolved O₂.

The observation above seems to indicate that O₂ dissolved in an electrolyte adjacent to the semiconductor surface induces at least two phenomena: (1) a structural change in the electric double layer due to the adsorption of oxygen on the semiconductor surface, (2) removal of electrons from the semiconductor surface due to oxygen reduction current, resulting in the increase of band bending in the semiconductor. The relative impact of these phenomena on the band alignment may depend on several factors such as illumination intensity, O₂ concentration in an electrolyte and the atomistic structure of the surface. The combination of Mott-Schottky analysis and OCP measurement as a function of light intensity will provide quantitative clues for the fundamental clarification of such impact of dissolved O₂ in an electrolyte.

SESSION EN07.04: Collaborative Modelling and Experiments for Water Splitting
Session Chairs: Anja Bieberle-Hütter and Elizabeth Gibson
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Liberty BC

1:30 PM *EN07.04.01
Oxygen Electro-Adsorption Kinetics on Well-Defined Oxide Surfaces Ding-Yuan Kuo, Hanjong Paik, Darrell G. Schlom and Jin Suntivich; Cornell University, United States

We present our measurements of the oxygen electro-adsorption kinetics on IrO₂ and RuO₂ surfaces and their implications for our oxygen evolution reaction (OER) understanding. The slow kinetics of the OER is currently the largest source of inefficiency in water-splitting devices. The common picture is that the slow OER kinetics is a reflection of the OER’s multi-electron nature; as the OER takes place, the catalyst must stabilize a series of proton and electron transfer events via surface electro-adsorption. We present our measurements of the kinetics of these electro-adsorption events, specifically the deprotonation of H₂O* to OH* and OH* to O*, two of the elementary steps of the OER. Our approach uses rate-dependent cyclic voltammetry to isolate the electro-adsorption rate constants from the electrochemical driving force. We further vary the electrolytes to examine how the rate constant varies with pH to reveal the nature of the proton and electron transfers on IrO₂ and RuO₂. Our measurement provide insights into the electro-adsorption process on oxides and information on the kinetics of the elementary steps within the OER.

2:00 PM EN07.04.02
BSE Calculations for Hematite Water Splitting Nadav Snir and Maytal Caspary Toroker; Technion-Israel
Hematite is a widely-studied photo-anode in photoelectrochemical cells (PEC) due to its visible-light band-gap (~2.2 eV) and chemical stability. There are many DFT+U studies for the electronic structure of hematite. In current work we go into more accurate calculations of hematite's absorption spectrum using the one-shot Green's functions (\(G_0W_0\)) and Bethe-Salpeter equations (BSE) methods which take excited states into account. We compared the calculated absorption spectra to experimental spectra and found a match in peak energy position. Furthermore, we found anisotropy of the absorption spectrum that is concurrent with the crystallographic structure of hematite. We also calculated the absorption spectra of hematite intermediates during the oxygen evolution reaction using the \(G_0W_0\)-BSE method and found that the *O intermediate is the dominant species under bias.

2:15 PM EN07.04.03
Sn-Addition on Polycrystalline Hematite Reduces the Grain Boundary Blocking Effect Enhancing the Electronic Conductivity
Mario R. Soares¹, Edson R. Leite¹ and Flavio L. De Souza²; ¹UFSCar, Brazil; ²University Federal-ABC, Brazil

The poor electronic properties of polycrystalline hematite have been prevent its potential application as photoanode for light induced water splitting. Despite some progress have been made overcome this limitations remains as important challenge in the solar fuel production field [1-2]. The present work showed that the Sn-addition enhances the electronic transport of polycrystalline hematite (α-Fe₂O₃) by reduces the grain boundary block effect. A controlled sintering process allowed us freezing the state of electronic defects, in which the electrical properties of hematite are governed by the grain boundary and Sn segregation. Electrical measurements showed that the current flows preferentially through the grain boundary with presence of Sn-segregated. Sn-addition probably leads to decrease the grain boundary resistance. Atomic force microscopy and electric force microscopy (AFM/EFM) measurements confirm the results of the impedance analysis. The identification of preferential grain boundaries for electrical conductivity may have a direct influence on the light-induced water splitting performance of the hematite photoanode.


2:30 PM EN07.04.04
Optimization of Photoelectrochemical Performance of Hematite for Solar Water Splitting
Mmantsae M. Diale; University of Pretoria, South Africa

Hematite has attracted much attention due its superior properties for applications as a photoanode in a solar water splitting. Thin films and nanostructures of hematite were synthesized on fluorine-doped tin oxide by spray pyrolysis, dip coating and spin coating. X-ray diffraction results revealed (104) and (110) planes for all films, describing the rhombohedral structure of hematite. Raman spectra of the films confirmed two A₁g and five E₅g vibrational phonon modes of hematite. Scanning electron microscopy films showed nanoparticles of grain sizes varying from 30 to 40 nm. Cross-sectional images revealed film thickness of 430, 452 and 622 nm 521 nm for films prepared by spray pyrolysis, dip and spin coating techniques respectively. The films had an indirect band gap ranging from 1.96 to 2.30 eV. We carried out pump probe spectroscopic measurements on spin-coated samples to determine the electron-hole recombination rates in photo-excited samples. We obtained three distinct relaxation decay and recombination lifetimes in the ranges of sub-picosecond, hundreds of picoseconds and single digit nanoseconds. Furthermore, ab-initio studies of surface doped hematite films using Cu, Zn and Cu/Zn co-doping showed thermodynamic stability.

2:45 PM EN07.04.05
Engineering IT-MoS₂ with Transition Metal Doping as Efficient Electrocatalysts for Alkaline Hydrogen Evolution Reaction
Nuwan H. Attanayake¹, Lakshay Dheer², Sasitha C. Abeyweera¹, Umesh V. Waghmare² and Daniel R. Strongin¹; ¹Temple University, United States; ²Jawaharlal Nehru Centre for Advanced Scientific Research, India
Molecular hydrogen is considered as one of the most promising energy carriers due to their high energy density and environmental friendliness. The emission of unprecedented amounts of greenhouse gases during the combustion of fossil fuels is believed to be a major cause in climate change. Thus, greener fuels are sought after more than ever. The production of hydrogen gas by electrolysis of water or hydrogen evolution reaction (HER) using energy from renewable sources is one of the most evaluated areas as a viable solution. These extensive studies have identified many earth abundant materials to perform with high energy efficiency in the reduction of protons to hydrogen gas in acidic media. Nevertheless, there are few studies to accommodate materials as catalysts to reduce water to hydrogen gas in alkaline conditions. This would be a vital factor since the more challenging oxygen evolution reaction (OER) catalysts show good efficiencies in alkaline conditions (i.e. pH 14). Thus, materials which would split water to generate hydrogen in alkaline conditions are sought after as it would allow the water splitting reaction to be carried out in one electrolyte. MoS$_2$ gained a lot of attention as an efficient catalyst in reducing protons to hydrogen in acidic conditions. Nevertheless, they suffer in stability and activity in alkaline conditions. In this study we report the synthesis of doped 1T phase of MoS$_2$ to gain stability and provide improved activity than the pure 1T phase of MoS$_2$. The metallic 1T phase of MoS$_2$ was successfully doped with with varying concentrations of Co and Ni atoms in the basal planes of these MoS$_2$ sheets. This doping reduced the overpotential (@10 mA/cm$^2$) for the HER to 110 mV from 220 mV, relative to pure 1T phase in alkaline conditions with 10% of Co dopants in them. 10% Ni doping gives 120 mV overpotential for the HER at the same current density. These doped materials show low tafel slopes (~125 mV/dec) and good stability for the HER for more than 24 hours. We use density functional theory (DFT) calculations to explain the improvement in the catalytic activity and stability in these doped materials. These calculations suggest that the introduction of the impurities in these sheets lowers the energy required for the water dissociation step and reduces the binding energy towards the hydroxyl ions that wouldn’t leave the surface on pure MoS$_2$. Furthermore, the calculations show that the introduction of the dopants reduce the H binding energy on the active sites which is a crucial factor in efficient HER catalysis.

3:00 PM BREAK

3:30 PM *EN07.04.06 Multiscale Modelling Strategies for Alloy Design Javier Llorca$^{1,2}$; $^1$IMDEA Materials Institute, Spain; $^2$Technical University of Madrid, Spain

Materials are transversal to all technologies and they are always at the core of the major disruptive discoveries. Either the synthesis of a material with novel properties leads to a technological breakthrough or current engineering materials are introduced and slowly improved for novel applications following a trial-and-error strategy. Both circumstances act as limiting factors of technological progress but advances in computer power and modeling tools have changed this scenario. In particular, a large number of modeling tools are nowadays available for particular ranges of length and time scales (density functional theory, molecular mechanics, computational thermodynamics, finite elements and finite differences, etc.). They have already proven their potential to predict the formation, structure and properties of materials and have been used to design materials with improved properties or unexpected structures, such as new catalysts or Li-based materials for batteries.

These success stories were possible because the critical structure or properties depended on phenomena with a particular time and length scale, which could be simulated using only one of the techniques mentioned above. This is not always the case and, in fact, it is unlikely to occur in materials for engineering applications. For instance, balanced mechanical properties (stiffness, strength, toughness) depend on many different processes which take place along nine or more orders of magnitude in length scales (from nm to m) and this dependence on different length scales is more evident in multifunctional (smart) materials.

In this talk, a roadmap for multiscale modelling of engineering materials for structural applications is presented around two pillars of virtual processing and virtual testing. In the first pillar, the microstructural development during processing is simulated through a cascade a simulation tools including ab initio calculations, cluster expansion and kinetic Monte Carlo to determine the phase diagram and the interface mobility. This information is used in combination with classical nucleation theory and phase-field modelling to obtain the microstructure (grain size, size, shape and spatial distribution of second phases). Virtual testing is accomplished by means of computational homogenization of a representative volume element of the polycrystalline microstructure, in which the properties of the single crystals and grain boundaries were obtained from ab initio, molecular dynamics and dislocation dynamics.
in combination with transition state theory. The roadmap is demonstrated in the development of Al-Cu alloys for aerospace applications. Future applications of this strategy to design new materials for enhanced electrocatalytic water splitting by elastic strain engineering is outlined.

4:00 PM EN07.04.07
Carbon-Based Heterojunction with Optimizing Oxygen Concentration for Photoelectrochemical Water Splitting Minyeong Je†, Yelyn Sim‡, Uk Sim‡ and Heechae Choi†; †University of Cologne, Germany; ‡Chonnam National University, Korea (the Republic of)

Recently, two-dimensional (2D) carbon-based heterojunction materials have exhibited high photocatalytic activities for water splitting and hydrogen evolution reaction (HER). Reduced graphene oxide (rGO) and graphitic carbon nitrides (C,N) have attracted strong research interests in junctions because of excellent compatibility with other 2D materials and versatile functionalities. However, the functionality of rGO-C,N heterojunction is not very reliable, which means that the water splitting photocatalytic activity largely fluctuates with fabrication conditions. In this study, the effect of oxygen/carbon (O/C) ratio of rGO and C-O binding chemistry on the physicochemical properties and possibility to fine tune the photocatalysis of rGO-C,N composite was systematically and theoretically investigated using density function theory (DFT) calculations. Interestingly, from DFT calculations results, the work functions of pristine rGO (PrGO) and defective (DrGO) were found to be linearly increase with O/C ratio. Especially, it indicated that PrGO and DrGO with O/C ratio range from 4% to 13% have a suitable work function value for the photocatalyst in junctions with C,N, considering feasibilities of charge separations and water redox levels. It revealed that the charge transfer only occurs in PrGO with 4% O/C ratio and DrGO with 8% and 13% O/C ratio. Free energy diagram and volcano plot of H adsorbed on PrGO and C,N/DrGO heterojunction was investigated to further understand the HER mechanisms. Furthermore, the experimental results were well verified that the rGO-C,N heterojunction having the proper O/C ratio shows the enhanced water splitting photocatalytic activity. Thus, it was demonstrated through DFT calculations and experimental results that controlling the proper O/C ratio is very important in the rGO-C,N heterojunction.

4:15 PM EN07.04.08
Zn:BiVO₄/Mo:BiVO₄ Homojunction as Efficient Photoanode for Photoelectrochemical Water Splitting Jae Myeong Lee¹, Ji Hyun Baek¹, Xinjian Shi², Gill Sang Han¹, Dong Hoe Kim¹, Hyun Suk Jung¹ and Xiaolin Zheng²; ¹Sungkyunkwan University, Korea (the Republic of); ²Stanford University, United States; ³Sejong University, Korea (the Republic of)

Photoelectrochemical (PEC) water splitting has been extensively studied as a method to convert sunlight and water to hydrogen. Among the many obstacles facing PEC water splitting, a critical challenge is the lack of efficient photoanodes for the water oxidation reaction. Here, we demonstrate a n-n+ type-II homojunction of Zn:BiVO₄/Mo:BiVO₄, which enhance the bulk transport and surface charge transfer processes of the well-studied BiVO₄ photoanode. In this homojunction, the Zinc and Molybdenum dopants move the BiVO₄ Fermi level closer to valence band maximum and conduction band minimum, respectively, establishing a n-n+ type-II homojunction. The staggered band alignment between Zn:BiVO₄ and Mo:BiVO₄ facilitates electron-hole separation between the interface of two layers. The Molybdenum is a well-known donor dopant for BiVO₄ and increases the donor concentration, leading to higher electrical conductivity. The Zinc dopant increases the number of oxygen chemisorption sites at the surface layer, reducing surface recombination rate. In summary, we demonstrate that a Zn:BiVO₄/Mo:BiVO₄ homojunction structure improves both charge transport and transfer efficiency.

4:30 PM EN07.04.09
Investigation of Highly Stable Proton Exchange Membrane Water Electrolyzers with Low Catalyst Loading and Reduced Hydrogen Crossover Ryan Ouimet¹,¹, Reza Mirshekari¹, Haoran Yu¹, Zhiqiao Zeng¹, Leonard Bonville¹, Prasanna Mani², Allison Niedzwiecki², Chris Capuano², Katherine Ayers² and Radenka Maric¹,¹; ¹University of Connecticut, United States; ²Nel Hydrogen, United States

Hydrogen, with a global production rate of about 50 billion kg/year, is one of the world’s most important chemicals [1]. Today, hydrogen is mainly produced from natural gas and coal, generating CO₂ as a byproduct. Recently, Proton Exchange Membrane Water Electrolyzers (PEMWEs) have been gaining in interest worldwide as a renewable energy source for hydrogen production. However, the product costs have not yet reached the market targets, mainly due to the immaturity of the manufacturing processes and materials cost. The catalyst coated membrane (CCM) is
the largest cost contributor to the cell, due to the high catalyst loadings of platinum group metals (PGMs) and the current labor-intensive methods for CCM fabrication. In order to address the catalyst cost issue, there is a need to reduce the catalyst loading and develop the manufacturing process. Furthermore, stability and long-term operation at high current density has been challenging for electrodes with low PGM loading (less than 1 mg cm$^{-2}$). Recent literature has shown long-term catalyst stability from hundreds to several thousand hours of cell operation. Lewinski et al. [2] have demonstrated a nano-structured thin film (NSTF) cell with Ir anode loading of 0.25 mg cm$^{-2}$ which achieved stability of 5000 h at 2 A cm$^{-2}$. Rozain et al. [3] have also studied a low-loaded Ti supported Ir oxide anode catalyst (0.12 mg cm$^{-2}$) which showed more than 1000 h of operation at 1 A cm$^{-2}$. On the other hand, one of the principal technical issues hampering the extensive use of PEMWEs is hydrogen crossover which causes a serious safety hazard in the anodic compartment where oxygen is produced as the lower explosion limit of hydrogen in oxygen is about 4 vol%. It has been shown that the integration of a recombination layer incorporated directly into the membrane has significantly improved the hydrogen crossover with the ability to decrease this safety hazard [4]. In this work, a novel single-step electrode fabrication process, Reactive Spray Deposition Technique (RSDT), was employed to reduce the electrode manufacturing cost and develop 86 cm$^{2}$ full CCMs with low catalyst loadings (cathode: Pt/Vulcan XC-72R with loading of 0.3 mgPt cm$^{-2}$, anode: IrO$_2$/Nafion® with loading of 0.2-0.3 mgIr cm$^{-2}$) which meet the desired stability of >1000 h at 1.8 A cm$^{-2}$, 50 °C, 400 psi hydrogen pressure. A Pt recombination layer directly introduced into the membrane was also used to reduce hydrogen crossover to the commercial threshold. The microstructural characteristics of the RSDT-derived CCMs were studied by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Stability and cell performance of the RSDT-derived CCMs were investigated using diagnostic tests including polarization analysis, cyclic voltammetry and electrochemical impedance spectroscopy.

References

4:45 PM EN07.04.10
From Rusting to Solar Power Plants—A Successful Nano-Patterning of Stainless Steel 316L for Visible Light-Induced Photoelectrocatalytic Water Splitting Nageh K. Allam; American University in Cairo, Egypt

A novel propitious nanoporous anodized stainless steel 316L (NASS316L) photoanode was developed for water splitting. The anodization could successfully produce a uniform nanoporous (∼ 90 nm in pore diameter) array (∼ 2.0 m thick) of NASS316L with a high pore density. Several techniques, including FESEM, EDX, XRD, XPS, ICP-OES, and UV–vis-NIR spectrophotometry, were employed to characterize the catalyst and to assess and interpret its activity toward water splitting. Surprisingly, the NASS316L retained almost the same composition of the bare stainless steel 316L, which recommended a symmetric dealloying mechanism during anodization. It also possessed a narrow band gap energy (1.77 eV) and a unique photoelectrocatalytic activity (∼ 4.1 mA cm$^{-2}$ at 0.65 V versus Ag/AgCl, 4-fold to that of α-Fe2O3) toward water splitting. The onset potential (∼0.85 V) in the photocurrent-voltage curve of the NASS316L catalyst demonstrated a negative shift in its Fermi level when compared to α-Fe2O3. The high (23% at 0.2 V vs Ag/AgCl) incident-photon-to-current conversion efficiency and the robust durability revealed from the in situ analysis of the produced H2 gas continued recommending the peerless inexpensive and abundant NASS316L catalyst for potential visible-induced solar applications.

SESSION EN07.05: Poster Session
Session Chairs: Maytal Caspary Toroker, Francesc Illas, Michele Pavone and Guofeng Wang
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B
EN07.05.01

Understanding the Reasons for the Absence of Photoactivity in β Manganese Vanadate (Mn$_2$V$_2$O$_7$) Yash Gargasya; University of California, Irvine, United States

With depleting fossil fuels reserves and their possible role in accelerating climate change, solar energy stands out as one promising source for providing clean energy at a multi-terawatt scale to meet ever-increasing global energy demand. The challenge of its intermittent nature can be tackled by storing it in an energy dense material like chemical fuel. Water can be the abundant raw material for this conversion process. Thus, photoelectrochemical water splitting can be one possible route to solve the energy crisis.

Till date, no semiconductor deployed for photoelectrochemical water splitting has met the stringent criteria of the right bandgap of 1.6-2 eV, optimal band edge positions (CBM, few mV negative of HER and VBM, 300-500 mV positive of OER), electrochemical stability (at alkaline pH for OER) and good electron transport properties. However, manganese vanadate (Mn$_2$V$_2$O$_7$), has been reported to have 1.8 eV bandgap, near optimal band edge positions, electrochemical stability in the alkaline pH and Mn 3d orbital based valence band leading to curvature in the valence band light holes.

In this work, we have developed a simple spin coating method to fabricate tunable, nanoporous thin films of manganese vanadate. The grain size can be tuned from 20nm to 200nm whereas the film thickness can be tuned from 100nm to 1.5 microns. The direct bandgap has been found to be 2 eV. Contrary to previous reports, the material is found to suffer from serious stability issues. It dissolves in neutral, acidic and mildly acidic pH within minutes, and undergoes vanadium leaching and amorphousization at alkaline pH. It is relatively stable in mildly alkaline pH, but, use of common buffer ions like phosphate accelerate the film dissolution even in this pH due to low Ksp of manganese phosphate.

Also, unlike previous reports, the material shows no photoactivity in pristine form or when stabilized by atomic layer deposited TiO$_2$. Photoluminescence spectrum suggests the possibility of very small charge carrier localizing domains resulting in an uncharacteristically broad PL peak. Further studies have been done using transient absorption spectroscopy to study the carrier lifetime to probe long-lived traps and bulk charge carrier recombination. XPS measurements have been conducted to study the chemical environment of the film surface and exchange current density and impedance has been measured to probe the presence of any resistive surface layer impeding the charge transfer across the interface.

EN07.05.02

Developing Stable and Efficient Water Splitting Devices for Solar H$_2$ Production under Concentrated Light Mohd A. Khan$^1$, Purushothaman Varadhan$^2$, Hicham Idriss$^1$ and Jr-Hau He$^2$; $^1$SABIC, Saudi Arabia; $^2$King Abdullah University of Science and Technology, Saudi Arabia

Photoelectrochemical (PEC) water splitting into hydrogen and oxygen molecules has been touted as the most promising route for converting solar energy into a storable form. After decades of research solar-to-hydrogen (STH) efficiencies are now approaching 20% using III-V semiconductor solar cells, making the process close to implementation. Yet, the high cost and instability of these cells prohibit their practical use. Stable water splitting reactions should yield stoichiometric hydrogen and oxygen and these are seldom reported. Herein this work we demonstrate the importance of measurement of gaseous products (H$_2$ and O$_2$), and show cases where total inactivity was observed due to corrosion while current measurements indicated stable and high performances. At the same time, we demonstrate integrated water splitting devices that use nickel for stoichiometric (2:1) hydrogen and oxygen production. Specifically we demonstrate over 400 hours of stability @ 12 % STH under 1 sun condition. In parallel we also demonstrate the use of concentrated light for as means for lowering the cost of H$_2$ production. Specifically we report demonstrate devices that work under 25 suns @ 10% STH with stability of more than 250 hours, paving the way to developing practical solar H$_2$ generators.

EN07.05.03

Activation of Reaction Sites in Multinary Phyllosilicate Catalysts for Electrochemical Water Oxidation Byunghoon Kim, Ju Seong Kim and Kisuk Kang; Seoul National University, Korea (the Republic of)

The practical realization of a water-splitting system necessitates the development of high-performance oxygen
evolution reaction (OER) catalysts. Despite tremendous research efforts aimed at identifying earth-abundant 3d transition-metal-based catalysts, their insufficient catalytic efficiencies continue to jeopardize their real-world application. Herein, we introduce amorphous cobalt–iron phyllosilicates (ACFPs) as highly efficient OER catalysts. The ACFPs were designed by tailoring the metal chemistry of the phyllosilicate framework and prepared using a facile room-temperature precipitation method. Structural characterization using X-ray diffraction, Fourier-transform infrared spectroscopy, and X-ray absorption spectroscopy revealed that the ACFP structure consists of laminations of silicate (SiO₄) layers and layered Co–Fe (oxy)hydroxide motifs. The OER properties of the ACFP series were also sensitively affected by the Co/Fe ratio, with an exceptionally low overpotential (η ~ 329 mV for a current density of 10 mA cm⁻²) delivered at the optimized composition of 40 at.% Fe. This catalytic efficiency is greater than that of the structurally analogous Co–Fe (oxy)hydroxide as well as those of pure Co phyllosilicate and pure Fe phyllosilicate, suggesting the beneficial role of the phyllosilicate framework along with the synergistic interplay of Co and Fe ions in the framework. Density functional theory calculations revealed that the introduction of Fe at the surface of Co phyllosilicate perturbs the local structural environment of oxygen sites, providing additional active sites. This work enables more rapid optimization of novel phyllosilicate-based OER catalysts and suggests a valid strategy for the design of high-performance catalysts by chemically tuning both the redox-active and redox-inert elements concomitantly.

EN07.05.04
Quantification of Surface Reactivity and Step-Selective Etching on Single-Crystal BiOI(001) Julia Martin, Roy Stoflet, Katarina Himmelberger, Alexander D. Carl and Ronald L. Grimm; Worcester Polytechnic Institute, United States

We synthesized single-crystal BiOI to characterize the interplay between etching chemistry and interfacial chemical and electronic structure at the (001) face of this emerging solar-relevant, 2-D-layered material. Experiments utilized BiOI single-crystals grown from BiOI powder via physical vapor transport (PVT) and via chemical vapor transport (CVT) with elemental I₂ as a transport agent. Optical images of nascent crystals reveal 1–10 mm² (001) facets but microscopic defects and pitting. Etching studies alternatively included ten-second exposures to 6 M aqueous HF, 6 M HCl, and a stepwise treatment of HF with an acetone rinse. Optical images of HF- or HCl-etched samples demonstrate clean terrace-rich regions and increased scattering at step-rich regions. X-ray photoelectron spectra (XPS) of HF- or HCl-etched, step-dense regions reveal increased iodine as well as fluoride or chloride features, while XRD presents BiI₃ features. We attribute optical, XPS, and XRD results to the dissolution of interfacial bismuth oxides and the concomitant formation of BiI₃ at the steps of the BiOI(001) face. Surface analyses of samples subjected to sequential HF and acetone rinsing demonstrate no detectable BiI₃ by XRD, and Bi:O:I photoelectron area ratios demonstrative of stoichiometric BiOI. In concert with separate studies demonstrating high solubility of BiI₃ in polar organic solvents, the sequential HF and acetone treatments appear to yield chemically pristine BiOI(001). Ultraviolet photoelectron spectra (UPS) of these surfaces demonstrate significant differences in work-function and Fermi-edge values for nascent, for HF-etch, and for HCl-etched BiOI(001) as compared to tape-cleaved, pristine BiOI(001). Importantly, UP spectra of BiOI(001) subjected to a sequential HF and acetone treatment resemble spectra of tape-cleaved, pristine BiOI(001). In concert, the sequential HF and acetone treatment yields BiOI(001) that best mimic the chemical and electronic structure of tape-cleaved surfaces. We discuss these results in the context of polycrystalline BiOI samples for tandem junction photovoltaics (PV).

EN07.05.05
Doped Diamond-Like Carbon Films for Electronic Applications Philip Schneider¹, Marie Francoise C. Millares¹, Iulian Gherasoiu² and Harry Efstathiads³; ¹SUNY Polytechnic Institute College of Nanoscale Science and Engineering, United States; ²State University of New York Polytechnic Institute, United States

Diamond is rapidly emerging as an outstanding semiconductor material for the 21st century. New device applications are envisioned based on its superior properties such as an ultrawide bandgap, the highest electron and hole mobilities, high electric field breakdown strength, all combined with unmatched thermal conductivity and radiation hardness. Toward the realization of its promises as a material for electronic devices, the successful doping of the diamond with boron and phosphorus are important stepping stones. Various techniques are used for the synthesis of diamond including detonation that results in the formation of micron-sized aggregates of nanometer scale diamonds, high-pressure, high-temperature chemical vapor deposition (CVD) or plasma-enhanced CVD. This work focuses on the fabrication of Diamond-Like Carbon (DLC) through Plasma-Enhanced Chemical Vapor Deposition, and on the
measurement of the properties of the material doped with boron and phosphorus from surface a source. The drive-in and activation of the dopants is done through thermal annealing. By testing different annealing temperatures, we are able to observe how the structural, optical and electrical properties of the carbon films were affected. It was found that synthesizing DLC at low temperatures (~100°C) in conjunction with annealing enhances the material crystallinity, its conductivity and allows higher transparency of the film.

**EN07.05.06**
**Sodium Flame Synthesis of Nano-Structured Powders for Catalytic Applications** Mary Krause, Geoff Smith, Nick Yin, Larry Wang and Grodon Smith; Global Advanced Metals USA, Inc., United States

Nano-structured, high surface area metal or ceramic powders have a growing interest within many markets including energy conversion, catalysts, and electronic materials. Manufacturing high purity metal powders at an industrial scale is a challenge due to trace impurities impacting powder performance. In particular, oxygen, nitrogen, and carbon impurities can adversely affect the physical and chemical properties of refractory metals such as titanium, tantalum, tungsten, and niobium. Here we present a nano-structured powder produced using a scalable sodium synthesis technology. Primary particle size and aggregate morphology of the resulting powder can be optimized for the given application by adjusting process parameters including optional metal or gas doping. In one such application, we adapt the powder for photocatalytic applications with promising performance.

**EN07.05.07**
**Synthesis, Characterization and Application of MoO₃ by Hydrothermal Route Assisted by Microwaves as an Adsorbent of Organic Dyes** Larissa O. Garcia¹, Fenelon M. Pontes¹, Rafaela F. Silva¹, Regina A. Capeli¹ and Elson O. Longo²; ¹UNESP São Paulo State University, Brazil; ²UFSCAR- Federal University of São Carlos, Brazil

Dyes and pigments, released from several industries such as textile, food, paper and cellulose, cosmetic and plastic industries, are the main organic pollutant compounds in wastewaters. The presence of dyes in water sources, even at low concentrations is very harmful to human beings and microorganisms. A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied and is used to impart color to materials of which it becomes an integral part. Most of the current treatment methods work through biological treatment processes, coagulation, oxidation, filtration, membrane separation, and adsorption. Among these methods, Adsorption presents advantages due to its simplicity, effectiveness, and cost-benefit. As adsorbent material, we have the MoO₃, an example of transition metal oxides has been widely used because of their different properties such as electrochromism, thermochromism, and photochromism, as well as having three polymorphs, which are called α-MoO₃, β-MoO₃, h-MoO₃. [1-4] In this work were synthesized MoO₃ nanostructures characterized by the techniques of XRD and BET where it was possible to observe that the prepared samples had the hexagonal, h-MoO₃ phases with a surface area of 6.5 m²/g and a mean crystallite size of 50,56 nm, and orthorhombic, α-MoO₃ with surface area of 14 m²/g mean crystal size of 25.80 nm for the sample using 20 mL of 6M HNO₃. MEV and TEM analyzes showed hexagonal prisms and nanobelts with a diameter of 200 nm and a length of 2μm. The spectra in the Infrared Region allowed identifying the presence of residual organic matter in the synthesis process. Diffuse reflectance spectra in the ultraviolet and visible region allowed to calculate the Band-Gap of h-MoO₃, in the value of 2.65 eV and 2.90 eV for the α-MoO₃ phase. For the adsorption study using different concentrations of Rhodamine B and Methylene Blue, was obtained spontaneous, endothermic, chemical nature adsorption.


**EN07.05.08**
**The Importance of the Interfacial Contact—Is Reduced Graphene Oxide Always an Enhancer in Photo(Electro)Catalytic Water Oxidation?** Zhirun Xie¹, Hui Ling Tan² and Yun Hau Ng³; ¹University of New South Wales, Australia; ²Kyushu University, Japan; ³City University of Hong Kong, Hong Kong
Optimization of the interfacial contact between graphene and semiconductor has been proposed to be essential to improve their charge interactions. Herein, we fabricate bismuth vanadate-reduced graphene oxide (BiVO$_4$/rGO) composites with tailored interfacial contacting extent and reveal their opposite behaviors in the photoelectrochemical (PEC) and powder suspension (PS) water oxidation systems. The BiVO$_4$/rGO with high rGO coverage (BiVO$_4$/rGO HC) features a remarkable superiority in PEC photocurrent enhancement to its low rGO coverage analogue composite (BiVO$_4$/rGO LC). On the contrary, BiVO$_4$/rGO HC shows detrimental effect while BiVO$_4$/rGO LC exhibits an enhanced performance for oxygen evolution in the PS system. This phenomenon is attributed to the changes in the hydrophobicity of BiVO$_4$/rGO composite in conjunction with the interfacial contact configuration. Enriched BiVO$_4$/rGO interfacial contact is found to improve the charge separation efficiency and charge transfer ability as well as the energetics of the composite material, explaining the superior PEC performance of BiVO$_4$/rGO HC. However, the highly hydrophobicity of BiVO$_4$/rGO HC ensuing from the higher rGO reduction degree triggers poor water miscibility, reducing the surface wettability and therefore hampering the photocatalytic O$_2$ evolution activity of the sample. This work also highlights water miscibility as the governing issue in the PS system.

EN07.05.09
The Remarkable Structure of Surface-Terminated Grain Boundary in Perovskite Oxides and Implications for Oxygen Electrocatalysis Yoon Heo, Hyung Bin Bae, Seungkyu Choi and Sung-Yoon Chung; KAIST, Korea (the Republic of)

A grain boundary forms as an internal interface when two crystalline grains with mutually different crystallographic orientations are in direct contact with each other. As a result, atomic arrangement at grain boundaries differs from that of the bulk, showing serious displacements deviating from the original symmetric positions. As these symmetry-broken configurations are difficult to achieve in the bulk crystals, grain boundaries are considered distinctive platforms that can exhibit new physical properties. By using both sintered polycrystals with various grain sizes and thin films on bicrystal substrates, it is directly verified that surface-terminating grain boundaries in LaCoO$_3$ and LaMnO$_3$ are exceptional in oxygen evolution electrocatalysis, showing more than an order of magnitude higher activity. A combination of atomic-scale structure observation and density functional theory calculations demonstrates that the displacement of atoms in metal–oxygen octahedra correlates with significant splitting of the degenerate transition-metal 3d orbitals, and subsequently much easier charge transfer between metals and oxygen is attained. In addition to identifying the grain boundaries as strikingly active sites, the findings suggest that symmetry breaking by atom displacements in metal–oxygen octahedra is an efficient approach to remarkably enhance the oxygen electrocatalytic efficiency in perovskite oxides.

EN07.05.10
Tailoring the d-Band Center and Electronic Structure of Co-N$_4$ Electrocatalyst for Hydrogen Evolution Reaction Sabhapathy Palani$^{1,2,3}$, Indrajit Shown$^1$, Wei-Fu Chen$^2$, Kuei-Hsien Chen$^{1,2}$ and Li-Chyong Chen$^{2,2}$; $^1$Academia Sinica, Taiwan; $^2$National Taiwan University, Taiwan; $^3$National Tsing Hua University, Taiwan

Electrochemical hydrogen generation via the hydrogen evolution reaction (HER) offers a promising solution for a green renewable-energy generation. Platinum (Pt) and Pt-based nanomaterials are mostly served as an efficient electrocatalyst for HER; however, due to its high cost and low abundance limits its large scale commercial application. Therefore, developing nonprecious metal based electrocatalyst for HER is highly necessary for large scale hydrogen production. Over the past decades, tremendous efforts have been made for Pt free electrocatalysts for HER. Recent advances in carbon nanomaterials (RGO, CNT, etc.) have shown their promising future in energy-related electrocatalytic reactions (ORR, OER, and HER) especially, after heteroatom (such as N, B, P, and S) doping, the catalytic activity enhanced. Among all the reported electrocatalysts, the co-doping of trace transition metals on heteroatoms doped carbon materials leads to form metal complexes (Ex. Co-Nx), showing promising HER activity in the aqueous electrolyte. In addition, the reported density functional theory (DFT) simulation shows that when combining both coordinations into one complex, the optimized charge distribution results in an ideal value of $\Delta G_0$ in Metal-Carbon-Nitrogen (M-C-N) hybrid system and which is much better than the single or mixture system of M-C and M-N.

In this presentation, we will demonstrate a new HER electrocatalyst based on Co-N$_4$ system. The cobalt-based catalysts are prepared by a one-step pyrolysis process at the high temperature in which vitamin-B12 (metal precursor) and thiourea (sulfur precursor) together with reduced graphene oxide (RGO). We observed that the electrocatalytic activities of synthesized catalysts are strongly related to the pyrolysis temperature, metal loading,
and acid leaching. The as-synthesized catalyst was characterized by XRD, XPS, and XAS. The results indicate that Co-corrin complexes (Vitamin B12) together with RGO have been decomposed at the high temperature to form new structure (ex. N-Co-C and N-Co-S). Furthermore, the density functional theory (DFT) calculation reveals, this conjugation induces downshift of the d-band center of cobalt, which decreases its hydrogen binding energy. The downshift of d-band center favors the electrochemical desorption of adsorbed hydrogen and leads to a relatively moderate Co–H binding strength, which helps for enhanced hydrogen evolution reaction. The comparison of HER activity and stability of cobalt electrocatalyst in alkaline and all pH electrolytes will be discussed at the meeting.

EN07.05.11
Ni(OH)2-WP Hybrid Nanorod Arrays for Superior Electro catalyst toward Hydrogen Evolution Reaction in Alkaline Media Kijung Yong and Dokyoung Kim; Pohang University of Science and Technology, Korea (the Republic of)

The development of efficient non-noble hydrogen evolution electrocatalysts in alkaline media is crucial for sustainable production of H2 through water electrolysis. Generally, the mechanism of hydrogen evolution reaction (HER) consists of a generation of hydrogen intermediates (Volmer reaction) and followed electrochemical desorption (Heyrovsky reaction) or H2 recombination (Tafel reaction). Compared with the process in acidic media, HER in alkaline solution requires extensive energy barrier owing to slow kinetics of water dissociation step caused by different reacting species in Volmer and Heyrovsky reaction in acidic (H3O+) and alkaline (H2O/OH−) media. To overcome this problem, an alkaline HER catalyst composed of Ni(OH)2-WP nanorod arrays on carbon paper was synthesized via thermal evaporation and electrodeposition. This hybrid catalyst exhibited outstanding HER activity and required a low overpotential of only 77 mV to drive current density of 10 mA/cm2 and a Tafel slope of 71 mV/dec. The hybrid catalyst also showed long-term electrochemical stability, maintaining its activity for 24 h. This improved HER efficiency was attributed to the synergetic effect of WP and Ni(OH)2: Ni(OH)2 effectively lowers the energy barrier during water dissociation and also provides active sites for hydroxyl adsorption, whereas WP adsorbs hydrogen intermediates and efficiently produces H2 gas. This interfacial cooperation offers not only excellent HER catalytic activity but also new strategies for the fabrication of effective non-noble-metal-based electrocatalysts in alkaline media.

EN07.05.12
NiCoP Double Transition Metal Phosphide/Ti3C2 MXene 3D Architecture as Efficient Bifunctional Photocatalyst for Solar Water Splitting Jiyeon Kang1, Seulgi Kim1, Sungho Song2 and Dongju Lee1; 1Chungbuk National University, Korea (the Republic of); 2Kongju National University, Korea (the Republic of)

Hydrogen energy is the ultimate challenge for achieving clean and sustainable energy in the current situation of environmental destruction caused by fossil fuels. Photocatalytic and photoelectrochemical water splitting under irradiation by sunlight has received much attention for production of renewable hydrogen from water on a large scale. Among various photocatalytic materials, transition metal phosphides have been studied as promising catalysts for hydrogen evolution reaction (HER) in solar water splitting, but have issues due to their low conductivity and stability.

Herein, three-dimensional (3D) porous architecture was fabricated with Double transition metal phosphide and conductive two-dimensional MXene hybrids. Ti3C2 MXene was used as a co-catalyst for exciton separation and charge transfer acceleration as well as a support material for the stability of NiCoP catalyst, due to its high conductivity and mechanical strength. Not only the 3D interconnected architecture with large electrochemically active surface area and structural stability but also the synergistic effect between the electrochemical activities of NiCoP and MXene Ti3C2 leads to excellent electrochemical performance.

EN07.05.13
Engineering Facet-Heterojunction Rutile TiO2 Photocatalyst for Highly Efficient Overall Water Splitting Chaomin Gao, Lina Zhang, Shenguang Ge, Xin Cheng and Kang Cui; University of Jinan, China

Rutile TiO2 in principle is a more potential photocatalyst owing to its narrower bandgap, higher thermodynamically stability and less intragrain defects when compared with anatase TiO2. Nevertheless, rutile TiO2 still hasn’t achieved the comparable photocatalytic activity with anatase-based TiO2 on account of its high recombination rate of electron-hole pairs. Electrons in rutile are deep trapped, which shows shorter lifetime in picosecond region,
however, the amount of electrons in microsecond to millisecond region is larger. In order to effectively separate the long-life electron, a novel rutile facet heterojunction TiO₂ with long-distance electronic pathway was firstly proposed to match the transportation of long-life electron, aiming to suppressing the carrier recombination and improving the photocatalytic activity. Here, a structural rutile TiO₂ with facet heterojunction mechanism, which could promote the separation of charge carriers efficiently, was designed for photocatalytic overall water splitting with the two-step hydrothermal strategy. In addition, compared with rutile TiO₂ nanorod, more than 60 and 25 times higher of generated photocurrent and H₂ productive rates are obtained for rutile facet heterojunction TiO₂, respectively.

EN07.05.14
Realizing Multiple Heterojunction within Single Titanium Dioxide Nanoparticles for Highly Efficient Solar Hydrogen Production Yoonjun Cho and Jong Hyeok Park; Yonsei University, Korea (the Republic of)

The surface disorder-engineering of TiO₂ has been drawing intensive interests in tuning surface energy states and thus boosting photocatalytic activity, but yet remains on application as in surface disorder layer. Selective localization of this disorder layer has not been reported so far, of which it can provide unpredictable strategy within the heterojunction interfaces to achieve novel metal-free photocatalysis. Conventional TiO₂ polymorph with mixed-phase heterojunction (anatase and rutile, Degussa P25) possessing energetic type-II band alignment at the interface, outperforming single-phase TiO₂ is employed in this work for single material photocatalyst.

Here we report conceptually different synthetic process to selectively localizing the crystal disorder layer between the anatase and rutile phase of a single TiO₂ nanoparticle, for highly efficient photocatalytic hydrogen (H₂) generation. Phase selective disorder-engineering of rutile TiO₂ followed by thermal re-oxidation below the phase transformation temperature could realize multiple heterojunction of anatase/disorder layer/rutile within a single P25 nanoparticle (denoted as DE-P25). The multiple heterojunction was thoroughly confirmed and analyzed by electron energy-loss spectroscopy (EELS) and electron holography mapping for the first time. EELS Ti-L₂,₃ spectrum geometry of DE-P25 showed distinctive oxygen-deficient variation between the two crystals which corresponds with the drastic decrease of potential and negative charge density within the disordered layer due to localized unpaired electrons. Also, PL decay profiles exhibiting dramatically enhanced charge separation efficiencies of DE-P25 indicate that the rutile phase incorporated with the disordered layer in the TiO₂ nanoparticle induces dominant direct excitation formation and reduces the self-trap of charge carriers, thus suppressing the electron/hole recombination.

The novel designing of multiple heterojunction in single TiO₂ nanoparticles could not only demonstrate efficient charge separation through interfacial charge polarization, but also novel metal-free H₂ generation rate of 3.994 μmol/cm² h⁻¹, which is ~11 times higher than that of Pt-decorated P25. This rational approach can provide breakthrough in stagnated efficiencies of metal oxide-based materials for commercial-scale photocatalytic H₂ production.

EN07.05.15
Effect of the Potential Deposition on the Photoelectroactivity of the SnSₓ/ SbₓS₃ Thin Films Moisés A. de Araújo¹, Francisco Willian d. Lucas² and Lucia Helena Mascaro¹; ¹Universidade Federal de São Carlos, Brazil; ²Universidade de São Paulo, Brazil

Semiconductor-based materials containing earth-abundant and low-toxicity elements are preferably desired to be applied either in photoelectrochemical or photovoltaic cells. Fitting these conditions, there are tin sulphide and antimony sulphide. Both materials have a narrow band gap and a high absorption coefficient. Most of the methodologies developed so far for the production of these materials are based on vacuum technique, which is a high cost method. Very little attention has been given for other methods known to be low-cost, such as, electrodeposition. In light of all these, the aim of this work is to evaluate the electrodeposition potential of ShSn followed by sulphurisation on the photoelectroactivity of this material. Additionally, the microstructure, morphology and optical properties of the unsulphured and sulphurised films were also studied. The electrodeposition of the films were carried out potentialistically at -1.07, -1.14 and -1.18 V vs Ag/AgCl/Cl⁻(sat. KCl) on FTO substrate with a deposition charge density of -332 mC cm⁻². The bath composition was 2 mM SnCl₂ and 4 mM K₂Sb₂(C₂H₂O₆)₂ dissolved in 0.1 M KNa(C₂H₂O₃) pH 6.0. The electrodeposited films were subsequently sulphurised at 270 °C per 3 h under sulphur vapour and argon gas flux. The XRD data for all unsulphured films were indexed to the SbSn and Sb phases, which was additionally confirmed by Raman spectra. Once sulphurised, the XRD and Raman data
indicated the Sb$_2$S$_3$ and SnS phases for all the electrodes. The SnS$_2$ phase was detected for the sulphurised films electrodeposited at -1.07 and -1.14 V. Regarding the optical properties, the estimated optical band gap for a direct (allowed) electronic transition of all the sulphurised films were around 1.8 eV. This value can be attributed to both Sb$_2$S$_3$ and SnS phases. Concerning the morphology of the films, the SEM images showed dendritic like morphology for the unsulphured films electrodeposited at -1.14 and -1.18 V, whilst the film obtained at -1.07 V presented cubic like morphology. The sulphurised films obtained at -1.07 and -1.14 V showed rode like morphology and the sulphurised one which was electrodeposited at -1.18 V had needle and small rods like morphologies. The photoelectrochemical assessments were performed in 0.5 M Na$_2$SO$_4$ + 1 mM 4-nitrophenol at pH 2.0 and under a solar simulator (100 mW cm$^{-2}$, AM 1.0 G). The results revealed that the electrodeposited film at -1.14 V resulted in the highest cathodic photocurrent density once sulphurised which was -113 μA cm$^{-2}$ at -0.315 V. We believe that the SnS$_x$, (SnS + SnS$_2$) and Sb$_2$S$_3$ phases formed a heterostructure SnS$_x$/Sb$_2$S$_3$ in the film which facilitates carriers separation and transportation and improves photocurrent density values. In order to confirm it, Sn and Sb films were prepared from the optimal electrodeposition condition and then sulphurised at the same condition as mentioned previously. The characterisation analysis showed that the sulphurised Sn film was made up of SnS and SnS$_2$, whilst Sb$_2$S$_3$ phase was identified for the sulphurised Sb film. In terms of photocurrent density values, sulphurised Sn and Sb films had cathodic photocurrent densities of -2.4 and -12.2 μA cm$^{-2}$, respectively. These results confirm the existence of the heterostructure SnS$_x$/Sb$_2$S$_3$ as its photocurrent density value was higher than the photocurrent density for the individual sulphurised phases SnS$_x$ and Sb$_2$S$_3$. Band diagrams for the sulphurised Sn and Sb films were constructed from Mott-Schottky analysis and band gap data. The results showed that the valence band maximum (VBM) and conduction band minimum (CBM) of the Sb$_2$S$_3$ film are shifted to lower energy vs. vacuum compared to the SnS$_x$ film. This band energy position favours the transportation of the photogenerated minority carriers from SnS$_x$-CBM to Sb$_2$S$_3$-CBM, increasing the charge separation and, consequently, the photocurrent.

**EN07.05.16**

**The Effect of Electrochemical Pre-Treatment in Sulfide Solutions on the Performance of Iron-Based Oxygen Evolution Catalysts**

Billal Zayat, Debanjan Mitra and Sri Narayanan; University of Southern California, United States

Electrochemical splitting of water is a very attractive technique for the production of clean hydrogen. Water electrolysis under alkaline conditions is particularly attractive compared to acidic water electrolysis because of the potential for a lower cost system. The alkaline system avoids the need for precious metals and perfluorinated membranes. However, the oxygen evolution reaction (OER) has sluggish kinetics leading to increased voltage losses and hence, reduced energy efficiency.\(^1\) Therefore, the development of a robust and low-cost alkaline water electrolyzer relies on developing inexpensive, durable, and efficient electrocatalysts for OER. Due to the instability and high cost of noble metal oxides such as RuO$_x$ or IrO$_x$,\(^2\) transition metal oxides anchored on a nickel substrate are commonly used for OER in alkaline conditions.\(^3,4\) The overpotential for these electrocatalysts is approximately 300 mV at 10 mA/cm$^2$.\(^5\) This relatively high overpotential coupled with the still expensive cost of a nickel substrate shows that there is a need to improve the catalyst performance and also reduce the cost of nickel-based substrates.

We report here on the performance characteristics of an inexpensive, durable, and efficient OER electrocatalyst with a high-surface area low-carbon steel mesh substrate. The first step in the electrode fabrication involved pre-treating the steel mesh by polarizing the electrode under alkaline conditions in a solution of sodium sulfide. This pre-treatment step increases the surface area of the steel mesh substrate by forming iron hydroxides. The modified steel substrate is then treated with nickel nitrate and annealed at 200°C to form a catalytically active nickel hydroxide layer. The electrode is rendered exceptionally robust in 30% potassium hydroxide and highly active towards OER in alkaline conditions by surface modification with nickel.\(^6,7\)

This electrode has the dual advantage of having a low overpotential of 227 mV at 10 mA/cm$^2$ while being significantly less expensive than common electrodes with nickel-based substrates. In addition, it shows excellent stability over 100 hours of continuous oxygen evolution with no loss in performance. This enhanced activity compared to what has been previously reported by our group\(^6,7\) is attributed to the increased catalytic surface area due to the sodium sulfide pre-treatment. Furthermore, we have examined the effect of changing the pre-treatment conditions, especially the number of pre-treatment cycles, and studied its effect on the surface area and catalyst performance. We have also studied the electrochemical and morphological characteristics using electrochemical impedance spectroscopy, SEM, and XPS.

Finally, we demonstrated a fully-functioning “all-iron” alkaline electrolyzer that uses the surface-modified steel for the OER electrode and nickel-molybdenum co-sputtered steel for the hydrogen evolution reaction electrode. The cell
achieves a voltage of 1.7 V at 100 mA/cm² at 70°C. The cell also shows outstanding stability during a 100-hour test at 1000 mA/cm² at room temperature with a cell voltage of 2.1 V.

References


EN07.05.17

Electron Transfer in the Solid State—Extension of the Corresponding Orbitals Transformation for Calculating Electron Transfer Parameter VAB to Periodic Systems Payan Kumar Behara and Michel Dupuis; University at Buffalo, The State University of New York, United States

We are interested in the fundamental characterization of solar-to-fuels conversion systems in the three phases of ‘light absorption’, ‘carrier transport’, and ‘carrier reactivity’, all contributing to the overall photo-electro-conversion efficiency. Our major focus is on ‘carrier transport’, specifically the modeling of transport of photo-generated electrons and holes in complex crystalline materials.

Our approach is based on the two-state model of Emin/Holstein/Marcus1–2 in which a key quantity is the electron-transfer coupling matrix element, V_AB, a measure of the strength of overlap between the initial and final electron-localized states. We report on the extension of the molecular method of Farazdel et al.3 to solid state periodic systems. The implementation handles any periodic HF- or DFT-based spin-constrained initial and final states and is carried out in the framework of the CP2K code.4 Test cases will be presented.

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EN07.05.18

Cobalt Molybdate-Based Electrocatalyst for Efficient Hydrogen Evolution in Alkaline Media Siyu Zhao; University College London, United Kingdom

Nowadays, much attention has been put on green energy production. Hydrogen is one of the most promising energy sources in the future. Electrolysis of water to generate hydrogen is one of the important strategies to produce hydrogen and much effort has been paid to develop costless, efficient and long lifetime electrocatalysts. Recently, transition metal phosphides (TMP) are largely explored due to its excellent hydrogen evolution reaction (HER) performance and low cost. However, the stability of TMP for long-time use is restricted due to its intrinsic structure and therefore HER performance is restricted. Moreover, although the HER mechanism in acid media is well documented, there is still large to explore in alkaline media for HER reaction. In this work, cobalt molybdate phosphides was successfully prepared to make a self-standing electrode. The optimised electrodes showed a small overpotential to reach a current density of 10 mA cm⁻² in alkaline media. The electrocatalysts also showed an excellent stability in a 48h test. Furthermore, DFT calculation combined with XPS tests revealed the whole process to induce P in the reaction and could give some insights to explain the role of P in HER. Results of in situ techniques showed some interesting phenomenon happened at the interface and gave some insights in explaining the HER.
mechanism in alkaline media.

**EN07.05.19**

**Enhanced Photoelectrochemical Performance of Ternary Ag/PaNi/NaNbO3 Nanocomposite Photoanode for PEC Water Splitting**

Dheeraj Kumar and Neeraj Khare; Indian Institute of Technology Delhi, India

The consumption of petroleum derivatives, for example, coal, oil and gaseous petrol have turned into a worldwide issue of environmental concern. The energy utilization is quickly increasing with rising population because of which there is a necessity of using sustainable green renewable energy sources to satisfy the needs of energy supply [1]. The solar based energy can be converted and stored in the form of fuels, for example, hydrogen (H2) by water splitting [2]. Hydrogen is an ideal green fuel and can replace fossil fuels in the future Photoelectrochemical (PEC) water splitting is one of the most promising methods for H2 generation on a large scale using a semiconductor nanocomposite materials. [3, 4].

In the present work, a ternary Ag/PaNi/NaNbO3 nanocomposite photoanode has been successfully fabricated by chemically grafting of Ag nanoparticles (NPs) over binary PaNi/NaNbO3 nanocomposite for PEC water splitting applications. The Ag NPs on the surface of binary PaNi/NaNbO3 nanocomposite, act as a photosensitizer under visible-light illumination due to the surface plasmonic effect. The ternary Ag/PaNi/NaNbO3 nanocomposite photoanode exhibit an enhancement in the PEC activity as compared to binary PaNi/NaNbO3 and NaNbO3 photoanodes. Under light illumination, the current density of the ternary Ag/PaNi/NaNbO3 nanocomposite has been achieved to be ~ 5.93 mA/cm² (at 1V vs. Ag/AgCl), which is ~5 fold and ~2 fold higher than pristine NaNbO3 and binary PaNi/NaNbO3, respectively. The enhanced PEC activity of ternary Ag/PaNi/NaNbO3 composites is attributed to the improved light absorption in the visible part of the solar spectrum due to (1) the surface plasmonic effect (as Ag NPs act as photosensitizer for visible-light harvesting), because of coupling with PaNi intermediate material which is used as a remarkable electron transporter which easily effectively separate the e- - h+ pairs and decrease the recombination rate, and due to type-II heterojunction formation between PaNi and pristine NaNbO3. The results show the potentiality of fabricated ternary Ag/PaNi/NaNbO3 photoanode materials towards improved PEC water splitting application.

References

**EN07.05.20**

**Exfoliated NiPS3 Nanosheets as an Oxygen Evolution Reaction Electrocatalyst**

Raksha Dangol1, Zhengfei Dai1,2, Apoorva Chaturvedi1 and Qingyu Yan1; 1Nanyang Technological University, Singapore; 2State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, China

Nanostructuring is an important aspect of synthesis of nanomaterials. 2D materials, considered as promising group of materials for electrocatalysis, can be easily exfoliated into nanosheets by ultrasonic-sum-solvent assisted methods. Nanosheet structures, thus formed, have a large surface area which, expose higher active sites and give rise to fast electron transport during water splitting process. Hence, this process is used to exfoliate bulk NiPS3, a representative material from MPX3 family synthesized using Chemical Vapour Transport method, by the application of ultrasonic bath for a good yield of NiPS3 nanosheets. Various solvents were systematically investigated for obtaining high yield of the nanosheets, whereby Formamide had the highest yield among the ten commonly used solvents. Thus-obtained nanosheets are employed as an oxygen evolution reaction (OER) catalyst. The NiPS3 nanosheets demonstrate an excellent electrocatalytic OER properties, like a low overpotential of 301 mV at the current density of 10 mA cm² and a small Tafel slope of 43 mV dec⁻¹ and a remarkable long-term stable performance. Upon further investigation on the performance, it was observed that the improved catalytic activity was due to a large electrochemically active surface area and high intrinsic activity. It was also found that the in-situ formation of NiOOH and its interface enhances the OH⁻ adsorption and reduces Gibbs free energy of the reaction intermediates.

**EN07.05.21**

**In Situ Raman Spectro-Electrochemical Studies of Support-Catalyst Interface of Nanocarbon Florets**
Supported Co₃O₄ with an Energy Efficient Electrocatalysis under a Magnet  
Jayeeta Saha; Indian Institute of Technology Bombay, India

The demand for worldwide energy calls for the need to build up an effective technology for the manufacture of a clean and sustainable energy source as a fuel cell. Hydrogen is considered as the cleanest and high specific energy density fuel source. The object is to provide catalysts with a catalyst-support which can produce maximum hydrogen with a minimum applied energy, i.e., high current density with low overpotential. For this purpose, comprehending the mechanistic involvement of support-catalyst interface is critical for effective designing of industrially relevant electrocatalytic processes such as alkaline hydrogen evolution reaction (alHER). The understanding of kinetically sluggish alHER exhibited by both Pt and Pt-group-metal-free catalysts is primarily derived from indirect electrochemical parameters such as Tafel slope. Addressing these lacunae, we establish the critical role of nanocarbon florets (NCF) based electrochemical support in generating key cobalt-oxohydroxo (OH-Co=O) intermediate during alHER through operando Raman spectro-electrochemistry. Specifically, interfacial nano-engineering of a newly designed carbon support (NCF) with a spinel Co₃O₄ nanocube catalyst is demonstrated to achieve facile alHER (-0.46 V @10 mA/cm²). Such efficient alHER is mainly attributed to the unique lamellar morphology with high mesoporous surface area (936 m²/g) of NCF that catalyzes the rate-determining water dissociation step and facilitates rapid ion diffusion. The dissociated water drives the formation of OH-Co=O intermediate, spectroscopically captured for the first time through the emergence of \(\text{OH-Co} = \text{O} \) Raman peak (1074 cm⁻¹). Subsequent alHER proceeds through Volmer-Heyrovsky route (119 mV/dec) via \(T_{\text{d}}\) Co\(^{2+}\leftrightarrow Co^{3+}\leftrightarrow Co^{4+}\) oxidative pathway. Concomitant graphitization of NCF through the disappearance of \(\text{sp}^3\text{C-H (2946 cm}^{-1})\) supports the cooperative dynamics at the Co₃O₄-NCF interface. Thus, NCF positively contributes to the lowering of overpotential with low charge-transfer resistance (\(R_{\text{ct}}=35.8 \, \Omega\)) and high double layer capacitance (\(C_{\text{dl}}=410 \, \text{mF/cm}^2\)). Thus, the participation of both catalyst and its support to enhance HER activity is thereby confirmed in contrast to conventionally established understanding of passive support.

Further, for the mass production of hydrogen, the term “magneto-electrolysis” plays a crucial role, where the magnetic fields influence the performance of electrocatalysis processes. Thus we explore the interactions of magnetic fields with electrocatalysts and the control to the formation of the diffusion layer over the electrode-electrolyte interface. This effect in the reaction interface directs the mass transport of reactive components at the electrode surface and control the reaction rate at the electrode-electrolyte interface. This magnetization behavior is present after removal of the small disc magnets, indicating the remanent magnetization of the para/ferromagnetic catalyst, which plays a crucial role in the electrocatalytic enhancement process. Therefore, by using a 0.05 T magnetic field the overpotential of Co₃O₄-NCF was reduced by 12%. The total energy saved by using the 0.05 T magnetic field is 13% of its normal usage. Thus, magneto-electrocatalysis can be the next energy efficient technique for hydrogen evolution and subsequently magneto-catalysis become the alternative of electrocatalysis for water splitting.

EN07.05.22
Triggering Catalytic Active Sites for Hydrogen Evolution Reaction by Intrinsic Defects in Janus Monolayer MoSSe  
Wenwu Shi and Zhiguo Wang; University of Electronic Science and Technology of China, China

Janus transition-metal dichalcogenides have been predicted to be promising candidates for hydrogen evolution reaction (HER) due to their inherent structural asymmetry. However, the effect of intrinsic defects, including vacancies, antisites, and grain boundaries, on their catalytic activity is still unknown. MoSSe provides an ideal platform for studying such defects, since theoretical calculation has indicated that the formation energies of point defects and grain boundaries on MoSSe were lower than that of pristine MoS₂ monolayer. In this work, density functional theory is utilized to study all of the possible intrinsic defects on the MoSSe monolayer for HER. The MoSSe monolayer with 4/4, 4/8a, 5/7b, 8/10a GBs, vacancies (Vs, Vsₐ, Vsₐₐ, Vₘ₉, Vₘ₉₃), and antisite defects (MoSSe, Seₘ₉, Sₘ₉) shows enhanced HER performance. The adsorption behaviors of hydrogen on defects were explained by using a “states-filling” model. The adsorption energy of hydrogen during catalysis changes linearly with the work required to fill unoccupied electronic states within the catalysts. The work required to fill the unoccupied electronic states of MoSSe monolayer can be described via an integral formulation of the DOS of catalyst.

The electronic structures of Janus MoSSe were further analyzed to reveal the deep mechanism of enhanced catalytic activity for HER by introducing defects. The pristine Janus MoSSe shows a direct band gap of 1.55 eV. It is difficult for H to donate its electron to Janus MoSSe by overcoming large barrier of 1.55 eV. Therefore, unstable adsorption states were formed when the H atom adsorbed on the MoSSe surface. However, for MoSSe with Vs and 8/10a GBs, defective states appear below and above the Fermi energy. The gap states would provide an unoccupied state near
the Fermi energy. The Fermi energy level shifts up after H adsorption, which is due to the transfer of charge from H atom to MoSSe. Our calculation reveal that the introduction of gap states in hydrogen adsorbed systems is the origin of enhanced HER activity.

**EN07.05.23**

**Microkinetic Modeling of Water Oxidation in Photoelectrochemical Cells—The Impact of Surface States on the Electrochemistry**

Kiran George¹, Tigran Khachatrjan¹, Matthijs van Berkel¹,²,³ and Anja Bieberle-Hütter¹;

¹DIFFER, Netherlands; ²Technische Universiteit Eindhoven, Netherlands; ³Vrije Universiteit Brussel, Belgium

Water splitting in photoelectrochemical (PEC) cells involves two set of reactions: the hydrogen evolution reaction and the oxygen evolution reaction (OER). We focus on the OER at the semiconductor-water interface to identify limiting processes at the interface. Recently, we have developed a general approach to relate electrochemical measurements to the kinetics of multistep reactions at the semiconductor-electrolyte interface¹. The hematite (Fe₂O₃) – water interface is used as model system in this study. A microkinetic model of OER is developed and is formulated as a state-space model (SSM); the applied potential is the input and the current density is the output. By solving the model, j-V plots and impedance spectra can be simulated similar to experimental measurements.¹

According to the literature, charge transfer under illumination happen directly via the valence band and indirectly via surface states. In our model, we use Gerischer theory and hence the electron transfer rates are defined in terms of empty and occupied energy states on either side of the interface. For any given surface state the charge transfer rate can be calculated similar to the calculation of charge transfer rates via valence band or conduction band.² By using these rates in the state space model, indirect charge transfer via surface states is simulated. Charge transfer via both valence band and surface states are modeled and compared. The impact of surface state properties on the electrochemical measurements is investigated. Steady state j-V plots, impedance spectra, and linear sweep voltammetry curves simulated from the model will be presented for different energy states within the band gap. The sensitivity of these measurements to the intermediate reaction rates, voltage-scan-rate, semiconductor parameters, and other interface parameters is discussed.


**EN07.05.24**

**Bimetallic Phosphide Encapsulated on Carbon Matrix Derived from Metal-Phenolic Network as Stable and Efficient Electrocatalysts for Oxygen Evolution Reaction**

Gwan Hyun Choi, Clament Sagaya Selvam Neethinathan and Piljin Yoo; Sungkyunkwan University, Korea (the Republic of)

Rational design of electrocatalyst with high activity and stability is imperative for developing sustainable water electrolysis. In this work, we have developed bimetallic phosphide embedded in P-doped carbon layers as a stable electrocatalyst for oxygen evolution reaction (OER). Here, distinct from other metal/carbon sources, tannic acid (TA)-based metal-phenolic networks (MPNs) are utilized to design stable and efficient hybrid structures. Especially, thanks to the strong coordination between the phenolic ligands and metal ions in atomic/molecular scale, which facilitates the nanometer-sized hybrids formation with evenly distributed/embedded metal nanoparticles in few layers of graphitic carbons without any aggregations. It has been observed that every single nanoparticle (transition metals=Fe, Co and Ni) in the hybrid can serve as active site while carbon layers can prevent massive surface oxidation and poisoning under OER conditions. Precisely defined metal/carbon interface structure was achieved via simple carbonization step. The subsequent phosphidation results in metal phosphides that remarkably increases the number of active sites. Meanwhile, controlling the appropriate atomic ratio of metal and electronegative P atoms enhances the conductivity of the hybrid electrocatalyst. Since phosphidation process is diffusion-driven reaction from outmost carbon layer to inner metallic phases, the final product has the unique structural characteristics that consist of core metallic phase and peripheral metal phosphide phase with P-doped carbon layers. We have demonstrated that the bimetallic phosphide shows enhanced activity (~270mV at 10mA cm⁻², under 1M KOH alkaline condition) compared with monometallic phosphides, state-of-the-art IrO₂ and other benchmark electrocatalysts. The structural contributions to the electrocatalyst activity and long-term stability (~100 hours) has been systematically investigated by using synchrotron-based X-ray absorption spectroscopy (XAS) and photoelectron spectroscopy (XPS). Combining with structural investigations and electrochemical studies, it can be concluded that its enhanced activity stems from synergistic function of each of metal phosphide species with its
EN07.05.25

Visible/Near-Infrared Driven Photocatalyst Based on Upconversion Nanoparticles and Graphitic Carbon Nitride Yong Il Park; Chonnam National University, Korea (the Republic of)

Graphitic carbon nitride ($g$-C$_3$N$_4$) is a promising visible-light-driven photocatalyst. $g$-C$_3$N$_4$ is inexpensive, air-stable, and non-toxic material and they have been proven to exhibit high performance in photocatalysis. To use solar energy more efficiently, it is necessary to broaden the light absorption of $g$-C$_3$N$_4$ is required. To take advantage of the near-infrared (NIR) region of solar energy, the $g$-C$_3$N$_4$ was combined with upconverting nanoparticles (UCNPs). The UCNPs convert NIR photons to visible light which can activate the $g$-C$_3$N$_4$ photocatalyst. The use of visible and NIR light source improves the photocatalytic activity of the UCNP@$g$-C$_3$N$_4$ nanocomposites. In order to optimize the photocatalytic efficiency of the nanocomposite, the absorption and emission wavelengths of the UCNPs were tuned by controlling the lanthanide dopant composition. The nanocomposite exhibited excellent photocatalytic activity under simulated solar light illumination.

EN07.05.26

Effect of Electronic and Structural Properties of Transparent Conductive Colloid Mediator on Z-Scheme Water Splitting over Printable Photocatalyst Sheets Hiromasa Tokudome1,2, Sayuri Okunaka1,2, Shingo Oozu1,2, Takeshi Ikeda1,2 and Kazunari Domen3,4; 1TOTO Ltd, Japan; 2Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), Japan; 3The University of Tokyo, Japan; 4Shinshu University, Japan

Photocatalytic water splitting is attracted a significant attention as a low-cost production process for renewable hydrogen using abundant sunlight. In the reaction system using photocatalyst particles, Z-scheme system via two-step excitation can be a practical candidate instead of one-step reaction on visible-light-responsive single photocatalyst particle with difficult development. Z-scheme water splitting can drive by employing two kinds of visible light responsive photocatalysts selectable from various ones in the presence/absence of appropriate mediators such as redox ions or conductive materials. We previously reported that a Z-scheme-type printable photocatalyst sheet exhibited the solar-to-hydrogen energy conversion efficiency (STH) of 0.1%. This sheet is fabricated by screen printing and consisted of mixed films of two kinds of visible-light-active photocatalysts and a conductive mediator nanocolloid on a glass substrate. 1) Recently, we designed a new photocatalyst sheet based on transparent colloidal indium-tin-oxide mediator, attaining the STH of 0.4%. 2) In this study, we fabricated a Z-scheme-type photocatalyst sheet composed of a new transparent and low-cost mediator, antimony (Sb) -doped tin oxide (ATO), and examined the water splitting activity.

Z-scheme-type sheets were prepared via screen-printing on borosilicate glass substrates using a viscous paste including Rh-doped SrTiO$_3$, BiVO$_4$ and ATO particles. The sheets produced hydrogen and oxygen from pure water in the stoichiometric ratio under visible light irradiation. This result showed that the ATO colloid acted as an electron mediator between the two photocatalysts. Moreover, it is found that the water splitting activity varied with Sb doping concentration and particle morphology of ATO colloid.

EN07.05.27

Aerosol-Assisted Chemical Vapour Deposition of alpha-Fe$_2$O$_3$ Thin Films for Water-Splitting Matthew K. Surman, Andrew Johnson, Michael Hill and Salvador Eslava; University of Bath, United Kingdom

The global interest in developing renewable fuels as an alternative to fossil-based fuels has supported a resurgence in the use of hydrogen; at present, hydrogen is produced predominantly through the steam reformation of methane, and so research has been focused on producing hydrogen more cost-effectively from sustainable sources with a smaller carbon footprint.
Semi-conducting materials with an appropriate band-gap are able to absorb photons emitted by the Sun in order to drive the conversion of water into hydrogen and oxygen. In order for this photoelectrochemical water-splitting to take place, the band-gap of the semi-conducting material must bridge the redox potentials of the two relevant water-splitting half-reactions.

Hematite (alpha-Fe₂O₃) is a well-studied material for photoelectrochemical water-splitting; it has reported optical band-gaps between 1.9–2.2 eV, giving it a theoretical solar-to-hydrogen efficiency of around 15 %. Iron is also an earth-abundant metal, making hematite an inherently cheap-to-produce material, which raises few concerns about supply longevity.

This work focuses on the designing and synthesis of new iron(II) complexes as single-source precursors for hematite deposition using AA-CVD, which can affect the structure and morphology of the resultant films, and thus alter the optical and electronic properties of the film for more favourable photoelectrochemical water-splitting.

References

**EN07.05.28**
**Growth and Characterization of Tantalum Oxynitrate Thin Film for Solar Water Splitting**
Roberto Masso-Ferret, Javier Wu and Ratnakar Palai; University of Puerto Rico at Rio Piedras, United States

In the view of the current global energy crisis and environmental problems, it is a pressing need to explore and exploit some sustainable energy systems. Oxynitrdes are considered as important materials for photocatalytic water splitting applications. In this paper, we report on growth, optimization, and characterization of TaON thin films by sputtering on Si, glass, and sapphire substrates. Structural, electrical, and optoelectronic properties of TaON thin films were investigated using various characterization techniques. The crystalline structure of the films was analyzed using X-ray Diffraction XRD. In order to understand the conduction mechanisms of the samples, we performed current-voltage characteristics. Hall Effect measurements were done on the samples in order to determine band gap and charge carrier’s mobility. The electronic and photocatalytic properties of a prototype for water splitting will be discussed in detail.

**EN07.05.29**
**Enhancement of Photocatalytic Oxygen Evolution Reaction of Nanoscale BiFeO₃ Using IrO₂ Nanoparticles**
Wegdan Ramadan¹,² and Detlef Bahnemann¹,³; ¹Leibniz Universität Hannover, Germany; ²Alexandria University-Faculty of Science, Egypt; ³St Petersburg State University, Laboratory “Photoactive Nanocomposite Materials, Russian Federation

BiFeO₃ (BFO) is a multiferroics that combines antiferromagnetic and ferroelectric order well above room temperature also it is narrow band gap semiconductor (~ 2.2-2.7 eV) hence, it can harvest significant amount of visible light. Combining such desired properties on simple ternary compound makes it easier to utilize in many different folds. However, the performance of BFO in overall water splitting is still poor due to the fast recombination of the photogenerated charges and the position of its conduction band with potential less negative than that for water reduction meanwhile its valence band potential is more positive than that required for water oxidation. Here we report on the enhancement of the photocatalytic oxygen evolution reaction, OER, of BiFeO₃ nanoparticles using IrO₂ nanoparticles loaded on the BFO surface using impregnation method. OER showed two folds enhancement upon loading with 2wt% IrO₂. IrO₂ is one of the best catalyst for OER, unfortunately it is also one of the most expensive rare elements hence their applicability is limited by the high cost. Reducing IrO₂ content onto the system should be an option to make its application feasible and cost effective and loading on IrO₂ nanoparticles on the surface could be one feasible solution. Scanning the loaded IrO₂ content from 0.5 wt% to 4 wt% showed a maximum of OER at 2wt % followed by a decrease in activity. XPS showed the formation of Ir (IV) and TEM indicated non uniform distribution of it on the surface. Charge carrier life time and dynamics for pure BFO and IrO₂ loaded BFO have been studied by means of diffuse reflectance laser flash photolysis spectroscopy. Transient absorption of the charge carriers indicated a significant increase in the charge life time in the case of 2wt% IrO₂ loading compared to the other IrO₂ contents. Band positions between BFO and IrO₂ favors the formation of heterojunction at the interface between IrO₂ and BiFeO₃ that enhances the separation of the photogenerated charges
and the photocatalytic OER performance. The position of the conduction band could be manipulated by forming solid solution with SrTiO3 towards formation of Sr1−xBixTi1−xFexO3 having different x values and/or doping BFO to achieve overall water splitting which is our future work.

EN07.05.30
Effect of Hf Doping on ZnO Photo-Anode
Boulos AlFakes1,1, Corrado Garlisi1, Nituil S. Rajput1,1, ChunYu Lu1,1, Ibraheem Almansouri1, Giovanni Palmisano2 and Matteo Chiesa1,1,2; 1Khalifa University of Science and Technology, United Arab Emirates; 2UiT The Arctic University of Norway, United Arab Emirates

The urgent need for a sustainable storable alternative to oil, boosts the research on hydrogen generation using water splitting. ZnO is a promising material in this context, and has been widely studied as an anode in a water splitting solar cell. Different dopants, such as Al, Cu, Ag and N, were utilized to enhance the ZnO performance for this type of applications. In this work, ALD grown Hf doped ZnO is presented as a valid material for utilization as an anode in PEC cell. The effect of Hf doping on the photoelectrochemical performance is studied optically, structurally and electrically. A decrease in the anode resistivity, as well as an increase in the carrier concentration was observed. As a result, an impressive 250% increase in the photocurrent was obtained in the Hf doped sample in comparison to the undoped ZnO. Furthermore, DFT simulations are presented to compliment the detailed experimental characterization, to support the interpretation for this enhanced performance. Those results open the research for utilizing this material into more common water splitting structures, such as nanorods and nanowires, which can be efficiently and conformably coated through atomic layer deposition.

EN07.05.32
A Band Diagram Based Device Modeling Approach for Designing Photoelectrochemical Anodes
Botong Miao, Asif Iqbal and Kirk Bevan; McGill University, Canada

Photoelectrochemical (PEC) cells offer a promising route towards combating climate change through the production of hydrogen fuel. However, PEC cells have remained inefficient due to the sluggish oxygen evolution reaction present at the photoanode. This key inefficiency bottleneck remains a major obstacle to the large-scale commercialization of PEC cells. In this regard, operational photovoltage and photocurrent trends provide key metrics for characterizing and improving the performance PEC photoanodes. However, a quantitative band diagram approach for systematically engineering these properties is still lacking. Here, we discuss how self-consistent solutions to the semiclassical equations governing PEC cells can provide fundamental band diagram based insights into improving their operation. Our work focuses on modeling the ultimate factors determining the photovoltage and photocurrent under active operation and how these quantities can be directly correlated with electron and hole densities in illuminated PECs. In general, this study underscores the engineering opportunities provided by a rigorous device modeling based design approach.

EN07.05.33
Fabrication Process Analysis of Non-Precious Metal Electrochemical Water Oxidation Catalysts of MOx (M = Mn, Fe, Co, Ni) by Raman Spectra
Katsushi Fujii, Kayo Koike, Kei Morishita and Satoshi Wada; RIKEN, RAP, Japan

Non-precious metal oxides are often used materials for electrochemical catalysts and photoelectrochemical co-catalysts of water oxidation. The mechanisms of water oxidations on these catalysts are complicated. Not only -O but also -OOH is believed to play an important role in the water oxidation. Especially, the Fe oxide site for the case in the Fe oxide mixed in the other non-precious metal oxides is said to be the active site [1]. Unfortunately, non-precious metal oxides are usually stable in basic solution but not stable in neutral and acidic solutions even the abilities are comparable to precious metal oxide (IrOx for example) electrochemical water oxidation catalysts. The MnOx is, however, reported to be relatively stable even in the acidic solutions when the applied potential is selected [2]. The water oxidation properties of non-precious metal oxides are still obscure and discussed. The reasons for the complexity of the non-precious oxides electrocatalytic properties are probably the effects that the oxides have multi oxidation numbers, multi-crystal polymorphism, and wide nonstoichiometric compositions. Therefore, the chemical states and bonds of the metal atoms are important characteristics to analyze the properties. One of the non-precious metal oxide formations is thermal oxidation of metal nitrate aqueous solution. In this report, the chemical state
changes of the MOx (M = Mn, Fe, Co, Ni) during the catalyst formation process were observed by Raman spectra as the first step of the analysis of the metal oxide catalysts. The Raman spectra for Mn and Ni nitrate aqueous solution are relatively strong compared to those for Fe and Co nitrates. The spectra show the difference between the different metals. Comparison from their (Ni and Co) reported solid oxide Raman spectra [3,4], some of the peaks are close to its TO related modes and 2LO. The peak around 1000 to 1100 cm⁻¹, which is close to the peak assigned as 2LO in the solids, are most strong. It should be noted that the metal oxides Raman spectra were different with changes in its concentration of metal nitrate in water. The Raman spectra after dropping the nitrates on carbon paper were similar to the form in aqueous solution but changed. The Raman spectra were weakened after the anneal at 250°C for 2.5 hrs in the air. These results probably show that nonprecious metal can change its chemical form easily.


EN07.05.34
Method for Determining Bond Energy in Nanostructured Water Vitaly Bondarenko, Svetlana A. Volchek, Vladimir A. Petrovich, Valentina A. Yakovtseva, Sergey Redko and Alexander Grigoriev; Belarusian State University of Informatics and Radioelectronics, Belarus

Today, there are the following basic ideas about the structure of water as a partially self-organizing system with a dipole as an elementary structural element: (1) in addition to neutral dipole water molecules, water also contains the OH⁻ and H⁺ ions that are products of the water dissociation; (2) water contains water molecules that are linearly associated with hydrogen bonds, and the closed (by the ring principle) structural organization of water is not excluded at that; (3) water forms three-dimensional nanoclusters. Each nanocluster can contain from 100 to 500, and even up to 910 water molecules. The nanocluster size is estimated to be equal to 1.5 nm. The basis for the cluster construction is a tetragonal cell, at the vertices of which water molecules linked by the hydrogen bonds are located. This paper discusses the study of the change in the loss tangent for deionized water in the frequency range from 25 to 10⁶ Hz. The water temperature during the loss tangent registration was 293 and 323 K. The acidity value of deionized water was regulated by hydrochloric acid. Using water as an example, it is shown that monitoring the change in the loss tangent is a high sensitive method that allows determining the activation energy of relaxation processes in nanostructured water with high accuracy. The paper presents an analysis of the use of open- and closed-type sensors. The use of closed-type sensors, the electrodes of which are not in direct contact with the liquid under study, is justified for monitoring the properties of aqueous solutions. When studying the properties of water using a closed-type sensor, the sensor electrodes together with the fluoroplastic coating serve essentially to create an electric polarizing field in the volume of the liquid studied. When registering the dispersion of the loss tangent and other immittance characteristics, electrode reactions associated with the electric current passage through the metal-dielectric-liquid interface (Faraday currents) do not affect the results—they simply do not exist. At the same time, in the bulk of water and its solutions, not only polarization processes, but ion transfer processes take place as well. These processes occur simultaneously. Thus, a closed-type sensor registers mainly the volume properties of water and allows, the acidity values of the solution to be unambiguously determined at any frequency not exceeding 10⁵ Hz.

SESSION EN07.06: Novel Water-Splitting Catalysts I
Session Chairs: Jin Suntivich and Guofeng Wang
Wednesday Morning, December 4, 2019
Sheraton, 2nd Floor, Liberty BC

8:30 AM *EN07.06.01
Nanometal for Hydrogen Evolution De-en Jiang; University of California, Riverside, United States

Hydrogen in metals underpins many key technologies in energy storage and conversion such as hydrogen storage.
and metal-hydride batteries, but little is known about hydrogen in many nanosystems such as gold nanoclusters. In this talk, I will discuss our recent computational efforts to elucidate the role of hydrogen in metal nanoclusters and the relevant catalytic impact. Especially, we focus on the energetics of H-metal interaction and how it changes the electronic structure of the nanosystems and impacts hydrogen evolution.

9:00 AM
EN07.06.02
Interfacial Engineered Colloidal “giant” Core/Shell Quantum Dots Sensitized Carbon Nanotubes-TiO2 Hybrid Photoanode for High-Efficiency Hydrogen Generation Gurpreet S. Selopal1,2, Mahyar Mohammadnezhad2, Omar Abdelkarim2, Haiguang Zhao3, François Vidal2, Zhiming Wang1 and Federico Rosei2,1; 1IFFS-UESTC, China; 2INRS-EMT, Canada; 3Qingdao University, China

Solar-driven photoelectrochemical (PEC) hydrogen (H2) generation is an attractive approach for the sustainable production of clean and renewable fuels, to address future global energy demands [1-2]. However, the low photon-to-fuel conversion efficiency and long-term stability of PEC devices are major challenges to be addressed to enable large-scale commercialization. The sensitization of the wide band gap semiconductors with colloidal chalcogenide quantum dots (QDs) as light harvesters is an effective approach to extend the absorption spectrum toward the visible and near infrared region (NIR) region, leading to significant improvement of the PEC performance[3]. A specially designed “giant” core/shell QDs exhibit superior optoelectronic properties such as better photophysical/chemical stability, suppressed non-radiative Auger recombination, improved quantum yield (QY), and improved exciton lifetime and the formation of quasi-type-II core/shell by tailoring the shell thickness/composition as well as the core size [4]. Also, the carbon nanomaterials such as carbon nanotubes (CNTs), graphene, graphene nanoribbons and graphene oxide are widely used in various optoelectronic devices due to their unique structural and optoelectronic properties such as excellent conductivity, high mechanical strength and optical transparency [5]. Herein, for the first time, we explore a simple, fast and cost-effective approach to fabricate high efficiency and stable PEC devices for H2 generation, by using a specially designed colloidal “giant” CdSe/(CdSe,S1-x)5/(CdS)2 core/shell QDs as sensitizer and a hybrid photoanode with small amounts of CNTs into a TiO2 mesoporous film.

We will discuss the synergistic effect of promising optoelectronic properties of specially designed colloidal giant” CdSe/(CdSe,S1-x)5/(CdS)2 core/shell QDs and improved electron transport (reduced charge transfer resistance) within the TiO2-CNTs hybrid anodes enabled by the directional path of CNTs to the photo-injected electrons towards FTO. Resulting, PEC devices based on TiO2/QDs-CNTs (T/Q-C) hybrid photoanode with optimized amount of CNTs (0.015 wt%), yield a saturated photocurrent density of 15.90 mA.cm-2 (at 1.0 VRHE) under one sun illumination (AM 1.5 G, 100 mW×cm-2), which is 40% higher than the reference device based on TiO2/QDs (T/Q) photoanodes. In addition, enhanced stability of the PEC device based on T/Q-C hybrid photoanodes (~19% loss of its initial photocurrent density) as compared with the T/Q photoanode (~35% loss) after two hours of continuous one sun illumination will be also presented and discussed in details. These results provide fundamental insights and a different approach to improve the efficiency and long-term stability of PEC devices and represent an essential step towards the commercialization of this emerging solar-to-fuel conversion technology.

References

9:15 AM
EN07.06.03
Molecular Insight into the Osmolality of Ionic Liquid with Lower Critical Solution Temperature Transition Behavior Hyungmook Kang1,2, Akanksha K. Menon1, Robert Kostecki1, Chris Dames2 and Jeffrey Urban1; 1Lawrence Berkeley National Laboratory, United States; 2University of California, Berkeley, United States

A subclass of ionic liquids (ILs) undergoes a thermoresponsive liquid-liquid phase transition of lower critical solution temperature (LCST). In liquid-liquid mixtures with an LCST transition, a single and miscible phase appears at lower temperatures, whereas the single-phase mixture separates into two immiscible phases upon heating above a critical temperature. The IL-based mixtures as draw solutes have opened up new water purification potentials such...
as forward-osmosis desalination. This study tracks the changes in long-range order and local-molecular environment of an IL-water mixture with LCST transition, experimentally and theoretically. In the mixture, the IL forms loosely hold aggregate structures that grow in size leading up to a critical temperature, whereas the aggregation of a fully miscible aqueous mixture by minor chemical modification of the anion shrinks versus increasing temperature. Radial distribution functions from Molecular Dynamics simulations support the observation of aggregation phenomena in the IL-water mixtures. For the usage as the osmosis draw solutes for water purification, the osmolality of the IL in water is measured as a function of concentration. The geometric nature of ILs introduce steric hindrance and strong attractive interaction between cation and anion causes a non-monotone trend of the osmolality. Molecular approaches considering the interaction between ions and the number of water molecules near each ion from Molecular Dynamics simulation suggest a method to define free ions in the mixture, which can improve the osmotic pressure.

9:30 AM EN07.06.04
A Combined Spectroscopic and First-Principles Approach for the Atomistic-Level Description of Semiconductor/Electrolyte Interface
Masahiro Sato, Yuki Imazeki, Takahito Takeda, Masaki Kobayashi, Susumu Yamamoto, Iwao Matsuda, Jun Yoshinobu, Yoshiaki Nakano and Masakazu Sugiyama; The University of Tokyo, Japan

Photocatalytic water splitting is one of the most attractive technologies for storing sunlight. However, today’s photocatalysts (photoelectrodes) still suffer from low efficiency or poor stability [1], and to overcome these problems, the physical basis of photoelectrochemical reactions has to be understood in more detail. Band alignment (i.e., the relative position between the conduction band minimum (CBM) or the valence band maximum (VBM) of the semiconductor and the redox potentials in the electrolyte at the semiconductor/electrolyte interface,) determines whether the reaction of interest proceeds or not, and therefore is the key factor for photoelectrochemical reactions. Nevertheless, from an atomistic point of view, little is known about the photocatalyst(semiconductor)/electrolyte interface, and the relationship between the band alignment and the geometric structure at the interface remains unrevealed.

The recent development of ambient pressure X-ray photoelectron spectroscopy (AP-XPS) has made it possible to probe the electronic structure of the semiconductor/electrolyte interface under nearly in situ conditions [2]. However, XPS results are not self-explanatory in the sense that it requires XPS signatures obtained from other experiments in order to identify the chemical elements and the nature of their chemical bonds. Considering the above, in this contribution, we probe the relationship between the band alignment and the geometric structure at the semiconductor/electrolyte interface by combining AP-XPS measurements and first-principles calculations. As a starting point, we investigate water adsorption on crystalline GaN (0001) surface to avoid excessive complexity.

The band alignment between semiconductors and electrolytes are determined by both the intrinsic and non-intrinsic properties. The non-intrinsic properties, that is, ones that cannot be determined from the bulk properties of the materials alone, are: the (1) band bending and (2) the surface dipole layer.

AP-XPS analysis allowed us to evaluate the band bending from the energy difference between the VBM and the Fermi level of the n-GaN substrate. In line with previous studies [3], the results have showed that the water adsorption on the GaN substrate reduces the band bending. The first-principles calculations have showed that the density of mid-gap states are reduced upon O, OH, or H adsorption. Taking both experimental and computational results into account, one can conclude that the band bending is reduced by the dissociative adsorption of water molecules. In addition, the O 1s spectra, which are interpreted using the computed O 1s binding energies, indicates that some portion of water molecules dissociates into O atoms as well as OH groups.

The potential shift due to the surface dipole layer is roughly estimated from the AP-XPS experiments by detecting the change in the O 1s binding energy of the water molecules in the gas phase. By comparing the results with the computed surface dipoles of various interface models and the amount of surface species estimated from the AP-XPS O 1s spectra, we have shown that the surface dipole is determined not only by the dipole of the adsorbates but also by the charge transfer between the substrate and the adsorbates.

In conclusion, we have found that it is possible to obtain an atomistic-level description of the interface-specific properties that determine the band alignment at the semiconductor/electrolyte interface. The approach described above will help us decide how to realize the desired band alignment at the photocatalyst/electrolyte interfaces.

Earth-Abundant Metal-Metalloid Materials as Highly-Efficient Oxygen-Evolving Electrocatalyst Jean Marie Vianney Nsanzimana and Vikas Reddu; Nanyang Technological University, Singapore

Abstract: Electrochemical energy conversion and storage devices, including metal-air batteries, regenerative fuel cells, and water-splitting cells are critical to satisfy the future energy demand of human society. Though electrochemical water splitting technology has been well-established among other techniques as a clean and efficient technology for hydrogen production because of the possibility of coupling to other renewable sources, such as solar and wind energy, it is still limited by the sluggish anodic oxygen evolution reaction (OER).[1] As this sluggish electrochemical reaction is also involved in many energy storage and conversion technologies, it has become a hot topic over the last decades.[2] Precious metal-based catalysts such as Iridium- and Ruthenium-based oxides and their composites are used predominantly, but the scarcity and low stability limit their application at large scale.[3] As a consequence, intensive efforts have been devoted to developing cost-effective catalysts with superior oxygen-evolving activity and stability.[4] The earth-abundant metal-metalloid materials represent an emerging family of highly efficient oxygen-evolving catalysts due to their ability for charge transfer between different elements and modified electronic structures lowering the kinetic energy barriers of the electrochemical processes.[5] Herein, we present a fast and simple method of synthesizing iron-doped amorphous nickel boride on graphene oxide sheets. The hybrid exhibits outstanding OER performance and stability in prolonged OER operation. In 1.0 M KOH, only an overpotential of 230 millivolts is required to afford a current density of 15 milliampere cm$^{-2}$ and showed outstanding stability in alkaline solution. The superior OER activity of the as-prepared catalyst is attributed to (i) unique amorphous structure to allow abundant active sites, (ii) synergistic effect of constituents and, (iii) strong coupling of active material and reduced graphene oxide. This work not only provides new perspectives to design highly effective material for OER, but also opens a promising avenue to tailor the electrochemical properties of metal boride which could be extended to other materials for energy storage and conversion technologies.

References
Hierarchical Sb$_2$Se$_3$ Light Absorber—Nanostructured Photocathode for Highly Efficient Solar to Hydrogen Conversion
Jaemin Park, Wooseok Yang, Jeiwan Tan, Hyungsoo Lee, Sang-gi Shim and Jooho Moon; Yonsei University, Korea (the Republic of)

For practical hydrogen production via photoelectrochemical (PEC) water splitting, proper nanostructuring enabling of sufficient light absorption and effective charge carrier transport to the electrolyte is of immense importance. In this study, we propose novel nanostructure for photocathode using Sb$_2$Se$_3$ which is nontoxic, low band gap and earth-abundant materials. The planar Sb$_2$Se$_3$ film is fabricated with molecular precursor ink to avoid direct contact of conductive substrate and electrolyte then the branch-like Sb$_2$Se$_3$ nanowires sequentially decorate the planar film by an additional facile spin coating. UV-vis spectroscopy shows that internal scattering at nanowires enables the reduced reflectance by bilayer structure. After the surface modification with TiO$_2$ and co-catalyst Pt, impedance spectroscopy and intensity-modulated photovoltage spectroscopy are also conducted to examine the charge transport of the film in which the electrons are easily transported to the electrolyte due to higher surface area. Furthermore, incident photon to current efficiency at the long wavelength for hierarchically bilayer Sb$_2$Se$_3$ based photocathode reveals increases dramatically compared with monolayer film, indicating more efficient light harvesting in wide wavelength area. Consequently, improved optical and electrical characteristics allow us to demonstrate the record high photocurrent at 0 V versus reversible hydrogen electrode up to 28.5 mA cm$^{-2}$. This implies the successful achievement of the highly efficient Sb$_2$Se$_3$ based photocathode with a hierarchically bilayer structure. Our findings clearly illustrate the impact of our Sb$_2$Se$_3$ device as a promising candidate for practical PEC water splitting.

Development of a Method to Characterize Active Sites in Photocatalysis Using Operando Transmission Electron Microscopy
Eric A. Stach, Vincent A. Verret, Pawan Kumar, Noah Glachman, Khim Karki, Daan Hein Alsem and Deep M. Jariwalla; 1University of Pennsylvania, United States; 2Hummingbird Scientific, United States

Hydrogen gas has the potential to be a clean source of sustainable energy due to its high energy density. However, greenhouse gas emissions are still a major byproduct of current hydrogen production methods. Photoelectrochemistry provides a promising, environmentally friendly route to hydrogen production. However, the atomic scale mechanisms of the photocatalysts that facilitate the water splitting reaction are currently poorly understood. Further understanding of the chemical physics governing the active hydrogen evolution sites would allow for better design of photoelectrochemical devices and thus lead to improved reaction efficiencies. This will overcome one of the major barriers impeding this promising technology. We have developed a unique operando photoelectrochemistry transmission electron microscope liquid cell sample holder which can be used to characterize these reactions in real time at nanometer length scales. This system builds upon our prior developments of operando electrochemical liquid cell holders, by including the additional provision of an optical fiber directed at the sample to provide full solar spectrum illumination. In order to provide accurate, quantitative information, it is necessary to accurately deposit the photocatalyst of interest onto microfabricated electrodes. In this research, a precise sample deposition technique utilizing an inkjet printer has been developed along with stable suspensions of known photocatalysts, leading to site-specific deposition onto the electrode chips. Specifically, this experimental design allows for correlation between I-V characteristics and real time, high magnification imaging and spectroscopy, elucidating information about photocatalytic mechanisms at the nanoscale. The following photocatalysts used were chosen because the proposed mechanism for each exhibits a spatial dependence: plasmonically enhanced catalysis for Au nanoprisms and catalytically active edge sites for MoS$_2$ flakes. These experiments will lay the groundwork for the use of this novel experimental design to investigate a wide variety of photoelectrochemical systems and will allow determination of the mechanisms by which selected photocatalysts induce water splitting and the identification of defect features that serve as the active sites.

Hydrogenated TiO$_2$-Silicon Tandem Cell Platelets for Direct Water Splitting
Helmut Karl; University of Augsburg, Germany

Hydrogenated TiO$_2$ (H:TiO$_2$ or black titania) shows highly increased absorption in the visible frequency spectrum of light in parallel with an improved photoelectrochemically (PEC) water splitting activity. These findings dragged...
interest on the properties and in particular on the synthesis, electrical properties and stability of H:TiO₂.

It became also apparent that there might be no single compound which simultaneously fulfills all requirements for unassisted (i.e. without externally applied electric fields) direct PEC water splitting, which are firstly band edge energy levels and quasi-Fermi energy level positions providing over potentials needed to enable hydrogen (HER) and oxygen evolution (OER) reactions, secondly a potential difference of more than 1.23 V, and thirdly chemical stability under highly photo corrosive working conditions.

Coupling of H:TiO₂ with a mobility energy gap E₉ of 1.5-3.2 eV with amorphous a-Si:H (E₉ = 1.1-1.8 eV), which results in a theoretical maximal solar to hydrogen (STH) efficiency of 20% in thin film tandem cell structures, could be a route toward low cost PEC water splitting systems.

Nanoparticle suspensions might play a key-role in achieving efficient and cost effective PEC water splitting. The reason for this is, that nanostructured semiconductors possess a large surface to volume ratio and by choosing an appropriate particle size, particle geometry (e.g. platelet) and catalysts mutually dependent conversion steps, which crucially determine photovoltaic and PEC performance in their bulk counterparts, can be decoupled. This concerns in particular the generation and selective separation of photogenerated electron-hole (e-h) pairs which are mainly controlled in bulk materials by diffusion, gradients of the electrical potential and finally by gradients of the quasi-Fermi energies. In nanostructures localized surface states with extremely fast charge carrier transfer times and charge carrier transport times to the interfaces much smaller than e-h pair recombination times in the bulk determine the selectivity and efficiency.

A very important feature of the here proposed PEC tandem cell platelets is the very short charge carrier transport length to the facing large surfaces. The thickness of the tandem top- and bottom-electrode can be adjusted independently from their lateral dimension and adapted to optimize photogenerated electron-hole pair separation. In contrast to conventional solar tandem cell architectures, where thick absorbing semiconductor layers are applied and carrier diffusion is important, ballistic transport of photogenerated electrons and holes to the liquid/solid and solid/solid interfaces by utilizing very thin top- and bottom-layers with H:TiO₂ and a-Si:H can be achieved.

In this work H:TiO₂ thin films were grown in-situ by fully reactive sputtering of a metallic Ti target on silicon and silica substrates. We mapped the critical process parameters consisting of the sputter gas ratio and the RF-sputter power over a wide range for determining growth condition resulting in maximal hydrogen incorporation. Quantitative depth profiling of the H-content in the H:TiO₂ thin films was performed by helium elastic recoil detection analysis (He-ERDA) which revealed an H-content of more than 2.7 at.%. The optical absorption coefficient and temperature dependent electrical conductivity will be discussed in context of the thermal stability and hydrogen content. The temperature dependent resistivity and Seebeck coefficient of H:TiO₂ thin films were determined by consecutive temperature cycles up to 723K and show to be stable up to 673 K, above which a slight increase in the resistivity was observed. First H:TiO₂-silicon-iridium tandem cell platelets will be presented an their properties discussed.

Combinatorial Thin-Film Deposition for High-Throughput Electrocatalyst Testing Anthony Thompson¹, Hector Colon-Mercado¹, Elise Fox¹, Larry Scipioni², James Greer² and Adam Shepard²; ¹Savannah River National Laboratory, United States; ²PVD Products, United States

Catalytic processes can often be improved and optimized by changing the composition of the catalyst, but it is often not feasible to explore the entire compositional space because of the time and cost of performing multiple syntheses. High-throughput methods allow for the exploration of a wide range of variables in a relatively short period of time.

Here we demonstrate the high-throughput testing of electrocatalysts for SO₂ oxidation, the electrochemical step of the Hybrid Sulfur (HyS) process for water splitting, over a full range of compositions of Au, Pt, and V. Catalysts were synthesized by combinatorial sputter deposition of multiple thin film patches onto a glassy carbon substrate and compositions were confirmed by XPS. A scanning electrochemical microscope (SECM) with a scanning droplet system (SDS) attachment was used to obtain CV curves and map electrochemical activity across the entire glassy carbon plate, allowing rapid optimization of metal ratios for the reaction.
1:30 PM EN07.07.01
Electrocatalysis with Graphitic Carbon Catalysts Troy Van Voorhis; Massachusetts Institute of Technology, United States

Pyrolytic graphitic carbon materials possess tantalizing activity toward a range of reactions - from hydrogen evolution, to oxygen reduction and oxygen evolution. However, the uncontrolled nature of their synthesis makes it virtually impossible to rationally improve them. Recently, graphitic carbon catalysts (GCCs) - small molecule catalysts that are directly conjugated to the edges of graphitic carbon - have been shown to possess similar reactivity but with controllable synthesis. This presentation will give an overview of the mechanism of oxygen reduction (ORR) in GCCs and present the results of several large-scale computational screening experiments aimed at improving the activity and selectivity of the catalysts. In particular, we find that the GCCs do not obey the commonly accepted scaling relations that limit ORR performance in traditional heterogeneous catalysts. We hypothesize this is due to the fact that these are organic and organometallic complexes, which are empirically known to provide a greater degree of chemical specificity than inorganic solids and surfaces. We conclude with an analysis of the transferrability of these ideas to the reverse reaction of ORR.

2:00 PM EN07.07.02
First-Principles Predictions of Photoelectrode Materials—From Bulk to Complex Interfaces Tuan Anh Pham¹, Tyler Smart², Yuan Ping², Brandon Wood¹ and Tadashi Ogitsu¹; ¹Lawrence Livermore National Laboratory, United States; ²University of California, Santa Cruz, United States

The generation of hydrogen from water and sunlight through photoelectrochemical cells (PECs) offers a promising approach for producing scalable and sustainable carbon-free energy. The design of high-performance PECs requires a detailed understanding of physicochemical properties of not only the semiconductor photoelectrode, but also the interface between the material and liquid water. In this presentation, we discuss how first-principles simulations can be utilized to unravel the key chemical and electronic properties of photoelectrode materials in the bulk phase and at the interface with liquid water. Specific discussion focuses on how hybrid density functional theory and many-body perturbation theory can be used to provide high-fidelity description of the electronic properties of photoelectrode materials, including their band gap and band edge positions. In addition, we show how first-principles molecular dynamics simulations can be coupled with near-ambient-pressure XPS experiments for the identification of solid/liquid interfacial chemical composition and speciation, which is necessary for devising meaningful strategies to improve PEC performance and durability. Examples for different materials, from Co₃O₄ to III-V semiconductors will be discussed, based on which we suggest a more general roadmap for obtaining a realistic and reliable description of the chemistry of complex.

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2:15 PM EN07.07.03
Estimation of Electronic Entropy Contributions to Oxygen Vacancy Formation Reaction in Nonstoichiometric Oxides via Analysis of Electronic Structure Properties Conrad R. Cole; University of Florida, United States

The primary motivation of this work is to develop a method through which the entropy change of oxygen vacancy formation may be computed from first principles for strongly correlated metal oxides which exhibit intrinsic spin polarization. Namely, a methodology via which the electronic structure may be utilized to predict electronic entropy contributions to the overall free energy change. Leveraging electronic structure properties facilitates the process by circumventing the need for extensive combinatorics and statistical methods which are conventional approaches for entropy calculations within the realm of statistical physics. Nonstoichiometric cerium dioxide (CeO₂) and the manganite perovskites (AMnO₃) form a prototypical composition space meeting the criteria above and possessing a high degree of versatility with applications ranging from electrocatalysis and solar thermochemical energy storage to electronic and magnetic devices. The acquisition of a fundamental understanding of the mechanisms governing entropy in these materials would enhance the rate at which they may be optimized and tailored for current applications and potentially enable the discovery of novel applications for which they are ideal candidates.
It is commonly assumed that finite temperature electronic contributions to the free energy of insulators and semiconductors may be neglected due to the lack or absence of electron density near the Fermi level. This may be the case when treating ideal, pristine systems since there are no electronic levels available for population due to thermal excitation of electrons near the valence band maximum. This sizable bandgap in medium to wide gap materials limit the number of electronic configurations accessible to the highest occupied levels. The validity of this assumption is highly questionable however, especially when charged defect levels are present within the energy gap increasing the density of states near the Fermi level. Shallow defect levels with unpaired electrons near the VBM would allow for an increase in the number of microstates for thermal population of electrons contributing to the electronic configurational free energy.

The electronic density-of-states data from a structural relaxation at the HSE06 level of theory with a 12-atom Ce4O8 bulk supercell was implemented to calculate the Fermi level (electron chemical potential) as a function of temperature. The Fermi-Dirac distribution along with the normalized DOS were utilized to estimate the majority carrier concentration (assuming only electronic charge carriers) via the difference between the conduction band and valence band integrals. A greedy algorithm is utilized to evaluate the Fermi level at which the error between the calculated carrier concentration (via above parameters) at a given temperature and the predicted/estimated carrier concentration is minimized.

The corresponding electronic entropy agrees relatively well with results from work by Naghavi et al. in magnitude and variation with respect to temperature. Further validating the significance of electronic entropy contributions to the energetics of oxygen vacancy formation in ceria and other similar mixed conducting oxides which may be comparable to if not greater than structural configurational and vibrational entropic terms. Recent work by Lany highlighted this relationship between temperature, Fermi level and charged defect formation energies specifying that electronic entropy is the physical or thermodynamic consequence of this phenomenon. Specifically, the energy level of the oxygen vacancy, the conduction band effective mass and the temperature dependence of the conduction band minimum were claimed to be the electronic structure properties that govern the electronic entropy contribution to vacancy formation free energies. The work presented herein provides numerical evidence to support the claims made by Lany in a purely analytical deduction.

2:30 PM BREAK

3:30 PM EN07.07.04
Multiscale Modeling of Charge Carrier Dynamics in Complex Metal Oxides for Solar Water Splitting—The Case of Anion Doping in BiVO4
Viswanath Pasumarthi, Pavan Kumar Behara and Michel Dupuis; University at Buffalo, The State University of New York, United States

This presentation will deal with computational modeling dealing with doping strategies toward enhanced carrier transport and overall photo-electro-conversion (PEC) efficiency of semiconductor electrodes, in particular BiVO4, the best anode material to date. We carried out multiscale modeling, combining DFT+U calculations of e/h polaron hopping by Marcus/Holstein theory and Kinetic Monte Carlo (KMC) modeling of collective charge carrier transport at the mesoscale. We will highlight the approach first for a stoichiometric bulk BiVO4 where simulations revealed that hole transport is bimodal, featuring fast rattling but transport-inefficient hops and slower transport-efficient hops, while electron transport is slower yet. We will then discuss the structure and stability of electron and hole polarons in the presence of sulfur doping. DFT calculations reveal that sulfur atoms substitute oxygen and act as hard traps (~ 14 k_BT) for electrons in their vicinity. We will describe how sulfur incorporation affects electron and hole transport dynamics resulting in enhanced transport efficiency. If time permits, we will highlight modeling of cation doping by W/Mo, including the design of homo-junctions for enhanced carrier separation.

Photoelectrochemical (PEC) water splitting is a renewable energy conversion process in which hydrogen and oxygen are generated from water using energy from sunlight that is attracting much interest in a sustainable energy economy. However, there exist several scientific and engineering challenges in implementing this technology at industrial scale. A broad critical challenge is to identify suitable semiconductor materials for photoelectrodes in PEC cells: they must exhibit good visible light absorption and carrier generation, good carrier transport, and good redox reactivity. Metal oxides have the promising advantages of stability in aqueous medium and wide and inexpensive availability of the constituent elements. Bismuth vanadate (BiVO4), a ternary metal oxide is one of the best performing photoelectrode material to date, with its most photoactive monoclinic phase having a wide band gap of
~2.4-2.5 eV. Systematic investigations of the performance limiting factors have led to significant progress over the past decade. Engineering the material using strategies such as nanostructuring, or metal-ion doping by tungsten (W) and molybdenum (Mo) have resulted in photocurrents to reach ~6.7 mA/cm², ~90% of theoretical maximum of ~7.5 mA/cm². Recently, anion doping with nitrogen/sulfur was found to decrease the bandgap by up to ~300 meV for improved solar spectrum absorption.

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3:45 PM EN07.07.05

Phenyl Oxidation at Oxygen Evolution Potentials—Impact on Alkaline Membrane Electrolyzer Durability

Dongguo Li, Ivana Matanovic, Albert S. Lee, Hoon T. Chung and Yu Seung Kim; Los Alamos National Lab, United States

The durability of alkaline membrane/ionomer is a critical requirement for commercially viable alkaline membrane water electrolysis. In this presentation, we report the oxidation of the phenyl group in the ionomer adsorbed on the oxygen evolution catalysts, which may cause performance deterioration in AEM electrolyzers. The 1H-NMR analysis in combination with rotating disk electrode studies shows that the oxidation of phenyl group occurs at oxygen evolution potentials, ca. 1.6 V under both low and high pH conditions. Further study indicates that the phenyl oxidation also depends on the nature of catalysts. Commercial Pt/C and IrO₂ noble metal catalysts exhibit much faster phenyl oxidation compared with La₀.₈₅Sr₀.₁₅Co₃ perovskite oxide. Density functional theory calculations also confirm that the phenyl adsorption is significantly less pronounced on the perovskite oxide catalyst, implying phenyl adsorption at the oxygen evolution potentials is a critical factor determining the phenyl oxidation. This research provides a path for the development of more durable AEM electrolyzers with components that can minimize the adverse impact induced by the phenyl group oxidation, such as the development of novel ionomers with fewer phenyl moieties or catalysts with less phenyl-adsorbing characteristics.

SESSION EN07.08: Fundamental Mechanisms for Water Splitting I
Session Chairs: De-en Jiang and Gideon Segev
Thursday Morning, December 5, 2019
Sheraton, 2nd Floor, Liberty BC

8:30 AM *EN07.08.01

Linking Surface Properties to Electrochemical Activity of Water Splitting Catalysts

Yelena Gorlin; Research and Technology Center, Robert Bosch LLC, United States

Improvements in water splitting technology requires detailed understanding of associated electrochemical reactions, the oxygen evolution reaction and the hydrogen evolution reaction, as well as catalyst surfaces on which these reactions occur. This talk will first focus on the oxygen evolution reaction and present examples of how X-ray absorption spectroscopy characterization can be combined with electrochemistry to study the oxidation state of the catalysts under reaction conditions. Then, it will transition to hydrogen evolution reaction and reexamine electrochemical activity of precious-metal catalysts in alkaline environment. In this example, detailed analysis of the micropolarization region of rotating disc electrode experiments will be combined with calculations of the relevant surface conditions, in order to interpret the characterized exchange current densities in the context of surface properties of the catalysts.

9:00 AM EN07.08.02

Unravelling the Structure—Properties Relationship of MOCVD Co₃O₄/TiO₂ Heterojunctions for Solar Water Splitting

Adeline Miquelot¹, Olivier Debieu², Stephanie Roualdes³, Christina Villeneuve³, Nathalie Prud’homme³, Jeremy Cure³, Vincent Rouessac⁴, George Papaveros⁵, Vassilios Constantoudis⁶ and Constantin Vahlas⁷;

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Green H₂ production by solar water splitting entirely relies on the intrinsic properties of the photocatalyst. Among
the numerous photocatalytic materials investigated on purpose, heterojunctions based on TiO₂, the quintessential component of state of the art photocatalytic systems, are expected to expand the photocatalytic activity to the visible domain of the solar spectrum. In this perspective, literature reports on the p/n Co₃O₄/TiO₂(anatase) heterostructure are contradictory as they mention either improvement or degradation of their photocatalytic activity with regard to the single anatase photoanode. The aim of the present contribution is to contribute to the elucidation of this question and, subsequently to the illumination of the impact of the intrinsic properties of this material, explored at nanoscale, on its photocatalytic activity under visible light illumination.

We process the Co₃O₄/TiO₂ heterostructure in the form of a two films stack by a sequential MOCVD process, starting from cobalt 2,2,6,6-tetramethyl-3,5-heptanedionato, Co(dmp)₃, and titanium tetra-isopropoxide, TTIP. Deposition in the temperature range 350 to 550 °C provides Co₃O₄ and anatase films with variable characteristics. We implement a multiscale, holistic microstructural, optical and electrical characterization of the two types films alone and of various Co₃O₄/TiO₂ bilayers, using state of the art techniques, microscopic (SEM-FEG including advanced image analysis, AFM, HRTEM, EBSD/TKD), spectrometric (FTIR, Raman, UV-Vis-NIR, ellipsometry, XPS, XRD, EPMA, EDX), and electrical/electronic (conductive AFM, Hall and Van der Pauw resistivity, Seebeck coefficient).

We show that, with increasing deposition temperature, anatase films evolve from dense to porous, nanotree-like columnar structures. This evolution results in a remarkable increase of the exchange surface, coinciding with a change of growth direction, from <110> to <001> and to the increase of the porosity, to a decrease of the optical absorption, and to an increase of both the electrical resistivity and the carriers density.

In the same conditions, the morphology of the Co₃O₄ films evolve in the opposite direction, from columnar to dense. These films show a minimum room temperature resistivity of 21.4 Ω.cm, and Hall resistivity measurements establish their p-type semiconducting behavior with a maximum holes density of 1.8 ± 0.8×10¹⁸ cm⁻³, and a maximum holes mobility of 0.16 cm² V⁻¹ s⁻¹. We attribute the linear T⁻¹/₄ temperature dependence of the film conductivity to a 3-dimension variable range hopping conduction mechanism of holes. The surface topographies of the deposition temperature dependent morphologies perfectly match the current maps at the AFM scale, demonstrating that the variable range hopping conduction of holes occurs through the Co₃O₄ nanocrystallites. The 66 h cumulative H₂ photogeneration from the single anatase films increases from 4.4 to 78.9 mmol.m⁻² with increasing the deposition temperature from 325 to 450 °C. This result points out the importance of the beneficial effect of the morphological nano-complexification, and of the crystallographic diversification of the exchange facets on the photocatalytic performance over detrimental aspects inherent in this evolution, namely, the decreases of the optical absorption and the increase of residual stress, also described here. We process heterojunctions by cross combining dense and columnar single layers of the two semiconductors. The resulting H₂ photogeneration is strongly reduced with regard to the anatase films, despite a strong decrease of the thickness of the external Co₃O₄ layer to less than 50 nm, aiming at the exposure of both semiconductors and of their interfacial zones to the light. This result is in agreement with the strong decrease of the electrical conductivity perpendicular to the stack. Detailed analysis of the interface is actually in progress in order to reveal the reasons of this behavior.

9:15 AM EN07.08.03
Unfolding the Effect of the O₂ and N₂ Plasma on Hydrogen Evolution Reaction of MoS₂ Lalita Sharma; Indian Institute of Technology, India

Defect engineering is widely adopted technique to increase the density of exposed active sites. Plasma technique is proved as an effective technique to tune the surface properties and edge reactive sites for greatly improving the electrochemical activities. In this report, controlled oxygen (O) and nitrogen (N) plasma used to generate defects and introduce dopants N and O in MoS₂ nanosheets to form defect-induced nanocomposite material MoS₂₋ₓₓ (X= N, O) with sulphur vacancies. Defects in the MoS₂ nanosheets help to improve the number of active sites but extra defects deteriorate electron mobility. So here mild plasma technique is used to (1) increase the hydrogen evolution reaction (HER) catalytic activity of MoS₂ S-edge and (2) electron mobility of MoS₂ nanosheets for fast electron transfer which are one of the responsible factors to increase the electrochemical activities. Electrochemical measurements prove that with the combination of both active sites along with the incorporation of O & N dopants enhance HER activities. The superior activity and stability for the hydrogen evolution reaction with low overpotential and fast electron transfer is derived from the coexistence of both doping effect and sulphur vacancies.

9:30 AM EN07.08.04
Comparison of Light-Intensity-Dependent Open-Circuit Potential among TiO₂, SrTiO₃ and GaN Single-Crystalline Photoanodes Supawan Ngamprapawat¹, Yuki Imazeki¹, Tsutomu Minegishi¹, Masahiro Sato¹, Katsushi
Photoelectrochemical (PEC) water splitting is a promising technology that converts solar energy into a storable energy carrier, hydrogen. Many signs of progress have been reported. Nevertheless, the efficiency and the stability of PEC water splitting is still unsatisfactory. Finding a photoelectrode material which has an appropriate alignment of quasi-Fermi energies under illumination with respect to redox potentials of water is an essential condition for the progress of PEC water splitting.

Semiconductor photoelectrodes are a key component. They are often selected based on the band-edge energies, assuming a flat-band situation. However, band bending generally exists at the semiconductor/electrolyte interface, which makes the flat-band condition unattainable under insufficient light intensity. When the light intensity exceeds a certain value, the band bending is reduced by an accumulation of photo-generated carriers. By comparing the light intensity dependence of band bending among a variety of materials, it would be possible to explore the fundamental processes governing the function of semiconductor photoelectrodes from the viewpoint of semiconductor physics, similarly to the analysis for photovoltaic devices.

In this study, light-intensity-dependent open-circuit potential (OCP) of three types of single crystalline photoelectrodes: (i) undoped and 0.05 wt% Nb-doped TiO$_2$, (ii) 0.01 wt% and 0.05 wt% Nb-doped STO, and (iii) n-type GaN on Si was investigated with varied photon flux from $10^9$ to $10^{17}$ s$^{-1}$cm$^{-2}$. A He-Cd laser (325 nm) was used as a light source. The light-intensity-dependent OCP of all materials showed a similar tendency. Plateau of OCP versus light intensity was observed at the photon flux less than $10^{11}$ s$^{-1}$cm$^{-2}$. The positions of the plateau for all materials range between -0.3 and 0 V vs SHE. These positions depend on several factors: surface condition of the photoelectrode, impurity in semiconductor, and dissolved gas in the electrolyte. Conversely, when the photon flux exceeded $10^{11}$ s$^{-1}$cm$^{-2}$, the linear relationship was clearly observed between the logarithm of photon flux and OCP, indicating the accumulation of charge carriers in the bulk of semiconductor and the reduction in band bending, in a similar manner to solid-state junctions of semiconductors.

Furthermore, the ideality factor of a diode was evaluated from the slope of the plots of OCP versus the logarithm of photon flux. The ideality factors of the doped photoelectrodes, TiO$_2$ and STO, were in a range of 1.0 – 1.3, while that of the undoped TiO$_2$ was 1.6. The ideality factor of GaN photoelectrode, prepared by the hetero-epitaxial growth on Si, was larger than 2.0. The distribution of interface states and defects, and the recombination of carriers in the depletion region could be the main reasons for the deviation from unity. These results also showed that the better crystal quality resulted in ideality factors close to unity, indicating the suppressed recombination of photo-generated carriers in the semiconductor bulk.

As the photon flux increased, the OCP shifted toward the flat-band potential. At the photon flux of $10^{17}$ s$^{-1}$cm$^{-2}$, OCP of all materials exceeded the hydrogen evolution potential, i.e. hydrogen evolution reaction (HER) became possible at the counter electrode. The difference between the OCP and the flat-band potential at high photon flux depends on materials and doping concentration; an ideal photoelectrode should show virtually no difference.

In summary, all three materials exhibited the linear relationship in the plot of OCP versus the logarithm of photon flux as it is observed in photovoltaic devices. Ideality factor of a diode at solid-liquid interfaces close to unity was obtained only for photoelectrodes fabricated from single-crystalline wafers with low defect density. The study of light-intensity-dependent OCP allows us to determine which material has a suitable photo-response for HER under certain light intensity.

### 9:45 AM EN07.08.05
**Fields Matter—Better Water Splitting Through Magnetic Field-Assisted Processing of Hematite Thin Films**

Myeongwhun Pyeon$^1$, Vanessa Rauch$^1$, Daniel Stadler$^1$, Mehmet Gursoy$^2$, Meenal Deo$^1$, Yakup Gönnülü$^1$, Thomas Fischer$^1$, Taejin Hwang$^3$ and Sanjay Mathur$^1$; $^1$University of Cologne, Germany; $^2$Selçuk Üniversitesi, Turkey; $^3$KITECH, Korea (the Republic of)

Even though the potential of hematite thin films for water splitting applications are widely accepted, researchers are still tackling the ‘rust challenge’. We report here on the influence of external magnetic fields applied parallel or perpendicular to the substrate during plasma enhanced chemical vapor deposition (PECVD) of hematite ($\alpha$-Fe$_2$O$_3$) nanostructures. Hematite films grown from iron precursors showed pronounced changes in crystallographic textures.
depending upon whether PECVD was performed with or without the influence of external magnetic field. Static magnetic fields created by rod-type (RTMs) or disk-type magnets (DTMs) resulted in hematite films with anisotropic or equiaxed grains, respectively. Using RTMs, a superior photoelectrochemical (PEC) performance was obtained for hematite photoanodes synthesized under perpendicularly applied magnetic field (with respect to substrate), whereas parallel magnetic field resulted in the most efficient hematite photoanode in the case of DTM. Our experimental data on microstructure and functional properties of hematite films showed that application of magnetic fields parallel and perpendicular have a significant effect on the crystallite size and texture with preferred growth and/or suppression of grains with specific texture in α-Fe₂O₃films. Investigations on the water splitting properties of the hematite films in a photoelectrochemical reactor revealed that photocurrent values of hematite photoanodes were remarkably different for films deposited with (0.659 mA/cm²) or without (0.484 mA/cm²) external magnetic field.

10:00 AM BREAK

10:30 AM *EN07.08.06
Adsorption Energetics and Surface Phase Transformations in Iridium and Ruthenium-Based Oxygen Evolution Reaction Catalysts Geoffroy Hautier; University Catholique de Louvain, Belgium

Important devices such as electrolyzers or fuel cells depend on the control and understanding of electrocatalytic processes. Ab initio techniques have been extremely useful in providing the needed insight in the catalytic mechanisms leading even to computationally-motivated design of new electrocatalysts. There remain, however, many open questions in the field and fundamental studies of the adsorption processes on model single-crystals are strongly called. In this talk, I will present recent results on combined theory-experiment approaches towards the understanding of important oxide catalysts for oxygen evolution reaction (OER) using molecular-beam epitaxy (MBE) grown single-crystals and ab initio techniques. I will especially focus on the comparison between computed and experimental adsorption energies in two model systems: RuO₂ and IrO₂, helping estimate the typical errors on the very common DFT adsorption computations performed in electrocatalysis. Finally, I will discuss more recent results on the understanding of complex phase transformations during hydrogen desorption and cyclic voltammetry especially on IrO₂ and using a combination of DFT and statistical mechanics.

11:00 AM EN07.08.07
Surface and Sub-Surface Structure of Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋δ Perovskite Particles for Oxygen Evolution Reaction Probed by Electron Microscopy Techniques Tzu-Hsien Shen¹, Liam Spillane², Yang Shao-Horn³ and Vasiliki Tileli¹; ¹École polytechnique fédérale de Lausanne, Switzerland; ²Gatan Inc., United States; ³Massachusetts Institute of Technology, United States

Water splitting is seen as a promising way to store clean energy. However, the sluggish oxygen evolution reaction (OER, 4OH⁻ → O₂ + 2H₂O + 4e⁻) at the anode is the bottleneck that limits the water electrolysis efficiency. Perovskite family with the ability of tunable electronic structure is considered as a strong candidate to replace precious metal catalysts that currently dominate the market for oxygen evolution reaction [1]. Understanding the surface of perovskites is one of the keys to design protocols for next-generation OER electrocatalysts as most of catalytic processes occur at the surface. In this study, transmission electron microscopy (TEM) based techniques with exceptional spatial resolution are used to fulfill this purpose and perovskite Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋δ (BSCF), a highly active OER catalyst in alkaline electrolytes [2], is taken as the target catalyst. Electron energy-loss spectroscopy (EELS) operated under scanning TEM (STEM) mode is performed by probing the surface of the as-synthesized BSCF particles dispersed in KOH. The EELS results show a profile of decreasing Ba concentration from bulk toward the surface and a reduced valence of Co ions at the very surface of BSCF. Quantitative analysis using simulated EEL data confirms the compositional alteration of the surface structure. Selected area fast Fourier transform patterns of high resolution TEM images of BSCF reveal a spinel structure of surface Co-rich phase as well as the lowering of the crystallinity as approaching the surface. STEM-EELS of the identical BSCF particle after chronoamperometric measurements in OER regime shows that the reduced oxidation state of surface Co-rich phase remains after OER.

In order to further understand how the BSCF surface structure evolves during electrochemical processes, in situ TEM methodologies are applied [3]. Real-time structural monitoring during cyclic voltammetry shows surface dissolution which is likely A-site Ba²⁺/Sr²⁺ leaching at BSCF surface [4,5]. The expansion of the BSCF particle due
to OER is also observed during cycling. In conclusion, the electron microscopic studies give information on complex surface structure of BSCF which might be related to the OER catalytic properties, and in situ TEM observation provides possible degradation mechanisms of BSCF perovskite catalysts.

References

11:15 AM EN07.08.08
Programmable NiFe/Au Barcode Nanomesh for Enhanced Oxygen Evolution Can Cui and Liao Yong Wen; University of Connecticut, United States

The oxygen evolution reaction (OER) is the most important half-reaction in renewable electrochemical energy storage and conversion, including water splitting, CO₂ reduction, and metal-air batteries. First-row transition metal oxides and hydroxides (e.g., Ni, Co, Fe and Mn) is one of the most promising alternatives to replace the precious metal oxides (e.g., Ir and Ru) in alkaline conditions. To address the large overpotential and poor stability of the low-cost transition metal oxides based OER catalysts, many strategies have been explored, including elemental doping, surface decoration by noble metal, nanostructurering et al.. However, these challenges still exist, which greatly hinder their large-scale applications.

Here, we report a novel three-dimensional NiFe/Au barcode nanomesh based on alumina nanoporous template to pursue a desirable OER catalyst. The morphological feature and composition of the NiFe/Au barcode nanomesh can be easily tuned by using different templates and electrodeposition processes. The spatial confinement effect of the uniform porous structure in a range of hundreds of nanometers could efficiently facilitate the oxygen gas evolution with small bubbles. Most importantly, the synergistic interaction of the alternating layered NiFe alloy and Au structure could not only provide a large number of active sites, but also decrease the intrinsic resistance of the formed NiFe alloy oxides during the OER, which in turn significantly decreases the required overpotential. By choosing suitable thickness ratios of NiFe and Au layers, respectively, a very low overpotential below 300 mV was obtained under a current density of 10 mA/cm², which is one of the lowest reported values from the NiFe based composites. A negligible decrease of the potential was observed even after a 3-day test. These programmable three-dimensional NiFe/Au nanomeshs may provide a new type of cost-effective and long-term stable electrocatalysts for scalable energy applications.

11:30 AM EN07.08.09
Design and Preparation of CNTs Aerogel/Wood Bilayer-Structures for Solar Steam and Sewage Treatment Lei Miao, Xiaojing Mu and Jianhua Zhou; Guilin University of Electronic Technology, China

The shortage of clean water is one of the predominant causes of human mortality, especially in remote rural areas. Currently, solar steam generation is being adopted as an efficient, sustainable, and low-cost means for water desalination to produce clean water¹. CNTs aerogel is a good solar absorber with huge surface area, high absorptance of solar irradiation, light weight and good insulation. However, the strong hydrophilicity of aerogel hinders heat localization in the pore and further decreasing water evaporation rate for pure CNTs aerogel solar evaporator. Here, in this work, we designed CNTs aerogel/wood bilayer-structures, i.e.; insertion of natural wood sheet between aerogel and evaporation interface to control the hydrophilicity of the whole evaporator and make the absorbed heat more compatible with the water to be evaporated, then the evaporation rate could be improved greatly. Chitosan and CNTs composed aerogels were prepared by one-step freeze-drying treated Chitosan and CNTs mixture. The highest evaporation rate reached up to 1.64 kg m⁻² h⁻¹ in the evaporation system with pure CNT aerogels as absorber. While, for the bilayer structure with wood as interface layer, the evaporation rate reached up to
2.22 kg m\(^{-2}\) h\(^{-1}\) which increased by about 40\% comparing to the pure CNT aerogels absorber. Infrared imager was used to record the temperature of evaporator in the process of evaporation. It is obvious that the thermal insulation and local heating properties of the composite material are much better than that of CNT aerogel. Desalination result shows that although the evaporation rate decreases slightly, it can still reach 1.86 kg m\(^{-2}\) h\(^{-1}\), which providing a new idea for efficient desalination. In addition, the two-stage filter effect can be achieved by wood sheet and aerogel composite. The macropore of the wood sheet is a primary filtration, which can be used to preliminarily remove the larger pollutants or harmful substances in the sewage. The mesoporous and microporous of aerogel are secondary filtration, which can further remove the smaller particles or harmful substances in sewage. Driven by solar energy, the whole filter system could purify waste liquid and domestic sewage effectively. Cost-effective bilayer structures could prepare solar absorber with good steam generation performance and sewage treatment capacity in large quantities, which holds great potential for practical applications, especially in remote rural areas and environmental polluted area.

References

11:45 AM EN07.08.10
Li and P Co-Doped Heptazine Based g-C\(_3\)N\(_4\) Monolayer Deepak K. Gorai and Tarun Kumar Kundu; Indian Institute of Technology Kharagpur, India

In this work, quantum chemical first principle density functional theory calculations are performed by using VASP and Gaussian09 software to investigate the geometric, electronic and optical properties of Li and P co-doped carbon nitride (g-C\(_3\)N\(_4\)) monolayer. The co-doping process results in significantly narrow the band gap of g-C\(_3\)N\(_4\). The optical absorption shows better visible-light response. Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) show strong delocalization and hence photo-generated e\(^-\)/h\(^+\) pair separation abilities of them are better than pristine monolayer g-C\(_3\)N\(_4\). The theoretical evidence for the possibility of using g-C\(_3\)N\(_4\) with excellent photocatalytic properties has been provided.

keywords: Density Functional Theory, Co-doping, VASP, Gaussian09, g-C\(_3\)N\(_4\) Monolayer, Photo-catalyst

SESSION EN07.09: Fundamental Mechanisms for Water Splitting II
Session Chairs: Troy Van Voorhis and Hua Zhou
Thursday Afternoon, December 5, 2019
Sheraton, 2nd Floor, Liberty BC

1:30 PM *EN07.09.01
Halide Perovskites—From Understanding Fundamental Physics to Optoelectronic Applications Sergei Tretiak and Dibyajyoti Ghosh; Los Alamos National Laboratory, United States

Hybrid organic—inorganic perovskites (HOPs) have demonstrated an extraordinary potential for clean sustainable energy technologies and low-cost optoelectronic devices. This talk overviews the main features of three dimensional (3D) and layered two-dimensional (2D) HOPs by combining solid-state physics concepts with simulation tools based on density functional theory. A comparison between layered and 3D HOPs highlights differences and similarities such as spin-orbit effects, quantum and dielectric confinements and excitonic properties. In 3D HOPs we study in depth the effects of electron-phonon coupling leading to polaron formation across the broad range of materials. Calculated electronic structure, charge density, changes the geometry, and reorganization energies are further related to experimentally measured specific vibrational modes, Huang-Rhys parameters and Jahn-Teller like distortions. These effects lead to formation of meta-stable deep-level charge states, which potentially responsible for photocurrent degradation in thin-film perovskite devices. The photophysics of 2D materials is defined by an interplay of strongly bound excitons and lower-energy states associated with the edges of the perovskite layers. The latter provide a direct pathway for dissociating excitons into longer-lived free carriers that substantially improve the performance of optoelectronic devices. Our theoretical simulations rationalize specifics of electronic structure of these materials, dynamics and a role of interfacial states. We also outline specific ways to rationally control geometry of edges in 2D HOP materials via external fields, contact interfaces and composition of organic compound. Overall, our results provide insights towards the material design for various applications.
Mechanisms for Hydrogen Evolution on Transition Metal Phosphides and Pt

Chenyang Li1, Per Lindgren2, Georg Kastlunger2, Andrew A. Peterson2 and Tim Mueller1; 1Johns Hopkins University, United States; 2Brown University, United States

Water splitting for renewable energy storage and conversion is limited by the high cost of Pt-based catalysts used for the hydrogen evolution reaction (HER). Earth-abundant transition metal phosphides have emerged as active HER catalysts with lower cost than Pt. However, the catalytically active sites and reaction mechanisms on these catalysts remain unclear. Here we present models of the HER on four different transition metal phosphide surfaces (Co2P, CoP, Fe2P, and FeP) using cluster expansions parameterized by density functional theory. By running Monte Carlo simulations, we predict the structures and energetics of adsorbed hydrogen as a function of temperature and applied potential, allowing us to determine the potential-dependent activities of different sites while fully accounting for interactions among adsorbed hydrogen atoms. For comparison, we have used the same approach to model the HER mechanisms on Pt surfaces – including Pt(111), Pt(110), and Pt(100). We demonstrate the effects of potential-dependent surface coverage on HER current density and propose mechanisms for the HER on these model surfaces. The present model provides a general and effective approach to study catalytic reaction mechanisms and probe catalytically active sites, which can facilitate the design of highly active catalysts.

Investigation of the Influence of Electrolyte Temperature on the Performance of Cu2O towards Solar Water Splitting

Iqra Reyaz Hamdani and Ashok N. Bhaskarwar; Indian Institute of Technology Delhi, India

Cuprous oxide (Cu2O) is a nontoxic and inexpensive semiconductor with the direct bandgap of 2.0 eV. It is an excellent material for solar driven water splitting, having a good theoretical solar to hydrogen conversion efficiency of 18%. Various deposition techniques have been explored for Cu2O thin film deposition, such as spray pyrolysis, sputtering, and electrodeposition, and chemical vapor deposition, thermal and chemical oxidation. However, electrodeposition is the most convenient method since it is economical and provides an easy control on the properties of the film, such as thickness, crystallinity, and roughness. Thus, Cu2O deposited by electrodeposition method is a low cost, sustainable and an efficient material. In this work, Cu2O thin films were electrodeposited on FTO substrates at different bath temperatures, at a constant bias potential of -0.4 V with respect to Ag/AgCl. A comprehensive study was carried out to investigate the effect of bath temperature on the morphological and optical properties of Cu2O. The performance of Cu2O as a photocathode in a photoelectrochemical device, and hence its application in photoelectrolysis of water towards hydrogen evolution, was determined and analyzed at three different temperatures i.e., at room temperature (25°C), 65°C and 85°C. The electrolyte used was 0.4 M copper sulfate hexahydrate and 3 M lactic acid. The pH of electrolyte was kept at 9 by the addition of 4 M aqueous NaOH. From the SEM images, the surface morphology was found to change from crystalline small grain sizes through polyhedral structures to amorphous structured fine grains as the temperature was increased from 25°C to 85°C. From the XRD studies, films deposited at higher temperature of 85°C showed the presence of CuO which was also visually detectable by the black color. All the films showed the presence of phase (111), however its intensity was highest at temperature of 65°C. The thickness of films increased from ~150 nm to 10 μm as the temperature was increased. However, in this range their uniformity decreased. The charge carrier density as evaluated from the Mott-Schottky equation, was highest for the films deposited at 65°C, and its magnitude was about 1.5 x 1029 cm–3. From the photoelectrochemical measurements, the films synthesized at 65°C exhibited the highest performance and generated a maximum photocurrent density of 1.6 mA/cm2.

Highly Flexible and Porously Structured Metal Phosphide/MXene Arrays as Efficient Bifunctional Electro catalysts for Overall Water Splitting

Clament Sagaya Selvam Neethinathan, Gwan Hyun Choi and Piljin Yoo; Sungkyunkwan university, Korea (the Republic of)

The development of efficient and stable bifunctional electrocatalysts that outperform noble metal electrocatalysts is an important task and an ongoing challenge for sustainable hydrogen generation. To accomplish this goal, an ordered hierarchical structure with more exposed active sites for strong electrolyte contact should be designed. Herein we report a synthetic strategy of binder free, free-standing and flexibly structured Mx-Py (M=Fe, Co and Ni) decorated MXene arrays as efficient bifunctional electrocatalysts. Specifically, 2-dimensional (2D) MXene sheets
prepared by improvised etching method render a flexible platform for the hierarchical decoration of highly mesoporous CoP, allowing them to exhibit remarkably high electrocatalytic performances. The phosphidation process provides enhanced conductivity and increased number of active sites for the hybrid. As a result, CoP/MXene electrocatalyst shows enhanced oxygen evolution reaction (OER) activity, with substantially lower overpotential (230 mV at 10 mA cm⁻²) compared to those of state-of-the-art IrO₂ (270 mV). Furthermore, a hybrid bifunctional electrode (CoP/MXene/CoP/MXene) exhibits highly stable and efficient overall water splitting performance (1.56V at 10 mA cm⁻²) as compared to the benchmark electrode couple IrO₂/C//Pt/C (1.62V at 10 mA cm⁻²) in alkaline solution. The hybrid electrocatalyst having Co atoms with exposed active sites accelerates the OER kinetics. Likewise, the negatively charged MXene sheets enriched with functional groups increase the proximal migration of H⁺ ions toward the cathode, thereby facilitating the HER kinetics as evidenced by DFT calculation. This study also provides a better understanding of the electronic effect induced by the MXene termination groups. Furthermore, under the OER conditions, the CoP/MXene is partially oxidized to Co-(oxy) hydroxide clusters, acting as a real active species for the efficient electrocatalytic performance. Furthermore, the post-stability analysis indicated that the massive oxidation of M-P bond (under OER experimental conditions) is suppressed by MXene layer. These promising results demonstrate the structural and compositional merits of CoP/MXene hybrid for scalable electrochemical applications. Our findings also reveal that rational tuning of Metal/MXene interface can remarkably promote the OER/HER electrochemistry. We conclude that the as-fabricated flexible and free-standing MXene-based films can be directly used as electrodes for various electrochemical applications.

2:45 PM EN07.09.05
Wafer Scale Synthesis of MoS₂-Graphene Heterostructure at Low Temperature and its HER Application
Kubra Aydin¹, Hyeong-U Kim², Vinit K. Kanade¹, Mansu Kim³, Hyunho Seok¹, Changmin Kim³, Dongmok Whang³, Jae-Hyun Lee⁴ and Tae Sung Kim³,¹; ¹Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); ²Northwestern University, United States; ³Sungkyunkwan University, Korea (the Republic of); ⁴Ajou University, Korea (the Republic of)

In this research, we successfully indicate the fabrication and characterization of MoS₂-graphene heterostructure (MGH) using Plasma enhance chemical vapor deposition (PECVD) and its HER activity. Graphene is a material that has two-dimensional (2D) planar structure of carbon atoms with small overlap between the valence and conduction bands. 2D planar structure of graphene can agree to hybrid with different materials and this agreement can lead to enhanced catalytic activity and stability. Therefore, Transition-metal dichalcogenides (TMDs) is one of materials for enhancement performance with graphene. TMDs are atomically thin semiconductors of the type MX₂, where M is a transition metal (Mo, W) and X is a chalcogen (S, Se, or Te). In addition, band gap of MoS₂ is depending on the number of MoS₂ layers. MoS₂ can be applied wide application areas because of its tunable band gap like hydrogen storage, capacitors.

Heterostructure was distinguished as lateral and vertical heterostructure. Lateral heterostructure includes different 2D layers on one plane. Vertical heterostructure is that different 2D layers are stacked up onto one plane. When graphene forms vertical heterostructure with MoS₂, the Dirac cone of graphene splits. Therefore, it can be tuned band gap of material using heterostructure method. When we consider regarding its tunable band gap and relatively high carrier mobility, MoS₂ has been investigated for applications in future electronic devices. Especially, the combination of MoS₂ with graphene opens up new possibilities in electronic applications and also shows great potential as a catalyst. Perfectly, this various band gap material finds many uses; for example, in hydrogen storage, capacitors, electrochemical devices.

First of all, Graphene was synthesized on Cu foils using chemical vapor deposition (CVD) process. Graphene was growth using CH₄:H₂ (30:50 sccm) at 1040 celsius degree for 1h and then furnace was rapidly cooled to room temperature under same atmosphere. The synthesized graphene was transferred on substrate (SiO₂/Si or glassy carbon electrode). Mo was deposited by 1 nm of thickness on transferred graphene by E-beam evaporator. it was loaded into PECVD chamber for sulfurization at 150 celsius degree under H₂S and Ar plasma for 1.5 h. Finally, MoS₂ was directly growth on graphene layer as a vertical heterostructure layer. It was characterized by using Raman spectroscopy and high-resolution transmission electron microscopy. The MoS₂ was confirmed as 5-6 layers using Raman and HR-TEM analysis. XPS analysis with depth profiling can confirm chemical states of both top MoS₂ layer and bottom graphene layer in MGH. Furthermore, hydrogen evolution reaction (HER) of MGH and bare MoS₂ was evaluated. MGH electrodes shows lower over potential and Tafel slope than bare MoS₂ electrode, which is indicating their enhanced catalytic performance. This rising up can be attributed to the high density of defects (grain boundaries and sulfur vacancies) present in MoS₂ synthesized on graphene, which is increasing the total number of active sites and then provide an effective charge transport pathway through the highly conducting
graphene layer.

3:00 PM BREAK

3:30 PM *EN07.09.06
Understanding Photoelectrode/Catalyst Interface for Solar Water Splitting Dunwei Wang; Boston College, United States

As a potentially low-cost, high-efficiency solar energy storage solution, solar water splitting faces great challenges. One of the issues is the poor catalytic activity and low stability. Applications of co-catalysts have been shown effective to correct the deficiency by promoting desired chemical reactions so as to minimize charge recombination at the surface and to reduce parasitic corrosion reactions. The detailed behaviors of the light absorber/catalyst interface, however, remain poorly understood. Here we present our recent research in this area. We show that the application of the co-catalysts may greatly influence the charge separation behaviors of the photoelectrode. Detailed thermodynamic and kinetic measurements support our understanding. Furthermore, we show that the photoelectrode substrate also exerts great influences on the co-catalyst behaviors. A strong interaction between the photoelectrode and the catalyst can be beneficial. The combined system may also serve as a new platform to understand heterogeneous catalysis such as water oxidation at a level previously inaccessible. The knowledge generated by our work will likely contribute significantly to the development of solar water splitting technology for a future powered by renewable energies.

4:00 PM EN07.09.07
Water Oxidation by Manganese Oxide Systems—Molecular and Layered Catalysts Inspired by Nature Michael J. Zdilla1, Daniel R. Strongin1, Eric Borguet1, John P. Perdew1, Michael L. Klein1, Ian G. McKendry2, Haowei Peng1, Richard Remsing1 and Ran Ding1; 1Temple University, United States; 2Los Alamos National Laboratory, United States

An overview of our recent progress in two areas of biologically inspired water oxidation chemistry is presented. 1) The preparation of synthetic manganese clusters that mimic the active site of the oxygen evolving complex Photosystem II has given catalysts that are able to activate water for redox reactions at low overpotentials, and has offered insights into mechanistic chemistry at these systems of potential relevance to nature. 2) The synthetic modification and optimization of layered manganese oxide catalysts, guided by theory, has offered clues into the electronic, structural, defect, and geometric features that favor redox chemistry in the interlayer of the manganese oxide phase birnessite. By a combination of theory, simulation, and experiment, the optimization of birnessite to turn it from a poor catalyst into an excellent catlayst for electrochemical water oxidation will be presented.

4:15 PM EN07.09.08
InGaAsP as a Promising Narrow Band Gap Semiconductor for Photoelectrochemical Water Splitting Joshua Butson, Parvathala Narangari, Mykhaylo Lysevych, Jennifer Wong-Leung, Yimao Wan, Siva Karuturi, Hoe Tan and Chennupati Jagadish; The Australian National University, Australia

While photoelectrochemical (PEC) water splitting is a very promising route towards zero-carbon energy, conversion efficiency remains limited. Semiconductors with narrower band gaps can absorb a much greater portion of the solar spectrum, thereby increasing efficiency. However, narrow band gap (~1 eV) III-V semiconductor photoelectrodes have not yet been thoroughly investigated. In this study, the narrow band gap quaternary III-V alloy InGaAsP is demonstrated for the first time to have great potential for PEC water splitting, with the long-term goal of developing high-efficiency tandem PEC devices, which require both wide and narrow band gap absorbers. TiO2-coated InGaAsP photocathodes generate a photocurrent density of over 30 mA/cm2 with an onset potential of 0.45 V versus RHE, yielding an applied bias efficiency of over 7%. This is an excellent performance, given that nearly all power losses can be attributed to reflection losses. X-ray photoelectron spectroscopy and photoluminescence spectroscopy show that InGaAsP and TiO2 form a type-II band alignment, greatly enhancing carrier separation and reducing recombination losses. TiO2 also greatly improves the stability of InGaAsP, which is susceptible to corrosion in acidic electrolyte. Future work will include the minimisation of reflection losses. This can be achieved by fabricating InGaAsP nanostructures, for which a large-area top-down random nano-mask technique has been developed. Beyond water splitting, the tunable band gap of InGaAsP could be of further interest in other areas of photocatalysis, such as CO2 reduction.
Identifying Active Surface Entities on Metal Oxides for Oxygen Evolution by Multimodal Surface X-Ray Probes

Hua Zhou; Argonne National Laboratory, United States

Electrocatalysts are materials designed to provide a facilitating environment for electrochemical conversion and synthesis of materials and fuels from atmospheric molecules, which is one of the most important challenges facing societal need of energy in 21st century. One of the major hurdles developing electrocatalysts is the lack of holistic information of the evolving surface structure of materials during electrochemical operation. This is particularly formidable for oxygen evolution reaction (OER), where the oxidizing environment is corrosive and can significantly rearrange the electrocatalyst surface structure. Therefore, identifying how the surface structure of materials evolves during the OER is essential to the development of more active and stable electrocatalysts and broadly to the prospect of materials and energy sustainability. Surface-sensitive X-ray probes from modern synchrotron sources including surface X-ray scattering and grazing incidence X-ray spectroscopy provide a very powerful suite of toolkits to decipher the surface subtlety and evolution. If utilizing these techniques in a well-coordinated approach, one can deliver thorough and deep fundamental insights of surface transformations (e.g. structural, chemical and electronic) during the electrocatalytic process.

In this talk, we will firstly render a brief survey of various surface sensitive X-ray techniques to specifically probe structural and chemical aspects of electrocatalytic materials, in particular the combined approach to differentiate the contribution from surface and bulk layers. Following the survey, we would like to present a few prototypic studies of metal oxide model systems for surface OER processes. First example is the detailed understanding of the interaction between water and single crystal RuO2 (110) in acidic electrolytes under OER conditions, especially surface atomic structure rearrangements as a function of potential quantified by X-ray crystal truncation rods. Unique oxygen absorbent species on the Ru sites were detected at an OER relevant potential. A new OER pathway with the rate-limiting deprotonation of the –OH group can be suggested by integrating potential-dependent surface structures with DFT-calculated energetics. The second demonstration is to present a comprehensive study of the emergent surface transformation of SrIrO3, the most active OER electrocatalyst reported to date, especially the amorphous boundary layer that forms from the pristine crystalline structure on the surface with OER cycling. In virtue of multimodal X-ray probing, a step-by-step transformation mechanism of the amorphization process could be explicitly illuminated. Our X-ray results show that the amorphization is triggered by the lattice oxygen activation and the structural reorganization facilitating coupled cation and anion diffusions is key to the realization of the OER active structure in the final SrIrO3 form which exhibits stronger disorder than conventional amorphous IrOx, partially explaining its champion OER activity.

Self-Assembling Oxide Catalyst for Electrochemical Water Splitting

Ilia Valov1, Daniel Bick2, Deok-Yong Cho3, David N. Mueller4 and Rainer Waser2; 1Research Center Juelich, Germany; 2RWTH Aachen University, Germany; 3Chonbuk University, Korea (the Republic of)

The demand on efficient and economically reasonable conversion and storage of energy from renewable power sources is an essential challenge and existential task for the modern society. Emerging technologies like metal-air batteries, fuel-cells and electrolyzers, which are mostly limited by the oxygen electrocatalysis, depend on reliable catalyst materials suited for long term application in alkaline environments. Candidates for precious metal free catalyst materials range from metal alloys to oxides and nitrides. Several perovskites have been suggested as economically reasonable catalysts for the oxygen evolution reaction (OER) and showed eligible overpotentials. Among these, the perovskite system BaCoO3 (BCO), and especially the double perovskite PrBa1-xCoO3-δ (PBCO) has shown superior properties (low overpotential) and has been identified as one of the most promising OER materials.
Application of oxides as OER electrocatalysts is limited by two general problems. The first one is their insufficient electronic conductivity. The second and main problem for all OER catalysts is the degradation of the structure (amorphisation) and electrocatalytic properties during long-term operation.

We report on a new perovskite self-assembling material system BaCo$_{0.98}$Ti$_{0.02}$O$_{3-\delta}$.Co$_3$O$_4$, which exhibits higher current densities for the OER and over 10-fold increased lifetime in comparison to the most reliable electrocatalyst (PBCO) reported up-to-date. Importantly, all electrolysis experiments were performed at temperatures typical for industrial application i.e. 353 K. By systematic modification of chemical composition/doping and defect chemistry in binder free BCO perovskite-based catalyst films, simultaneous aging and characterisation with electrochemical methods, XRD, XPS, XANES and EXAFS we were able to identify the degradation mechanism related to cation leaching and amorphization. We demonstrate that the initial crystalline structure rapidly and completely transforms to an amorphous electrochemically active material, which retains its electrochemical properties until its service life end.

Based on the combination of analysis, calculation and aging experiments, a model is derived, which is able to explain the connection between short-range order, defect chemistry and catalyst stability. This model is capable of making predictions to future OER catalyst material design.

9:15 AM EN07.10.03
In Situ Probing of Ultrafast Electrochemical Reactions with High Catalyst Mass Activities for Efficient Water Splitting Feng-Yuan Zhang; University of Tennessee, United States

Water splitting into hydrogen/oxygen with Proton exchange membrane electrolyzer cells (PEMECs) has become more attractive due to their high efficiencies even at low-temperature operation. In this talk, the ultrafast and multiscale electrochemical reactions in an operating PEMEC, including oxygen evolution reactions (OERs) and hydrogen evolution reactions (HERs), will be revealed. The in-situ probing results shows the OERs and HERs mainly occur on catalyst layers at the rim of the pores of the thin/tunable liquid/gas diffusion layers (TT-LGDLs), and there is a large portion of catalysts being not effectively utilized. Based on these discoveries, a novel thin/tunable gas diffusion electrode (GDE) is developed by depositing the catalyst on a tunable pattern that is observed to be active for the OER/HER. The thin GDEs with a total thickness of about 25 µm significantly improve the catalyst mass activity and utilization and exhibit excellent PEMEC performance with a very simple fabrication process and low cost.

9:30 AM EN07.10.04
Tailored Nickel-Iron Layered Double Hydroxide Platelet Size for Optimized Oxygen Evolution Reaction Catalysis Daire P. Tyndall, Valeria Nicolosi, João Coelho and Sonia Jaskaniec; Trinity College Dublin, Ireland

The oxygen evolution reaction (OER) has drawn significant interest in the field of renewable and sustainable energy in recent years, with potential applications for hybrid electric vehicles (HEV) in the form of electrolyzer cells for hydrogen production, fuel cells or metal-air batteries, among others. Perhaps the most significant feature of OER is the fact that it is a necessary ‘step’ in the evolution of H$_2$ gas by water electrolysis, bringing with it an associated potential (E $\approx$ 1.23 V). To overcome this potential barrier with minimum overpotential (\(\eta\)), an effective electrocatalyst is required to facilitate the reaction. Nickel-Iron Layered Double Hydroxide (NiFe-LDH) has been shown to exhibit efficient catalysis of the OER, demonstrating overpotentials in composite systems which are competitive with previously studied electrocatalysts based on rare earth metals such as ruthenium and iridium\([1]\), as well as being competitive in an economic perspective. NiFe-LDH has other advantages over rare earth catalysts such as earth abundance, cost and stability (in operating conditions)\([2]\). The nature of the material in question is that the vast majority of catalytic active sites are located at open coordination sites at the edge of the NiFe-LDH hexagonal platelets. This means that average particle dimensions will play an important role in determining the density of active sites within a NiFe-LDH electrode and hence, it’s catalytic ability.

Synthesis of high quality, planar NiFe-LDH platelets with regular hexagonal morphology was achieved using a wet chemistry method at a relatively low temperature (100 °C) using triethanolamine (TEA) as a ‘capping agent’ to allow homogeneous coprecipitation of both the nickel and iron metal centres within brucite-lake layers. Using platelets synthesized in this way, OER catalysis has been demonstrated with \(\eta = 0.36\) V, a competitive value when compared to many state-of-the-art OER electrocatalysts in the same conditions\([3]\) (5 mVs$^{-1}$, quoted at current density j $= 10$ mAcm$^{-2}$). The work aims to develop methods of post-synthetic treatment of NiFe-LDH dispersions to reduce lateral platelet dimensions and further improve edge-site density for electrocatalytic optimization. This study comes
in accordance with the growing number of high-performance electrocatalysts being studied for OER\[4\]. In this work, a combination of platelet size reduction and selection techniques are utilized to isolate particle dispersions with controlled mean platelet dimensions \(<L>\) with the aim of elucidating the relationship between \(<L>\) and \(\eta\). To do so, methods of tip-sonication and centrifugation were employed. Tip-sonication (7 h) alone can reduce \(<L>\) from 0.78 ± 0.01 µm to 0.29 ± 0.01 µm while further centrifugation in the relatively narrow range of centrifuge rates 1000 – 5000 rpm can isolate useable dispersions with \(<L>\) as low as 0.20 ± 0.01 µm. When tested in electrolyzer cell working conditions (1 M KOH, 0 – 0.6 V) electrodes based on size-selected material exhibited a clear reliance of electrocatalytic performance on the mean platelet size \(<L>\). Further, composite studies are carried out to establish ideal materials for optimizing the NiFe-LDH performance to achieve \(\eta\) values which are competitive in the field of OER catalysis.


9:45 AM EN07.10.05
Synthesis of Titanium Oxynitride Thin Films with Tunable Bandgaps for Alternative Energy Applications in the Full Solar Spectrum Range Nikhil R. Mucha\(^1\), Surabhi Shaji\(^1\), Manosi Roy\(^1\), Balamurugan Balasubramanian\(^2\), Prakash Apte\(^1\) and Dhananjay Kumar\(^1\); \(^1\)North Carolina A&T State University, United States; \(^2\)University of Nebraska–Lincoln, United States

A novel Ti\(_x\)N\(_y\)O\(_z\) (TiNO) material system with a range of \(x\) (0≤\(x\)≥1) and \(y\) (0≤\(y\)≤2) values has been synthesized in thin film form using the non-equilibrium nature of a pulsed laser deposition process. A proper control of \(x\) and \(y\) values has been found to result in the material system transformation from a metallic rock-salt structure to an insulating rutile structure (TiO\(_2\)). The in-between \(x\) and \(y\) values yield compounds with a range of bandgap materials capable of absorbing radiation in the full solar spectrum. When N atoms in TiN are partially substituted by O atoms, the top of the valence band (valence band maxima) shifts down leaving the bottom of the conduction band (conduction band minima) unaffected. Since, the valence band maximum of the oxynitride compounds is located at higher potential energy than that for pure TiO\(_2\) due to the contribution of N 2p orbitals, the partial substitution of N by O result in the reduction of bandgap values with respect to those of the extreme compounds, i.e. TiN or TiO\(_2\).

X-ray diffraction and x-ray photoelectron spectroscopy measurements have been carried out that lend evidence in support of the realization of the aforementioned values of \(x\) and \(y\). The optical measurements on TiNO films involving photoluminescence and ultra violet studies have established the existence of bandgaps in the range of 1.6 to 3.0 eV. The current voltage characteristics recorded from ITO/TiNO/Cu(Au) configurations have shown that the current (\(I\)) and corresponding voltage (\(V\)) lie in the same quadrant with a similar polarity in the dark conditions while the current and the corresponding voltage lie in quadrants with different polarity. The positive sign of power (\(I\) times \(V\) positive) under dark conditions indicates dissipation of power in TiNO while the negative of sign of the power (\(I\) times \(V\) negative) indicates the power generation capability of TiNO system. The fabrication of TiNO system via controlled oxidation has an advantage over conventional methods of bandgap manipulation of TiO\(_2\) via nitridation due to the higher activation energy of a nitridation process (672 kJ/mol) than that of an oxidation process (496 kJ/mol). As the number of photocatalysts/semiconductors that are active under visible light irradiation is very limited, our approach to develop a unique visible-light-driven TiNO photocatalytic and photovoltaic material system can open a new avenue for solar devices.

10:00 AM BREAK

10:30 AM *EN07.10.06
Electrocatalytic Activity of Pd-\(\text{CeO}_2\) Catalysts for Anion Exchange Membrane Fuel Cells Pamir Alpay\(^1\), Sanjubala Sahoo\(^1\), Hamish A. Miller\(^2\) and Dario R. Dekel\(^3\); \(^1\)University of Connecticut, United States; \(^2\)Istituto di Chimica dei Composti Organometallici, Italy; \(^3\)The Wolfson Department of Chemical Engineering, and the Nancy
There is significant interest in the development of platinum-free electrode materials for Anion Exchange Membrane Fuel Cells (AEMFCs) \cite{1,2}. Here we present a combined experimental and theoretical study of the Hydrogen Oxidation Reaction (HOR) activity in alkaline medium for Pd-CeO$_2$ anode catalysts. Specifically, we model Pd-CeO$_2$ substrates where Pd atoms are either adsorbed or embedded on (111) CeO$_2$ surfaces. The computations are performed using density functional theory using the generalized gradient approximation and the necessary Hubbard corrections. The HOR activity is explored using the Tafel-Volmer mechanism. The Tafel reaction is one of the rate-determining steps for HOR activity, which involves the dissociation of the H$_2$ molecule. The activity descriptors for the HOR under alkaline conditions however, have been suggested to be the H bonding energy (HBE) and the OH bonding energy (OHBE), which provides a quantification of the H and OH bond strength onto the Pd and ceria. We determine dissociation pathways for H$_2$ molecules on both Pd-CeO$_2$ substrates. Our findings show that the Pd adsorbed (111) CeO$_2$ becomes highly reactive for H$_2$ dissociation, exhibiting a low dissociation barrier compared to that of a pure CeO$_2$. Our computations are in agreement with experiments where a high HOR performance has been achieved for a bifunctional Pd-CeO$_2$ system compared to CeO$_2$ \cite{3}. Additional calculations are carried out to understand the HOR activity as a function of the concentration of adsorbed Pd atoms. Oxidized single Pd atoms or very small clusters coordinated to the CeO$_2$ oxygens show improved HOR activity. Our research provides the underlying principles towards the design of highly active HOR catalysts for AEMFC without utilizing platinum.

\begin{thebibliography}{4}
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\bibitem{3} Davydova \textit{et al.}, ACS Catal. \textbf{8}, 6665 (2018)
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\section*{11:00 AM EN07.10.07}
Enhancing the Activity of Molybdenum Diselenide for Electrocatalytic Hydrogen Evolution via Transition-Metal Doping

\textbf{Akash Jain$^1$}, \textbf{Vasu Kuraganti$^{2,3}$}, \textbf{Maya Bar-Sadan$^{2,3}$} and \textbf{Ashwin Ramasubramaniam$^1$}; \textit{1}University of Massachusetts Amherst, United States; \textit{2}Ben-Gurion University of the Negev, Israel

Electrochemical water splitting is a promising fossil-fuel free route for hydrogen production. However, the hydrogen evolution reaction (HER) is most efficiently catalyzed by expensive platinum group metals and there is significant interest in finding alternative, earth-abundant replacements. Recently, there has been progress in employing relatively inexpensive transition-metal dichalcogenides (TMDCs) like MoSe$_2$ for HER but these materials still require an appreciably larger overpotential than Pt, which reduces their efficiency. Here, we show that the catalytic activity of MoSe$_2$ can be improved significantly by doping with earth-abundant transition-metal (TM) dopants such as Mn, Fe, Co and Ni. Using density functional theory (DFT) calculations, we study the influence of these substitutional dopants on the thermodynamics of H adsorption at edges, Se-vacancy, and basal plane sites, and explain trends in adsorption energies via electronic structure considerations and structural changes arising from the atomic-size mismatch between Mo and dopant atoms. A key finding from our studies is that selected TM-dopants promote the formation of highly active Se-vacancy sites—in some cases even making these vacancies thermodynamically favorable—thereby increasing the activity of the native MoSe$_2$ catalyst. DFT calculations shed light on recent experiments on Mn-doped MoSe$_2$ nanoflowers that display improved HER charge-transfer kinetics, smaller Tafel slope, and overpotential than undoped MoSe$_2$. Overall, our work suggests that the electrocatalytic activity of MoSe$_2$ and similar transition-metal dichalcogenides can be enhanced by employing substitutional dopants, not for their inherent activity, but as promoters of highly active chalcogen vacancies.

\section*{11:15 AM EN07.10.08}
Role of Defects and Polaron in Surface Morphology and Electronic Structure in BiVO$_4$

\textbf{Wennie Wang$^1$} and \textbf{Giulia Galli$^{1,2}$}; \textit{1}The University of Chicago, United States; \textit{2}Argonne National Laboratory, United States

As one of the most widely-studied oxides for photocatalysis, bismuth vanadate (BiVO$_4$) is a highly promising material candidate as a photoanode for water photocatalysis. In addition to having strong absorption across the visible spectrum and a conduction band edge near the hydrogen evolution potential, BiVO$_4$ is stable under aqueous conditions and relatively facile and cheap to synthesize. It has been reported that charge transport, interfacial charge transfer, and recombination events are limiting factors for photoelectrocatalytic (PEC) performance. Thus,
significant effort has gone into optimizing PEC devices based on BiVO₄, including doping, nanostructuring, and pairing with other catalysts or semiconductors. However, a major challenge in the field has been to have well-defined experimental samples and computational methodologies to disentangle the influence of surface/interface morphology, defects, and the presence of water.

Our objective is to holistically understand the connections between surface morphology and PEC performance, and bridge gaps between theoretical and experimental methods by making direct comparison between computed and measured electronic properties. Using first-principles calculations, we study the surface morphology and electronic structure of BiVO₄, and compare with single-crystalline and epitaxially-grown samples. We present our work on pristine and defective surfaces, and connect our calculations with measured band edges, work functions, and STM images. In particular, we discuss the role and formation of polarons in the bulk and at the surface [1], and their influence on PEC performance.


11:30 AM EN07.10.09
Enhanced Catalytic Activity of Edge-Exposed 1T Phase WS₂ Grown Directly on WO₃ Nanohelical Array for Water Splitting
Noho Lee, Il Yong Choi, Kyung-Yeon Doh, Jaewon Kim, Hyeji Sim, Donghwa Lee, Si-Young Choi and Jong Kyu Kim; POSTECH, Korea, Korea (the Republic of)

Among various candidates for renewable energy sources, much attention has been given to hydrogen (H₂) produced by hydrogen evolution reaction (HER) via electrochemical water splitting. As promising materials for electro-catalytic electrodes, layered 2 dimensional (2D) transition metal dichalcogenides (TMDCs) such as MoS₂ and WS₂ have drawn great attention as alternatives to precious metals such as platinum (Pt) and gold (Au). On the other hand, it is highly desirable to control the morphology and phase of electrodes materials to optimize the catalytic activity. For example, edge planes of layered TMDCs are known to be catalytically more active than basal planes due to nearly thermoneutral properties in proton adsorption. Morphological controls of TMDCs were investigated to expose edge sites effectively by tuning nucleation and growth behaviors, for example, double gyroid MoS₂ thin film using atomically controlled surface, vertically aligned TMDCs by rapid sulfurization and defects-mediated formation of in-plane edges of MoS₂ nanosheets. Controlling crystallographic phase is also important since the atomic configuration of TMDCs affects the catalytic activity substantially. Greater catalytic performances of metallic 1T phase MoS₂ and WS₂ than semiconducting 2H phase ones due to improved intrinsic reactivity and charge transfer kinetics for HER process, and strain-induced preferential formation of 1T phase WS₂, MoS₂ and MoSe₂ have been reported. Therefore, it would be very advantageous to develop an engineered nanostructure whose surface can be easily modified to facilitate the nucleation and strain-induced growth of edge-plane-exposed TMDCs with 1T phase preferentially.

Herein, hierarchical electrode consisting of edge-exposed 1T phase WS₂ grown on the array of surface-modified WO₃ nanohelices (NHs) and its enhanced catalytic performance in hydrogen evolution reaction (HER) are presented. Oxygen-deficient WO₃ NHs surface modified by a controlled annealing facilitates the formation of a rich edge-exposed WS₂ during sulfurization. In addition, metallic 1T phase WS₂ is preferentially grown on the WO₃ NHs owing to the strain induced between WS₂ and curved WO₃ NHs. Such desirable structural properties, metallic 1T phase and a rich edge-exposed morphology, for a catalytic electrode directly resulted in an enhanced HER performance in water splitting.

11:45 AM EN07.10.10
“All Electric” Ion Pumps
Gideon Segev¹,², Shane Ardo³,³, Rylan J. Kautz², David M. Larson¹,¹, Joel W. Ager¹,¹,4 and Francesca Maria Toma¹,²;¹ Lawrence Berkeley National Laboratory, United States; ²Tel Aviv University, Israel; ³University of California, Irvine, United States; ⁴University of California, Berkeley, United States

Ion pumps are devices that use external power to introduce a net ionic flux. For example, in the photosynthetic process, light is used to pump protons up a concentration gradient which will be used in sequential steps to generate fuels. In living cell membranes, nano scale channels pump different types of ions against a concentration gradient consuming energy from the hydrolysis of ATP. Although widely used in nature, there are very little technologies that can unleash the vast potential of ion pumps. Unlike electrons in electronic devices where contacts serve as nearly ideal sources and sinks for charge carriers, ions are sourced and removed by chemical reactions. These reactions are in many cases energetically expensive and require tailoring specific catalysts to the specific ions to be
pumped. In this contribution we report a first of its kind “all electric”, ion pump based on an electronic ratchet mechanism.

Electronic ratchets are devices that utilize modulation in a spatially varying electric field to drive steady state current. Similar to peristaltic pumps, where the pump mechanism is not in direct contact with the pumped fluid, electronic ratchets induce net current with no direct charge transport between the power source and the pumped charge carriers. Thus, electronic ratchets can be used to pump ions in steady state with no electrochemical reactions between the power source and the pumped ions resulting in an “all electric” ion pump.

Porous capacitor based ion pumps were fabricated by coating the two surfaces of nano-porous alumina wafers with gold. The electric field within the nano-pores is modulated by oscillating the capacitors voltage. Thus, when immersed in solution, ions within the pores experience a modulating electric field resulting in ratchet based ion pumping. The device pumping performance was studied for various input signals, geometries and solutions. The proposed ion pumps may be used as building blocks in a wide range of applications such as artificial photosynthesis, water desalination, chemical separations and many others.

SESSION EN07.11: Novel Water-Splitting Catalysts II
Session Chairs: Pamir Alpay and Dunwei Wang
Friday Afternoon, December 6, 2019
Hynes, Level 2, Room 203

1:30 PM *EN07.11.01
Implicit Solvation with Periodic Boundary Conditions—Implementation and Application to Reactions at Interfaces Carlo Adamo1,2; 1Chimie Paristech-CNRS, France; 2Institut Universitaire de France, France

We present the implementation of an implicit solvation model in the periodic CRYSTAL code. The solvation energy is separated into two components: the electrostatic contribution arising from a self-consistent reaction field treatment obtained within a generalized finite-difference Poisson model, augmented by a nonelectrostatic contribution proportional to the solvent-accessible surface area of the solute. A discontinuous dielectric boundary is used, along with a solvent-excluded surface built from interlocking atom-centered spheres on which apparent surface point charges are mapped. The procedure is general and can be performed at both the Hartree–Fock and density functional theory levels, with pure or hybrid functionals, for systems periodic in 0, 1, and 2 directions, that is, for isolated molecules and extended polymers and surfaces [1].

As application of the implemented solvent model, we consider the reaction of CO and H2O to form CO2 and H2 on Pt(111), using periodic density functional theory (DFT) calculations. Since this reaction has already been investigated at the DFT level with different mechanisms proposed (see [2] for instance), it therefore offers a suitable playground to investigate the role of different effects on the proposed mechanisms. In particular, we compare GGA to hybrid DFT models, considering both dispersion and implicit solvation effects. We discuss the results obtained on the full reaction paths, in which transition states are fully characterized.

References:

2:00 PM EN07.11.02
Anchoring Ir Single Atom Sites on NiFe Oxyhydroxides for High-Efficient Water Oxidation Reaction Xueli Zheng and Yi Cui; Stanford University, United States

The efficiency with which renewable fuels and feedstocks are synthesized from electrical sources is limited at present by the sluggish water oxidation reaction. Here, using density functional approach, we predict that the optimal energetics for water oxidation could be achieved by systematic increase of the oxidation of the Ir active sites within typical NiFe framework. We successfully anchored Ir single sites on NiFe oxyhydroxides (Ir0.1/Ni0.9Fe) via a unique cryogenic (cryo)-photochemical reduction method. Ir0.1/Ni0.9Fe catalyst exhibits the lowest overpotential (166 millivolts) at 10 milliamperes per square centimeter and retains its performance following 200 hours of operation in 1 M KOH electrolyte. In situ grazing incidence X-ray absorption spectroscopy measurements/simulations reveal that
and Bader charge analysis indicate the charge transfer between Ir and Ni/Fe/O which reveals an average oxidation state of +5.3 on Ir sites under operating conditions. The favorable coordination environment of such single sites plays important roles for the enhanced water oxidation activity.

2:15 PM EN07.11.03
Kinetics of Photogenerated Charge Carriers at Semiconductor-Electrolyte Interface in Photoelectrochemical Water-Splitting
Chang-Ming Jiang1, Jason K. Cooper2 and Ian D. Sharp1; 1Technical University of Munich, Germany; 2Lawrence Berkeley National Laboratory, United States

Understanding the identity of surface states, as well as their roles in catalyzing photoelectrochemical (PEC) reactions, is imperative for achieving efficient solar fuel production. Copper vanadate (CVO) is an emerging semiconductor photoanode material system that supports a variety of room temperature stable phases depending on the Cu:V stoichiometry. This feature of CVO provides a unique opportunity to study the role of composition, phase, and surface states on key PEC characteristics. In this work, thin films of four CVO phases: Cu5V2O10, Cu11V6O26, γ-Cu3V2O8, and β-Cu2V2O7, were prepared by reactive co-sputtering. A suite of complimentary experimental tools (including spectroscopic ellipsometry, transient absorption, and transient photocurrent) were applied to determine trends in basic optical properties, photocarrier dynamics, and surface state-induced charge trapping. Analysis of these results reveals competing bulk and surface properties; increasing Cu content provides stronger light absorption but reduces oxygen evolution activity. The rate constants for water oxidation and surface recombination are quantified as a function of composition, applied electrochemical potential, and incident light intensity. Composition trends for interfacial charge transfer and recombination rate constants indicate that Cu cations near the surface serve as trap states for photogenerated holes. Surprisingly, it is found that the surface recombination rate remains nearly constant with illumination intensity over the range of 0.1 – 1.5 suns. At the same time, the heterogeneous charge transfer rate constant is enhanced by a factor of 2 to 6, depending on composition and applied potential, over the same intensity range. Based on these results, we propose modifications to the existing kinetic model and provide insights into the kinetic factors that underlie competitive recombination and charge transfer at transition metal oxide photoelectrode surfaces.

2:30 PM BREAK

3:00 PM EN07.11.04
InGaN-Si Tandem Photoelectrodes for Photoelectrochemical Water Splitting by MOCVD—Understanding System Design Considerations Necessary to Bridge Theory and Experiment
Andrew B. Wong1,2, Ye Sheng Yee1, Thomas F. Jaramillo1,2 and James S. Harris1; 1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States

For some time, it has been predicted that the development of tandem absorber photoelectrodes can allow for superior utilization of the solar spectrum for photoelectrochemical water splitting. Based on stoichiometry, InGaN has a variable band gap that can span from 3.4 to 0.7 eV, which makes it ideal for pairing with Si in tandem photoabsorber devices, in principle. Furthermore, MOCVD of InGaN directly onto a Si p-n junction can provide a path to reducing the cost of tandem absorbers towards commercialization. In this presentation, our work into the development of tandem InGaN-Si photoelectrodes via MOCVD will be discussed. Specifically, our successful growth of the designed InGaN-Si system and the performance of this system will be presented. Our efforts elucidate necessary considerations when pursuing design of photoelectrochemical systems that are relevant for discussions between experimentalists and theorists during system design. These inter-related considerations include:
- Controlling electronic trap and surface states within the absorber materials and defect tolerance
- Controlling crystallization, growth, and morphology of absorber materials
- Controlling carrier concentration and carrier type
- Reducing the density of structural defects in the absorber materials
- Managing lattice strain resulting from mismatches in lattice constant and thermal expansion coefficients
Overall, this work on tandem InGaN-Si photoelectrodes for photoelectrochemical water splitting can provide a useful case study that can inform the dialog for the coordination between experimentalists with theorists for the discovery of the next generation of materials for water splitting. This dialog continues to grow in importance as the interface between theory and experiment continues to become more robust.

3:15 PM EN07.11.05
Novel Stable Three-Dimensional (3D) Stainless Steel-Based Electrodes for Efficient Water Splitting

Haojie Zhang¹, Juliana Martins de Souza e Silva¹, Xiaopeng Li², A. Wouter Maijenburg¹, Stefan Schweizer¹ and Ralf B. Wehrspohn¹,³; ¹Martin-Luther-Universität Halle-Wittenberg, Germany; ²Shanghai Advanced Research Institute, Chinese Academy of Science (SARI-CAS), China; ³Fraunhofer-Institut für Mikrostruktur von Werkstoffen und Systemen IMWS, Germany

Stainless steel (SS) is a promising material for the preparation of high-active electrode for efficient water splitting. However, the stability of coupled electrocatalysts on the surface of SS is a significant challenge for the construction of three-dimensional stable electrodes. In this work, we present an efficient and universal process to enhance the interfacial interaction between SS and highly-active electrocatalysts for the preparation of 3D electrodes through the formation of an interfacial network of carbon nanotubes (CNTs) on the surface of SS. The strongly-interconnected CNTs network increases the surface area of the SS support that benefits the modification of highly-active electrocatalysts and also serves as an electron/charge-conductive highway between the electrocatalysts and the support. The modified electrocatalysts on CNTs further improve the performance of the water splitting. The 3D structure of the prepared 3D electrode was visualized and analyzed by X-ray microscopy. Our strategy is an efficient approach to combine highly-active electrocatalysts with SS for the preparation of active and stable 3D electrodes, that can be used further explored in various areas.

SYMPOSIUM EN08

TUTORIAL: Processing and Device Optimization Strategies for High Efficiency Solar Cells
December 1 - December 1, 2019

* Invited Paper

TUTORIAL
Processing and Device Optimization Strategies for High Efficiency Perovskite Solar Cells
Sunday Afternoon, December 1, 2019
Hynes, Level 2, Room 204

Halide perovskites are currently one of the hottest research topics due to their potential use in a wide variety of optoelectronic devices. Especially in the field of photovoltaics this material now outperforms most other thin-film solar cell technologies, reaching efficiencies well above 20%.

In this tutorial, we will introduce material researchers to the most important aspects related to the preparation of state-of-the-art perovskite solar cells. The first part will cover fundamental concepts regarding the preparation of perovskite films and discuss stability effects when tuning the elemental composition. The second part will cover reproducible fabrication protocols and design rules for single cell applications, with a special focus on charge carrier recombination. Finally, in the third part, aspects regarding the preparation, challenges, and prospects of perovskite-based tandem solar cell devices will be examined. The overarching goal of this Tutorial is to provide a comprehensive overview regarding important aspects in material and device preparation; this will enable students and researchers who are new to this topic to pick up the necessary knowledge needed to participate in this exciting research field.
1:30 PM  
Processing, Stabilizing, and Detoxifying Perovskites  Yuanyuan Zhou, Brown University

The first session of this tutorial will discuss the fundamental materials science that governs the most outstanding issues of scalability, stability, and toxicity in the commercialization of perovskite optoelectronics. First, fundamental understandings on the structure, formation, and degradation of halide perovskites will be elaborated with specific examples from the literature. Then, typical materials-engineering strategies that mitigate these issues will be demonstrated. Finally, a perspective on the future directions in this research area will be provided.

2:30 PM  
BREAK

3:00 PM  
How to Make Efficient Perovskite Solar Cells  Martin Stolterfoht, University of Potsdam

The second section will focus on conveying reproducible fabrication protocols for preparing p–i–n type perovskite solar cells with efficiencies above 20% efficiency. The optimization strategies are particularly focused on suppressing non-radiative interfacial recombination which is the main bottleneck of today's perovskite solar cells. Necessary measurement techniques are introduced in this tutorial which will allow researchers to quantify recombination losses in their perovskite solar cell stacks in order to identify the origin of efficiency losses.

4:00 PM  
Perovskite-based Multijunction Solar Cells  Jérémie Werner, University of Colorado Boulder

The third part of this course will cover relevant aspects related to the field of perovskite-based multijunction solar cells. First, a comprehensive overview will be given on how developments in stack design enabled the swift rise in efficiency from 0 to >28% which took place in the last 5 years. Both all-perovskite as well as hybrid perovskite-based tandem solar cells will be introduced and the pros and cons discussed. Finally, the remaining challenges and future directions of this technology will be addressed.

SYMPOSIUM EN08

Halide Perovskites for Photovoltaic Applications—Devices, Stability and Upscaling  
December 2 - December 6, 2019

Symposium Organizers  
Shengzhong (Frank) Liu, Shaanxi Normal University  
Selina Olthof, University of Cologne  
Yabing Qi, Okinawa Institute of Science and Technology  
Kai Zhu, National Renewable Energy Laboratory

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* Invited Paper
8:30 AM *EN08.01.01
Understanding and Designing Interfaces and Defects in Perovskite Solar Cells Juan Pablo Correa Baena; Georgia Institute of Technology, United States

Perovskite solar cells promise to yield efficiencies beyond 30% by further improving the quality of the materials and devices. Electronic defect passivation, and suppression of detrimental charge-carrier recombination at the different device interfaces has been used as a strategy to achieve high performance perovskite solar cells.

In this presentation, I will discuss the role of electronic defects and how these can be passivated to improve charge-carrier lifetimes and to achieve high open-circuit voltages. I will discuss the characterization of 2D and 3D defects, such as grain boundaries, crystal surface defects, and precipitate formation within the films, by synchrotron-based techniques. The importance of interfaces and their contribution to detrimental recombination will also be discussed. As a result of these contributions to better understanding 2D and 3D defects, the perovskite solar cell field has been able to improve device performance. Albeit the rapid improvements in performance, there is still a need to improve these defects to push these solar cells beyond the current state-of-the-art.

9:00 AM *EN08.01.02
Materials and Processing for Scalable Perovskite Solar Cells Nam-Gyu Park; Sungkyunkwan University, Korea (the Republic of)

Since the first report on the 9.7% efficiency, 500 h-stable solid-state perovskite solar cell (PSC) in 2012 by our group, following two seed works on perovskite-sensitized liquid junction solar cells in 2009 and 2011, a power conversion efficiency (PCE) of 24.2% was recorded in 2019. According to Web of Science, publications on PSC increase exponentially since 2012 and total number of publications reaches over 12,000 as of May 2019, which indicates that PSC is considered as promising photovoltaics. Although high photovoltaic performance was achieved from small area cell, scalable technologies are required for commercialization of PSC. In order to shift from small-area device to large-area module, the cheap materials and an effective coating procedure are highly required. We developed cost-effective materials based on delta FAPbI3 powder for high efficiency PSC. The best PCE of 22.6% was achieved using the synthesized perovskite powder. For large-area uniform perovskite coating, a precursor solution containing perovskite cluster was developed. Homogeneous MAPbI3 perovskite film (>100 cm2) was D-bar coated within 20 s, which demonstrated the PCE approaching 18%. Bifacial stamping technique was developed, which led to both high quality FAPbI3 and MAPbI3 on a large scale at milder condition.

9:30 AM EN08.01.03
Combined Surface and Additive Engineering for High Efficiency Flexible Perovskite Solar Cells Shengzhong (Frank) Liu1,2, Yucheng Liu1 and Xuejie Zhu1; 1Shaanxi Normal University, China; 2Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

An effective surface engineering is developed to prepare effective SnO2-based electron transport layer (ETL). Together with an additive engineering strategy, solar cell efficiency is improved to 22% when rigid glass is used as the substrate. When PET substrate is used, flexible solar cells are designed and fabricated with the cell efficiency improved to as high as 20.9%, the highest efficiency for this category of flexible solar cells. It is found that by using an additive to react with Pb2+ to form an intermediate complex. Crystallization process is slowed down during the perovskite formation, leading to enlarged grain size and improved crystalline quality. In fact, using the SnO2 ETL and the additive engineering, the trap state density of the resultant perovskite thin films is effectively reduced comparing to the films without it, demonstrating that the additive effectively retards transformation kinetics during the thin film formation process. Meanwhile, the surface modification is found critical to form a nucleation layer and a good interface for the perovskite thin film development. Furthermore, the environmental stability of the flexible solar cells is significantly enhanced comparing to the devices without them. Large area solar cells are fabricated to demonstrate its scalability.
9:45 AM EN08.01.04  
**Bottom-Up Interfacial Modification with Inorganic and Organic Materials for Highly Efficient and Stable Perovskite Cells**  
Antonio Facchetti\(^1,2\); \(^1\)Northwestern University, United States; \(^2\)Flexterra Corp, United States

Hybrid organic-inorganic perovskite solar cells (PSCs) are promising for applications due to unparalleled processing-performance characteristics. Due to improvements in both perovskite active layer composition and the use of newly-developed interfacial materials, PSC PCEs have increased steadily from ~4% to >23%. High-performance PSCs relies on: (1) Appropriate interfacial energy level alignment for reducing energy losses. (2) Minimize defects and ion vacancies at the perovskite interface and bulk to maximize charge transfer. Here, we report two complementary strategies for fabricating/modifying the device electron transporting layer (ETL) based on inorganic and organic materials. In the first strategy, we demonstrate high-quality and dense ZnO films with negligible organic impurities, high crystallinity, and a self-passivated surface by combustion synthesis enabling cells with a PCE of 19.69 %. In the second strategy, we introduce two non-conjugated multi zwitterionic organic small-molecule electrolytes (NSEs) as effective bottom-up modifier to passivate not only interfacial but the bulk defects of perovskite for solution-processed PSCs. These NSEs enable to achieve an ideal WF for the ETL of 3.78 eV, thus resulting in a barrier free electron transfer, as well as to passivate interfacial defects between perovskite and ETL, preventing back electron transfer and suppressing charge recombination. Cells based on SnO2/NSE deliver PCEs surpassing 21.18% with an ultra-high VOC of 1.19 V. Both approaches strongly suppressed hysteresis and enhance environmental stability.

10:00 AM BREAK

10:30 AM *EN08.01.05  
**Breaking the Defect Bottleneck in Halide Perovskite Semiconductors**  
Aron Walsh; Imperial College London, United Kingdom

The physical properties of semiconducting solids depend on the imperfections they contain [1]. Defects come in a few flavours: conductivity-promoting defects create free carriers that enable electronics; killer defects (deep, charged centres) trigger recombination; and charge scattering defects reduce mobility.

Our understanding of the defect chemistry and physics of halide perovskites is limited in comparison to inorganic semiconductors. I will discuss recent progress, from theory and experiment, to identify, characterise and control point defects and defect processes in this family of compounds. I will cover charge compensation mechanisms [2], carrier trapping phenomena [3], the effect of grain boundaries [4], and how this understanding can be applied to engineer defect populations and distributions. The use of ‘defect tolerance’ as a metric to develop and screen post-perovskite materials will be critically addressed.

[1] "Instilling defect tolerance in new compounds" Nature Mater. 16, 964 (2017); https://www.nature.com/articles/nmat4973


[4] "Accumulation of deep traps at grain boundaries in halide perovskites" ACS Energy Lett. 4, 1321 (2019); https://doi.org/10.1021/acsenergylett.9b00840

11:00 AM EN08.01.06  
**Surface Molecule Doping of Metal Oxide Nanocrystals to Enhance Carrier Transport of Perovskite Solar Cells**  
Zhubing He\(^1,2\); \(^1\)Southern University of Science and Technology, China; \(^2\)Shenzhen Key Laboratory of Full Spectral Solar Electricity Generation (FSSEG), China

Molecular doping of inorganic semiconductor is a rising topic in the scope of organic/inorganic hybrid electronics.
In this talk, we present two typical molecular doping for NiO and SnO₂, both of which play a crucial role in carrier transport in perovskite solar cells. First, NiO hole-transport-layer was realized p-doping successfully by 2,2’-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6TCNNQ). Determined by XPS and UPS, the Eₚ of NiOx HTLs is increased from -4.63 eV to -5.07 eV and VBM-EF declines from 0.58 eV to 0.29 eV after F6TCNNQ doping. The energy level offset between the VBMs of NiO, and perovskites declined from 0.18 eV to 0.04 eV. Combining with first-principles calculations, electrostatic-force-microscopy was the first time applied to verify directly electron transfer from NiOx to F6TCNNQ. The average PCE of CsFAMA mixed cations PSCs were boosted by ca. 8% depending on F6TCNNQ doped NiOx HTLs. Strikingly, the champion cell conversion-efficiency of CsFAMA mixed-cations and MAPbI₃ based devices got 20.86% and 19.75%, respectively.

However, it’s difficult for n-doping, especially for oxides, because rare molecules own both strong reducibility and stability simultaneously in ambient atmosphere. In the second work, a simple, air-robust and cost-effective triphenylphosphine oxide molecule successfully realizes n-doping of SnO₂. Strikingly, we discovered that electrons were transferred from the R₃P⁺-O⁻ σ-bond to the peripheral tin atoms other than the directly interacted ones at the surface. That means those electrons are delocalized. The course was verified by multi physical characterizations. This doping effect accounts for the enhancement of conductivity and the decline of work function of SnO₂, which enlarges the built-in field from 0.01 eV to 0.07 eV and decreases the energy barrier from 0.55 eV to 0.39 eV at the SnO₂/Perovskite interface enabling an increase in the conversion efficiency of perovskite solar cells from 19.01% to 20.69%.

Our discoveries offer an extremely promising molecular doping method for inorganic carrier transport layers in PSCs. This methodology definitely paves a novel way to modulate the doping in hybrid electronics more than perovskite and organic solar cells.
transformation mechanism and effective manipulation for the complex phase transformation from disordered precursors to intermediate phases and perovskite crystal during solution-casting, and the equilibrium between nucleation and growth during single-crystal fabrication. [1-8] Our findings suggest an important role of the phase transformation control for dimensional tailoring, scalable fabrication, and flexible single-crystal of perovskite. In addition, I will briefly discuss the relationship of phase transformation-crystal quality-device performance in terms of solar cells and optoelectronics.

11:45 AM EN08.01.09
Mixed Dimensional 2D/3D Perovskite Solar Cells Using Double-Sided 2D Perovskite Passivation Md Arafat Mahmud, The Duong, Yiliang Wu, Jun Peng, Heping Shen, Kylie Catchpole, Klaus Weber and Thomas White; Australian National University (ANU), Australia

Conventionally, 3D perovskite materials are used for fabricating high-efficiency perovskite solar cells (PSCs), but they demonstrate poor device stability due to their high moisture sensitivity. Conversely, 2D Ruddlesden-Popper perovskite materials exhibit high moisture stability, but render lower device performance. Therefore, mixed dimensional 2D/3D PSCs have gained substantial research interest recently due to their high efficiency and ambient stability. Contemporary studies on mixed 2D/3D PSCs are based on either a thin 2D perovskite surface layer on top of 3D perovskite at perovskite/ hole transport layer (HTL) interface or 2D perovskite incorporated in the bulk of 3D perovskite. This work demonstrates that the application of 2D surface material with appropriate energy band alignment can be as effective for perovskite/ electron transport layer (ETL) interface, as reported for perovskite/HTL interface. Using such double-sided 2D surface passivation of n-butylammonium iodide (C₄H₁₂IN) sandwiching the bulk 3D quadruple cation Cs₀.₀₇Rb₀.₀₃FA₀.₇₆₅MA₀.₁₃₅Pb₁.₅₅Br₀.₄₅ [(CH₃NH₃ (MA), CH(NH₂)₂ (FA)] perovskite enabled over 22% stabilized power conversion efficiency (PCE) with mixed dimensional 2D/3D PSCs in n-i-p device configuration. Compared to the control 3D PSCs, mixed 2D/3D PSCs demonstrate an average open circuit voltage (VOC) enhancement of 20-40 mV and enhanced fill factor (FF) by 4% absolute value. The 2D surface layer contributes to the suppression of nonradiative recombination at perovskite/ETL and perovskite/HTL interfaces, which leads to enhanced photovoltaic performance with mixed 2D/3D PSCs. XRD spectral analysis also suggests reduced surface strain of perovskite film with 2D passivation layer that contributes to the superior device performance of 2D/3D device.

SESSION EN08.02: Perovskite Solar Cell—Interface and Transport Layers
Session Chairs: Pablo Docampo, Yabing Qi, Aron Walsh and Kai Zhu
Monday Afternoon, December 2, 2019
Sheraton, 2nd Floor, Back Bay AB

1:30 PM *EN08.02.01
Perovskite Stability—Challenges and Solutions Pablo Docampo; Newcastle University, United Kingdom

Hybrid halide perovskites combine top-notch optoelectronic properties with solution-deposition. This unprecedented combination has led to the development of solar cells that outperform established industry staples such as poly-Si. The road towards these achievements has been marked by a constant improvement of perovskite deposition techniques fuelled by our increasing understanding of the crystallization processes. However, stability still remains a key challenge. Here, I will focus on the effects of moisture-induced degradation on state-of-the-art perovskite materials and put forward several strategies to minimize the effect. I will show that the composition of the perovskite critically affects its stability while popular stabilization routes, such as introducing bulky hydrophobic cations - forming 2D/3D hybrid materials - in fact do not prevent moisture ingress into the structure. Our results show that the perovskite exhibits a surprisingly effective self-healing effect when combined with a thin 2D/3D hybrid perovskite bi-layer configuration. Furthermore, the effect can be minimized by the choice of hole transporter used where our developed amide-based hole transporting materials enhance both the performance and stability of the system.

2:00 PM *EN08.02.02
Interfacial Engineering of Carbon-Based Perovskite Solar Cells Tingli Ma¹,², Fanning Meng³ and Liguo Gao³;
Using carbon materials as the back electrode for perovskite solar cells (C-PSCs) has attracted significant attention due to their low cost and excellent stability. In general, the device structure of based C-PSCs has two types, one is hole transport layer (HTL) free and another one is with HTM. For these two cases, the carbon paste electrodes (CPEs) need directly collect the photo-generated holes or/and transport the holes. Therefore, interfacial engineering between the perovskite and CPE plays a crucial role in charge collection and affects the performance of C-PSCs. Our group have been carried out the interfacial engineering between carbon layer and perovskite layer using several methods to improve the performance of the C-PSCs. Herein, we will report our recent results, including development a simple process and an effective sandwich structure-based on coal carbon materials and 2D titanium carbide for improving the efficiency of PSCs. We also review the current progress in the studies on the carbon-based PSCs.

References:

Metal halide perovskite solar cells are now effectively competing with their inorganic counterparts in terms of power conversion efficiencies. However, state-of-the-art perovskite solar cells still suffer from limited fill factor (FF), open circuit voltage (V_{oc}) and long-term stability. Charge transport layers (CTLs) are key components of diffusion-controlled perovskite solar cells, however, we found that the CTL/perovskite interfaces induce additional non-radiative recombination pathways, which limit the V_{oc} of the cell. In order to harvest the full thermodynamic potential of the perovskite absorber, the interfaces of both the electron and hole transport layers (ETL/HTL) must be properly addressed and improved. Given the knowledge obtained from our previous studies, we developed a novel polymeric surface treatment based on poly(ionic-liquid) (PIL) materials. Notably, the application of this surface modification to a triple cation Cs$_5$(MA$_{0.17}$FA$_{0.83}$)$_9$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ perovskite in pin-type solar cell enables a concomitant improvement of the FF and the V_{oc}. The resulting solar cell devices show outstanding FF values of up to 83% and V_{oc} of 1.17V, which lead to extraordinarily high PCEs up to 21.5%. Through combined photoluminescence and cathodoluminescence studies we find that the PIL treatment helps to reduce the non-radiative recombination at the perovskite surface by acting as a defect passivating agent in the bare material. Additionally, we find that the recombination of charges across the perovskite/C_{60} interface is strongly reduced, increasing the V_{oc} in the actual device. Moreover, photoemission spectroscopy and conductive atomic force microscopy highlighted a specific charge redistribution at the perovskite surface upon PIL treatment, which conceivably leads to increased conductivity and charge extraction, consistently with the enhanced FF. Ultimately, the hydrophobic nature of the PIL provides a shielding coverage of the perovskite which helps to prevent degradation of the active material by moisture and air. The PIL modified devices show exceptionally long dark storage stability and enhanced lifetimes under maximum power point tracking (MPP). We show that by addressing and carefully modifying the perovskite surface/interface with this novel material, it is possible to efficiently suppress the non-radiative recombination of charges, promote the charge extraction and improve the stability at the same time. Additionally, given the simplicity of this post-treatment, our results can be representative of a more general methodology for device modification, therefore, potentially applicable to other compositions and cell architecture, including tandem solar cells. Finally, our results could open the doors to e new class of materials to be implemented in perovskite solar cells for future development.

State-of-the-art halide perovskite solar cells employ semiconductor oxides as electron transport materials. Defects in
these oxides, such as oxygen vacancies (O_{vac}), act as recombination centres and, in air and UV light, reduce the stability of the solar cell. Under the same conditions, the PbZrTiO$_3$ ferroelectric oxide employs O_{vac} for the creation of defect-dipoles responsible for photo-carrier separation and current transport, evading device degradation. Here, we report the application of PbZrTiO$_3$ as the electron extraction material in triple cation halide perovskite solar cells. The application of a bias voltage (poling) up to 2 V, under UV light, is a critical step to induce charge transport in the ferroelectric oxide. Champion cells result in power conversion efficiencies of $\sim$11% after poling. Stability analysis, carried out at 1-sun AM 1.5 G, including UV light in air for unencapsulated devices, shows negligible degradation for hours. These devices show also switching properties and thus, are also applied as solar transistors. Our results demonstrate, the application of ferroelectric/ferroelectric interfaces for efficient and stable PSCs and Solar transistors. These findings are also a step forward in the development of next generation ferroelectric oxide-based electronic and optoelectronic devices.


3:00 PM BREAK

3:30 PM *EN08.02.05
Stable Perovskite Solar Cells by Compositional and Interface Engineering Mohammad K. Nazeeruddin; Ecole Polytechnique Fédérale de Lausanne, Switzerland

Organic/inorganic lead halide perovskite solar cells (PSCs), reaching over 24% power conversion efficiency demonstrates that they are the most promising class of materials for next-generation thin film photovoltaics. The unprecedented increase in the device performance in less than ten years is because of improved processing protocols, and compositional engineering of cations, and anions of the perovskite material. Nevertheless, the remarkable power conversion efficiency (PCE) progression of perovskite solar cells, confronts with serious stability concerns, due to an intrinsic decomposition of the materials compromising their potentiality as a future market technology. In this talk, we discuss how to mitigate the stability of perovskite solar cells by compositional and interface engineering.

4:00 PM EN08.02.06
Inverted (p-i-n) Perovskite Solar Cells Prepared by Complex Assisted Gas Quenching on Hydrophobic Hole Transport Layers—Overcoming the De-Wetting Issues Kai O. Brinkmann$^1$, Junjie He$^{1,2}$, Felix Schubert$^1$, Jessica Malerczyk$^1$, Cedric Kreusel$^1$, Frederic van gen Hassend$^1$, Sebastian Weber$^1$, Jun Song$^2$, Junle Qu$^2$ and Thomas Riedl$^1$; $^1$Bergische Universitat Wuppertal, Germany; $^2$Shenzhen University, China

Lead halide perovskite solar cells are attractive because they can be processed from solution at low temperature. Nevertheless, the perovskite community adheres to relatively strict processing protocols to form high-performance perovskite layers with the frequently used “anti-solvent” procedure. Thus, to establish a perovskite process in a lab is closely linked with cumbersome fine-tuning, processing practice and ambient control (temperature, atmosphere). As a result, reproducibility issues from lab to lab are frequently encountered. Some of the issues associated with the anti-solvent approach can be overcome by the so called “complex assisted gas quenching” (CAGQ) technique, that replaces the anti solvent exposure by a nitrogen flow driven drying process. In any case, the perovskite precursor inks usually consist of highly polar solvents, which gives rise to de-wetting issues, especially if hydrophobic organic hole transporting layers, like poly triarylamine (PTAA), are considered. Here, we will show, that for the most frequently used solvent system of DMSO:DMF precursor de-wetting is of
particular importance as the wetting behavior deteriorates during the gradual formation of supersaturation. We unambiguously identify DMSO to be the main reason for de-wetting of the precursor solution and the consequent pinhole formation on hydrophobic hole transport layers. In striking contrast, we will show that n-methyl-2-pyrrolidon (NMP), which has a lower hydrophilic-lipophilic-balance, can be favorably used instead of DMSO to strongly mitigate these de-wetting issues. The resulting high-quality perovskite layers are extremely tolerant with respect to the mixing ratio (NMP:DMF), process handling and timing. Thus, our findings afford an outstandingly robust, easy to use and failsafe deposition technique yielding single (MAPbI3) and double (FA0.94Cs0.06PbI3) cation perovskites as well as mixed halide (FA0.6Cs0.4PbI2Br) perovskites for solar cells with high efficiencies without the need to adjust process parameters when switching between material systems. Most notably, the statistical variation of the devices with NMP:DMF solvent system is significantly reduced, even if the deposition process is performed by different persons with no significant lab experience whatsoever.[4]

We foresee, that our results will further the reliable preparation of perovskite thin films and mitigate process-to-process variations that still hinder the prospects of upscaling perovskite solar technology.


4:15 PM EN08.02.07
2D/3D Hybrid Perovskite Interfaces and Physics therein for Stable and Efficient Solar Cells Giulia Grancini1 and Valentin I. Queloz2,1; 1Università di Pavia, Italy; 2Ecole Polytechnique Fédérale de Lausanne, Switzerland

Solar energy can lead a “paradigm shift” in the energy sector with a new low-cost, efficient, and stable technology. Nowadays, three-dimensional (3D) methylammonium lead iodide perovskite solar cells are undoubtedly leading the photovoltaic scene with their power conversion efficiency (PCE) >23%, holding the promise to be the near future solution to harness solar energy [1]. Tuning the material composition, i.e. by cations and anions substitution, and functionalization of the device interfaces have been the successful routes for a real breakthrough in the device performances [2]. However, poor device stability and still lack of knowledge on device physics substantially hamper their take-off. Here, I will show a new concept by using a different class of perovskites, arranging into a two-dimensional (2D) structure, i.e. resembling natural quantum wells. 2D perovskites have demonstrated high stability, far above their 3D counterparts [3]. However, their narrow band gap limits their light-harvesting ability, compromising their photovoltaic action. Combining 2D and 3D into a new hybrid 2D/3D heterostructure will be here presented as a new way to boost device efficiency and stability, together. The 2D/3D composite self-assembles into an exceptional gradually organized interface with tunable structure and physics. To exploit new synergistic function, interface physics, which ultimately dictate the device performances, is explored, with a special focus on energy and charge transfer dynamics, as well as charge recombination and trapping processes happening over a time scale from fs to ms. As shown in Fig.1, when 2D perovskite is used on top of the 3D, charge transfer happens, while electron hole recombination at the perovskite/hole transporter interface is prevented. This results in improved device efficiency. In concomitance, the stable 2D perovskite is used as a sheath to physically protect the 3D underneath, with the aim to enhance the device stability. The joint effect leads to PCE=20% which is kept stable for 1000 h [3,4]. Incorporating the hybrid interfaces into working solar cells is here demonstrated as an interesting route to advance in the solar cell technology bringing a new fundamental understanding of the interface physics at multi-dimensional perovskite junction. The knowledge derived is essential for a deeper understanding of the material properties and for guiding a rational device design, even beyond photovoltaics.

4:30 PM EN08.02.08
Enhanced Nucleation of Atomic Layer Deposited Contacts Improves Operational Stability of Perovskite Solar Cells James A. Raiford1, Caleb C. Boyd1,2, Axel F. Palmstrom2, Eli J. Wolf1,2, Benjamin A. Fearon1, Joseph J. Berry3, Michael D. McGehee3 and Stacey F. Bent1; 1Stanford University, United States; 2National Renewable Energy Laboratory, United States; 3University of Colorado Boulder, United States

Various strategies have been explored to improve the long-term stability of metal halide perovskite solar cells, including the use of barrier and passivation layers and device encapsulation. Atomic layer deposition (ALD) has emerged as an effective tool for all of these applications, due to the precise control it affords over film thickness and
composition and the excellent barrier properties of the resultant films. In practice, ALD metal oxides are often grown on top of organic carrier transport layers in devices. For example, ALD SnO₂ grown on fullerenes is widely used for high-efficiency all-perovskite, perovskite-Si and perovskite-CIGS tandems.¹⁻³ The physical barrier and electronic properties of an ALD film grown on an organic substrate, such as a polymer, small molecule, or self-assembled monolayer largely depend on the structure of the organic material. To ensure the formation of an abrupt organic/oxide interface and avoid subsurface growth, a high density of functional sites (e.g. hydroxyls, amines) at the surface are desired to facilitate ligand-exchange reactions with the ALD metal-organic precursors.

In this work, we apply these insights to improve the nucleation, and consequently the barrier properties, of ALD metal oxides as selective contacts, with a focus on improving operational device stability. We demonstrate the application of a thin (~1 nm), nucleophilic polymer to promote the growth of ALD SnO₂ on C₆₀ as electron contacts in n-i-p devices. The nucleation-enhanced SnO₂ effectively protects against the degradation of Cs₀.₂₅FA₀.₇₅Pb(Br₀.₂₀I₀.₈₀)₃ films held at 200°C in air for up to 2 hours and upon direct exposure to water for at least 10 minutes. Ultimately, we show the integration of nucleation layers into single-junction, opaque devices with a champion power conversion efficiency (PCE) of 18.5%. On average, devices with nucleation-enhanced ALD SnO₂ and no further encapsulation maintain 82% of their initial PCE after 250 hours of continuous, illuminated operation at maximum power in air at 60°C, demonstrating a 150% improvement in stability at these harsh conditions over devices with ALD SnO₂ grown directly on C₆₀. These results highlight the impact that a high-quality contact/barrier layer can have on protecting the perovskite from various degradation pathways, such as moisture or oxygen ingress, halide egress, or metal-halide reactions. This study also presents a framework upon which to further improve the quality of barrier/encapsulation layers for various configurations and architectures of perovskite optoelectronic devices.


SESSION EN08.03: Poster Session I: Perovskite Solar Cell—Interface and Transport Layers
Session Chair: Shengzhong (Frank) Liu
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

**EN08.03.01**
A Novel NDI-Based Polymer Adopted as the Electron Transport Layer in Inverted Planar Flexible Perovskite Solar Cell

Hyuntae Choi, Jihyun Min, Dohyun Kim and Taiho Park; POSTECH, Korea (the Republic of)

A novel naphthalene diimide (NDI)–based polymer (P(NDI₂DT–TTCN)) which has strong electron withdrawing dicyanothiophene group is employed as the electron transport layer (ETL) in place of the conventional fullerene-based ETL in inverted–structure perovskite solar cells (Pero–SCs). A variety of characterization techniques are used to observe and analyze the interface between perovskite and P(NDI₂DT–TTCN) or [6,6]–phenyl–C₆₁–butyric acid methyl ester (PCBM). It is confirmed that P(NDI₂DT–TTCN) helps not only to facilitate the electron extraction but also to prevent ambient atmosphere interference by forming a hydrophobic ETL surface. Furthermore, P(NDI₂DT–TTCN) shows excellent mechanical stability in flexible Pero–SCs. With these improved properties, the device performance based on P(NDI₂DT–TTCN) is superior to that of based on PCBM from 14.3% to 17% with negligible hysteresis.

**EN08.03.02**
A Superficial New Solid-State Synthesis of SnO₂ for High-Performance and Stable Perovskite Solar Cells

Mriganka Singh¹,²,³, Hong-Cheu Lin¹, Chih Wei Chu² and Gang Li³; ¹National Chiao Tung University, Taiwan;
Metal oxide carrier transporting layers have been investigated widely in organic/inorganic lead halide perovskite solar cells (PSCs). Tin oxide (SnO$_2$) is a promising alternative to the titanium dioxide commonly used in the electron transporting layer (ETL), due to its tunable carrier concentration, high electron mobility, amenability to low-temperature annealing processing, and large energy bandgap. In this study, a facile method was developed for the preparation of a room-temperature-processed SnO$_2$ electron transporting material that provided a high-quality ETL, leading to PSCs displaying high power conversion efficiency (PCE) and stability. A novel physical ball milling method was first employed to prepare chemically pure ground SnO$_2$ nanoparticles (G-SnO$_2$), and a sol–gel process was used to prepare a compact SnO$_2$ (C-SnO$_2$) layer. The effects of various types of ETLs (C-SnO$_2$, G-SnO$_2$, composite G-SnO$_2$/C-SnO$_2$) on the performance of the PSCs are investigated. The composite SnO$_2$ nanostructure formed a robust ETL having efficient carrier transport properties; accordingly, carrier recombination between the ETL and mixed perovskite was inhibited. PSCs incorporating C-SnO$_2$, G-SnO$_2$, and G-SnO$_2$/C-SnO$_2$ as ETLs provided PCEs of 16.46, 17.92, and 21.09%, respectively. In addition to their high efficiency, the devices featuring the composite SnO$_2$ (G-SnO$_2$/C-SnO$_2$) nanostructures possessed excellent long-term stability—they maintained 89% (with encapsulation) and 83% (without encapsulation) of their initial PCEs after 105 days (>2500 h) and 60 days (>1400 h), respectively, when stored under dry ambient air (20 ± 5 RH %).

EN08.03.03
BaSnO$_3$ Electron Transport Layer as an Alternative to TiO$_2$ for Efficient and Stable Perovskite Solar Cells
Chung Jaehoon, Seong Sik Shin and Jangwon Seo; Korea research institute of chemical technology, Korea (the Republic of)

For commercializing perovskite solar cells (PSCs), moisture-tolerant materials are required for each component of PSCs, such as electron transport layer (ETL), perovskite layer, and hole transport layers (HTL), because low relative humidity (RH) under 10–20% cannot be controlled in actual production line. Most of conversional PSCs with a high power conversion efficiency (PCE) over 20% have widely implemented Li doped mesoporous titanium oxide (mp-TiO$_2$:Li) as an n-type semiconductor for ETL. This Li treatment could facilitate an electron extraction of ETL, but could affect the device stability during the fabrication of PSCs under humid atmospheric environment due to its hydroscopic nature.

In this work, we employ mesoporous BaSnO$_3$ (mp-BSO), which is moisture tolerant ETL, and fabricate stable PSCs without sacrificing the performance. The mp-BSO based PSCs show certified PCE of 21.3% and steady-state PCE of 21.4%, which is comparable to that of mp-TiO$_2$:Li based PSCs. However, with respect to the storage stability, each device exhibits different behavior according to the humidity in air. Both devices are stable at RH-10% atmosphere. At high humid environment (RH 40%), mp-TiO$_2$:Li based device shows severe degradation even after 24 hours, whereas mp-BSO based device shows good stability similar to the result at RH 10%. This is mainly attributed to the formation of Li$_2$O on TiO$_2$ surface analysis of mp-TiO$_2$:Li (i.e. IR, XPS, and TEM). For resultant device with mp-TiO$_2$:Li as ETL, electron transfer/transport could be impeded at the interface between ETL and perovskite layer at a high humid condition. On the other hand, the device with mp-BSO exhibits a superior moisture stability. It is also supported by transient photocurrent/photovoltage and time resolved photoluminescence studies. Along with outstanding performance, mp-BSO based PSCs show excellent storage and light stability during 500 hours. We believe that this strategy of introducing mp-BSO ETL into PSCs will accelerate the commercialization of PSCs.

EN08.03.04
Complimentary Heterogenous Electron Transporting Layers to Fabricate Highly Consistent, Stable and Efficient Planar Perovskite Solar Cells
Shini Foo, Thambidurai Mariyappan, P. C. Harikesh, Nripan Mathews, Yi Zhong Huang and Cuong Dang; Nanyang Technological University, Singapore

Unlike the mesoporous configuration in which efficient charge extraction is derived from its high contact area, planar perovskite device places heavier dependence on the intrinsic characteristics of the electron transporting layer (ETL) to effectively transport photoexcited electrons from the organometal-halide absorber layer to the anode. Furthermore, the planar configuration generally demonstrates poorer power conversion efficient (PCE), device stability, and reproducibility. In this work, we present the systematic study of heterogeneous ETLs comprising of solution-processed optimized AlIn-TiO$_2$ (AITO) and SnO$_2$ as a highly effective approach to overcome these
shortcomings. By depositing a thin SnO₂ interlayer between the AITO/perovskite interface, significant improvement in recombination resistance and PCE was observed. As a result, the heterogeneous AITO/SnO₂ ETL based device exhibited nonpareil PCE of 18.9% and notable long-term stability through which 93% of its initial PCE was retained after 25 days in the absence of encapsulation. On the other hand, remarkable device stability was obtained from the consistent AITO ETL in which interquartile range (IQR) of the efficiency boxplot revealed 2.8 times reduction in the heterogeneous ETL based devices compared to the homogeneous SnO₂ ETL based devices. In essence, our results suggest the use of favourable ETLs as a straightforward yet powerful method to cover the weaknesses of individual ETLs while providing synergistic enhancements in device stability, reproducibility, and various photovoltaic parameters in planar perovskite solar cells.

EN08.03.05
Digital Alloy Contact Layers of ZnO and MgZnO for Perovskite Solar Cells Ekrai Dahal¹, Bin Du¹, Ben Isenhart¹, Olivia Sergiovanni¹, Sean Dunfield², Joseph J. Berry³ and Matthew S. White¹; ¹The University of Vermont, United States; ²University of Colorado Boulder, United States; ³National Renewable Energy Laboratory, United States

Perovskite solar cells are considered the photovoltaics technology of the future due to their low manufacturing costs and potential for high performance. Perovskite solar cells often use oxides to perform multiple functions; oxides such as TiO₂, SnO₂, and ZnO are used as electron transport layers (ETL) and NiO, WO₃ as hole transport layers (HTL). The ETL material must simultaneously have optimal conduction band alignment, facilitate carrier extraction, prevent recombination, and provide a chemically stable interface with the volatile perovskite semiconductor. The multiple requirements placed on this one layer dictate different material properties at different positions within the film, specifically bulk and interfacial properties. Given that the layer thickness ranges from 10 nm to 200 nm, the requirements demand positional control of the material composition at the nano-scale. By using the pulsed laser deposition (PLD) technique to control the chemical composition at nanometer scale to form material alloys of ZnO and MgZnO as ETL for the perovskite solar cell device, we demonstrate that digital alloy gradients can be tuned to significantly outperform either of the parent materials in perovskite solar cells.

EN08.03.06
Effect of Conduction Band Offset between SnO₂-Based ETL and Perovskite Absorber on Device Performance Ji Won Lee¹, Jin Hyuck Heo²,³, Seong Yeon Kim¹,³, Fei Zhang¹, Ji-Sang Park¹, Sang Hyuk Im², Kai Zhu¹, Joseph J. Berry³ and Jun Ho Kim¹,³; ¹Incheon National University, Korea (the Republic of); ²Korea University, Korea (the Republic of); ³National Renewable Energy Laboratory, United States; ⁴Imperial College London, United Kingdom

SnO₂-based oxide is very promising electron transport layer (ETL) for high efficient and stable perovskite solar cell. However, electron affinity of SnO₂ is rather low, considering the optimal conduction band offset (CBO) between ETL and absorber layer. We studied device simulation to get optimal CBO by tuning the electron affinity of SnO₂-based ETL and perovskite absorber. SCAPS simulation showed that power conversion efficiency (PCE) is increased from cliff-type CBO to spike-type CBO, and decreased with larger spike-type CBO. With the obtained simulation result, we fabricated SnO₂ and doped-SnO₂ ETLs with up-shifted conduction band edge and compared performance of fabricated device with simulation result. This research indicates that CBO should be optimized for higher efficiency SnO₂-based perovskite solar cell.

EN08.03.07
Effect of p-Type Doping to Dithiophene-Benzene Copolymer as Hole Transporting Layers in Perovskite Solar Cells Yoshihiko Nishihara¹,², Nobuko Onozawa-Komatsuzaki¹, Hiroaki Tachibana¹, Masayuki Chikamatsu¹ and Yuji Yoshida¹,²; ¹National Institute of Advanced Industrial Science and Technology, Japan; ²University of Tsukuba, Japan

We have investigated perovskite solar cells (PSCs) employing novel polymer semiconductor as hole transporting material (HTM). Dithiophene-benzene (DTB) copolymer-based PSCs have been reported higher short circuit current density than other polymer-based PSCs. In addition, it was expected that DTB was low cost and high stability compared to typical HTM of Spiro-OMeTAD. However, the influence of oxygen and dopant on DTB have not been examined in detail yet. In this research, we fabricated mesoporous-type PSCs employing DTB copolymer as HTM without and with dopant
under nitrogen atmosphere and measured the device performance in air. We used a lewis acid tris(pentafluorophenyl)boran (BCF) as a dopant. In case of the device without dopant, initial power conversion efficiency (PCE) showed 2.98% after exposure to air for 5 hours. However, the device performance gradually improved by keeping in dry air. After keeping in dry air for 1 week, PCE greatly improved to 16.15%. These results indicate that increase of carrier density in DTB occurred due to oxygen-doping. In case of the device with BCF dopant, initial PCE showed 13-14% after exposure to air for 5 hours. The PCE improved to 15-16% by keeping in dry air. The cause of this improvement of the initial device performance was due to increase of carrier density in DTB by BCF dopant.

EN08.03.08
Enhanced Transport and Carrier Selectivity at Perovskite Interfaces Enabled by Ordered Perylene Monolayers
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Tandem-junction perovskite/silicon devices present the potential for highly efficient solar energy conversion devices. We investigate low-temperature organic monolayer functionalization of silicon substrates to chemically and electrically tether perovskite thin-films while maintaining carrier selectivity and a soft, flexible interface. We have covalently grafted vertically oriented perylene diimide overlayers on oxide-free Si (111) through and imide linkage to a surface-bound aniline. Secondary functionalization of the terminal anhydride with phenylenediamine yields A-type cation moieties that serve as a chemical hook for perovskite deposition. UPS characterized the band-energy levels of functionalized surfaces aligned to facilitate electron transport from MAPbI3 to the silicon substrate. Transfection Infrared Spectroscopy and X-ray photoelectron spectroscopy revealed a high coverage of vertically oriented perylene diimides. Liquid-junction photoelectrochemical experiments of MAPbI3/perylene diimide terminated, oxide-free silicon interfaces yield improved energy conversion relative to long-chain alkyl terminated silicon surfaces. We ascribe these improvements to enhanced carrier selective transport and reduced recombination. This work presents a bench-top functionalization of soft, robust, electron transport layers to further integrate low-cost perovskites with mature silicon PV.

EN08.03.09
Enhancing Electron Transport via Graphene Quantum Dot-Tin Oxide Composites for Efficient and Durable Flexible Perovskite Photovoltaics
Yu Zhou and Hong Lin; Tsinghua University, China

Recent advances in flexible perovskite solar cells (PSCs) have attracted considerable attention owing to their great potential for bendable and wearable electronic devices. Particularly, developing high-quality low-temperature processed electron transport layers (ETLs) plays a pivotal role in realizing highly efficient flexible PSCs. Herein, we develop a facile strategy to fabricate graphene quantum dot/SnO2 composites (GQD@SnO2) as effective ETLs for PSCs. Through systematically optimizing GQDs' size and concentration, higher film conductivity, better film coverage uniformity, and raised fermi energy level matching with perovskite were reached, which is remarkably beneficial to facilitate electron transfer and suppress interfacial charge recombination, resulting in great enhancement of photovoltaic performance. As a result, PSCs based on SnO2 blending with GQD of ca. 5 nm in diameter (G5@SnO2) exhibit superior photovoltaic performance with a champion power conversion efficiency (PCE) of 19.6% and an average PCE of 19.0%. Significantly, flexible PSCs based on G5@SnO2 obtain a best PCE and stabilized PCE of 17.7% and 17.2%, respectively. Moreover, these flexible devices demonstrate outstanding durability, retaining 91% of their original PCE after 500 bending cycles at a radius of 7 mm. This work provides a facile route to develop effective ETLs for high-performance flexible PSCs and paves the way for further advances in flexible photovoltaic devices and optoelectronic applications.

EN08.03.10
Fabrication and Properties of Inverted Perovskite Solar Cells with Surface-Treated Hole Transport Layer
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Organic–inorganic hybrid perovskite solar cells have attracted great attentions in recent years, because they can be fabricated by solution processes and the power conversion efficiency (PCE) has been drastically improved up to more than 24%. In a normal type perovskite solar cells having mesoporous structure, a metal oxide layer such as titanium oxide is used. However, it is not suitable for the application to flexible solar cells because it requires high temperature treatment for film formation. Therefore, studies on the inverted type perovskite solar cells which can be
formed a thin film at low temperature have attracted attention. Poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS) widely used for the hole transport layer, is considered to have a negative influence on the solar cell characteristics due to strong acidity, hygroscopicity, etc. Therefore, the development of chemically inert hole transport layers is one of the important challenges.1)2) Interface engineering of heterojunction interfaces which reducing the surface recombination is also a crucial strategy to improve the performance of the perovskite solar cells. In this study, inverted perovskite solar cells using metal oxide as the hole transport layer are prepared, and the effect of various acid treatments on the surface of the metal oxide layer such as NiOx, WO3, MoO3 and V2O5 on its local structure, charge transport characteristics and photovoltaic characteristics were investigated systematically. It was found that the perovskite layer prepared on the acid-treated metal oxide film exhibits higher PL quenching ratio than that on the non-acid-treated metal oxide film. In this presentation, we will report the detailed experimental results on the effect of acid treatment to metal oxide film on solar cell characteristics under various conditions.

EN08.03.11
Fully Metal Oxide Charge Selective Layers for n-i-p Structure Perovskite Solar Cells Employing Nickel Oxide Nanoparticles Kerem C. Icli1 and Ahmet Macit Ozenbas2; 1Middle East Technical Univ, Turkey; 2Middle East Technical University, Turkey

An alcohol based nickel oxide nanoparticle dispersion was prepared and used to deposit hole conductor medium for a polymeric substance free perovskite solar cell in mesoscopic n-i-p configuration. In contrast to conventional p-i-n configuration or inverted type perovskite solar cells, nickel oxide layer was spin coated directly on perovskite layer and the perovskite layer was sandwiched between two metal oxides, TiO2 and NiO, resulting in n-i-p configuration. High surface area nickel oxide nanoparticles were synthesized by precipitation and successfully dispersed in isopropanol with the aid of ball milling, which was confirmed to breakdown the aggregates and stabilize the dispersion without the assistance of a stabilizing agent. This strategy leads to deposition of nickel oxide nanoparticles on perovskite layer without damaging the underneath perovskite layer and inhibiting the charge transfer between individual nanoparticles, confirmed by scanning electron microscopy, photoluminescence quenching and J-V measurements. Ultraviolet photoelectron spectroscopy analysis showed excellent matching of the band alignment of nickel oxide layers with that of perovskite. An efficiency of 10.89% was achieved after optimizing the nickel oxide layer thickness and comparing with a hole conductor free device using J-V measurements and electrochemical impedance spectroscopy revealed that nickel oxide layer possesses excellent electron blocking ability and reduces the recombination rate, which also in turn stabilizes the power output and hysteresis of the cells. This strategy is believed to be applicable for other metal oxides employed in charge selective layers of perovskite and organic solar cells.

EN08.03.12
High Performance Inverted Perovskite Solar Cells by Reducing Electron Capture Region for Electron Transport Layers Shengnan Zuo; Shaanxi Normal University, China

The power conversion efficiency (PCE) of inverted perovskite solar cells (i-PSCs) is lower than the normal structures. The low efficiency is mainly ascribed to the inferior properties of commonly-used [6,6]-phenyl C61 butyric acid methyl ester (PCBM) electron transport layers (ETLs) such as complexity in achieving high quality films, low electron mobility, imperfect energy level for electron extraction, and large electron capture region. Herein, we develop the bulk heterojunction (BHJ) ETLs, which compose of PCBM and conjugated polymer materials. The electron mobility of BHJ film is enhanced by more than 3 times compared to pristine PCBM, and its Fermi level is close to the conduction band of perovskite. The high electron mobility and suitable energy level result in efficient electron extraction. Further, the electron capture region of BHJ film significantly decreases to 1.20 × 10^-18 cm^3 from 3.70 × 10^-17 cm^3 for pristine PCBM due to increased relative permittivity (enhanced to 5.32 from 3.66 for PCBM), leading to reduced trap-assistant recombination at perovskite/ETL interface. As a result, the PCE of i-PSCs is up to 18.84%, increased by about 15% compared to pristine PCBM. Under ambient air after 30 days, the PCE of unsealed devices based on BHJ ETLs keeps about 85% of the initial efficiency, while the devices with PCBM retain only about 49% of the initial value under the same aging conditions. Meanwhile, the unsealed devices with BHJ ETLs show about 83% of the initial efficiency under continuous illumination for 60 hours, while the devices based on pristine PCBM give about 63% of the initial value. The excellent stability is attributed to the more hydrophobic BHJ films and full coverage of perovskite surface, which effectively prevent the moisture permeation.
High Performance Perovskite Solar Cells by Using Low-Temperature-Processed Brookite-Based TiO2 Heterophase Junction

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In the design of electron transport layers (ETLs) to enhance the performance of perovskite solar cells (PSCs), efficient electron extraction and transport are important aspects. Herein, we examine the effect of different titanium oxide (TiO2) polymorphs such as anatase and brookite in the resultant PSCs performance. In this work, pure-phase, high-stable, high conductive, and single-crystalline brookite TiO2 nanoparticles (NPs) with an average diameter of approximately 30 nm ~ 50 nm were synthesized by a facile, nontoxic, environmentally friendly hydrothermal method by using a water-soluble titanium complex as the titanium source that helps for green and scalable fabrication of the PSCs. We design and fabricate, single-crystalline and high-phase-purity brookite-based TiO2 heterophase junctions on fluorine-doped tin oxide (FTO) as the substrate. We attempt to investigate and compare single phase anatase (A) and brookite (B) and heterophase anatase–brookite (AB) and brookite–anatase (BA) as ETLs in PSCs. The PCE of PSCs with single crystalline FTO-B only layer as the ETL was as high as 14.92% that is the highest reported efficiency of FTO-B-based single-layer PSC (Nano Lett., 2019, 19, 598). This result suggests that FTO-B acts as an active phase, which can be a potential candidate as an ETL scaffold in planar PSCs. Hetero junction FTO-AB ETLs based PSCs showed PCEs as high as 16.82%, which is higher to those of PSCs with single-phase anatase (FTO-A) and brookite (FTO-B) as the ETLs (13.86% and 14.92%, respectively). The large surface area of brookite TiO2 NPs facilitates more electron injection and subsequent transport, which can balance the electron current density and hole current density in the resultant PSCs and, therefore, can promote high performance. This facile synthesis and employing of brookite TiO2 NPs provide a clean and eco-friendly fabrication of PSCs with respect to an alternative approach to anatase TiO2 phase as the ETL bilayer.

High Power Conversion Efficiency of Perovskite Solar Cells Based on Low-Temperature Zn-Doped TiO2 Electron Extraction Layer

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Perovskite solar cells (PSCs) has remarkably increased its power conversion efficiency (PCE) to 23.7% due to its high open-circuit voltage (VOC) and photocurrent. To make it commercialized, the modification of electron extraction layer (EEL) for improving the photovoltaic performance became another important issue. For the EEL, TiO2-based material is widely applied for the next-generation solar cells because of its non-toxicity, chemical stability, inexpensiveness, and high charge transportability. Doping Zn into TiO2 could accelerate the photo-induced electron-hole separation and could tune the bandgap of TiO2-based material. To further enhance the photovoltaic performance of PSC, we systematically study the effect of different Zn-doped TiO2 (Zn:TiO2) EEL on PSCs, including (1) planar Zn:TiO2 EEL, (2) mesoscopic Zn:TiO2 EEL, and (3) low-temperature Zn:TiO2 EEL. For the planar Zn:TiO2 EEL, it demonstrates serious hysteresis and it is unstable in the atmosphere. Although the mesoscopic Zn:TiO2 EEL based PSCs shows higher PCE than planer Zn:TiO2 EEL, the high-temperature calcination leads to cost increment and energy consumption and hinders the commercial potential. Therefore, the low-temperature process to prepare the nanostructure TiO2 layer has been regarded as a breakthrough. By optimizing the parameters of PSCs and the energy band alignment between perovskite absorber layer and 3 types of Zn:TiO2 EEL, the average PCE for PSCs based on (1) planarZn:TiO2 EEL is ~14.0%, (2) mesoscopic Zn:TiO2 EEL is ~16.8%, and (3) low-temperature Zn:TiO2 EEL reached as high as 20.4%.

High-Efficiency Flexible Solar Cells Based on a Low-Temperature UVO-Treated SnO2

Xuediao Cai, Yefang Jiang, Zhike Liu and Shengzhong (Frank) Liu; Shaanxi Normal University, China

The new perovskite material has wide application prospects in the field of photovoltaics, because of its excellent photoelectric properties such as bipolar transmission characteristics, large extinction coefficient, long carrier diffusion length, high carrier mobility, and low trap-state. However, there are still some problems that need to be
solved in the commercial application. For example: How to improve the power conversion efficiency? How to improve device stability? How to find alternative materials for Pb? How to prepare large area and flexible devices? In this work, we propose a low temperature thermal annealing and UV-ozone (UVO) assisted treatment of SnO₂ electron transport layer for rigid and flexible perovskite solar cells. It has been found that using UVO-assisted annealing treatment of SnO₂ is more conducive to form tin oxide network structure than only after thermal annealing. After UVO-assisted annealing treatment, the perovskite precursor solution can be easily spread on the surface of the SnO₂ film, the perovskite crystal has better crystallinity and larger grain size, and the perovskite film is more uniform. Furthermore, the performance of the PSC is improved, through which more sunlight could be absorbed and recombination could be efficiently reduced. A highly efficient rigid PSC with a PCE of 19.7% is obtained based on low temperature and UVO-treated SnO₂ ETLs. Based on lower temperature and UVO-treated SnO₂ ETL, flexible perovskite solar cell exhibited a high PCE of 18.88%. It is worth noting that 18.88% is higher than currently reported device efficiency, which at the world's leading level.

EN08.03.16
High-Performance and Stable Semi-Transparent Perovskite Solar Cells with Cross-Linked Hole Transport Layer
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Organic–inorganic hybrid perovskites have emerged as an attractive candidate for semi-transparent solar cells (ST-SCs) due to their superior optoelectronic properties and transparency. In general, the appropriate selection of charge transport layers is considered to be the most crucial factors to both the efficient and the stability of perovskite solar cells (PeSCs). Spiro-OMeTAD with Li-TFSI and TBP dopants has been widely used as the hole transport layer in conventional opaque and ST solar cells because it has suitable energy level matching and good hole extraction ability. However, the hygroscopic nature of these dopants tends to reduce device stability because it can cause both phase segregation after moisture absorption and corrosion of the perovskite film, thereby limiting the applicability in commercial application.

Here, we demonstrated highly efficient and stable semi-transparent PeSCs (ST-PeSCs) introduced the cross-linked polymer (i.e. VNPB) as hole transport layer and dielectric-metal-dielectric (DMD, MoO₃/ultra-thin gold/MoO₃) as transparent electrode. We also explored post annealing as a facile approach towards optimizing the doping levels at our VNPB/MoO₃ interface. Experimental and analytical investigations revealed that a post annealing treatment of the VNPB-based ST-PeSCs remarkably increased charge extraction and reduced recombination of charge carriers. After optimization of post annealing treatment, we achieved a significantly improved power conversion efficiency of 16.7% with 10% average visible transmittance (AVT) compared to the device without post annealing treatment (10.9%). Moreover, the VNPB-based ST-PeSCs showed high long-term stability, maintaining 80% of the initial PCE after 360 h under continuous illumination and 50% of the initial PCE after 30 day under humid air conditions, whereas Spiro-OMeTAD-based ST-PeSCs showed a significant reduction in PCE. We emphasize that our approach can provide a new pathway to hole transport layer for hugely enhancing the efficiency and stability of ST-PeSCs.

EN08.03.17
High-Performance Perovskite Solar Cells Employing Solution-Processed Double-Walled Carbon Nanotubes
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Organometallic halide perovskite solar cell (PSC) is the next generation thin film photovoltaic that harvests infinite solar energy. The strength of PSC lies in its potential price competitiveness from solution process availability and its ability to be made thin and be flexible due to high absorption coefficient of organometallic halide perovskite. However, use of brittle, indium-embedded, high-cost transparent conducting oxide (TCO) limits the commercialization of PSCs and their application to flexible devices.

Carbon nanotube (CNT) has received a lot of spotlight as a transparent electrode for electronic devices on grounds of its high conductivity, good transmittance, and abundance of elements. Single-walled carbon nanotube (SWNT) has been a subject of much research because of its low light density. However, its poor solubility restricts SWNT from cost-effective, large area available solution processes, preventing the commercialization of SWNT. Double-walled carbon nanotube (DWNT) is structurally midway between SWNT and multi-walled carbon nanotube (MWNT), with high transparency of SWNT and excellent dispersibility of MWNT. Taking advantage of these
features, we demonstrate solution processed DWNT electrodes and apply them to the PSCs. We treat nitric acid and trifluoromethanesulfonic acid (TFMS) on DWNT for optimization of sheet resistance and duration of doping effect. We systematically study the effect of the two dopants on the outer- and inner-wall through Raman spectroscopy and near-infrared (NIR) spectroscopy, and the results are consistent with the trend obtained from DFT calculation. We analyze PSCs based on DWNT with photoluminescence (PL) and dark current density-voltage (Dark J-V) measurements. Maximum power point tracking (MPPT) shows that optimized device exhibits stabilized power conversion efficiency (PCE) of 17.2% under 1 sun illumination.

EN08.03.18
Interfacial Engineering for Stability of Perovskite Solar Cell Molang Cai, Songyuan Dai and Yong Ding; North China Electric Power University (NCEPU), China

Perovskite solar cells (PSCs) are the most promising low-cost photovoltaic technology, whose power conversion efficiency has increased rapidly in a few years. In approaching the Shockley limit on a single-junction solar cell, one of the major challenges lies in interface properties of working devices. The energy alignment, charge transport and collection as well as electrical potential distribution are critical to device performances. We start with the electronic properties of perovskite layer to investigate the effect of dopant on heterojunction property, electron recombination as well as charge collection. Kelvin probe force microscopy, were employed to gain a mechanistic understanding of charge transportation in different structure of perovskite solar cells. We further use the C60/TiO2 bilayer to restrain the trap states at interfaces for achieving 83% of its initial performance after 312 h UV irradiation.

EN08.03.19
Interfacial Engineering of the Electron Transporting Layers by Self-Assembled Monolayers for High Performance and Long-Term Stable Perovskite Solar Cells Jinyoung Han1, Haejung Son2 and Dong Ha Kim1; 1Ewha Womans University, Korea (the Republic of); 2Korea Institute of Science and Technology, Korea (the Republic of)

Developing perovskite solar cells (PSCs) with a high performance and a low-temperature process has great potential for the scalable, economic renewable photovoltaic devices. Among critical elements, ZnO has many advantages as electron transporting layer (ETL) in PSCs, due to promising features including a suitable energy structure and a high electron mobility, which can potentially reduce the recombination loss as ETL. Also, ZnO can be easily solution-processed at low temperature. Despite these advantages, several obstacles must be resolved to utilize ZnO for viable perovskite-based devices; one of them is the thermal instability of CH3NH3PbI3 photoactive layer deposited on ZnO ETL. The basic nature of the ZnO surface can induce the proton transfer reaction taking place between ZnO and CH3NH3PbI3 layer, which can reduce the device performance.

In this work, we demonstrated modification of the ETL by self-assembled monolayers (SAMs) to suppress the decomposition of perovskite for low-temperature processed and high performance PSC. The SAM layer was deposited on ZnO ETLs by dip coating for several hours to induce the condensation reaction between the hydroxyl group of ZnO ETL and the carboxylic acid group of the SAM layer. It was found that utilization of SAMs, especially 4-methoxybenzoic acid (MBA), 3, 4-dimethoxybenzoic acid (DMBA) and 3, 4, 5-trimethoxybenzoic acid (TMBA) on ZnO ETL prevents the direct contact between the perovskite and ETLs, avoiding the proton transfer reaction between perovskite and ZnO ETL. Also, strong dipole effect induced by a methoxy functional group of SAM interlayer can enhance the LOMO energy level and the work function of ZnO ETL, resulting in a reduction of electron transport barrier at the ZnO/CH3NH3PbI3 interface and enhancing the built-in voltage of the device. We verified the decrease in the energy gap between LOMO level of ZnO ETL and that of perovskite by photoluminescence quenching. PL intensity of ZnO/CH3NH3PbI3 was quenched after applying SAM interlayer, proving that charge transfer at ZnO/CH3NH3PbI3 interfaces was significantly facilitated via insertion of SAM interlayer. The effect was maximized when the ZnO was modified with TMBA which has the highest dipole moment among the SAM materials employed. Also, microscopic studies revealed that the perovskite active layer on TMBA modified ZnO ETLs showed optimized morphology. The power conversion efficiency (PCE) of the device was enhanced from 0.86 to 12.65% after optimizing a SAM interlayer, which was mainly ascribed for the highly increased short circuit current (JSC).
Investigation of CuSCN Hole Transport Layer for High Reliability Perovskite Solar Cells JungYup Yang1, NamHee Kwon1, MiJoung Kim1, JungSeock Oh1, MoonHoe Kim1, Daseul Hyun2 and Jinpyo Hong2; 1Kunsan National University, Korea (the Republic of); 2Hanyang University, Korea (the Republic of)

Recent advances in photovoltaic research have proved the great potential of copper(I) thiocyanate (CuSCN) as a hole transport layer (HTL) for organic inorganic hybrid perovskite solar cells. Here, we have investigated CuSCN as HTL instead of conventional 2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamini)-9,9'-spirobifluorene (Spiro-OMeTAD) and systematically observed the relationships with methyl ammonium lead iodide (MAPbI3) perovskite absorber layer. The CuSCN was completely dissolved in diethyl sulfide solvent and then deposited by spin coating method on the MAPbI3 absorber layer. For the creation of compact CuSCN layer the post-annealing process was performed with various temperatures and times using hot plate. However, we observed the undesirable decomposition from MAPbI3 to PbI2 because post-annealing process performs feature long time annealing steps at elevated temperature. To solve this problem we were investigated by the increasing of methyl-ammonium iodide (MAI) ratio in MAPbI3 precursor solution. The device and material properties were analyzed by current-voltage curve, quantum efficiency, scanning electron microscopy, UV-visible spectroscopy, and x-ray diffraction for finding the optimum condition of MAPbI3 solar cells with CuSCN HTL. When excess MAI ratio is present in MAPbI3 precursor solution, it can be compensates for the loss of any MAI and suppresses or delays the formation of a PbI2 phase during annealing.

EN08.03.21
Long-Term Thermal and Operational Condition Stable Perovskite Solar Cells with Inorganic Charge Transport Layers Grown via Atomic Layer Deposition Seongrok Seo, Seonghwa Jeong, Changdeuck Bae and Hyunjung Shin; Sungkyunkwan University, Korea (the Republic of)

Despite the high power conversion efficiency (PCE) of perovskite solar cells (PSCs), poor long-term stability is one of the main obstacles preventing their commercialisation. Several approaches to enhance the stability of PSCs have been proposed. However the accelerating stability test of PSCs at high temperature under the operating conditions in ambient air remains still to be demonstrated. Herein, we show interface engineered stable PSCs with inorganic charge transport layers (p-NiO and n-Al:ZnO grown via atomic layer deposition). First of all, NiO has been chosen as hole transporting layers due to its a wide band gap (~3.6 eV) and p-type semiconducting properties. It also has good optical transparency and high chemical stability, and thus has the capability aligning the band edges to the perovskite (CH3NH3PbI3) layers with efficient energy transfer. Ultra-thin and un-doped NiO films with much less absorption loss were prepared by atomic layer deposition with highly precise control over thickness without any pinholes. Thin enough (5–7.5 nm in thickness) NiO films with the thickness of few time the Debye length (L_D = 1–2 nm for NiO) show enough conductivities achieved by overlapping space charge regions. Second, the highly conductive Al doped ZnO films have been chosen as an efficient electron transporting layers while acting as dense passivation layers. This layer prevents underneath perovskite from moisture contact, evaporation of component, and reaction with a metal electrode. Finally the inverted-type PSCs with inorganic charge transport layers exhibited a PCE of 18.45 % and retained 86.7 % of the initial efficiency for 500 hours under continuous 1-sun illumination at 85 °C in ambient air with electrical biases (at maximum power point tracking).

EN08.03.22
Manganese Doped Solution Processed Nickel Oxide Hole Transport Layer for Perovskite Solar Cell Merve D. Oflaz, Hava Z. Kaya, Wiria Soltanpoor, Cem Sahiner, Gorkem Gunbas and Seleuk Yerci; Middle East Technical University, Turkey

The electrical and optical properties of the transport layers play an important role in achieving efficient and hysteresis-free perovskite solar cells. Nickel oxide (NiOx) with its wide band gap and suitable valance energy band alignment with perovskite is a promising candidate for hole extraction. Although hysteresis-free and rather stable perovskite solar cells were developed by utilizing NiOx hole transport layer, its relatively small mobility and carrier concentration prevent achieving perovskite solar cells over 20% efficiency. On this respect, there are numerous studies in the literature on doping of NiOx with various elements (i.e. Cu, Y, Li, etc.) to increase its mobility and carrier concentration. In this study, the impact of manganese (Mn) incorporation into the NiOx thin film (Mn: NiOx) is investigated to enhance the charge extraction capability of NiOx without compromising its optical properties. Nickel(II) acetate tetrahydrate and different amounts of manganese(II)acetate tetrahydrate salts are used to prepare the Mn: NiOx precursor solutions and spin coated on TCO substrates. While transmission and reflection, and
spectroscopic ellipsometry measurements are performed to determine the optical properties of uniform Mn: NiOx films, ultraviolet spectrum is utilized to determine their work function and valance energy band position. Impedance spectroscopy is carried out to determine surface passivation property and measure the mobility of the layers. We demonstrate the Mn doping into NiOx thin films provides to enhanced efficiency in hysteresis-free perovskite solar cells.

EN08.03.23
Molecular Doping of CuSCN for Hole Transporting Layer in Inverted-Type Planar Perovskite Solar Cells
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Among many strategies to develop high-performance perovskite solar cells, the interface engineering is considered as a promising approach for achieving high power conversion efficiency. Specifically, high optical transparency and excellent electrical properties are essential in optimized hole transport materials in the inverted-type planar perovskite solar cells. In this study, we demonstrate the molecular doping of copper thiocyanate (CuSCN) by 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) significantly enhances the photovoltaic performance of perovskite solar cells. The incorporation of F4TCNQ in CuSCN leads to successful electron transfer from CuSCN to F4TCNQ, which affords more balanced energy level alignment at the interface of perovskite layer for hole conduction. The device analyses reveal faster charge transport and less carrier recombination in the F4TCNQ-doped CuSCN-based devices, contributing to not only the improved efficiency but also the hysteresis elimination. At the optimized doping concentration, the doped CuSCN exhibited ~35% increased efficiency as high as 14.19% in the inverted-type planar perovskite solar cells.

EN08.03.24
Normal and Planar Type Perovskite Solar Cells Based on Inorganic Electron Transporting Layers (ETLs) of SnO2 via Atomic Layer Deposition (ALD)
Seonghwa Jeong, Seongrok Seo, Hyoungmin Park and Hyunjung Shin; Sungkyunkwan University, Korea (the Republic of)

SnO2 has received a great deal of attention in normal and planar type perovskite solar cells with its excellent optical and electrical properties; i.e., wide bandgap, good chemical stability and can be grown by low temperature processing as an electron transporting layer (ETL). Among various deposition methods, SnO2 thin films used as ETL are deposited by Atomic Layer Deposition (ALD). ALD shows numerous advantages of being able to control film thicknesses with nanometer precision and to produce high quality thin films without any pinholes. SnO2 has a deeper conduction band, compared to TiO2 deposited by ALD which has energy level mismatch with MAPbI3, thus energetic alignment of SnO2 is more appropriate for extracting photogenerated electrons than TiO2, resulting in high power conversion efficiency (PCE ; ~ 18.3 % with pure MAPbI3 based PSCs). In addition, processing temperature of ALD-SnO2 thin films (at ~ 180 °C and/or even R.T.) is much lower than that of ALD-TiO2 thin films (~ 400 °C). Furthermore, thin films of Zn doped SnO2 also prepared in this study and showed enhanced conductivity compared to undoped ones, as a result, photovoltaic performances are improved in the normal planar structure (FTO / Zn:SnO2 / Perovskite / Spiro-OMeTAD / Ag) of the perovskite solar cells.

Keyword : perovskite solar cell, atomic layer deposition, SnO2

EN08.03.25
Organic Monomolecular Layers Enable Energy-Level Matching for Efficient Hole Transporting Layer Free Inverted Perovskite Solar Cells
Guojun Mi, Weiguang Kong, Xiao Duan and Chun Cheng; Southern University of Science and Technology, China

For perovskite solar cells (PSCs) without hole transport layer (HTL), the hole transport energy barrier (ΔEh) is defined as the energy difference between the Fermi level (EF) of the electrode and the valence band maximum (VBM) of the perovskite. Highly efficient HTL-free PSCs require that ΔEh should be reduced or eliminated to improve hole collection. In order to minimize ΔEh, one strategy is to adjust the VBM of the perovskite closer to the EF of the electrode. However, it is rather challenging because the electronic structure of the perovskite depends, to a large extent, on the specifics properties of the system, as well as the preparation and environmental conditions. Another strategy to minimize ΔEh is to shift the EF of ITO closer to the VBM of the perovskite. In this way, organic monolayer (ML) materials which have been widely used in organic electronics can adjust the electrode EF. However,
to date organic ML is rarely used to prepare efficient HTL-free PSCs. Besides, the energy level arrangement between electrode and HTL still needs optimization, and the feasibility of using organic ML to construct highly efficient PSC without HTL remains to be explored. We report the monomolecular layer strategy toward barrier-free contact of the energy level arrangement at the electrode/perovskite interface, facilitating efficient charge transfer and inhibiting non-radiative carrier recombination. The HTL-free PSCs based on ML-modified ITO produced an efficiency of 19.4%, much higher than the HTL-free PSCs (10.26%) on the original ITO, and it is even comparable to the PSCs with HTL. This study provides an in-depth understanding of the interface level layout mechanism and is helpful in designing advanced interface materials for simplified and efficient PSCs.

EN08.03.26
Perovskite Solar Cells with a Hybrid Electrode Structure Askhat Jumabekov¹, Yinghong Hu² and Gede Adhyaksa³; ¹Nazarbayev University, Kazakhstan; ²Ludwig-Maximilians-Universität München, Germany; ³FOM Institute AMOLF, Netherlands

Many factors govern the performance of back-contact perovskite solar cell (BC-PSC) devices, with the design and dimensions of the electrodes being among the key factors influencing the charge carrier collection properties, and thereby the final device performance.

The back-contact architecture for a PSC is realized by arranging both the anode and cathode on a substrate surface, with the perovskite photovoltaic layer then deposited on top. This affords a device with the perovskite photovoltaic layer in contact with both electrodes on one side (substrate side), while directly exposing the perovskite surface to illumination on the other side (front side).¹ Unlike in conventional sandwich-type architectures for PSCs, this approach reduces transmission losses and exposes the active layer for surface passivation or the application of an antireflective coating.² This new concept has recently been highlighted as a route to further increasing the efficiency of PSC devices.³

To realize the full potential of back-contact architectures for high-efficiency PSC, a deeper understanding of the underlying device physics is required. While standard models developed for sandwich-type PSC with p-i-n or n-i-p device configurations adequately describe the physical processes in the device, they cannot be as readily applied to BC-PSCs due to the nature of their architecture. This makes it challenging to contrast the performance and behavior of BC-PSCs with standard sandwich-type PSCs.

Here we present an example of a PSC device with a hybrid electrode structure, in which a single device can operate with either a vertical (sandwich-type) or lateral (back-contact) configuration of contacts. The hybrid structure was achieved by depositing an additional anode on top of a prefabricated back-contact PSC device with transparent back-contact electrodes. Comparative analysis between the sandwich and back-contact operation modes have been performed. The device performance analysis reveals that the efficiencies of PSC devices in back-contact mode is inferior when compared to sandwich mode operation. Coupled opto-electronic simulations determined that due to the intrinsically narrow depletion region near the contact interfaces, the charge collection efficiency in the back-contact device structure appears to be significantly lower compared to the sandwich device structure. These findings provides an insight into the cause of the performance disparity between these two architectures.

References

EN08.03.27
Practical, Thermal Atomic Layer Deposition of p-type NiO Thin Films as Hole Transporting Layers for Organic-Inorganic Hybrid Perovskite Solar Cells Hyoungmin Park, Seongrok Seo, Seonghwa Jeong, Changdeuck Bae and Hyunjung Shin; Sungkyunkwan University, Korea (the Republic of)

Efficiency of the halide perovskite solar cells (HPSCs) has recently reached over 24% by solution-based compositional engineering as well as surface passivation technique. Low stability of halide perovskite materials still
remains many challenging problems. Inverted configuration of HPSCs with a hole transporting layer (HTL) of inorganic materials have shown great promise to improve the resulting stability. In this study, ultra-thin films of NiO as HTLs were deposited by thermal atomic layer deposition (ALD) with H2O2 and O3 as an oxygen source. We were able to identify the difference between Ni and O compositions in the deposited thin films either by H2O2 or O3 as oxygen sources. Band diagrams of HPSCs with ultra-thin NiO layers were revisited on the basis of the optical property, and the analysis of valence band maximum and work function using ultraviolet photoelectron spectroscopy. The present study shows that a couple of nanometers-thick and pin-hole-free NiO films could be successfully prepared by ALD and served as HTLs by modifying interfacial characteristics to halide perovskite layers and by demonstrating improved stability of HPSCs.

EN08.03.28
Preparation of High Efficiency Flexible Solar Cells by Inserting KCl Modified Layer at the Interface between SnO2 and Perovskite Ye Xiaofang, Hongkun Cai and Jianjun Zhang; Nankai University, China

In recent years, flexible perovskite solar cells have received extensive attention and rapid development due to their advantages of light weight, portability, wearability, and applications in near-space. However, due to the limitations of its preparation process and other factors, high-efficiency and large-area flexible perovskite solar cells still have a lot of room for development. In our work, a flexible perovskite solar cell was prepared using a low temperature (not more than 100 °C) solution method (PEN/ITO/SnO2/KCl/Cs0.05(MA0.17FA0.83)0.95Pb(I0.83Br0.17)0.05), and the device with the highest efficiency of 17.20% was obtained by adjusting the concentration and rotation conditions of the KCl modified layer. Meanwhile, the efficiency of the large-area (1 cm2) flexible solar cell was more than 13%. At the same time, the passivation of the KCl interface modification layer inhibits the formation of the defect state, which reduces the surface composite of the perovskite and improves the carrier transport performance, and the hysteresis effect of the device is also reduced accordingly.

EN08.03.30
The Effect of Underlying Layer on Sequential Deposition of Methylammonium Lead Halide Shu-Chen Kao, Yu-Sheng Chen and Chih-Liang Wang; National Chung Hsing University, Taiwan

Perovskite solar cell (PSC) has been considered one of the most promising candidates for the next generation renewable energy device due to its power conversion efficiency over 22% in a short time. Many fabrication methods for the perovskites have been reported, such as one-step deposition, sequential deposition, vapor assisted deposition. The sequential deposition involving the conversion of perovskite from lead halide is particularly attractive because of its controllability of perovskite property via crystallization kinetics. Though previous studies have correlated the microstructure of lead halide, solution concentration, and loading time with the resulting perovskite film, the effect of underlying layer on the sequential deposition seemingly remains few.

In this regard, a series of TiO2 nanorods with the length from 200 nm to 800 nm on FTO are grown by the hydrothermal process, followed by the sequential deposition of CH3NH3PbI3. In order to investigate the effect of underlying layer, the SEM and XRD are carried out to analyze the properties of the sequential deposited CH3NH3PbI3, such as the morphology, crystallization and conversion level, on a series of TiO2 nanorods. The UV-Vis and EIS are performed to detect the optical property and charge transport, respectively, of perovskite films deposited on different length of TiO2 nanorod. J-V characteristics of the perovskite solar cells using different TiO2 nanorods are tested under AM 1.5G illumination. Our results show that the different length of TiO2 nanorod can potentially affect the level of PbI2 residue and the perovskite morphology after the sequential deposition. An optimized length of TiO2 nanorod is simultaneously beneficial for obtaining a high quality perovskite film along with the improved charge collection. More details of the performance of perovskite solar cells, influence by the underlying TiO2 nanorods, will be discussed in the presentation.

EN08.03.31
The Use of Optimized Ternary Metal Oxide and Binary Oxide as Effective Bilayer Electron Transport Layer for Highly Efficient and Stable Planar Perovskite Solar Cells Thambidurai Mariyappan, Foo Shini, P. C. Harikesh, Nripan Mathews and Cuong Dang; Nanyang Technological University, Singapore

An ideal planar electron transport layer (ETL) should possess little surface defects, high electron mobility, and well-aligned energy level with the absorbing layer. Ternary oxides exhibit promising potentials as effective electrontransportmaterialas the optical and electrical properties are easily manipulated using simple compositional
adjustments. In this paper, we examine various solution-processed ternary zinc-tin oxide (ZTO) compositions as plausible compact ETL candidates in planar perovskite cell application. Through the use of the ZTO ETLs, chemical instability previously observed in pristine ZnO ETL based device was greatly reduced with improved device stability and power conversion efficiency (PCE) of 16.41% attained in the Z1T1O ETL based device. We further explored the use of SnO2 interlayer between the ZTO/perovskite interface to form a bilayer ETL structure. Apart from prohibiting the unfavourable contact between the ZnO film with the perovskite layer, the bilayer ETL structure showed further enhancement in reproducibility, charge transfer, recombination resistance, device stability, and efficiency. Paramount PCE of 19.01%, with an average PCE of 18.18%, was demonstrated in the ZTO/SnO2 ETL based device. In addition, exceptional stability was obtained in which 90% of its initial PCE was maintained after 90 days without encapsulation. The superior performance and device stability are attributed to the improved charge extraction, favourable energy alignment, and suppressed charge recombination derived from the compatible ZTO/SnO2 bilayer. Hence, our work demonstrates the viability of ternary metal oxides as effective ETL candidates for perovskite solar cell application whereby stability and performance were further enhanced with the addition of a compatible SnO2 interlayer.

EN08.03.32
Towards Efficient and Stable Perovskite Solar Cells Employing Non-Hygroscopic F4-TCNQ doped TFB as Hole-Transporting Material

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Organic-inorganic halide perovskites have found increasing potential in a wide range of optoelectronic applications due to their excellent optoelectrical properties e.g., low energy bandgaps ($E_g \sim 1.6$ eV), low exciton binding energy ($<10$ meV), long diffusion length (up to 1 μm), and high absorption coefficients ($1.5 \times 10^4$ cm$^{-1}$ at $\lambda = 550$ nm). In this context, perovskites solar cells (PSCs) have reached a rapid development of best power conversion efficiency (PCE) with a certified 23.7% efficiency up to date. In this work, we have focused our attention on the design of efficient and stable hole transporting layer (HTL) materials in organic-inorganic PSCs, towards a facile hole extraction and enhanced photocurrent generation. To date, cost ineffectiveness, insufficient hole mobility ($\sim 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$), and low electrical conductivity ($\sim 10^{-5}$ S cm$^{-2}$) have hindered the commercialization of the reference 2,2',7,7'-Tetrakis-(N,N'-di-4-methoxyphenylamo)-9,9'-spirobi fluorore (Spiro-OMeTAD) HTL material. Similarly, conventional additives and dopants e.g., lithium bis (trifluoromethylsulfonyl)-imide (LiTFSI) and 4-tert-butylpyridine (TBP), have been shown to enhance moisture absorption, leading to inherently low stability and reproducibility, and to disturb the equilibrium between the CH$_3$NH$_3$PbI$_3$ and its degraded components, respectively. In this work, we have developed for the first time a novel and efficient HTL material by optimized doping of a conjugated polymer, poly[(9,9-diocetylfluorenyl-2,7-diyl)-co-(4,4’-(N-(4-sec-butylphenyl)diphenylamine)] (TFB), with a non-hygroscopic p-type dopant, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ). The F4-TCNQ-doped TFB PSC exhibited a PCE of 17.46%, which surpassed that of 16.64% and 11.01% for the reference LiTFSI+TBP-doped Spiro-OMeTAD and LiTFSI+TBP-doped TFB-based devices, respectively. The appropriate band alignment of the introduced F4-TCNQ-doped TFB HTL material with the highest occupied molecular orbital (HOMO) of the perovskite was proposed as primary factor to facilitate efficient charge extraction from the perovskite to the electrode as well as increased short-circuit current. Conducted steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) analyses have herein further corroborated a reduced charge recombination. Most importantly, the hydrophobic nature of F4-TCNQ-doped TFB was shown to dramatically improve the long-term stability of the device under an ambient condition with RH of 45%. In detail, the device herein reported maintained ca. 80% of its initial efficiency after 10 days, significantly superior to both LiTFSI+TBP-doped Spiro-OMeTAD (ca. 30%) and LiTFSI+TBP-doped TFB (ca. 10%) counterparts. This simple, yet novel strategy is believed to reflect a promising route for a wide range of highly efficient solar cells and other photovoltaic applications.

EN08.03.33
Fluorinated Dication Templated 1D Spikes for Stable and High-Performance Perovskite Solar Cells

Jue Gong1, Zhenghong Dai1, Mingyu Hu1,2, Yuanyuan Zhou1 and Nitin P. Padture2; 1Brown University, United States; 2Kunming University of Science and Technology, China
Further improvement of environmental stability of perovskite solar cells at operation conditions is still a critical issue for matured and practical commercializations in the future. In this study, we utilize fluorinated organic cation, as in the form of 2,6-difluoro-4-ammonium pyridinium (2F4AP2+), to realize solar cell applications with power conversion efficiencies exceeding 13% and stable across 500 hours in high moisture contents (>60%) under constant illumination. Most interestingly, when 2F4AP2+ composition is highest with respect to PbI2 precursor, (2F4AP)PbI4 compound has a 1D spike-like crystal structure. Such low-dimension structure, as due to strong quantum confinement effects and special electron-phonon interaction, additionally enables broad yellow emission upon UV excitation at room temperature. Our studies demonstrate the rich chemistry and versatile optoelectronic functions of fluorinated organic-inorganic hybrid perovskite materials, and with careful tuning of the 2F4AP compositions, continuous increase in photovoltaic performance of solar cell devices with long-term stability are promisingly achievable.

Defect Engineering as a Tool to Enhance Stability in Perovskite Thin Films and Solar Cells

Katelyn P. Goetz1, Fabian Thome1, Paul Fassl2, Lukas M. Falk1, Vincent Lami1, David Becker-Koch1, An Qingzhi1, Alexander Taylor1, Fabian Paulus1 and Yana Vaynzof1; 1Universität Heidelberg, Germany; 2Karlsruhe Institute of Technology, Germany

Environmental stability remains one of the most significant challenges impeding the commercialization of perovskite solar cells. The presence of defects has been linked to the stability of perovskite devices, for example, the photoinduced formation of superoxide upon oxygen exposure in the presence of iodine vacancy defects has been shown to play a key role in the degradation of methylammonium lead iodide (MAPbI3) perovskite thin films [1]; however, the details of this process remain unclear. Recently, our group has demonstrated that the type and density of defects on the surface of MAPbI3 perovskites can be tuned by incrementally adjusting the stoichiometry of the precursor solution [2]. Herein, we exploit this method to elucidate the interaction between specific defects in MAPbI3 and the environment, and further expand it to understand these effects in bromide-based perovskites (MAPbBr3).

Our methodology is based on a multi-technique approach. X-ray photoelectron spectroscopy is used to identify the density and type of surface defect in each type of perovskite film. To then isolate the interaction of the defect with the environment, films are exposed to environments of nitrogen mixed with varying (but controlled) oxygen and water content and completed with extraction layers and an electrode. In parallel, the changes in optoelectronic properties are monitored with photothermal deflection spectroscopy and photoluminescence spectroscopy, allowing us to correlate the changes in defect type and density with changes in photovoltaic performance. Finally, the PV performance and optoelectronic properties are monitored over time to assess the shelf-storage stability as a function of defect density and type.

We find that the photovoltaic performance of the MAPbI3 samples deficient in iodine shows a tremendous drop in the short-circuit current ($J_{sc}$) upon exposure to oxygen and light, while samples with excess iodine show performance that is similar to pristine films. While the latter show low photoluminescence quantum efficiency (PLQE) and high Urbach energies, suggesting the presence of deep trap states, these states do not interact with oxygen under illumination. In contrast, the PLQE of iodine-deficient samples initially increases upon exposure to oxygen, indicative of trap healing; but this process is short lived, with significant degradation taking place after 2h, in agreement with the decline in PV performance of these samples. The bromide-based perovskite solar cells show little dependence of the initial photovoltaic performance on the trap density, but upon exposure to air and light, bromide-deficient solar cells undergo a large $J_{sc}$ boost, resulting in a near tripling of their initial PCE. These results highlight the strong role that chemical composition plays in the stability of perovskite PVs and suggest that defect engineering is a potential strategy for enhanced stability, especially in the single-cation perovskite compositions.

Recently, solar cells using an organic-inorganic hybrid perovskite (OIH) as a light absorber have attracted tremendous attention considering the unique advantages such as high absorption coefficient, favorable bandgap, fast charge transport, high dielectric constant, long carrier lifetime, and high doping tolerance etc. In just a few years, the power conversion efficiency (PCE) of perovskite solar cell (PSC) has experienced a skyrocketing increase, which has been enhanced from 3.8% in 2009 to 24.2% according to the latest report. However, the long term stability of the PSC is still a big issue. It is well known that most of the PSCs, the perovskite films are prepared by solution process. However, besides the low-cost fabrication, solution process would also introduce lots of defects at the surface and grain boundaries. In the perovskite, the defects would not only influence the performance but also have a detrimental impact on the stability of perovskite solar cell.

In this work, we try to introduce a new thieno[3,4-b] thiophene-based small molecular donor, named as 4FK, into perovskite solar cell. The 4FK could not only help separate and then further extract the carriers, but also passivate the surface defects through the formation of the Lewis adduct with the Pb\(^{2+}\) of the perovskite. Consequently, with the cooperation of passivation effect, better band alignment, and carrier extraction effect, a champion device with PCE of 19.9% for MA-based perovskite solar cell has been achieved. Our results provide a reliable way to enhance the performance and also the long term stability of perovskite solar cells.

EN08.03.36
Grain Boundary Passivation for Efficient and Stable Halide Perovskite with Suppressed Iodide Migration via Direct Backbone Attachment of Polyester Yuchen Zhou\(^1\), Yifan Yin\(^1\), Likun Wang\(^1\), Xianghao Zuo\(^1\), Chang-Yong Nam\(^2\) and Miriam Rafailovich\(^1\); \(^1\)Stony Brook University, United States; \(^2\)Brookhaven National Laboratory, United States

Organic-inorganic halide perovskites (OIHP) remains as one of the hottest research topics in the past several years due to their exceptional optoelectronic properties in broad fields relating light emitting, photovoltaic, photo-detecting, gas sensing and even photosynthesis, etc. However, the exist of grain boundaries in OIHP thin films made using current preparation method creates large number of defects/traps, resulting in possible low photo conversion efficiency (PCE) of its corresponding devices. The presence of grain boundaries can also become a “starting point” for structural degradation to take place, which makes the film highly degradable when exposing to excessive environmental stress, such as moisture, heat and light.

In this study, we effectively passivated the grain boundaries in methylammonium lead iodide (MAPI) perovskite thin films using one type of the polyester called polycaprolactone (PCL). We observed the successful attachment of PCL on MAPI grains using FTIR, AFM and (HR)TEM. The blueshifts of C=O group were found both in PCL incorporated MAPI layer and the PCL mixed PbI\(_2\) sample, which indicated the formation of coordination between electron donating O-C=O group on PCL and electron acceptor Pb\(^{2+}\) complex in MAPI via Lewis acid and base adduct. We also visualized the presence of PCL polymer on grain boundaries of MAPI by using friction mode AFM and (HR)TEM. The brighter boundaries and darker grains on friction AFM for MAPI with PCL indicated stronger interaction of AFM tip on the boundaries and implied the gathering of softer polymeric materials between the grains, while the pure MAPI barely showed the contrast difference using same AFM operation mode. The HRTEM images on both surface and the focused ion beam (FIB) prepared cross-sectional samples further proved the passivation of PCL at the boundaries with highly crystalline MAPI grain areas being separated by amorphous PCL polymer channels. The passivation has also been confirmed by showing increased photoluminescence (PL) emission intensity and decay lifetime due to reduce of boundary- borne defects/traps, which can act as centers for the non-radioactive recombination. Such optoelectronic improvement by PCL directly promoted the photovoltaic performance of the corresponding device, showing an increased open circuit voltage with the highest PCE exceeding 19%. More importantly, the direct boundary passivation by PCL greatly enhanced the stability of MAPI thin films against three major environmental stresses (moisture, heat and light). All samples with PCL incorporation largely maintained pure MAPI crystal structure with much suppressed growth of PbI\(_2\), while the reference MAPI films became degraded with obvious PbI\(_2\) appearing after the exposure. Moreover, we used the SIMS to reveal the suppression effect of ion migration (especially for iodide ion) due to the increase of the activation energy of MAPI film with PCL passivation. After heating the corresponding devices, the PCL passivated one presented only little, if any, migration of iodide towards the HTM and electrode layer, while significant migration with much stronger iodide ion signal has been detected at the HTM layer for the reference MAPI device.

We believe that the unique chain structure of PCL with the functional ester groups (O-C=O) on backbone offered the outstanding passivation by forming direct backbone attachment of PCL on the grain boundaries of MAPI. The
repeating backbone segments composed of six methylene between two attaching ester groups can serve as a strong hydrophobic moisture repellent layer and can also help maintain high structural purity of MAPI when exposing to heat and light, as well as hinder the mobile of iodide ion by increasing the activation energy of MAPI after the direct polymer chain attachment. (This work was supported by the Morin Foundation Trust and the NSF, Inspire program #1344267)

EN08.03.37
Passivated Tin Oxide Based on Acetylacetonate Complexes for High Performing Planar Perovskite Solar Cells Mousa Abuhelaiqa, Pak Sanghyun, Yonghui Lee and Mohammad K. Nazeeruddin; École Polytechnique Fédérale de Lausanne, Switzerland

Perovskite-based solar cells have overseen tremendous development reaching power conversion efficiencies exceeding 24% in the laboratory scale. Part of the development was made possible by utilizing passivated SnO\textsubscript{2} as an electron transporting layer. Chlorinated and colloidal precursors such as SnCl\textsubscript{4} and SnO\textsubscript{2} nanoparticles are usually used to fabricate efficient SnO\textsubscript{2} films. In this work, we explore the effect of halogen additives on the passivation properties yielded on SnO\textsubscript{2} films. This was done by employing three novel acetylacetonate-based precursors of which one is halide-free and two are halogenated with Cl and Br respectively. These precursors form stable, non-colloidal solutions that yield a unique SnO\textsubscript{2} film morphology as we show with TEM. Additionally, we demonstrate that the halide additives electrically passivate the SnO\textsubscript{2} film and alter the optimum annealing temperature of SnO\textsubscript{2} film formation. Our optimized SnO\textsubscript{2} films achieved high-performing planar perovskite solar cell devices with a power conversion efficiency of 22.19% (21.4% certified by Newport) with 0.16 cm\textsuperscript{2} active area, and 16.7% for mini-modules with 15 cm\textsuperscript{2} active area.

EN08.03.38
Quantum Dots Supply Bulk- and Surface-Passivation Agents for Efficient and Stable Perovskite Solar Cells Xiaopeng Zheng\textsuperscript{1}, Joel Troughton\textsuperscript{1}, Nicola Gasparini\textsuperscript{1}, Yuanbao Lin\textsuperscript{1}, Mingyang Wei\textsuperscript{2}, Yi Hou\textsuperscript{2} and Osman M. Bakr\textsuperscript{1}; \textsuperscript{1}King Abdullah University of Science and Technology, Saudi Arabia; \textsuperscript{2}University of Toronto, Canada

Defect passivation and surface modification of hybrid perovskite films are essential to achieving high power conversion efficiency (PCE) and stable perovskite photovoltaics. Here, we demonstrate a facile strategy that combines high PCE with high stability in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} (MAPbI\textsubscript{3}) solar cells. The strategy utilizes inorganic perovskite quantum dots (QDs) to distribute elemental dopants uniformly across the MAPbI\textsubscript{3} film and attach ligands to the film’s surface. Compared with pristine MAPbI\textsubscript{3} films, MAPbI\textsubscript{3} films processed with QDs show a reduction in tail states, smaller trap-state density, and an increase in carrier recombination lifetime. This strategy results in reduced voltage losses and an improvement in PCE from 18.3\% to 21.5\%, which is among the highest efficiencies for MAPbI\textsubscript{3} devices. Ligands introduced with the aid of the QDs render the perovskite film’s surface hydrophobic—inhbiting moisture penetration. The devices maintain 80\% of their initial PCE under 1-sun continuous illumination for 500 h and show improved thermal stability.

EN08.03.39
Surface and Interface Passivation of Perovskite PV Materials Hela Liber Sasson\textsuperscript{1,2} and Iris Visoly-Fisher\textsuperscript{1,2}; \textsuperscript{1}Ben Gurion University of the Negev, Israel; \textsuperscript{2}Ben-Gurion University of the Negev, Israel

Organometallic halide perovskites attract much attention in the field of optoelectronics and in photovoltaic research thanks to its high performance. However, perovskite photovoltaics have yet a major obstacle to overcome - stability. The perovskite surface plays an important role in the cells’ stability and efficiency. Surface states were previously found to induce recombination and accelerated degradation. Passivation of the surface and interfaces of the perovskite film and neutralizing surface states can be achieved by various techniques. In this research we focus on the effect of passivation using conjugated small molecules on the perovskite photo-stability. The perovskite surface is modified using porphyrin molecules resulting in the formation of new hybrid films. The molecules are added into the precursor solution and are aimed to be located at the perovskite grain boundaries. The additive porphyrins differ by their functional group while each group is designated to passivate specific surface dangling bonds towards increasing the photo-stability. We find that different functional groups differently affect the perovskite crystallization, hence the resulting solar cell efficiency and stability.

EN08.03.40
To Greatly Reduce Defects via Photoannealing for High-Quality Perovskite Films  

Duo Wang, Cuncun Wu, Wei Luo, Xuan Guo, Xin Qi, Yuqing Zhang, Zehao Zhang, Ning Zhu, Bo Qu, Lixin Xiao and Zhijian Chen; Peking University, China

The performance of perovskite solar cells (PSCs) depends on the crystallization of the perovskite layer. Herein, we demonstrate an effective photoannealing (PA) process by a halogen lamp. During the PA process, on the one hand, the lower energy photon, that is, near IR up to $\sim 1015$ nm photon, drives the crystallization of the perovskite film, similar to the conventional thermal annealing (TA). On the other hand, the higher energy photon of PA can excite the trapped carriers and release the space charges, thus leading to an ideal perovskite layer with better crystallinity and lower density of defect when compared to that of TA. A maximum power conversion efficiency (PCE) has been obtained to be 20.41% in the CH$_3$NH$_3$PbI$_3$-based planar PSCs based on PA because of the increase of J$_{sc}$ and V$_{oc}$, much higher than the control device based on the conventional TA with a maximum PCE of 18.08%. Therefore, this result demonstrates that PA is an effective method to promote the device performances and reduce the fabrication cost, which provides a potential approach for the commercial application of perovskite devices.

EN08.03.41

Trap State Passivation in Perovskite Solar Cells Using a Bifunctional Organic Molecule as a Lewis Acid-Base Adduct  

Sandeep B. Satyanarayana and Praveen C. Ramamurthy; Indian Inst of Science, India

Organic-inorganic hybrid lead halide perovskites have become the most sought-after materials for various optoelectronic applications. Their low-temperature (<150°C) and solution processability enable them to function on flexible platforms. The power conversion efficiencies of perovskite solar cells have reached 22%. Interdisciplinary efforts are going into realizing perovskite-silicon tandem cells for the better utilization of the solar bandwidth. The major drawback of these devices is their inferior stability. The high diffusivity of iodide ions in the perovskite lead to chemical reactions with atmospheric oxygen and moisture. This in turn disintegrates the perovskite structure and hence, photon absorptivity is lost. Encapsulation of these devices does improve the stability but is nowhere near standards needed for commercialization.

The shallow and deep trap states play a major role in determining the performance and stability of perovskite solar cells. These states are created by ionic defects at the at the grain boundaries and surface respectively. The use of Lewis acids and bases have been demonstrated to pacify these defects. The Lewis base interacts with the cation and the acid with the anion. The interaction of a Lewis acid or base at a grain boundaries results in defect states. These states hinder inter-grain transport and act as parasitic resistances.

In this work, we propose to design a bifunctional organic molecule with HOMO and LUMO matching the band edges of the perovskite absorber. The bifunctionality (Lewis acid and base) enables passivation of both cations and anions simultaneously. The trap state passivation inhibits ion migration in the crystal and hence improves the stability of the device. It also helps in impeding trap assisted recombination to in turn enhance device performance. The band edge matching on the HOMO and LUMO levels empowers inter-grain transport of charge carriers. This will result in larger charge carrier diffusion lengths and lower bimolecular recombination. The overall performance and stability of the device is augmented. The use of organic molecule for passivation also increases the hydrophobicity of the perovskite layer. This results in better moisture resistance for the perovskite.

The stability of the passivated perovskite is monitored through JV measurements, X-ray diffraction and absorption measurements. The interaction of the passivation molecule with perovskite is estimated using FTIR spectroscopy and is mapped using an X-ray synchrotron source. The effect of passivation is estimated by calculating the trap density of states and also observing the long-term aging behavior.

EN08.03.42

Corrosive Processing on Top of Perovskite Solar Cells Enabled by SnO$_{2}$ as Internal Barrier Layer  

Kai O. Brinkmann$^1$, Tobias Gahlmann$^1$, Junjie He$^{1,2}$, Christian Tückmantel$^1$, Tim Becker$^1$, Manuel Theisen$^1$, Johannes Bahr$^1$, Cedric Kreusel$^1$, Jun Song$^2$, Junle Qu$^2$ and Thomas Riedl$^1$; $^1$Bergische Universitat Wuppertal, Germany; $^2$Shenzhen University, China

With power conversion efficiencies (PCE) of more than 24%, halide perovskites (HAPs) now even rival silicon as photoactive semiconductor in solar cells.$^{[1]}$ At the same time, serious concerns about material stability are still inevitably linked with HAPs, e.g. when in contact with water etc.$^{[2,3]}$ The sensitivity of HAPs not only states a challenge with respect to long term stability, but likewise limits the choice of processes for the deposition of subsequent functional materials, such as charge transport layers and electrodes.
Processes involving polar solvents such as water or ethyl acetate are typically excluded as candidates for follow-up processing, as they have been shown to severely damage the HAP. Unfortunately, a wide variety of solvents that would be desirable for “green” upscaling classify as corrosive for HAPs.

In this work we will show that the use of an ultrathin, impermeable, yet conductive AZO/SnOx hybrid layer that serves as electron transport material is able to mitigate most of the above issues. This is possible due to the unique nature of the ALD grown SnOx, which is transparent, conductive and, most importantly, physically dense and impermeable to a wide variety of corrosive solvents.[4] Based on the AZO/SnOx hybrid we were able to realize perovskite solar cells with semitransparent top electrode based on silver nanowires (Ag NWs), that were spray coated from an aqueous dispersion. The resulting semi-transparent cells showed a PCE exceeding 15%. In a similar sense a carbon electrode could be doctor bladed from a paste based on ethyl acetate. This afforded the first p-i-n (inverted) perovskite solar cells with carbon top-electrode. Most importantly, if both processes were used without the AZO/SnOx protection layer, the solar cells turn out to be non-functional.

The now functional devices comprising the Ag-NW top electrode reveal a further important issue related to the interface of Ag-NW and SnOx, which shows rectifying behavior, due to a parasitic Schottky barrier between Ag-NW and SnOx. We have conducted an in-depth study using Kelvin probe analysis, photoemission spectroscopy and specific unipolar test devices. We demonstrate that the issues associate with the interfacial barrier can either be eliminated by UV-light soaking or by the introduction of a dedicated interlayer with a high carrier density n > 10^{18} cm^{-2} between Ag-NW and SnOx. Taken together, we will present the first perovskite solar cells with a water processed Ag NWs top electrode and as well as the first proof of concept p-i-n (inverted) perovskite solar cell with a carbon top electrode.


SESSION EN08.04: Perovskite Solar Cell—Processing, Additives, Material Development
Session Chairs: Henk Bolink, Shengzhong (Frank) Liu, Selina Olothof and Yabing Qi
Tuesday Morning, December 3, 2019
Sheraton, 2nd Floor, Back Bay AB

8:30 AM *EN08.04.01
Up-Scalable Fabrication of Metal Halide Perovskite Solar Cells and Modules Luis K. Ono, Longbin Qiu, Sisi He, Zonghao Liu, Zhifang Wu and Yabing Qi; Okinawa Institute of Science and Technology, Japan

After a decade of metal halide perovskite solar cell research and owing to the intensive research efforts across the world, there is no doubt that power conversion efficiencies (PCEs) comparable to several other photovoltaic technologies (e.g., multicrystalline Si, CIGS, CdTe) are achievable [1]. However, when moving perovskite solar cell technology from laboratory to industrial products, high-PCE, low-cost, and up-scaling are key metrics [2]. At OIST, a team of researchers in the Energy Materials and Surface Sciences Unit is making concerted efforts to develop processes (i) aiming at high PCE, (ii) high-throughput, (iii) minimum batch-to-batch variation, and (iv) compatible with large-area perovskite solar cells and modules. In this talk, we will present our recent progress on the use of chemical vapor deposition CVD [2-4] to fabricate perovskite solar cells and modules.

9:00 AM *EN08.04.02
**Vapor Phase Deposited Perovskites** Henk J. Bolink, Ana Maria Igual-Muñoz, Jorge Ávila, Daniel Pérez-del-Rey, Kassio P. Zanoni, Maria Grazia I. La-Placa, Azin Babaei, Chris L. Dressen, Yousra El Ajjouri, Francisco Palazón, Sang H. Chin, Michele Sessolo and Pablo Boix; University of Valencia, Spain

We will report on the progress on vapor phase deposited perovskites, including low bandgap Pb-Sn and wider bandgap multiple cation versions. The performance of these materials in both single and double junction solar cells will be reported. The influence of the use of thin organic charge extraction layers, using strong dopants, ionic compounds and conjugated polymers will be described.

9:30 AM EN08.04.03
**The Next Big Thing—Single-Crystal Perovskite Solar Cells With 21% Power Conversion Efficiency** Bekir Turedi1, Zhaolai Chen1, Abdullah Alsalloum1, Chen Yang1, Xiaopeng Zheng1, Issam Gereige2, Ahmed Alsaggaf2, Omar A. Mohammed1 and Osman M. Bakr1; 1King Abdullah University of Science and Technology, Saudi Arabia; 2Saudi Aramco, Saudi Arabia

Developments in perovskite photovoltaics dominantly rely on thin films of polycrystalline morphology. The record efficiency for PSCs which is 24.2% [1] is still far from their Shockley-Queisser (SQ) limit which is ~30.5% power-conversion efficiency (PCE) for methylammonium lead iodide (MAPbI3).[2] Despite the marked efforts in improving polycrystalline perovskite films, they have significant parasitic non-radiative recombination due to their inherent grain size and surface defects.[3] In contrast to polycrystalline perovskite films, single-crystal perovskites are orders of magnitude superior in terms of defect density, charge carrier mobility, and diffusion length.[4] These advantages make the single-crystal perovskites a strong candidate to achieve their SQ limit. Unfortunately, there are a limited amount of studies on single-crystal perovskite solar cells (SC-PSC), most of which show inferior PCEs compared to polycrystalline counterpart. The highest PCE so far for SC-PSCs was reported in 2017 is 17.8% by Huang and co-workers.[5]

Here, we achieved highly efficient SC-PSCs with PCEs reaching 21.1% and FFs of up to 84.3% (under 1-sun illumination).[6] This is the first time for an SC-PSC to exceed the 20% PCE benchmark. These devices, based on a ~20 micrometers-thick MAPbI3 single-crystal active layer in an inverted p-i-n structure, set a new record for SC-PSC efficiency and a new potential benchmark for FFs that PSCs should aim for, which polycrystalline PSCs have struggled to achieve. We describe the crucial fabrication steps and measurement conditions required to achieve these high efficiencies. Additionally, our study is also answering an ongoing debate over the diffusion length of carriers in perovskite single-crystals. The different methods like 1D, SCLC, and 3D methods showed a diverse range from several microns to mm. Our work confirms the extraction length should be over 40 μm since the external quantum efficiency (EQE) is over 80% all over the absorbed spectrum. While there is still room for substantial interfacial optimization, our findings highlight the promise of single-crystals for advancing perovskite optoelectronic technology, which could be a parallel growing path to the one taken by their polycrystalline counterparts.

**Bacteriorhodopsin Enhances Efficiency of Perovskite Solar Cells by Forster Resonance Energy Transfer Mechanism**

Subhabrata Das¹, Congcong Wu², Zhaoning Song¹, Yuchen Hou³, Ponisseril Somasundaran¹, Shashank Priya², Bernardo Barbìellinì⁴,⁵ and Renugopalakrishnan Venkatesan⁵,⁶; ¹Columbia University, United States; ²The Pennsylvania State University, United States; ³University of Toledo/Bowling Green University, United States; ⁴Lappeenranta University of Technology, Finland; ⁵Northeastern University, United States; ⁶Harvard University, United States

In recent years, halide perovskites have upstaged decades of development in solar cells by reaching power conversion efficiencies that surpass polycrystalline silicon performance. The efficiency improvement in the perovskite cells is related to repeated recycling between photons and electron-hole pairs, reduced recombination losses and increased carrier lifetimes. Here, we demonstrate a novel approach towards enhancing the efficiency of perovskite solar cells by invoking the Forster Resonance Energy Transfer (FRET) mechanism for predicting the strength and range of exciton transport between separated molecules based on Born-Oppenheimer approximation. FRET occurs in the near-field region as photosensitive protein, bacteriorhodopsin (bR) and perovskite have similar optical gaps. Titanium dioxide functionalized with bR protein is shown to accelerate the electron injection from excitons produced in the perovskite layer. FRET predicts the strength and range of exciton transport between separated perovskite and bR layers. We show that the cells incorporating bR/ TiO₂ layers exhibit much higher photovoltaic performance. These results open the opportunity to develop a new class of bio-perovskite solar cells with improved performance and stability.

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**Polyelemental, Multicomponent Perovskite Semiconductor Libraries through Combinatorial Screening**

Michael Saliba; Technical University of Darmstadt, Germany

Perovskites have emerged as low-cost, high efficiency photovoltaics with certified efficiencies of 24.0% approaching already established technologies. The perovskites used for solar cells have an ABX₃ structure where the cation A is methylammonium (MA), formamidinium (FA), or cesium (Cs); the metal B is Pb or Sn; and the halide X is Cl, Br or I. Unfortunately, single-cation perovskites often suffer from phase, temperature or humidity instabilities. This is particularly noteworthy for CsPbX₃ and FAPbX₃ which are stable at room temperature as a photoinactive “yellow phase” instead of the more desired photoactive “black phase” that is only stable at higher temperatures. Moreover, apart from phase stability, operating perovskite solar cells (PSCs) at elevated temperatures (of 85 °C) is required for passing industrial norms.

Recently, double-cation perovskites (using MA, FA or Cs, FA) were shown to have a stable “black phase” at room temperature.(1,2) These perovskites also exhibit unexpected, novel properties. For example, Cs/FA mixtures supress halide segregation enabling band gaps for perovskite/silicon or perovskite/perovskite tandems.(3) In general, adding more components increases entropy that can stabilize unstable materials (such as the “yellow phase” of FAPbI₃ that can be avoided using the also unstable CsPbI₃). Here, we take the mixing approach further to investigate triple cation (with Cs, MA, FA) perovskites resulting in significantly improved reproducibility and stability.(4) We then use multiple cation engineering as a strategy to integrate the seemingly too small rubidium (Rb) (that never shows a black phase as a single-cation perovskite) to study novel multication perovskites.(5) One composition containing Rb, Cs, MA and FA resulted in a stabilized efficiency of 21.6% and an electroluminescence of 3.8%. The Voc of 1.24 V at a band gap of 1.63 eV leads to a very small loss-in-potential of 0.39 V, one of the lowest measured on any PV material indicating the almost recombination-free nature of the novel compound. Polymer-coated cells maintained 95% of their initial performance at 85°C for 500 hours under full illumination and maximum power point tracking. This is a crucial step towards industrialisation of perovskite solar cells.

Lastly, to explore the theme of multicomponent perovskites further, molecular cations were revaluated using a globularity factor. With this, we calculated that ethylammonium (EA) has been misclassified as too large. Using the multication strategy, we studied an EA-containing compound that yielded an open-circuit voltage of 1.59 V, one of the highest to date. Moreover, using EA, we demonstrate a continuous fine-tuning for perovskites in the “green gap” which is highly relevant for lasers and display technology.

The last part elaborates on a roadmap on how to extend the multication to multicomponent engineering providing a...
series of new compounds that are highly relevant candidates for the coming years.(6,7)

(3) McMeekin et al. Science (2016)
(4) Saliba et al., Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. Energy & Environmental Science (2016)

11:00 AM *EN08.04.06
Processing Approaches for High-Performance and Versatile Halide Perovskite Semiconductor Films and Devices David B. Mitzi; Duke University, United States

Halide-based perovskite semiconductors (e.g., CH3NH3PbI3 and lower-dimensional analogs) have attracted substantial recent interest for photovoltaic and other optoelectronic application, due to large optical absorption coefficients, high carrier mobilities, long minority carrier lifetimes, and relatively benign defects and grain boundaries achieved within these materials. Coupled with the demonstrated high performance of associated films/devices, the ability to employ a diverse array of simple and low-temperature film deposition approaches provides an opportunity for very low processing costs and wide-ranging substrate form factors (e.g., flexible, light weight, curved surface). This talk will explore several recently described pathways for versatile thin-film deposition [1], including additive engineering [2], melt-processing [3,4], lamination and resonant-infrared matrix-assisted pulsed-laser evaporation (RIR-MAPLE) [5]. Considerations will include focus on grain growth, interfacial reactivity/passivation and deposition pathways for more complex 2-D hybrid perovskite films. Advances in film deposition and control offer promise of enhanced device performance, improved operational stability and greater device form factor flexibility.


11:30 AM EN08.04.07
Almost Hysteresis-Free Vacuum-Deposited Organic-Inorganic Perovskite Solar Cells Enkhtur Erdenebileg, Martin Kroll, Ran Ji, Zongbao Zhang, Tim Schramm, Changsoon Cho, Reinhard Scholz, Frederik Nehm and Karl Leo; IAPP, Germany

Organic-Inorganic Perovskite solar cells (PSCs) have attracted great interest over the past few years due to their outstanding power conversion efficiencies. However, operational stability still needs to be improved for broad commercial application. A commonly observed phenomenon for PSCs is hysteresis in their current–voltage characteristics, which has been suggested to be related to issues with long-term stability. Understanding of the processes involved in hysteresis may also guide the way to further improving the cells efficiencies. We fabricate planar pin organic–inorganic hybrid PSCs using three different organic transport layer architectures by vacuum deposition in a new multi-source tool and measure their hysteresis and long-term stability behavior. The organic transport layer architectures use controlled doping methods based on our pioneering work on organic doping, which is currently broadly commercially used in OLED displays.

Our results show that all-vacuum-deposited PSCs show much weaker hysteresis than in previous studies, where many types of PSCs were involved. For our devices, we also report an inverted hysteresis, where efficiency is somewhat higher for a voltage sweep from short circuit to forward-bias conditions than for the reverse sweep at lower scan rates, which has not commonly been observed in previous studies of PSCs.

11:45 AM EN08.04.08
Investigation of the Optoelectronic Properties and Stability of Coevaporated $\gamma$-CsPbI$_3$ Perovskites

Pascal Becker$^1$, Jose Marquez Prieto$^1$, Justus Just$^2$, Amran Al-Ashouri$^1$, Charles J. Hages$^3$, Hannes Hempel$^1$, Marko Jost$^1$, Steve Albrecht$^1$ and Thomas Unold$^1$; $^1$Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; $^2$MAX IV Laboratory, Sweden; $^3$University of Florida, United States

High-throughput experimentation can be of great advantage for exploring the complex compositional phase space of halide perovskites. Here we demonstrate the application of such techniques for the investigation of CsPbI$_3$ thin-films and solar cells. Cesium lead iodide thin films were fabricated with a lateral compositional gradient by co-evaporation of CsI and PbI$_2$ onto a non-rotating substrate. The composition, crystal structure, grain size, charge carrier mobility, lifetime and photoluminescence external quantum yield (PLQY) were determined by mapping these properties on the 5x5cm samples. Correlation of these results provides complete structure-property relationships and shows that stable high quality $\gamma$-CsPbI$_3$ can be obtained by Cs-rich low temperature deposition, without need of a high temperature annealing step. 12% efficient solar cells are demonstrated based on these results.[1]

Furthermore, samples obtained at different substrate temperatures, containing both the $\gamma$-phase and the $\delta$-phase, were annealed at 320 °C for a comparison of the properties of the as-deposited $\gamma$-phase with the $\gamma$-phase obtained after high temperature annealing. It is found that grain sizes increase from ~100 nm in the as-deposited films to ~500 nm in the annealed films, accompanied by an increase in the PLQY by about an order of magnitude (only). The degradation/conversion to the $\delta$-phase is investigated systematically for various deposition temperatures and Cs/Pb composition ratios in a humidity-controllable environmental chamber. Overall, a significantly enhanced stability is observed for the Cs-rich deposited perovskite samples.


SESSION EN08.05/EN09.05: Joint Session: Perovskite Solar Cell—A 10-Year Anniversary

Session Chair: Philip Schulz
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Back Bay AB

1:30 PM *EN08.05/EN09.05.01

Prospects of Perovskite PV Research Based on All-Inorganic Absorbers and New Dopant-Free Carrier Transporters

Tsutomu Miyasaka; Toin University of Yokohama, Japan

This year, we are celebrating 10 years of perovskite solar cell (PSC). Since our first discovery of PSC in 2009, enormous efforts have been put into different aspects of PSCs and the progress has been incredibly fast on all fronts. While preparing a comprehensive review[1] on the background, on-going R&Ds, and future direction of PSC research recently, we realized that, although efficiency level has gone beyond 24%, PSCs face serious challenges of practical stability and durability required for industrialization. Although compositional engineering of perovskites by mixing different cations and anions, using modulator molecules and mixing 2D and 3D structures have doubtlessly improved the stability of perovskites against heat and moisture, use of organic moieties still remain a challenge to improve the stability further. Intrinsic stability of the perovskite crystal structure and robust properties of carrier transport materials are going to be the keys to the long term durability of the device. In this respect, use of all-inorganic perovskite materials and combination with dopant-free carrier transport materials are highly desired. We have conducted some work in this direction which includes stabilization of CsPbI$_3$ black phase[2] and use of dopant-free hole transport materials (HTMs). Dopant-free HTMs combined with all-inorganic perovskites have yielded sufficiently high efficiency of 15%. Intrinsic thermal stability of the device was improved without using diffusible dopants. In our collaboration with JAXA, stability of perovskites was investigated in space environment for satellite applications. Here, organic cations in perovskite such as methyl ammonium are instable under exposure to vacuum and high temperatures >100°C. Perovskite materials demonstrate its high stability against exposure to high energy particle radiations (proton and electron beams) up to dose of $10^{15}$ particles/cm$^2$ due to use of thin absorber films that can avoid accumulation of particles and also exhibit defect tolerant nature. The lecture will also introduce our current efforts in making PSCs based on both lead and lead-free perovskites, and future perspectives of perovskite photovoltaics.

2:00 PM *EN08.05.02/EN09.05.02
Stabilizing Halide Perovskites—Self-Repair, Defects and Sealing David Cahen1,2; 1Weizmann Institute of Science, Israel; 2Bar-Ilan University, Israel

Halide Perovskites (HaPs) present a remarkable case of just stable (against decompositon into binaries) compounds that can function as active component for PV, light-emission and radiation detection, all demanding functions, over time periods that seem incompatible with their free energy of formation (again, from the binaries). Actually, the Achilles heel of the materials is their surface, true to Pauli’s famous dictum, because of the law of mass-action: as long as the system remains a hermetically close one, it can withstand the onslaught of electronic carriers and photons. Add to that that it are to a large extent the interfaces that make the devices function (again following a famous dictum, this time from Kroemer) and.. those are made with surfaces. Thus, what might appear esoteric materials chemistry and physics issues, are highly relevant for device design. In principle, apart from the remarkable self-healing ability (known to some extent also for CIGS) this is not new as nearly every (inorganic) semiconductor material that we use today went through the process of taming its surfaces to get control over interfaces made with them. In this talk I will, depending on developments in the half year between abstract writing and presentation, present data on the self-healing and (de)stabilization processes of HaPs and put their behaviour in perspective with respect to some other semiconductors, to arrive at insights that should be useful to device design and building.

2:30 PM *EN08.05.03/EN09.05.03
Molecular Dopants on Metal Halide Perovskite Surfaces—What Do We Learn? Antoine Kahn, Fengyu Zhang, Scott Silver, Joseph C. Hamill, Nakita K. Noel, Barry P. Rand and Lynn Loo; Princeton University, United States

Surfaces of metal halide perovskites (MHP) present an interesting set of questions and challenges that are only beginning to be addressed, namely the existence, origin, density and energy of electronic surface gap states. MHP surfaces are prone to ion diffusion and chemical reactions, and to degradation under various environmental conditions and probing tools, all of which likely induce some density of electronic gap states. In sufficient density, these states affect the electronic structure and optoelectronic performance of all MHP interfaces and devices. There is currently no consensus on potential profile and occurrence of band bending in perovskite films, from substrate to surface. Available data point to a strong dependence of these profile on the nature and surface potential of the substrate on which the films are fabricated, and on the perovskite processing conditions. Limits in Fermi level excursion have been observed and also point to some low density of (surface or bulk) gap states.[1] To address some of these issues, several groups have started to use organic molecular dopants (reductants and oxidants), as “gentle” probes of the electronic occupation and density of surface states, and as modifier agents of these states. [2,3] This talk describes our recent investigations of the interaction between molecular reductants (mostly [RuCp*Mes]2+) and oxidants (Mo(tfd)3 and derivatives) and surfaces of 3D MHPs CsPbBr3 and FAxMA1-xPb(IyBr1-y)3, and the 2D Ruddlesden-Popper phase BA2PbI4. Using a combination of electron spectroscopies and contact potential measurements, we determine the sign and magnitude of surface photovoltage occurring at these free surfaces, and the extent of surface energy level shifts resulting from charge exchange with the molecular dopants. We also show evidence obtained via photoemission spectroscopy of a density of (surface) filled states above the valence band maximum of FAPbBr3 following electron bombardment, and of MAPbI3, likely due to the presence of DMSO in the precursor solution. The role of surface doping in changing the occupation of these states will be discussed.


3:00 PM BREAK

3:30 PM *EN08.05.04/EN09.05.04
Understanding Defect Physics to Stabilize Metal-Halide Perovskite Semiconductors for Optoelectronic Applications Annamaria Petrozza; Istituto Italiano di Tecnologia, Italy
Semiconducting metal-halide perovskites present various types of chemical interactions which give them a characteristic fluctuating structure sensitive to the operating conditions of the device, to which they adjust. This makes the control of structure-properties relationship, especially at interfaces where the device realizes its function, the crucial step in order to control devices operation. In particular, given their simple processability at relatively low temperature, one can expect an intrinsic level of structural/chemical disorder of the semiconductor which results in the formation of defects.

Here, first I will summarize our understanding of the nature of defects and their photo-chemistry, which leverages on the cooperative action of density functional theory investigations and accurate experimental design. Then, I will show the correlation between the nature of defects and the observed semiconductor instabilities. Instabilities are manifested as light-induced ion migration and segregation, eventually leading to material degradation under prolonged exposure to light. Understanding, controlling and eventually blocking such material instabilities are fundamental steps towards large scale exploitation of perovskite in optoelectronic devices. By combining photoluminescence measurements under controlled conditions with ab initio simulations we identify photo-instabilities related to competing light-induced formation and annihilation of trap states, disclosing their characteristic length and time scales and the factors responsible for both processes. We show that short range/short time defect annihilation can prevail over defect formation, happening on longer scales, when effectively blocking undercoordinated surface sites, which act as a defect reservoir. Finally, based on such knowledge, I will discuss different synthetic and passivation strategies which are able to stabilize the perovskite layer towards such photo-induced instabilities, leading to improved optoelectronic material quality and enhanced photo-stability in a working solar cell.

4:00 PM *EN08.05.05/EN09.05.05
Understanding Surface Passivation in Methylammonium Lead Tribromide Single Crystals Maria Antonietta Loi; University of Groningen, Netherlands

The surface of hybrid perovskites plays a crucial role in the performance and stability of optoelectronic devices, as it strongly influences the recombination rate of excited charge carriers. Recently, it has been reported that molecular ligands such as benzylamine are capable of significantly reducing the surface trap state density in thin films. Here I will report on the mechanism that governs the surface passivation of hybrid perovskites by benzylamine. To this end, we developed a versatile approach to investigate the influence of benzylamine passivation on the well-defined crystal surface of freshly cleaved methylammonium lead tribromide single crystals. We show that benzylamine is capable of permanently passivating surface trap states in these single crystals, resulting in enhanced photoluminescence intensities and charge carrier lifetimes. Additionally, we show that exposure of the perovskite surface to benzylamine leads to replacement of the methylammonium cations by benzylammonium, thereby creating a thermodynamically more stable two-dimensional perovskite (BA)2PbBr4 on the surface of the 3D crystal. This conversion from a 3D to 2D perovskite drives an anisotropic etching of the crystal surface, with the {100} planes being most prone to etching.

4:30 PM RUMP SESSION: PANEL DISCUSSION—FUNDAMENTAL RESEARCH AND THE 10-YEAR ANNIVERSARY OF THE PEROVS KITE SOLAR CELL

SESSION EN08.06: Poster Session II: Perovskite Solar Cell—Processing, Additives, Material Development Session Chair: Kai Zhu
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EN08.06.01
Tungsten Trioxide (WO₃) as an Electron-Selective Transporting Layer for Perovskite Solar Cell Funsoo Kim, Seongrok Seo, Hyoungmin Park and Hyunjung Shin; Sungkyunkwan University, Korea (the Republic of)
Tungsten trioxide electron-selective transport layer (ETL) was formed by sol-gel method using acetylated peroxotungstic acid (APTA) solution as a precursor. The formed layer was in triclinic phase, as shown by the x-ray diffraction patterns. Both compact and mesoporous structure can be made using the same precursor solution and process, but with the Polyethylene glycol as an additive for the mesoporous films. Electronic and optoelectronic properties of the synthesized WO₃ ETL was determined from electrochemical impedance spectroscopy, photoluminescence, and UPS measurement. Three types of WO₃ layer was used for the cell fabrication, which were in compact, mesoporous, and mesoporous/compact double layer. Also, the effect of TiO₂ interlayer for the cell performance was also studied.

EN08.06.02
The Power of the Crowd—What Could be Learned by Collective Pooling of All the World’s Perovskite Device Data and How Do We Get There? Tor J. Jacobsson¹ and Eva L. Unger¹,²; ¹Helmholtz-Zentrum Berlin fur Materialen und Energie GmbH, Germany; ²Lund University, Sweden

Much research related to perovskite solar cells follows a familiar pattern. A group of postdocs and PhD students enter the lab where they with skill and determination meticulous handcraft a staggering number of solar cells, where after they carefully measure the device characteristics of the cells. This process triggers the writing of papers in which insights are summarised, and where a subset of the generated data is used for plotting figures and filling tables. Over the last ten years, this has been repeated about 10000 times. Sadly, much of the data presented in figures are non-trivial to extract, and much of the raw data newer leaves the hard drives of the students doing the work, and when they move on, the data is many times forever lost in the growing heap of unconsidered data. We firmly believe that much could be gained if more of this data could be stored in one place where it is easily accessible for the research community. So is also an increasing number of funding agencies. Such a collection of data could lead to new insights that are hard to get when the data is scattered over thousands of articles, and it could thus be a way to accelerate the pace of development. In this project, we are working on creating a platform for what could be described as a Wikipedia of perovskite device data. We will in this presentation describe what we have created, what can be conclude from the data so far accumulated, as well as the potential benefits for the perovskite community and beyond if this approach to data sharing reach full penetration in the field.

EN08.06.03
Recrystallization Mechanism of Pure and Binary MASn,Pb₁₋ₓIₓ Perovskite Complex with Methylamine Vapor Akash Singh¹,² and Sushobhan Avasthi¹; ¹Indian Institute of Science, India; ²Duke University, United States

With the advent of the deployment of halide perovskites in optoelectronics, various combinations of precursor halide salts have been tried to tune the perovskite’s photophysical properties which include changing the stoichiometric ratio of different ions that make up the perovskite structure. Simple compositional engineering opens a new world to tune the bandgap from 1.1 to 3.0 eV making the fabrication of all perovskite tandem devices and IR-RGB LED’s possible. One way to achieving efficient and stable perovskite photovoltaic devices is through improving the crystallinity and morphology of the active absorber layer. Due to the different chemistry of various halide precursors in solution, it is difficult to develop a common processing condition for thin film deposition of all the compositionally engineered perovskite.

In this work, we demonstrate a common post-deposition vapor annealing technique that improves the quality of pure and binary MASₙPb₁₋ₓIₓ perovskite thin-films. MAPbI₃ perovskite forms an optically bleached frustrated intermediate complex (MAPbI₃-xMA) when exposed to methylamine (MA) vapor for 3 seconds at room temperature. Upon removal at 25°C, the complex decomposes and gives back MAPbI₃ parent phase in the next 2-3 seconds with degassing of MA gas. This increases the surface coverage from 90 to 100% with uniform grains of 200 nm size as compared to needle-like non-uniform crystals obtained in as-deposited control films. MA exposure improved the crystallinity and carrier lifetime of these films by two times. The grain sizes are further increased to 10-15 microns by prolonging the recrystallization time to 90 minutes in a MA filled pressure-controlled glass reactor heated at 140°C.

In the case of pure MASnI₃ films, the MA exposure results into optically bleached stable Lewis pair amorphous complex of SnI₂-xMA at room temperature, with MAI crystalizing out of the film as confirmed by XRD. We find that prolonged heating of MA exposed film at 140-150°C breaks the complex back to SnI₂ which simultaneously
reacts with MAI resulting into MASnI$_3$ parent phase. Annealing below 150°C results into partial conversion to perovskite with remnant MAI primary XRD peak appearing at $\sim$10°. Annealing beyond 150°C leads to degradation of films into SnI$_2$. A step-annealing technique on MA exposed films is employed whereby the temperature is progressively increased from 25°C to 150°C and maintained at 150°C for 60 minutes to control the nucleation and grain-growth kinetics. This technique increases the grain size from 100-150 nm in as-deposited films to 1-2 microns in step-annealed films along with 7 times improvement in film crystallinity. Due to lower grain boundary density, the oxygen and moisture permeation is checked leading towards 75 nm of Burstein-moss red-shift in the absorption onset. This reveals that step-annealed MASnI$_3$ films (1.2 eV) are fairly less doped as compared to degenerate p-type self-doped as-deposited MASnI$_3$ films (1.3 eV).

For the binary MASn$_{0.5}$Pb$_{0.5}$I$_3$ (1.2 eV) perovskite films, the MA exposure forms an intermediate stable complex, but it doesn’t show any characteristic XRD peak of MAI instead, an unknown peak at 11.3° is observed, which diminishes as the film is annealed. At 85°C, the parent MASn$_{0.5}$Pb$_{0.5}$I$_3$ perovskite phase is fully recovered. Annealing below 85°C results into partial conversion to perovskite, whereas annealing beyond 85°C results into the small appearance of PbI$_2$ peak at 12.6° suggestive of degradation onset. The recrystallization temperature increases with increase in Sn content in MASn$_x$Pb$_{1-x}$I$_3$ films from 25°C, 85°C to 150°C for x = 0, 0.5 and 1.0 respectively suggestive of different affinity towards MA following different complex formation and recrystallization mechanism. The MA vapor annealing method provides a way to obtain high quality pure and binary MASn$_x$Pb$_{1-x}$I$_3$ perovskite thin-films to be employed in tandem and singlet fission devices leading towards enhanced efficiency.

EN08.06.04
Understanding the Role of Antisolvent Quenching in Film Formation, Device Performance and Reproducibility of Triple Cation Perovskite Solar Cells Alexander Taylor, Qing Sun, Fabian Paulus and Yana Vaynzof; University of Heidelberg, Germany

Hybrid organic-inorganic perovskite materials have taken the photovoltaic (PV) research world by storm, setting new power conversion efficiency (PCE) records at an unprecedented rate. However, significant irreproducibility issues continue to plague the field, even at world-leading laboratories. These issues are often due to small, unnoticed factors. For example, our group recently demonstrated that fractional variations in the precursor solution stoichiometric ratio significantly impact subsequent device performance. These findings motivated us to look for other hidden variables affecting the performance and reproducibility of perovskite PVs. Herein, we seek to further our understanding of the root causes of this irreproducibility by closely examining the fabrication procedure of cutting edge triple cation perovskite solar cells. Through a variety of characterization techniques including electron microscopy, x-ray diffraction, and others, we reveal that subtle differences during the critical “antisolvent” fabrication step lead to significant microstructural changes, and thus dramatically affect the final PV performance. By deliberately introducing device-to-device variation in this step, we find that perovskite film formation is highly altered, and show that the resulting PCE can vary from over 21% to less than 15%, for devices fabricated in the same batch and from the same precursor solutions. Additionally, we performed these experiments with 15 different antisolvents, and find that they fall into four categories based on their physical and chemical properties, with each possessing significantly different optimal processing conditions. Furthermore, by careful control over the antisolvent fabrication step, high performance (~20% PCE) can be obtained using almost all studied antisolvents. These results challenge some of the prevailing beliefs currently held by the research community, regarding not only what the highest performing antisolvents are, but also in general the role of the antisolvent in fabricating high performance perovskite solar cells.


EN08.06.05
Maximizing the External Radiative Efficiency of Hybrid Perovskite Solar Cells Dane W. deQuilettes; Massachusetts Institute of Technology, United States

Despite rapid advancements in power conversion efficiency in the last decade, perovskite solar cells still perform...
below their thermodynamic efficiency limits. Non-radiative recombination, in particular, has limited the external radiative efficiency and open circuit voltage in the highest performing devices. I will review the historical progress in enhancing perovskite external radiative efficiency and determine key strategies for reaching high optoelectronic quality. Specifically, I will focus on non-radiative recombination within the perovskite layer and highlight novel approaches to reduce energy losses at interfaces and through parasitic absorption. I will highlight a rapid photoluminescence method capable of quantifying non-radiative loss throughout the device stack. By strategically targeting defects, it is likely that the next set of record performing devices with ultra-low voltage losses will be achieved.

EN08.06.06
Extending the Photovoltaic Response of Perovskite Solar Cells into the Near-Infrared with a Narrow Bandgap Molecule
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Metal halide perovskite solar cells (PSCs) have attracted much attention due to the rapid increase in their power-conversion efficiencies (PCEs), and their amenability to solution-processing and low-cost manufacturing. Typical lead (Pb)-based 3D perovskites show an onset of light absorption around 800 nm; extending light absorption beyond 800 nm into the near-infrared (NIR) of such photoactive layers should increase photocurrent generation and further improve photovoltaic efficiency. While efforts to tune and formulate new materials compositions have resulted in tin (Sn)-containing perovskites with narrower bandgaps than their Pb-counterparts, these new materials exhibit low chemical stability, and are often more prone to oxidation compared to Pb-based perovskites. Tandem structures composed of two or more sub-cells with complementary absorption profiles serially connected have also demonstrated enhanced photo-response compared to single-junction Pb-based perovskite solar cells. The use of a tandem structure, however, necessarily complicates processing and dramatically increases device complexity. There currently does not exist a simple and effective strategy to enhance the NIR photovoltaic response of PSCs. Here, we demonstrate a facile approach to incorporate a NIR-chromophore that is also a Lewis-base, namely IEICO-4F, into an active layer comprising CsFAMAPbI3 to broaden its photo-response and increase its photovoltaic efficiency. Given the energy-level alignment between the organic chromophore and perovskite, efficient hole and electron transfer take place readily. Compared with control experiments conducted on PSCs without IEICO-4F, these solar cells generate photocurrent in the NIR, beyond the band edge of perovskite. Given the Lewis-basic nature of IEICO-4F, its addition to the photoactive layer also effectively passivates perovskite defects. These films thus exhibit significantly reduced trap densities, enhanced hole and electron mobilities, and suppressed illumination-induced ion migration. As a consequence, perovskite solar cells with IEICO-4F exhibit an enhanced PCE of 21.6% relative to those without IEICO-4F at 20.0%, and substantively improved operational stability under continuous one-sun illumination. Borrowing from the organic photovoltaic playbook, we have successfully demonstrated the effectiveness of incorporating a narrow bandgap chromophore to extend the photoresponse of perovskite absorber. The judicious selection of the organic chromophore simultaneously increases photovoltage and photocurrent generation to PSCs, and imbues enhanced stability to their operation.

EN08.06.07
Improved Perovskite Solar Cell Efficiency by Tuning the Colloidal Size and Free Ion Concentration in Precursor Solution Using Formic Acid Additive
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Improving the quality of the perovskite active layer is crucial to obtaining high performance perovskite solar cells (PSCs). In this work, by introducing formic acid into the formamidinium lead iodide (FAPbI3) precursor solution, we managed to achieve reduced colloidal size in the solution, leading to more uniform deposition of FAPbI3 film with lower trap state density and higher carrier mobility. The solar cells based on the FAPbI3 absorber layer modified with formic acid show significantly better photovoltaic performance than that on the reference FAPbI3 film without formic acid. The device performance shows a close correlation with the colloidal size. Within the range studied from 6.7 to 1.0 nm, the smaller the colloidal size is, the higher the solar cell efficiency. More specifically, the cell efficiency is improved from 17.82% for the control cell without formic acid to 19.81% when 0.764 M formic acid was used. Formic acid has also been added into a CH3NH3PbI3 (MAPbI3) precursor solution, which exhibits a similar effect on the resulting MAPbI3 films and solar cells, with efficiency improved from 16.07% to 17.00%.
Ordered Orientation and Compact Molecule Packing Due to Coplanar Backbone Structure of Interlayer—Improvement in Fill Factor for Photovoltaic Device

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A novel alcohol/water-soluble small molecule was obtained using a p-type planar backbone. The synthesized molecule was dissolved in organic solvents and highly polar solvents. The 3,3’-((3,3”-dimethyl-[2,2’;5’,2’’:5’’,2”’-quarterthiophene]-5,5”-diyl)bis(4,1-phenylene))bis(oxy))bis(N,N-dimethylpropan-1-amine) (QTA) film exhibited a red-shifted spectrum compared with the solution spectrum owing to its many more planar molecular conformations in the solid state. According to X-ray diffraction (XRD) measurements, the QTA film showed sharp diffraction peaks near 3.6–11.0°, which indicates the formation of an interdigitated and ordered structure as an out-of-plane peak (100) due to the alkyl side chain of the quarter-thiophene backbone. A comprehensive analysis of the out-of-plane and in-plane XRD data suggests that a large fraction of the QTA derivatives was oriented edge-on relative to the substrate. A photovoltaic device containing QTA exhibited an open-circuit voltage of 0.85 V, current density of 15.5 mA/cm², fill factor of 62.9%, and power-conversion efficiency of 8.4%. The photovoltaic device containing the QTA derivative exhibited improved power conversion efficiency compared with those containing PFN (8.0%) due to the ordered orientation and compact molecule packing of QTA. Moreover, the PCE values of the device with QTA decreased by only approximately 91 ~ 92 % after 450 hours, which showed superior durability compared with that with PFN (68 ~ 69 % after 450 hours) because of the electrochemical stability of QTA.

Influence of Antisolvent Dropping Speed and Time for Perovskite Layer Morphology

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Organic-inorganic hybrid halide perovskite has emerged as a light harvest material for solar energy. Perovskite has a lot of advantages such as low manufacturability cost, unique photoelectric properties and so on. Those properties are related to the morphology of perovskites such as grain size, pinhole, and thickness. Moreover, the most common method to synthesis perovskite is a solution process method. In that method, anti-solvent plays a critical role to get the optimal perovskite layer. The kind and volume of anti-solvent have been studied in recent years. Only a few people study influence about dropping speed and time of the anti-solvent. In our research, we use a fancy perovskite, triple cation perovskite (Cs0.17(MA0.83)100−XPb(I0.83Br0.17)3). Three anti-solvents (TL, TFT, and 1,2-DCB) were used to study which is the best one for the triple cation perovskite. We try the anti-solvent dropping speed from 0.6 ml/min to 4.8 ml/min under a constant time condition and dropping time from the 10s to 60s in certain dropping speed. The changes of morphology and phase have been observed. Grain size is decreased by increasing the speed and time. The density of pinhole and thickness also decreased. The amount of black α-FAPbI3 phase is increased when we increase speed and time. We can show that the performance of perovskite solar cell is increased to 7.66% in the normal environment by changing the anti-solvent dropping speed and time.

Thermal Evaporation Applied to Perovskite Materials—Chances and Challenges

Nadja I. Klipfel, Cristina Momblona, Hiroyuki Kanda, Cristina Roldan Carmona and Mohammad K. Nazeeruddin; Ecole polytechnique fédérale de Lausanne, Switzerland

Organic-inorganic metal halide perovskite solar cells are an emerging photovoltaic technology that has the potential to compete with commercially available silicon solar cells. Over the last decade, perovskite solar cells have have undergone significant development; reaching a high power conversion efficiency of 24.2% with low material and processing costs. However, most of these certified solar cells are processed from solution, depositing the perovskite layer from solvents such as dimethyl sulfoxide (DMSO) or dimethyl formamide (DMF). Solvent-free, vacuum-based methods are mature technologies widely adopted in the semiconductor industry but marginally explored for perovskite optoelectronics. Its suitability for large-scale fabrication of high-purity systems merges with the ability of precise control over film thickness and composition, low-temperature processing and the possibility of preparing multilayer structures. All these advantages call for more in-depth investigation of this alternative device preparation method. Here we present a detailed study of the chances and challenges of the vacuum-deposition process of hybrid inorganic/organic lead halide perovskites, which once completed, will facilitate the transfer from lab scale to large-
scale application.

2J. Avila; C. Momblon; P. P. Boix; M. Sessolo; H. J. Bolink, Joule 2017, 1, 431-442.

EN08.06.11
Mapping the Photocurrent and Photovoltage of Perovskite Films at the Nanoscale for Stability Studies
Chandra Shakher Pathak and Iris Visoly-Fisher, Ben-Gurion University of the Negev, Israel

Perovskite solar cells based on methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) and related materials have emerged as an exciting development for next generation photovoltaic technologies. Solar cells based on them have achieved impressive energy conversion efficiencies, but their stability is still limited. Understanding degradation mechanisms in such materials is key to developing strategies to increase their lifetime. The present work reports on the nanoscale characterization of perovskite photovoltaic films with respect to their stability and degradation mechanisms. We investigated the local conductance and surface potential variation of perovskite films at the nanoscale using conducting atomic force microscopy (CAFM) and Kelvin probe force microscopy (KPFM). CAFM measurements revealed that the current is larger at grain boundaries. The surface potential at grain boundaries and on top of the grain is almost similar which suggests a negligible energy barrier at grain boundaries. We investigated the effect of sunlight exposure on the nano-scale conductance and surface potential of perovskite thin films towards better understanding of photo-induced degradation mechanisms.

EN08.06.12
High Performance UV Photodetector Based on Perovskite-ZnO Heterojunction Structure
Dali Shao, Weiguang Zhu, Guoqing Xin, Jie Lian and Shayla Sawyer; Rensselaer Polytechnic Institute, United States

A high performance heterojunction ultraviolet (UV) photodetector was fabricated by growing vertical aligned ZnO nanowire arrays (ZnO NWAs) on ITO substrate followed by deposition of novel wide-bandgap inorganic perovskite Cs$_2$SnCl$_6$ nanoparticles (NPs) thin film on the top. The ZnO-Cs$_2$SnCl$_6$ heterojunction photodetector demonstrated a high external quantum efficiency of 86% at the wavelength of 378 nm and fast response speed with rise and fall time on the order of $\mu$s. In addition, the photodetector achieved a large linear dynamic range of 178dB. The excellent performance of this photodetector originates from enhanced separation and collection efficiency of the photo-generated carriers at the ZnO-Cs$_2$SnCl$_6$ hetero-interface, which will be discussed in details in terms of the energy band diagrams of the device and the carrier dynamics upon UV illumination. The results presented in this work may trigger further research interest in development of perovskite based heterojunction photodiodes.

EN08.06.13
Relationship between Lattice Strain Relaxation and Enhancement of Efficiency During Storage for Pb-Free Perovskite Solar Cells
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The certified efficiency of Pb perovskite solar cells (PSCs) with more than 1 cm$^2$ cell is reported to be 20.9%. In the smaller cells, the cell efficiency with 23.3% has been reported, which is close to those of multi-crystalline inorganic solar cells such as 22.3% of multi Si solar cells. However, the use of Pb in electronic is limited according to the EU RoHS Directive. Thus, it is desirable to develop Pb-free PSCs. Among Pb-free perovskite candidates, Sn perovskite is one of the most promising candidates for the light harvesting layer for the Pb-free PSCs, because they have perovskite structure similar to Pb-perovskite. The efficiency with more than 9% have been reported for Sn-PSC consisting of 2D and 3D structures. In this report, the efficiency increases during the storage in N$_2$. However, no clear explanation is given regarding this observation. We have also seen similar phenomena with our SnGe PSCs where the initial efficiency is 4.48% increased to 6.90% after 3 days. Here, we will discuss the efficiency enhancement from the viewpoint of perovskite lattice relaxation during storage time. The inverted structure of ITO / PEDOT:PSS / FA$_{0.70}$MA$_{0.25}$SnI$_3$ + GeI$_2$ (5 mol%) / C$_{60}$ / BCP / Ag / Au showed an efficiency of 6.3 % immediately after fabrication and the value increased up to 7.6 % after 6th day. The increased is mainly contributed by the
improvement of $V_{OC}$ and a slightly improved FF. Interestingly, the $J_{SC}$ remains the same throughout the study. Photoluminescence peak shifted from 920nm (1st day) to 910 nm (5th day). The lattice strain determined from the Williamson-Hall plot showed a value of 1.56% on the 1st day, and decreased gradually to 0.26% on the 5th day. These results show that the efficiency enhancement during storage phenomena can be explained through lattice strain relaxation.

**EN08.06.14**

**Hybrid Perovskites for Solar Cells—Atomic-Scale Insights into Local Structure, Defects and Charge Dynamics**

Dibyajyoti Ghosh$^{1,2}$, Amanda Neukirch$^1$ and Sergei Tretiak$^1$; $^1$Los Alamos National Laboratory, United States; $^2$University of Bath, United Kingdom

Further breakthroughs in perovskite solar cells require advances in new compositions and underpinning materials science. Indeed, a greater fundamental understanding of perovskite materials requires atomic-scale characterization of their underlying structural, defect and transport behaviour. In this context, combined modelling-experimental work is now a powerful approach for investigating these properties at the atomistic level. In my talk I will describe such studies on hybrid perovskites [1-3] into two related areas: (i) the beneficial impact of partial A-site substitution on the iodide ion diffusion in methylammonium lead iodide (MAPI). Combining ab initio modelling and multiple spectroscopic techniques, we demonstrate for the first time that partial guanidinium substitution into MAPI strongly suppresses iodide ion transport; [1] (ii) Application of strain for systematically modifying the photovoltaic performance of halide perovskites. Charge carrier generation, transport and recombination in these materials can be largely modified by controlled lattice distortion. [2-4] These insights are very important for the future design of stable perovskite solar cells with enhanced performance.


**EN08.06.15**

**Modeling of Aggregate State Effects on Electronic Properties of Hole Transporting Materials for Perovskite Solar Cells**

Yingqian Chen$^1$, Qian Liu$^2$, Aidan Brock$^2$, Steven Bottle$^2$, John Bell$^2$, John McMurtrie$^2$, Prashant Sonar$^2$ and Sergei Manzhos$^3$; $^1$National University of Singapore, Singapore; $^2$Queensland University of Technology, Australia; $^3$Institut National de la Recherche Scientifique, Canada

A key bottleneck on way to practical application of perovskite solar cells (PSC) is the development of non-expensive, sustainable and stable hole-transporting materials (HTM). Molecular HTMs hold much promise and already allowed obtaining power conversion efficiencies (PCE) in excess of 20% while often providing better stability than the reference Spiro-OMeTAD. Further developments are still needed to improve stability, cost, and efficiency.

Ab initio - typically at the DFT level - modeling is useful to obtain and compare key electronic properties of such materials which helps rationalize their performance and helps design them rationally. While it is relatively easy to perform molecular-level DFT modeling, as is done in much of the literature, ultimately solid HTM layers are used in devices, and it is important to include effects due to molecular aggregation. Specifically, at the single molecule level, there are no significant changes in the electronic properties such as frontier orbital energies or absorption spectra of molecules differing by the length of alkyl chains. Chain length is an important design variable; redox potentials and other properties of films are known to change with chain length; there can also be strong effect on charge transport which is not captured in molecular calculations.

We will present a combined Density Functional Theory (DFT) - Density Functional Tight Binding (DFTB) and Time-dependent (TD-) DFT/DFTB modeling of the effects of aggregate state on electronic properties of diketopyrrolopyrrole based molecular HTMs which showed PCEs of about 20%. Based on experimentally measured packing structures and computed electronic properties, we show that alkyl chain length can have effects on electronic properties which would be missed in molecular calculations and which are important to understand the differences in device performance with molecules featuring different chains.

**EN08.06.16**
Towards Light-Rechargeable Batteries Using Hybrid Perovskites  

Angus Mathieson, Felix Deschler and Michael De Volder; University of Cambridge, United Kingdom

Increases in the global energy demand necessitate the development of new approaches to energy conversion and storage. In particular, the utilisation of solar energy could provide a basis of evolving technologies capable of meeting modern and future demands.

By combining the photovoltaic and newfound electrochemical properties of organo-metal hybrid perovskite materials in a single device, a novel photobattery technology is proposed [1]. Utilising the photovoltaic performance of perovskite materials in combination with the intercalation and conversion mechanisms available to Lithium ion species, a device with the ability both to convert light to electrochemical energy and store it is demonstrated. The motivation for such a device will be discussed, with its inherent impact in areas such as off-grid energy solutions and the internet of things. The fabrication techniques are described and characterisation techniques common to both photovoltaic and electrochemical disciplines, with their recent results are discussed. Modifications are made to conventional electrochemical coin cells and pouch cells, in order to facilitate optical access to the electrode material. Using in-operando x-ray diffraction and optical probing, the fundamental mechanisms of charge storage and ion conversion are investigated both in the presence of light, to replicate a light-charging cycle and in the absence of light.


EN08.06.17

Halide Segregation in Perovskites—Unraveling the Impact on Open-Circuit Voltage  

Suhas Mahesh¹, James M. Ball¹, David P. McMeekin², Pabitra Nayak¹ and Henry J. Snaith¹; ¹University of Oxford, United Kingdom; ²Monash University, Australia

The success of perovskite-perovskite tandem solar cells hinges crucially on the development of efficient wide-bandgap cells. However, when the Bromide content is increased to widen the bandgap, cells cease to deliver the expected increase in open-circuit voltage ($V_{oc}$). This loss is usually attributed to halide-segregation in the perovskite. Naturally the question arises: how much voltage loss does halide-segregation incur? Our work answers this question by quantifying the $V_{oc}$ loss due to halide segregation using Fourier Transform Photocurrent Spectroscopy (FTPS) coupled with thermodynamic calculations. Our results show that the main voltage loss in contemporary Br rich perovskite cells is not due to halide segregation, but the relatively low initial luminescent radiative efficiency in the mixed halide thin films. We also present a model that quantitatively predicts expected voltage loss due to halide-segregation at different bandgaps and segregation severities. Our results suggest that $V_{oc}$ of up to 1.33V is within reach, even if halide segregation cannot be suppressed, and that focusing upon maximising the initial radiative efficiency of the mixed halide films is more important than attempting to suppress halide segregation.

EN08.06.18

Light Intensity Modulated Ion Transport in p-i-n MAPb(I1-xBrx)3 Perovskite Solar Cells  

Hamza Javaid, Christie L. Ellis, Emily C. Smith and Dhandapani Venkataraman; University of Massachusetts Amherst, United States

We studied ion migration in p-i-n MAPb(I1,xBrx)3-based solar cells at varying AM1.5G light intensities with electrochemical impedance spectroscopy (EIS). We calculated the diffusion coefficients ($D$), ionic conductivities ($\sigma_{ion}$), and capacitive elements for each hybrid organic-inorganic perovskite (HOIP)-based device. We found that $D$ values increase with increasing illumination intensity in MAPbI3, MAPb(I0.8Br0.2)3, and MAPb(I0.6Br0.4)3, whereas in MAPbBr3, MAPb(I0.4Br0.6)3, and MAPb(I0.2Br0.8)3 compositions, $D$ values exhibit a weak dependence on light intensity. Furthermore, we compared the magnitude of ion diffusion in different compositions of MAPb(I1,xBrx)3 (x= 0.2 to 0.8) and found that MAPb(I0.8Br0.2)3 has the highest resistance to ion diffusion. Interestingly, the MAPb(I0.8Br0.2)3 devices show a superior charge extraction capability to both MAPbI3 and MAPbBr3 devices. Based on our impedance analysis, we expect the MAPb(I0.8Br0.2)3 composition to be more stable and efficient than pristine MAPbI3.
Lower Toxicity Solvents for High Speed Manufacturing Richard M. Swartwout, Dak B. Dou and Roberto Brenes; Massachusetts Institute of Technology, United States

Metal organic perovskite materials have shown promise as solution processable, high efficiency, optically active semiconductors for a variety of applications. This amazing property has led many to believe these materials are capable of high-speed roll-to-roll manufacturing for large solar cells and LED displays. However, the main solvents used to dissolve traditional precursor materials are undesirable from a toxicity, coating and manufacturing perspective. Solvents like DMF and Acetonitrile are readily absorbed through the skin and are highly toxic. DMF has high surface tension, viscosity and a high boiling point limiting upper manufacturing speeds. In addition, these solvents have legally regulated exposure limits in both the United States by the Occupational Safety and Health Administration (OSHA) or by the European Union Agency for Safety and Health at Work (EU-OSHA). These exposure limits have the overall effect of practically limiting coating speed under normal ventilation conditions or requiring specialized equipment for vapor management.

To solve this problem we turn to Lead-Alkylamine complex systems as they show promise for being able to extend the solubility of lead halides into additional organic solvents. We use the Hansen solubility model to dissolve solar cell perovskite precursors into a more benign and less limited mixed solvent system of Tetrahydrofuran and Methanol. Although the resulting perovskite film crystalizes in milliseconds, we show that high power conversion efficiency is only achieved when the solution is doped with multiple organic halides improving charge carrier diffusion length as well as external photoluminescence quantum yield. This work provides a path forward for a more benign and industry focused solvent system for perovskite devices.

EN08.06.20

Machine-Learning-Assisted Design of 2D Capping Layer for Improving Perovskite Solar Cells Stability Noor Titan Putri Hartono, Shijing Sun, Zhe Liu, Armi Tiilhonen, Felipe Oviedo, Jason Yoo, Janak Thapa, Jose D. Perea, Rafael Gomez-Bombarelli and Tonio Buonassisi; Massachusetts Institute of Technology, United States

Despite perovskite solar cells (PSCs) efficiency reaching 24.2%, PSCs stability is still well behind 25-year-stable silicon wafer solar cells. To push PSCs into commercialization, improving their environmental stability is a critical step. Recent studies by Zhou et al., and Dong et al. have suggested that depositing 2D perovskite capping layer, which is also known as buffer layer in PV community, between perovskite absorber and hole-transport layers in a device can improve both environmental stability under ambient temperature with 40%-50% relative humidity (RH) and efficiency by up to 20% relative improvement [1], [2]. Understanding how various 2D perovskim capping layers can be optimized will help improving the cells stability and device architecture design process in the future. We propose a detailed study exploring 7 different types of 2D perovskites for interface layer with methylammonium lead iodide (MAPI) as the photon-absorber layer. The samples are degraded in a well-controlled environmental chamber, under high humidity (85% RH), heat (85°C), and illumination (0.17 sun). In order to accelerate the exploration process of 7 different types of 2D perovskites and numerous deposition conditions, Bayesian optimization (BO) algorithm is used to rapidly optimize each capping layer’s stability based on their deposition conditions. The preliminary results show that optimized tetrabutylammonium iodide capping layer lasts 3.6 times longer than bare MAPI films. Furthermore, by comparing the stability of various types of 2D perovskites through X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscope (SEM) data analysis, we can deduce a capping layer design guideline in terms of grain size and film thickness for more stable perovskite solar cells.

References

EN08.06.21

Exploring the Limiting Open–Circuit Voltage by a Large Band Offset at the Interface between Electron Transport Layer and Tin-Based Halide Perovskite Layer Tomoyasu Yokoyama, Yu Nishitani, Yumi Miyamoto, Shohei Kusumoto, Taisuke Matsui, Kenji Kawano and Yukihiro Kaneko; Panasonic Corporation, Japan
Organic–inorganic lead halide perovskite materials have attracted great attention to realize low–cost and high–efficiency solar cells. The power conversion efficiency of Pb–based halide perovskite solar cells (PSCs) has increased from 3.8 % to above 20 % in the last decade[1,2]. Nevertheless, the toxicity and instability of Pb–based perovskite materials are preventing their commercial implementation. So far, Sn–based PSCs showed the most promising results in Pb–free perovskite solar cells with enough efficiencies. However, Sn–based PSCs showed a much smaller open–circuit voltage ($V_{oc}$) than Pb–based PSCs[3]. Many previous studies have focused on improve the quality of Sn-based perovskite layers, but the $V_{oc}$ of Sn–based PSCs has still been much lower than Pb–based PSCs

To increase the $V_{oc}$ of Sn–based PSCs, we focused on the interface between Sn–based perovskites and electron transport layers (ETLs). There is a large conduction band offset at the interface between Sn–based perovskites and TiO$_2$, which is often used as ETLs in both Pb–based and Sn-based devices. Such offset is essentially caused by the fact that Sn–based perovskites have the shallower electron affinity (EA) of -3.5 eV than Pb–based perovskites of -4.0 eV. Moreover, $p$–$n$ junction is mainly formed at interface between ETLs and Sn-based perovskite layers because Sn–based perovskites show $p$–type characteristics. So we investigated the relationship of the $V_{oc}$ and the conduction band offset between a perovskite layer and an ETL.

In this work, we use three oxides with different EA, SnO$_2$, TiO$_2$ and Nb$_2$O$_5$, as ETLs of formamidinium tin iodide (FASnI$_3$) PSCs. Each oxide was fabricated by the spin–coating or sputtering method. We measured that the EA of SnO$_2$, TiO$_2$ and Nb$_2$O$_5$ are -4.6 eV, -4.0 eV and -3.3 eV, respectively using the ultraviolet photoelectron spectroscopy and the UV–Vis spectroscopy. We demonstrated the performances of Sn-based PSCs in a planar $n$–$i$–$p$ heterojunction device (ITO/ATO/ETL/FASnI$_3$/PTAA/Au) using each oxide as ETLs. The $V_{oc}$ of 100 mV, 300 mV and 420 mV were obtained using SnO$_2$, TiO$_2$ and Nb$_2$O$_5$, respectively. The device with power conversion efficiency (PCE) reached 5.1 % using Nb$_2$O$_5$, which was higher than PCE of 2.5 % and 0.5 % using TiO$_2$ and SnO$_2$, respectively. As the conduction band offset between FASnI$_3$ and the ETL oxide become smaller, a $V_{oc}$ and a PCE of the device increase. Consequently, for Sn–based PSCs a conduction band offset of interface between ETLs and perovskites layers is an important factor to increase $V_{oc}$, and Nb$_2$O$_5$ is a good ETL material for high performance of Sn–based device.


EN08.06.22
The Fundamental Efficiency Limit of Perovskite-Perovskite Tandems and the Role of Light Coupling between Sub-Cells Alan Bowman, Edoardo Ruggeri, Miguel Anaya, Mojtaba Abdi-Jalebi and Samuel D. Stranks; University of Cambridge, United Kingdom

Metal halide perovskites have properties including strong absorption coefficients and long charge diffusion lengths (relative to film thickness) making them close to ideal for solar cells. For perovskite devices to achieve their efficiency limits, charge carrier recombination and the role of photon recycling within films must be better understood and controlled.

Current approaches to measure charge carrier recombination rates are typically based on time intensive and expensive transient spectroscopic measurements. Here we demonstrate that we can employ steady state approaches to extract these parameters, thereby allowing for faster screening of materials. We show the potential of this approach by a comparison with results from transient absorption spectroscopy.

To further understand photon recycling we use our methodology to quantify the photon escape probability. While there are some calculations of the escape probability in the literature, this quantity has not been previously quantified in metal halide perovskites, despite its importance for solar cell operation including photon recycling. We present measured values and compare with those previously calculated.

Using results from our rapid screening process we calculate the limiting efficiency and number of photon recycling events per initially absorbed photon within devices. We carry out calculations for a range of materials including low bandgap and wider gap mixed-halide perovskites. Our results show that in addition to minimising the charge trapping rate it is necessary to maximise the escape probability for optimal efficiency, thereby reducing the number of photon recycling events. We extend our analysis to two and three bandgap tandem configurations, demonstrating that photon recycling between absorber layers has a relatively small effect on efficiency at the maximum power
point. Our combined experimental and modelling approach allows us to target specific device parameters to reach limiting efficiencies.

References

EN08.06.23
Recovery of Decomposed MAPbI₃ Films Fabricated via Three Different Fabrication Routes Priyanka Chhillar, Bhanu P. Dhamaniya and Sandeep Pathak; Indian Institute of Technology Delhi, India

Mixed organic-inorganic or fully inorganic halide perovskite solar cells (PSCs) have drawn appreciable interest of research community as highly efficient light harvesters reaching efficiency of about 24% in a past few years. Despite its promising potentials to replace the other commercialized technologies, the principal hurdle is the instability issue when exposed to ambient environment. On the other one cannot wish away from the fact that lead (Pb) which is highly toxic and carcinogenic is an inseparable part of PSCs. Researchers worldwide have tried hard to replace it with some other non-hazardous counterparts but failed to achieve similar optoelectronic properties. Disposal of hazardous waste is also a major issue because of its high expenses, so safe disposal becomes a major hurdle especially for the developing countries.¹ Cost analysis studies of similar architectures have shown that a major fraction (40-60%) of the total cost embedded is owned by fluorine doped tin oxide (FTO) substrate.² Other profound contributor to the cost of the technology is the expensive spiro-OMeTAD hole transporting layer, but a number of efficient alternatives to spiro-OMeTAD have been testified. Compact titanium dioxide (TiO₂) which serves as electron transporting layer though not much cost intensive but consumes a good amount of primary energy owing to its high sintering temperature requirement. In our work we have tried efficient recycling of the final decomposed product, which is PbI₂ back to perovskite. The reuse of same Pb and hence underneath TiO₂ and FTO layers will cut down the cost of the technology, decreasing the payback time even further. This work renders a comparative study of the feasibility of efficient recycling in three different fabrication routes i.e. single step mixed halide, single step acetate and sequential deposition route. We encountered that all the films cannot be recovered expeditiously, which was corroborated from the XRD spectra. XRD spectra elucidated that the degraded sequentially deposited films cannot be completely recovered back to methyl ammonium lead iodide perovskite on incorporation of methyl ammonium iodide. Degraded sequentially deposited films have shown drastically improved crystallinity, which if somehow can be converted back to perovskite completely will result in altogether superior optoelectronic properties. Films deposited via single step acetate and sequentially deposition route has shown efficient recovery of optoelectronic properties as compared to single step mixed halide route, as ascertained from the steady state photoluminescence. Absorption spectra recorded have shown the recovery of the characteristic wide absorbance range back upon recycling. Reusing the same Pb multiple times without compromising with the optoelectronic properties will move the technology a step ahead in the path of commercialization.

References

EN08.06.24
Characteristics of Lead Iodide Deposited by Sputtering Method and Perovskite Preaparred from the Sputtered Lead Iodide WonKyu Lee1, Sang-Won Lee1, Jae-Keun Hwang1, Solhee Lee1, Soohyun Bae1, Yoonmook Kang2,3, Hae-Seok Lee2,1 and Donghwan Kim1,2; 1Korea University, Korea (the Republic of); 2KU-KIST Green School, Korea (the Democratic People's Republic of)

Perovskite solar cell shows great possibilities for the solar power field as exhibiting uprising power conversion efficiency from 3.81% to 23.7%. Recent study has been focused on how to get market competitiveness between other solar cells. Those attempts include deposition of perovskite on texture and large-area substrate such as textured silicon.
Perovskite layer has been mainly deposited on mesoporous or compact layer by spin-coating perovskite solution on substrate. Spin-coating method has its limitation in deposition on textured, large-area surface. It also uses a poisonous solvent such as dimethylformamide, dimethyl sulfoxide. Other deposition methods such as evaporation, electroplating and slot die coating have also been proposed as methods for depositing perovskite layer. To obtain conformal and uniform layer of perovskite material on a large-scale and textured substrate, radio-frequency (RF) magnetron sputtering can be used to deposit a uniform lead iodide film on the substrate first. Conformal perovskite layer can be prepared by sequentially interacting the lead iodide film with methylammonium iodide (MAI). Lead iodide deposited through sputtering shows uniformly packed and conformal films on planar or textured substrate. RF magnetron sputtering is competitive with other deposition methods because highly uniform and conformal lead iodide films can be deposited on textured and large-area substrate and mass production is available. Unlike evaporation method, it does not need high temperature environment hindering coating film on flexible substrate.

In this study, lead iodide films were deposited by RF magnetron sputtering. Uniform and dense lead iodide films are obtained on a 1.5 cm x 1.5 cm FTO-glass substrate coated with c-SnO2. Characteristics of film deposited under various sputtering conditions were analyzed and compared with conventional spin-coated lead iodide film. Lead iodide films deposited using same method on textured silicon were also investigated. Perovskite layer are prepared by loading certain amount of MAI solution on sputtered lead iodide films. The effect of loading time and concentration of MAI solution on formation of perovskite layer were studied. Several measurement methods were used including X-ray diffraction method, Raman spectroscopy, X-ray photoelectron spectroscopy, Ultraviolet-visible spectroscopy, Transmission electron microscopy and Atomic force microscope.

EN08.06.25

New Techniques to Extract Local Performance Parameters in Metal-Halide Perovskite Solar Cells Kyle Frohna, Miguel Anaya and Samuel D. Stranks; University of Cambridge, United Kingdom

Polycrystalline metal-halide perovskite thin films share many optoelectronic properties of their high quality, inorganic semiconductor counterparts. However, local heterogeneity of the perovskite has been shown to limit device performance. [1] Fundamental semiconductor properties such as the quasi-Fermi level splitting (QFLS), absorptance, Urbach energy and photoluminescence quantum efficiency (PLQE) energy are important metrics that determine the upper bound efficiency of solar cells made with these materials, however complete microscale measurements of these properties in perovskites have not been performed. While photoluminescence mapping is common in the field, confocal illumination and collection geometries are often employed which necessitates much higher illumination intensity and real effects can be masked by carrier diffusion away from the illuminated area. [2, 3] Wide-field illumination microscopy, where the entire imaged area is illuminated simultaneously, enables microscopy at solar cell relevant carrier densities. This technique has been used to investigate the local QFLS in perovskites, [4] and in other thin film technologies such as CIGS. [5]

Here we use a wide-field illumination, spectrally and spatially calibrated microscope to study thin films of MAPbI3 and triple cation perovskites (Cs0.05FA0.79MA0.16Pb(I0.83Br0.17)3) at 1 sun equivalent illumination intensities. We develop novel methods to measure absolute reflectance, transmittance and absorptance spectra of these films in addition to absolute-intensity calibrated photoluminescence spectra with diffraction limited resolution. Correlating these spectra allows the extraction of local QFLS, Urbach energy and PLQE. We examine local spatial correlations between these properties in order to test the assertions of detailed-balance at the scale of individual grains. The results reveal considerable microscale heterogeneity in many fundamental, device relevant parameters that, on average, match with macroscale observations. We see grain to grain heterogeneity in the emission, but also larger scale heterogeneity over clusters of tens of grains. Strikingly we find local PLQE variation by up to an order of magnitude. We also use the technique to identify the most effective defect passivation treatments to our films resulting in enhanced device performance. Finally, we note the potentially wide applicability of these methods to a broad range of other emerging semiconductor technologies.

4. El-Hajje, G., et al., Quantification of spatial inhomogeneity in perovskite solar cells by hyperspectral

EN08.06.26
Impact of Partial Pb\textsuperscript{2+} Substitution on Photostability and Photovoltaic Performance of APbX\textsubscript{3} Perovskites
Marina Ustinova\textsuperscript{1}, Nadezda Dremova\textsuperscript{2}, Keith J. Stevenson\textsuperscript{1} and Pavel Troshin\textsuperscript{1,2}; \textsuperscript{1}Skolkovo Institute of Science and Technology, Russian Federation; \textsuperscript{2}Institute for Problems of Chemical Physics of RAS, Russian Federation

Perovskite solar cells represent one of the most promising photovoltaic technologies. Over the past few years, the performance of perovskite solar cells was gradually improved up to >23%, which is close to the characteristics of crystalline silicon photovoltaics. However, high toxicity and low stability of complex lead halides used as absorber materials hamper commercialization of this technology. The compositional engineering of lead perovskites was actively pursued in order to improve their stability and/or performance. In particular, a partial or full replacement of Pb\textsuperscript{2+} in MAPbI\textsubscript{3} is highly desirable in terms of developing more environmentally friendly materials. Here we present a systematic study of lead substitution in MAPbI\textsubscript{3} with >20 different cations introduced in atomic concentrations ranging from 10\textsuperscript{-5} to 20\textsuperscript{-30%}. It was shown that replacing even minor fraction of lead could change significantly the perovskite film crystallinity and morphology. Importantly, the efficiency and stability of p-i-n and n-i-p perovskite solar cells were improved considerably by appropriate modification of MAPbI\textsubscript{3} films. Moreover, important relationships were established between the nature of the substituting ions (e.g. ionic radius or charge) and their effects on electronic properties and photovoltaic performance of the resulting hybrid perovskites. The obtained results should facilitate the rational design of more stable and less toxic absorber materials for advanced perovskite solar cells.

EN08.06.27
Degradation of Hybrid Perovskite Absorber Layers from an Optical Perspective—An Ellipsometry Study
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Organic-inorganic hybrid perovskites are a class of semiconducting materials with great potential for solar cell absorbers. This is due to their high absorption coefficients, tunable direct bandgap, demonstrated high power conversion efficiencies in devices, and disruptively low manufacturing costs. However, they are currently limited by their tendency to degrade under strong (UV-)illumination, and elevated temperatures, both critical issues for a photovoltaic material. While these degradation effects have been widely reported in their electrical behavior, there is comparatively little information on the effects on their optical constants, the refractive index and absorption coefficient.

In this work we investigate the changes in optical constants of a variety of device relevant multi-cation perovskite compositions under the effects of UV light soaking and high temperatures. The compositions investigated include the widely used triple cation perovskite (Cs\textsubscript{0.05}(MA\textsubscript{0.17}FA\textsubscript{0.83})\textsubscript{0.95}Pb(Br\textsubscript{0.17}I\textsubscript{0.83})\textsubscript{3}), Rb-stabilized and methylammonium-free compositions (Rb\textsubscript{0.05}Cs\textsubscript{0.05}(MA\textsubscript{0.17}FA\textsubscript{0.83})\textsubscript{0.90}PbI\textsubscript{3}, Rb\textsubscript{0.05}Cs\textsubscript{0.10}FA\textsubscript{0.85}PbI\textsubscript{3}), as well as MAPbI\textsubscript{3} for comparison. UV light soaking was performed with a Xe lamp in air, and heating was done in a high temperature stage with nitrogen purging at 100°C and 120°C. The optical measurements were carried out using Variable Angle Spectroscopic Ellipsometry in the wide wavelength range of 190 nm – 25 μm, from the UV to the Middle Infrared (MIR). We demonstrate that it is possible to observe degradation effects around the bandgap and high absorption regions, which are of interest for solar cell performance, while changes in chemical composition can be observed at the same time through the MIR absorption bands.

A variety of behaviors were observed with increasing degradation time under both UV and heat exposure. The most recurring was a rapid loss of methylammonium ions from the film. This was visible as a reduction of IR peaks associated to methylammonium and a decrease in film thickness, which was confirmed by SEM imaging. IR peaks related to formamidinium ions also showed a decrease, but the rates were much lower. The loss of methylammonium was coupled with phase segregation and the formation of PbI\textsubscript{2} in the film: at energies above 2 eV, a superposition of the absorption coefficients of PbI\textsubscript{2} and the base perovskite was observed, with the bandgap of PbI\textsubscript{2}
clearly visible at 2.4 eV. Overall, the most UV stable composition was the standard triple cation perovskite, closely followed by the methylammonium-free \( \text{Rb}_{0.05}\text{Cs}_{0.10}\text{FA}_{0.85}\text{PbI}_3 \), which showed the best thermal stability.

**EN08.06.28**

**Synthesis and Characterization of Halide Hybrid Perovskites by Sequential Physical Vapor Deposition**  
Juvet N. Fru, Nolwazi Nombona and Mmantsae M. Diale; University of Pretoria, South Africa

Recently, the interest in low-cost hole-conduction-layer-free perovskite solar cells is growing rapidly due to the high-power conversion efficiencies (exceeding 17 \%) recorded [1]. Previous studies have reported that halide hybrid perovskites thin films produced a more stable and efficient hole-conduction-layer-free solar cell when compared with its non-hybrid halide perovskites components, owing to their excellent blend of light absorption and hole-conduction properties [2]. However, far too little attention has been paid to their synthesis by physical vapor deposition, which may further increase stability. Herein, a hybrid methylammonium lead tri-iodide/methylammonium lead tri-bromide (MAPbI\(_3\)/MAPbBr\(_3\)) perovskite thin film was prepared by sequential physical vapor deposition of MAPbBr\(_3\) on MAPbI\(_3\) thin film. The structural, optical, morphological and electrical properties of the MAPbI\(_3\), MAPbBr\(_3\), and MAPbI\(_3\)/MAPbBr\(_3\) thin films were compared. X-ray diffraction patterns confirmed the tetragonal crystal structure of MAPbI\(_3\), a cubical structure of MAPbBr\(_3\) and the two clearly separate phases for MAPbI\(_3\)/MAPbBr\(_3\) [3]. In addition, the crystallite sizes were observed to decrease from 32.74 to 22.06 nm while dislocation density increased from 9.33 x 10\(^{10}\) to 2.05 x 10\(^{11}\) cm\(^{-2}\) for MAPbI\(_3\), MAPbI\(_3\)/MAPbBr\(_3\), and MAPbBr\(_3\) respectively. UV-Vis absorption spectra revealed onsets of absorption for MAPbI\(_3\), MAPbI\(_3\)/MAPbBr\(_3\), and MAPbBr\(_3\) at 760, 628 and 550 nm respectively, which correspond to respective optical bandgaps of 1.63, 1.97 and 2.25 eV. Scanning electron microscopy micrographs depicted densely packed grains which fully covered the substrates, required to minimize leakage currents. Electrical properties showed that the trap densities increased from 2.56 x 10\(^{15}\) to 1.89 x 10\(^{16}\) cm\(^{-3}\) whereas the carrier mobilities decreased from 2.34 x 10\(^{-1}\) to 1.89 x 10\(^{-2}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for MAPbI\(_3\), MAPbI\(_3\)/MAPbBr\(_3\), and MAPbBr\(_3\) respectively. This study introduces a facile way of growing hybrid halide perovskites thin films for efficient hole-transport-layer-free solar cells.

Keywords: Hybrid methylammonium lead tri-iodide/methylammonium lead tri-bromide; sequential physical vapor deposition; hole-conduction-layer-free solar cell.

References


**EN08.06.29**

**Reap-Rest-Recovery Cycle in Perovskites Solar Cells from the Macro- to the Nanoscale**  
John M. Howard, Richa Lahoti, Erica S. Lee and Marina S. Leite; University of Maryland, United States

To date, the primary limitation of perovskite solar cell is still related to device instability. Because intrinsic and extrinsic factors such as light, temperature, bias, humidity, and oxygen can all contribute to material degradation, we propose the use of machine learning (ML) as a strategy to identify the individual and combined contribution of each aforementioned factor through a reap-rest-recovery cycle, which will be discussed in details. Moreover, we will present the dynamic electrical and optical behavior of MAPbI\(_3\), MAPbBr\(_3\), and multi-cation perovskites (including Cs and Rb ions) by implementing environmental atomic force microscopy (AFM) and micro-photoluminescence (micro-PL) microscopy. In the realm of the perovskite’s electrical response, we use Kelvin probe force microscopy (KPFM) and photoconductive (pc-) AFM to map changes in voltage and current that occur upon submitting the devices to different light treatments. Through fast-KPFM we quantify, in real-time, a dynamic open-circuit voltage (Voc) response as a function of chemical composition, resulting from ion motion. Optically, we resolve the correlation between the luminescence response of the perovskites and its chemical composition by exposing the perovskites to different environments, including loops in relative humidity ranging from < 5\% to 55\%. Combined, our microscopy probes enable us to define the contribution of each stressor to device instability, elucidating their effects on the physical behavior of the grains and boundaries composing the perovskite solar cells.

**EN08.06.30**

**Route to Efficient and Stable Perovskite Solar Cell—Interfacial Modification and Defect Passivation**  
Alan
Understanding the degradation mechanisms and realizing high operational stability have become major issues in perovskite photovoltaics. Especially, recent researches point that stable perovskite solar cells can be enabled by controlling defects of conventional devices, as well as developing novel materials.[1,2] Herein, based on our comprehension upon the defect characteristics and analyses,[3,4] we introduce our approaches for efficient and stable perovskite solar cells via the development of materials and trap controls. Using copper thiocyanate (CuSCN) for the inorganic hole-transport layer, we suggest polydimethylsiloxane (PDMS) as a novel crosslinking material for the interlayer between perovskite and CuSCN, which brings the effect of interfacial modification and defect passivation. With its unique crosslinking behavior observed, PDMS mitigates the trap formation and enhances the charge extraction at the interface realizing thermally stable perovskite solar cells with high power-conversion efficiency over 19%. By extension, further modification on the hole-transport layer is applied in order to prevent degradation of electrode and ionic interdiffusion, the dominant factors deteriorating the device performance under light and applied bias. Embracing our recent research on the stability of perovskite solar cells, the correlation between the interfacial defects and device stability will be discussed, with future insights to realize highly stable and efficient perovskite solar cells.


EN08.06.31
Enhanced Near-Infrared Photoresponse of Inverted Perovskite Solar Cells Enabled by Rational Design of Electron-Transporting Layer Chih-I Chen and Chu-Chen Chueh; National Taiwan University, Taiwan

Organic-inorganic hybrid perovskites solar cell (PVSC) has received worldwide attention in the past decade. Its power conversion efficiency (PCE) has struck to 24.2% from 3.8% since its first debut in 2009. Even though the perovskite materials possess exceptional semiconducting properties, such as ambipolar charge-transporting capability, low exciton binding energy, long carrier diffusion length, their generally light-harvesting range is limited in the visible-light region, from 300 nm to 800 nm, which engender great loss in spectral while illumination pass through the device. The enhancement in near-IR (NIR) region usually could be attained by composition engineering but the results were not significant, on the other hand, it could also be reached through device engineering but the researches mostly focused on conventional configuration. Herein, we describe a simple and accessible method to enhance the NIR photoresponse of inverted PVSC by rational design of electron-transporting layer.

In general, fullerene is the most commonly used ETL for inverted PVSCs. However, owing to its symmetric geometry, the light absorption of fullerene is quite weak. Recently, low bandgap non-fullerene acceptor (NFAs) with NIR light absorption has been vigorously develop in the field of organic photovoltaics. As inspired by this impressive progress, we herein conceive a study to enhance the NIR response of inverted PVSC by engineering the fullerene ETL with NFAs with NIR light absorption. Owing to the low bandgap, the NFA can form type II charge transfer with fullerene to dissociate the photoexcitation induced by NIR absorption. However, our result manifests that such binary blend is not sufficient to enhance the NIR photoresponse of derived inverted PVSCs. The ETL consisting of PCBM and NFA blend could not convert any near-IR photons into resulting photocurrent, as evidenced by the corresponding EQE spectrum. Intriguingly, we demonstrated a strategy to efficiently intercept the near-IR light and convert the photons into current through further modification of this hybrid ETL with NIR absorbing capability. As a result, the optimized near-IR ETL can enable its derived inverted PVSC to possess an extended photoresponse from visible region to 950 nm and present 40% EQE in the NIR region, contributing to 8.4% of the overall photocurrent (22.5 mA/cm²). Combined with the high Voc of 1.15 V and decent FF of 70%, an inverted PVSC with a high PCE of 18.1% was finally demonstrated. Our study unveils an effective approach to enhance the NIR photoresponse of inverted PVSCs through simple design of compatible charge-transporting layer.

EN08.06.32
Hyperspectral Photoluminescence Imaging of Spatial Inhomogeneities in Multi- Cation and –Anion Perovskite Absorbers Aslihan Babayigit1, Derese Desta1, Laura-Isabelle Dion2, Nicolas Rivas Rivas1, Frank
Renner¹, Koen Vandewal¹ and Hans-Gerd Boyen¹; ¹Hasselt University, Belgium; ²Photon Etc., Canada

Metal halide perovskites have witnessed a remarkable growth in efficiency that has yet to be recorded for any other photovoltaic technology to date (1). At the heart of these high performances lie exceptional material properties, which only in the recent years have started to be studied more profoundly alongside research efforts focusing on boosting the efficiency. An aspect attracting particular recent interest in this respect has been the significant impact of low fractional Cs substitution of the composition and the addition of sacrificial additives containing elements such as Rb, K and Na on the stability and/or performance of perovskite solar cells (2,3). Already clearly linked to effects such as halide homogenization in the light harvester, there are also strong indications that these compounds have an influence on crystallographic and phase intermediates of the soft and forgiving semiconductor (2,3,4). In an attempt to unravel the mechanism underlying the effect of these operations, this work studies the spatial photoluminescence of multi-cation and –anion perovskites by hyperspectral imaging. We demonstrate that sacrificial and substitutional compounds result in the elimination of distinct domains with varying intensities and emission maxima, which cannot be correlated to compositional inhomogeneities. Instead, we link this observation to effects inherent to the deposition method used to fabricate the absorber, and hypothesize that the observed results are due to strain effects in the semiconductor grains (5). In addition, we also elaborate on the stability of these PL inhomogeneities in terms of exposure to circumambient atmosphere, and reflect on their potential effects in corresponding devices.

References:
(1) NREL efficiency chart, 13th June 2019.

EN08.06.33
Electronic Structure Analysis of an Organometallic Halide Perovskite via Photoemission Yield Spectroscopy in Air for Stability Study Daisuke Yamashita¹, Yoshiyuki Nakajima¹, Satoshi Uchida² and Hiroshi Segawa²; ¹Riken Keiki Co., Ltd, Japan; ²The University of Tokyo, Japan

An open counter [1] is a unique detector that can operate in air at atmospheric pressure to detect and count a small number of low-energy photoelectrons. Therefore, photoemission yield spectroscopy in air (PYSA) can be performed by employing an open counter as the detector [2]. PYSA has the unique advantage of measuring high energy-resolution and low photo-excitation energies in a non-vacuum environment. After the commercial model was released, it was used to analyze industrial materials, e.g., semiconductors, organic photoconductors, toners, organic light-emitting diodes, and magnetic disk drives. Furthermore, the successive change on the practical surfaces, such as fresh Al surface exposed to air [3], has been successfully observed.

PYSA measurement was performed as follows. UV light emitted from a deuterium lamp was monochromatized using a grating monochromator, which was then focused on the sample surface. The number of photoelectrons emitted from the sample surface was counted using an open counter.

In recent years, PYSA has been applied to measure halide perovskites [4, 5]. Last year, we proposed a novel PYSA measurement technique and examined the change in the threshold energy of photoemission, which corresponds to the first-ionization potentials, at approximately the phase transition temperature of CH3NH3PbI3 [6]. Here, we discuss the applicability of PYSA for evaluate the long-term stability of halide perovskites.

EN08.06.35
Spatial Correlation of Organolead Halide Perovskite Nanocrystals Photoblinking and Photodegradation by Single-Particle Photoluminescence Microscopy Juvinch R. Vicente\textsuperscript{1,1,2} and Jixin Chen\textsuperscript{1,1}; \textsuperscript{1}Ohio University, United States; \textsuperscript{2}University of the Philippines- Visayas, Philippines

Organolead halide perovskites (OHP) have emerged as a promising material for applications in photovoltaics, LEDs and light detectors. This group of materials offers the simplicity of wet-chemistry methods while keeping competitive optoelectronic properties. However, photodegradation of OHPs especially under ambient conditions and high intensity illumination has been a significant bottleneck for its commercialization. Although the actual mechanism for this detrimental phenomenon is still under debate, the role of surface defects has been proposed. Recently, the presence of these surface defects has also been associated to the stochastic photoblinking of OHP nanocrystals. Employing super-resolution localization methods, we were able to estimate the spatial distribution of these surface defects along a single OHP nanocrystal. We then deliberately expose the particles at elevated light intensity and ambient conditions and observe the spatial evolution of its photodegradation and correlated it with the estimated localization of surface defects.

EN08.06.36
Design of Structures in Lead Halide Perovskite Solar Cells by Optimizing Interfacial Charge Transfer and Transport Dynamics Yasuhiro Tachibana\textsuperscript{1,2}; \textsuperscript{1}RMIT University, Australia; \textsuperscript{2}Osaka University, Japan

Perovskite solar cells have been recognized as a newly emerging solar cell with the potential of achieving high efficiency with a low cost fabrication process. In particular, facile solution processed cell fabrication facilitated rapid development of optimum cell structure and composition. Over the last few years, the cell efficiency has exceeded 23%.

A typical perovskite solar cell employs a perovskite layer sandwiched by p-type semiconductor (such as spiro-OMeTAD, PEDOT or NiO) and n-type semiconductor (such as TiO\textsubscript{2}, ZnO or PCBM) layers. Following light absorption, an electron and a hole are separated at the perovskite film interface, and are collected at the back electrodes. Choice of the most suitable solar cell structure is crucial to improve the performance further. In this presentation, we will present parameters controlling charge separation and recombination dynamics at the perovskite interfaces employing a series of transient absorption and emission spectroscopies. Nanosecond transient emission spectroscopy (Vis-ns-TES) clarifies charge separation processes, while Vis-NIR submicrosecond-millisecond transient absorption spectroscopies (VisNIR-smm-TAS) identify charge separation efficiency and charge recombination rates. The mechanisms of interfacial charge transfer and recombination processes have been clarified. Correlation of the dynamics results with the solar cell performance will be discussed [1-4]. An optimum cell structure for methylammonium lead iodide (MAPbI\textsubscript{3}) perovskite sandwiched by TiO\textsubscript{2} and spiro-OMeTAD layers, among planar heterojunction, mesoporous structure and extremely thin absorber structure will be identified. The method to determine the best structure will be applied to a different type of semiconductor.

This work was financially supported by the JST PRESTO program (Photoenergy Conversion Systems and Materials for the Next Generation Solar Cells) and partly by JSPS KAKENHI Grants (16K05885) and (19H02813) and the Collaborative Research Program of Institute for Chemical Research, Kyoto University (grant number 2019-50), Japan. The author also acknowledges Australian Research Council (ARC) LIEF grant (LE170100235) and the Office for Industry-University Co-Creation, Osaka University, for the financial supports.

References
Hight throughput Fabrication of Efficient Perovskite Solar Modules and Tandem Solar Cells
Jinsong Huang; University of North Carolina at Chapel Hill, United States

The efficiencies of small-pixel perovskite photovoltaics have increased to well above 20%, while the question is whether fabrication methods can be transferred to scalable manufacturing process. Here we report a method of fast blading large area perovskite films at an unprecedented speed of 99 millimeter-per-second or higher in ambient condition by tailoring solvent coordination capability. Combining volatile non-coordinating solvents to Pb2+ and low-volatile, coordinating solvents achieves both fast drying and large perovskite grains at room temperature. The reproducible fabrication yields a record certified module efficiency with aperture area of 63.7 cm². The perovskite modules also show a small temperature coefficient of -0.13%/°C and nearly fully recoverable efficiency after 58 cycles of shading, much better than commercial silicon and thin film solar modules. The application of the coating method to perovskite/silicon tandem cells and will also be presented. We will answer the question whether the perovskite layers can be fabricated at the speed of silicon cells are produced in the regular production lines.

Correlating the Performance of Perovskite/Silicon Tandem Solar Cells with Their Nanostructure
Quentin Jeangros1, Florent Sahli1, Peter Fiala1, Ricardo Z. Razera1, Fan Fu1, Daniel Jacobs1, Chien-Jen Yang1, Vincent Paratte1, Olivier Dupré1, Gizem Nogay2, Brett A. Kamino2, Saeid Rafizadeh2, Arnaud Walter2, Soo-Jin Moon2, Adriana Paracchino2, Marion Dussouillez2, Bertrand Paviet-Salomon2, Aïcha Hessler-Wyser1, Matthieu Despesse2, Mathieu Boccard1, Sylvain Nicolay2, Andrea Ingenito1 and Christophe Ballif1,2; 1EPFL PV-LAB, Switzerland; 2CSEM, Switzerland

Crystalline Si (c-Si) solar cells are driving the progression of renewable electricity generation technologies thanks to lowering costs and increasing efficiencies. One solution to maintain this cost-competitiveness on the long-term involves increasing efficiencies beyond the limit of c-Si by stacking a perovskite solar cell on a commercial c-Si one to form a photovoltaic tandem device. The tunable bandgap, soft processing conditions and high single-junction performance of perovskites indicate that this approach could upgrade c-Si solar cells to efficiencies >30% through a few extra process steps with low additional process costs.

For maximum photocurrent and compatibility with existing c-Si process flows, the perovskite solar cell should be deposited directly on the textured front side of the c-Si solar cell, a texture that improves light management in the c-Si. But this pyramidal texture imposes several microfabrication challenges as the perovskite absorber is typically deposited via solution processing, and is about one order of magnitude thinner than the height of the pyramids it needs to cover. Achieving a conformal deposition of all the layers on the top cell on this pyramidal texture and hence maximum performance requires a fine control over the layer formation to avoid pinhole formation.

In that regard, electron microscopy techniques, notably analytical transmission electron microscopy (TEM), can shed some light on the device nanostructure and its dependence on processing/operation conditions, guiding the development of devices. However, the fragile nature of perovskite solar cells complicates their preparation into thin cross-sections necessary for TEM observations and their analysis with high-energy electrons. This presentation will review artifacts that may occur during TEM sample preparation and observation, elaborate several strategies to identify and mitigate them, before discussing several topics correlating nanostructure and performance of perovskite single-junction and tandem solar cells. This contribution will present how electron microscopy data coupled with other techniques provide valuable inputs to guide the development of high-efficiency (>25%) tandems featuring textured n- and p-type c-Si solar cells1,2, notably by i) identifying optimal bottom cell contact nanostructures, ii) isolating crystallographic and chemical features enabling the recombination junction to quench shunts,2 iii) guiding
the removal of shunts running through the perovskite absorber on textured c-Si by adapting process conditions and iv) visualizing the dewetting of charge-selective layers during the crystallization of the perovskite solar cell on certain recombination junctions. In addition, degradation pathways triggered by reverse voltages (also investigated through TEM in situ biasing experiments) during long-term operation at maximum power point at various temperatures, or during damp heat tests (85°C/85% relative humidity) will be examined. These results highlight the dynamic nature of the perovskite nanostructure (ionic migration within the absorber and into the contacts, volatilization of species, crystallographic phase change/decomposition) depending on the external stimuli and its influence on the solar cell performance.


9:30 AM *EN08.07.03/EN11.07.03
Towards Highly Efficient Monolithic Tandem Devices with Perovskite Top Cells Steve Albrecht1,2, Marko Jost1, Eike Köhnen1, Amran Al-Asghouri1, Lars Korte1 and Bernd Stannowski1; 1Helmholtz-Center Berlin, Germany; 2Technical University of Berlin, Germany

Integrating metal halide perovskite top cells with crystalline silicon or CIGS bottom cells into monolithic tandem devices has recently attracted increased attention due to the high efficiency potential of these cell architectures. To further increase the tandem device performance to a level well above the best single junctions, optical and electrical optimizations as well as a detailed device understanding of this advanced tandem architecture need to be developed. Here we present our recent results on monolithic tandem combinations of perovskite with crystalline silicon and CIGS, as well as tandem relevant aspects of perovskite single junction solar cells.

By selecting a front contact layer stack with less parasitic absorption and utilizing the p-i-n perovskite top cell polarity, a certified conversion efficiency of 25.0% for a monolithic perovskite/silicon tandem solar cells was enabled. Further fine-tuning of the stack optics as well as contact layers improved the efficiency to 26.0% (0.8 cm² area) and we present how especially the fill factor of highly efficient tandem solar cells behaves under current-mismatch conditions. In strong mismatch the FF of the tandem cell is enhanced which reduces the sensitivity of efficiency to spectral mismatch. Additionally, the introduction of light trapping foils with textured surfaces is presented together with the influence on texture position on lab performance and outdoor energy yield.

The monolithic combination of perovskite and CIGS was highly challenging up to now as the CIGS surface is rather rough. By implementing a conformal hole transport layer, an 21.6% efficient monolithic perovskite/CIGS tandem (0.8 cm² area) was realised. Absolute photoluminescence of the perovskite and CIGS sub-cells gives insights into the contributions to the tandem open-circuit voltage (Voc). To further improve the tandem efficiency, the Voc of perovskite top cells needs to be enhanced via reduction of non-radiative recombination at the interface between perovskite and the charge selective layers. This can either be done via proper interlayers or via fine-tuned charge selective contacts.

Recently we have shown that self-assembled monolayers (SAM) could be implemented as appropriate hole selective contacts. The implementation of new generation SAM molecules enabled further reduction of non-radiative recombination losses with Voc’s up to 1.19 V and efficiency of 21.2% for p-i-n perovskite single junctions with band gaps of 1.63 eV and 1.55 eV, respectively.

References:

10:00 AM BREAK

10:30 AM *EN08.07.04/EN11.07.04
Efficient and Stable Wide-Bandgap Perovskite Solar Cells for Tandem Solar Cell Applications Yanfa Yan; University of Toledo, United States

Wide-bandgap (~1.7-1.8 eV) perovskite solar cells have attracted substantial research interest in recent years due to
their great potential to fabricate efficient tandem solar cells via combining with a lower bandgap (1.1-1.3 eV) absorber (e.g., Si, copper indium gallium diselenide, or low-bandgap perovskite). However, wide-bandgap perovskite solar cells usually suffer from large open circuit voltage ($V_{oc}$) deficits caused by small grain sizes and photoinduced phase segregation. We show that in addition to large grain sizes and passivated grain boundaries, controlling interface properties is critical for achieving high $V_{oc}$’s in the inverted wide-bandgap perovskite solar cells. We adopt guanidinium bromide solution to tune the effective doping and electronic properties of the surface layer of perovskite thin films, leading to the formation of a graded perovskite homojunction. The enhanced electric field at the perovskite homojunction is revealed by Kelvin probe force microscopy measurements. This advance enables an increase in the $V_{oc}$ of the inverted perovskite solar cells from an initial 1.12 V to 1.24 V. With the optimization of the device fabrication process, the champion inverted wide-bandgap cell delivers a power conversion efficiency of ~19% and sustains more than 72% of its initial efficiency after continuous illumination for 70 h without encapsulation. The improvement on performance of wide-bandgap perovskite subcells enables us to fabricate efficient and stable perovskite tandem solar cells.

11:00 AM *EN08.07.05/EN11.07.05

Tuning the Composition of Metal Halide Perovskites and Passivating Their Surfaces for Tandem Applications

Michael D. McGehee1,2; 1University of Colorado, United States; 2National Renewable Energy Laboratory, United States

The record power conversion efficiency is 28 % for perovskite-silicon tandems and 23.2 % for perovskite-perovskite tandems. One of the challenges that must be overcome to achieve efficiency greater than 30% is to reduce the voltage loss in high bandgap perovskite cells and prevent light-induced phase separation. We have found that treating the surface of perovskites can dramatically reduce the extent of light-induced phase separation, which has interesting implications for how the process occurs. We have also developed new strategies for increasing the bandgap in perovskite compounds that have modest amounts of bromine. We have been able to make semitransparent high bandgap solar cells with greater than 20% power conversion efficiency that do not suffer from light-induced phase separation. These advances in combination with improvements in the atomic layer deposition of highly impermeable metal oxide contacts enable the fabrication of highly efficient and stable tandems.

SESSION EN08.08: Perovskite Solar Cell— Stability and Degradation

Session Chairs: Prashant Kamat, Yabing Qi, Michael Saliba and Kai Zhu

Wednesday Afternoon, December 4, 2019
Sheraton, 2nd Floor, Back Bay AB

1:30 PM *EN08.08.01

Tracking Photo and Thermally Driven Halide Ion Movement in Metal Halide Perovskites

Prashant Kamat and Tor Elmelund; University of Notre Dame, United States

Halide ion mobility in metal halide perovskites plays an important role in determining the performance of perovskite solar cells. For example, the high ionic conductivity in MAPbI3 compared to the electronic conductivity along with high native ionic disorder leads to the trapping of the electronic carriers. The intrinsic ionic defects, specifically halide ion vacancies, often dictate the mobility of halide species within the perovskite film during the operation of solar cells. Whereas entropy of mixing explain the thermally activated mixing of halide ions to yield mixed halide perovskite, an opposite trend is observed when the mixed halide film is subjected to photoirradiation. This process, commonly referred as photoinduced phase segregation or halide segregation, yields Br-rich and I-rich perovskite domains. The interesting part is the total recovery when the film is left in the dark as thermal activation drives back to original composition. Formation of such Br-rich and I-rich domains severely affects the solar cell performance. The kinetic and thermodynamic arguments that explain the photoinduced halide segregation and dark recovery will be discussed.

2:00 PM EN08.08.02

Passivation Engineering for High Performance Perovskite Solar Cells

Damir Aidarkhanov1, Zhiwei Ren1,
The promising photovoltaic properties of organometallic halide perovskite based solar cells (PSCs) make it highly competitive with the existing solar technologies. Recently, the record power conversion efficiencies (PCEs) of 24.2 % for the single junction perovskite solar cell and 28 % for the monolithic perovskite/silicon tandem solar cell were reported. The rapid enhancement in device efficiency has attracted increasing attentions in the field of photovoltaics. Tremendous research efforts have been devoted to optimizing the performance of perovskite solar cells and increasing the device area to meet the criteria for future commercialization. Passivation engineering is an effective approach to enhance the stability and PCE of PSCs. In this work, we demonstrated effective passivation strategies for the bulk of mixed perovskite and the electron transport layer (ETL). Systematic experiments were conducted to investigate the electron transport materials (ETM) and their layer architecture. It is found that the SnO2 based ETM in a multilayer structure is superior in suppressing the $I-V$ hysteresis and enhancing the performance of PSCs due to the optimized morphology of the ETL and the passivation effects attributed to the presence of additional nanoparticles and thin films between the ETL/perovskite interface. The performance of PSCs can be further improved by incorporating a controlled amount of organic cross linker in the perovskite absorber. The experimental results obtained from photothermal thermal deflection spectroscopy, time resolved photoluminescence and scanning confocal microscopy show that an optimal amount of the organic cross linker can passivate the defect states in the bulk of mixed perovskite. However, excessive organic cross linkers will significantly lower the device performance of PSCs due to the generation of new defects and the insulating properties of the organic cross linker itself. A PCE of 19 % with negligible hysteresis can be achieved after careful optimizations of the perovskite absorber and material interfaces in PSCs. This work will provide useful information for the photovoltaic community to optimize the fabrication process of PSCs through the passivation engineering.

2:15 PM EN08.08.03
All-Vapor Processed Perovskite Thin Films by Close Space Vapor Transport Alexander Harding, Austin G. Kuba, Brian McCandless, Ujjwal Das, Babatunde Ogunnaike and William Shafarman; University of Delaware, United States

As the stability and efficiency of perovskite solar cells improve, methods for scaling laboratory performance to industrial production are increasingly sought after. Current efforts focus primarily on transferring the chemistry of spin-coating to high-throughput, continuous processes. However, perovskites are also compatible with vapor-processing, meaning that established thin film PV manufacturing methods could be used to address scale-up challenges. For instance, First Solar’s Vapor Transport Deposition (VTD) process has made CdTe the dominant thin film PV on the market; and VTD is particularly appealing for perovskites due to its high-throughput, dry processing and its highly efficient use of toxic material.

Here, an all-vapor process for CH$_3$NH$_3$PbI$_3$ perovskite deposition using close-space vapor transport (CSVT) is described, and its viability as a fabrication route is confirmed. The film is formed in a 2-step process with deposition of a PbI$_2$ precursor layer followed by its reaction in CH$_3$NH$_3$I vapor. A pilot C SVT reactor was designed and constructed with control of critical process variables including: source temperature, substrate temperature, system pressure, carrier gas flow rate, and the distance between the source and the substrate. As a result, a range of deposition rates, reaction rates, mass transport regimes, and morphologies are accessible which can be used to improve device performance.

Films of PbI$_2$ were deposited on CdS/ITO/SLG substrates in low vacuum at pressures ranging from 1 to 10 torr. CdS was chosen as the electron-selective contact due to its favorable band alignment with CH$_3$NH$_3$PbI$_3$ and its low-temperature, robust processing through chemical surface deposition. Temperatures, pressures, and deposition times were optimized for deposition of 200 nm films of PbI$_2$. At a source temperature of 260 °C, substrate temperature of 215 °C, and pressure of 1 torr, full coverage of the CdS substrates at the 200 nm target thickness was achieved after a 20 min deposition. Control of morphology and crystallinity in highly-oriented PbI$_2$ films was demonstrated, and their dependence on processing conditions will be described.

For the 2nd processing step, PbI$_2$ films were reacted with CH$_3$NH$_3$I vapor by CSVT to form CH$_3$NH$_3$PbI$_3$. 

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Temperature was found to have a significant effect on the rate of reaction and control of film morphology. At 160 °C, complete conversion from PbI$_2$ to CH$_3$NH$_3$PbI$_3$ is achieved within 10 min, but the CH$_3$NH$_3$PbI$_3$ grains coalesce at this temperature, leaving the CdS substrate exposed in the form of large pinholes. On the other hand, at 100 °C reacted films are pinhole-free with full surface coverage, but they require 150 min for complete conversion.

While isothermal reactions at 100 and 160 °C produced single-phase perovskites, reactions with a temperature gradient between the source and substrate promoted the formation of uncharacterized secondary phases. A brief rinse in isopropanol removes these phases, leaving behind only single-phase tetragonal CH$_3$NH$_3$PbI$_3$. The structure and composition of these secondary phases are under investigation, but it is possible that the temperature gradient promotes CH$_3$NH$_3$I deposition which drives an alternate chemical reaction.

Devices with CSVT CH$_3$NH$_3$PbI$_3$ films were completed with spin-coated, hole-selective spiro-OMeTAD and evaporated gold back contacts, and a 12.1% efficient cell with $V_{OC} = 980$ mV, $J_{SC} = 21.9$ mA/cm$^2$, and FF = 56.6% was measured. This result demonstrates the viability of CSVT as an all-vapor processing method for perovskite solar cells.

2:30 PM BREAK

3:30 PM *EN08.08.04

Ingenious and Multifunctional Synthesis Approach of In:CuCrO$_2$ nanoparticles for Highly Performed Perovskite Solar Cells Wallace C. Choy$^1$, Boping Yang$^2$ and Dan Ouyang$^1$; $^1$University of Hong Kong, China; $^2$Yancheng Institute of Technology, China

When there is no clear study of doped ternary metal oxide for efficient hole transport layers (HTL), we propose the ingenious and multifunctional synthesis approach of In doped CuCrO$_2$ nanoparticles (NPs) HTL including simplifying the synthesis requirements, enabling doping and achievement treatment-free HTLs. To be more specific, we demonstrate an azeotropic promoted approach (APA) to synthesize In doped CuCrO$_2$ nanoparticles (NPs) [1]. Remarkably, compared with the conventional method for synthesizing CuCrO$_2$ NPs, the reaction time is dramatically shortened by 90% and the calcination temperature is lowered by one-third, which not only promote the high throughput production but also reduce power consumption and cost in synthesis. Equally important, we successfully dope Indium into CuCrO$_2$, which is fundamentally difficult to low temperature process. The In doping offers less d-d transition of Cr$^{3+}$ and p-type doping characteristics for improving the transmittance and conductivity of the hole transport layer (HTL) respectively. Interestingly, the In doped CuCrO$_2$ HTL with these improvements can be achieved by simple ambient condition process and exhibits thermal stability up to 200 °C, which is beneficial for realizing highly performed perovskite solar cells (PSCs). Our results show that PSCs with the power conversion efficiency (PCE) of 20.54 % has been achieved with higher short-circuit current density ($J_{SC}$) and fill factor (FF) than that of the control PSCs with pristine CuCrO$_2$ NPs. Meanwhile, the devices show good repeatability and photostability. Consequently, we demonstrate an effective approach for realizing efficient HTL from the synthesis of material all the way to film formation featuring with substantial simplification of in synthesis conditions of In doping CuCrO$_2$ NPs to treatment-free high-quality film process for favoring the practical applications of highly performed PCSs.


4:00 PM EN08.08.05

High Efficient and Stable Organic Inorganic Hybrid Perovskite Solar Cells by Modulating Triple B Cations Using Ge-Pb-Sn Gyu Min Kim and Tsutomo Miyasaka; Toin University of Yokohama, Japan

With the development of compositional engineering, the power conversion efficiencies (PCE) and air stabilities of organic-inorganic hybrid perovskite solar cells (OlHPs) have been greatly improved. Triple A cations of Cs, MA and FA are the most popular compositions used in OlHPs recording high PCEs over 22%. Different from the modulation of cations in A site, manipulation of cations in B site is relatively limited compared to the cations in A site due to the quite unstable properties of elements used in B site such as Ge and Sn. Recently, the use of Ge$_2$I$_4$ in perovskite solar cells was reported to improve the PCEs and efficiencies of cells. However, Ge-Pn or Ge-Sn systems
were mainly focused on inorganic based perovskite solar cells because of extremely poor stability of GeI$_2$ when organic cations in A site such as MA and FA are used, leading to poor electronic performances. We found out that the incorporation of MACl in the precursor significantly improves the solubility of GeI$_2$ in the precursors. Based on this fact, the triple B cations composed of Pb-Sn-Ge were used in OIHPs based on organic A cations composed of MA and FA. As a result, general optoelectronic properties were improved with high Jsc and Voc leading to superior PCEs.

4:15 PM EN08.08.06
Towards Industrialization of Perovskite Solar Cells Using Slot Die Coating Anand Verma$^1$, David Martineau$^2$, Jakob Heier$^1$, Rene Schneider$^1$, Frank Nuesch$^1$ and Toby Meyer$^2$; $^1$Empa, Switzerland; $^2$Solaronix, Switzerland

Perovskite solar cells are the fastest developing solar cell technology till time. In a short span of time, power conversion efficiencies exceeding 23% in laboratory cells were reported by different research groups, hereby challenging existing dominant photovoltaic technologies. The focus of PeroPrint and the follow up project Upero-fundied by the Swiss Federal Office for Energy is to develop perovskite solar cells with high efficiency, using industrially relevant printing and coating techniques. The layered architecture of perovskite solar cells, as well as the ability of raw materials to disperse and dissolve into inks, opens the doors for solution processing of the cells. On the other hand, printing and coating technologies are large area deposition methods, which can drastically reduce production costs, especially when performed under ambient conditions. This is contrary to existing industrial photovoltaic products, which rather employ energy and waste intensive manufacturing techniques, such as high-purity ingot growth or vacuum deposition. The latter techniques also require huge capital expenditure to get production plants up and running at a profitable scale, a domain where simpler printing and coating techniques could lower the entry barrier to production.

In this project, we were able to develop novel inks to efficiently slot die coat the full stack of carbon based monolithic perovskite solar cells (Glass/FTO/compact TiO$_2$, mesoporous TiO$_2$, mesoporous ZrO$_2$, carbon with infiltrated MAPbI$_3$ into the porous structure) with power conversion efficiencies exceeding 12% for a large area cell. Here we also demonstrate an inventive co-firing method to fabricate monolithic perovskite solar cells where only one high temperature step is required in comparison to four reported till time for this architecture, thus reducing the fabrication time from 14 hours to 3.5 hours. We also demonstrate high shelf-life of the slot die coated cells exceeding 1 year when stored under ambient condition without any encapsulation.

4:30 PM EN08.08.07
Thermal Stability and Degradation Mechanism of Halide Perovskites Arising from Interaction with Oxide Transport Layer Materials Sampreetha Thampr, Boya Zhang, Weijie Xu and Julia W. Hsu; The University of Texas at Dallas, United States

Long-term stability has been a key challenge towards commercialization of organic-inorganic metal halide perovskite solar cells despite their high-power conversion efficiency and low-cost. To enable improvements in stability, it is of paramount importance to understand the chemical processes that could trigger degradation and the associated reaction pathways within the perovskite as well as its interaction with other materials. To this end, we employ temperature programmed desorption (TPD) and Fourier transform infrared (FTIR) spectroscopy techniques to study the thermal stability and decomposition of organic halide precursors (e.g. methylammonium (MAX), formamidinium (FAX), X = I, Cl, Br) and halide perovskites by themselves, as well as when they are in contact with metal oxide materials used as transport layers. In our experiments, the powder sample is heated with a controlled rate at atmospheric pressure. The gases evolved during heating from desorption, reaction, or decomposition are carried using an inert gas to a mass spectrometer and FTIR connected inline with the furnace and are simultaneously analyzed. The composition of these released gases as a function of temperature enables direct deduction of the thermal processes and helps elucidate the reaction steps involved in the degradation mechanism. Using this approach, we determine that the decomposition of MAI (CH$_3$NH$_3$I) proceeds via the formation of CH$_3$I and NH$_3$ above 250 °C. However, when MAI is mixed with NiO, the decomposition temperatures lowers to 175 °C with release of CH$_3$NH$_2$ and H$_2$O. Although, both NiO and SmO$_2$ reacts with MAI, NiO is found to be more reactive, consistent with n-i-p devices with SnO$_2$ are more stable than p-i-n devices with NiO. Studies will also be performed on other halide precursors, halide perovskites, and other commonly used metal oxide transport layer materials. These studies provide fundamental knowledge that will facilitate the choice of suitable perovskite and transport layer materials and processing conditions to further engineering of perovskite solar cells with enhanced stability.
Clean Production of Plastic Perovskite Solar Cell from Aqueous Lead Nitrate Tzu-Chien Wei; National Tsing Hua University, Taiwan

Lightweight, plastic photovoltaic (PPV) devices are attractive renewable energy devices because they can be fabricated using high-throughput printing process and they enable the possibility to use solar power on curved surfaces. Generally, the power conversion efficiency (PCE) of a PPV is lower than that of its rigid counterpart, primarily owing to the limitations of the low thermal budget of plastic substrates. Apart from this problem, its flexibility is, ironically, another troublesome factor that causes PCE low due to insufficient light capture from its thin absorbing layer. Perovskite solar cells (PSCs) utilizing organometal halide perovskite absorber is considered a favorable candidate of PPV because of its unrivaled extinction coefficient, low exciton binding energy and low formation temperature. However, most published processes to deposit perovskite absorber involves the use of polar organic solvent such as DMF or DMSO, which is toxic and can not be vastly used in production scale. In the past few years, we devoted ourselves to develop a low-toxic process to fabricate high PCE PSC using only water as the primary solvent.

In this presentation, the journey of our efforts in this protocol and our targets in near future is shared. The conversion mechanism, morphology control and device engineering will be highlighted. Currently, we have achieved 16.5% plastic PSC using Pb(NO3)2/water as the starting material to prepare organometal halide perovskite layer.

Abnormal Aging and Recovery Processes in Perovskite Solar Cells with Metal Electrodes Dong Geon Lee1, Min-cheol Kim2, Shen Wang2, Byeong Jo Kim3,1, Sangwook Lee4, Shirley Meng2 and Hyun Suk Jung1; 1Sungkyunkwan Univ, Korea (the Republic of); 2University of California, United States; 3Uppsala University, Sweden; 4Kyungpook National University, Korea (the Republic of)

Perovskite solar cells (PSCs) have been rapidly improved in their energy converging performances, currently exhibiting up to 24.2 % of power conversion efficiencies (PCEs). Despite their great performances, they still suffer from various issues such as stabilities and scaling-up problems. PSCs struggle to maintain their performance owing to fast chemical decomposition or performing instability caused by hysteretic behavior or ion migration. Large-area perovskite film fabrication and cost problems of electrodes should be resolved for practical photovoltaic application. Among present problems, electrode selection is one of most important assignments in solving both hurdles for commercialization because the most popular metal electrodes, Au or Ag, are instable chemically and it is too much expensive to be used in mass production system, especially Au electrode. PSCs with Ag electrode performs low PCEs with low open circuit voltage and fill factor showing an s-shape kink in current density-voltage (J-V) curves at first. However, with aging time, the performance of PSCs recovers to the normal level and such abnormal performing instability can be a huge obstacle for commercial application of Ag electrode. The s-shape J-V curves are mainly attributed to inferior majority charge carrier extraction from the photo-absorbing area to the cathode or anode, however, the underlying reason for these phenomena, especially for the abnormal aging and recovery mechanism in PSCs with Ag electrode has not been elucidated at all. It is important to understand the origin of the s-shape J-V curves of PSCs with Ag electrode at early stage and the mechanism of aging and recovery phenomena with elimination of s-shape for securing the possible use of Ag electrode in commercialized PSCs. Here in this work, we present the different time-dependent performance change trends of PSCs with regard to metal electrodes (Au and Ag). PSCs with Ag electrode exhibit a clear s-shape J-V curves in early stage, however they recover to their best performance with 12 h of aging time. On the other hands, PSCs with Au electrode exhibit their best performance from the beginning. In order to clarify this abnormal aging and recovery process in PSCs with Ag electrode, we also investigate the time-dependent carrier dynamics alteration by photo-luminescence behaviors.
which proves the performance changes with aging time. By the measurement and simulation results, we are able to verify that the work function difference between Ag electrode and hole transport materials, Spiro-MeOTAD, induces a significant injection barrier for holes, and it clearly cause the formation and alleviation of the s-shape J-V curves in PSCs with Ag electrode. We finally address the potential of Ag electrodes for commercial use by demonstrating highly stable PSCs with Ag electrode for durations exceeding 350 h under light-illumination, which is close to the results of PSCs with Au electrode.

Advances in the Triple Mesoscopic Perovskite Solar Cells

Wenhao Zhang and Hongwei Han; Huazhong University of Science and Technology, China

Perovskite solar cells (PSCs) have attracted intensive attention from many researchers due to the excellent properties of perovskite materials and simple device fabrication process. Thanks to worldwide efforts, PSCs have achieved the most rapid development with certified efficiencies rising from 3.8% in 2009 to 24.2% in 2019. Different from mesoscopic structure or planar structure, the triple mesoscopic perovskite solar cells are based on a TiO₂/ZrO₂/carbon triple-layer mesoporous scaffold, acting as the electron transporting layer, spacer layer and counter electrode, respectively. All these functional layers are fabricated by screen printing along with subsequent sintering. Innovatively, the triple mesoscopic PSCs eliminate the use of noble metal electrodes and hole transport materials, which can simplify the fabrication procedures and reduce the fabrication cost. More impressively, the stability of PSCs with the triple mesoscopic structure is quite superior and different groups have confirmed it in recent years. Photostability of more than 1000 h in ambient air under full sunlight irradiation was first reported in 2014. Subsequently, stability of more than 10,000 h with zero loss in performances was obtained under controlled standard conditions in 2017. In addition, thermal stability of the triple mesoscopic PSCs is also excellent for they can maintain initial efficiency for over 1500 h during the 100°C thermal test in the dark. Based on these advantages, the triple mesoscopic PSCs have drawn lots of interest and become a competitive candidate for the new generation of photovoltaic technology. And a series of work have been performed to improve the performance of the triple mesoscopic PSCs, including perovskite modification, interface engineering, optimization of each functional layers, post-treatment and encapsulation. Up to now, the state-of-the-art power conversion efficiency of 15.77% has been obtained, exhibiting promising future of commercialization for the triple mesoscopic PSCs.

Comprehensive Investigation of Thermochemical Stability of Perovskite Layer and Perovskite Solar Cells with Zinc Oxide Electron Transport Layers

Wenjing Zhao, Dapeng Wang and Shengzhong (Frank) Liu; Shaanxi Normal University, China

In an efficient perovskite solar cell (PSC), the quality of the charge transport layers should be significantly considered. In case of the electron transport layer (ETL) materials, TiO₂ is a most commonly used inorganic semiconductor as ETL. However, due to the limitation of the intrinsic properties of TiO₂, it always suffers from high processing temperature, low electron mobility, and strong photocatalytic activity, resulting into the undesirable carrier recombination for TiO₂ based PSCs. Comparatively, zinc oxide (ZnO) is an alternative metal oxide ETL owing to its high electron mobility and comparable energy level as well as low temperature fabrication. In addition, ZnO films can be simply prepared through the various solution- or vacuum-based techniques, which is beneficial to the mass and low-cost production of photovoltaic devices. Although the solution processed ZnO-based PSCs have acquired the significant achievements, some problems still need to be settled for the future commercial applications. An important issue is the hydroxyl groups and/or residual acetate ligands remained on the solution-processed ZnO surface, which accelerates the chemical decomposition of the perovskite film during the fabrication processing. In comparison to various solution methods, magnetron sputtering technique is a traditional vacuum-deposition approach to form stoichiometry and morphology controlled metal oxide semiconductors at a desirable temperature. On the basis of sputtered ETLs-based normal or inverted PSCs, the thermochemical stability of the devices is rarely discussed. Most importantly, the sputtered samples contain few hydroxyl groups because the hydrogen-free ceramic target and working gases are used during the whole fabrication process, which effectively avoid the chemical decomposition of the perovskite layer and is beneficial to enhance the stability of the devices. Hitherto, the ETLs with various amounts of hydroxyl groups prepared by vacuum and solution methods are seldom considered. In this study, the thermochemical stability of the perovskite layer and PSCs on ZnO substrates containing the different amount of hydroxyl groups is investigated. To evaluate the chemical decomposition of the perovskite layer caused by the amount of hydroxyl groups remained on the interface of ZnO/perovskite films, ZnO films with
different amount of hydroxyl groups are prepared by magnetron sputtering and spin-coating methods. The sputtered ZnO film contains the negligible hydroxyl groups because the hydrogen-free working gases of argon and oxygen are introduced during the sputtering process. In case of the optimized deposition condition under Ar/O2 ratio of 1:4, the sputtered ZnO film shows larger grain size, bigger water contact angle, higher energy-level matching, better optical transmission, and higher conductivity in comparison with the spin-coated ZnO film. Moreover, the planar perovskite solar cells (PSCs) based on the sputtered ZnO electron transport layers (ETLs) yields an optimal power conversion efficiency of 17.22%, sharply outperforming that based on the spin-coated ZnO ETL (14.24%). More notably, the thermochemical stability of the device based on the sputtered ZnO ETL was also significantly improved.

EN08.09.04
Dual Function SBOET Glass Improves the Stability and Efficiency of Perovskite Solar Cell Jing Gou; Shaanxi Normal University, China

The performance of perovskite solar cells has been developing rapidly since 2009, the certified power efficiency has exceeded 24% in a few years. It has a very broad application prospect on basic research fields and new energy development, thus which has attracted great attentions. Ultraviolet radiation in solar spectrum is inevitable that can destroy the performance of perovskite solar cells in the same time. In order to solve this problem, we introduced photoluminescent glass in perovskite solar cells replacing traditional glass basement. The key point is SBOET photoluminescent glass, which can convert high-energy ultraviolet light to visible light for improving the stability and efficiency of perovskite solar cells. On the one hand, it can decrease the decomposition of perovskite material because less ultraviolet radiation can pass through SBOET glass. On the other hand, it can increase visible radiation by photoluminescence conversion. So that utilization of dual function SBOET glass can both improve stability and efficiency of the perovskite device.

EN08.09.05
Electric Field Induced Degradation in MA-Free Perovskite Solar Cells Erjin Zheng, Zhiyin Niu, Hao Dong, Gabriella A. Tosado and Qiuming Yu; University of Washington, United States

Small cation (Cs+ and Rb+) doped formamidinium lead triiodide (FAPbI3) is one of the most promising perovskite materials for solar cell applications because of the elimination of thermally unstable methylammonium (MA) cation and the reduced phase transition of FAPbI3 from photoactive α-phase to photo-inactive δ-phase. Comprehensive studies have been performed on the stability of small cation doped FAPbI3 perovskites with respective to oxygen, humidity, and temperature. However, the stability under the operational condition, such as applied electric bias and solar illumination, is equally important, yet has not been well studied.

In this work, we fabricated MA-free Rb0.05Cs0.10FA0.85PbI3 perovskite via hot casting and anti-solvent method. Diethyl ether and chlorobenzene were applied as the anti-solvent. Diethyl ether served as a better anti-solvent than chlorobenzene, yielding densely packed, uniform α-phase Rb0.05Cs0.10FA0.85PbI3 perovskite thin films confirmed by SEM and XRD. Perovskite solar cells with the structure of ITO/PEDOT:PSS/Rb0.05Cs0.10FA0.85PbI3/PC60BM/BCP/Ag exhibited an average PCE of 12.14% and a steady Jsc at the maximum power for 60 min. The PCEs of the devices, stored in N2 glove box, dropped to ~60% of the initial value over the first 15 days and retained the same level for the next 15 days with a testing interval of 3 days in these 30 days, and kept the same PCEs when tested in another 20 days later. No interfacial degradation was confirmed via light intensity- and effective voltage-dependent Jsc measurements. SEM images showed that the perovskite thin film still remained crystalline grains with clear grain boundaries over the entire cross-section. However, XRD patterns showed that small amount of photo-inactive δ-phase perovskite formed in the region right under the electrodes while the region in between electrodes remained photoactive α-phase, indicating the initial PCE drop is due to the δ-phase perovskite formation and electric-field plays an important role.

The impact of precursor preparation on the formation of phase pure Rb0.05Cs0.10FA0.85PbI3 perovskite was further investigated. Rb/CsPbI3 phase segregation occurred in the formation of Rb0.05Cs0.10FA0.85PbI3 perovskite thin film if the precursor solution was not well mixed before spin coating. While a higher average PCE of 13.23% and a steady Jsc at the maximum power for 60 min were achieved from the devices prepared with the unwell-mixed precursor solution, the devices exhibited an accelerated degradation and strong dependence on testing frequency, which means the exposure to the applied electric field. With the testing intervals of 3, 15, and 30 days, the PCE reduced to 8, 20, and 44% of the initial values, respectively. The perovskite under electrodes turned to yellow while in between electrodes were still black. No interfacial degradation was confirmed. The perovskite material degradation was investigated via SEM, which showed small pin holes in the cross-sectional area right under the electrode, and XRD,
which showed the significantly decreased α-phase peaks accompanied by the significantly increased δ-phase peaks. The perovskite in between electrodes, again, remained crystalline grains with clear grain boundaries and α-phase with trace δ-phase formation. We proposed that the electric field induced degradation via small cation migration between vacancies could be a possible mechanism. More experiments were conducted to verify this proposal. Furthermore, the possible reducing phase segregation methods were also proposed and experimentally tested. This work provides an insight on the selection of anti-solvent for making mixed-cation perovskite thin films, demonstrates the importance of precursor preparation to the operational stability of devices, reveals a perovskite solar cell degradation mechanism via the electric field driven phase segregation, and offers the means to reduce such phase segregation and to enhance perovskite solar cell stability.

EN08.09.06
Enhanced Water-Resistance of Perovskite Solar Cells by Grain Boundary Passivation with Polydimethylsiloxane-Woochul Kim, Yusin Pak and Gun Young Jung; Gwangju Institute of Science and Technology (GIST), Korea (the Republic of)

Organic-inorganic hybrid perovskite solar cells (PSCs) have attracted considerable attention due to their remarkable power conversion efficiency (PCE) that lately exceeds 22 %. However, stability issue remains regarding their use in real-life environments with the most urgent matter being their long-term stability under humid conditions. The hybrid perovskites are inherently vulnerable to water molecules, which can induce degradation of perovskite photoactive chemicals such as MAPbI3, FAPbI3. Therefore, to realize the commercial-level long-term PSC stability, the adsorption and infiltration of water into perovskite films must be minimized. Herein, it is demonstrated that polydimethylsiloxane (PDMS) introduced simultaneously during perovskite spin-coating is highly beneficial to passivate perovskite grains and adjacent grain boundaries (GBs). It promotes the formation of lead oxide (PbO) bonding that prevent a water-perovskite reaction and contributes to reducing a Pb defect density related to trap-assisted recombination. Owing to the reduced trap-assisted recombination, the best PDMS-passivated PSC exhibits a PCE of 16.16 %, FF of 70 % and $J_{sc}$ of 21.10 mA/cm². The photovoltaic performance of the PDMS-passivated PSC is notably enhanced compared to a reference PSC (without PDMS). Furthermore, the PDMS with abundant methyl moieties is hydrophobic, effectively limiting water infiltration into the perovskite film and PbO bonding formed by PDMS passivation can prevent catalytic reaction between Pb atoms and water molecules. Thus surprisingly, more than 90 % of the initial PCE (~15 %) is sustained after laboratory storage of 5000 h under 70 % relative humidity, while only 20 % of original PCE of reference PSC is retained after 2000 h under the same conditions. These results will pave the way for developing commercial perovskite optoelectronic devices.

EN08.09.07
Enhancement of Humidity Stability by Cation Engineering in Perovskite Solar Cells Bohyung Kim; UNIST, Korea (the Republic of)

Many organic cations in halide perovskites have been studied for their application in perovskite solar cells (PSCs). Most organic cations in the PSCs are based on protic nitrogen cores, which are susceptible to deprotonation. Here, a new candidate of fully alkylated cation (target cation) was designed and successfully assembled into PSCs with the aim of increasing humidity stability. To ensure promising photovoltaic performance of three-dimensional perovskites, trace amount of target cation was assembled into perovskite solar cells by using typical solution spin-coating method. From the results of the structural and morphology studies combined with XPS analysis, it was evident that the target cation was introduced in the grain boundaries and/or surface of perovskites without change in 3-D perovskite lattice, which resulted in the comparable photovoltaic performance (η ~ 19 %) of 3-D MAPbI3 under 100 mWm⁻² irradiation. Regarding the stability of perovskite film on moist, it was found that the generic feature of A-site cations in the form of ABX₃ perovskites significantly affected humidity stability of perovskites, with ammonium-based perovskites giving a poor moisture-tolerance. However, the target cation-driven perovskites showed a much more pronounced effect on the increase in humidity stability, which emphasizes a generic electronic difference between protic versus aprotic cation. From the point of view on the humidity stability, it should be added that not only hydrophobic alkyl (or aromatic) chain but also basicity of cations should be considered when engineering large cations for their use in perovskites. Based on the prominent photovoltaic performance and stability of target additive-driven PSCs, current additive is considered as logical cations for further design of 2-D, 3-D, or 2D/3D hybrid perovskite.
EN08.09.08
Evaluation of Durability of Organic-Inorganic Perovskite Compound Films II Yuki Fukazawa1, Masato Gocho1, Kazunori Ito1, Toshiya Kobayashi1, Ryusuke Umeda1 and Hironori Ogata1,2,3; 1Hosei Univ. Grad. Sch., Japan; 2Hosei University, Japan; 3Research Center for Micro-Nano Tech, Japan

In organic-inorganic hybrid solar cells using a lead halide-based perovskite compound as a light absorbing layer, improvement in durability is one of the major issues in practical use. Several studies have been reported on improving the durability of the perovskite layer. In particular, it have been reported that the stability of the compounds is enhanced by mixed crystal formation of lead halide perovskite compounds. In particular, it has been reported that stability is improved by mixing inorganic cations such as Cs and Rb with organic cations such as CH3NH3+ (MA+) and HC (NH2)2+(FA+) (1) (2). In addition, recently, it has been reported that energy conversion efficiency and stability are improved by mixing CH6N3+ as an organic cation (3), but these deterioration suppressing mechanisms have not been sufficiently elucidated yet. We are conducting research focusing on the durability mechanism of the perovskite layer with mixed cations and halide anions.

In this study, the effects of temperature and humidity on the crystal structure, morphology, charge transport properties and photovoltaic properties of the mixed perovskite compound films based on FAPbI 3-y Br self were systematically investigated. Furthermore, the results of evaluating the influence of the ratio of the inorganic cation (Cs or Rb) and the organic cations of the mixed perovskite compound thin film on the durability are also reported. Detailed results will be discussed on the conference.

EN08.09.09
Impacts of Secondary Phase on Performance of Formamidinium-Based Perovskite Solar Cells—Mechanisms and Solutions Linfeng Cai and Furong Zhu; Hong Kong Baptist University, China

Solution-processable perovskite materials have already been proven the potential for applications in optoelectronic devices, including solar cells, photodetectors, light-emitting diodes etc. Stability of the perovskite solar cells is particularly important for the eventual application. The formation of secondary phase in the complex perovskite active layer, typically with multiple ions, is one of the causes leading to the deterioration in the cell performance. In this work, we report our effort to understand the thermal stability of the solution-processed methylammonium- and bromine-free formamidinium-based perovskite (FA0.85Cs0.1Rb0.05PbI3) layers, and the relationship between the formation of secondary phase and long-term stability of the FA0.85Cs0.1Rb0.05PbI3-based perovskite solar cells. It shows that the emergence of secondary phase in the perovskite layer is closely associated with the storage time of the perovskite precursor solution. An obvious decrease in power conversion efficiency was observed when the secondary phase was formed in the perovskite active layer in the cells. The formation of the secondary phase in the perovskite active layer leads to an increase in charge recombination, due to the reduction in the built-in potential across the cell. The improved understanding of the formation mechanism of the secondary phase and the solutions to supress the formation of the secondary phase are the prerequisite for attaining high performing perovskite solar cells.

EN08.09.10
Influence of Guanidinium on the Stability and Performance of the Multi-Cation Perovskite Solar Cells Eunhwan Jung, Senol Oez, Feray Uenlue, Heechae Choi and Sanjay Mathur; University of Cologne, Germany

Here we present the preparation of solution processed mixed cation GAx(Cs0.05MA0.15FA0.8)1-xPb(I0.85Br0.15)3 (GA= guanidinium; MA= methylammonium; FA= formamidinium) organic-inorganic hybrid perovskite films and their incorporation into mesoporous perovskite solar cells by spin coating solution processing. We found that incorporation of GA into Cs, MA, and FA triple cation perovskite enables the formation of highly crystalline black phase perovskite which enhance charge carrier transfer and inhibits charge recombination at the perovskite/spiro-OMeTAD interfaces and therefore improves short-circuit current density of the device. Time-resolved photoluminescence (TRPL) data confirm a faster decay of the PL signal in the presence of the perovskite/spiro-OMeTAD with GA incorporation perovskite solar cell in comparison with triple cation perovskite solar cell. The effect of GA substitution was systemically investigated, and the 5% GAI was the optimum condition to achieve high performance perovskite solar cells. This study will provide a basic insight for the mixed-cation perovskite for the future energy harvesting applications.

EN08.09.11
Investigation of Air Stability in Different Perovskite Semiconductors Abhishek Kumar Chauhan, Pankaj Kumar
Organo-metal halide perovskite semiconductors have attracted especial attention of the entire photovoltaic community as they have shown excellent properties for photovoltaic applications. They have shown unprecedented improvement in their ability of converting solar energy into electricity from 3.8% in 2009 to certified 22.1% in 2016. Perovskite photovoltaic technology is considered to be the most cost effective technology and the devices are very thin, light weight and compatible to roll-to-roll fabrication on flexible substrates, making them mountable on any kind of building surfaces. Ease in band gap tuning of perovskite semiconductors have paved the path for overcoming the efficiency limitations in tandem structures. Scientist are applying perovskite semiconductors on the commercial solar cell technologies and c-Si/Perovskite tandem solar cells have already crossed 23% in monolithic architecture and 26% in mechanical stacking. Unfortunately perovskite semiconductors are very sensitive and lose their optical and electrical properties in the presence of moisture, oxygen, UV light and high temperature. Rapid degradation in perovskite semiconductors is keeping this technology away from the market. Application of stable perovskite semiconductors will provide the solar cells a longer stability. Keeping this objective in our mind we have synthesized a number of perovskite semiconductors by varying the composition of precursors and using double or triple cations along with different halides. Thin films of these perovskites were prepared via spin coating technique and subjected to different test conditions to investigate their stability and degradation mechanisms. The films were characterized by the important tools, used for understanding of degradation, like UV-vis absorption spectroscopy, scanning electron microscopy, optical microscopy, X-ray diffraction technique etc. From these studies we were able to identify the stable perovskite materials for stable solar cells and the results will be discussed in more detail during the conference.

EN08.09.12
Perovskite Solar Cell Operational Stability under Vacuum for Space Application Yan Jiang, Shih-Chi Yang, Stefano Pisoni, Thierry Moser, Fan Fu, Stephan Buecheler and Ayodhya N. Tiwari; Swiss Federal Laboratories for Materials Science and Technology, Switzerland

High power conversion efficiency,$^1$ high specific power (W/g) and stowed packing efficiency (W/cm$^3$),$^2$ low processing cost (US cents/kWh)$^3$ and high tolerance against space environmental threats (high energy and charged particle radiation)$^4,5$ makes perovskite solar cell (PSC) a promising candidate as space-based photovoltaics. However, vacuum causes outgassing of perovskite absorber,$^4$ raising concerns on its long-term reliability. In this work, we investigated how different pressure levels affect the operational stability of non-encapsulated PSCs with the state-of-the-art (SOA) architecture. Stability of PSCs decreases upon reducing the operational pressure while they are kept at the maximum power point (MPP) condition under 1 sun continuous illumination. By performing XRD, UV-Vis, SEM and SIMS measurements, we reveal the vacuum induced efficiency loss mechanism. In addition, we developed two PSC architectures that effectively delay/mitigate these vacuum induced detrimental effects. PSCs with one of the new developed device architectures show a low PCE loss rate of 0.007%/h in 1037 h at MPP condition under 50 mbar, equaling to a projected T$^0$ lifetime of 4750 h. The findings present in this study lay the foundations towards highly stable PSC structures for applications in low-pressure environment, as encountered in outer space.

Reference:

EN08.09.13
Qualifying Cesium as a Stabilizer for Effective Perovskite Solar Cells Denice N. Feria$^1$ and Yu-Chiang Chao$^2$; $^1$Chung Yuan Christian University, Taiwan; $^2$National Taiwan Normal University, Taiwan
The rapid increase in global demand for energy paved the way for finding renewable and efficient energy source. With this, a cost-effective and environment friendly hybrid organic-inorganic lead halide perovskites have gained attention as an absorber layer for effective solar cells. The perovskite device performance is more efficient not only because of its distinct properties. But also, the flexibility of the perovskite material to be tuned in different structures to enhance its stability under ambient conditions. The process of interchanging cations to the perovskite material became a feasible route to further improve its efficiency which contributes to its fast development over the past years. By replacing Methylammonium (MA) cation to Formamidinium (FA) cation, it created a new perovskite structure that can be utilized for better device performance. A pristine FAPbI₃-based solar cells exhibited good characterizations and desirable device performance but its stability is inconsistent under ambient conditions. This can be attributed to the non-perovskite property of the FA cation which often exhibits during exposure to air and inappropriate fabrication process. Thus, in this study, creating a double or mixed cation perovskite solar cells (PSCs) were observed to solve the instability issue of HC(NH₂)₂PbI₃ /FAPbI₃ making it more photo and structurally-stable under environmental factors.

The idea of double cation PSC was done by incorporating small amounts of Cesium (Cs) in FA-based perovskite absorber layers. This incorporation pushed the photo-active black perovskite phase of FA-based solar cells which made it more suitable for the effective perovskite solar cell fabrication. The CsFA-based structure also avoids the phase transition of the perovskite material from perovskite to non-perovskite property. This PSC was enhanced both in its efficiency and stability under thermal and moisture exposure. With thorough investigation on the different techniques in PSC fabrication such as addition of poor solvent, delay time and annealing conditions, perovskite samples have shown more developed characterizations compared to the pristine FAPbI₃. Fabricated in different delay time conditions, the most stable photo-active black perovskite phase was detected from the structure, FA₀.₉ Cs₀.₁ PbI₃. Flat and smooth surface which has a full perovskite coverage and appropriate thickness were found from dark and bright optical images and scanning electron microscope (SEM) observations. Also, it contributed to the perovskite samples to have broader absorption and stronger photoluminescence that developed its device performance. Moreover, X-Ray Diffraction (XRD) patterns and its full-width half-maximum (FWHM) values showed that when a correct amount of Cesium was incorporated to the pristine FAPbI₃, a pure perovskite film with high crystallinity will be obtained. Because of these enhanced properties, the PSC exhibited an efficiency of 8.74% with good reproducibility. A stable device was also observed which is highly needed for fabricating an effective solar cell. As a whole, the perovskite solar cell in FA₀.₉ Cs₀.₁ PbI₃ demonstrated enhanced device properties over the FAPbI₃-based device on the influence of other variables. The observation in the fabrication techniques made the PSC to be structurally and thermally stable which were also useful for future experiments and large-scale applications.

EN08.09.14
Semi-Locked Tetrathienylethene as a Building Block for Hole-Transporting Materials—Toward Efficient and Stable Perovskite Solar Cells Chao Shen; East China University of Science and Technology, China

The construction of state-of-the-art hole-transporting materials (HTMs) is challenging regarding the appropriate molecular configuration for simultaneously achieving high morphology uniformity and charge mobility, especially because of the lack of appropriate building blocks. Herein a semi-locked tetrathienylethene (TTE) serves as a promising building block for HTMs by fine-tuning molecular planarity. Upon incorporation of four triphenylamine groups, the resulting TTE represents the first hybrid orthogonal and planar conformation, thus leading to the desirable electronic and morphological properties in perovskite solar cells (PSCs). Owing to its high hole mobility, deep lying HOMO level, and excellent thin film quality, the dopant-free TTE-based PSCs exhibit a very promising efficiency of over 20% with long-term stability, achieving to date the best performances among dopant-free HTM-based planar n-i-p structured PSCs.

EN08.09.15
Sn–Zn-Oxide Nanocomposites (TZO) Electron Transport Layers for Efficient and Stable Perovskite Solar Cells Nageh K. Allam; American University in Cairo, Egypt

Tin–zinc-oxide nanocomposites (TZO) with various Sn:Zn ratios were successfully fabricated and tested as electron transport layers (ETLs) in perovskite solar cells (PVSs). The fabricated nanocomposites showed good crystallinity, good contact between layers, good electrical conductivity, and favorable light absorption, resulting in an enhancement in the net efficiency of CH₃NH₃PbI₃ (MAP) based perovskite solar cells. The device made of TZO–
Sn0.05 as an ETL showed a maximum power conversion efficiency (PCE) of 17.81% with a short-circuit current density (Jsc) of 23.59 mA cm^{-2}, an open-circuit voltage (Voc) of 1 V, and a fill factor (FF) of 0.754. However, the ETL containing lower Sn ratios showed PCEs of 12.02, 13.80 and 15.86% for pure ZnO, TZO–Sn0.2 and TZO–Sn0.1, respectively. Meanwhile, the reproducibility of 30 fabricated devices proved the outstanding long-term stability of the cells based on TZO nanocomposites, retaining 85% of their PCE over 1200 h of operation. In addition, the incident photon-to-current efficiency (IPCE) exceeded 90% over the entire wavelength range from 400 to 800 nm. The current results suggest that our synthesized tin–zinc-oxide nanocomposite is an effective electron transport layer for efficient and stable perovskite solar cells.

EN08.09.16
Study of the Stability of Lead Halide Perovskite under Two Different Fluoropolymer Top Coatings Fatemeh Khorramshahi and Arash Takshi; University of South Florida, United States

In this work, two lead halide perovskite photodetector were fabricated by laser-assisted rapid fabrication method. A microchannel was engraved on an indium tin oxide (ITO) coated polyethylene terephthalate (PET) conductive flexible substrate using a CO2 laser source. The channels were filled by methylammonium lead halide perovskite (CH3NH3PbI3) using the capillary motion of perovskite precursor. CYTOP and the low-cost commercially available FluroPel were used as a top protective coating layer to suppress the decomposition of the perovskite channel. X-ray diffraction pattern (XRD) was used to measure the stability of the perovskite. Strong humidity resistant and self-healing behavior were observed in both devices. The performance of the two photodetectors was compared by measuring electrical and optical characteristics over time. This study will help in the low-cost fabrication of perovskite-based devices.

EN08.09.17
Concentrated Sunlight for Studying Bias-Dependent Stability of Perovskite Solar Cells Anoop K M1, Mark Khenkin1, Renjun Guo3, Eugene A. Katz1, Yulia Galagan3, Francesco Di Giacomo2, Stav Rahmany3, Lioz Etgar3 and Iris Visoly-Fisher1; 1Ben-Gurion University of the Negev, Israel; 2TNO-Solliance, Netherlands; 3The Hebrew University of Jerusalem, Israel

Perovskite solar cells have exhibited impressive power conversion efficiency, but to be considered for large scale commercial applications these cells have to be stable under operating conditions including exposure to sunlight, heat and electric bias. Here we present stability studies using concentrated sunlight, which allows rapid screening of the degradation parameters in the cells. Specifically, accelerated degradation studies to determine factors affecting degradation at different bias conditions were performed. Our experimental methodology allows independent control of sunlight intensity, the sample temperature and environment during the exposure. Stress testing of perovskite solar cells showed that faster degradation was found for cells held at SC under concentrated sunlight and on the initial stage of outdoor exposure. However, cells kept at short circuit (SC) showed better long-term stability compared to cells kept at open circuit (OC) upon real operational conditions. We also found that intensity was more important than dose for cells degradation at SC conditions, while dose was the determining factor at OC. This indicates that different degradation mechanisms are dominant at different degradation stages and under different bias conditions and that nano-scale understanding of degradation mechanisms is required to suggest ways to increase the device life-time.

EN08.09.18
Sunlight Concentration-Dependent Degradation of Perovskite Solar Cells Anoop K M1, Mark Khenkin1, Eugene A. Katz1, Yulia Galagan3, Francesco Di Giacomo2, Lioz Etgar3, Stav Rahmany3 and Iris Visoly-Fisher1; 1Ben-Gurion University of the Negev, Israel; 2TNO-Solliance, Netherlands; 3The Hebrew University of Jerusalem, Israel

Over the last few years, perovskites have emerged as promising photovoltaic materials because of their ease of fabrication and high power conversion efficiency. However, their long-term stability remains a major concern for their commercialization. Here we present stability studies using concentrated sunlight, which allows rapid screening of the degradation parameters in the cells. Studies conducted on dual cation perovskite solar cells revealed that there are two different degradation mechanisms being dominant at different exposure intensities. At 10 to 30 suns exposure, the PCE degradation behaved entirely...
different from that of 40 and 50 suns exposed samples. We have studied the mechanisms behind this PCE degradation with the help of photoluminescence mapping and by electrical measurements including photo-induced charge carrier extraction by linearly increasing voltage (photo-CELIV), transient photo-current and impedance, using the PAIOS instrument. PL mapping shows non-homogeneous degradation only at intensities of 40-50 suns, which is non-reversible, in contrast with that at lower sunlight concentrations. Electrical measurements showed that cell degradation up to 30 suns can be due to the generation of traps. The different acting degradation mechanisms indicate that accelerated stability testing using concentrated sunlight is limited to smaller sunlight concentrations.

EN08.09.19
Thermochemical Stability of Hybrid Halide Perovskites  Alessandro Senocrate1,2, Gee Yeong Kim1, Davide Moia1, Michael Graetzel1,2 and Joachim Maier1; 1Max Planck Institut for Solid State Research, Germany; 2École Polytechnique Fédérale de Lausanne, Switzerland

Hybrid halide perovskites (HOIHPs) have been extensively studied in recent years due to their potential use as light-harvester in photovoltaic devices. While the efficiencies of such devices pose no limitation to commercial applications, the severe lack of stability of the materials remains an important issue to be overcome. Indeed, HOIHPs are known to easily degrade under moderate thermal stress,[1] or upon oxygen[2] and/or light exposure.[3] Notably, recent calorimetric studies even suggested that, in agreement with DFT calculations,[5] some HOIHPs (MAPbI3 in particular and MAPbBr3 to a lesser extent) could be thermodynamically unstable[4] with respect to decomposition into their binary precursors. In contrast, other studies indicate the materials to be intrinsically stable.[1,6] Obviously these questions need to be unambiguously answered. In this contribution, we discuss the underlying thermodynamics of HOIHPs. We treat the intrinsic (vs temperature) and the extrinsic (vs oxygen) stability, as well as decomposition processes induced by light and applied bias. Intrinsically, we find the materials to be stable under standard conditions (albeit, in the case of MAPbI3, only marginally), and we also can assess the favourable degradation path upon heating. A strong tendency towards instability is expected under real conditions. Extrinsically, our considerations reveal a large tendency towards degradation of HOIHPs in the presence of oxygen, which is especially severe under real conditions. Notably, light itself can activate a relevant photodecomposition pathway.[7] We discuss these issues on a quantitative level, in conjunction with experimental observations of the degradation phenomena.

References

EN08.09.20
Thermomechanical Behaviour of Halide Perovskites  Srinivas K. Yadavalli, Zhenghong Dai, Yuanyuan Zhou and Nitin P. Padture; Brown University, United States

Organic-inorganic halide perovskite (OIHP) based solar cells have rapidly emerged as a promising photovoltaic technology because of fascinating optical and electronic properties of OIHPS. However, perovskite solar cells (PSCs) are extremely fragile and have cohesion energy values lower than that of even the organic solar cells. Also, the devices have multi-layered structures with functional layers possessing different thermal and mechanical properties. So, thermal cycles during device fabrication can induce macroscopic residual stresses in the OIHP film. The possibility of these stresses leading to different modes of film fracture (surface cracks, channelling cracks and interface cracks) is evaluated. The behaviour of the devices is also studied under externally applied stresses. The effect of interface modification on the cohesion energy of the devices is demonstrated, leading to more mechanically reliable PSCs. The OIHP film’s mechanical stability is evaluated by subjecting the films deposited on flexible substrates to high strains. The microstructural and the residual stress changes during a bending cycle are characterized to understand the mechanisms of failure. This brings insights to the fundamental aspects of the mechanical behaviour of OIHPS which is very likely to be critical inorder to emerge as a highly reliable solar cell technology.
EN08.09.21
Understanding Intrinsic Instability of Perovskite Solar Cells at Outdoor Operation Settings
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Thin film solar cells based on organo-metal halide perovskite have reached efficiencies above 24%, promising to be part of next generation photovoltaics. However, one of the preconditions for its commercialization is performance stability. In recent years, extrinsic stability of perovskite solar cells (PSCs) has significantly improved due to better encapsulation. As a follow, increasing attention has been attracted towards the intrinsic stability of PSCs. In this regard, many PSCs have been reported to be stable for over 1000 hours under continuous illumination at constant temperature in inert environment. However, in real life outdoor operation solar cells undergo light-dark cycling and temperature variation due to day-night periods. Thus, it’s necessary to understand PSC performance changes due to these variable conditions.

Motivated by this cause, we have tracked the changes in the maximum power of PSCs in three scenarios progressively evolving from conventional laboratory settings to approximate diurnal outdoor settings, i.e. from continuous light at constant temperature to light-dark cycling with respective constant temperatures ending with light-dark cycling with temperature variation under light. Study shows that first and second scenarios do not significantly affect PSC performance, while the third scenario results in irreversible performance degradation. Based on analysis using numerical simulation and advanced electrical characterizations, we arrive at the understanding of this degradation with respect to defect dynamics.

To conclude, this work reveals the combination of day-night cycling and varying temperature causes PSC degradation, owing to the intrinsically unstable property of perovskite, i.e. defects generation and migration. Thus, this work further accents the necessity to control defects formation in polycrystalline perovskite films in order to achieve stable PSCs at outdoor operation settings.

EN08.09.22
Engineering Hybrid-Processed Metal-Halide Perovskites on Textured Interfaces for Perovskite/Silicon Tandem Solar Cell Applications
Erkan Aydin, Michele De Bastiani, Furkan H. Isikgor, Jiang Liu, Thomas G. Allen, Emmanuel Van Kerschaver and Stefaan De Wolf; King Abdullah University of Science and Technology, Saudi Arabia

In recent years, metal-halide perovskites (MHPs) have drawn significant attention as a new class of photovoltaic (PV) materials. In a short period after the first solid-state perovskite solar cells (PSCs) were reported, rapid progress followed, culminating recently in single junction devices with a reported power conversion efficiency (PCE) of 24.2%. The excellent optoelectronic properties of the MHPs together with their band gap tunability make them also promising for tandem solar cells. Considering their dominance in the current PV market, the marriage of the perovskite and crystalline silicon (c-Si) solar cells seems very promising for large scale deployment of the PSCs, potentially enabling >30 PCE in the near future.

Such an appealing concept comes nevertheless with some constraints in terms of device processing. Although MHPs processed using a variety of techniques, the community still widely relies on spin-coating, owing to its easy and cost-efficient employment in the lab. Several reports have been published utilizing spin-casted PSCs on ‘flat’ c-Si bottom cells achieving >25% PCE in a monolithic tandem configuration. However, micron-sized textured surfaces play a critical role in efficient light-coupling into c-Si solar cells. This is also true when used as bottom cells, ensuring thereby well-matched high photocurrents between the subcells. Moreover, the use of textured Si wafers is standard in existing c-Si solar cell processing lines, with little incentive to change this. Therefore, the development of the conformal and high-quality PSCs on such textured interfaces is the critical step towards the >30% PCE target. Solution-based techniques may have limitations to produce conformal layers on textured interfaces. However, ‘hybrid’ processing is very promising to this end, which requires first (co)evaporation of the inorganic part of the perovskite, followed by the conversion of this layer to the final perovskite structure by a solution-based technique, relying on the inter-diffusion of the halides. In hybrid processing, achieving high-quality perovskite absorbers depends on several critical parameters such as evaporation rate, film thickness, solution concentration, annealing temperature, ambient conditions (relative humidity), etc. In this study, we investigate the role of these parameters
and report the optimal processing conditions.
Non-optimized, the hybrid deposition method may suffer from the incomplete transformation of PbI₂; residual PbI₂ remains as a secondary domain at the interface, limiting device performance. We found that the porosity of the PbI₂ films is critical for their full conversion; notably, co-evaporation of CsBr together with PbI₂ enables this needed porosity with controlled Cs/Pb elemental ratio. To obtain fully converted perovskites, the solution concentration is another parameter which requires a good balance between film thickness and solution concentration. We found that a low concentration causes non-converted films, whereas a high concentration results in segregated phases and residual FAI on the surface of the films, which limits the device performance. Since the thermal evaporation is a directional deposition technique, the top of the pyramidal texture and deepest point of the valleys are always thicker than the flanks of the pyramidal texture. Increasing the number of such points results in poorly converted films.
With this motivation, we compared different pyramid sizes and found the optimal range. Finally, we looked into the different recombination junctions such as TCOs and nc-Si and correlated these results with shunt problems.
Overall, in this study, we deeply investigated critical processing parameters in hybrid processing of perovskite on textured interfaces by correlating these results with monolithic tandem solar cell performances. This study reveals the potential of the hybrid processing method for tandem applications and gives an insight into the further progress of the field.

EN08.09.23
Fabrication of Uniform Perovskite Films on 4-inch Textured Silicon Surface Using Sputtering and Chemical Vapor Deposition Process Jae-Keun Hwang¹, WonKyu Lee¹, Sang-Won Lee¹, Soohyun Bae¹, Solhee Lee¹, Yoonmook Kang²,¹, Hae-Seok Lee²,¹ and Donghwan Kim¹,²;¹ Korea University, Korea (the Republic of); ²KU-KIST Green School, Korea (the Republic of)

Perovskite solar cells (PSCs), reported for the first time in 2009, are experiencing rapid increase in efficiency from 3.81% at the initial efficiency to 24.2% at present, attracting many researchers with the next generation solar cells. Basically, CH₃NH₃PbI₃ perovskite films (PFs) can be fabricated through the synthesis of the precursor (ex:PbI₂) and CH₃NH₃I. One of the key factor for producing a highly efficient PSCs is to produce a uniform thin films on substrates.

One of the major research topic in the future of PSCs is commercialization strategy, and it is important to deposit thin films uniformly over a large area. However, it is expected that the conventional solution process will have a limitation in uniformly depositing PSCs on a large area. In order to fabricate a large-area PSCs, a method of depositing PFs through the vacuum process is required.

In addition, the vacuum process is also needed from the viewpoint of silicon/perovskite tandem solar cells, deposition of conformal PFs over silicon pyramids is limited by solution processes on textured commercial silicon substrates. For this reason, the silicon/perovskite tandem solar cell has been fabricated to have a flat structure at the front face so that a lot of reflection loss was generated. Recently, there has been a report on fabricating silicon/perovskite tandem solar cell with double-sided texture through evaporation process to reduce reflection loss and increase current density.

In this study, the PFs were fabricated by sputtering and chemical vapor deposition process which are widely used in commercial applications. Perovskite precursor were deposited by sputtering, followed by chemical vapor deposition process for phase converted into the PFs. The films were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM). A PSCs with glass/FTO/compact-TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD/Au structure were fabricated. Finally, it was confirmed that the PFs were conformally deposited on the 4-inch textured silicon substrate. The uniformity of reflectance and thickness was higher than 86% and 92%, respectively. This fabrication processes of the PFs are expected to be applicable to silicon/perovskite tandem solar cells.

EN08.09.24
Optimization of Device Design for Low Cost and High Efficiency Planar Monolithic Perovskite/Silicon Tandem Solar Cells Chan Ul Kim, Jae Choul Yu, Eui Dae Jung, In Young Choi, Wonjin Park, Hyungmin Lee and Kyoung Jin Choi; UNIST, Korea (the Republic of)

Currently, various multi-junction solar cell structures are being studied to overcome the theoretical limitation of silicon solar cell. The III-V tandem structure can achieve high efficiency, but it can not be commercialized because of a high cost. In order to overcome this problem, research on perovskite / silicon tandem solar cell using a low cost perovskite solar cell which is rapidly emerging as a next generation solar cell is being conducted. However, most
hybrid tandem cell research is based on n-type heterojunction silicon cells, which occupy only a small fraction of the total solar market. Therefore, for commercialization, research on perovskite / silicon tandem solar cell based on PERC structure emerging as the mainstream of next-generation silicon solar cell and Al-BSF structure which is mainstream of silicon solar cell is essential.

Here, we have fabricated perovskite / silicon tandem solar cells by introducing Al-BSF structure and PERC structure. Optimized tandem cells based on Al-BSF structure, fabricated with a 310-nm-thick perovskite layer of (FAPbI3)0.8(MAPbBr3)0.2 and a hole transport layer of PTAA, have significantly increased efficiency of 21.19% compared to stand-alone 13.4% perovskite and 12.8% Si cells. Our tandem cell represents the highest efficiency increment among all monolithic perovskite / silicon tandem cells and the highest efficiency among monolithic perovskite / silicon tandem cells based on p-type homojunction silicon cell with Al back-surface field at the same time. The design rules suggested in this study can be applicable to different types of perovskite / silicon tandem cells as well. We believe that this approach opens up a pathway for the commercialization of perovskite solar cells with industry-standard monocrystalline Si solar cells as highly efficient monolithic tandem devices.

EN08.09.25
Perovskite and Quantum Dot Tandem Solar Cells with Optimized Semitransparent Middle Electrode Aneta H. Andruszkiewicz and Erik Johansson; Uppsala University, Ångström laboratoriet, Sweden

In recent years the significant effort has been made to develop new photovoltaic materials configurations and architectures, among which the considerable attention was drawn to tandem cells. It was theoretically proven that tandem configuration involving two or more solar cells has a great potential to overcome the Shockley-Queisser single-junction efficiency limit. Theoretical calculations predict that the combination of large band gap energy (~1.5 eV) material as top cell and low band gap energy (~1.0 eV) material as bottom cell can allow the conversion efficiency of around 30%. Among solution-processed photovoltaic materials, metal halide perovskites with their broad light absorption spectrum, tunable band gaps, long charge carrier diffusion, and low fabrication cost together with lead sulfide (PbS) colloidal quantum dots (QDs) with highly tunable band gap and strong infrared absorption, shows great opportunity to create such highly efficient tandem cells. However, the biggest challenge here is to incorporate the sensitive and unstable perovskite film into such tandem structure. Herein, I will demonstrate efficient solution-processed tandem solar cells using Methylammonium Lead Iodide (MAPbI3) Perovskite in the front cell and PbS QDs in the rear cell and discuss the progress on developing and optimizing semitransparent middle interlayer in such tandem solar cell configuration. Also, further strategies for improving this interlayer together with short overview of other challenges on how to provide even more complementary absorption will be discussed.

EN08.09.26
Sandwiched Gold Nanomesh Electrode for Ultrahigh Near-Infrared Transmittance for High-Efficiency Multijunction Perovskite Solar Cells Ziyu Wang; Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

The crystalline Si-based solar cells have been dominating the ever-expanding global PV market with about 95% market share. With its highest cell efficiency of 26.6% reaching its theoretical limit, there is little hope to raise its performance by just device optimization within the single-junction cell architecture. As the PV market is so huge with its annual revenue in the order of trillion US dollars, even 1% cost reduction would mean net profit of billions of US dollars per year. Since efficiency increase is proven to be the most reliable means to reduce cost, it makes sense for industries like Hanergy and Shanghai Institute of Microsystem and Information Technologies to support us to develop the tandem cells with potential of significantly increased cell efficiency. There are two basic designs for the tandem cells: (1) two-terminal configuration in which the perovskite top-cell is deposited on the silicon bottom-cell; and (2) four-terminal design in which both the perovskite top-cell and the silicon bottom-cell are completed independently. For the first, in case the top-cell is degraded for any reason, the integrated tandem cell is affected by the same proportion. For the latter, if the perovskite goes bad for any reason, it can be simply removed from the integration and the silicon cell will work just fine. Considering that the silicon solar modules are so robust with product warranty of 25-35 years, and the perovskite solar cells are still in the research stage without any reliability data from the market, the 4-terminal cell design is therefore selected in the present work to not only taking the advantages of higher cell efficiency for reduced cost, but also minimized influence of uncertain reliability of perovskite on the silicon solar modules.
Semi-Transparent Perovskite Solar Cells with Two-Step InZnSnO Top Electrodes Deposited by Damage-Free Linear Facing Target Sputtering Sang-Hwi Lim\textsuperscript{1}, Jin H. Park\textsuperscript{1}, Han-Ki Kim\textsuperscript{1} and Seungju Nam\textsuperscript{2};
\textsuperscript{1}Sungkyunkwan University, Korea (the Republic of); \textsuperscript{2}Korea Electric Power Research Institute, Korea (the Republic of)

Recently, semi-transparent perovskite solar cells (PSCs) have been investigated as building integrated photovoltaics (BIPV) for next generation smart building. To realize semi-transparent PSCs, both anode and cathode electrodes have a high transparency and conductivity. However, unlike bottom anode electrodes prepared by typical sputtering, the preparation of top cathode electrode is very difficult because the semi-transparent PSC is severely damaged by irradiation of high energy plasma during the sputtering process. Here, we reported semi-transparent perovskite solar cells (PSCs) with InZnSnO (IZTO) top cathode prepared by two-step sputtering at room temperature. At first sputtering process, 30 nm thick IZTO top cathode was very slowly sputtered at a low DC power to minimize the direct plasma damage of PSCs. Then, thick IZTO top cathode was directly sputtered on the thin IZTO buffer layer to obtain high conductivity\textsuperscript{1} and transparency of the IZTO cathode electrode. LFTS-grown IZTO top cathode sputtered at an optimized condition has a sheet resistance of 20.95 Ohm/square and optical transmittance of 85.97% at wavelength 550 nm. In addition, we confirmed LFTS-grown IZTO top cathode has appropriate energy band structure as a top cathode for semi-transparent PSC by using ultraviolet photoelectron spectroscopy (UPS). The semi-transparent PSCs with LFTS-grown IZTO top cathode has comparable power conversion efficiency (PCE) of 14.08% to PCE(16.46%) of reference opaque PSC with Ag top cathode. Similar PCE value of the semi-transparent PSC prepared by LFTS indicates that the LFTS is a promising thin film process to make IZTO top cathode on the PSCs without plasma damage which was easily found in typical DC or RF magnetron sputtering of TCO top cathode in semi-transparent PSCs.

Subcells Characterization of Highly Efficient Perovskite-Based Tandem Solar Cells Jae Hyun Park, Ik-Jae Park, Su Geun Ji and Jin Young Kim; Seoul National University, Korea (the Republic of)

The tandem solar cells based on perovskite top cells are attracting significant interest due to its high conversion efficiency and decent stability.[1,2] The theoretical calculation shows that the combination of a top cell with a large bandgap energy (1.5–1.7 eV) and a bottom cell with a low bandgap energy (1.0–1.1 eV) can lead to a conversion efficiency higher than 40%. Given that the bandgap energy of most commercial single junction solar cells is around 1.1 eV, the perovskite solar cell with a bandgap energy around 1.6 eV must be a very promising candidate for the top cell of tandem solar cells.

Although the efficiency of the perovskite-based tandem solar cells is rapidly increasing, the accurate characterization of their photovoltaic/electrical properties is quite tricky due to their monolithic device structure. We have recently demonstrated that the photovoltaic/electrical properties of the highly efficient (~24%) perovskite-Si tandem solar cells and each subcell can be accurately characterized using a 3-terminal characterization platform.[3] where we used subcell EQE spectra for precise current matching. In this presentation, the concept of 3-terminal characterization platform and how we utilized it for developing highly efficient perovskite-Si tandem solar cells will be introduced. In addition, some of our recent studies focusing on the unique photovoltaic/electrical properties of each subcell in the monolithic tandem solar cells such as the effect of the subcell illumination on the electron dynamics and the effect of the current mismatching on the photovoltaic properties will be discussed.

References

Carbon-Based Electrode Engineering Boosts the Efficiency of All Low-Temperature Processed Perovskite Solar Cells Sisi He, Longbin Qiu, Luis K. Ono and Yabing Qi; Okinawa Institute of Science and Technology Graduate University, Japan
Using carbon to function as both hole transport layer (HTL) and back contact electrode in perovskite solar cells (PSC) can significantly lower the cost, improve the device stability and expand applications to flexible substrates [1]. The interface between HTL and the perovskite layer which is the only effective hole extraction interface in this device is expected to have a significant impact on the device performance [2]. Besides the effective HTL, a high open-circuit voltage (Voc) of carbon-based PSCs is also key to achieving high performance. One of the reasons responsible for the low Voc in carbon electrode-based PSC devices is the energy level mismatch between the carbon electrode (e.g., graphite, carbon black) and the perovskite film (e.g., CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$), CH(NH$_2$)$_2$PbI$_3$, CH$_3$NH$_3$PbBr$_3$) [3]. In this work, we develop an elaborate process to engineer carbon paste to optimize the properties of carbon electrodes and the perovskite/carbon interface to fabricate all low-temperature processed carbon electrode-based lead halide perovskite solar cells. In addition, the low-temperature coating process is fully compatible with large scale and continuous fabrication. Carbon electrode-based flexible solar cells can be also fabricated on flexible conductive substrates thanks to the low-temperature process and their compatibility with printing processes.


EN08.09.30
Engineering an Open-Air Process Window for Rapid Spray-Plasma Fabrication of Stable, Highly Reproducible Perovskite Solar Cells William J. Scheideler, Nicholas Rolston, Austin Flick, Oliver Zhao, Justin Chen, Jinbao Zhang and Reinhold H. Dauskardt; Stanford University, United States

Hybrid metal halide perovskite solar technology poses exciting global potential for terawatt-level generation and penetration of solar energy into new markets such as transportation and lightweight wireless devices. However, large area scaling and operational reliability remain formidable challenges hindering commercialization. High-throughput open-air fabrication methods such as spray coating and printing could offer low capital-expenditure routes to continuous manufacturing of perovskites, but understanding and overcoming ambient factors such as relative humidity (RH) has been a persistent challenge for achieving high performance and device stability.

In this work, we present moisture-immune open-air spray-plasma processing of high-performance double cation perovskite solar cells that leverages solvent engineering and dual source annealing to precisely control film drying kinetics. Rapid plasma curing and air blade drying of perovskite films (< 100 ms) at elevated substrate temperatures > 100 °C and high processing speeds (>20 cm/s) afford immunity to ambient moisture ingress even under high humidity conditions (up to 50% RH). Our study of the influence of precursor composition, processing speed, and perovskite plasma curing kinetics on film morphology and crystallinity, as well as solar cell performance, allows a generalizable correlation of micron-scale morphologies with photovoltaic efficiency.

This detailed understanding of open-air perovskite processing allowed fabrication of highly reproducible planar inverted Cs$_{17}$FA$_{83}$Pb(Br$_{17}$I$_{83}$)$_3$ cells with stabilized PCE > 16 %, fill factors as high as 78 %, and standard deviation < 1.5% absolute PCE among independent batches fabricated from 25%-50% RH. Importantly, these devices are processed exclusively by scalable methods (no spin coating), utilizing spray deposited inorganic NiO hole transport layers to complete a highly photostable cell architecture that retains 98% of initial PCE over the course of 5•10$^4$s of maximum power point tracking under illumination. This combination of rapid open-air processing methods with an efficient and highly stable multiple cation perovskite composition can offer a viable path towards module upscaling.

EN08.09.31
Flexible Perovskite Solar Cells via Gravure Printing toward Roll-to-Roll Manufacturing Young Yun Kim¹, Tae-Youl Yang¹, Riikka Suhonen², Antti Kemppainen² and Jangwon Seo¹; ¹KRICT (Korea Research Institute of Chemical Technology), Korea (the Republic of); ²VTT Technical Research Centre of Finland, Finland

Perovskite solar cells (PSCs) have been of great interest due to the inherent superior optoelectronic properties of organometallic halide perovskite itself, such as high absorption coefficient, long carrier diffusion length, ambipolar charge transport and solution-processability. Over 24 % of power conversion efficiency (PCE) have been achieved recently for PSCs by virtue of composition engineering, optimization of interlayer, and defect management. Aside from the high PCE, flexibility and light-weight are the most unique and promising characteristics of PSCs. To utilize
such advantages the PSCs, the fabrication of large-area PSCs via scalable deposition process is prerequisite. The several successful demonstrations of scalable production of PSCs have been reported by blade, slot-die, and inkjet coating, yielding uniform perovskite films with a high quality. Nevertheless, the direct printing of the desirable layer with arbitrary shape and size at a relatively high deposition speed remains a great challenge for flexible PSCs. In this presentation, we will present the fabrication of all-printed PSCs with a n-i-p structure on flexible substrates using gravure printing, which is a roll-to-roll compatible deposition method enabling a realization of the desirable image pattern. The successful formation of Methylammonium (MA)-based perovskite layer is demonstrated by gravure printing using the one-step method employing printing and successive antisolvent-bathing process. The SnO2 and Spiro-OMeTAD as electron- and hole-transporting layer are also gravure-printed. As a result, the all-printed PSCs showed a PCE of 17.2% in reverse scan and a stable power output over 1000 s. [1] For a better performance, Formamidinium (FA) based, multi-cation perovskite films are prepared by gravure printing. Eco-friendly and efficiently extracting antisolvent is newly suggested so as to successfully form a uniform FA-based perovskite layer and extend the process to roll-to-roll scale. Consequently, gravure-printed cells exhibited PCE of over 18% for table-top printing and over 15% for partial roll-to-roll process, respectively. Furthermore, the gravure-printed perovskite layers fabricated by the two-step method via mediator extraction treatment (MET) will be discussed in this presentation. [2]

References

EN08.09.32
High-Performance, Stable and Flexible Perovskite Solar Cell for Wearable Photovoltaic Systems Janak Thapa, Sai Nithin Reddy Kantareddy, Noor Titan Putri Hartono, Ian Mathews, Sanjay Sarma, Ian Marius Peters, Shijing Sun and Tonio Buonassisi; Massachusetts Institute of Technology, United States

Perovskite solar cells (PSCs) show great promise as an emerging photovoltaic technology (PV) because of their low cost and relative ease of manufacturing. In a previous study, we demonstrated the application of flexible solar cells for wireless systems, using them as external power sources for radio-frequency identification (RFID) sensors [1]. Traditionally, the performance of PSCs deposited on plastics is inferior to their on-glass counterparts, both in terms of efficiency and stability. We, therefore, performed a diagnostic study to determine the key performance limiting factors and understand the root-cause of the performance drop. Our results identified shunting effect as a major contributor for low efficiency in flexible cells. Hence, we performed process optimization through cleaning, etching, morphology control and chemical doping, and achieved an improvement in efficiency from 10% to over 13% in an ongoing process. We evaluated the device stability via an accelerated aging test in our in-lab stability chamber and performed a comparative study on the degradation mechanisms of PSCs deposited on glass and plastics, respectively. Our study shows significant improvement in the performance of flexible PSCs and contributes to the development of flexible PSCs for wearable technologies, such as solar-powered RFID.


EN08.09.33
Large-Scale Deposition of Copper (I) Thiocyanate Hole Transport Material for Use in Perovskite Solar Cells Lokeshwari Mohan1,2, Martyn McLachlan1 and Joe Briscoe2; 1Imperial College London, United Kingdom; 2Queen Mary University of London, United Kingdom

Copper (I) thiocyanate (CuSCN) is an optically transparent, wide bandgap (3.4-3.9 eV), p-type semiconductor used in organic and perovskite solar cells. In comparison to other hole transporting materials (HTMs), CuSCN is economically favourable and comparable in performance, with efficiencies for hybrid organic-inorganic metal halide perovskite solar cells exceeding 20% [1].

Current research involves several solution-processable methods such as spin coating, spray coating and doctor blading. This study reports the first ever deposition of CuSCN via aerosol assisted chemical vapour deposition (AACVD). AACVD is a scalable ambient-pressure technique with low processing costs and simple reactor design. An added advantage is the flexibility over material choice due to the process being dependent on the solubility of the precursor, rather than the volatility as in conventional chemical vapour deposition techniques [2].
The study involves deposition of CuSCN using three different solvents: dipropyl sulfide, diethyl sulfide and ammonium hydroxide. For each CuSCN/solvent combination, deposition temperature, concentration of solution and amount of precursor solution deposited were varied. CuSCN films produced by diethyl sulfide solvent were further optimised by studying the growth characteristics. CuSCN films deposited via AACVD were compared to films produced by conventional spin coating methods. Scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible spectroscopy (UV-Vis) were used to determine morphological, structural and optical information.

Using the optimised conditions, AACVD CuSCN was incorporated into a working methylammonium lead iodide perovskite solar cell. Addition of interlayers, different electron transport layers and device architectures were explored to determine structure with highest performance. Studies into the solar cell performance allowed further understanding of the less well-known CuSCN HTM. Solar cells were tested under AM 1.5 and a champion efficiency of 10.44% was achieved, which represents the first ever working solar cell using AACVD CuSCN.


EN08.09.34
Laser Scribing of Organometal Halide Perovskite Solar Cells for See-Through Module Fabrication David Hwang¹, Zhen Wang¹, Seungkuk Kuk¹ and Jeung-hyun Jeong²; ¹State University of New York at Stony Brook, United States; ²Korea Institute of Science and Technology, Korea (the Republic of)

Organometal–halide perovskite solar cells (PSC) have attracted attention by its unprecedented rise in device efficiency. However, the PSCs were mostly tested for the unit cell of small area. Therefore, it is important to upscale to solar modules that provide desired voltage and power output. Laser scribing technology, proven for the conventional thin film solar cell fabrication process, can be effectively extended for PSC module fabrication. The P1 scribing to isolate the transparent bottom electrode layer is essentially identical to the conventional laser scribing task. However, the P2 laser scribing to expose the bottom electrode for serial interconnect with the minimal contact resistance has been recognized as a challenging process; it is important to develop reliable single-step P2 process removing necessary stack of films, e.g., including hole blocking layer, without damaging bottom electrode, depending on the PSC material architectures selected. Although the P3 laser scribing to isolate the top electrode layer has been assumed to be less difficult, close examination of possible electrical shunt and/or unwanted damage of underlying structures are required. On the other hand, the P4 laser scribing to fabricate see-through patterns should minimize electrical shunt and/or degradation of surrounding structures with high optical transmissivity or visuality. Current study will focus on addressing the aforementioned challenges by exploring the optimal PSC laser scribing parameters based on pico- and nano- second lasers of various wavelengths from ultraviolet to visible and near-infrared, illuminated both from film and substrate sides. Relevant mechanisms and further improvement plans will be also discussed based on the measured module performance in conjunction with morphological, compositional, optical and spectroscopic characterization results.

EN08.09.35
Engineering of the Back Contact between PCBM and Metal Electrode for Planar Perovskite Solar Cells with Enhanced Efficiency and Stability Shaobing Xiong and Qinye Bao; East China Normal University, China

The cathode interface plays a critical role in achieving high-performance fullerene/perovskite planar solar cells, governing the charge extraction and transport behaviors between the perovskite layer and the electrode. However, there is a high energy mismatch between PCBM and the commonly used metal cathode electrode aluminum (Al) and silver (Ag), severely restricting the electron extraction at the contact and therefore leading to poor device performance. [1]

Herein, organic dyes, Isatin and Isatin-Cl, which are abundant, cheap, air stable, and easy to modify in terms of their chemical structure, are introduced at the back contact PCBM/Al as a cathode modification interlayer due. [2] It is revealed that the Isatin interlayers facilitate electron transport/extraction and suppress electron recombination, attributed to the formation of negative dipole potential steps and the passivation of the interfacial trap density. The
average power conversion efficiencies of the resulting devices are significantly improved by 11% from 17.68 % to 19.74%, with an enhancement in all device parameters including short-circuit current, open-circuit voltage and fill factor. The hysteresis index is found to disappear. In addition, such interlayer enhances device stability under ambient conditions compared to the control devices due to suppression of moisture-induced degradation of the perovskite films. Our findings provide a comprehensive understanding of the engineering of the back contact between PCBM and the metal electrode to improve efficiency and stability of perovskite solar cells.


EN08.09.36
Analyzing the Reactivity of Surface Ligands with MAPbI3 Films and Their Influence on Photoluminescence, Stability and Photovoltaic Performance
So Min Park, Ashkan Abtahi and Kenneth R. Graham; University of Kentucky, United States

Surface ligand treatment provides a promising approach to passivate defect states and improve the photoluminescence quantum yields (PLQY), charge-carrier mobilities, material and device stability, and photovoltaic (PV) device performance of organic metal halide perovskites (OMHPs). Numerous surface treatments have been applied to OMHP thin films and shown to passivate defect states and improve the PLQY and PV performance of OMHPs, but it is not clear which surface modifiers bind to the surface and to what extent. As surface ligands have the potential to passivate defect states, alter interface energetics, and manipulate material and device stability, it is important to understand how different functional groups interact with the surfaces of OMHP thin films. In this study, we investigate a series of ligand binding groups and systematically probe the stability of the bound surface ligands, how they influence PL properties, film stability, and PV device performance. We observe phosphonic acids (PAs) form reasonably stable surface bonds, whereas carboxylic acids (CAs) and thiols do not. Trichlorosilane (SiCl3) groups react rapidly and lead to thicker surface layers that restrict charge transfer at the perovskite/electron transport layer (ETL) interface. Ammonium salts react rapidly to displace the methylammonium cations, thus resulting in less control over formation of only a surface layer. Despite the fact that we do not detect thiol or CA binding with XPS measurements, both of these surface ligands lead to increased PL intensity and increased stability. Furthermore, toluic acid treatment of MAPbI3 based inverted PV devices results in an improved power conversion efficiency from 16.5% to 19.3%.

EN08.09.37
Chemomechanical Effect of Cutting Fluid Affects Ductile Mode Material Removal in Slicing Silicon Wafers for Photovoltaics
Arkadeep Kumar1,2 and Shreyes Melkote2; 1Lawrence Berkeley National Lab, United States; 2Georgia Institute of Technology, United States

Mechanical strength of crystalline silicon wafers sliced by diamond wire sawing process depends on the surface and subsurface damage (in form of microcracks) caused by material removal processes. The type and the extent of damage depends on material removal being ductile or brittle. In this work we investigated the chemo-mechanical effect of cutting fluid on material removal mechanisms in single crystal silicon by scribing experiments, which simulates the material removal mode of industrial diamond wire slicing process. We show experiments between of scribing single crystal silicon in dry and in presence of water-based cutting fluids. Our results show more ductile material removal of silicon in presence of the cutting fluid – such chemomechanical effect of fluid on silicon has not been reported in literature, and provide new ways of reducing surface and subsurface damage in silicon wafers.

EN08.09.38
Effect of Polycrystalline Silicon on Wear of Diamond In Scribing
Arkadeep Kumar1,2 and Shreyes Melkote2; 1Lawrence Berkeley National Lab, United States; 2Georgia Institute of Technology, United States

Multi-crystalline silicon (mc-Si) is cheaper than single-crystalline silicon and hold promise of delivering affordable photovoltaic energy. However, manufacturing process of multi-crystalline silicon wafers by slicing with diamond wire sawing faces challenges of reduced efficiency with increased consumption of the diamond abrasives on the wire. We simulate the cutting process by fundamental scribing or scratch experiments with diamond on single and multi-crystalline silicon substrates. We used two tips of same geometry conical diamond indenters, and monitored the wear of diamond by microscopy and radius of curvature measurements, apart from contact forces for mc-Si
versus single-crystal silicon. We found that the forces are higher for diamond contacting for mc-Si, and corresponding increase in tip radius being higher in mc-Si versus single-crystal silicon, due to higher stresses and wear of the tip. We found the fracture surfaces of diamond show micro-fracture and blunting from high resolution scanning electron microscopy and confocal microscopy. Stress induced phased transformation of diamond along with compressive residual stresses were measured using Raman spectroscopy for difference in silicon material structure. We explain the results using material inhomogeneity of multi-crystalline silicon for increased wear of diamond cutting the material, compared to single crystal silicon.

SESSION EN08.10: Perovskite Solar Cell—2D, Stability, Nanostructures
Session Chairs: Selina Olthof and Yixin Zhao
Thursday Morning, December 5, 2019
Sheraton, 2nd Floor, Back Bay AB

8:30 AM *EN08.10.01
Two Dimensional Organic-Inorganic Perovskite from Nanostructures to Solar Cells Lioz Etgar; Hebrew University, Israel

Perovskite is a promising light harvester for use in photovoltaic solar cells. In recent years, the power conversion efficiency of perovskite solar cells has been dramatically increased, making them a competitive source of renewable energy. This work will discuss new directions related to organic inorganic perovskite and their applications in solar cells. In low dimensional systems, stability of excitons in quantum wells is greatly enhanced due to the confined effect and the coulomb interaction. The exciton binding energy of the typical 2D organic-inorganic perovskites is up to 300 meV and their self-assembled films exhibit bright photoluminescence at room temperature. *In this work we will show the dimensionality in the perovskite structure. The 2D perovskite structure should provide stable perovskite structure compared to the 3D structure. The additional long organic cation, which is added to the perovskite structure (in the 2D structure), is expected to provide hydrophobicity, which will enhance the resistivity of the perovskite to humidity. Moreover we will demonstrate the use of 2D perovskite in high efficiency solar cells.

* Organic-inorganic halide perovskite is used mainly in its “bulk” form in the solar cell. Confined perovskite nanostructures could be a promising candidate for efficient optoelectronic devices, taking advantage of the superior bulk properties of organo-metal halide perovskite, as well as the nanoscale properties. In this talk, I will present our recent progress related to the synthesis and characterization of perovskite NPs - i.e. Inorganic and hybrid organic-inorganic NPs. New nanostructures such as: NRs and NWs will be presented and the introduction of other cations such as Rb will be shown.

9:00 AM *EN08.10.02
Crystal Orientation Drives the Interface Physics at 2/3-Dimensional Hybrid Perovskites Marine E. Bouduban1, Valentin I. Queloz1, Valentina Caselli2, Kyung Taek Cho1, Ahmad R. Kirmani1, Sanghyun Paek1, Cristina Roldan Carmona1, Lee Richter1, Jacques E. Moser1, Tom J. Savenije2, Mohammad K. Nazeeruddin1 and Giulia Grancini1; 1EPFL, Switzerland; 2Delft University of Technology, Netherlands; 3National Institute of Standards and Technology, United States

Combining halide perovskites with tailored dimensionality into two/three-dimensional (2D/3D) systems has revealed a powerful strategy to boost the performances of perovskite photovoltaics (PVs). Despite the recent advances, a clear understanding on the intimate link between interface structure and physics is still missing, leading so far to a blind optimization of the 2D/3D PVs. Here, we reveal the impact of 2D/3D crystal alignment in driving the interface charge-recombination dynamics. The 2D crystal growth and orientation is manipulated by specific fluorination of the phenethylammonium (PEA), used here as the organic cation backbone of the 2D component. By means of time-resolved optoelectronic analysis from femto- to microsecond, we demonstrate a static function of the 2D as electron barrier and homogeneous surface passivant, together with a dynamical role in retarding back charge recombination. Our results reveal a crucial dependence of such beneficial effect with the 2D crystal orientation, leading to enhanced open circuit voltage (V_{OC}) if 2D lies parallel on the 3D. Such findings provide a deep
understanding and delineate precise guidelines for the smart design of multi-dimensional perovskite interfaces for advanced PV and beyond.

9:15 AM EN08.10.03
From 2D to 1D Electronic Dimensionality in Halide Perovskites with Stepped and Flat Layers Using Propylammonium as a Spacer
Justin M. Hoffman1, Xiaoyang Che2, Siraj Sidhik3, Xiaotong Li1, Ido Hadar4, Jean-Christophe Blancon5, Hisato Yamaguchi6, Mikael Kepenekian7, Claudine Katan8, Jacky Even9, Constantinios Stoumpos1, Aditya D. Mohite3 and Mercouri G. Kanatzidis1; 1Northwestern University, United States; 2Université de Rennes, France; 3Rice University, United States; 4Los Alamos National Laboratory, United States

Two-dimensional (2D) hybrid halide perovskites are promising in optoelectronic applications, particularly solar cells and light emitting devices (LEDs), and for their increased stability compared to 3D perovskites. Here, we report a new series of structures using a propylammonium (PA+) cation which results in a series of Ruddlesden-Popper (RP) structures with the formula (PA)2(MA)n-1PbnI3n+1 (n = 3, 4) and a new homologous series of “step-like” (SL) structures where the PbI6 octahedra connect in both a corner- and face-sharing motif with the general formula (PA)2m+4(MA)m-2Pb2m+1I7m+4 (m = 2, 3, 4). The RP structures show a blue-shift in bandgap for decreasing n while the SL structures have an even greater blue-shift. DFT calculations show that, while the RP structures are electronically 2D quantum wells, the SL structures are electronically 1D quantum wires with the chains of corner-sharing octahedra “insulated” by blocks of face-sharing octahedra. These blocks form an additional lateral carrier confinement barrier that prevents any significant electronic coupling across the face-sharing octahedra and results in 1D electronic dimensionality. Dark measurements for RP crystals show high resistivity perpendicular to the layers but a lower resistivity parallel to them. The SL crystals have varying resistivity in all three directions, confirming both RP and SL crystals’ utility as anisotropic electronic materials. The RP structures show strong photoresponse and are utilized in solar cell devices. Solar cells were made with n = 3 using “hotcasting” and solvent engineering methods giving an efficiency of 7.04% (average 6.28 ± 0.65%) with negligible hysteresis.

9:30 AM EN08.10.04
Uniformly Arranging Different-n-Value Nanoplates for Developing Highly Efficient Quasi-2D Perovskite Solar Cells
Jia Zhang1, Jiajun Qin2, Miaosheng Wang1, Yujie Bai2, Han Zou1, Hengxing Xu1, Jong K. Keum4, Haomiao Yu5 and Bin Hu1; 1University of Tennessee, United States; 2Fudan University, China; 3University of Strasbourg, France; 4Oak Ridge National Laboratory, United States; 5Beijing Jiaotong University, China

Quasi-2D perovskites are inevitably formed with multi-layer nanoplates of different n values. Normally, the nanoplates are vertically arranged from small-n-value to large-n-value structures between bottom and top surfaces in quasi-2D perovskite films, forming a common approach to facilitate charge transfer for developing high-performance optoelectronic devices. Here, we report a different strategy of uniformly arranging different-n-value nanoplates (PEA2MAn-1PbnI3n+1) between bottom and top surfaces in quasi-2D perovskite films to generate high-performance solar cells by introducing vacuum poling treatment right after spin-coating of precursor solution. By mechanically peeling off the monolayers of nanoplates with our delicate scotch-tape method while monitoring the photoluminescence (PL), we un-ambiguously show that our vacuum poling method can create the uniform dispersion of different-n-value nanoplates between bottom and top surfaces in quasi-2D perovskite films, as compared to the conventional ordered dispersion of nanoplates from n = 1 to n = 5 prepared without vacuum poling treatment. The transient absorption (TA) measured through bottom and top surfaces show that the efficient carrier transfer occurs within 10 ps from small-n-value nanoplates to large-n-value nanoplates under uniform dispersion, presenting an efficient carrier extraction mechanism. The PL dynamics indicate that uniformly arranging different-n-value nanoplates leads to small-n-value and large n-value nanoplates functioning as passivation agents and light-emitting centers with significantly enhanced PL intensity and lifetime. Moreover, the record-high fill factor (FF) of 82.4 % was realized with the power conversion efficiency (PCE) of 18.04% (Voc = 1.223V and Jsc = 17.91 mA/cm2), showing an extremely efficient carrier extraction occurring in the quasi-2D perovskite device (ITO/PTAA/quasi-2D perovskites/PC61BM/PEI/Ag) based on this new strategy. Therefore, uniformly arranging different-n-value nanoplates offers a new materials engineering strategy to enhance carrier transfer and extraction for developing high-performance quasi-2D perovskite solar cells.

9:45 AM BREAK
SESSION EN08.11: Perovskite Solar Cell—All Inorganic Solar Cells
Session Chairs: Lioz Etgar and Shengzhong (Frank) Liu
Thursday Morning, December 5, 2019
Sheraton, 2nd Floor, Back Bay AB

10:15 AM *EN08.11.01
All-Organic CsPbI₃ Perovskite for High Efficiency Photovoltaics Yong Wang, Taiyang Zhang and Yixin Zhao; Shanghai Jiao Tong University, China

The all-inorganic lead halide perovskite without volatile component would be a promising alternative candidate for high efficiency photovoltaics. However, the all inorganic CsPbI₃ with most suitable band gap face the challenges of low room temperature phase stability and relative low efficiency. To enhance the performance and stability of all-inorganic CsPbI₃ perovskite, the 2D/3D configuration especially the (110) oriented 2D perovskite component was introduced to stabilize the α-CsPbI₃. The (110) oriented 2D based on EDAPbI₄ help stabilize α-CsPbI₃ to achieve up to >11% efficiency. Impressively, the Cs cation in CsPbI₃ would not ion exchanged with organic cation, which is significantly different from the hybrid and a signal for the promising cation stability of inorganic perovskite. Therefore, a facile organic cation surface termination approach was developed to significantly enhance the stability and performance of α-CsPbI₃ solar cell with >15% efficiency. The bifunctional stabilization of CsPbI₃ with gradient Br doping and organic cation termination finally improve the efficiency of CsPbI₃ perovskite solar cells to a record value of 17% with enhanced stabilities.

10:45 AM EN08.11.02
High Efficiency 16.37% of Cesium Bromide-Passivated All-Inorganic CsPbI₂Br Perovskite Solar Cells Yuqing Zhang, Cuncun Wu and Bo Qu; Peking University, China

Recently, the all-inorganic CsPbI₂Br perovskite attracts increasing attention owing to its outstanding thermal stability and suitable bandgap for optoelectronic devices. However, the substandard power conversion efficiency (PCE) and large energy loss ($E_{\text{loss}}$) of CsPbI₂Br perovskite solar cells (PSCs) caused by the low quality and high trap density of perovskite film, still limit the application of devices. Herein, we utilize the post-treatment of evaporating cesium bromide (CsBr) on top of perovskite surface to passivate the CsPbI₂Br/hole-transporting layer interface and reduce $E_{\text{loss}}$. The results of micro zone photoluminescence indicate that the evaporated CsBr gathered at grain boundaries of CsPbI₂Br layers and Br-enriched perovskites (CsPbIₓBr₃₋ₓ, x<2) are formed, which can provide protection for CsPbI₂Br. Therefore, the gaps between crystal grains are filled up and the recombination loss of the all-inorganic CsPbI₂Br PSCs is reduced accordingly. The champion device exhibits the high open-circuit voltage and PCE of 1.271 V and 16.37%, respectively. To the best of our knowledge, it’s the highest PCE among all-inorganic CsPbI₂Br PSCs reported so far. In addition, the stability of CsPbI₂Br PSCs is effectively improved by CsBr passivation and the device without encapsulation can retain 86% of its initial PCE after storage of 1368 hr, which is beneficial to the practical application.

11:00 AM EN08.11.03
Straining to be Black—On the Thermal Unequilibrium of Metastable Perovskite Thin Films Julian A. Steele, Johan Hofkens and Maarten Roefraers; KU Leuven, Belgium

The all-inorganic CsPbI₃ perovskite offers the prospect of a more stable alternative to hybrid organic-inorganic perovskites. Unfortunately, like many other polymorphic perovskite systems, the metastability of its high-temperature black phase (l) stands in the way of realizing room-temperature (RT) stable optoelectronic devices. It is of interest to find ways to shift the energetics of CsPbI₃, in order to secure RT black phase formation over its yellow non-perovskite phase (2). In this presentation, we outline the role of glass substrate clamping and biaxial strain (induced by the large thermal expansion mismatch) to realize RT stable black-phase CsPbI₃ thin films. Employing synchrotron-based grazing incidence wide angle X-ray scattering with extremely fast acquisition time (~0.1 s), we track the introduction of crystal distortions and texture formation within black CsPbI₃ thin films as they are cooled from annealing temperatures. The thermal stability of black CsPbI₃ thin films are vastly improved by the strained interface, a response verified by ab initio thermodynamic modelling. This contribution introduces substrate clamping as an important parameter in the rational design of stable RT black inorganic halide perovskite thin films.
11:15 AM EN08.11.04
High-Stability All-Inorganic Perovskite Solar Cells  Jia Liang and Jun Lou; Rice University, United States

Hybrid organic-inorganic halide perovskite solar cells (PSCs) have attracted a great deal of attention as they show promises toward the development of next generation solar cells, with the highest power conversion efficiency (PCE) reaching 24%. However, these types of PSCs, such as PSCs based on methylammonium lead iodide (MAPbI3) or formamidinium lead iodide (FAPbI3), exhibited poor stability against moisture and heat. Moreover, hole transport materials (HTMs) in these traditional PSCs (Spiro or PTAA) are very expensive and need some additives to improve their mobility. In order to overcome these disadvantages, we develop all-inorganic PSCs based on CsMX3 (M = Pb, Sn, In; X = I, Br, Cl) and low-cost carbon films. First, we employed CsPbBr3 as the absorb layer in the all-inorganic PSC, which showed excellent stability even under environmental stress and without any encapsulation. However, because the bandgap of CsPbBr3 was 2.3 eV, the light absorption for CsPbBr3 was only up to ~540 nm, which led to the low PCE. As CsPbI3 possesses a smaller bandgap (1.7 eV) than CsPbBr3, CsPbI3-based all-inorganic PSCs are subsequently developed. However, they still exhibited lower PCEs because of the existence of defects and poor stability. Therefore, in our recent work, we engineered the defect densities in CsPbI3, and a new all-inorganic perovskite material, CsPbI3:Br:InI3, was prepared. This new perovskite retained the same bandgap as CsPbI3, while the intrinsic defect concentration has been largely suppressed. Moreover, it can be prepared under extremely high humidity atmosphere thus a glovebox was not required. By completely eliminating the labile and expensive components in traditional PSCs, the all-inorganic PSCs based on CsPbI3:Br:InI3 and carbon electrode exhibited the PCE and open-circuit voltage as high as 12.04% and 1.20 eV, respectively. More importantly, the encapsulated all-inorganic PSCs based on CsPbI3:Br:InI3 demonstrated excellent stability in air for more than two months, while those based on CsPbI3 can just survived a few days in air. The progresses reported here open the door for all-inorganic PSCs with long-term stability under harsh conditions, making practical application of the PSC with high performance a real possibility.

11:30 AM EN08.11.05
Highly Efficient CsPbBr2 Perovskite Solar Cells—Interface Modification and Heteroatom Substitution  Kai Wang1, Waqas Siddique Subhani1 and Shengzhong (Frank) Liu1,2; 1Dalian Institute of Chemical Physics, China; 2Shaanxi Normal University, China

The state-of-the-art organic-inorganic halide perovskite solar cells (PSCs) have scored tremendous achievements as reflected by the highest power conversion efficiency (PCE) skyrocketing to over 24.2% in just a few years.[1] Nevertheless, the long-term stability of the hybrid perovskite inherited from its organic moiety remains a major hurdle preventing it from commercialization. For further development of PSCs, a more robust inorganic cesium halide perovskite (CsPbX3, X = I or Br) without a fragile organic component and possessing a range of spectacular advantages, including superb thermal stability (> 300 °C) and high electron mobility, is considered to have more potential than the organic-inorganic hybrid material. As such, it is extremely crucial to design inorganic perovskite-based solar cells possessing both excellent photovoltaic performance and outstanding stability. Among the shared inorganic perovskite employed in PSCs, CsPbBr2 is considered a feasible material for tandem solar cells after balancing the band gap and stability of the inorganic perovskite. Nevertheless, the performance of CsPbBr2 PSCs has lagged behind that of other analogs, far from its highest theoretical efficiency. In general, the inferior performance is attributed to substantial interface recombination and non-radiative recombination within the perovskite.

Accordingly, we report a facile interface modification strategy for inorganic PSCs, wherein a low-cost lanthanide halide, SmBr3, is incorporated to modify the TiO2/CsPbBr2 interface.[2] Apart from its effects at the interface, SmBr3 can diffuse into the perovskite layer and induce a blocking layer with a gradient energy band gap. Therefore, SmBr3 interface modification can not only optimize the charge transfer process and restrain interface recombination, but also suppress the non-radiative recombination within the perovskite material. Finally, the devices with SmBr3 interface modification yield a high PCE of 10.88%.

In addition, Ba2+ was doped in CsPbBr2 to suppress the inside non-radiative recombination.[3] Ba2+ with large radius can result in an undesired tolerance factor less than 0.8, but strikingly, the Ba2+-doped CsPbBr2 has beneficial
morphology and excellent crystallinity as well as suppressed carrier recombination. Compared with the control sample, Ba\(^{2+}\) doping boosts the device efficiency from 8\% to 10.5\%. This finding indicates that the perovskite films are tolerant to Goldschmidt-rule-deviating homovalent heteroatoms, extending the substitution engineering of inorganic perovskite.

References:

11:45 AM EN08.11.06
Effective Strategies to Improve the Performance and Operational Stability of Perovskite Solar Cells

M Ibrahim Dar; University of Cambridge, United Kingdom

Over a span of a decade, perovskite solar cells have evolved as a promising photovoltaic technology by displaying a meteoric rise in the power-conversion efficiencies. However, it is equally important that the performance of perovskite solar cells sustains under operating conditions over a long period of time. Therefore, their stability under different conditions such as illumination, humidity, and thermal stress needs to be thoroughly investigated. It is well known that the stability problems of perovskite solar cells arise from the degradation of the light-absorbing and/or charge extraction layers and the deterioration of various interfaces across the solar cell. We have employed three main strategies to develop better perovskite-based devices that are not only efficient but also stable. We have investigated the interfaces on both sides of the hole transporting material (HTM) i.e., perovskite absorber/HTM and HTM/back contact interface in a solar cell device to mitigate the catastrophic stability issues associated with perovskite solar cells. We explored three main strategies including employing all-inorganic charge extraction layers [1]. This has led to the CuSCN hole extraction layer based devices with stabilized efficiencies exceeding 20\%. Another strategy involves using highly water-repellent wide bandgap perovskite layer inserted between the 3D light-harvesting perovskite film and HTM. This approach combines the suitable properties of 2D layer (ultrahydrophobicity, improved interfacial hole extraction, enhanced operational stability under humid conditions) enabling perovskite solar cells with 3D/2D architecture with efficiencies exceeding 22\% [2]. The third strategy is to introduce electrochemically stable or inert layers, which, respectively, facilitate or allow the transport of holes, either in between perovskite and hole transporting layer or in between hole conductor and metallic back contact [1, 3]. It is worth emphasizing that these approaches not only allowed us to realize high efficiencies but also outstanding stability under operational conditions for perovskite solar cells. In my presentation, important fundamental insights gained through various structural, morphological, and spectroscopic characterization techniques directly impacting the performance and stability of perovskite solar cells will be discussed.

References
1:30 PM *EN08.12.01  
**Stability of Perovskite Solar Cells—Molecular Design and Defects Passivation**  
Songyuan Dai, Molang Cai and Yong Ding; North China Electric Power University, China

The photovoltaic efficiency of perovskite solar cells (PSCs) has remarkably developed, while poor stability is a huge barrier for the commercialization of PSCs. The strategies to enhance stability are portrayed in terms of moisture and illumination endurance of photoactive layer as well as defects at interfaces of different layers. Here we effectively improve the stability of perovskite solar cell by molecular design and defects passivation. Firstly, the quasi 2D molecular with several ammonium salts are design for enhance the hydrophobic properties of photoactive layer. The halogen functional groups are further introduced to improve the poor charge transport with high-quality perovskite films with better crystallization. The optimal 2D PSCs exhibit high efficiency of 20.08% as well as retain 92% initial PCE after aging at 50 ± 5% relative humidity for 2400 h. Moreover, the defects of photoactive layer are reduced by controlling the growth and nucleation of perovskite film and adding passivation additives. The C60/TiO2 bilayer were employed to gain intimate contact between the ETL and perovskite, which results in an enhanced perovskite crystallization and a reduced charge recombination at the interface. The bilayer-based PSC shows outstanding stability, retaining 83% and 90% of its initial performance after 312 h UV irradiation and 1000 h exposure to ambient air, respectively.

2:00 PM EN08.12.02  
**Enhancing Electron Diffusion Length in Narrow-Bandgap Perovskites for Efficient Monolithic Perovskite Tandem Solar Cells**  
Zhenhua Yu, Zhibin Yang and Jinsong Huang; University of North Carolina at Chapel Hill, United States

Developing multijunction perovskite solar cells (PSCs) is an attractive route to boost PSC efficiencies to above the single-junction Shockley-Queisser limit. However, commonly used tin-based narrow-bandgap perovskites have shorter carrier diffusion lengths and lower absorption coefficient than lead-based perovskites, limiting the efficiency of perovskite-perovskite tandem solar cells. We discover that the charge collection efficiency in tin-based PSCs is limited by a short diffusion length of electrons. Adding proper additive into tin-perovskite precursors reduce the background free hole concentration and electron trap density, yielding a long electron diffusion length of 2.72±0.15 µm. It increases the optimized thickness of narrow-bandgap perovskite films to 1000 nm, yielding exceptional stabilized efficiencies of 20.2% and 22.7% for single junction narrow-bandgap PSCs and monolithic perovskite-perovskite tandem cells, respectively. This work provides a promising method to enhance the optoelectronic properties of narrow-bandgap perovskites and unleash the potential of perovskite-perovskite tandem solar cells.

2:15 PM EN08.12.03  
**High-Efficiency Solution-Processed Perovskite—Colloidal Quantum Dot Tandem Solar Cells**  
Afshal Manekkathodi1, Bin Chen2, Junghwan Kim1, Benjamin Scheffel2, Yi Hou2, Maksud Saidaminov2, Oleksandr Voznyy2, Vinod Madhavan1, Abdelhak Belaidi1, Sahel Ashhab1 and Edward H. Sargent2; 1Hamad Bin Khalifa University (HBKU), Qatar; 2University of Toronto, Canada; 3Photo-electronic Hybrids Research Center, Korea Institute of Science and Technology, Korea (the Democratic People's Republic of)

Multi-junction solar cells composed of complementary absorber layers with appropriate bandgaps offer avenues to improve the AM1.5 power conversion efficiency (PCE) beyond the Shockley-Queisser (SQ) limit of single-junction solar cells. In particular, PV technologies based on low-temperature solution processing have attracted interest in the pursuit of low-cost, flexible, and lightweight solar cells. Solution-processed perovskite/perovskite tandem solar cells have achieved significant progress in recent years. However, face a fundamental limitation on the path to reaching their full tandem potential due to the lack of efficient low-temperature processed IR back solar cell technology. Perovskite:colloidal quantum dot (CQD) hybrid tandems offer a route to overcoming this limitation. PbS CQDs are desirable for third-generation solar cell technology, owing to their superior photoelectric properties, facile bandgap tunability, and low-temperature solution-processability. The band gaps of CQDs can reach 0.5 eV providing a path to harness photons in the near to deep infrared region of the solar spectrum, beyond the capacity of crystalline silicon and perovskites. Here we report a solution-processed four terminal (4T) tandem solar cell composed of a perovskite front cell and a PbS CQD back cell, with a PCE exceeding 21% and a stabilized efficiency of 20%. This is the highest reported PCE of the perovskite/CQD tandem solar cell to date, and it surpasses the performance of
both the perovskite and the CQD single junction double-pass solar cells. We developed a dielectric-metal-dielectric (DMD) electrode to enable semi-transparent perovskite solar cells that combine enhanced transmittance and conductance for record-performing front cells. The DMD structure is designed to have high IR transmittance by optimizing the thickness of top dielectric oxide based on the zero-reflection condition in the optical admittance diagram. As a result, we achieved an increase of 25% in IR transmittance, and this enabled us to take advantage of CQDs as IR absorbers and boost the photon collection beyond the capacity of prior solar cells. The semi-transparent perovskite solar cell has a best PCE of 19.0% and a stabilized efficiency of 17.5%. The back cell is fabricated based on the IR PbS CQD absorber layers that is complementary to the IR transmittance characteristic of semi-transparent perovskite solar front cell for the optimized 4T tandem performance. The CQD:perovskite 4-terminal tandem is designed by mechanically stacking the 1.15 eV PbS-CQD solar cell as the back cell to the semi-transparent perovskite (1.63 eV) front cell. The EQE measurements of 1.15 eV and 0.95 eV CQD absorbers showed high EQE values at the exciton peaks; which indicates that the solar cells have an excellent IR charge collection efficiency from light harnessed beyond the perovskite absorption at ~750 nm. The short circuit current of the filtered CQD solar cell were ~6 mA/cm2 after filtering the perovskite front sub-cell. The Voc of the device is only marginally reduced, while a small increase in the fill factor is obtained. In the 4T measurement of the CQD solar cell, for the best performing cell, we were able to get a filtered PCE of 2.11%. Together with the 19.02% efficiency of the perovskite front cell, this gives 21.13% efficiency for the tandem device. Significant progress could be achieved in this perovskite:CQD tandem device in future, with concurrent advances in the light management in the perovskite sub-cell and IR charge collection techniques in the CQD sub-cell. Solution-processed hybrid tandem photovoltaics combining these two emergent PV technologies open the possibility to realize not only high-efficiency solar cells with substantial reductions in the cost of solar electricity but also next-generation flexible photovoltaic (PV) devices.

2:30 PM EN08.12.04
Efficient and Stable Monolithic All-Perovskite Tandem Solar Cells Renxing Lin1, Ke Xiao1, Chunfeng Zhang1, Edward H. Sargent2 and Hairen Tan1; 1Nanjing University, China; 2University of Toronto, Canada

Combining wide-bandgap and narrow-bandgap perovskites to construct monolithic all-perovskite tandem solar cells offers avenues for the continued increase in photovoltaic power conversion efficiencies (PCEs). However, the actual efficiencies of all-perovskite tandem solar cells today are diminished by the subpar performance of narrow-bandgap subcells. Here we report a strategy to reduce Sn vacancies in mixed Pb-Sn narrow-bandgap perovskites. We increase thereby the charge carrier diffusion length in narrow-bandgap perovskites, and we obtained a PCE higher than 20% for 1.2-eV narrow-bandgap solar cells. We then developed a recombination junction that avoids sputtered transparent-conductive-oxide and takes advantage instead of robust and compact recombination layer processed via atomic layer deposition. We fabricated monolithic all-perovskite tandem solar cells with PCEs beyond 23%. The tandem solar cells retained 90% of their performance after more than 400 hours of operation at the maximum power point under full one-sun illumination.

2:45 PM BREAK

3:15 PM *EN08.12.05
Materials and Process Issues in Facilitating Commercialization of Perovskite Solar Cells Hyun Suk Jung; Sungkyunkwan University (SKKU), Korea (the Republic of)

All solid-state solar cells based on organometal trihalide perovskite absorbers have already achieved distinguished power conversion efficiency (PCE) to over 24% and further improvements are expected up to 25%. Now, the research on perovskite solar cells has been moving toward commercialization. To facilitate commercialization of these great solar cells, some technical issues such as long-term stability, large scale fabrication process, and Pb-related hazardous materials need to be solved. Also, exploitation of flexible solar cell is of great importance for commercialization in niche markets. This talk is dealing with our recent efforts to facilitate commercialization of perovskite solar cells. For examples, we introduce a recycling technology of perovskite solar cells, which covers the regeneration process of Pb contained perovskite layer as well as recycling process of Au electrodes and transparent conducting oxide glass. Also, simple fabrication technologies for large scale perovskite module is going to be introduced. Finally, recent interesting results regarding ultra-flexible perovskite cells will be discussed in terms of stress analysis.
Improved Performance of Printable Perovskite Solar Cells with Bifunctional Conjugated Organic Molecules
Yue Hu and Yaoguang Rong; Huazhong University of Science and Technology, China

The past few years have witnessed a rapid evolution of hybrid organic-inorganic perovskite solar cells (PSCs) with both low cost and boosted high power conversion efficiency (PCE) over 22%. Despite the achievements, MAPbI$_3$ suffers from inherent instability over ambient operation conditions due to the low formation energy of the material itself and the high hydrophilicity of the organic cations. Efforts such as developing novel device architectures as well as exploring novel materials have been tried to improve the device stabilities. Among them, the two-dimensional (2D) perovskites that are crafted using bulkier alkylammonium cations in place of methylammonium exhibit appealing environmental stability. However, the insulating alkylammonium spacer cations hinder charge transport and limit the efficiencies of the devices based on such perovskites. In this scenario, an exploration of alternative yet effective organic spacer cations that increase the charge transfer is imperative to enhance the efficiency.

Herein, we design such an alternative bi-functional conjugated cation AB. We report the first time the incorporation of AB in 2D/3D perovskites and its implementation on solar cells. The use of bi-functional conjugated cations enhances significantly the performance of the cells, reaching a highest power conversion efficiency of 15.6% with improved stability. The efficiency remained around 90% of the initial value after 100 h continuous illumination, much more stable than MAPbI$_3$ perovskite. By comparing this cation with a mono-functional cation and a bi-functional non-conjugated cation with similar structure, we found that the bi-functional conjugated cation not only benefits the growth of perovskite crystals in the mesoporous network, but also facilitates the charge transport. Our approach helps explore new rational designs of cations in perovskites.

Carrier Lifetimes of >1 μs in Sn-Pb Perovskites Enable Efficient All-Perovskite Tandem Solar Cells
Jinhui Tong and Kai Zhu; National Renewable Energy Laboratory, United States

All-perovskite–based polycrystalline thin-film tandem solar cells have the potential to deliver efficiencies of >30%. However, the performance of all-perovskite–based tandem devices has been limited by the lack of high-efficiency, low–band gap tin–lead (Sn–Pb) mixed-perovskite solar cells (PSCs). We found that the addition of guanidinium thiocyanate (GuaSCN) resulted in marked improvements in the structural and optoelectronic properties of Sn–Pb mixed, low–band gap (~1.25 electron volt) perovskite films. The films have defect densities that are lower by a factor of 10, leading to carrier lifetimes of greater than 1 microsecond and diffusion lengths of 2.5 micrometers. These improved properties enable our demonstration of >20% efficient low–band gap PSCs. When combined with wider–band gap PSCs, we achieve 25% efficient four-terminal and 23.1% efficient two-terminal all-perovskite–based polycrystalline thin-film tandem solar cells.

Low-Bandgap 1.2 eV Tin-Lead Perovskite Solar Cells and All-Perovskite Tandem Solar Cells with Improved Device Stability
Jeremie Werner$^{1,2}$, Rohit Prasanna$^{1,2}$, Giles Eperon$^2$, Tomas Leijtens$^4$, Eli J. Wolf$^{1,2}$, Daniel J. Witter$^{1,2}$, Caleb C. Boyd$^{1,2}$, Luca Bertoluzzi$^3$, Axel F. Palmstrom$^2$, Sean Dunfield$^{1,2}$, Maikel F. Van Hest$^2$, Glenn Teeter$^2$, David T. Moore$^2$, Joseph J. Berry$^2$ and Michael D. McGehee$^1$; $^1$University of Colorado Boulder, United States; $^2$NREL, United States; $^3$Stanford University, United States; $^4$Swift Solar, United States

All-perovskite tandem solar cells have the potential to reach high efficiency but still suffer from limited stability. While a large effort of the community has been focused on improving the efficiency and stability of wide-gap (E$_g$>1.5eV) perovskite solar cells, Tin-based low-gap (E$_g$=1.2eV) perovskites still have a large room for improvement, especially in terms of stability, hindered by potential problems of Tin oxidation and improper charge selective contacts.

We will present our latest development on designing the Tin-Lead perovskite absorber composition and deposition conditions to reach high efficiency and high stability in tandem configuration. The growth conditions of the absorber are adapted to yield smooth, compact and large grained films. Then, we will discuss the crucial role of the hole selective contact in the efficiency/stability compromise. Several hole transport materials are under investigation. In particular, we will show low gap cells that can maintain >95% of initial efficiency after 1000hrs at 85°C, in air with no encapsulation. This can be achieved by eliminating the commonly used hole transport layer PEDOT:PSS and use instead the band bending effect existing at the ITO/perovskite heterojunction [1]. Further adapting an ALD-
deposited barrier and sputtered TCO layer for the Sn/Pb perovskites can improve the device environmental stability. Overall, Tin-Lead perovskite solar cells having a bandgap of ~1.25 eV will be presented with >16% efficiency and improved light, thermal and environmental stability. We will also present our progress at integrating these low gap cells into efficient and stable all-perovskite tandem solar cells. In that respect, a new perovskite tandem structure in substrate orientation will be introduced and discussed at the conference, including its potential for easier industrial penetration and lower module fabrication costs.

[1] Rohit Prasanna, et al. in peer review

4:30 PM EN08.12.09
High-Resilience Compounds Enabling Monolithic Perovskite-Si Tandem Solar Cells Exceeding 27% Efficiency Yen-Hung Lin and Henry J. Snaith; University of Oxford, United Kingdom

Hybrid organic-inorganic metal-halide perovskites stand out as obvious candidates for solar energy generation and photovoltaic applications owing to their much-heralded material property trio: remarkable absorption coefficients, long-lived photocarriers and tuneable bandgaps. After the first introduction of the solid-state device architectures in 2012,1,2 tremendous efforts from both academia and industry have been devoted to research fundamental properties of metal-halide perovskites as well as to advance relevant photovoltaic technologies. Power conversion efficiency (PCE) of perovskite solar cells has since continued to soar over the past years. This skyrocketing progress has reflected on a recent record breaking PCE over 24% certified for perovskite single-junction cells, fast-approaching the performance offered by incumbent crystalline-silicon (c-Si) technologies.3 Such rapid development of perovskite photovoltaics has directly led to their emergence in the hope of preventing natural resource depletion as well as mitigating global climate change. Among the applications of perovskite photovoltaics pioneered so far, perovskite-Si tandem solar cells that feature two sub-cells operating in their optimised absorption spectrum appear to be one of the most promising photovoltaic technologies to achieve remarkable energy conversion efficiency in a cost-effective manner. The latter is largely thanks to the simplicity and versatility of metal-halide perovskite material processing.4

In this contribution, we will present high-durability metal-halide perovskite compounds enabled by a series of additives. Our approach allows ultra-high-longevity perovskite solar cells to sustain an aggressive ageing condition that combines high-strength light and heat. With numerous material and spectroscopic characterisation techniques, we will shed light on the mechanism and factors that could eventually help perovskite solar cells to resist extreme environmental conditions. Integrating our high-resilience compounds into monolithic two-terminal perovskite-Si tandem solar cells has led to a 27% PCE, surpassing the highest recorded efficiencies for single-junction c-Si solar cells. Our demonstration represents a significant advancement that validates the approach of using perovskite-Si tandem configurations to ultimately enhance the absolute performance of market-dominating Si-based photovoltaics.5,6

References

4:45 PM EN08.12.10
Efficient and Stable Printable Mesoscopic Perovskite Solar Cells Yaoguang Rong, Yue Hu, Zhengyang Fu, Yanjun Guan and Da Li; Huazhong University of Science and Technology, China

Perovskite solar cells (PSCs) have attracted much attention in the past several years due to the ever-increasing power
conversion efficiency (PCE) and simple fabrication process. Particularly, we developed a printable triple mesoscopic architecture for PSCs, which uses carbon electrodes instead of traditional noble metals and can be fabricated with screen printing process. Through optimizing the material systems, modifying the interfaces, and diversifying the device structures, the efficiency of such printable triple mesoscopic PSCs has increased from the initial ~6% in 2013 to ~18% in 2019. Besides the lower material cost and simpler fabrication process, printable triple mesoscopic PSCs also have shown promising stability under various conditions, such as high temperature (85 °C), continuous illumination (AM1.5G), and outdoor conditions. In 2018, we enlarged the cell area to module level (3600 cm2) and installed a power system for outdoor exposure.

SESSION EN08.13: Poster Session IV: Perovskite Solar Cell—Upscaling and Tandem Device
Session Chair: Selina Olthof
Thursday Afternoon, December 5, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EN08.13.01
Dynamical Transformation of Two-Dimensional Perovskites with Alternating Cations in the Interlayer Space for High-Performance Photovoltaics
Ya L. Zhang¹, Sheng Z. Liu¹,² and Kui Zhao¹; ¹Shaanxi Normal University, China; ²Dalian Institute of Chemical Physics, China

The two-dimensional (2D) perovskites stabilized by alternating cations in the interlayer space (ACI) define a new type of structure with different physical properties than the more common Ruddlesden–Popper counterparts. However, there is a lack of understanding of material crystallization in films and its influence on the morphological/optoelectronic properties and the final photovoltaic devices. Herein, we undertake in situ studies of the solidification process for ACI 2D perovskite (GA)(MA)nPbnI3n+1 (n=3) from ink to solid-state semiconductor, using solvent mixture of DMSO:DMF (1:10 v/v) as the solvent and link this behavior to solar cell devices. The in situ grazing-incidence X-ray scattering (GIWAXS) analysis reveals a complex journey through disordered sol−gel precursors, intermediate phases, and ultimately to ACI perovskites. The intermediate phases, including a crystalline solvate compound and the 2D GA2PbI4 perovskite, provide a scaffold for the growth of the ACI perovskites during thermal annealing. We identify 2D GA2PbI4 to be the key intermediate phase, which is strongly influenced by the deposition technique and determines the formation of the 1D GAPbI3 byproducts and the distribution of various n phases of ACI perovskites in the final films. We also confirm the presence of internal charge transfer between different n phases through transient absorption spectroscopy. The high quality ACI perovskite films deposited from solvent mixture of DMSO:DMF (1:10 v/v) deliver a record power conversion efficiency of 14.7% in planar solar cells and significantly enhanced long-term stability of devices in contrast to the 3D MAPbI3 counterpart.

EN08.13.02
In Situ Grain Boundary Modification via Two-Dimensional Nanoplates to Remarkably Improve Stability and Efficiency of Perovskite Solar Cells
Xuejie Zhu; Shaanxi Normal University, China

Even though a record efficiency of 24.2% has been achieved in organic–inorganic hybrid perovskite solar cells, their stability remains a critical issue, which greatly depends on the morphology of perovskite absorbers. Herein, we report a practical grain boundary modification to remarkably improve the humidity and thermal stability by gradually growing in situ two-dimensional nanoplates between the grain boundaries of perovskite films using phenylethylammonium iodide (PEAI). The experimental results show that PEAI nanoplates play a critical role in stabilizing perovskite thin films by reducing the moisture sensitivity and suppressing phase transition at the grain boundaries. In addition to the significant improved ambient stability, the grain boundary modification by PEAI can effectively suppress the nonradiative charge recombination at grain boundaries. As a result, the efficiency of perovskite solar cells is up to 20.34% with significant humidity and thermal stability.

EN08.13.03
MACI Doping for High-Performance ACI Perovskite Solar Cells Tao Luo¹, Yalan Zhang¹, Kui Zhao¹ and Shengzhong (Frank) Liu¹,²; ¹Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, China; ²Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

Organic–inorganic perovskite structured compounds recently have emerged as attractive materials in the photovoltaic fields due to their exciting optical properties and easy syntheses, as well as exceptional structural and optical tunability. Recently, we have reported a layered two-dimensional (2D) perovskite with an alternating cation of C(NH₂)₃(CH₃NH₃)₃Pb₃I₁₀ (ACI) (n≥3) in the interlayer space by anti-solvent engineering with an efficiency of 14.7%. Based on the previous work, we further improved the quality and stability of the film by using CH₃NH₃Cl (MACI) as additive, and achieved a record efficiency of 18.48% for low-dimensional perovskite. In addition, the optimized device retained approximately 90% of the original PCE after 60 days at 30% relative humidity (RH) at ambient condition, and 80% of the original PCE after 65 hours at 80 °C without any encapsulation. This work will be useful to achieving more desirable outcomes and increase in photovoltaic performance.

EN08.13.04 Structure-Photophysics-Function Relationship of Quasi-2D Perovskite Solar Cells Chengbin Fei, Meng Zhou, Julio Sarmiento and He Wang; University of Miami, United States

Quasi-2D perovskite has higher stability and easier tunability compared with conventional 3D organic-inorganic hybrid perovskite. Tuning the phase distribution according to the device structure is necessary. We manipulate the structure of quasi-2D perovskite film and probe how the structure affects the solar cell device performance and stability. To better understand the structure-function relationship, we utilize femtosecond laser spectroscopy to study photophysics of different structures.

The addition of a small amount of hydrophobic cation of large size into 3D perovskite can improve both efficiency and stability. We find that the propylammonium is the most effective by comparing a family of different cations. The cations of large size preferentially segregate at the grain boundaries and surface, verified by transient absorption and reflection spectroscopy. Such passivation enhances device efficiency up to 20.1% and improves both device and precursor stabilities. The efficiency of devices with treatment only decreases by ~3% after 600 hours under low (10-15% RH) and high humidity (45–50% RH). (J. Mater. Chem. A, 2019, DOI:10.1039/C9TA01755K)

We also manipulate the phase purity and vertical distribution of quasi-2D perovskite. Ethyl acetate is utilized as antisolvent to tune the vertical phase distribution and the direction of carrier transfer is reversed accordingly. CH₃NH₃Cl and dimethyl sulfoxide are used to control the phase purity. These phenomena are proved by transient absorption spectroscopy. We find that solar cell performance is more sensitive to phase purity than vertical phase distribution. (Solar RRL, 2019, 3, 1800359)

EN08.13.05 Chlorine Doping for Black γ-CsPbI₃ Solar Cells with Stabilized Efficiency beyond 16% Kang Wang¹, Zhiwen Jin² and Sheng Z. Liu¹; ¹Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology; School of Materials Science & Engineering, Shaanxi Normal University, China; ²School of Physical Science and Technology & Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, China

Although the solar cells based on the α-CsPbI₃ presents very impressive power conversion efficiency, it suffers from insufficient crystalline structure stability even in ambient condition. Herein, the black orthorhombic γ phase based CsPbI₃ is successfully fabricated with its performance further optimized by doping chlorine ions. It is found that the chlorine incorporation improves crystallization dynamics for favorable surface morphology and crystalline orientation. In particular by doping 3 mol% chlorine into the CsPbI₃ film, its trap density is minimized with enhanced black phase stability and much improved thin film characteristics, including conductivity, electron and hole mobilities. Consequently, the solar cell efficiency is increased to as high as 16.07%. More importantly, the PCE of the optimized device shows only 0.45% degradation after continuous light soaking for 200 h. It retains as much as 94% of its initial PCE even after being exposed in air (relative humidity of 20%-30% at 25 °C) for 60 days.
Fabrication and Characterization of All-Inorganic Lead Halide Perovskite Films

Ryusuke Umeda1, Kazunori Ito1, Masato Gocho1, Toshiya Kobayashi1, Yuki Fukazawa1 and Hironori Ogata1,1,2; 1Hosei University, Japan; 2Research for Micro-Nano Technology, Japan

In recent years, perovskite solar cells that can be easily manufactured at low cost by solution processing have achieved high energy conversion efficiency exceeding 24%. Halide perovskites of an ABX3 structure [A=CH3NH3+(MA), HC(NH2)2+(FA), Cs+; B=Pb2+, Sn2+; X=I-, Br-, Cl-] are used photovoltaic materials. In perovskite solar cells, a perovskite compound containing methylammonium or formamidinium, which is an organic cation is widely used as a photoactive layer because it exhibits high energy conversion efficiency, but its durability against heat and moisture is low.

It has been reported that thermal resistance is improved by using an inorganic cation such as an alkali metal instead of an organic cation. In addition, it has been reported that the CsPbX3 thin film using cesium as an inorganic cation changes in band gap energy and durability due to mixed crystallization of halide ions. Furthermore, it has been reported that CsPbX3 thin film causes a structural change δ phase which is non perovskite phase by moisture, which is a problem for practical use.

In this study, the effects of temperature and humidity on the crystal structure, morphology and charge transport properties and durability of several kinds of CsPbX3-yX'y thin films with different proportions of halide ions (X and X') were systematically investigated. Detailed experiment results will be presented.

Fabrication of High-Efficiency Planar CsPbBr3 Perovskite Film Solar Cells by One-Crucible Thermal Evaporation of PbBr2 and CsBr

Juan Li, Rongrong Gao, Fei Gao, Xin Wu, Jie Lei, Haoxu Wang, Jianbo Li, Xiaodong Hua, Hao Liu and Shengzhong (Frank) Liu; Shaanxi Normal University, China

It is promising to improve the stability of organic–inorganic hybrid halide perovskite solar cells by using all-inorganic perovskite materials. Herein, a facile one-crucible single-source vacuum thermal evaporation (VTE) approach is developed, which is used to evaporate two different melting points materials CsBr (630 °C) and PbBr2 (370.6 °C) to deposit high-quality inorganic CsPbBr3 perovskite films. Molar ratio of PbBr2 to CsBr in their mixture in the crucible is a key factor influencing the stoichiometry, structure, photoelectrical and photovoltaic properties of the CsPbBr3 films. The other important factor is the thickness of the CsPbBr3 films. High-quality CsPbBr3 films with good uniformity and compact and large grains are prepared. Planar CsPbBr3 perovskite solar cells are fabricated giving a high power conversion efficiency of 8.65%. The fabricated CsPbBr3 solar cells exhibit a good stability in air without encapsulation. This study opens up the possibility to deposit multi-element compound thin films by facile single-source VTE of different melting points materials.

Graded Bandgap CsPbI2+xBr1-x Perovskite Solar Cells with a Stabilized Efficiency of 14.4%

Hui Bian, Zhiwen Jin and Shengzhong (Frank) Liu; School of Chemistry and Chemical Engineering, China

All-inorganic perovskite shows great potential for photovoltaic applications due to its excellent solar cell performance and atmospheric stability. Herein, CsPbI2Br1-x perovskite solar cell with a graded bandgap is explored using CsPbBrI2 and CsPbI3 quantum dots as component cells. Four strategies were pursued to boost the device performance. First, CsPbI2Br film was fabricated as the main absorber, with the component cell showing remarkable power conversion efficiency (PCE) as high as 13.45%. Second, by Mn2+ substitution, SCN- capping and [(NH2)2CH]+ treatment, stable and high-mobility CsPbI3 QDs film was attained. Third, a halide-ion-profiled heterojunction was designed at the CsPbBrI2/CsPbI3 QDs interface to achieve proper band edge bending as graded bandgap for improved carrier collection. Finally, the CsPbI3 QDs layer was optimized in the graded bandgap structure to achieve maximum overall light harvesting. As a result, the device achieved PCE with 14.45%. This is the highest efficiency ever reported for inorganic perovskite solar cells.

High Efficiency Inorganic CsPbBrI2 Perovskite Solar Cell via Iodine Salts Optimized Interface

Jingru Zhanag and Shengzhong (Frank) Liu; School of Materials Science & Engineering, China

The inorganic CsPbBrI2 perovskite has attracted ever-increasing attention for its outstanding optoelectronic
properties and ambient phase stability. However, to achieve high power conversion efficiency (PCE), it is imperative to minimize recombination at interface between the CsPbBrI₂ and the hole-extraction layer (HEL) for maximized carrier extraction efficiency. Herein, we developed the AI treatment to provide a general method for optimizing the interfacial properties. In our present work, quantum-dots (QDs) were firstly used to form dimension-graded heterojunction structure with the CsPbBrI₂ perovskite bulk film for optimized energy alignment in the solar cell (PSC) structure. Then, we ventured to conduct interface engineering by post treatmentment of the CsPbBrI₂ perovskite film with a series of A-site cation based iodine salts (AI, where A = formamidinium (FA⁺), methylammonium (MA⁺), ethylenediamine (EDA⁺), phenylethylammonium (PEA⁺) or n-butylammonium (BA⁺)) to achieve further improved device performance. In the applied QDs/film structure, an ultra-thin iodine-ion-enriched perovskite layer was formed on the top of CsPbBrI₂ film, and QDs surface were proved capped with AI after AI salt post-treated. We found such a phenomenon leads to proper band edge bending, decreased surface defects, and high-quality QDs modified layer. As a consequence, these changes proved effectively decreased recombination loss with improved hole extraction efficiency. More specifically, the FAI treated device yields an ultra-high PCE of 14.12% which positioning above the best reported PCE for CsPbBrI₂ PSCs to date. We believe such strategy should have significant potential for future applications in other optoelectronic devices.

EN08.13.10
High-Voltage CsPbBr₃-Based Fully Inorganic Planar-Type Perovskite Solar Cell Youhei Numata¹ and Tsutomu Miyasaka²; ¹The University of Tokyo, Japan; ²Toin University of Yokohama, Japan

Up to now, the best conversion efficiency of perovskite solar cells (PSCs) has reached over 23%, which is approaching to theoretical limit, and therefore, not only high efficiency, but also development of related technologies and new applications such as flexible device, module, lead-free material, high voltage, X-ray detector, and power source for IoT device are focused as next targets of researches. Recently, Cs-based all inorganic perovskite solar cells are energetically developed due to their high thermal stability. CsPbX₃ (X = I, Br and their mixture) perovskites possess wide band gap compared to the FA and MA-based perovskites, enabling to obtain high-voltage PSCs. Unfortunately, a-phase of iodide-rich CsPbX₃ perovskites such as CsPbI₃ and CsPbI₂Br is unstable under ambient condition, because of too small Cs ion size to form 3-D cubic perovskite structure at room temperature. Therefore, various effort to stabilization of the a-phase is devoted. On the other hand, reports of pure bromide, CsPbBr₃ is increasing because of high phase stability and high open-circuit voltage (VOC) up to 1.6 V. We focused on CsPbBr₃ and developed a fully inorganic planar-type PSCs using TiOX compact layer and a carbon-based electrode. Because of very poor solubility of the CsPbBr₃ perovskite in any solvent (maximum less than 0.5 mM for DMF and DMSO), the CsPbBr₃ film is commonly prepared sequential deposition method; a precursor PbBr₂ film was treated with CsBr solution. The CsBr treatment is repeated four times to perfectly convert the PbBr₂ to CsPbBr₃ perovskite. However, because of no TiO₂ mesoporous scaffold, CsPbBr₃ film converted on the TiOX CL became very rough and there are many pinholes due to low adhesion power between perovskite and TiOX surface. To obtain pinhole-free and high-quality perovskite film, we modified a recipe of precursor solution and CsBr treatment procedure, and obtained pinhole-free CsPbBr₃ film on the TiOX CL by CsBr treatment once. Furthermore, by passivation of surface of the TiOX CL, VOC of up to 1.5 V was obtained.

EN08.13.11
In Situ Structural and Optical Studies of Phase Transformations of CsPbI₃ from Atomic Scale to Macroscopic Properties Jose Marquez Prieto¹, Pascal Becker¹, Justus Just², Hampus Nässström¹, Chen Li³,⁴, Thomas Unold¹ and Roland Mainz²; ¹Helmholtz Zentrum Berlin, Germany; ²Lund University, Sweden; ³Max Planck Institute for Solid State Research, Germany; ⁴University Antwerpen, Belgium

Understanding the phase transitions in inorganic halide perovskites is crucial to increase the stability of solar cells and to allow possible application of these materials in thermochromic solar cells and phase-change based optoelectronic devices [1, 2]. Here we present a combination of several in-situ techniques to reveal the phase transformation relations between the α, β and γ (black) perovskite phases and the δ (yellow) non-perovskite polymorph in thin films. Structural changes were tracked as a function of relative humidity (RH) and temperature by in-situ X-ray diffraction with a liquid-metal jet X-ray source. We find that at room temperature, the transition from the γ-black to the δ-yellow phase is exclusively triggered by the % of RH whereas O₂ is not involved in the mechanism. The transformation is preceded by an expansion of the unit cell volume of the perovskite phase
Spectrally filtered in-situ optical microscopy reveals that this transformation does not affect the grain structure. An intermediate state is observed, where the optical transmission at 700 nm is significantly reduced, suggesting a pseudo-amorphous state during the atomic reordering.

For a detailed understanding of the atomic motion during the phase transitions we also studied the conversion from the yellow non-perovskite to the black-perovskite polymorph during in-situ heating using scanning transmission electron microscopy (STEM) revealing the transition from the δ- to the α-phase with atomic resolution where a layered structure is observed as intermediate.


EN08.13.12
Pb-Bi Binary Metal Absorber Layer for Stability Enhancement in Perovskite Solar Cells Jin Huang1,2; 1Shanxi Normal University, China; 2Shanxi University of Science &Technology, China

A lead-bismuth (Pb-Bi) binary metal based perovskite film is successfully fabricated and applied as absorber layer to enhance the stability of perovskite solar cells (PSCs). Unlike the Pb-only perovskite-based device, the Pb-Bi binary metal perovskite based one shows better tolerance to humidity and oxygen. High power conversion efficiency (PCE) of 11.1% is obtained for the PSC. Noticeably, the PCE only reduced by 15% under atmospheric humidity of 30% in four weeks. An electron-only device also shows reduced trap states. The improved stability and PCE is ascribed to higher quality perovskite film with less trap states and smaller series resistance (Rs) in the device.

EN08.13.13
Perovskite Solar Cell towards Lower Toxicity—A Theoretical Study of Physical Lead Reduction Strategy Yifan Zheng; Peking University, China

The huge performance enhancements of the organometal halide perovskite solar cells (OHPSCs) have appealed enormous attention within recent ten years. Although the rapid growth of the device power conversion efficiency (PCE) has attained over 24%, the contamination of health-hazardous components still holds back its sustainable applications. To reduce the lead usage, many groups have tried chemical lead reduction solutions: substituting the lead by other group 14 metal elements to realize the low-lead OHPSCs. Unfortunately, neither the PCE nor the stability, low-lead OHPSCs all lag far behind the state-of-the-art conventional lead-based OHPSCs. In this work, we present a physical lead reduction (PLR) concept by reducing the perovskite film thickness to restrict the perovskite hazard risk with minor scarification in device performances. Through the simulation of transfer matrix model, we theoretically demonstrated that by introducing the optical space layer, the device PCE could maintain 96% of the original maximum value while attenuating the perovskite film thickness to one-third. This means that the usage of lead can be reduced by ~70% with PLR concept, which could have broad appeal as a new lead reduction strategy towards high performance OHPSCs.

EN08.13.14
Rapid Architecture-Specific Toxicity Screening of Lead-Based Emerging Thin-Film Photovoltaics Nicole Moody1, Dasol Yoon2, Anna Johnson1, Dak B. Dou1, Vladimir Bulovic1 and Mounig G. Bawendi1; 1Massachusetts Institute of Technology, United States; 2Wellesley College, United States

While lead-based perovskite and quantum dot (QD) solar panels are rapidly approaching the technological maturity for widespread commercialization, their environmental impacts and end-of-life disposal requirements have been largely uncharacterized. Here we present the United States Environmental Protection Agency Toxicity Characteristic Leaching Procedure (TCLP) as a means of rapidly characterizing the human and environmental health impacts of laboratory-scale solar cells and their resulting disposal requirements. We employ the TCLP to screen the toxicity and regulatory requirements of perovskite solar cells on various substrates, revealing increased lead leaching and potentially higher disposal costs for perovskite solar cells on lightweight, flexible substrates compared to heavier, rigid ones. We also use the TCLP to guide the development of a lower-toxicity manufacturing method for lead sulfide (PbS) QD solar cells. By developing a new solution-phase QD ligand exchange method that employs tetrabutyl ammonium iodide (TBAI) as the source of ligands, we maintain high device performance while reducing the total lead content in the synthesis byproducts by nearly 250 times and the total volume of solvents used.
by 80% compared to previous methods that employ lead halides. TCLP analysis reveals that QD solar cells made with this ligand exchange method leach less lead than the EPA limit, and as a result are unlikely to cause environmental harm during end-of-life disposal in municipal landfills. Further, the TBAI ligand exchange method offers significant cost savings compared to previous lead-halide-based methods, reducing synthesis costs by more than 70%. By using the TCLP to obtain architecture-specific toxicity information of lab-scale devices, we are able to design new solar technologies with low environmental risk.

EN08.13.15
The Phase Segregation in CsPbI2Br Inorganic Perovskite Solar Cells Haoxu Wang, Fei Gao and Shengzhong (Frank) Liu; Shaanxi Normal University, China

The rapid development of organic-inorganic hybrid and all-inorganic pervoskite materials have drawn widely attention in energy field. Within a decade, the PCE of perovskite solar cells has exceeded 24.2% from 3.8%. With such a promising commercialization potential, the perovskite solar cells still have many problems to be solved, such as poor ambient stability, heavy metal toxicity and expensive additives. Herein, we fabricated high performance CsPbI2 solar cells and studied the phase segregation mechanism of CsPbI2 thin films.

In this work, we explored the CsPbI2 thin films and solar cells fabrication via dual-source thermal evaporation. A best device performance up to 7.4% was gained through adjustment of molar ratio, substrate temperature, annealing temperature and annealing time. The device performance decay in ambient with 25%-35% relative humidity is less than 10% for 30 days. And two different methods to prepare the CsPbI2 thin films and solar cells were compared. The advantage of dual-source thermal evaporation was proved by superior quality and performance of CsPbI2 thin film and solar cells. Furthermore, the mechanism of the intrinsic phenomenon of phase segregation in CsPbI2 thin films was demonstrated via EDX characterization. Due to different formation energy, the I atom is intended to be replaced by Br atom spontaneously during power injection from external thermal source such as annealing process. The phase segregation is intrinsic characteristics of CsPbI2 thin films which will not be eliminated completely.

EN08.13.16
All-Inorganic Cesium Tin Halide Perovskite for Photodetector Junhua Shen; Rensselaer Polytechnic Institute, United States

Inorganic halide perovskite materials have attracted wide attention for optoelectronic applications due to its high mobility, long diffusion length and outstanding visible light harvesting performance. However, there are two major challenges for industrial applications, stability, and toxicity. By introducing environmental benign element Tin (Sn), toxicity problem could be addressed. Compared with divalent Sn-based perovskite which must be handled in an inert condition, tetravalent Sn-based perovskite materials are stable in ambient condition.

In this work, we demonstrate a novel solution processed all-inorganic perovskite Cs2SnI6 with excellent optoelectronic properties. At room temperature, the solution processed Cs2SnI6 photodetectors are sensitive to red-light(650nm), exhibiting a high detectivity. These Sn-based devices possess good linearity photo-response, and their optoelectronic performance is comparable to most of the all inorganic perovskite photodetectors. Our results indicate that with proper synthesis and device construction, lead-free inorganic perovskite materials are promising for stable, low-cost, environmentally-benign and high-performance photodetectors.

EN08.13.17
Humidity Controlled Fabrication of Methylammonium Lead Iodide and Spiro-OMeTAD Layer for High Efficiency Perovskite Solar Cells Junyeong Lee, Jiyoon Nam, Changgyun Kim, Kyudong Kim and Sungjin Jo; Kyungpook National University, Korea (the Republic of)

Perovskite solar cells (PSCs) have advanced intensively over the last few years and have reached in 24.2% power conversion efficiency (PCE). Because the achievement of high efficiency is enough for commercial applications, the stability and scalability issues have attracted attention for the potential commercialization of PSCs. However, when exposed to moisture, methylammonium lead iodide (MAPbI3), which is used as the active layer of PSCs, decomposes into methylammonium iodide (MAI) and lead iodide (PbI2), thereby degrading the device performance. For this reason, PSCs have to be fabricated under humidity-controlled environments. Recently, it is reported that the humidity plays an important role in the crystallization of the MAPbI3 and MAPbI3 fabricated in ambient conditions has had a higher performance than that coated at low humidity. Thereafter, studies
were conducted to fabricate the MAPbI₃ layer at various humidities, and it has been shown that when moisture is absorbed, the adjacent grain merges and the grain size increases. However, while the Spiro-OMeTAD material that is often used as a HTL has the property of absorbing moisture like MAPbI₃, few studies have reported on Spiro-OMeTAD coated at various humidities.

In this report, we investigate the tendency of characteristic changes when both Spiro-OMeTAD and MAPbI₃ were fabricated at relative humidity (RH) 20%, 40%, 60%, and 80%. As a result, PSCs fabricated at RH 60% showed PCE 15.5%, which is higher than the PCE 12.9% fabricated at RH 20%. We demonstrated that MAPbI₃ is more critical for the PCE of PSCs than Spiro-OMeTAD when we deposited MAPbI₃ and Spiro-OMeTAD separately under different humidity conditions. In this regard, the amount of PbI₂ produced by the humidity condition was characterized by employing an X-ray diffractometer and an ultraviolet–visible spectrophotometer. The surface morphology of the MAPbI₃ image were obtained by a scanning electron microscope and the charge lifetime of the MAPbI₃ surface was analyzed by steady-state photoluminescence (PL) and time-resolved PL. In this result, we can confirm that the efficiency increases when all experimental processes were performed in ambient condition at RH 60%. We expect this to be useful for commercialization because the fabrication of PSCs in ambient environment does not require expensive equipment to maintain low humidity.

EN08.13.18

Large Single-Crystal Grains for Highly Efficient Integrated Back-Contact Perovskite Solar Cells Teng Ma and Ayumi Hirano; Tohoku University, Japan

The perovskite solar cells (PSCs) have been attracting great attention due to their promising high performance and low fabrication cost. Researchers have put a huge amount of effort to optimize the bulk and interfaces of perovskite layer in the PSCs to achieve high power conversion efficiency (PCE) and high stability at the same time. As a result, the PCE of PSCs has increased from 3.8% to 24.2% in only 10 years. However, as the internal quantum efficiency of the PSCs approaching 100%, the space left for further optimization is getting smaller. Previously, by using numerical simulation methods, we have demonstrated that the performance of the PSCs could be improved by 11% by replacing the widely-used sandwich structure with an integrated back-contact (IBC) structure. However, the reported PCEs of the IBC-PSC are still lower than that of their sandwich-PSC counterparts.

Here, based on our simulation and experiment results, we propose that the grain boundary is one of the main factors limiting the performance of IBC-PSCs. In IBC structure, since the photo-generated charges need to travel laterally through a longer distance than that in a sandwich structure, if the distance of the electrodes is larger than the grain size, the charges might have to cross several grain boundaries to reach the electrode, resulting in a high recombination possibility. To reduce grain boundaries in the charge transporting path, we adopt a unique method to form a uniform perovskite layer with large single crystal grains as large as 50 µm. In the fabricated IBC devices, most of the adjacent electrodes were connected by a single crystal of perovskite material. The performance of the IBC-PSCs was therefore significantly improved due to the reduced grain boundaries.

Reference

EN08.13.20

Probing Perovskite Crystal Quality to Drive Process Development for Flat and Textured Perovskite Solar Cells Peter Fiala1, Florent Sahli1, Ricardo Z. Razera1,2, Jeremie Werner1,3, Fan Fu1,4, Terry C. Yang1, Daniel Jacobs1, Beat Ruhstaller5,6, Quentin Jeangros1 and Christophe Ballif1; 1Ecole Polytechnique Federale Lausanne, Switzerland; 2Instituto de Física, Brazil; 3University of Colorado Boulder, United States; 4Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; 5Fluxim AG, Switzerland; 6Zurich University of Applied Sciences, Switzerland

In the field of perovskite thin-film solar cells (PSC), the formation of the perovskite absorber via hybrid thermal evaporation / spin-coating processes represents an important step towards large-area deposition methods and potential industrial feasibility, while also enabling deposition on textured substrates. One caveat of this hybrid method is that it requires two physically separate layers of precursors to interdiffuse and crystalize, forming the perovskite absorber. This interdiffusion is complex, and many process parameters influence the resulting perovskite
crystal quality and associated interfaces. In turn, these material qualities strongly affect the photovoltaic performance of the fabricated PSC. Directly measuring the perovskite material quality would be an ideal shortcut to drive process development without the need to make large numbers of full devices. In this work, photo-thermal deflection spectroscopy (PDS), atomic force microscopy (AFM), and X-Ray diffraction (XRD) measurements were used to investigate material quality in perovskite films formed via a hybrid evaporation/spin-coating process. Specifically, the temperature, dew point, and anneal time of the interdiffusion process were investigated. This led to insights about the crystal quality and stoichiometry of the perovskites, which was shown to directly link back to PSC performance, with efficiency gains of over 3% absolute. However, verification by PSC production revealed that these metrics (PDS, AFM, XRD) did not tell the whole story of the interdiffusion process. The remaining effects were attributed to modification of the perovskite layer interfaces. Further investigations into this phenomenon will be discussed at the conference.

The understanding of this hybrid fabrication method was then applied to PSC deposited on textured substrates. In theory, PSC employing a textured absorber interface could eschew the optical losses typical of thin films via improved light management. As our hybrid method allows for perovskite deposition on textured surfaces, textured PSC development focused more on optimization of the substrate texture. Along this route, we first performed optical ray-tracing simulations using AFM scans of textured surfaces formed by KOH-etched silicon (c-Si) wafers, as demonstrated in our previous publications. Optimal BZO and c-Si textured surfaces were then used to fabricate PSC in the p-i-n architecture, with the perovskite layer deposited via the optimized hybrid method. Demonstrated PSC verified the trends predicted by simulation, with increased short-circuit current density (JSC) and removed interference fringes from external quantum efficiency curves. However, improved optical performance and JSC are not the only factors relevant to the overall performance of our PSC. Optimization of the full device and the impact of textured interfaces on other device parameters will be discussed at the conference.

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EN08.13.21
Record Efficiency Stable Flexible Perovskite Solar Cell Using Effective Additive Assistant Strategy Feng Jiangshan; Shaanxi Normal university, China

Even though the power conversion efficiency (PCE) of rigid perovskite solar cells is increased to 22.7%, the PCE of flexible perovskite solar cells (F-PSCs) is still lower. Here, a novel dimethyl sulfide (DS) additive is developed to effectively improve the performance of the F-PSCs. Fourier transform infrared spectroscopy reveals that the DS additive reacts with Pb2+ to form a chelated intermediate, which significantly slows down the crystallization rate, leading to large grain size and good crystallinity for the resultant perovskite film. In fact, the trap density of the perovskite film prepared using the DS additive is reduced by an order of magnitude compared to the one without it, demonstrating that the additive effectively retards transformation kinetics during the thin film formation process. As a result, the PCE of the flexible devices increases to 18.40%, with good mechanical tolerance, the highest reported so far for the F-PSCs. Meanwhile, the environmental stability of the F-PSCs significantly enhances by 1.72 times compared to the device without the additive, likely due to the large grain size that suppresses perovskite degradation at grain boundaries. The present strategy will help guide development of high efficiency F-PSCs for practical applications.

EN08.13.22
Stable High Efficiency Two-Dimensional Perovskite Solar Cells via Cesium Doping Xu Zhang1,2; 1Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China; 2University of Chinese Academy of Sciences, China

Two-dimensional (2D) organic–inorganic perovskites have recently emerged as one of the most important thin-film solar cell materials owing to their excellent environmental stability. The remaining major pitfall is relatively poor photovoltaic performance in contrast to 3D perovskites. In this work we demonstrate cesium cation (Cs+) doped 2D (BA)2(MA)3Pb4I13 perovskite solar cells giving power conversion efficiency (PCE) as high as 13.7%, the highest
among reported 2D perovskite based devices. In addition, it has excellent humidity stability. The enhanced efficiency is attributed to perfectly controlled crystal orientation, increased grain size of 2D planes, superior surface quality, reduced trap-state density, enhanced charge-carrier mobility and charge-transfer kinetics. To our surprise, the Cs+ doping yields superior environmental stability and humidity tolerance. The device doped using 5% Cs+ degrades only ca. 10% after 1400 hours exposure in 30% relative humidity (RH), and exhibits significantly improved stability under heating and high moisture environment. Our results provide an important step toward air-stable and fully printable low dimensional perovskite as a next-generation renewable energy source.

EN08.13.23
Interfacial Chemical States, Reactivity and Stability of Antifluorite Cesium Titanium Bromide, Cs₂TiBr₆
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Cesium titanium bromide, Cs₂TiBr₆, has attracted research interest as a semiconductor due to its ~1.8 eV band gap, which makes it desirable for forming tandem junctions with silicon. However, little is known about the surface of the material. To ascertain stability of the material in ambient air we conducted controlled air exposure experiments, and to determine the reactivity and basicity of interfacial halides, we reacted the surface with a series of Lewis acids. X-ray photoelectron spectroscopy (XPS) established correct synthesis, effects of atmospheric exposure, and surface coverage of Lewis adducts. Powder X-ray diffraction (pXRD) quantified the effects of atmospheric exposure to the crystal over time. Temperature programmed desorption (TPD) quantified bond strengths of resulting Lewis adducts. The presence of Lewis adducts at the surface of Cs₂TiBr₆ demonstrated consistent loss of cesium bromide on the surfaces and surface exposure to ambient air resulted in rapid surface oxidation. These results elucidate the reactivity of the chemical states on Cs₂TiBr₆ surfaces, and future routes through which interfacial reactivity may be used to improve atmospheric stability.

EN08.13.24
Lead-Free Double Perovskite Cs₂AgBiBr₆ Quantum Dots Excited State Interactions and Solar Cell Applications Junsang Cho¹ and Prashant Kamat¹,²; ¹Radiation Laboratory, University of Notre Dame, United States; ²University of Notre Dame, United States

Lead-free double perovskites of Cs₂AgBiBr₆ wherein two divalent Pb²⁺ cations are substituted by one monovalent Ag⁺ cation and one trivalent Bi³⁺ cation, respectively, are considered as potential candidates for developing materials for perovskite solar cells. We have now prepared 8—10 nm diameter Cs₂AgBiBr₆ nanocrystals using a hot-injection method and investigated their excited state properties. In addition, we have also probed the excited state interactions of double perovskite quantum dots (QDs) with various metal oxides (TiO₂, ZnO, SnO, and ZrO₂) and established the electron transfer kinetics between the two. Spin-coated QD films were annealed (at 225 °C) to obtain bulk double perovskite films. UV-vis absorption, high resolution SEM images, and X-ray diffraction have been employed to track the transformation of QDs to bulk films. The annealed films can be directly employed in the fabrication of solar cell architecture: FTO/c-TiO₂/m-TiO₂/Cs₂AgBiBr₆/Spiro-oMeTAD/Au. The double perovskite solar cells show relatively low solar energy conversion efficiency (less than 1.0 %) with Jsc of 0.40 mA/cm² and Voc of 0.65 V. Understanding of nanocrystal growth mechanism and correlation between the grain size and solar cell efficiency is important for improving the efficiency of double halide perovskite for solar cells.

EN08.13.25
Lead-Free Perovskite (-Like) Solar Cells Qiaohui Zhang, Cuncun Wu and Lixin Xiao; Department of Physics, Peking University, China

Organic-inorganic hybrid perovskite solar cells (SCs) have emerged as one of the most promising contenders to traditional silicon solar cells, due to their active layers outstanding photoelectric properties, such as appropriate direct bandgap, balanced high carrier mobility and long carrier diffusion length, the identified power conversion efficiency (PCE) has reached to 24.2 %. But the toxic lead, a key component in the archetypical light harvesting material, is a large obstacle to commercialization.

Double perovskite Cs₂AgBiBr₆ has emerged as a promising optoelectronic material due to its excellent physics and photoelectric properties. We first reported double perovskite planar heterojunction SC with a high quality Cs₂AgBiBr₆ film, fabricated by a low-pressure assisted solution processing method under ambient conditions, which presents a highest PCE of 1.44 %. Moreover, we reported highly efficient and stable self-powered ultraviolet and
deep-blue photodetector based on Cs$_2$AgBiBr$_6$/SnO$_2$ heterojunction with two responsivity peaks at 350 and 435 nm, which is suitable for ultraviolet-A (320–400 nm) and deep-blue light detecting. A high responsivity of 0.11 A/W at 350 nm and a quick response time of less than 3 ms are obtained, which is significantly higher than other semiconductor oxide heterojunction based UV-detectors. More importantly, the stability is significantly better than most of the hybrid perovskite photodetectors reported so far. Its photocurrent shows no obvious degradation after more than six months storage in ambient condition without any encapsulation. Consequently, the utilization of Cs$_2$AgBiBr$_6$ film is a practical approach for high performance, large-area lead-free perovskite photodetector application. The low toxicity and high stability of this double perovskite active layer make it very promising for practical application. For mechanism, we found that photogenerated carriers in Cs$_2$AgBiBr$_6$ film are separated at Cs$_2$AgBiBr$_6$/SnO$_2$ heterojunction interface by its build-in field, which is very important for the future double perovskite based optoelectronic device structure design.

Silver bismuth iodide (Ag–Bi–I) as an environmentally friendly semiconductor with suitable band gap and high stability has been regarded as a potential photovoltaic material, while the reported mesoscopic devices all showed poor open circuit voltage ($V_{oc}$) of 0.5–0.6 V. We reported silver bismuth iodide-based solar cells with a planar heterojunction structure of “ITO/SnO$_2$/AgBiI$_4$/PTAA/Au” by a solution method. Li-TFSI additive (2 wt %) was added into the AgBiI$_4$ precursor and induced a fully covered pinhole-free morphology. The readily coordinated organic component, TFSI$^-$, was proven to play a role of assisting the film growth. The optimal device could achieve a $V_{oc}$ of 0.82 ± 0.01 V and PCE up to 2.50 ± 0.20 %, much higher than the one without Li-TFSI of 0.66 ± 0.02 V and 1.67 ± 0.09 %. Moreover, we fabricated AgBiI$_4$ SC with a thicker absorber film, which could even have a record $V_{oc}$ of 0.88 V, but the depressed $J_{sc}$ implied its limited carrier diffusion length. In addition, the double layer devices with a structure of “ITO/SnO$_2$/AgBiI$_4$/Au” or “ITO/AgBiI$_4$/PTAA/Au” showed the carrier separation occurred in the interface of SnO$_2$/AgBiI$_4$. Above results pointed out the significance of film quality improvement and interface charge extraction in further research.

EN08.13.26
Lead-Free Tin Halide Perovskite Material and Interface Energetics and Iodide Diffusion Into Electron Transport Layers

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Halide perovskites have generated tremendous interest as low-cost semiconductors for optoelectronic applications such as photovoltaics. The bulk of work surrounding halide perovskites has centered around Pb-based perovskite derivatives; however, recent years have seen a rise in Pb-free perovskites which are less harmful and more environmentally friendly. In this regime the leading alternative to Pb is Sn, which has successfully been used in photovoltaics to achieve over 9% power conversion efficiency. The further development of Sn based perovskite photovoltaics necessitates a firm understanding of the material properties and the ways in which tin derivatives differ from their lead counterparts. One key property is the energetic structure of Sn-based perovskites and the energetic alignment of their transport states with those in adjacent layers. Herein lies an issue where current literature regarding the valence and conduction band energies cannot reach consensus even for formamidinium tin iodide (FASnI$_3$), the most popular tin-based composition, for which reported ionization energies (IEs) already span a range greater than 1 eV. Using low energy ultraviolet and inverse photoelectron spectroscopy, we find the IE and electron affinity (EA) to equal 5.3 and 3.9 eV for FASnI$_3$. In addition, we observe that the amount of tin(II) fluoride, a nearly ubiquitous additive employed to reduce tin oxidation, shifts these energetics by hundreds of meV. Further, we find that short air exposures (<1 minute), synonymous with sample transfer, result in minimal changes to IE, EA, and PV performance, whereas longer exposure times (5-10 minutes), analogous of a sample measurement in air, shows changes of hundreds of meV in both IE and EA as well as degradation of device performance. At the interface between FASnI$_3$ and C60 we detect migration of iodide from the perovskite into the fullerene and the formation of a surface dipole. Additional fullerene derivatives are examined to elucidate the prevalence of iodide migration and the impacts on energy level alignment with the perovskite and photovoltaic performance. Finally, surface modifiers are explored to prevent iodide diffusion out of the perovskite layer. These results are important for understanding the electronic structures of tin-based perovskites, how interface energetics influence charge extraction in perovskite photovoltaics, and minimizing iodide diffusion is critical to improving stability.

EN08.13.27
Research Pertaining to Fabricate Efficient Tin/Lead Perovskite Solar Cells

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Tin-lead (Sn-Pb) perovskite exhibits an ideal band gap (1.2 eV-1.4 eV) to achieve higher power conversion efficiency (PCE) than pure Pb based PSCs [1]. However, being a low band gap material and prone to oxidation of Sn²⁺ to Sn⁴⁺, Sn-Pb solar cells exhibit low open circuit voltage (Voc) [2,3]. To increase the Voc, a spike structure strategy was reported by our group, Voc of 0.75 V and PCE of 17.6% were obtained [2]. To further improve Voc, in this work we will demonstrate that by decreasing the strain in the Sn-Pb perovskite lattice, Voc more than 0.80 V can be obtained. Also, we will show that with the change in conducting glass substrate, i.e by selecting a conducting glass with better IR transmittance, short circuit current density (Jsc) more than 30 mA/cm² can be obtained. The methodology discussed in the work can direct to PCE of more than 20%

Cs⁺ added triple cation-based Sn-Pb perovskites, (CsxFA₁₋ₓSnI₃)₀.₅(MAPbI₃)₀.₅, were prepared. Voc was improved from 0.76V to 0.81V with the addition of optimized amount of Cs⁺. This observation was well supported by the decrease of lattice strain at the optimized concentration of Cs⁺. In the work, we will discuss in detail about the characterization techniques such as X-ray diffraction (XRD), UV-Vis spectroscopy, Trap density measurement by Thermally stimulated current (TSC) measurements, etc, which led to the conclusive discussions regarding the optimized precursor for Sn-Pb PSCs.

Strain relaxation in Sn-Pb PSCs was reported which led to the increase in Voc more than 0.80 V. It was demonstrated that better transmittance of conducting glass in infrared region can increase Jsc of Sn-Pb PSCs more than 30 mA/cm². Furthermore, PCE of more than 20% can be achieved in the case of Sn-Pb PSCs despite of oxidation problem. Also, the results obtained in the work encourage implementation of Sn-Pb PSCs as a low band gap solar cell in tandem solar cells.

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Role of Water Vapor in the Thermal Deposition of MAPbI₃ Ke Wang, Benjamin Ecker and Yongli Gao; University of Rochester, United States

Organometal halide perovskites have received a lot of attention in recent years as an efficient light absorbing material for use in a solar cell, where the device efficiency has reached 24.2% in early 2019. Compared to traditional silicon solar cells, the perovskite thin films can readily be made in a lab environment with techniques such as spin coating, blade coating, and thermal vapor deposition. In particular, thermal deposition is well-known for its ability to grow highly uniform perovskite thin films, often times with fewer defects and a more ideal chemical stoichiometry than films grown by solution-based techniques. The interactions of the prototypical perovskite precursors, lead iodide (PbI₂) and methylammonium iodide (MAI), while in the vapor phase and their depositions are poorly understood, despite their role they play in perovskite film growth. Herein, we observed the partial pressure changes of the perovskite precursors in the vapor phase with a residual gas analyzer, and each precursor was individually evaporated in a vacuum chamber which was continually pumped by a turbomolecular pump. No increase in the MAI partial pressure was observed during the MAI evaporation and this suggested that it was not evaporating as a whole compound, but rather it was dissociating into several other species including CH₃NH, CH₃NH₂, and HI.

Surprisingly, residual water vapor was also observed to behave differently in the two different individual evaporation. During the MAI evaporation, the water vapor pressure was reduced and this indicated that the water vapor was being consumed either by MAI or MAI dissociation products. This was not observed during the evaporation of PbI₂ or the heating of an empty tungsten boat used as a control investigation. This was surprising as the water vapors initial pressure was 5*10⁻⁷ torr, and such a low amount of water vapor was not expected to influence the depositions. In literature, it had previously been thought that MAI depositions were problematic due to a low sticking coefficient. However, this work suggests that the MAI’s and its dissociation component’s vapor pressures in previous investigations may have unknowingly also been reduced due to residual water vapor in the vacuum growth chambers. This reduction effect of the MAI related vapor pressures may play a critical role in the initial deposition of MAI films, and subsequently, any deposition of perovskite thin films by vapor deposition.

Rubidium-Dopped Cs₂AgBiBr₆ Double Perovskite Solar Cell Zehao Zhang, Cuncun Wu, Duo Wang, Ganghong Liu, Qiaohui Zhang, Wei Luo, Xin Qi, Xuan Guo, Yuqing Zhang, Yinan Lao, Bo Qu, Lixin Xiao and Zhijian Chen; Peking University, China
Cs$_2$AgBiBr$_6$ has received great attention as an emerging double perovskite material. Some researches shown that the performance of the double perovskite material can be improved by doping other elements, but there is no report about solar cell with doping. We demonstrate Rb$^+$ doping in Cs$_2$AgBiBr$_6$ can effectively increase the current and PCE of the device. Doping Rb$^+$ can effectively modify the perovskite to reduce the density of defect states, while the absorption of long-wavelength is strengthened. We also found the optimizing ratio of Cs$^+$ and Rb$^+$ is 9:1. The device with (Cs$_{0.9}$Rb$_{0.1}$)$_2$AgBiBr$_6$ achieves a maximum PCE of 1.52% and an ultra-high FF of 0.788 with the planar structure. And the average PCE is nearly 15% higher than the devices with Cs$_2$AgBiBr$_6$. However, excessive Rb$^+$ would lead to formation of Rb$_3$Bi$_2$Br$_9$, that means the degradation of the double perovskites.

EN08.13.30
Metal Encapsulation of Scalable Perovskite Devices for Operation Under High-Moisture Environments

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Research in perovskite photovoltaics (PV) has witnessed a tremendous development over the last decade, as leaps in efficiency and stability were achieved by improvements in the device architecture. Progress in the charge selective layers led to better charge collection and band alignment, whereas development of multiple cation mixed halide perovskite phases resulted in robustness beyond 500 h under harsh environmental conditions.[1,2] Yet, the broad commercialization of perovskite PV panels has remained an elusive goal, as issues remain regarding the modules’ scalability and their long-term moisture- and air-sensitivity.

While typical stability tests employ high ambient humidity and elevated temperatures to accelerate device degradation, it must be pointed out that real-life module operation involves device soaking, mechanical stress and temperature changes, as experienced by a solar panel under say a heavy rain. Accordingly, the investigation of device robustness when submerged in aqueous, potentially corrosive electrolyte solutions may provide a more realistic benchmark for evaluating encapsulation strategies.

In this contribution, we introduce photoelectrochemical (PEC) device testing as a way to evaluate encapsulation methods, which are employed for perovskite PV devices of different sizes. Accordingly, we will focus on the recent advances in solar cell encapsulation achieved using a thin layer of Field’s metal (FM), a low melting InBiSn alloy.[3,4,5] The metal layer has a dual function, as protective barrier and electrical contact, which can act as an electronic interface to a surface-bound catalyst for PEC applications. In particular, the FM encapsulation demonstrates an advantage for the J-V characterization of larger single pixel perovskite solar cells, which can be straightforwardly employed as hydrogen-evolving photocathodes after electroless deposition of a platinum nanoparticle catalyst.[5] In this respect, we will also place special focus on the scalability of FM encapsulated solar cells, highlighting the interplay between device performance and serial resistance losses for single pixel perovskite PV devices of sizes of up to 10 cm$^2$.

In this context of photoelectrochemical benchmarking, we will also give a brief introduction to the basic principles of solar-fuel research and its advantages in terms of simultaneous energy production and storage,[6] showcasing our recent progress in the development of perovskite-BiVO$_4$ PEC tandem devices for unassisted water splitting.[5] Taking our current progress on 300 cm$^2$ large scale BiVO$_4$ panels into account,[7] we envision rooftop PEC devices by combining the BiVO$_4$ photoanodes with perovskite photocathodes of matching sizes. In the context of commercial applications, we will further address the potential of lowering down the overall device costs by appropriate choice of components.

Photonic Curing to Increase Throughput in Halide Perovskite Solar Cell Fabrication

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Halide perovskite solar cells (PSCs) have leap-frogged many photovoltaic systems in the past decade due to their excellent optoelectrical properties and solution-processability. Meanwhile, metal oxide (MO) transport layers have been shown to exhibit better stability, lower cost, and more tolerant processing parameters than their organic counterpart, leading to a promising path towards PSC commercialization. However, the bottleneck to high-throughput manufacturing of PSCs is the thermal annealing step in both the perovskite active layer and the MO transport layer, especially for mixed-cation perovskite materials and sol-gel MO films, which both require long thermal annealing time and high temperature. Conventional thermal annealing methods are not conducive to high-throughput manufacturing of large area PSCs because they translate to hundreds of meters long annealing tools and tremendous energy consumption due to the heat loss. In this work, we explored photonic curing as a rapid thermal annealing technique to replace conventional thermal annealing for both the bottom MO transport layer and the perovskite layer. Photonic curing, which is often used to sinter conductive nanoparticles on flexible substrates, delivers intense pulsed light on a sample within ~1ms. The absorption of light by the precursor film can increase its temperature by several hundreds of degrees within a short time window while minimizing heating of the substrate due to overall low energy. Thus, it is suitable for plastic substrates that can only be processed at low temperatures, e.g. PET. In addition, many photonic curing parameters—pulse length, pulse shape, pulse rate, energy per pulse, and number of pulses—can be optimized to process different materials due to their different light absorption coefficients and thermal properties. Our p-i-n PSCs are fabricated on PET/ITO substrates using NiOx as the hole transport layer. We spin coat and photonic cure NiOx sol-gel precursor films and perovskite precursor films sequentially. The materials’ properties, including optical absorption, crystallinity, surface morphology and roughness, and work function, as well as device performance are compared for films processed by photonic curing vs. conventional thermal annealing. We also compare the processing time and cost between photonic curing and hot plate annealing to demonstrate photonic curing as a potential candidate in high-throughput manufacturing of halide PSCs.

Showerhead-Assisted Chemical Vapor Deposition of Perovskite Films for Solar Cell Application

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Organic-inorganic halide perovskite solar cells have shown a rapid increase of performance with a maximum power conversion efficiency (PCE) up to 24.2 % in 2019, making these devices promising alternatives to those of established solar cell technologies. Besides the toxicity of the commonly used Pb-based compounds, the lack of deposition tools for large areas is one of the major challenges for the commercialization of perovskite photovoltaics. Chemical vapor deposition (CVD) is an appealing choice because it furthermore features high purity and superior process control.

In this work, we present a custom-developed showerhead-based perovskite CVD tool as well as novel low-vacuum (total pressure 10 hPa) CVD processes to fabricate dense perovskite films by simultaneous deposition of the precursors from the gas phase. We employ an organo-halide compound (CH3NH3I (MAI)) and a metal halide (either PbI2 or BiI3 as a non-toxic alternative) to obtain either MAPbI3 or (MA)3Bi2I9 (MBI) perovskite layers on a typical solar cell anode stack (glass / FTO / compact TiO2 / mesoporous TiO2, substrate size 2.5 cm x 2.5 cm). The thermally sublimated precursors are transported via N2 carrier gas (500 sccm) through the heated showerhead. The carrier gas flow is spread homogeneously enabling deposition on large-area substrates. Condensation and reaction of the precursors occur on the temperature-controlled substrate. A quartz crystal microbalance (QCM) is used to determine the deposition rates, usually between 3 and 7 nm/min for perovskite growth. For morphological, structural and optical characterization of fabricated layers, scanning electron microscopy (SEM), X-ray diffraction (XRD) and absorption measurements are performed. To obtain stoichiometric perovskites, we analyze the impact of the deposited-volume ratio between MAI and PbI2/BiI3 (adjusted by the QCM rates). In case of the Pb-based perovskite, an excessive supply of MAI (volume ratio MAI/PbI2 > 5) was found to be responsible for the formation of the
dihydrate perovskite phase \((\text{CH}_3\text{NH}_3)_4\text{PbI}_6\cdot2\text{H}_2\text{O}\) (XRD reflex at 11.3 °, measured in ambient air), leading to fast degradation of the perovskite layer. Providing the right amount of MAI during deposition (volume ratio between 2 and 4) results in stoichiometric perovskite films without any residues of the precursors (XRD spectrum perfectly matches the calculated pattern). We fabricated dense layers with thicknesses of 400 nm, exhibiting a cubic morphology with grain sizes of 200 nm.

For the MBI perovskite, a volume ratio of 5 was found to be sufficient for a complete conversion of BiI₃. Depositions with MAI/BiI₃ volume ratios exceeding 5 do not exhibit XRD peaks which can be assigned to either MAI or a perovskite hydrate. Obviously, the simultaneous deposition of BiI₃ and MAI has a self-limitation for MAI incorporation, still leading to the formation of stoichiometric MBI. Furthermore, we investigated the influence of the substrate temperature and layer thickness on film properties. Decreasing the substrate temperature from 88 to 50 °C leads to a more rounded grain morphology. The size of the crystallites scales to some extent with the layer thickness. Large grains up to 500 nm diameter are formed for a film with 225 nm layer thickness. The MBI films were implemented in non-inverted solar cell structures (Spiro-MeOTAD / Au contacts on top) with a maximum PCE of 0.016 %. Most likely, higher efficiencies can be achieved by optimizing the device architecture as the mesoporous TiO₂ matrix is not penetrated by the perovskite film. Finally, we deposited and characterized dense MBI films on large-area FTO substrates (12 cm x 9 cm), demonstrating the high degree of homogeneity. The formation of dense perovskite layers combined with the versatility and scalability of the process render this technology to be an auspicious candidate for commercial large-area production.

EN08.13.33
Upscale of Perovskite Solar Cells—Impacts of Drying Processes on Growth Mechanisms and Layer Properties of the Absorber

Sophie Bernard¹,²,³, Sébastien Jutteau¹,², Frédéric Sauvage³ and Jean Rousse³¹,², IPVF, France; ²EDF R&D, France; ³UPJV, France

For the past few years, perovskite solar cells have known a tremendous development among photovoltaic technologies. Since 2012, their performances rapidly increased from 2% to 24.2% efficiency. Nonetheless, most of the research occurs on lab scale substrates with an active area in the range of 0.1 cm². One challenge for the future of perovskite solar cells is the device up-dimensioning to modules, larger than 1 m². To do so, it first requires a better understanding and a good control of nucleation and growth mechanisms, but also the development of large scale fabrication processes, including deposition and drying methods.

Fabrication of a thin film on large-scale by solution coating is very demanding. To address this issue, various techniques have been previously developed, such as blade-coating, screen printing or slot-die coating [1]. However, none of this processes have achieved the small-scale performances yet. For now, the best efficiency for slot-die coated perovskite reached 18% [2] on lab-scale cell and 10.1% for a 160 cm² module [3]. To enhance the performances, it is necessary to deeply understand the influence of coating processes and drying methods.

First, we noticed that DMF/NMP offer a larger window coating, which can be optimized for slot-die systems. In fact, NMP get a similar coordination potential with PbI₂ than DMSO, usually used in spin coating solutions, but evaporate slower. Varying NMP ratio in DMF solvent mix allowed us to investigate different crystallization mechanisms in order to fit upscale conditions. Moreover, depending on NMP ratio, it is possible to enhance perovskite film coverage. Then, using an ideal DMF/NMP ratio, we developed a vacuum aspiration protocol. Inspired by X.Li and al.’s work on VASP (Vacuum flash-assisted solution process) for small scale spin-coated perovskite solar cells [4], we adapted this technology for 5x10 cm² slot-die coated perovskite layers. We studied different temperature and pressure conditions for quench and annealing stages in order to get an efficient and repeatable drying process.

On another hand, we studied several perovskite ink compositions. Besides solvent variation, it is possible to add different additives and surfactants to control adducts formation, making it more compatible with a slot-die coating system. We focused our work on FACs perovskite, excluding methylammonium cation. We adjusted the solid content and the ink formulation to improve uniformity, thickness and crystallization rate.

Through this work, we aim to demonstrate the influence of drying method on the absorber properties and how it is possible to control it to achieve high quality perovskite layers by slot-die system. We plan to transfer this achievements on mini-modules, with slot-die coated perovskite absorber.
EN08.13.35
P-type Conductors for Reducing Defect Density and Improving Stability in Invert Perovskite Solar Cells Lin Li; Huazhong University of Science and Technology, China

Perovskite solar cells (PSCs) are one of the most promising photovoltaic technology. However, lead perovskites face long-term instability issues under stimuli of heat, oxygen, moisture, electric field and light irradiation. Here we incorporate a series p-type organic conductors as additives in perovskite layer, increasing the device efficiency and markedly improving the long-time device stability. We close by positing organic conductor, reduce the defect density on the perovskite surface, by tying up both halide-rich antisites and undercoordinated lead center. After optimization, the carrier recombination lifetime was increased and the boost efficiency of 20.4% inverted perovskite solar cells was obtained. The thermal stability of the PSCs with passivation was evaluated, in which the devices were heated to 85°C inside a N2-filled glove box. there is almost no PCE reduction for the perovskite-conductor device after being heated for 24 hours.

EN08.13.36
Hydrophobic Perovskite Based on an Alkylamine Compound for High Efficiency Solar Cells with Improved Environmental Stability Mi Hee Jung; Sejong University, Korea (the Republic of)

Hybrid quasi-two dimensional perovskites (2D) have attracted significant scientific interest, because they have demonstrated excellent light absorbing materials in photovoltaic devices. However, the quasi-2D perovskites still perform poorly in high humidity, even though they have exhibited greatly improved stability compared to their three-dimensional (3D) counterparts. This is the biggest obstacle for the practical implementation and commercial viability of perovskite solar cells. Herein, we used hexylamine (CH3(CH2)4CH2NH2, HA) for a quasi-2D, HA(CH3NH3)n-PbnI3n+1 (n = 1, 2, 3, 4) perovskite, which has had sufficient long alkyl chain to maintain the chemical stability of perovskite. As the number of layers of quasi 2D HA(CH3NH3)n-PbnI3n+1 perovskites was increased, it exhibited an appropriate band gap as a light absorber to be applied to solar cells. The perovskite solar cell based on the 2D HA(CH3NH3)n-PbnI3n+1 perovskites showed an excellent power conversion efficiency of 5.90% with a short circuit current density of 13.61 mA cm⁻¹, an open circuit voltage of 0.72 V, a fill factor of 60.10%, and stability with solar cells to ambient air. The long alkyl chain of the hexylamine cation prevented degradation of the solar cell from the atmosphere with passivation of the perovskite films due to its high hydrophobic property. This investigation highlights the role of the organic cation to maintain the quality of the perovskite film and provides a critical solution for the poor stability of perovskites in ambient air.

EN08.13.37
Stacking of Layered Halide Perovskite from Incorporating a Diammonium Cation into Three-Dimensional Perovskites Mi Hee Jung; Sejong University, Korea (the Republic of)

Quasi two-dimensional (2D) layered perovskites have been emerging as promising candidates for a photovoltaic cell because they exhibit intrinsic stability and a higher tunability of optical properties compared to three-dimensional (3D) perovskites. However, since most 2D perovskites have bulkier groups as an organic space group, it will inevitably have a van der Waals gap between the inorganic layers, and their crystal growth directions orientate in a lateral direction. It also interrupts carrier transport across the conducting inorganic layer in the solar cell. Here, we presents the new homologous 2D layered perovskites, (HA)(A)n-PbnI3n+1, where HA stands for the histammonium ((C5N3H11)2+) as a diammonium cation, and A stands for methylammonium (CH3NH3+) or formammonium (HC(NH2)2+). Since the ditopic HA have diammonium cation, it connects the inorganic slabs stacked in the vertical direction. The inorganic layer is stacked on the other layer to form a layered structure, which results in rigid and stable structures. These materials (1.46 eV for (HA)(FA)n-PbnI3n+1 and 1.80 eV for (HA)(MA)n-PbnI3n+1) have significantly lower band gaps than the HAPbI4 (2.20 eV). Compared to the pure 2D and 3D perovskites, these perovskite have a longer electron lifetime due to the vertical crystal structure and show improved environmental...
stability for the perovskite solar cell application

**EN08.13.40**  
**A Chemically Inert Bismuth Interlayer Enhances Long-Term Stability of Inverted Perovskite Solar Cells**  
Chen Rui; Huazhong University of Science and Technology, China

Highly efficient and low-cost halide perovskite solar cells (HPVKSCs) are regarded as one of the most promising photovoltaic technologies to realize commercialization in the near future. However, the long-term stability of HPVKSCs under real working conditions, involving stresses from moisture, heat, light, and the electric field, is still a challenge that must be addressed. The irreversible degradation of HPVKSCs can be mainly attributed to three phenomena: (1) volatilization of the organic components in organic–inorganic hybrid perovskites, especially for the benchmark methylammonium lead triiodide (MAPbI3) under thermal aging conditions above 85°C, (2) permeation of external H2O/O2 and its induced degradation of perovskites, and (3) reactions between the normally used metal electrodes and halogens from the perovskites during prolonged operation. For the last two issues, especially the third one, their resolutions are largely related to the essential properties of the interfacial layers (i.e., morphologic pin-hole free, chemical resistivity to H2O/O2 and halides), which could act as robust permeation barriers to block the undesired processes. If the interfacial layers are permeable or have pin-holes, sufficient separation between the perovskites and electrode metals cannot be achieved, and the corrosive reaction could be fast.

Here, we demonstrate a facile processing strategy for highly stable HPVKSCs with the structure FTO/Li+-doped NiMgLiO/Perovskite (PVK)/PCBM/BCP/Bi/Ag by introducing the compact Bi interlayer. The devices and films were characterized by photoluminescence (PL), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), time of flight secondary ion mass spectrometry (ToF-SIMS), etc., which demonstrate that the Bi interlayer acts as a robust penetration barrier that blocks the unfavorable external molecules from diffusing into the devices and suppresses the diffusion of ions between the metal electrode and the perovskites. As a result, our unencapsulated MA-HPVKSCs retain 88% of their initial efficiency after being maintained in the dark in ambient air without humidity control for 6000h. During long-term light soaking or thermal aging at 85°C in the dark, the devices with Bi interlayers are considerably more stable than devices without Bi. This Bi-interlayer strategy is easily scalable and highly repeatable and may pave the way to the future practical application of large-area and highly stable HPVKSCs.

**EN08.13.41**  
**Inorganic Halide Perovskite Single Crystal—Growth Mechanism, Structural and Optical Properties**  
Sovesh Mohapatra, Naveen K. Tailor and Soumitra Satapathi; Indian Institute of Technology, India

Lead halide semiconductors with a perovskite crystal structure and APbX3 stoichiometry [A = Cs+; X = I−, Br−, Cl− or mixtures thereof have recently turned into the most strongly considered category of inorganic optoelectronic materials. These materials are now widely utilized in light-emitting diodes, lasers, photo-detectors as well as in X-ray and gamma-ray (γ-ray) detectors. In these applications, large single crystals (SCs) grown by precursors solutions of perovskites are mostly utilized because of low trap density and less grain boundary. Therefore, the rapid emergence of halide perovskite based single crystalline materials for a wide variety of as mentioned applications has drawn much research attention in recent years. Many efforts have been made in optimizing their macroscale device performance by improving material processing and device fabrication and over the last few years. But, to fully obtain and understand the intrinsic characteristics of perovskites, a variety of high-quality single-crystalline materials are genuinely necessary.

In our present study, we have reported the 3mm size lead free perovskite single crystals grown by the slow cooling method. The synthesis, crystal growth, and detailed structural and optical characterization have been carried out by Optical microscopy, FESEM, EDXA, single crystal XRD, UV-Vis, PL, and TCSPC. The synthesized single crystals have orthorhombic structure and Pnma space group and the corresponding lattice parameters and reciprocal lattice parameters are calculated. Moreover, symmetry operators in the crystal, hkl values, linear absorption coefficient and reciprocal lattice pattern of the synthesized single crystals have been calculated. Transmission microscope and FESEM images have shown clearly the single crystalline morphology and EDXA have shown the stoichiometry matching by means of elemental analysis of the crystals. The I-V characteristics of this lead-free perovskite single crystals are also discussed.
Grain Size Increase of MAPbI₃ Perovskite via Hot-Casting Technique for PV Application with Enhanced Efficiency

Jasmine Li¹, Aidan York², Yuchen Zhou¹, Yifen Yin¹ and Miriam Rafailovich¹; ¹Fairview High School, United States; ²Kellenberg Memorial High School, United States; ³Stony Brook University, United States

Perovskite solar cells (PSCs) demonstrated fast-raising power conversion efficiency (PCE) in past couple years. However, one of the problems associated with PSCs is the formation of small sized grains with large density of grain boundaries (GB) and defects within the perovskite layer, which largely results from the conventional post annealing method used in perovskite layer preparation. To promote crystalline quality and reduce GB density, we utilized a so-called “hot-casting” technique, in which the perovskite precursor solution and substrate are preheated at a relatively high temperature before spin-casting. This allows annealing and spin-casting to occur at the same time, prolongs the grain growth time, and as a result, enhances the crystal quality. Therefore, PSCs made by hot-casting can have promoted PCE by growing large crystal grains and decreasing defects/traps.

We compared the morphology and crystalline structure of perovskite layer and PV performance of corresponding devices prepared via conventional post annealing versus the hot-casting. We observed in scanning electron microscope (SEM) images that hot-casted samples produced an average grain size of 11.40 μm, nearly 60 times greater in size than the average grain size of 194 nm obtained for the post annealing method. Furthermore, we observed in atomic force microscopy (AFM) images that hot-casted perovskite demonstrated a canyon-like crystal growth due to such vigorous growth that neighboring grains collided at the edges, forming a uniform, fully covered, and highly crystalline film with micron sized grains; in contrast, perovskite made by post annealing produced a film with much smaller and nanosized grains. We also used x-ray diffraction (XRD) to confirm that hot-casting generated perovskites possessed the tetragonal crystal phase, same with the sample made by post annealing method; in fact, hot-casting enhanced the crystallinity of perovskite, which exhibited stronger XRD peak intensity than the conventional ones. Most notably, PV performance tests demonstrated a PCE increase of ≈15% when using hot-casting, from 12.2% prepared conventionally to 13.9% prepared via hot-casting. Thus, hot-casting has demonstrated to be an effective method to increase PCE of PSCs through the grain size management. (We acknowledge support from the Louis Morin Charitable Trust and NYS Department of Economic Development.)

Ion Diffusion and Surface Moisture-Induced Degradation Behaviors in Halide Perovskite Using Molecular Dynamics Simulations

Huanhuan Zhou¹, Mingchao Wang², Jingfan Wang¹ and Shangchao Lin³; ¹Florida State University, United States; ²Monash University, Australia; ³Shanghai Jiao Tong University, China

Organic-inorganic hybrid perovskites, such as the prototypical methylammonium lead iodide (CH₃NH₃PbX₃ or MAPbX₃, X=I-, Br-, Cl-), have emerged as promising light absorbers in photovoltaic (PV) cells or as emitters in light-emitting diodes (LEDs). However, they generally suffer from moisture instability, which limits the long-term use of perovskite-based devices in ambient environment and impedes the rapid commercialization. In this work, we have studied the ion diffusion and surface moisture-induced degradation behaviors for two types of perovskites: 3D MAPbI₃ and 2D MAPbBr₃. In order to greatly decrease the ion dissociation rate and improve the moisture stability, we have applied molecular dynamics (MD) simulations and first-order reaction kinetics theory to model the ion dissociation process and estimate the associated free energy barrier with and without ligand passivation. We design 3D MAPbI₃ and 2D MAPbBr₃ structures with ligand-passivated surfaces by replacing MA cations with ligands composed of long-chain alkyl-ammoniums. Ligands with different chain lengths, such as CH₃(CH₂)₇NH₃⁺ (n=7), and under different surface coverages (σ = 25%, 50%, 75%, 100%), are considered here. We discover that ligand passivation can greatly help 3D MAPbI₃ and 2D MAPbBr₃ perovskites protect MA cations on the surface due to the much higher dissociation energy barriers of these ligands compared to that of MA cations. For I anions, ligand passivation can also shield them from water contacts, except for long-chain ligands, such as CH₃(CH₂)₇NH₃⁺ (n=7) at full surface coverages (σ = 100%), due to the reduced dissociation free energy barriers of long-chain ligands. As an interesting finding, the reduced dissociation free energy barriers for long-chain ligands at high surface coverages could be explained by their larger tendencies to micellize, which serves as additional driving force for their dissociation. Additionally, water contact angle simulations have also been performed for 3D MAPbI₃ perovskites to compare the hydrophobicity of different ligand-passivated surfaces and verify that the surface moisture stability of 3D MAPbI₃ surface has been improved by the ligand passivation technique. We also observe suppressed and anisotropic ion diffusion in 2D MAPbBr₃ perovskites due to the layered ligand phase sandwiched by the PbI₂ crystals, which resembles an organic-inorganic superlattice. This work significantly motivates future experimental
efforts in designing new surface ligands to improve the moisture stability of halide perovskites.

EN08.13.45
Stability Enhancement of Perovskite Solar Cells Using Mixed Cation/Halide Perovskite Ethan Eisenberg¹, Jack Cox², Yuchen Zhou³, Yifan Yin³ and Miriam Rafailovich³; ¹George W. Hewlett High School, United States; ²South Side High School, United States; ³Stonybrook University, United States

Within the last decade, perovskite (PVSK) has emerged as a solar cell material rivaling those of silicon and quantum dots due to their increasing power conversion efficiency (PCE). PVSK serves as the active layer within a planar solar cell and have the common hybrid organic inorganic halide structure ABX3. The increasing efficiency of these cells can be attributed to several optoelectronic characteristics such as a high absorption coefficient, tunable bandgap and ambipolar carrier transport. However, PVSK is limited because the ABX3 classic structure is unstable. The most common ABX3 structure is methylammonium lead iodide (MAPbI3). The organic cation of methylammonium (MA) is hygroscopic, causing the cell to degrade under conditions of moisture, heat, oxygen, and light [3]. To reduce degradation and enhance efficiency, Cs and formamidinium (FA) cations and Br halide are introduced to create a mixed cation/halide structure CsFAMAPbIxBr1-x. The combination of these cations and halides can allow for increased stability and optoelectronic performance by reducing transformation into a photo inactive delta phase, while maintaining the preferable bandgap produced by the FA structure.

Pervious research studies have used different pure PVSK compounds such as CsPbI3 or FAPbI3 to either prevent degradation or to optimize absorption. However, due to the existence of inactive phases, these materials suffer from structural instability. Furthermore, studies that have observed mixed structures that do not include FA (CsxMA1-xPbI3 for example) can exhibit lower efficiencies due to a bandgap increase. This study tries a combination of Cs, FA, MA, and Br with a spin-coating method to optimize both efficiency and stability of the cell. One-step spin coating was used to prepare the PVSK film. PbI2, MAI, CsI, FAI, and PbBr2 at a molar ratio of 1:0.7:0.15:0.15 were placed in a mixed solvent of DMF and DMSO (8:2). Titanium dioxide was spin coated onto FTO substrates and annealed to form the electron transport layer (ETL). The precursor PVSK solution was then deposited via spin coating and chlorobenzene was applied onto the surface as an anti-solvent for crystal generation. Spiro-OMeTAD was coated as a hole transport layer (HTL) and physical vapor deposition (PVD) was used to add the gold electrodes.

UV-Visible Spectroscopy indicated that the changing of the cation/halide component did not influence the absorption of the photoactive layer. Scanning electron microscopy (SEM) morphology results showed increased grain size for the mixed PVSK. Atomic force microscopy showed correspondent morphologies to SEM results, but with an increase in roughness, which is within acceptable range. Moreover, XRD results implicated that the mixed PVSK had two possible crystal phases (α and phases) compared to the single peak of (110) of MAPbI3 PVSK, while only the cubic α phase is photoactive. Therefore, the mixed PVSK layer was annealed at various conditions to optimize the cubic alpha photoactive phase. This is because the partial phase segregation can lead to increased recombination at Iodine rich centers, and would therefore hinder PCE. After the optimization, results revealed that at a temperature of 120 Celsius and a time of 10 minutes allowed for the preferable crystallization of the mixed PVSK with a strong alpha peak and negligible delta phase. Furthermore, the PCE measurement indicated the mixed PVSK has higher PCE, probably due to increased grain size. The moisture and heat stability tests (XRD) revealed enhanced structural stability against excessive heat, supporting that the mixed structure can successfully generate better performance and enhance the durability. (We acknowledge support from the Louis Morin Charitable Trust and NYS Department of Economic Development.)

EN08.13.46
127I NQR Study of Methylammonium Lead Iodide MAPbI3 YoHan Kim, BeomJe Jo and Moohee Lee; Konkuk University, Korea (the Republic of)

The single crystals of methylammonium lead iodide (MAPbI3) CH3NH3PbI3, which recently draws much research interest as light-harvesters in dye-sensitized solar cells because of the high photovoltaic efficiency and the structural flexibility for all solid-state devices, were prepared by the solution growth method and characterized by 127I NQR (nuclear quadrupole resonance) techniques. 127I NQR spectrum, linewidth, spin-spin relaxation rate 1/T2, and spin-lattice relaxation rate 1/T1 were measured as a function of temperature down to 70 K to microscopically understand the iodine dynamics associated with the ionic conductivity. As temperature decreases, 127I NQR frequency slightly increases from ~ 82 MHz at room temperature and then disappears around 180 K with the rapidly increasing linewidth. At lower temperatures, the NQR signal appears again with the fast increase of resonance frequency but
the narrowed linewidth remains almost same. The spin-echo signal is observed below 120 K and $1/T_2$ decreases quickly at low temperatures. $1/T_1$ increases down to 180 K, below which it starts to decrease. Based on these NQR data, we conclude that the iodine dynamics change significantly around 180 K.

EN08.13.47
Moisture Induced Structural Degradation in Methylammonium Lead Iodide Perovskite Thin Films Panteha Toloueiinia, Hamidreza Khassaf, Alireza Shirazi-Amin, Anne Mirich, Chris Monteleone and Steven L. Suib; University of Connecticut, United States

Methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$, MAPbI$_3$) belongs to the group of organic-inorganic halide perovskite (OIH) that exhibit exceptional electrical and optical behavior for photovoltaic applications. However, its structural and chemical stability and robustness remain a challenge in order to be considered a feasible active material in optoelectronic devices. Therefore, it is crucially important to understand mechanisms by which MAPbI$_3$ undergoes chemical degradation under operating conditions such as a relatively humid environment. We use dark pulse discharge measurements and current-voltage (I–V) variations of MAPbI$_3$ under different moisture levels to investigate the nature of structural degradation in (OIHs). We show that while relatively low levels of humidity (RH<65%) have limited impact on structural stability, exposure to higher levels of moisture results in the formation of PbI$_2$ and CH$_3$NH$_3$I which fundamentally change the charge transport phenomenon in MAPbI$_3$. Our findings suggest an explanation of the ongoing debate on the presence of a critical level of humidity that triggers irreversible structural transformation that leads to full degradation of MAPbI$_3$.

SESSION EN08.14: Perovskite Solar Cell—High Efficiency
Session Chairs: Shuzi Hayase, Shengzhong (Frank) Liu and Selina Olthof
Friday Morning, December 6, 2019
Hynes, Level 2, Room 204

8:00 AM *EN08.14.01
Understand the Stability Limitation of Perovskites and Strategies to Enhance the Stability Jinsong Huang; University of North Carolina at Chapel Hill, United States

The efficiencies of small-pixel perovskite photovoltaics have increased to well above 20%, while the question is whether fabrication methods can be transferred to scalable manufacturing process. Here we report a method of fast blading large area perovskite films at an unprecedented speed of 99 millimeter-per-second or higher in ambient condition by tailoring solvent coordination capability. Combining volatile non-coordinating solvents to Pb$^{2+}$ and low-volatile, coordinating solvents achieves both fast drying and large perovskite grains at room temperature. The reproducible fabrication yields a record certified module efficiency with aperture area of 63.7 cm$^2$. The perovskite modules also show a small temperature coefficient of -0.13%/°C and nearly fully recoverable efficiency after 58 cycles of shading, much better than commercial silicon and thin film solar modules. The application of the coating method to perovskite/silicon tandem cells and will also be presented. We will answer the question whether the perovskite layers can be fabricated at the speed of silicon cells are produced in the regular production lines.

8:30 AM *EN08.14.02
Surface Passivation for Efficient Perovskite Solar Cells Jingbi You; Chinese Academy of Sciences, China

It is known that the $V_{OC}$ of solar cells are strongly related to the defects recombination in the bulk or on the surface of absorber layer. Solution processed perovskite film is usually polycrystal, which contains substantial structural disorder such as grain boundary defects, crystallographic defects. Although it was theoretically predicted that most of the defects formed in perovskite layer could be shallow defects, several experimental results still showed that the suppression of defects in the solution-processed perovskite films are very critical for further enhancing the performance of PSCs toward their thermodynamic limits. Surface is the place where the defects could be easily formed, passivation of the surface defects is always the most important tasks in any type of solar cells. In PSCs, several efficient surface passivation methods have been adopted previously. Recently, we developed an organic halide salt phenethylammonium iodide (PEAI) for post-treatment of mixed perovskite to suppress the surface
defects of perovskite polycrystal film for efficient solar cells. We find that the PEAI can form on the perovskite surface and results in higher efficiency cells by reducing the defects and suppressing non-radiative recombination. As a result, planar PSCs with a certificated efficiency of 23.32% (Quasi-steady-state) are obtained. More recently, we have pushed the efficiency of PSCs beyond 24%.

References

9:00 AM EN08.14.03
Application of 2D Materials in Fabrication of Efficient and Stable Perovskite Solar Cells Mohammad Mahdi Tavakoli and Jing Kong; Massachusetts Institute of Technology, United States

Organic-inorganic perovskite materials, due to their excellent optoelectronic properties and low-cost processing have attracted many research groups nowadays. These materials with ABX₃ crystal structure (A: cesium (Cs), methylammonium (MA) or formamidinium (FA), B: Pb or Sn, and X: Cl, Br or I) have been a good candidate for the fabrication of highly efficient perovskite solar cells (PSCs) with a certified power conversion efficiency (PCE) of 24.2%. Interfacial engineering is one of the effective strategies for improving the efficiency and stability of PSCs. In this regard, combination of two-dimensional (2D) materials with PSCs would be so effective to improve the photovoltaic properties of devices. Here, we study the applications of monolayer graphene synthesized by chemical vapor deposition (CVD), MoS₂, and BN in the perovskite architecture. We considered graphene as top and bottom electrodes in the device and found that this would be a great way to replace metal electrode such as gold and fabricate efficient semi-transparent PSCs. Based on graphene as a top electrode in CsPbI₃ QDs PSC, we achieved a PSC with power conversion efficiency (PCE) of 6.8%, which is slightly lower than the reference cell (9.6%). Additionally, by tuning the thickness of the active layer, a PSC with PCE of 4.95% and average visible transmittance (AVT) of 53% is demonstrated, indicating the potential of CsPbI₃ QDs for the fabrication of semi-transparent devices applicable in windows.

Moreover, we employed MoS₂ as an electron transporting layer (ETL) in the PSCs and a PSC with PCE of 18% was achieved with this architecture, indicating the potential of 2D materials in the PSCs. In addition to the above study, we considered BN monolayer as an interface layer in inverted PSC device. Based on this modification, we improve the open circuit voltage (Voc) and stability of the PSCs drastically. Based on this modification, a PSC with PCE of over 20% was achieved.

9:15 AM EN08.14.04
Stable and Efficient Perovskite Solar Cells by Thiophene-Based 2D Perovskite Functionalization Albertus Adrian Sutanto¹, Nikita Drigo¹, Inés García Benito¹, Valentin I. Queloz¹, Kyung Taek Cho¹, Giulia Grancini² and Mohammad K. Nazeeruddin¹; ¹École polytechnique fédérale de Lausanne, Switzerland; ²University of Pavia, Italy

Hybrid metal halide perovskite materials have become a leading technology in the photovoltaic scene since its first application in solar cells in 2009. The power conversion efficiency (PCE) of perovskite solar cells (PSCs) has been reached from 3.8 to 24.2% in the past ten years. Compositional tuning, i.e., by substituting the anions or cations, and interface functionalization have been the key to the breakthrough of the device performances. However, the state-of-art device performance is, so far, achieved by employing three-dimensional (3D) perovskite materials as the light absorber. The major drawback in using 3D perovskites is the poor stability against moisture, which hinders the widespread application of this technology. On the other hand, two-dimensional (2D) perovskite materials have demonstrated superior stability compared to the 3D counterparts. However, 2D perovskites have limited light-harvesting ability, resulting in low PCE. Combining 2D and 3D into a new hybrid 2D/3D has been a popular alternative to boost both device efficiency and stability. In this work, we design and employ a family of thiophene-based organic cations, as building blocks for layered two-dimensional (2D) perovskites. The 2D layer functionalizes the interface between the optimized triple-cation (formamidinium (FA), methylammonium (MA), and cesium) lead halide perovskite layer and the organic hole transporting material (HTM) employed in n-i-p solar cells configuration. As an immediate result, the functional 2D interlayer actively improves device performances by significantly improving the long-term device stability by retaining up to 90% of the initial efficiency after continuous illumination and delivering efficiency of >20%. In parallel, the thiophene-based 2D capping layer reduces the commonly observed current voltage hysteresis behavior to a great extent.

9:30 AM EN08.14.05
Surface Tailoring and Passivation for Both Enhanced Efficiency and Stability of Perovskite Solar Cells
Shangshang Chen and Jinsong Huang; University of North Carolina at Chapel Hill, United States

Lead halide perovskites have drawn extensive research attention due to their excellent optoelectronic properties and remarkable performance in photovoltaic devices. The power conversion efficiency of perovskite solar cells has already reached over 24 %, surpassing those of mainstream thin film photovoltaic technologies like CdTe and CIGS. Despite these encouraging progresses, perovskite solar cells still suffer from poor stability owing to their vulnerability to oxygen, moisture and light.

It has been demonstrated that the degradation of perovskite initializes from the defective surface and grain boundaries, due to the higher reactivity of defects site, making them vulnerable to be attacked by moisture and oxygen.[1] Therefore, the passivation of these defects is imperative for the commercialization and large-scale production of this photovoltaic technology.

Here we present a simple strategy via the in-situ conversion of surface perovskite to water-insoluble lead salts, which exhibits dual effects: 1) passivate the surface defects and thus enhance the power conversion efficiency to over 21 %; 2) the formation of compact surface lead salt layer exhibits good resistance to hazardous stimuli under ambient atmosphere and light irradiation. Consequently, our encapsulated devices show excellent stability after operation at maximum power point under simulated AM 1.5G irradiation for over 1000 hours at 65 °C.

References:

9:45 AM EN08.14.06
Ultrafast Thin-Film Perovskite Solar Cells Exian Liu¹, Kai Zhu² and Jianbo Gao¹; ¹Clemson University, United States; ²NREL, United States

To reveal the device physics of solar cells, various photoconductivity approaches such as time-resolved microwave photoconductivity (TRMC), time-of-flight (TOF), and photo charge extraction by linearly increasing voltage (CELIV) are used in-situ. However, their time resolution is within the range of couple nanoseconds to microsecond due to the device structure, resulted in that the carrier dynamics study is dominated by trapping states, rather than trapping-free phenomena. Therefore, it remains a challenge to study in-situ solar cells in an ultrafast fashion.

In this report, we use a more than 20 % perovskite thin film solar cell as a test-bed, and integrated them into an ultrafast photocurrent spectroscopy with sub-40 ps time resolution to study the carrier dynamics from the sub-40 ps to couple microseconds. We address the evolution of carrier dynamics such as relaxation, recombination, transport, and trapping.

10:00 AM BREAK

10:30 AM *EN08.14.07
New Nanostructures, Interfaces and Crystallization Modes for Efficient and Stable Perovskite Solar Cells Shihe Yang; Peking University Shenzhen Graduate School, China

Nanostructures, interfaces and active layer crystallization are critical to the functioning of the new generation solar cells. The hybrid organic/inorganic halide perovskite solar cells have emerged as among the most competitive photovoltaic technologies of the future thanks to their superb and rapidly improving power conversion efficiencies (PCEs). For realistic deployment of the perovskite photovoltaic technology in large scale, however, device stability has become more and more important issue of the day. I will update our recent work on the development of high-efficiency and high-stability perovskite solar cells. First, we have developed a new hole transport material by embedding an ultra-low concentration of gold nanoparticles into a NiO film, significantly boosting the performance of the p-i-n perovskite solar cells. Second, by incorporating an ultrathin ferroelectric oxide PbTiO₃ layer between the electron transport material and the halide perovskite, we are able to significantly increase both PCE and stability of the perovskite solar cells. Finally, we discovered that a large excess of cesium iodide induces spinodal decomposition of CsPbI₂Br perovskite films, and these films could also be made into high performance perovskite solar cells. Implications of these results on the future development of perovskite solar cells will be discussed.
Compared with silicon-based solar cells, organic-inorganic hybrid perovskite solar cells (PSCs) possess a distinct advantage, i.e., its application in flexible field. However, the efficiency of flexible device is still lower than that of rigid one. Firstly, we found that dense perovskite film can be obtained with the help of N-methyl-2-pyrrolidone (NMP) by low pressure assisted method (LPAM). In addition, CH$_3$NH$_3$Cl (MACl) as the additive could preferentially form MAPbCl$_{3-x}$I$_x$ perovskite seeds to induce perovskite phase transition and crystal growth. Finally, by using FAI-PbI$_2$-NMP+x%MACl as the precursor, i.e., ligand and additive synergetic process (LASP), FA-based perovskite film with large grain size, high crystallinity and low trap density was obtained on a flexible substrate in ambient due to the synergetic effect, e.g., MACl could enhance the crystallization of the intermediate phase of FAI-PbI$_2$-NMP. As a result, a record efficiency of 19.38% in flexible planar PSCs was achieved by using FAI-PbI$_2$-NMP+15%MACl as the precursor, and it could retain about 89% of its initial PCE after 230 days without encapsulation in ambient. The PCE retained 92% of the initial value after 500 bending cycles with a bending radii of 10 mm. Our results show a robust way to fabricate highly efficient flexible PSC.

Perovskite solar cells are approaching silicon photovoltaic counterparts in performance, but mostly on a small area. To commercialize this low-cost technology, scalable fabrication is one of the main challenges to be addressed, for both perovskite active layers and charge transport layers [1]. For large-area, uniform and high-quality perovskite deposition, we have developed industry compatible hybrid chemical vapor deposition (H-CVD) to deposit MAPbI$_3$, FAPbI$_3$, and C$_x$FA$_{1-x}$PbI$_3$ films with high quality for solar cells/modules [2-5]. In this talk, I will focus on fully scalable perovskite solar modules with high-geometric fill factor by a further optimized hybrid chemical vapor deposition process and scalable sputtering deposition of electron transport layer SnO$_2$ [6-7]. With optimized interface structure between SnO$_2$ and C$_x$FA$_{1-x}$PbI$_3$, 10 cm x 10 cm solar modules showed a designated area efficiency approaching 10% with a geometric fill factor greater than 90%. We show that H-CVD is capable of fabricating large-area and high performance perovskite solar modules.

References:

The past ten years have witnessed the booming development of perovskite solar cell (PSC) with efficiency exceeding 24%, which is recognized as a superstar in photovoltaic research fields. However, the stability issue still limits their further development and commercialization. One of the main factors which lead to the instability issue is the ion diffusion between metal electrodes (Ag or Au) and perovskite absorbers. Carbon nanotubes have attracted tremendous attention with merits of low cost, outstanding electrical and mechanical properties, great chemical stability as well as large-area fabrication. Aiming at improving the long-term stability and reducing the fabrication cost of PSCs, we have devised several high-performance PSCs based on cross-stacked superaligned carbon nanotube
electrodes (CSCNT). Via subtly optimizing the device architecture and chemically modifying the CNT electrodes, we have significantly enhanced the photovoltaic performance and stability of CNT based PSCs under multi-environment. We first modify CNT with iodine and polyethylenimine (PEI) for regular HTM-free PSCs and inverted planar PSCs, respectively. Devices show better photovoltaic performance than that of the pristine CNT based ones owing to the enhanced charge transfer. Then we successfully construct inverted PSCs with all inorganic charge transport layer based on SnO$_2$@CNT electrode and obtain a champion power conversion efficiency (PCE) of 14.3% and 10.5% on the rigid and flexible substrate, respectively. Meanwhile, devices retain 88% of their original PCE aging at light illumination in air or thermal treatment in N$_2$ for 550 h. Finally, we design all-carbon-electrode based flexible PSCs with graphene as anode and CNT as cathode with a best PCE of 11.9%. Our devices show outstanding stability and durability under continuous light soaking in air for 1000 hours or bending cycles over 2000 times, retaining ca. 90% of their original PCEs respectively. Considering the increasing efforts dedicated to developing low-cost and stable energy conversion devices, the promising efficiency, flexibility, and long-term stability of CNT based PSCs clearly reveal sufficient compatibility. In addition, we have successfully developed a perovskite-thermoelectric tandem cell, which promotes the device PCE up to 23.2%.

Hysteresis-Free, Stable and Efficient Solution-Processed Perovskites Solar Cells by Hybrid Perovskites Co-Crystallized with Polymers

Hybrid perovskite materials have emerged as attractive alternatives for cost-effective solar cells. Impressive device performance has been realized through generic interface engineering. However, approaching hysteresis-free, stable and efficient solution-processed perovskites solar cells has remained a significant fundamental challenge. In this study, we report a strategy that utilizes polymer to anchor the counter ions in the perovskite lattices to suppress the formation of point defects, reduce the migration of ions/vacancy and to facilitate crystal growth in a more thermodynamically preferred orientation. Systematical investigations indicate that polymer indeed form hydrogen bonds at the crystal interface, which reduce the formation of kinetically-driven point defects, minimizes charge carrier recombination and maintains the sharp distribution of the density of states. As a result, un-encapsulated perovskite solar cells by novel hybrid perovskites thin film exhibit efficient, hysteresis-free characteristics and a decent device lifetime after being operated in air with 50% relative humidity in comparison to the reference perovskite solar cells by pristine hybrid perovskites thin film. Our studies demonstrate that development of hybrid perovskite materials crosslinked with polymers is one option to approach hysteresis-free, stable and efficient solution-processed perovskite solar cells.

Narrow Band Gap Perovskite Solar Cells Containing Sn

Perovskite solar cells in which metal halide perovskite layers are used as light harvesting materials are gaining much attention because of the high efficiency although these solar cell can be prepared by low temperature printing technology. The efficiency of Pb-perovskite solar cells with more than 1 cm$^2$ is 20.9% which became close to those of inorganic multi-crystalline solar cells such as MC-Si, CIGS, and CdTe. In small cells with less than 1cm$^2$, the efficiency of 24.2% has just been reported for the perovskite solar cells. Conventional perovskite solar cells consisting of Pb have band gap of 1.5-1.6 eV and can harvest the light in the visible region up to 850nm. According to Shockley-Queisser limit, light harvesting layer with 1.2-1.4 eV band gap gives the highest efficiency. Mixed metal PbSn perovskite materials have a narrow band gap of around 1.2 eV. Therefore, mixed metal SnPb perovskite solar cell is expected to give higher efficiency than Pb-perovskite solar cells. In addition, the narrow band gap solar cell is useful for bottom cells for all perovskite tandem solar cells. When SnPb mixed metal perovskite solar cells was firstly reported by us, the efficiency was around 4%. However,
the efficiency has been enhanced gradually and recently efficiency higher than 20% has been reported by several groups including our Lab. How the efficiency was enhanced will be discussed in the presentation1-3. The conventional perovskite layer consists of Pb ions. Therefore, the perovskite solar cells have to recover completely, for which a new business model is needed such as CdTe solar cells. In addition, the use of Pb ions is limited by the law such as RoHS directive in Europe. From this view point, there is a strong request for Pb-free perovskite solar cells solar cells. Bismuth halide compounds such as Cs$_3$Bi$_2$I$_9$, MA$_3$Bi$_2$I$_9$ Ag$_3$BiI$_6$, AgBiI$_3$, Cs$_2$AgBiBr$_6$, antimony halide compounds such as Rb$_3$Sb$_2$I$_9$, titanium halide compounds such as Cs$_2$TiBr$_6$, and copper halide compounds such as MA$_2$CuI$_4$ have been reported to replace lead. However, the solar cell efficiency based on these materials were less than 5% and was not satisfactory. Among all lead-free perovskite materials, Sn-based perovskite is one of the most promising candidates as the light harvesting layer for Pb-free PSCs, because they have perovskite structure similar to Pb perovskite. The efficiency has been enhanced to 10% by several research groups including us, however, the efficiency is not still satisfactory, when compared with Pb-perovskite. The cause of the low efficiency and how the efficiency will be enhanced is discussed4-7. In addition, wide gap perovskite solar cells needed for all perovskite tandem cells will be reviewed including our results on Pb-perovskite consisting of Ge ion6.

References

2:00 PM EN08.15.02
Suppression of Surface Recombination in Tin-Halide Perovskite Solar Cells via Lewis Base Post-Treatment
Muhammad Akmal Kamarudin1, Daisuke Hirotani2, Kengo Hamada3, Kohei Nishimura1, Qing Shen1, Taro Toyoda1, Satoshi Ikubo2, Takashi Minemoto3, Kenji Yoshino4 and Shuzi Hayase1,2; 1The University of Electro-Communications, Japan; 2Kyushu Institute of Technology, Japan; 3Ritsumeikan University, Japan; 4Miyazaki University, Japan

Tin perovskite solar cells (PSCs) show the most promise to replace the more toxic lead-based perovskite solar cells. However, the efficiency of tin-based PSCs falls short of that of lead-based PSCs by a large margin, as a result of low open-circuit voltage (Voc). This is due to the tendency of Sn$^{2+}$ to oxidize into Sn$^{4+}$ in the presence of air together with the formation of defects and traps caused by the fast crystallization of tin perovskite materials. Here, we performed post-treatment of tin perovskite layer with Lewis base to suppress the recombination reaction in tin halide PSCs resulting in efficiencies more than 10 %, which is the highest reported efficiency to date for pure tin-halide PSCs. The Voc increased by as much as 0.1 V with optimum concentration of the Lewis base. Upon analyzing the X-ray photoelectron spectroscopy and impedance spectroscopy data, we came to the conclusion that the amine-group bonded the under-coordinated perovskite, passivating the dangling bonds and defects resulting in suppressed charge carrier recombination. This also has the effect of prolonged lifetime and higher charge carrier mobility. Our findings will provide the groundwork for improving the efficiency of pure tin halide PSCs to compete with that of lead-based PSCs by simple post-treatment with organic molecules.

2:15 PM EN08.15.03
Rudorffites as Alternatives for Solution Processed Lead Halide Perovskite Solar Cells
Feray Ünlü1, Ashish Kulkarni2, Sanjay Mathur1 and Tsutomu Miyasaka2; 1Institute of Inorganic Chemistry, University of Cologne, Germany; 2Graduate School of Engineering, Toin University of Yokohama, Japan

Inorganic-organic hybrid lead halide perovskite solar cells have attracted tremendous research attention due to rapid rise in power conversion efficiency (PCE) from merely 3.8% to 24.2% within 10 years. Such rise in PCE is attributed to exceptional optoelectronic properties such as long charge carrier diffusion length, low exciton binding energy, ambipolar charge mobility, tunable narrow bandgap. Despite of these advantages, one of the major problems encountered with this new technology, apart from structural and chemical stability, is the toxicity associated with heavy metal lead. Among various metals explored, bismuth-based perovskite materials provide promising optoelectronic properties and can be processed from solution using a variety
of wet chemical deposition techniques and additives. In our research, we focused on different various bismuth-based perovskite materials having zero dimensional to higher dimensional networks and investigated their optical, morphological and photovoltaic properties. Interestingly, we could observe, that by increasing the bismuth halide network dimensionality, the power conversion efficiency could be improved. This increase in solar cell performance could be achieved by introducing monovalent noble metals. The incorporation of these monovalent cations lead to 3D networking of Bismuth halides, resulting in rudorfitte structure.

2:30 PM EN08.15.05
Stable and Efficient Tin-Based Halide Perovskite Solar Cells via Defects Passivation Min Chen, Yuanyuan Zhou and Nitin P. Padture; Brown University, United States

The state-of-the-art high efficiency perovskite solar cells (PSCs) contain lead and organic cations in the perovskite light-absorber. However, lead-toxicity and intrinsic instability of these PSCs are major hurdles in the path towards the commercialization of PSCs. While there has been effort towards replacing lead cation with less toxic cations, typical lead-free PSCs still suffer from the low power-conversion efficiency (PCE) and poor stability to ambient. Herein, we have utilized a defects passivation strategy in Sn-based perovskite materials, and realized PSCs with a promising PCE of up to 10%. Furthermore, the defects passivation via native oxides passivation layer or 2D phase passivation result in superior air-stability of Tin-based perovskite solars within 1000-hours continuous operation under one-sun illumination. Thus, this work provides a new avenue for the design and development of high performance and stable Sn-based PSCs.

2:45 PM BREAK

SESSION EN08.16: Perovskite Solar Cell—Large Area Fabrication
Session Chairs: Jingbi You and Kai Zhu
Friday Afternoon, December 6, 2019
Hynes, Level 2, Room 204

3:30 PM *EN08.16.01
The Challenges of Printable Mesoscopic Perovskite Solar Cells Hongwei Han; Huazhong University of Science and technology, China

Over the past few years, organic–inorganic hybrid perovskites have attracted significantly attention as light absorbers in efficient photovoltaics. While impressive power conversion efficiencies exceeding 24% have been attained within a period of only a few years, concerns have been raised about the viability of this class of photovoltaics as a scalable and long-term reliable energy source. In our group the printable perovskite solar cells were developed with triple mesoscopic layers1. The conjugated or non-conjugated bifunctional molecules were introduced into the perovskite materials to enhance their stability and efficiency2-4. The results indicated that the interface engineering plays a key role of directing the crystal formation and growth during the infiltration and precipitation of the perovskite within the mesoporous oxide scaffold. The fully printable mesoscopic perovskite solar cell presents no obvious decay within over 1000h light soaking and high efficiency of more than 18%. The crystals of the perovskite films are reconstructed by post-treating with methylamine gas and allows the regeneration of the photodegraded PSCs via the crystal reconstruction and the PCE can recover to 91% of the initial value after two cycles of the photodegradation-recovery process5-8. Meanwhile, the characterization of the mesoscopic perovskite solar cells under the UV light soaking condition was performed. A 110 m2 mesoscopic perovskite solar system was exhibited. These results offer a promising prospect for its commercial application.

References
Solution processing of organic-inorganic metal halide perovskites represents a major advantage for low-cost solar cell fabrication. However, scalable processes must be developed in place of spin-coating in order to successfully commercialize the technology. Slot die and ambient spray coating have emerged as alternatives, but like spin-coating, these methods require lengthy anneals that pose significant challenges for inline high-speed fabrication.

In this work, we fabricate all of the perovskite, charge transport, and barrier layers in open air with scalable processes. Using a p-i-n planar architecture, we first spray coat an aqueous NiO hole transport layer that demonstrates improved efficiency and fill factor relative to a spin coated organic NiO precursor. A double cation perovskite film consisting of Cs$_{0.17}$FA$_{0.83}$Pb(Br$_{0.17}$I$_{0.83}$)$_3$—a composition with excellent thermal and photostability—is then formed using the Rapid Spray Plasma Processing (RSPP) method, where films are sprayed and immediately exposed to a plasma at an ultrafast linear processing rate $> 10$ cm/s. The combination of reactive species (ions, radicals, metastables, and photons) and convective thermal energy produced by the plasma rapidly transfer energy to the perovskite-precursor solvate, enabling the growth of efficient and mechanically robust perovskite films in seconds with no post-annealing necessary.

A fiber laser (1064 nm) and CO$_2$ laser (10.6 μm) are used for the respective P1 and P2 scribes to create a monolithic, series-interconnected module. Module design is optimized for the RSPP process to achieve $>70\%$ Geometric Fill Factor. After completion of the module, an organosilicate barrier film is deposited with RSPP to improve thermal and environmental stability in addition to providing protection from thermal degradation of the perovskite during encapsulant lamination. A stabilized value of 12.4% PCE was achieved after 1000 s illumination in air for a 12.5 cm$^2$ series-connected module with six subcells and a module $V_{oc} > 6.2$ V. Additionally, encapsulated modules with in-situ barriers demonstrate validated reliability and retain $>80\%$ of their initial PCE after 500 hours of indoor (damp heat testing at 85 °C) and outdoor (full spectrum illumination) ageing tests.

The commercial application of perovskite based thin film photovoltaic technology requires highly efficient large area devices. A high drop in power conversion efficiency of 40%rel. is observed when comparing record solar cells of 0.1 cm$^2$ aperture area with the best 100 cm$^2$ modules. As Li et.al reported in Nature review in 2018, perovskite based TFPV still have higher upscaling loss than any other PV technology. Recently, with better understanding of perovskite crystallization dynamics, module efficiencies of 17% on 17 cm$^2$ and 12.6% on 355 cm$^2$ have been achieved.

Upscaling losses going from cell to module can be grouped into four types of losses: sheet resistance, interconnection resistance, inactive area and layer inhomogeneity loss. In order to achieve high performance upscaled devices, we process and analyze devices up to 156 cm$^2$, using techniques such as spin coating, blade and slot die coating. We employ integrated circuit-based simulation techniques, as well as electrical and optical
characterization methods including J-V measurements, transmission line measurement, luminescence imaging, thermography and electron spectroscopy to analyze each of the loss mechanism separately.

As a result, we identify specific process optimization steps that should be undertaken in order to minimize each performance loss, including module design, laser interconnection patterning, optimizing deposition method used, improving processing conditions and solvent engineering. Following an ideal process implementation, the relative upsaling losses going from cells to modules could decrease to 5 %, making large area perovskite modules with 20 % power conversion efficiencies a reality.

4:30 PM EN08.16.04
High-Throughput Vapor Transport Deposition of Organic-Inorganic Perovskite Films Anurag Panda, Ella Wassweiler and Vladimir Bulovic; Massachusetts Institute of Technology, United States

Development of large-area high-throughput deposition techniques is necessary to successfully commercialize perovskite solar cell technology. Vapor transport deposition (VTD) is one such potential technique that uses a carrier gas to transfer sublimed salts from source to substrate, where they react to form perovskite films. Unlike vapor thermal evaporation, during VTD the material deposition rate is decoupled from material temperature allowing for high throughput deposition. During the VTD process there is also independent control of chamber pressure and deposition rate, parameters which can be tuned to change the film crystallization kinetics. Similar to thermal evaporation, VTD allows for precise thickness control and eliminates hazardous solvents from device fabrication, allowing for facile growth of complex multi-layer device structures such as tandem solar cells. The high throughput deposition coupled with low vacuum operation reduces capex requirement for VTD deposition tools, and has already led to commercialization of the technique for CdTe and organic semiconductor materials manufacturing.1

In our work, through the use of a custom-built VTD setup2 we study perovskite film formation via co-evaporation of lead iodide and methylammonium iodide (MAI). We find that control of MAI degradation during vapor transport and its deposition rate is a critical challenge that needs to be overcome. We describe design parameters and deposition conditions necessary to incorporate undegraded MAI into the methylammonium lead iodide film. We describe numerical simulation of material diffusion and gas flow necessary to narrow the design parameter space. We study the impact of substrate temperature and carrier gas flow rate on film formation kinetics by examining metrics such as photoluminescence, x-ray diffraction, morphology, as well as device efficiency. Through this systematic study we demonstrate VTD to be a viable new deposition tool for large-area high-throughput deposition of perovskite solar cells.


SYMPOSIUM EN09

Advances in the Fundamental Science of Halide Perovskite Optoelectronics
December 2 - December 6, 2019

Symposium Organizers
Joseph Berry, National Renewable Energy Laboratory
Marina Leite, University of California, Davis
Philip Schulz, CNRS IPVF
Yuanyuan Zhou, Brown University
SESSION EN09.01: Theory, Modelling and Characterization—Materials by Design
Session Chairs: Paulina Plochocka and Philip Schulz
Monday Morning, December 2, 2019
Sheraton, 2nd Floor, Constitution B

8:30 AM *EN09.01.01
Theoretical Investigation of Halide Perovskites for Solar Cell and Optoelectronic Applications Su-Huai Wei;
Beijing Computational Science Research Center, China

Halide perovskites such as CH3NH3PbI3 have recently emerged as promising materials for low-cost, high-efficiency solar cells. The efficiency of perovskite-based solar cells has increased rapidly, from 3.8% in 2009 to more than 23% recently by modifying material compositions and engineering cell architectures and defect properties. The emergence of high efficiency perovskite solar cells can be attributed to the intrinsic properties that distinguish them from conventional semiconducting solar cell absorber materials. However, despite the enormous progress of the perovskites in solar cell applications, challenges are still standing in their way to large-scale commercial applications, including their poor long-term stability, which could be partially attributed to the intrinsic thermodynamic instability of CH3NH3PbI3 and related materials, and the toxicity of Pb, currently used in halide perovskite based solar cells with high power conversion efficiencies. Recently, various approaches have been proposed to overcome these bottlenecks, including defect control, alloying, as well as atomic transmutation. In this talk, I will discuss some of our recent theoretical investigations on ordered and disordered halide perovskites to understand their material properties and provide theoretical insights and possible solutions to the usage of halide perovskites for solar cell and other optoelectronic applications.

9:00 AM *EN09.01.02
Impurity and Dynamic Properties of Perovskites from First Principles Arun Kumar Mannodi Kanakkithodi and
Maria K. Chan; Argonne National Laboratory, United States

In this talk, we will discuss (1) electronic properties of MA-Pb-halide perovskites with at different halide compositions with various defects and impurities, obtained using first principles density functional theory calculations and machine learning; (2) dynamics of lattice thermal equilibration, especially between the organic and inorganic sublattices, from ab initio molecular dynamics simulations.

9:30 AM EN09.01.03
Persuasive Evidences for Hyperfine Interaction in Halide Perovskite Bulk Single Crystals Alyssa Kostadinov,
Arthur Shapiro, Yahel Barak, Shahar Zuri, Ellenor Geraffy and Efrat Lifshitz; Technion–Israel Institute of
Technology, Israel

Halide perovskite materials are at the forefront of scientific and technological interest in the last decade, due to their extraordinary physical properties and their indisputable performance in solar cells, and in other opto-electronic applications. The most studied halide perovskite has the chemical formula APbX3 (A = methylammonium, formamidinium, Cs; X = I, Cl, Br) prepared as bulk single crystals, thin films or nanostructures. Those were characterized by their long carrier diffusion length, unity emission quantum efficiency, tolerance for defects, anharmonicity, reduced elastic stiffness, strong carrier-phonon coupling and polaron formation. However, spin properties were investigated only to a lesser extent, albeit, they may be of a paramount importance in the control of
the optical properties of halide perovskites, thus demands further exploration. Most recent years studies uncovered the occurrence of a Rashba effect, related to the existence of an exotic spin-orbit field which split both valence and conduction band in k-space into two valleys, symmetrically spaces away from a Brillouin point with opposing спин helicity, hence dictating spin selective recombination.\(^1\)\(^2\) Other studies explored the g-factor of photo-generated carriers, as well as the carrier spin relaxation time (T\(_1\) ~ 1nsec) and dephasing time (T\(_2\) ~ 80 psec).\(^3\)\(^4\)

The current work reports magneto-optical measurements of MAPbBr\(_3\) high quality single crystal where the observation brought about for the first time, a strong evidence for the existence of an Overhauser effect, viz., occurrence of coupling between a photo-generated carrier' spins and nuclei spins, the last related to the existence of neutral absence isotopes. A photo-generated carrier applies a local field on nuclear spins via hyperfine interactions and induces their mutual alignment. Then, the effective magnetic field created by the nuclei acts back on a carrier, affecting its polarization and the helicity of a recombination emission. The effective nuclear field may enhance or suppress a Zeeman and Rashba fields. The current work exploited the counter balance between the Rashba, Overhauser and a Zeeman field. A follow up of the exciton emission intensity or its circular polarization versus strength of an external magnetic field, revealed a special trend corroborating the occurrence of an Overhauser field < 0.2 Tesla. Furthermore, the Rashba field is pronounced as a non-Zeeman behavior, as well as by occurrence of uniform ordering of exciton fine structure. The study discovered a dominant route causing de-coherence of carrier's spin, with significance impact on the perovskites use in quantum information or memory devices.


9:45 AM EN09.01.04

**Halide Perovskites as a Polymorphous Network with a Distribution of Local Motifs** \textit{Alex Zunger}; University of Colorado, United States

While octahedral tilting or B atom displacements as a single repeated structural motif are well known in perovskites, we find that removing the standard restriction to such a minimal unit cell size in total energy structural optimization, leads in some perovskites to the formation of a ‘polymorphous network’, manifesting a \textit{distribution of different tilt angles and different B-atom displacement in different octahedra}. Such systems cannot be described crystallographically by a small, repeated unit cell, and were generally described as thermally disordered compounds, modelled by high temperature molecular dynamics via time-dependent dynamic motions with entropy-driven disorder. What is different about the polymorphous network for the cubic halide perovskite FASnI\(_3\) (where FA\texttextsuperscript{=CH(NH\textsubscript{3})\textsubscript{2}}) is that the \textit{distribution of local motifs emerges already from the (density functional) minimization of the static, T=0 internal energy of a large supercell}, constrained to have the global cubic lattice vectors. This a-thermal distribution represents a correlated set of displacements and is very different from the time-dependent uncorrelated entropic thermal disorder calculated by MD, or from the single sharp monomorphous values of these deformation parameters . This distribution of local motifs is also different from the periodically repeated ordered double-potential well models that address anharmonic polar fluctuations. The existence of such a polymorphous distribution is easy to miss using standard energy minimization protocols (such as those based on following gradients to the nearest local minimum) but is revealed once one initially applies a \textit{random} atomic displacement (“nudge”) off the cubic sites and explores lower symmetries in the minimization process. These polymorphous networks represent a different paradigm in understanding cubic halide and oxide perovskites. Our finding suggests that the widely discussed single formula unit cubic Pm-3m structure of halide perovskites does not really exist, except as a macroscopically averaged fictitious structural model. Because X-ray diffraction has a rather long coherence length, such polymorphous systems were often fit in structure refinement models by a macroscopically averaged (“\textit{fictitious monomorphous}”) cubic Pm-3m unit cells. Significantly, compared to the monomorphous assumption, we show here that the cubic polymorphous network (i) fits much better the observed Pair Distribution Function (PDF), which probes the local environment. (ii) a significantly lowering of calculated total energies, by \textit{~70-150 meV/f.u.}, and (iii) up to 300% larger band gaps, on account of the reduced level repulsion afforded by larger octahedral tilting and rotations. Thus, (iv) the band gap renormalization energy (~200 meV) is now closer to experiment relative to the values computed with respect to the band gap of the monomorphous model (390-640 meV). (v) Use of the polymorphous structure leads to the reversal of the predicted sign of the mixing
enthalpies of the solid solutions from negative (ordering-like; not seen experimentally) to positive (experimentally observed phase-separating), in better agreement with observations. (vi) Remarkably, despite the existence of a distribution of motifs, the calculated band structure (unfolded to the primitive Brillouin zone from the supercell) shows sharp band edge states and a correspondingly fast rise of the absorption spectrum, and leads to a broad and slow rising absorption tail. Finally, relative to the monomorphous case, (vii) polymorphous networks have a much larger (by ~50%) calculated dielectric constant, where the ionic contribution now dominates the electronic contribution as expected from near ferroelectrics. The polymorphous approximant could thus serve as a useful practical structure to use with standard band structure approaches to predict properties, replacing the fictitious monomorphous structures. In collaboration with Xingang Zhao, Zhi Wei and Gustavo Dalpian.

10:00 AM BREAK

10:30 AM *EN09.01.05
Impact of Structural Dynamics on Optoelectronic Properties of Halide Perovskites—Insights from Theory
David Egger; Technical University of Munich, Germany

Halide perovskites (HaPs) are highly promising materials for a range of optoelectronic devices. HaPs are also very interesting scientifically because of the unusual structural dynamics that occur in the material. These include the appearance of complex structural disorder and sizable nuclear anharmonic effects already at room temperature, which challenge our basic understanding of coupling between nuclear vibrations and optoelectronic properties in a semiconductor.

In this talk, I will present our recent explorations of the consequences of the unusual structural phenomena in HaPs for their optoelectronic properties. Theoretical calculations based on density functional theory, molecular dynamics, and tight-binding modeling will be used to examine the impact of structural dynamics on pertinent device-relevant observables. Consequences of the structural dynamics and anharmonicity in HaPs will be discussed for the charge-carrier mobility, Urbach energy, and defect energetics. It will be shown that the impact of the unusual structural dynamics on the optoelectronic properties of HaPs cannot be neglected when understanding these materials microscopically and designing new functional compounds.

11:00 AM EN09.01.06
Determining the Changes in Electronic Structure of Lead and Tin-Based Perovskites—A Combined Experimental and Theoretical Approach
Selina Olthof1, Ines Schmidt1, Shuxia Tao2 and Geert Brocks2;3; 1University of Cologne, Germany; 2Eindhoven University of Technology, Netherlands; 3University of Twente, Netherlands

In recent years, the interest in halide perovskites rose at a rapid pace due to their tremendous success in the field of photovoltaic while other fields, like light emitting diodes, show great potential as well. One intriguing property of this material class is the wide tunability of the band-gap that can be induced by changing the perovskite composition. While changes in band gap are regularly reported, it is unclear how the respective conduction and valence band positions change and what the underlying origins of these changes are. Knowing the band positions is however crucial for device design, i.e. ensuring efficient charge transport across the various interfaces.

In this talk, I will discuss recent findings regarding the variations in ionization energy and electron affinity, covering the complete library of lead and tin based halide perovskite systems. [1] Using a combination of photoelectron spectroscopy, density functional theory, and a tight binding model we are able to reliably extract the relevant energy level positions. Furthermore, we are able to explain the origin of these changes based on changes in hybridization strength, atomic level positions, and lattice distortion.

References

11:15 AM EN09.01.07
The Bandgap Bowing Behavior and Its Origin in Perovskite-Inspired Lead-Free Cs3(Bi,Sb)2(I,Br)9Alloys
Anuj Goyal1,2, Shijing Sun3, Noor Titan Putri Hartono3, Tonio Buonassisi3 and Vladan Stevanovic1,2; 1Colorado School of Mines, United States; 2National Renewable Energy Laboratory, United States; 3Massachusetts Institute of
Lead-based hybrid organic-inorganic perovskite photovoltaic materials have been the focus of much research in recent years because of their low fabrication cost and extremely high photoconversion efficiencies. Inspired by the rapid rise in efficiencies of lead based perovskite solar cells and the environmental concern of the heavy metal content, lead-free alternatives are attracting increasing attention. Perovskite-inspired materials with 0D and 2D crystallographic structure with the formula A3B2X9, where A is the monovalent cation (methyl ammonium MA, formamidinium FA, Rb, or Cs), B is the metal cation (Sb and/or Bi), and X is the halide anion (I, Cl and/or Br), have recently attracted the attention of the researchers looking for the next lead-free material. Recently, dual-site alloys Cs3(Bi1-xSbx)2(I1-yBr y)9 exhibiting a transition between 0D to 2D crystal structures and a non-linear bandgap tunability, have been synthesized. The discovery of non-linear bandgap behavior (bandgap bowing) in this series has opened up a new pathway to achieve lead-free all-inorganic perovskites for multi-junction solar cells. However, compared to their lead-based counterparts, the origins of the bandgap bowing in these systems are not yet understood. In this study, we employ detailed first-principles DFT calculations to model Cs3(Bi,Sb)2I9, Cs3(Bi,Sb)2Br9, Cs3Sb2(I,Br)9, Cs3Bi2(I,Br)9 systems to better understand the pathways to reduced bandgaps in dual-site alloys, as well as to systematically decouple the structural and chemical origins to the bandgap bowing. Our results suggest that bandgap bowing is caused by mixing at the B-site and that the non-linearity in the bandgap exists regardless of the crystallographic dimensionality of the alloy. With better understanding of the bandgap behavior we aim to tailor these lead-free perovskite-inspired mixed systems to achieve optimum optoelectronic properties.

References:

Pressure-Induced Carrier Recombination in Halide Perovskite Light-Emitting Diodes

Young-Kwang Jung1, Mayami Abdulla2, Samuel D. Stranks2 and Aron Walsh1,3; 1Yonsei University, Korea (the Republic of); 2University of Cambridge, United Kingdom; 3Imperial College London, United Kingdom

Metal halide perovskites have been widely studied for light-emitting applications (LEDs) [1-2], as well as photovoltaics [3-4] showing drastic increase in efficiencies due to their unique opto-electronic properties. The control of non-radiative losses in the active perovskite layer is still one of limiting factors that diminishes the efficiency of devices below their theoretical performance limits. Recently, it has been shown that lattice strain present in halide perovskites correlated with non-radiative electron-hole recombination [5]. To prove the concept, we systematically investigate how volumetric strain affects the atomic and electronic structure, charged native point defect concentration, and luminescence properties by combining state-of-the-art simulations and experiment. Our first-principles density functional theory (DFT) calculations including relativistic effects show enhanced Rashba splitting and Schottky vacancy defect disorder under compressive pressure, while experiments of perovskite LEDs under hydrostatic pressure display a pronounced decrease in photoluminescence peak position and intensity under compressive pressure. The combination of theory and experiment provide a unified model of pressure-induced recombination in these soft semiconductors.

Ni Doping in CsPbX₃ Nanocrystals via Post-Synthesis Anion-Cation Co-Exchange

Arthur Shapiro¹,²,³, Markus W. Heindl⁴, Faris Horani¹,²,³, Meir H. Dahan⁵, Matan Menahem⁶, Yaron Amouyal⁵, Omer Yaffe⁶ and Efrat Lifshitz¹,²,³ ; ¹Technion–Israel Institute of Technology, Schulich Faculty of Chemistry, Israel; ²Technion–Israel Institute of Technology, Solid State Institute, Israel; ³Technion–Israel Institute of Technology, Russell Berrie Nanotechnology Institute, Israel; ⁴Technical University of Munich, TUM Department of Chemistry, Germany; ⁵Technion–Israel Institute of Technology, Department of Materials and Interfaces, Israel; ⁶Weizmann Institute of Science, Israel

In the last decade perovskite nanocrystals (NCs) burst into the consciousness of the scientific community as a new class of semiconductors and became the material class at the forefront of research efforts. Particularly, the topic of doping arose in recent years, involving doping or alloying by magnetic ions, which induced changes in the optical and magnetic properties.

In this work a novel dynamic cation exchange strategy driven by a simultaneous anion exchange was implemented¹ to incorporate Ni²⁺ ions into CsPbBr₃ perovskite nanocrystals² at room temperature and ambient conditions. Ni is especially interesting as a dopant, as it combines an electron spin of S=1, a lack of nuclear spins (with the exception of ⁶¹Ni with a low natural abundance of < 1%) and relatively weak spin-orbit coupling compared to Pb. Magnetic dopants in semiconducting materials induce spin-exchange interactions with the host carrier's spins, mostly leading to a giant magnetization within the host lattice. The lack of spin-orbit and nuclear spin coupling of the Ni dopants should preserve this giant magnetization and consequently the carrier's spin coherency for a length of time. Long spin coherence time is the holy-grail of spin-based devices.

The present work describes a thorough investigation of the doping mechanism into perovskite nanocrystals and characterization of the produced structures and composition, using electron microscopy and spectroscopic techniques. The doping of CsPbBr₃ NCs with Ni²⁺ ions was carried out using ion exchange procedures, involving post-treatment with either NiCl₂, PbCl₂, PbBr₂ or NiBr₂ precursors at room temperature. The reaction with NiCl₂ was utilized for the anion-cation co-exchange in order to achieve a uniform Ni incorporation into the lattice, and the use of all other reagents was dedicated to control experiments. The results indicate the essential need for co-exchange of cation and anion, enabling integration of Ni²⁺ ions with a concentration from < 1% to about 12%. The observations revealed a uniform distribution of the Ni ions across the nanocrystals. Moreover, the nanocrystals exhibit improved luminescence quantum yields beyond those of the non-doped CsPbCl₃ and CsPbBr₃. The observations were corroborated by a theoretical density functional theory calculation, confirming that the exchange of Ni is energetically favorable.

hybrid perovskite semiconductors. Using combinations of scanning-probe, electron backscatter diffraction (EBSD), and time-resolved photoluminescence microscopy and spectroscopy, we explore the microscopic origins of non-radiative recombination in both archetypal methylammonium lead tri-iodide (MAPI), and more advanced mixed-cation perovskites. Using EBSD, we image local grain orientation and strain, and correlate surface strain with increased non-radiative recombination in MAPI. We explore the interface between the perovskite and various common charge extraction layers, combining experiment and simulation to show that surface recombination at the charge extraction layers is a limitation in current perovskite solar cell architectures. Finally, we explore alternative passivation and extraction layers to propose ways to more routinely approach the theoretical voltage limits in perovskite photovoltaic using scalable process chemistry.

2:00 PM *EN09.02.02
Characterization of Electronic and Ionic Transport in Halide Perovskites by Multi-Dimensional Luminescence Imaging
Laurent Lombez1,2,3, Adrien Bercegol1,4, Stefania Cacovich1, Olivier Fournier1,4, Daniel Suchet1,2, Jean Rousset1,4, Jean-Francois Guillemoles1,2 and Daniel Ory1,4; 1IPVF Institut Photovoltaïque Ile de France, France; 2CNRS-IPVF, France; 3LPCNO, France; 4EDF R&D, France

The excellent photovoltaic performance of halide perovskites goes along with a high photoluminescence yield (PL) that makes them suitable for a wide range of photonic devices and various optoelectronic applications, such as photodetectors, lasers and light emitting diodes. However, due to the complexity of the materials and the related devices, often traditional macroscopic characterisation tools are not able to unveil the physical processes underlying the working principles of the solar cells, especially the transport properties. Indeed, electronic as well as ionic transport are still under investigation. Here we quantify electrons, holes and ions transport and investigate the mutual impact of both transport mechanisms.

To do so, we used innovative characterisation methods that combine hyperspectral imaging system (HI) and a time-resolved fluorescence imaging (TR-FLIM) set-ups. We employed these optical techniques to study lateral transport of charge carriers in hybrid perovskites and probe a large variety of transport parameters (diffusion length, mobility, lifetimes…) which are often cross-linked. Photonic transport is also observed. Besides, measuring the local variations of time resolved luminescence in the nanosecond scale under lateral electric bias allows a direct access to charge carrier collection and transport properties for each kind of charge carrier –electrons and holes-. At long time scale such experiment allows to probe the ionic transport, especially associated with iodine species. It is confirmed when looking at spectrally resolved images where we can monitor ionic transport a part of the electronic transport and see the impact of the ions migration on the material properties. More precisely, the iodine seems to affect the band structure and locally modify the bandgap; it also degrades the local quasi Fermi level splitting (i.e. the internal bias).

The novel experimental approach, can thus image and quantify the transport mechanisms occurring within the material, providing new insights on these complex transport phenomena.


2:30 PM EN09.02.03
Understanding Phase Stability by In Situ X-Ray Diffraction in Mixed A-Site Halide Perovskite Active Layers
Laura T. Schelhas1, Zhen Li2,3, Jeffrey A. Christians4, Anuj Goyal5, Paul Kairys5, Steven Harvey2, Donghoe Kim2, Kevin Stone1, Joseph Luther2, Kai Zhu2, Vladan Stevanovic5 and Joseph J. Berry2; 1SLAC National Accelerator Laboratory, United States; 2National Renewable Energy Laboratory, United States; 3Northwestern Polytechnical University, China; 4Hope College, United States; 5Colorado School of Mines, United States

Hybrid organic-inorganic perovskite photovoltaic materials have been the focus of much research in recent years due in part to their extremely high photoconversion efficiencies[1] and also their ability to be synthesized by solution processing. These materials crystallize in the perovskite, AMX₃ crystal structure where A is the monovalent cation (methyl ammonium, MA, formamidinium, FA, Rb, and/or Cs), M is the metal cation (Pb²⁺), and X is the halide anion (I⁻, Cl⁻, and/or Br⁻). As the field has progressed, formulations of halide perovskite solar cells (PSC) have evolved from the simple MAPbI₃ to more complex alloys, e.g. RbCsMAFA-perovskite.[2] With these more complicated formulations understanding the operation and stability of these materials becomes more challenging.
For example, it is important to understand the geometric constraints and so-called “tolerance factors” when formulating new mixed phases in order to target stable structures.[3] Additionally, the composition and phase homogeneity across the film can also influence device performance.

In this study we present results using operando X-ray characterization techniques previously developed by our groups coupled with standard laboratory device measurements.[4] Using this operando technique we are able to monitor the crystal structure by X-ray diffraction (XRD) of the PSC in full device stacks during operation. Here, we explore the phase stability of mixed A-site PSCs of the form X\(\text{PbI}_3\) where \(X = \text{FA}, \text{Cs}, \text{and/or MA}\). Simultaneous JV and XRD measurements on devices are measured in both inert and humid (~50% relative humidity) conditions, at room temperature for up to 15 hours. Here we observe degradation pathways for these mixed A-site formulations which result in phase segregated films in some formulations and greater stability in others. To explain the experimentally observed mixing and de-mixing in these systems, we present a hypothesized framework developed using complementary first-principles calculations of mixed A-site halide perovskites. This is then validated using in-situ X-ray diffraction and spatially resolved time of flight secondary ion mass spectrometry. With greater understanding of the structural stability of these alloys we aim to inform well-tuned alloy formulations targeting long term stability in devices.

References
Impedance spectroscopy is a non-destructive characterization technique that has been used for the characterization of perovskite solar cells since the beginning of this technology. Impedance spectroscopy is a characterization method in the frequency domain that allows to decouple physical processes with different characteristic times at the working conditions i.e. under illumination and applied bias. However, different models and interpretation have been employed to explain the impedance measurements. Despite the huge potentiality of this technique for the characterization of perovskite solar cell a complete model of impedance for this kind of cells applicable in all the conditions and configuration has been elusive for the moment. Undoubtedly, the combined action of electron and holes and ions in perovskite solar cell is at the base of the complex behavior observed in this kind of devices. In this presentation, we compare the well know dye sensitized solar cells with the perovskite solar cells highlighting similarities and differences, and studying the evolution from the former to the later. In addition the interest of impedance characterization of different types of perovskite optoelectronic devices is discussed.

Band Structure and Electronic Properties of Lead Halide Perovskites from Photoemission Studies

Photovoltaic devices based on halide perovskites with outstanding optoelectronic properties have exhibited tremendous progress in performance. To understand the origin of these properties comprehensively, detailed knowledge on the underlying electronic band structure is required. Here, we present complementary results from low-energy electron diffraction (LEED), angle-resolved photoelectron spectroscopy (ARPES), and density functional theory (DFT) calculations for CH3NH3PbBr3 and CH3NH3PbI3 single crystals. For both, sharp LEED patterns corresponding to the (001) surfaces of CH3NH3PbBr3 and CH3NH3PbI3 were observed together with well-resolved, dispersive valence band (VB) features. Noteworthy, the LEED patterns of CH3NH3PbI3 reveal a coexistence of the cubic and tetragonal phase at the sample surface already at room temperature. From ARPES, we determined a bandwidth of ~1.0 eV and of ~1.3 eV along the X-R direction in CH3NH3PbI3 and CH3NH3PbBr3 single crystals, respectively. In good agreement with results from DFT calculations, the hole effective-mass, mh*, with values as small as 0.18 m0 (CH3NH3PbI3) and 0.25 m0 (CH3NH3PbBr3) were found. Furthermore, the fundamental differences between linear and logarithmic methods in determining the VB onset are discussed and addressed, revealing the fact that logarithmic method is more preferable to determine the VB onset for perovskite systems.[1,2] In addition, surface photovoltage effect (SPV), which has so far hardly been discussed in this context, is found to play significant effect in photoemission studies. We provide evidence that due to the presence of surface band bending, not only visible light but also UV light, as used in ultraviolet photoemission spectroscopy (UPS), induces substantial SPV (over 700 meV) in four modern perovskites. Given such effect, the conflicting energy levels as probed by UPS can be better rationalized.[3] Within the framework laid out here, the consistency of relating the energy level alignment in perovskite-based photovoltaic and optoelectronic devices with their functional parameters is substantially enhanced.

Metal halide perovskites present ideal properties for both light absorbing and light emitting devices. Despite their promising optoelectronic properties and the progress made over the last decade, perovskites still display instabilities when exposed to environmental stresses such as moisture, oxygen, bias, temperature, and light [1]. Here, we present our ongoing study of the fundamental science surrounding this dynamic behavior, typically detrimental for optoelectronics. Our first focus is the impact of humidity cycling on charge carrier recombination through the use of in situ micro-photoluminescence (micro-PL) [2, 3]. Here, we consider a set of four benchmark compositions based on Cs$_x$FA$_{1-x}$Pb(I$_y$Br$_{1-y}$) known for their superior stability and suitability for tandem photovoltaics, where Cs varies between 10-17% and Br within 17-38%. Each of the films is exposed to identical relative humidity (rH) treatments (<5%, 15%, 35%, 55%, and <5% rH) while the luminescence is simultaneously monitored to understand the changes to the optical response. While all samples considered exhibit an increase in overall PL emission upon reaching 35% rH, their luminescence response bifurcates at 55% rH, when the 17%-Br samples sustain their previous enhancement but those containing 38%-Br display a marked reduction in light emission. After returning to a low humidity ambient, all compositions present PL hysteresis dependent on the Br/Cs ratio. The irreversibility of the luminescence after the humidity cycle is due to surface-limited degradation leading to the formation of additional trap states. Next, we evaluate the water-driven recombination dynamics in the prototypical MAPbI$_3$ and MAPbBr$_3$ compositions, capturing light emission every ~1 s as the films undergo multiple humidity cycles. Our results indicate that water modifies I-containing material quickly, with abrupt increases in emission when the film is first exposed to water (~30% rH), and as the film returns to a low moisture environment. Contrastingly, the Br samples are less affected by water, and require high humidity (>50% rH) for a modest luminescence enhancement. Given the dynamic behavior of the I-based films, we investigated the impact of excitation wavelength on light emission. Surprisingly, the energy of the incident photons is anticorrelated with the area contained within the rH-PL loop. Based on their absorption depth, shorter wavelength photons create electron hole pairs more likely to nonradiatively recombine at the new, near-surface defects created through our controlled moisture-induced degradation. Inspired by our wavelength-dependent PL measurements, we also measured the voltage dynamics across dark-light-dark cycles for both the MAPbI$_3$ and MAPbBr$_3$ compositions through the use of a Kelvin probe and a wavelength tunable light source [4]. While the I-containing film shows a wavelength-independent trend in voltage decay, the Br-containing sample exhibits a 10x slower wavelength-dependent voltage relaxation that displays an exponential trend across the range of 405-605 nm. The slower voltage process is associated with the MAPbBr$_3$ lattice constant that increases resistance to ion migration back to equilibrium under dark conditions relative to MAPbI$_3$. The methods employed above can be extended to include the other environmental stressors (temperature and bias) and are material independent, easily applied to other critical compositions, such as lead-free variants. Finally, we will discuss the use of machine learning to understand the impact of the environmental parameters on perovskites recovery [1].


4:30 PM EN09.02.08
Ultrafast Dynamics in Metal-Organic Halide Perovskites Revealed by Soft X-Ray Spectroscopy
Regan Wilks¹, Axel Erbing², Golnaz Sadoughi³, Evelyn Handick¹, David E. Starr¹, Monika Blum⁴, Frank Meyer⁶, Dirk Hauschild⁷, Wanli Yang⁴, Lothar Weinhardt⁵, Clemens Heske⁵, Henry J. Snaith¹, Michael Odelius² and Marcus Bär¹,³,⁸; ¹Helmholtz Zentrum Berlin, Germany; ²AlbaNova University Center, Stockholm University, Sweden; ³University of Oxford, United Kingdom; ⁴Lawrence Berkeley National Laboratory, United States; ⁵University of Nevada, Las Vegas, United States; ⁶Julius-Maximilians-Universität Würzburg, Germany; ⁷Karlsruhe Institute of Technology, Germany; ⁸Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy, Germany

CH$_3$NH$_3$PbI$_3$ perovskite layers on compact TiO$_2$ have been investigated using nitrogen and carbon K-edge x-ray
emission (XES) and absorption (XAS) spectroscopy. These techniques, and their combination in Resonant Inelastic X-ray Scattering (RIXS), probe the organic component of the metal-organic compounds and can be used to examine the local partial density of occupied and unoccupied states. The measured spectra are strongly influenced by ultrafast (femtosecond-scale) proton dynamic effects, as modelled using ab initio molecular dynamics combined with density functional theory calculations of the electronic structure. The dynamic effects at the organic component are very similar to what has been observed in comparable molecules in solid, liquid, and gas phase experiments [1-3], and can be well understood by comparing and contrasting with reference materials. The spectral signature and related dynamic effects are influenced by the interaction of the organic and inorganic components of the material. Experimentally, it is also shown that the organic portion of the perovskite is quickly and strongly influenced by radiation damage, with soft x-rays from a third-generation synchrotron light source undulator causing significant degradation of the material on the time scale of a few seconds. The degradation mechanisms will be discussed in terms of their influence on experimental studies, as well as in terms of the general decomposition of metal-organic perovskite materials.


4:45 PM EN09.02.09
Interfacial Hole Injection Dynamics in Organohalide Perovskite Probed by Femtosecond Tabletop Extreme Ultraviolet Spectroscopy Aastha Sharma, Max Verkamp and Josh Vura-Weis; University of Illinois at Urbana-Champaign, United States

Hybrid organic-inorganic halide perovskites, such as methylammonium lead iodide (CH₃NH₃PbI₃) have emerged as potential hot-carrier (HC) solar cell materials. Despite rapid progress in device performances, the feasibility of HC injection in hybrid perovskites before carrier cooling is not fully understood. One experimental challenge is the difficulty in using optical methods to independently measure electron vs hole dynamics. We have shown that extreme ultraviolet (XUV) spectroscopy in the 40 to 80 eV energy range measures Iodine 4d→5p transitions and provides separate and distinct signals for valence band and conduction band dynamics. We use this technique to measure the rate of electron and hole injection into charge collection layers such as TiO₂, NiO and Co octaethylporphyrin after visible light excitation of the perovskite layer. The intense 3p→3d absorption, also in the XUV energy range, provides a unique spectroscopic fingerprint of the transition metal electronic structure with distinct peak changes corresponding to photoinduced oxidation state changes. The tabletop instrument uses high-harmonic generation to produce 15 femtosecond XUV probe pulses, enabling us to observe both carrier cooling and charge injection on the femtosecond to picosecond time scales.

SESSION EN09.03: Poster Session I: Fundamental Materials Properties and Advanced Characterization of Halide Perovskites I
Session Chair: Ross Kerner
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EN09.03.01
Rationalizing the Impact of B-Site Metal Additives and Their Spatial Incorporation in Halide Perovskites Xueying Li¹, Yanqi Luo¹, Moses Kodur¹, Rishi Kumar¹, Martin V. Holt¹, Zhonghou Cai² and David P. Fenning¹; ¹University of California, San Diego, United States; ²Argonne National Laboratory, United States

Leveraging their structural and chemical flexibility, halide perovskites have shown significant optoelectronic performance and stability improvements over the last several years with addition of alkaline metals (e.g. Cs, Rb and K) to the major organic A-site constituents (methylammonium and formamidinium). More recently, several studies
have shown improved film quality and solar cell performance with addition of cations targeting B-site incorporation. However, the spatial distribution and actual incorporation of B-site cations has yet to be firmly established. To understand the distribution of these potential dopants and their local effects on optoelectronic properties, we use a combination of X-ray nanofluorescence to probe the elemental composition and nano-diffraction to identify changes in the local crystal structure. We pair these with correlative microscopic evaluations of optoelectronic quality via photoluminescence mapping and E-beam induced current measurements. We thus develop relationships between local chemistry, grain size, crystal quality, and optoelectronic enhancement to identify the impacts of a range of metal cations. This new information on the distribution of cations targeting B-site incorporation rationalizes the wider composition space available to tune the properties of halide perovskite materials.

EN09.03.02
TlBr and Tl2AgBr3 Nanocrystal Synthesis Timothy Siegler, Yangning Zhang, Tushti Shah, Mokshin Suri and Brian A. Korgel; The University of Texas at Austin, United States

We have become interested in the addition of thallium to halide perovskites, both in A-site and B-site substitutions. Cs2AgTlBr6 (CATB) double perovskite for example offers the lowest band gap in the halide perovskite family of materials with a direct band gap of 0.95 eV in single crystals. Additionally, thallium halides have applications in radiation detectors due to their high mobility and high average atomic number. Controlling the Tl oxidation state is one of the challenges facing the synthesis of these nanocrystals. For instance, we have found that Tl3+ readily reduces to Tl+ under most reaction conditions. Here, we report progress on thallium bromide nanocrystal chemistry and have developed chemical routes to cubic CsCl-type TlBr and trigonal dolomite-type Tl2AgBr3 nanocrystals. TlBr nanocrystal synthesis involves hot injection of trimethylsilyl bromide (TMSBr) into a thallium (III) acetate solution in octadecene, oleic acid, and oleylamine at 70 °C. Tl2AgBr3 nanocrystals are synthesized using the same reaction conditions with a both thallium (III) acetate and silver (I) acetate in the precursor solution. The nanocrystals are uniform with diameters between 10 and 15 nm. The Tl2AgBr3 nanocrystals exhibit an indirect band gap of 3.1 eV and a direct band gap of 3.7 eV. This is the first report of Tl2AgBr3 nanoparticle synthesis and the first characterization of the band gap of Tl2AgBr3. TlBr has a direct band gap of 3.05 eV, consistent with bulk band gap of TlBr in literature. We were able to assemble face centered cubic (FCC) superlattices of the TlBr and Tl2AgBr3 nanocrystals. The size of the TlBr nanocrystals could be varied by changing the reaction temperature, with smaller (~5 ± 3 nm) TlBr nanocrystals formed at higher reaction temperatures (110 °C).

EN09.03.03
Solvent Engineering for All-Inorganic CsPbIBr2 Perovskite Photodetectors Ting Zhang, Feng Wang and Shibin Li; University of Electronic Science and Technology of China, China

Photodetectors, which can convert light signals into electrical signals, are important opto-electronic devices in imaging, optical communication, biomedical/biological sensing. Currently, most of the commerical photodetectors are based on traditional inorganic semiconductors, such as Si, ZnO, GaN and InGaAs, which require expensive vacuum equipment. In recent years, organic-inorganic halide perovskites have drawn great attention and been a very promising candidate for opto-electronic applications due to their outstanding physical properties, including strong light absorption, low exciton binding energy, long carrier lifetime and low charge recombination rate. Here, through optimizing the film quality via precursor solvents and posttreatment process, high performance flexible photodetectors based on all-inorganic cesium lead halide perovskite (CsPbIBr2) are demonstrated. The device show a high response speed (rise time and decay time are 170 and 250 μs, respectively.), a large light on/off ratio of 105 upon illumination with 520 nm light, high specific detectivity (~1011 Jones). Moreover, the flexible photodetectors exhibit outstanding long-term environmental stability after being kept in ambient air for one month. The results demonstrate a great potential for the application of CsPbIBr2 perovskite in opto-electronic detection, and provide a promising route to enhance the film quality and achieve high performance.

EN09.03.04
Directly-Generated Acetate Ions Enable Efficient and Stable Surface Management of CsPbI3 Perovskite Quantum Dots for Improved Solar Cell Performance Jigeon Kim¹², Younghoon Kim¹, Changsoon Choi¹ and Min Jae Ko²; ¹Dague Gyoungbuk Institute of Science and Technology, Korea (the Republic of); ²Hanyang University, Korea (the Republic of)

Fully-inorganic CsPbX3 (X=Cl, Br, I) perovskite quantum dots (PQDs) are receiving much attention as a
photoactive semiconductor in various optoelectronic devices because of their excellent opto-electrical and photophysical features resulting from the intrinsic properties of lead halide PQDs such as size- and composition-tunable optical bandgap, high absorption coefficient, narrow emission, high photoluminescence quantum yield, and high charge-carrier mobility. Recently, CsPbI$_3$ perovskite quantum dot (CsPbI$_3$-PQD) solar cells have shown the best device performance in the field of colloidal quantum dot (CQD) solar cells, achieved by methyl acetate (MeOAc) and formamidinium iodide treatments for enhanced electronic coupling within CsPbI$_3$-PQD solids. MeOAc treatment for CsPbI$_3$-PQDs generates acetate ions, which substitute for the oleates (act as insulators) on the surface of CsPbI$_3$-PQDs, as a result of MeOAc hydrolysis. However, the by-products, which are formed during the hydrolysis of MeOAc, induce the cubic-phase lattice distortion, nanocrystal aggregation and undesired surface traps. Herein, we demonstrate a new surface management strategy for CsPbI$_3$-PQDs, which removes the oleates more effectively without any side effects. In this strategy, a solution of sodium acetate (NaOAc) in MeOAc directly releases acetate ions minimizing the hydrolysis of MeOAc. This approach improves the electronic coupling in CsPbI$_3$-PQD solids, by preservation of their nanocrystal size and minimization of surface trap states. As a result, the NaOAc-treated CsPbI$_3$-PQD solar cells showed a power conversion efficiency (PCE) of 13.3% (higher than a 12.4% of a lead nitrate-treated control device) by only the development of surface management of CsPbI$_3$-PQDs without the aid of antireflective coating layer. In addition, this performance is comparable to a PCE 13.4% of the previously reported best performance of CsPbI$_3$-PQD solar cells, which use an antireflective coating layer.

EN09.03.05
In Situ GIXRD Study of Two-Dimensional Organohalide Perovskite Quantum Wells Junwei Xu$^{1,2}$, Maged Abdelsamie$^{1,2}$, Haipeng Lu$^3$, Kai Zhu$^3$ and Michael F. Toney$^{1,2,3}$; $^1$SLAC National Accelerator Laboratory, United States; $^2$Stanford University, United States; $^3$National Renewable Energy Laboratory, United States

Two-dimensional (2D) layered organohalide perovskites form natural “multiple quantum wells” have emerged as more intrinsically stable materials for solar cells than conventional three-dimensional (3D) halide perovskites (such as MAPbI$_3$, CsPbI$_3$, et al). This is because long organic spacers are inserted between perovskite slabs which can stabilize the structure. The organic ligands are bonded to the perovskite sheet with hydrogen bonds and to each other with van der Waals interactions. It has been demonstrated that the diversity of spacer organic cations greatly impacts the tunability of 2D organohalide perovskites in structural dimensionality as well as optoelectronic properties. Initial work has shown that 2D layered perovskite based solar cell is able to work stably over 46 days in the air with high humanity, however, it has a relatively low power conversion efficiency (PCE) comparing to that of its 3D counterpart. The major reason is attributed to poor charge transport property of the insulating organic spacers. Although the recent finding suggests that the undesired charge loss in the 2D perovskite structure could be overcome by tuning the crystalline orientation, the underlying crystallization kinetics mechanism is largely unexplored. It thus requires enormous work to establish a fundamental understanding of crystallization and factors related to this process, which eventually contributes to the improvement of carrier transport in the 2D perovskite thin films and photovoltaic devices. In our study, synchrotron based in-situ GIXRD technique was used to study crystallization dynamics of 2D perovskite films during fabrication and learn how the length of the organic spacers (PMA, PEA, PPA, PBA) influence the orientation of crystallites. We investigated a fundamental understanding of 2D perovskite crystallization during spin-coating and thermal annealing, which will develop as a guideline for the fabrication of the highly crystallized, oriented, and stable 2D perovskite films.

EN09.03.06
Increasing Exciton Spin Lifetimes in Layered Hybrid Perovskites by Lattice Symmetry Modification Sean Bourelle$^1$, Tanja Schmitt$^2$, Nathaniel J. Tye$^1$, Thomas Winkler$^1$ and Felix Deschler$^{1,3}$; $^1$University of Cambridge, United Kingdom; $^2$Universität Heidelberg, Germany; $^3$Technische Universität München, Germany

2D metal-halide perovskites are self-assembled quantum well structures with excellent optoelectronic properties and strongly-bound excitonic states. In these systems, strong spin-orbit coupling and the presence of crystal lattice asymmetry leads to a Rashba type band splitting. We show that the crystal lattice space group and symmetry in layered metal-halide perovskites can be controlled by halogen para-substituents. We report the synthesis and ultrafast electronic state dynamics of layered benzylammonium lead iodide perovskites (4-XC$_3$H$_7$CH$_2$NH$_3$)$_2$PbI$_4$ with X = H, F, Cl and Br. We will present x-ray diffraction and second-harmonic generation experiments from which we extract information on the symmetry of the crystal structure. We demonstrate that the fabricated materials are non-centrosymmetric 2D Ruddlesden-Popper metal-halide perovskites with layer number n=1. Using circularly polarised broadband transient absorption spectroscopy (CTA) we track the spin-polarised populations of the optically active
Exciton species on ultrafast timescales and present how the modification of the 2D perovskite crystal structure leads to a significant enhancement of the exciton spin lifetime.

EN09.03.07
Microfluidic Studies of Anion Exchange Reactions of Inorganic Perovskite Quantum Dots Kameel K. Abdel-Latif, Robert W. Epps, Corwin Kerr, Christopher Papa, Felix Castellano and Milad Abolhasani; North Carolina State University, United States

Inorganic perovskite quantum dots (IPQDs) have demonstrated remarkable success as a more energy-efficient alternative to well-studied metal chalcogenide QDs, and are attracting attention from the energy and chemical industries for a wide range of applications including photovoltaic devices, LED displays, and solar-enabled organic synthesis (photocatalysis). The facile bandgap tunability at room temperature through anion exchange reactions, high photoluminescence quantum yield, and relatively high defect tolerance, differentiate IPQDs from the other colloidal semiconductor nanocrystals. Despite the groundbreaking advancements of IPQDs in the field, their unique ionic nature (different than metal chalcogenide QDs) require new colloidal synthesis routes and surface chemistries. Conventionally, batch synthesis methods are utilized to synthesize, screen, and optimize solution-processed QDs. However, the massive reaction parameter space associated with IPQDs, in combination with the inherent mass and heat transfer challenges of batch methods, necessitate the utilization of material- and time-efficient synthesis methods for fundamental and applied studies of IQPDs. In this work, we develop and utilize a modular microfluidic platform for accelerated in-situ studies of IPQDs anion exchange reactions with minimum reagent consumption. The developed flow synthesis platform enables precise process control of halide exchange reactions, isolating reaction kinetics from precursor mixing rates in a gas-liquid segmented flow system. Utilizing the modular microfluidic strategy, we study in detail the effects of halide composition, ligand ratios, and halide salt source across reaction (residence) times ranging from 0.5 to 90 s. Capitalizing on the wealth of the systematic studies of anion exchange reaction, enabled by the developed time- and material-efficient strategy, we postulate a three-stage reaction mechanism for the homogeneous IPQDs halide exchange reaction. We complement our in situ findings of IPQDs anion exchange reactions with off-line material characterization techniques, gleaning new insights on the overall understanding of the anion exchange reaction network. The results of our kinetic studies of IPQDs halide exchange reactions in combination with the versatility and performance efficiency of the developed modular microfluidic platform, enable on-demand synthesis of IPQDs with a desired bandgap (composition) for targeted applications in optoelectronics and energy technologies.

EN09.03.08
Optical, Thermal and Crystallographic Studies of a Highly Stable New Hybrid Perovskite Material Based on Tetraethylphosphonium Iodide as Alternative Organic Cation and Bismuth Iodide Diana F. Garcia-Gutierrez1, Sylvain Bernes2, Edgar Gonzalez-Juarez1, Domingo Ixcoatl Garcia Gutierrez1,3 and Eduardo M. Sanchez-Cervantes1; 1Universidad Autónoma de Nuevo León, Mexico; 2Benemérita Universidad Autónoma de Puebla, Mexico; 3Centro de Innovación, Investigación y Desarrollo en Ingeniería y Tecnología, Mexico

Nowadays the study of MAPbX (X=Halide I, Cl or Br) perovskites’ properties is common in the race for having high efficiency and stable solar cells based on these promising materials. The poor stability in the environment of solar cells made with MAPbI3 has received great attention from researchers, and, on the other hand, there is also a necessity to find lead-free alternatives. One of the alternatives explored to solve the stability problem proposes to replace the organic cation MA for a hydrophobic one; on this regard, phosphonium salts possess this characteristic and they have been used as ionic liquids, so they also have high ionic conductivity as well. In parallel, bismuth and antimony compounds have been studied to replace the lead in the perovskite structure; in most cases, these lead-free solar cells display lower efficiencies, nonetheless showing improved stability at ambient and working conditions. Moreover, the properties of these lead-free perovskites make them excellent candidates to be used in tandem solar cells or other kind of optoelectronic applications, such as light emitting diodes. Conversely, these new materials, in many cases, are not reported in the literature, nor in the materials data bases, hence it is required to perform thorough studies to measure and understand their characteristics and properties. In this work, single crystals of BiI3-tetraethylphosphonium iodide were obtained by the supersaturation method; this is a new, stable and highly luminescent hybrid perovskite. These (EtP)3Bi2I9 single crystals have displayed thermochromic properties and the single crystal XRD studies have shown that they possess a tetragonal crystalline structure with a space group I42-d and unit cell dimensions of $a = b = 27.42$ Å and $c = 13.72$ Å. Based on the results obtained for this new perovskite,
tetraethylphosphonium iodide proves to be a promising candidate as an alternative organic cation in the solution of the instability problem. Finally, optical characterization results of the (EtP)$_3$Bi$_2$I$_9$ perovskite show it can be useful in many optoelectronic applications, such as light emitting diodes, photodetectors and tandem solar cells.

**EN09.03.10**

**Structural Design of Two-Dimensional Lead Halide Hybrid Perovskites for Optoelectronics**

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Two-dimensional (2D) halide perovskites exhibit excellent potential for optoelectronics because of their outstanding physical properties and structural diversity. Although the optical properties are mainly decided by the inorganic parts, the structures are significantly influenced by the shape and size of the spacer cations. Despite the large amount of recent new 2D perovskite reports, there is no existing rule that can predict the structures of the perovskites before the synthetic experiments. To achieve this, we carefully design our experiments by changing one factor of the organic cation at a time to assess the role each may play. We start with primary diamines NH$_2$C$_{m}$H$_{2m}$NH$_2$ ($m = 4−9$), using both solution and solid-state grinding method, we get the series (NH$_3$C$_{m}$H$_{2m}$NH$_3$)(CH$_3$NH$_3$)$_{n-1}$Pb$_n$I$_{3n+1}$ ($m = 4−9$ / $n = 1−4$), where $m$ represents the carbon-chain number and $n$ equals layer-thickness number. Even when the carbon-chain length is as short as $m = 4$, the structures are still closer to the Ruddlesden−Popper (RP) phase. If the primary diamines are replaced by cyclic diamines, the uncommon Dion-Jacobson (DJ) phase can be achieved. Furthermore, when aromatic diamines are utilized instead of the aliphatic ones, fine tuning of the structures can provide better insight for what kind of cations can template the rare DJ phase. Fabrication of photovoltaic devices using these materials shows promising solar cell performances. By using smaller 3-aminopyrrolidinium cation, more unique (110)-oriented perovskites can be synthesized. The highly distorted structures give rise to white-light emission at room temperature. By rational design of the structures for 2D perovskites, we may achieve the optimal properties ideal for their optoelectronic applications.

**EN09.03.11**

**The Interplay Between Free Charges and Traps in Organic and Inorganic Semiconductors**

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Organometallic halide perovskites (OMHPs) have recently undergone a remarkable development as highly efficient optoelectronic materials for a variety of applications particularly solar cells, light emitting diodes and photodetectors. To fully use the potential of OMHPs, several important challenges must be overcome. One of these challenges is the understanding and control of their defect structures. The available data from multiple research studies suggest that trap-assisted recombination exists in OMHPs despite their large carrier lifetimes, which makes these materials highly attractive, and this has resulted in the perovskite boom over the last decade. Conventional spectroscopy faces serious obstacles in OMHPs due to their low defect concentrations and capture cross section, and therefore the electronic structure of such semiconductors remains poorly understood. Currently, such understanding is limited, restricting the power conversion efficiencies of OMHP solar cells from reaching their Shockley–Queisser limit. In more mature semiconductors like Si, the knowledge of defects is one of the major factors in successful technological implementation. This knowledge and its control can make a paradigm shift in the development of OMHP devices.

The detection of shallow and deep traps is extremely challenging due to non-radiative nature of electrical transitions which cannot be studied by photoluminescence measurements. Moreover, as a result of the low activation energy, shallow traps cannot be detected by thermal emission methods. Here, we report on a deep level and shallow levels defects parameters and their effect on the free charge transport properties of the single crystalline methylammonium lead bromide (MAPbBr$_3$) perovskite for the first time. The transport properties of single crystal MAPbBr$_3$ are investigated by Time of Flight (ToF) measurements at several biases. These measurements are further fitted by Monte Carlo simulation allowing us the detection of parameters of energy states in the band gap. The analysis of charge carrier transport by ToF and MC simulation explain the long hole carrier lifetime and memory effect in MAPbBr$_3$ devices. Here, our studies provide strong evidence for deep levels in OMHPs and open a richer picture of the role and properties of shallow levels in MAPbBr$_3$ single crystals as a system model for the first time. The presented electrical and charge transport properties are crucial for informing the processing conditions towards the
elimination of these defects as was done for classical inorganic semiconductors. The deeper knowledge of the electronic structure of OMHPs could open further opportunities in the development of more feasible technologies.

EN09.03.12
Chiral 2D Perovskites with a High Degree of Circularly Polarized Photoluminescence Jiaqi Ma and Dehui Li; Huazhong University of Science and Technology, China

Chiral materials are of particular interest and have a wide range of potential applications in life science, material science, spintronic and optoelectronic devices. Two-dimensional (2D) hybrid organic-inorganic lead halide perovskites have attracted increasing attention. Incorporating the chiral organic ligands into the layered lead-iodide frameworks have been suggested for achieving the chirality transfer in 2D perovskites, so that the pure 2D perovskites with strong chirality exhibit CD. Meanwhile, 2D perovskites that possess the merits of both chiral materials and perovskites can realize circularly polarized light (CPL) emission and detection and thus would be promising materials for many imaging applications including biomedical, optical and spintronic devices. Nevertheless, the study of chiral pure 2D perovskites is still in its infancy. Here we report on the strong CPL emission and sensitive CPL detection in the visible-wavelength range in pure chiral ($R$/$S$-MBA)$_2$PbI$_4$ (MBA = C$_6$H$_5$C$_2$H$_4$NH$_2$) 2D perovskites, which are successfully synthesized with a needle shape and millimeter size by incorporating the chiral molecules. The chiral 2D perovskites ($R$-MBA)$_2$PbI$_4$ and ($S$-MBA)$_2$PbI$_4$ exhibit an average degree of circularly polarized photoluminescence (PL) of 9.6% and 10.1% at 77 K, respectively, and a maximum degree of the circularly polarized PL of 17.6% is achieved in ($S$-MBA)$_2$PbI$_4$. The degree of circularly polarized PL dramatically decreases with increasing temperature, implying that the lattice distortion induced by the incorporated chiral molecules and/or temperature-dependent spin flipping might be the origin for the observed chirality. Finally, CPL detection has been achieved with decent performance in our chiral 2D perovskite microplate/MoS$_2$ heterostructural devices. The high degree of the circularly polarized PL and excellent CPL detection together with the layered nature of pure chiral 2D perovskites enables them to be a class of very promising materials for developing and exploring spin associated electronic devices based on the chiral 2D perovskites.

EN09.03.13
Impact of Processing Strategies on Phase Evolution of Cs$_x$FA$_{1-x}$PbI$_3$ Perovskite Solar Cells—In Situ Monitoring of Crystallization Pathways During Film Formation Maged A. Abdelsamie, Junwei Xu and Michael F. Toney; Stanford University, United States

Organo-metal-halide perovskites have gained tremendous attention as potential materials for photovoltaics, demonstrating efficiencies approaching the best silicon solar cells. Many approaches have been adopted to manipulate perovskite formation including anti-solvent processing, compressed-gas treatment, and post-deposition thermal annealing, where films can be deposited using different coating techniques such as spin-coating or blade-coating. Understanding the role of processing strategies on crystallization pathways is of crucial importance as crystallization strongly affects the perovskite film microstructure, its stability, and devices performance. Moreover, crystallization pathways become more complicated for perovskites with a mixed stoichiometric mixture such as Cs$_x$FA$_{1-x}$PbI$_3$ due to the thermodynamic and kinetic competition to form secondary phases. Herein, using time-resolved x-ray scattering, we investigate the film formation of Cs-FA-containing perovskites with stoichiometry [Cs$_0.15$FA$_{0.85}$PbI$_3$]$_{in situ}$ during spin coating, blade coating, and the subsequent post-deposition thermal annealing, while different processing approaches such as anti-solvent [chlorobenzene (CB)] and compressed-gas (N$_2$) treatments were applied during film casting. We show how different processing routes affect the competition between the formation of the non-perovskite δ-phase and perovskite α-phase during film formation. When either anti-solvent or compressed-gas treatment is used, both δ-phase and α-phase are induced during casting, with the δ-phase more dominant in the as-cast film. However, each approach works with different mechanisms; while anti-solvent induces immediate crystallization from the bulk wet film, applying compressed N$_2$ works by depleting volatiles from the top-surface leading to surface-induced crystallization that occurs after reaching supersaturation. When neither treatment is applied, the as-cast film is mostly amorphous with little non-perovskite δ-phase formation. In addition, we show the evolution of phases during thermal annealing. Our results reveal that, for the non-treated films, crystallization of perovskite α-phase occurs predominantly from amorphous phase rather than δ-phase to α-phase transformation during thermal annealing. However, direct phase transformation of δ-phase to α-phase is more dominant for CB- and N$_2$- treated films, while perovskite crystallization occurs from an initially ordered film compared to non-treated films. Furthermore, our findings reveal that using blade-coating promotes completely different crystallization pathways than spin-coating,
while solvothermal direct crystallization of perovskite α-phase occurs predominantly, leading to overcoming the non-perovskite δ-phase formation without the need for post-deposition thermal annealing. Our work highlights the importance of real-time investigation of film formation which can provide an in-depth understanding of the mechanisms of perovskite formation and help to establish processing-microstructure-functionality relationships.

**EN09.03.14**

**Exciton Dynamics in Perovskite Nanocrystal-Based Heterostructures** En-Ping Yao, Bernhard Bohn, Yu Tong, He Huang, Lakshminarayana Polavarapu and Jochen Feldmann; Ludwig-Maximilians-Universität München, Germany

Solution-processable perovskite nanocrystals (NCs) are gaining increasing interest in the field of photovoltaics because of their enhanced stability compared to their thin-film counterparts. However, charge transfer dynamics in perovskite NC based light-harvesting systems are not well understood. By applying femtosecond differential transmission (DT) spectroscopy we investigate the photoinduced charge transfer from inorganic perovskite CsPbBr₃ NCs to the fullerene derivative phenyl-C₆₁-butyric acid methyl ester (PCBM) for two fundamentally different architectures, namely layer-by-layer heterostructures as well as blend structures. Varying the thickness of the NC layer on top of the PCBM in the layer-by-layer heterostructure, an exciton diffusion length of 290 ± 28 nm for CsPbBr₃ NC is extracted. The diffusion process is followed by an ultrafast exciton dissociation (within 200 fs) at the CsPbBr₃ NC/PCBM interface. In blend structures an overall faster charge transfer process is observed. Furthermore, photoconductivity measurements on a blend structure-based photodetector reveal an effective charge extraction from the active layer resulting in a high photosensitivity. DT measurements on this blend structure including adjacent electron- or hole-transport layers give insight into the extraction process and suggest a certain degree of phase segregation, which assists the charge collection.

**EN09.03.15**

**Epitaxial Growth of Soft Perovskites and the Hidden Carrier Dynamics** Jie Jiang¹², Yiping Wang¹, Zhizhong Chen¹, Jing Feng² and Jian Shi¹; ¹Rensselaer Polytechnic Institute, United States; ²Kunming University of Science and Technology, China

High-temperature vapor phase epitaxy (VPE) has been proved ubiquitously powerful in enabling high-performance electro-optic devices in III–V semiconductor field. A typical example is the successful growth of p-type GaN by VPE for blue light-emitting diodes. VPE excels as it controls film defects such as point/interface defects and grain boundary, thanks to its high-temperature processing condition and controllable deposition rate. In this talk, we will present single-crystalline high-temperature VPE soft halide perovskite thin film as a unique platform on unveiling previously uncovered carrier dynamics in inorganic halide perovskites. With VPE, hot photoluminescence and nanosecond photo-Dember effect are revealed in inorganic halide perovskite. These two phenomena suggest that inorganic halide perovskite could be as compelling as its organic–inorganic counterpart regarding optoelectronic properties and help explain the long carrier lifetime in halide perovskite. The findings suggest a new avenue on developing high-quality large-scale single-crystalline halide perovskite films requiring precise control of defects and morphology.

**EN09.03.16**

**Efficient Perovskite Solar Cells by Hybrid Perovskites Incorporated with Heterovalent Neodymium Cations** Xiong Gong; Univ of Akron, United States

Recently, hybrid perovskite materials have emerged as attractive alternatives for realizing cost-effective efficient perovskite solar cells. To date, impressive efficiency has been realized from the state-of-the-art solar cells through generic interface engineering and film morphological manipulation of perovskite active-layer in macroscopic scale. To further boost the efficiency of perovskite solar cells, microscopically tuning optoelectronic properties of hybrid perovskite materials represents a promising direction. In this study, we report efficient perovskite solar cells by a novel hybrid perovskites material that is incorporated with heterovalent neodymium cations (Nd³⁺). As compared with pristine hybrid perovskite materials, Nd³⁺-doped hybrid perovskite materials possess superior film quality with highly reduced trap-states, significantly enlarged charge carrier lifetimes, dramatically enhanced and balanced charge carrier mobilities. As a result, planar heterojunction perovskite solar cells by Nd³⁺-doped hybrid perovskite materials exhibit highly reproducible power conversion efficiency of 21.15% and significantly suppressed photocurrent hysteresis. These findings open a new window of tuning the optoelectronic properties of hybrid
perovskite materials and boosting the device performance of perovskite solar cells.

**EN09.03.17**

**Ultrafast Probe at the Interfaces of Solar Energy Conversion Materials**

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Solar energy represents one of the most important renewable energy sources. It can be converted to electricity and chemical fuels by photovoltaics and photoelectrochemical devices. The efficiency of solar energy conversion is governed by ultrafast carrier dynamics at solar energy conversion material interfaces. To understand such interfaces and develop next generation of solar energy conversion devices, ultrafast spectroscopic probes are needed. By developing transient reflectance spectroscopy to monitor the surface carriers that are within ~ 10 nm of the surface emerging solar cell materials, crucial parameters such as surface recombination and carrier diffusion are determined. Our results indicate the formation of 2D layered structure on Sn based perovskite solar cell surfaces that could effectively reduce surface recombination by 10-fold and increase carrier diffusion length to 2.5 μm.

**EN09.03.18**

**Why are Hot Holes Easier to Extract than Hot Electrons from Methylammonium Lead Iodide Perovskite?**

Ibrahim Dursun, Partha Maity, Jun Yin, Bekir Turedi, Ayan A. Zhumekenov, Kwang Jae Lee, Omar A. Mohammed and Osman M. Bakr; King Abdullah University of Science and Technology, Saudi Arabia

The power conversion efficiency of light harvesting devices is limited by the rapid thermalization of charge carriers that are photoexcited with energies above the bandgap of the absorbing material. As these so-called ‘hot’ carriers are difficult to collect, their cooling places an upper bound on the available photon energy that a given solar cell may utilize. Recently, studies on hot carriers in methylammonium lead iodide (MAPbI$_3$) perovskite have noted that they cooldown at an appreciably slower rate than carriers in other photovoltaic materials. However, the relaxation rate is still rapid in absolute terms, and hence, their capture and collection (before relaxing to the band edge) have not been shown so far. **Here we demonstrate and explain the efficiency of hot carrier extraction from MAPbI$_3$ using TiO$_2$ and Spiro-OMeTAD as an electron transporting layer (ETL) and hole transporting layer (HTL), respectively, via real-time observation of the carrier dynamics with femtosecond transient absorption spectroscopy and supported by density functional theory (DFT) calculation.** Time-resolved experiments establish that a quasi-equilibrium distribution of the hot carriers is directly populated upon excess-energy excitation of the pristine perovskite. This quasi-equilibrium distribution of hot carriers while not appreciably affected by the presence of TiO$_2$, is virtually absent in the presence of Spiro-OMeTAD, which is indicative of efficient hot hole extraction at the interface of MAPbI$_3$. DFT calculations predict that deep energy levels of MAPbI$_3$ exhibit electronically delocalized character, causing a strong overlap with the localized charge of the valence band of Spiro-OMeTAD lying on the surface of MAPbI$_3$. Consequently, the hot holes could be easily extracted from the deep-energy levels of MAPbI$_3$ by the HTL. These findings reveal the origins of efficient hot hole extraction in perovskites and offer a practical blueprint for optimizing interlayers of perovskite solar cells in order to enable hot carrier utilization.

**EN09.03.19**

**Low-Temperature-Gradient Crystallization for Multi-Inch High-Quality Perovskite Single Crystals for High Performance Photodetectors**

Yunxia Zhang$, Yucheng Liu$ and Shengzhong (Frank) Liu$; $1Shaanxi Normal University, China; $2Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

With their excellent optoelectronic properties, the practical application of single-crystalline organolead halide perovskite materials is limited by the lack of a method to prepare high quality perovskite single crystals in large dimension. Herein, we report our development of a low temperature-gradient crystallization (LTGC) method for high-quality CH$_3$NH$_3$PbBr$_3$ (MAPbBr$_3$) perovskite single crystals with lateral dimension as large as two inches. The theoretical analysis suggests that a small temperature gradient should be used to restrain the growth condition, particularly the solution concentration, within the optimal single-crystal-growth (OSCG) zone. The solubility curve as a function of temperature reveals a sharp turning point at 60 °C, across which the first-order solubility derivative (dC/dT) shows very different behaviors: below this temperature, the dC/dT changes dramatically as the temperature increases, while above this temperature, the dC/dT enters a plateau where further temperature change has little effect on the derivative, meaning that one can attain both a substantial crystal growth rate and crystallization yield below this temperature. Utilizing this discovery, a MAPbBr$_3$ single crystal as large as 47 × 41 × 14 mm is obtained with high quality via the LTGC method. The single crystal exhibits the best optoelectronic quality among all MAPbBr$_3$
materials reported in the literature, including the best trap state density, mobility, carrier lifetime, and diffusion length. These superior optoelectronic properties are further transferred into a high-performance planar photodetector. The device exhibits high operational stability, high external quantum efficiency (13.453%), excellent detectivity as high as $8 \times 10^{13}$ Jones, and a fast response speed as quick as 15.8 µs.

EN09.03.20
Crystal Phase Control toward the Perovskite Superlattice Solar Cell Satoshi Uchida, Naoyuki Shibayama, Koichi Tamaki, Keishi Tada, Miwako Furue, Ludmila Cojocaru and Hiroshi Segawa; 1The University of Tokyo, Japan; 2University of Freiburg, Germany

Recently organic–inorganic halide perovskite solar cell have great attention for its high performance together with easy production and wide variety of the process & flexibility of substrate materials. The power conversion efficiency has already reached over 23% in 2019 much beyond another solar cells such as CIGS or amorphous Si. The further performance still looks promising toward the Shockley–Queisser limit at around 30%. For that purpose, physical chemistry understanding based on the crystallography must be essential to design the good light harvesting, good charge separation and good charge transfer. Recently we reported the scientific revelation that the crystal phase of thin film CH$_3$NH$_3$PbI$_3$ consists of the mixture of tetragonal phase and cubic phase. They are about 15-20 nm well crystallized domain and randomly oriented in high resolution TEM analysis. Furthermore, multi stack sequence such as tetra-cubic-tetra resulted to form the superlattice with d-spacing 10.989 Å (2θ=8.03° for CuKα). Such a superlattice may act beneficial for good charge separation & charge transfer that are well known property as a Type II superlattice. To make more efficient performance, the crystal phase control with some different approaches were examined as below.

(1) High pressure post treatment by cold isostatic pressing (CIP)
(2) Photo-flash rapid curing
(3) Crystal growth under the high voltage electrostatic field
Here in this research the results of advantage-disadvantage will be discussed.

EN09.03.21
On the Proximity of Formamidinium-Centered States in Formamidinium-Doped Methylammonium Lead Iodide and Formamidinium Lead Iodide Sergei Manzhos and Giacomo Giorgi; 1Institut National de la Recherche Scientifique, Canada; 2University of Perugia, Italy

Organic-inorganic halide perovskite (OIHP) materials beyond the classic methylammonium lead iodide (MAPI) are actively researched for use in perovskite solar cells (PSC) and perovskite-based light emitting diodes (PLED). Specifically, the use of other inorganic cations such for formamidium (FA) has been reported to be advantageous, in particular in PLED. While the minimum of the conduction band (CBM) and the maximum of the valence band (VBM) of OIHPs are typically dominated by states due to the inorganic sub-lattice (such as PbI), it was recently suggested (PCCP 2019, 21, 8161) based on cluster calculations of FA-doped MAPI that FA-centered states may be close to the CBM (with fractions of an eV). This could have significant effect on electronic properties, as such states could be occupied (forming neutral FA species) by photoexcitation (in PSC) or electron injection (in PLED).

Here, we compute ab initio the properties of bulk and nanoclusters of FAPI and compare them to those of FA-doped MAPI. We consider the effects of van der Waals interactions and of the choice of the functional (GGA or hybrid) on the bandstructure. We observe FA-centered states in proximity to the CBM and a strong nanosizing effect whereby FA-centered states may fall through the CBM of the PbI sub-lattice in small nanoparticles. The results suggest that one indeed should consider effects of FA-centered states in OIHP using formidium either as a dopant or as majority cation (FAI).

EN09.03.22
Quantitative Measures of Contact Selectivity and Interfacial Recombination of Spiro-OMeTAD-Modified Solar Cell Contacts and the Role of Li-TFSI Kira Egelhofer and Mark Lonergan; University of Oregon, United States

An ideal solar cell contact collects either the electron or hole with no energy loss while perfectly rejecting the other carrier. Nonideal charge transfer at the interface between absorber and contact can severely limit the efficiency of solution-processed solar cells like perovskites. Interfacial layers (IFLs) such as 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobiﬂuorene (spiro-OMeTAD) are frequently used to help improve charge transfer...
and therefore efficiency. However, the field lacks systematic methods of studying how IFLs impact efficiency due to a few key challenges. These include separating interface phenomena from bulk processes, separate quantification of contact selectivity and interfacial recombination, and measuring the effects of operando solar cell function on charge transfer. Our work seeks to address these challenges to answer lingering questions about IFLs. For example, there are mixed reports concerning whether the selectivity or recombination of spiro-OMeTAD-modified contacts is more influential in determining solar cell characteristics (primarily $V_{oc}$). It is well known that the addition of Li-TFSI (lithium bis(trifluoromethane)sulfonimide, a common additive) facilitates the oxidation of spiro-OMeTAD in air, effectively $p$-doping the film and shifting the Fermi level down. This shift would intuitively increase the hole selectivity of the contact and should therefore increase the $V_{oc}$. However, the $V_{oc}$ of perovskite cells decreases with increased Li-TFSI concentration. Because increased interfacial recombination theoretically decreases $V_{oc}$, recombination could be more influential in determining $V_{oc}$ than the selectivity. However, there are no quantitative reports of the selectivity or recombination of spiro-OMeTAD-modified contacts, which this study seeks to address.

To do so we use the silicon interdigitated back-contact solar cell as a tool to experimentally measure the selectivity and recombination. Additionally, we use numerical simulation to extract the corresponding exchange current densities ($J_{ex}$) as charge transfer parameters for both electrons ($J_{en}$) and holes ($J_{hp}$). We find that spiro-OMeTAD IFLs both with and without 25 mol% Li-TFSI strongly affect both the selectivity (defined as $J_{en}/J_{hp}$) and recombination (defined as $(J_{en}J_{hp})^{1/2}$) of gold contacts. Neat spiro-OMeTAD causes gold to become two orders of magnitude less hole selective while the addition of Li-TFSI causes it to become three orders of magnitude more hole selective (a five order of magnitude increase from neat). Neat spiro-OMeTAD causes the recombination to go down by six orders of magnitude while the presence of Li-TFSI causes it to go down by five orders of magnitude (an order of magnitude increase compared to neat). Recall that reported perovskite $V_{oc}$s go down with increasing Li-TFSI concentration; a decrease in hole selectivity or an increase in recombination would cause this to occur. We find that both the hole selectivity and recombination increase upon addition of Li-TFSI indicating that the recombination change dominates decreases in $V_{oc}$. We emphasize that only by measuring both selectivity and recombination can we definitively come to this conclusion. We also observe that when the solar cell using spiro-OMeTAD-modified gold as the hole selective contact is operated in the power quadrant, the recombination decreases and the hole selectivity increases. From these results we conclude that changes to the selectivity and recombination properties of spiro-OMeTAD-modified contacts contribute to hysteretic behavior in perovskite solar cells. Our methods of studying charge transfer at spiro-OMeTAD interfacial layer-modified solar cell contacts shed light on the complex interplay between contact selectivity, recombination, and solar cell parameters. These insights will help the field engineer target interfacial layers for improved perovskite and other solution-processed solar cell efficiency.

**EN09.03.23**

**Two-Dimensional Lead Halide Perovskites Incorporating Long Straight Chain Aliphatic Ammonium Ions—Crystal Structure, Optical Properties and Ferroelectricity**

Eugenia S. Vasileiadou, Qing Tu, Shiqiang Hao, Daniel Friedrich, Ido Hadar, Ioannis Spanopoulos, Christopher Wolverton, Vinayak Dravid and Mercouri G. Kanatzidis; Northwestern University, United States

Herein, we present a new family of bilayered lead bromide perovskites, incorporating long chain aliphatic alkylammonium cations as the organic spacer between the inorganic sublattices with formula $(C_{m}H_{2m+1}NH_{3})_{2}(CH_{3}NH_{3})Pb_{2}Br_{7}$ (m = 6–8). Structural characterization by single-crystal X-ray diffraction demonstrates uniaxial expansion of the stacking axis of the studied perovskites, as the length of the alkylammonium cation increases. Differential scanning calorimetry was used to study the reversible phase transitions of the reported bilayered 2D perovskites. The semiconducting properties of the materials were examined by UV-Vis absorption and photoluminescence (PL) emission measurements. The studied compounds have a similar absorption spectra that are typical of layered perovskites, with an absorption edge around 2.85 eV and an excitonic peak above the bandgap. PL at room temperature displays a strong narrow emission, close to the energy value of the excitonic peak in the absorption spectra. The band structure of the materials was calculated based on density functional theory (DFT), which affirms that the materials are direct band gap semiconductors. Film fabrication demonstrates that the layered perovskites can successfully be cast into thin films through the hotcasting technique. Switching spectroscopy-piezoresponse force microscopy (SSPFM) on thin films shows polarization switching, indicating ferroelectric behavior along with the non-centrosymmetric structures of the materials. Thus, tuning the spacer cation of the 2D hybrid lead bromide perovskite structure by incorporating long-chain alkylamines, provides a platform to combine ferroelectricity with the excellent optical properties and stability of layered perovskites for fundamental and applied studies.
Thermoelectric Properties of Lead-Free Halide Perovskites Solar Cells Tianjun Liu and Oliver Fenwick; Queen Mary University of London, United Kingdom

Halide perovskites have emerged as promising candidates for photovoltaics and light-emitting diodes. Recently, promising thermoelectric performance has been reported for single nanocrystals of a halide perovskite, but there is not yet a good understanding of how thermoelectric performance can be optimised in these materials, especially in thin films where a diverse range of structures and morphologies are accessible. In this presentation I will report a record thermoelectric figure of merit (ZT) for halide perovskites, using the example of CsSnI3 thin films. This result is in part due to the ultralow thermal conductivity of our films (0.38 W/mK at room temperature), as well as high electrical conductivity enabled by self-doping of the films through controlled Sn oxidation. I will also discuss the potential role of mixed-halide films in developing these materials further. Finally, charge and phonon transport mechanism in CsSnI3 thin films will be discussed, which would be helpful for improving its air stability and further photovoltaic applications.

Direct Measurement of Exciton Diffusion in Two-Dimensional Ruddlesden-Popper Perovskites Michael Seitz and Ferry Prins; Universidad Autonoma de Madrid, Spain

There is an increasing interest in two-dimensional (2D) Ruddlesden-Popper perovskites for solar harvesting as a result of their superior chemical stability as compared to their bulk counterparts.1,2 Both purely 2D and blends of 2D/3D phases have already been successfully employed in solar cells with reported efficiencies of >18% and >22%, respectively.3,4 With this increasing technological relevance of 2D perovskites, it is essential to understand the physical processes that govern their opto-electronic performance. Particularly, the reduced dimensionality in 2D perovskites results in excitonic excited states, dramatically modifying the dynamics of charge collection. While charge carrier dynamics in bulk systems is increasingly well understood, a detailed understanding about the spatial dynamics of excitons in 2D perovskites is lacking.5

Here, we present the direct measurement of the intrinsic diffusivities and diffusion lengths of excitons in single crystalline 2D perovskites using time-resolved microscopy.6 This technique allows us to follow the temporal evolution of a diffraction limited exciton population with sub-nanosecond resolution, revealing the spatial and temporal exciton dynamics.7 Using the versatility of perovskite materials, we study the influence of the organic spacer, the halide and cation composition, as well as the dimensionality (n = 1 and 2) on the diffusion dynamics of excitons in 2D perovskites. We find that changes in these parameters can lead to differences in diffusion lengths of up to two orders of magnitude. Our results provide important insights into the spatial exciton dynamics in 2D perovskites and yield clear design rules for more efficient 2D perovskite solar cells and light emitting devices.

Tuesday Morning, December 3, 2019
Sheraton, 2nd Floor, Constitution B

8:00 AM EN09.04.01
Overcoming the Large Exciton Binding Energy in Two-Dimensional Perovskite Nanoplatelets by Attachment of Strong Organic Electron Acceptors Ferdinand C. Grozema1, María C. Gélvez-Rueda1, Magnus B. Fridriksson1, Rajeev K. Dubey1, Wolter F. Jager1 and Ward van der Stam2;1, Delft University of Technology, Netherlands; 2University of Utrecht, Netherlands

Two-dimensional perovskites are an emerging new class of materials with potential application in a broad range of opto-electronic devices. These materials are formed by layers of inorganic metal-halide octahedrals separated by large organic cations. The organic cations improve the stability and give a large freedom to tune the opto-electronic properties. However, the organic cations used so far act only as a dielectric non-conductive layer that contributes to the large exciton binding energy of these materials. This large binding energy limits their application in opto-electronic devices in which efficient charge carrier separation is required (such as solar cells, photo-detectors and photo-catalysts). In order to achieve charge separation, we consider the replacement of non-functional organic cations by a strongly electron accepting moiety.

We have explored the introduction of functional organic chromophores theoretically by density functional theory calculations and show that it is possible to introduce conjugated molecules that have a significant effect on the electronic structure. Strong electron acceptors or donors lead to conduction band or valence band edges that are localized on the organic part of the materials. This could lead to enhanced charge separation.

To test this idea experimentally we have introduced strongly electron accepting perylene diimide (PDI) molecules in 2D CsPbBr3 nanoplatelets as a model system for 2D perovskites. We show by ultrafast transient absorption and fluorescence that photoexcitation of these perovskite nanoplatelet:PDI conjugates leads to fast quenching of the fluorescence, fast decay of the bleach of the nanoplatelets and the appearance of a photoinduced absorption feature specific for the PDI anion. This latter feature unequivocally shows that the fluorescence quenching is due to electron transfer to the PDI molecules. Finally, we show by time-resolved microwave conductivity (TRMC) measurements that this charge transfer leads to long-lived hole conduction (tens of microseconds) in the two-dimensional perovskite nanoplatelets. This opens up a new synergistic approach, where the properties of two-dimensional perovskites can be tuned for specific device applications by introduction of strong functional dyes in the organic component of the material.

8:15 AM *EN09.04.02
Multi-Modal Techniques Linking Carrier Behavior with Material Properties in Halide Perovskites Samuel D. Stranks; University of Cambridge, United Kingdom

Halide perovskites are generating enormous excitement for their use in high-performance yet inexpensive optoelectronic applications. Nevertheless, a number of fundamental questions about these materials still remain and need to be answered to push devices to their theoretical performance limits. For example, we still know very little about the specific nature of the defects leading to trap states, carrier recombination pathways or anisotropies of carrier diffusion.

In this talk, I will present a number of new techniques we are developing to try to address these open questions in 2D and 3D halide perovskite semiconductors. These techniques focus on understanding charge carrier behavior, including recombination, trapping and diffusion, and how these properties link to chemical and material properties. I will present a high-resolution luminescence microscopy technique employing two-photon excitation to allow us to visualize and time-resolve carrier diffusion in three-dimensions, revealing anisotropic and depth-dependent carrier diffusion properties. Furthermore, we link the local luminescence properties to high-resolution crystallographic and chemical properties using synchrotron nano-probe X-Ray beamlines and low-dose scanning electron diffraction measurements. Through these measurements, we start to reveal the nature of the defects associated with local non-radiative power losses and heterogeneous diffusion and provide guidelines about how we can ultimately eliminate these unwanted loss pathways and homogenize carrier diffusion.
Excitons and Polaron in Hybrid Perovskite

Paulina Plochocka; LNCMI, France

Organic and inorganic metal halide perovskites have emerged in recent years as revolutionary semiconductor materials for lighting and energy harvesting applications. Many of their fascinating properties originate from the fact that metal-halide perovskites should be classed as crystalline liquids rather than hard semiconductor materials. In this talk I will discuss excitons and polaron in perovskites.

I will start by describing the exciton fine structure splitting in semiconductors, which reflects the underlying symmetry of the crystal and quantum confinement. Since the latter factor strongly enhances the exchange interaction, most work has focused on nanostructures. Here, we report on the first observation of the bright exciton structure splitting in a bulk semiconductor crystal, where the impact of quantum confinement can be specially excluded, giving access to the intrinsic properties of the material. Detailed investigation of the exciton photoluminescence and reflection spectra of a bulk methylammonium lead tribromide single crystal reveals a zero magnetic field splitting as large as 200 µeV. The observed splitting can be understood in the exciton picture combined with symmetry considerations.

Next I will discuss the formation of the polaron, which is the result of the exciton – phonon coupling. The polaron formation is made in evidence by observation of the exciton effective mass enhancement. In the end I will describe some optical properties of a very new system: hollow perovskites, which exhibit optical properties of the excitons in 3D and quantum confinement regime.

On the Relation between Photoluminescence Quantum Efficiency, Minority Carrier Lifetime and Quasi-Fermi Level Splitting in Perovskite Solar Cells

Thomas Unold1, Martin Stolterfoht2, Christian Wolff2, Pietro Caprioglio2, Jose Marquez Prieto3, Dieter Neher2 and Thomas Kirchartz3; 1Helmholtz-Zentrum Berlin, Germany; 2University Potsdam, Germany; 3Forschungszentrum Juelich GmbH, Germany

The open-circuit voltage ($V_{OC}$) is currently considered to be the main limitation on the path to approach the radiative (Shockley-Queisser) efficiency limit in hybrid perovskite-type solar cells. The $V_{OC}$ is determined by recombination processes in the solar cell including bulk, interface and/or contact recombination.[1] Under ideal conditions the open-circuit voltage approaches the internal quasi-Fermi level splitting (QFLS), which may be estimated by measuring the external photoluminescence quantum yield (PLQY) and the absorption properties.[2] The PLQY and quasi-Fermi level splitting can also be estimated through time-resolved photoluminescence (TRPL) measurements, if the radiative recombination constants and photon recycling are taken into account properly.[3] A survey of the literature shows that the reported PLQY values for given open-circuit voltages sometimes vary by orders of magnitude which is difficult to reconcile from a theoretical perspective. In this contribution, we show that careful consideration of the above points leads to a consistent picture of the interrelation between the QFLS, PLQY and TRPL lifetime. Finally we discuss possible sources of error in the analysis and how to cross-check data.


How Charge Carrier Transport through Ferroelastic Twin Boundaries in Halide Perovskite?

Xun Xiao1, Wenhao Li2, Yanjun Fang3, Rashid Zia1 and Jinsong Huang1,3; 1University of North Carolina at Chapel Hill, United States; 2Brown University, United States; 3University of Nebraska–Lincoln, United States

Grain boundaries (GBs) have been established to play a vital role in determining the power conversion efficiency of organic-inorganic halide perovskite (OIHP) thin film solar cells. As a special category of GBs, ferroelastic twin boundaries (TBs) are recently discovered to exist in both CH$_3$NH$_3$PbI$_3$ thin films and single crystals (SCs), however their impact on the carrier transport and recombination in OIHP materials remains unexplored. Here, using the
scanning photocurrent microscopy, we have demonstrated the uniform distribution of electric field across the TBs in OIHP SCs as long as the influence of the crystal surface is well suppressed through surface passivation, suggesting that the TBs have little influence on the carrier transport across them. Also, the photoluminescence (PL) imaging and the spatial-resolved PL intensity and lifetime results confirm the electronic benign nature of the TBs, in strong contrast to regular GBs that will block the carrier transport and also behave as the non-radiative recombination centers. Our observations reveal the fundamentally different role of TBs and GBs played in carrier transport of OIHP materials, which will provide insights into the performance improvement of the OIHP based optoelectronic devices.

9:45 AM EN09.04.06
Exploiting Localized Charge Accumulation in Alloyed Perovskites for Highly Efficient Luminescence Sascha Feldmann1, Stuart Macpherson1, Satyaprasad P. Senanayak1, Mojtaba Abdi-Jalebi1, Jasmine P. Rivett1, Guangjun Nan2, Richard Ciesielksi3, Achim Hartschuh3, Emilie Ringe1, Richard H. Friend1, Henning Sirringhaus1, Michael Saliba4, David Beljonne5, Samuel D. Stranks1 and Felix Deschler1; 1University of Cambridge, United Kingdom; 2Department of Physics, China; 3Ludwigs-Maximilian-Universität München, Germany; 4University of Fribourg, Switzerland; 5Université de Mons, Belgium

Metal-halide perovskites have emerged as excellent solution-processable semiconductors for optoelectronic applications such as solar cells and light-emitting devices. Substitution of the monovalent cations has advanced luminescence yields and device efficiencies. Here, we control the cation alloying to push optoelectronic performance through alteration of the charge carrier dynamics in mixed-halide perovskites. In contrast to single-halide perovskites, we find high luminescence yields for photo-excited carrier densities far below solar illumination conditions. Using time-resolved spectroscopy we show that the charge-carrier recombination regime changes from second to first order within the first tens of nanoseconds after excitation in these films. Supported by temperature-dependent microscale-mapping of the optical bandgap and chemical composition, electrically-gated transport measurements and first-principles calculations, we demonstrate that spatially-varying energetic disorder in the electronic states causes local charge accumulation, creating photo-doped regions, which unearths a strategy for efficient light emission at low charge-injection in solar cells and LEDs.

10:00 AM BREAK

10:30 AM *EN09.04.07
Perovskite Solar Cells—Improving Device Efficiency and Stability and Understanding Optoelectronic Processes Henry J. Snaith and Yen-Hung Lin; University of Oxford, United Kingdom

Perovskite solar cells continue to gain momentum in research and gain in efficiency, and multijunction perovskite solar cells offer a roadmap to performance levels well beyond that possible with single junction silicon or other thin-film technologies. Operational stability is an area which is critical for any PV technology, and even more so for perovskites, which are dissimilar to conventional semiconductors in a number of ways. I will present different approaches we have adopted to improving the efficiency, and fundamental stability of the perovskite absorber materials and devices, and highlight degradations which can occur in the bulk of the perovskite absorber materials and induced by the charge extraction heterojunction. I will give further insight into what factors influence stability, and how to mitigate degradation. Beyond stability, I will highlight how moving from a single absorber layer, to a multijunction cell should lead to much higher efficiencies, and I will show experimental realisation of progress along such a roadmap, including record perovskite-on-silicon PV cells. Beyond research, I will highlight our progress towards manufacturing scale-up through the technology company, Oxford PV Ltd., and key challenges which need to be overcome to deliver an industrialised perovskite PV technology.

11:00 AM EN09.04.08
Strong Light-Matter Interactions in Hybrid Perovskites Madeleine Laitz1, Dane W. deQuilettes1, Jude Deschamps1, Roberto Brenes1, Inés García Benito2, Giulia Grancini2, Keith A. Nelson1 and Vladimir Bulovic1; 1Massachusetts Institute of Technology, United States; 2École Polytechnique Fédérale de Lausanne, Switzerland
State-of-the-art perovskite materials demonstrate photoluminescence quantum efficiencies (PLQE) above 90% due to low non-radiative recombination rates and unparalleled defect tolerance. The optoelectronic properties that have allowed perovskites to emerge as a leading active layer material in high efficiency thin film photovoltaics (PVs) – high absorption coefficient, high PLQE, solution processability, chemical tunability – simultaneously situate perovskites to function superbly as a coherent quantum material. In this work, we explore perovskites as a platform for strong light-matter coupling to sustain all-optical operations. Though light is weakly interacting, it is possible to form interacting quasi-particles, called exciton-polaritons, that have characteristics of both light and matter. Traditionally, polaritons have been studied at cryogenic temperatures in all-inorganic semiconducting materials (e.g. GaAs heterostructures). In this work, we study the room-temperature formation of exciton-polaritons with large Rabi splittings in semiconductor microcavities, using solution-processed 2D perovskites as self-assembled quasi-quantum well structures for the active layer. Polariton formation is probed by angle resolved reflectivity and photoluminescence measurements through a k-space imaging setup. The polariton-polariton interaction strength is explored by the confinement of photo-generated exciton-polaritons via modifications to the potential environment of the microcavity, presenting opportunities to study room-temperature Bose-Einstein condensation. The realization of facilely-fabricated room-temperature exciton-polaritons has the potential to revolutionize a wide range of devices, from PVs to low-threshold lasers to all-optical switches.

11:15 AM EN09.04.09
Free-Electron Screening and Mahan Excitons in MAPbI₃ from First Principles Theoretical Spectroscopy
Joshua A. Leveillee and Andre Schleife; University of Illinois at Urbana-Champ, United States

An unusual combination of low exciton binding energy and strong optical absorption renders hybrid organic-inorganic perovskites interesting candidates for efficient absorber materials in next-generation solar cells. This interesting behavior triggered numerous studies to better understand excitonic effects, e.g. in MAPbI₃. In experiment, exciton binding energies in this material range from as high as 62 meV to as low as 2 meV. At the same time, a line shape of the absorption edge similar to that of GaAs was reported, with no clear excitonic peak and a binding energy potentially less than 10 meV at room temperature. In contrast, cutting-edge first-principles simulations based on the Bethe-Salpeter framework seem to consistently overestimate exciton binding energies.

In this work, we use density-functional and many-body perturbation theory to study atomic geometries, electronic structure, and optical properties of MAPbI₃ and find good agreement with earlier results and experiment. Electronic band structures and gaps are predicted using Hedin’s $GW$ approximation, including the spin-orbit interaction. We account for free electrons within our first-principles theoretical spectroscopy and specifically study their impact on the electron-hole interaction. This allows us to conclude that additional screening due to free electrons can explain consistently smaller exciton binding energies, compared to those in the material without free electrons. Furthermore, we also observe that the absorption line shape in MAPbI₃ with free electrons strongly resembles that of the spectrum without free electrons up to high free-electron concentrations. Interestingly, our simulations show that this unexpected behavior can be explained by formation of Mahan excitons. These dominate the absorption edge and we show that this makes this material robust against free-electron induced changes of the optical absorption that are observed in other semiconductors.

11:30 AM EN09.04.10
Illuminating Charge Transfer at the Interfaces of Perovskite Solar Cells
Robert J. Westbrook¹,², Weidong Xu¹, Tracey Clarke², James R. Durrant¹ and Saif Haque¹; ¹Imperial College London, United Kingdom; ²University College London, United Kingdom

Perovskite solar cells (PSCs) have set themselves apart from their dye-sensitized (DSSC) and organic (OSC) predecessors, with impressive efficiencies at 24%. Despite the key role that charge transport layers (CTLs) have played in this success, researchers are still debating the importance of parameters that govern charge transfer at the PSC interfaces, namely: (i) the interfacial energy offset, $\Delta E$ between the perovskite and CTL; (ii) CTL structure; and (iii) intrinsic perovskite properties.

This talk will detail our progress in developing a complete picture of electron/hole transfer at PSC interfaces using a combination of time-resolved spectroscopy and device work.² Specifically, we will first outline our observation of highly efficient (>75%), nanosecond charge transfer to CTLs at remarkably low values of $\Delta E$ (<0.1 eV). We will also show that careful selection of CTLs with electron-donating functional groups can slow interfacial recombination by passivating surface traps, as has been previously observed with Lewis bases, inert polymers and
other molecules. Remarkably, the resulting coordination between the perovskite and CTL produces a 3-fold enhancement in charge transfer yield. Finally, we will discuss the impact of such passivation on device stability. This novel insight into the charge separation mechanism in PSCs goes some way to explaining the success of triarylamines (e.g., PTAA, PTPD) as HTLs in such systems and has important implications for the design of next-generation CTLs.

2. R J. E. Westbrook, W. Xu et al, *Manuscript in Preparation*
3. N. K. Noel *et al*, *ACS Nano*, 2014, 8(10), 9815
5. W. Xu *et al*, *Nat. Photonics*, 2019, 13, 418
7. X. Bu *et al*, *Solar RRL*, 2019, 3, 1800282

11:45 AM EN09.04.11
The Evolution of Ultrafast Carrier Dynamics In Situ Perovskite Optoelectronic Devices Kanishka Kobbekaduwa1, Exian Liu1, Pan P. Adhikari1, Yuanyuan Zhou2, Wanyi Nie3, Kai Zhu4 and Jianbo Gao1; 1Clemson University, United States; 2Brown University, United States; 3Los Alamos National Laboratory, United States; 4National Renewable Energy Laboratory, United States

Although significant progresses have been made toward to optoelectronics application including solar cells, large color gamut LEDs, photodetectors, and X-ray detectors, the fundamental understanding of ultrafast carrier dynamics of organic-inorganic perovskite materials remains unclear. The ultrafast dynamics, which reveals some novel physical phenomena such as hot carrier cooling, phonon bottle-neck effect was widely studied by ultrafast optical spectroscopies, which include pump-probe transient absorption (transmission, reflection, time-resolved THz, optical Kerr effect, and the most popular time-resolved photoluminescence (TRPL). However, it remains a challenge to study the perovskite optoelectronic devices in-situ in an ultrafast fashion.

In this talk, we use an ultrafast photocurrent spectroscopy with sub-25 picosecond time resolution to reveal the evolution of ultrafast carrier dynamics from sub-25 ps to microsecond in-situ perovskite solar cells and photoconductors. We address the basic questions of carrier photogeneration, recombination, transport, trapping, in addition to directly extracting carrier mobility, lifetime, and the property of trap states such as density, energy level, and capture cross-section.

SESSION EN09.05/EN08.05: Joint Session: Perovskite Solar Cell—A 10-Year Anniversary
Session Chairs: Shengzhong (Frank) Liu and Philip Schulz
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Back Bay AB

1:30 PM *EN09.05.01/EN08.05.01
Prospects of Perovskite PV Research Based on All-Inorganic Absorbers and New Dopant-Free Carrier Transporters Tsutomu Miyasaka; Toin University of Yokohama, Japan

This year, we are celebrating 10 years of perovskite solar cell (PSC). Since our first discovery of PSC in 2009, enormous efforts have been put into different aspects of PSCs and the progress has been incredibly fast on all fronts. While preparing a comprehensive review1 on the background, on-going R&Ds, and future direction of PSC research recently, we realized that, although efficiency level has gone beyond 24%, PSCs face serious challenges of practical stability and durability required for industrialization. Although compositional engineering of perovskites by mixing different cations and anions, using modulator molecules and mixing 2D and 3D structures have doubtlessly improved the stability of perovskites against heat and moisture, use of organic moieties still remain a challenge to improve the stability further. Intrinsic stability of the perovskite crystal structure and robust properties of carrier transport materials are going to be the keys to the long term durability of the device. In this respect, use of all-inorganic perovskite materials and combination with dopant-free carrier transport materials are highly desired. We have conducted some work in this direction which includes stabilization of CsPbI3 black phase 2 and use of dopant-
free hole transport materials (HTMs). Dopant-free HTMs combined with all-inorganic perovskites have yielded sufficiently high efficiency of 15%. Intrinsic thermal stability of the device was improved without using diffusible dopants. In our collaboration with JAXA, stability of perovskites was investigated in space environment for satellite applications. Here, organic cations in perovskite such as methyl ammonium are instable under exposure to vacuum and high temperatures >100°C. Perovskite materials demonstrate its high stability against exposure to high energy particle radiations (proton and electron beams) up to dose of $10^{15}$ particles/cm$^2$ due to use of thin absorber films that can avoid accumulation of particles and also exhibit defect tolerant nature. The lecture will also introduce our current efforts in making PSCs based on both lead and lead-free perovskites, and future perspectives of perovskite photovoltaics.


Stabilizing Halide Perovskites—Self-Repair, Defects and Sealing David Cahen$^{1,2}$; $^1$Weizmann Institute of Science, Israel; $^2$Bar-Ilan University, Israel

Halide Perovskites (HaPs) present a remarkable case of just stable (against decompositon into binaries) compounds that can function as active component for PV, light-emission and radiation detection, all demanding functions, over time periods that seem incompatible with their free energy of formation (again, from the binaries). Actually, the Achilles heel of the materials is their surface, true to Pauli's famous dictum, because of the law of mass-action: as long as the system remains a hermetically close one, it can withstand the onslaught of electronic carriers and photons. Add to that that it are to a large extent the interfaces that make the devices function (again following a famous dictum, this time from Kroemer) and.. those are made with surfaces. Thus, what might appear esoteric materials chemistry and physics issues, are highly relevant for device design. In principle, apart from the remarkable self-healing ability (known to some extent also for CIGS) this is not new as nearly every (inorganic) semiconductor material that we use today went through the process of taming its surfaces to get control over interfaces made with them. In this talk I will, depending on developments in the half year between abstract writing and presentation, present data on the self-healing and (de)stabilization processes of HaPs and put their behaviour in perspective with respect to some other semiconductors, to arrive at insights that should be useful to device design and building.

Molecular Dopants on Metal Halide Perovskite Surfaces—What Do We Learn? Antoine Kahn, Fengyu Zhang, Scott Silver, Joseph C. Hamill, Nakita K. Noel, Barry P. Rand and Lynn Loo; Princeton University, United States

Surfaces of metal halide perovskites (MHP) present an interesting set of questions and challenges that are only beginning to be addressed, namely the existence, origin, density and energy of electronic surface gap states. MHP surfaces are prone to ion diffusion and chemical reactions, and to degradation under various environmental conditions and probing tools, all of which likely induce some density of electronic gap states. In sufficient density, these states affect the electronic structure and optoelectronic performance of all MHP interfaces and devices. There is currently no consensus on potential profile and occurence of band bending in perovskite films, from substrate to surface. Available data point to a strong dependence of these profile on the nature and surface potential of the substrate on which the films are fabricated, and on the perovskite processing conditions. Limits in Fermi level excursion have been observed and also point to some low density of (surface or bulk) gap states.[1] To address some of these issues, several groups have started to use organic molecular dopants (reductants and oxidants), as “gentle” probes of the electronic occupation and density of surface states, and as modifier agents of these states. [2,3] This talk describes our recent investigations of the interaction between molecular reductants (mostly [RuCp*Mes]$_2$) and oxidants (Mo(tfd)$_3$ and derivatives) and surfaces of 3D MHPs CsPbBr$_3$ and FA$_x$MA$_{1-x}$Pb(I$_y$Br$_{1-y}$)$_{3}$, and the 2D Ruddlesden-Popper phase BA$_2$PbI$_4$. Using a combination of electron spectroscopies and contact potential measurements, we determine the sign and magnitude of surface photovoltage occurring at these free surfaces, and the extent of surface energy level shifts resulting from charge exchange with the molecular dopants. We also show evidence obtained via photoemission spectroscopy of a density of (surface) filled states above the valence band maximum of FAPbBr$_3$ following electron bombardment, and of MAPbI$_3$, likely due to the presence of DMSO in the precursor solution. The role of surface doping in changing the occupation of these states will be discussed.
Semiconducting metal-halide perovskites present various types of chemical interactions which give them a characteristic fluctuating structure sensitive to the operating conditions of the device, to which they adjust. This makes the control of structure-properties relationship, especially at interfaces where the device realizes its function, the crucial step in order to control devices operation. In particular, given their simple processability at relatively low temperature, one can expect an intrinsic level of structural/chemical disorder of the semiconductor which results in the formation of defects.

Here, first I will summarize our understanding of the nature of defects and their photo-chemistry, which leverages on the cooperative action of density functional theory investigations and accurate experimental design. Then, I will show the correlation between the nature of defects and the observed semiconductor instabilities. Instabilities are manifested as light-induced ion migration and segregation, eventually leading to material degradation under prolonged exposure to light. Understanding, controlling and eventually blocking such material instabilities are fundamental steps towards large scale exploitation of perovskite in optoelectronic devices. By combining photoluminescence measurements under controlled conditions with ab initio simulations we identify photo-instabilities related to competing light-induced formation and annihilation of trap states, disclosing their characteristic length and time scales and the factors responsible for both processes. We show that short range/short time defect annihilation can prevail over defect formation, happening on longer scales, when effectively blocking undercoordinated surface sites, which act as a defect reservoir. Finally, based on such knowledge, I will discuss different synthetic and passivation strategies which are able to stabilize the perovskite layer towards such photo-induced instabilities, leading to improved optoelectronic material quality and enhanced photo-stability in a working solar cell.

The surface of hybrid perovskites plays a crucial role in the performance and stability of optoelectronic devices, as it strongly influences the recombination rate of excited charge carriers. Recently, it has been reported that molecular ligands such as benzylamine are capable of significantly reducing the surface trap state density in thin films. Here I will report on the mechanism that governs the surface passivation of hybrid perovskites by benzylamine. To this end, we developed a versatile approach to investigate the influence of benzylamine passivation on the well-defined crystal surface of freshly cleaved methylammonium lead tribromide single crystals. We show that benzylamine is capable of permanently passivating surface trap states in these single crystals, resulting in enhanced photoluminescence intensities and charge carrier lifetimes. Additionally, we show that exposure of the perovskite surface to benzylamine leads to replacement of the methylammonium cations by benzylammonium, thereby creating a thermodynamically more stable two-dimensional perovskite $(BA)2PbBr4$ on the surface of the 3D crystal. This conversion from a 3D to 2D perovskite drives an anisotropic etching of the crystal surface, with the $\{100\}$ planes being most prone to etching.
EN09.06.01  
The Photo-Responsive Transfer Property of Perovskite Materials  
Weili Yu; Chinese Academy of Sciences (CAS), China

The fields of photovoltaics, photodetection and light emission have seen tremendous activity in recent years with the advent of hybrid organic-inorganic perovskites. Yet, there have been far fewer reports on the photo-responsive transfer property of perovskite materials. The lateral and interfacial transport requirements of transistors make them particularly vulnerable to surface contamination and defects rife in polycrystalline films and bulk single crystals. Here, we demonstrate a spatially-confined inverse temperature crystallization strategy which synthesizes micrometre-thin single crystals of organometal trihalide perovskite with sub-nanometer surface roughness and very low surface contamination. The photo-responsive transfer property of perovskite materials were investigated and record, room-temperature field-effect mobility in both p and n channel devices were reported, with $10^4$ to $10^5$ on-off ratio and low turn-on voltages. This work paves the way for integrating hybrid perovskite crystals into printed, flexible and transparent electronics.

Reference:

EN09.06.02  
Tailoring Vertical Phase Distribution for High Open-Circuit Voltage and Performance in Quasi Two-Dimensional Perovskite Solar Cells  
Tiefeng Liu and Yinhua Zhou; Huazhong University of Science & Technology, China

Organic-inorganic hybrid perovskites ABX₃ have emerged as revolutionary solar absorbers with power conversion efficiencies rapidly increasing from 3.8% in 2009 to 24.2%. However, perovskite solar cells suffer from poor long-term stability, especially the moisture. Hydrophobic cations such as aliphatic alkylammonium and aromatic alkylammonium have been used to improve the resistivity to moisture, leading to the formation of the quasi 2-dimensional perovskites (A₁)₂(A₂)ₙ₋₁B₂X₃n+1 (where A₁ is large-size bulky organic cation and A₂ is Cs, methylammonium or formamidinium).

Different from their 3D counterparts, previous reports have shown that the fabricated quasi-2D perovskite films are actually a mixture of multiple perovskite phases with different n values instead of a homogeneous perovskite phase with an identical n value. These multiple phases are arranged spontaneously along the direction perpendicular to the substrate from small-n to large-n (from substrate side to the top surface of films). Vertical phase distribution plays an important role in the quasi-2D perovskite solar cells. So far, the driving force and how to tailor the vertical distribution of layer number (n) have been not discussed.

In this work, we report that the vertical distribution of n in the quasi-2D perovskite films deposited on PEDOT:PSS is different from that on glass substrate. The vertical distribution of n could be explained by the sedimentation equilibrium because of the colloidal feature of the perovskite precursors. But the addition of acid will change the precursors from the colloid to solution that therefore changes the vertical distribution. A self-assembly layer of 4-bromobenzenediazonium tetrafluoroborate covalently anchored onto the PEDOT:PSS induces the appearance of desired vertical distribution. The quasi-2D perovskite solar cells (n = 4) with the surface anchoring layer display a higher open-circuit voltage of 1.11 V and a higher efficiency of 13.74% comparing to the reference quasi-2D perovskite cells. The enhanced performance is attributed to the faster charge transport and lower trap densities.

EN09.06.03  
Oriented Attachment as the Mechanism for Microstructure Evolution in Chloride-Derived Hybrid Perovskite
**Thin Films with Enhanced Photovoltaic Performance** Wen Liang Tan¹, Yen Yee Choo¹, Wenchao Huang¹, Xuechen Jiao¹, Jian-feng Lu¹, Yi-Bing Cheng¹,² and Chris McNeill¹; ¹Monash University, Australia; ²Wuhan University of Technology, China

Hybrid organic-inorganic perovskites with appealing opto-electronic properties have attracted significant interest for photovoltaic application. The use of chloride (Cl⁻)-containing precursor species to induce improved perovskite thin-film microstructure and improved optoelectronic properties is well-established. However, the mechanism for the formation of perovskite films with highly textured, micron-sized grains in the presence of Cl⁻ remains elusive. Using synchrotron-based, in situ two-dimensional grazing incidence wide-angle X-ray scattering (GIWAXS) complemented by scanning electron microscopy (SEM) imaging, we present an oriented attachment mechanism via mineral bridge formation for the microstructural evolution of chloride-derived perovskite films. We have identified the crucial role of the oriented chlorine-containing intermediate phase as the mineral bridge, which templates the reorientation of primary, nanoscale perovskite grains followed by fusion into a uniaxial oriented monolithic grain. The resulting perovskite films exhibit micron-sized grains with preferential orientation of the tetragonal (110) direction perpendicular to the substrate with improved solar cell efficiency. Further device physics analysis also shows that highly textured perovskite films exhibit improved charge transport across the interface between the perovskite (110) crystal facet and charge transporting layers (CTLs). Our findings pave the way for rational microstructural design of chloride-derived perovskite films and highlight control of perovskite grain orientation for further exploration of the relationship between perovskite thin film microstructure and photovoltaic properties.

**EN09.06.04**

**Simple Method to Screen New Hole Transport Materials with Organic Small Molecules for Perovskite Solar Cell Application by First Principles** Eunhwan Jung, Feray Uenlue, Alexander Moellmann, Heechae Choi and Sanjay Mathur; University of Cologne, Germany

Perovskite solar cells (PSCs) have attracted considerable attention due to their outstanding power conversion efficiency (PCE) as high as 24.2%. A conventional PSC consists of electrode, hole transport material (HTM), electron transport material (ETM), and a conductive substrate. HTMs, among them are of importance component for high performance PSCs due to their efficient hole extraction, transportation, and blocking the electron transfer to the electrode. The major concern for HTMs is the materials used, especially spiro-OMeTAD which may be prone to degradation. Therefore, developing novel HTMs to replace spiro-OMeTAD is required to enhance the stability and efficiency of PSCs. Here, we present DFT calculations combined with the Marcus theory to investigate the electronic and charge transport properties of porphyrin-based HTMs and device performance containing these materials. Based on the calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level of reference molecules, we screened molecules which can be suitable alternatives to spiro-OMeTAD. Among them, tetraphenylporphyrin (TPP) shows the most promising properties which are relatively low HOMO and high LUMO energy level that facilitate comparably high open-circuit voltage and low reorganization energy and high transfer integral ensuring high hole mobility. TPP was synthesized and utilized as a HTM in solar cell device. Interestingly, the PCE of TPP was shown to be comparable to that of spiro-OMeTAD. Here we proposed new strategy to develop novel organic small molecules as HTMs by DFT calculation for stable and efficient PSCs and showed TPP may become one of promising alternatives to spiro-OMeTAD.

**EN09.06.05**

**Relationship between the Nature of Monovalent Cations and Charge Recombination in Metal Halide Perovskites** Katelyn Dagnall¹, Benjamin J. Foley¹, Joshua Choi¹ and YingZhong Ma²; ¹University of Virginia, United States; ²Oak Ridge National Laboratory, United States

In this study, the effect of the monovalent cation on monomolecular and bimolecular recombination rate constants in halide perovskites (HaPs) was investigated. Based on ultrafast optical measurements on HaP thin films with consistent morphology and trap site densities, our results reveal a key insight: the monovalent cation plays a different role in monomolecular and bimolecular recombination mechanisms; indicating that this remarkably customizable optoelectronic material may be more tunable than previously thought.

**EN09.06.06**

**Understanding Methylamine-Induced Phase Transitions in Hybrid Perovskites and Their Impact on Film Quality and Composition** Jonathan K. Meyers, Lorenzo Serafin and James F. Cahoon; University of North
Lead halide perovskites (LHPs) continue to rise with promise for efficient optoelectronic applications including photovoltaics. A wide variety of deposition techniques and treatments have been developed for LHPs with the goal of improving crystallization and thus efficiency and stability. Of particular interest to us is the exposure of perovskite films to methylamine gas. Such treatment has been shown to liquefy the film and dramatically decrease grain boundary defects in the treated film, especially at elevated temperatures. To better understand this reaction, we applied in-situ UV-visible spectrophotometry in controlled conditions of temperature and methylamine gas pressure to obtain a quantitative phase diagram highlighting solid, solid intermediate, and liquid phases. In this presentation, we discuss the impact of forcing crystallization along paths through this phase diagram in a unique system with no foreign solvent. Additionally we stress the importance of the liquid-substrate interaction as evidenced by contact angles measured between liquid perovskite and various substrates. Lastly, we extend these findings and methods to the two-dimensional system of butylammonium lead iodide and demonstrate controllable partial conversion. These insights may lead to more rational tuning of crystal quality, grain size, and hybrid 3D/2D properties.

EN09.06.07
Defect Tolerance in All-Inorganic Halide Perovskite PV Materials Chen Ming and Yi-Yang Sun; Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

The success of halide perovskites has often been attributed to their defect tolerance. While there have been a number of studies showing that intrinsic defects in organic-inorganic hybrid halide perovskites tend to exhibit shallow defect levels only, whether such a conclusion can be extended to pure inorganic perovskite semiconductors is still an open question. In particular, in the past several months, pure inorganic perovskite solar cells have been demonstrated to achieve appealing efficiency (~17%). In this work, we systematically investigate the intrinsic defects in representative halide perovskites. We will present the results obtained with hybrid density functional including spin-orbital coupling (SOC) effect using large supercells with an aim of concluding the existence of defect tolerance based on the state-of-the-art computational technique. Several possible origins of the defect tolerance, including the SOC, the unusual bonding nature of the band edge states and the competition between ionicity and covalency will be discussed.

EN09.06.08
Pressure-Induced Crystallization of Halide Perovskites for High-Performance Photodetector Do Hyung Chun and Jong Hyeok Park; Yonsei University, Seoul, Korea (the Republic of)

Thanks to numerous studies focusing on enhancing performances of organic-inorganic halide perovskite (OIHP)-based photoelectronic devices, the impressive improvements have been reported. Representatively, since the emergence of OIHP-based photovoltaics in 2012, the powerconversion efficiency (PCE) of OIHP-based photovoltaics exceeds 24% nowadays. As strategies to enhance performance, compositional, interfacial engineering and developing novel deposition methods are utilized. However, as growth in the PCE has stagnated by 20%, another method is required for tuning intrinsic properties of OIHPs to ultimately overcome the hurdles, which block the way toward commercialization.

In this work, we suggest pressure-induced crystallization process as a technique for improving performance of OIHP-based photoelectronic devices by engineering intrinsic properties of OIHPs. As high-quality OIHP films can be fabricated with annealing anti-solvent washed intermediate-state, we exerted pressure during crystallization process with nanostructured polymer molds. By pressing OIHP films during annealing, nanostructures of OIHP films are controlled. By pressing the pre-crystallized film with intaglio nanohole-arrayed polyurethaneacrylate (PUA) molds, nanopillar structure emerges on the surface of OIHP films. Because of the aligned surficial nanostructure of OIHP films, light scattering effect was observed on the surface of OIHP films, which are induced by photonic crystal effect. Also, nanopillar arrays were clearly observed with scanning electron microscopic (SEM) and atomic force microscopic (AFM) images.

With nanopillar-structured OIH films, we developed 2-terminal photoconductors to confirm improved photoelectronic characteristics after the process. Firstly, we measured current-voltage (I-V) characteristics of devices employing OIH films, which exhibited increased photocurrent and decreased dark current and responsivity and detectivity are enhanced by an order. Furthermore, motivated by the fact that pressure-induced crystallization process contributes to improve OIH film quality, we analyzed trap-density and electrical properties with conductive AFM (c-AFM) and revealed that trap-density of film was reduced and electrical conductivity was
significantly enhanced. In conclusion, we fabricated a nanopillar structure on the surface of OIHP film through applying simple soft imprinting technology and confirmed the advantages of the process by investigating photophysical properties of films. Considering that the process we suggested can be conducted with low cost and high reproducibility, the pressure-induced crystallization process can be a promising solution that can overcoming recent stagnation in terms of OIHP-based device performance.

EN09.06.09
Fabrication of Cesium Lead Bromide Thick Films with Closely-Packed Columnar Crystals and High Carrier Mobility by Using a Mist Deposition Method Yuki Haruta, Takumi Ikenoue, Masao Miyake and Tetsuji Hirato; Kyoto University, Japan

X-ray imaging is an important technique used for medical imaging and the nondestructive inspection of industrial products. Highly sensitive X-ray detectors which enable X-ray imaging at low dose are strongly required to reduce the risk of cancer. Lead halide perovskites (APbX₃; A = CH₃NH₃⁺, Cs⁺, X = Br⁻, I⁻) are promising candidates for X-ray detectors due to their excellent physical properties including high absorption coefficients, high carrier mobility, and long carrier diffusion length. Y. C. Kim et al.[1] achieved CH₃NH₃PbI₃-based X-ray imaging devices with the high sensitivity of up to 11 μC mGy⁻¹ cm⁻² which is at least ten times as high as the sensitivities achieved with currently used amorphous selenium or thallium-doped cesium iodide detectors. W. Wei et al.[2] reported Si-integrated CH₃NH₃PbBr₃ single crystals for highly sensitive X-ray imaging with the sensitivity of 25 μC mGy⁻¹ cm⁻². The biggest problem of organic-inorganic hybrid perovskites, which is partly composed of an organic cation such as CH₃NH₃⁺, is instability to heat and moisture. To solve this problem, replacing the organic cation by Cs⁺ has been proposed[3]. For X-ray imaging, fabrication of thick CsPbBr₃ films over a large area is required. However, previous methods such as spin-coating are not applicable to the fabrication of CsPbBr₃ films with the thickness of more than 10 μm. Therefore, we are working on the fabrication of thick CsPbBr₃ films by using a mist deposition method. This method is good at large-area film fabrication[4]. In addition, this method seems to have potentials for the increase of film thickness by repeating fabrication process because a precursor solution is atomized and the mist is injected to the pre-heated underlying film, resulting in fast solvent-evaporation and the growth of the film without remarkable dissolution damages.

In this conference, we report the fabrication of thick CsPbBr₃ films with the thickness of 100 μm. The influence of substrate temperature and deposition rate on the orientation of CsPbBr₃ films were mainly investigated. At optimized fabrication conditions, the obtained CsPbBr₃ thick films were composed of columnar crystals and had high carrier mobility of 28 cm² V⁻¹ s⁻¹, which is comparable to that for single crystals.


EN09.06.10
The Role of the Substrate in Perovskite Precursor Thermal Evaporation Deposition Benjamin Ecker, Ke Wang and Yongli Gao; University of Rochester, United States

The energy level alignment that occurs at the interfaces in planar-hetero structured perovskite photovoltaic devices strongly influences the charge transport across the interface, and thus plays a crucial role in overall device performance. To directly observe the energy level alignment requires pristine homogeneous surfaces that are free of contamination including adventitious carbon. Coevaporation offers the ability grow perovskite thin films insitu, and the method involves thermally evaporating the perovskite precursors such as PbI₂ and CH₃NH₃I. Some early reports have shown that the perovskite film formation and stoichiometry are problematic at ultralow coverages when the film is just starting to form, often times it was reported that there was excess PbI₂ and a deficiency in CH₃NH₃I. Using photoemission spectroscopy, we investigated the perovskite precursors PbI₂ and CH₃NH₃I on gold and highly oriented pyrolytic graphite (HOPG) surfaces. Results show that the nature of the surface and the deposition conditions can strongly influence the film formation. Excessive iodine observed in the initial evaporation stages appears to be substrate dependent, and this may influence the overall energy level alignment.

EN09.06.11
Experimental and Computational Investigation of Sulfur-donor Solvents for Hybrid Organic-Inorganic
Perovskite Processing Oluwaseun Romiluyi; Johns Hopkins University, United States

The ability to be processed in solution, provides Hybrid Organic-Inorganic Perovskite (HOIP)-based solar cells a unique cost advantage over existing technologies for materials like silicon, chalcogenides or III-Vs. However, while the morphology of the final crystalline thin film is known to be heavily influenced by solvent selection, these effects remain poorly understood. Further, experimental routes to study the nucleation and early stage growth of these materials are limited in resolution and scope. In contrast, molecular simulation models and techniques have a significant role to play in this endeavour by providing exquisitely detailed thermodynamic and kinetic information that help uncover how solvent-solute interactions influence the formation of moieties that will ultimately nucleate and grow into thin films. These moieties chiefly include haloplumbate complexes (PbX2\(^{-}\)-PbX\(_6\)\(^{4-}\), where X = Cl, Br, or I). Experimental metrics like the Gutmann Donor Number (DN) have previously been used to predict the formation of these complexes in solution. It has been suggested that higher DN solvent environments limit the formation of higher order haloplumbate complexes (PbX\(_2\)\(^{-}\)-PbX\(_6\)\(^{4-}\)) and delay the nucleation of the perovskite crystal from solution, leading to desirable final film properties. Now, utilizing Density Functional Theory (DFT), we have suggested a DN cut-off value as a solvation threshold to guide the selection of solvents for HOIPs processing. This cut-off predicts whether the formation and distribution of lower order haloplumbates (PbX\(_2\)-PbX\(_4\)\(^{2-}\)) are preferred in certain solvent environments over undesirable, higher order haloplumbate complexes (PbX\(_2\)-PbX\(_4\)\(^{2-}\)). We identified this solvation threshold by comparing the enthalpic preferences of halide complexation to Pb\(^{2+}\) center against the surrounding solvent molecules. Our results identified a range of solvent environments, based on their DN values, that favour solvent coordination to the Pb\(^{2+}\) center over halide ions (Cl\(^{-}\), Br\(^{-}\), and I\(^{-}\)), limiting the rate of nucleation and Pb-X coordination in these solutions. It was revealed that higher DN solvents are required to outcompete halides for complexation to Pb\(^{2+}\) in chloride rich solutions than in solutions rich with bromide and iodide ions, following an electronegativity trend. This predictive model can be used to guide the selection of solvents for specific lead halide environments (PbCl\(_2\), PbBr\(_2\), or PbI\(_2\)) to optimize for an improved final film morphology.

EN09.06.12
Two-Dimensional Lead-Free Inorganic-Organic Hybrid Systems—Structural and Optical Tunability in (R-NH\(_3\))\(_2\)CuX\(_4\) Madhu Bochalya and Sunil Kumar; Indian Institute of Technology Delhi, India

Two-dimensional inorganic-organic (2D-IO) hybrid systems are Ruddlesden-Popper phase-like materials which can be tailor-synthesized to achieve desired and tunable thermoelectric, optoelectronic and multiferroic properties. The lead-free inorganic-organic hybrids are the demand of the day for real life applications. Much importantly, these 2D-IO hybrids are easy to synthesize and have shown excellent structural and chemical stability against heat, humidity, temperature and external environment conditions as compared to other inorganic-organic hybrid counterparts. We have investigated tunability in the structural and optical properties of solution processed lead-free 2D-IO hybrids, the (C\(_{12}\)H\(_{25}\)NH\(_3\))\(_2\)Cu(Cl\(_{1-x}\)Br\(_x\))\(_4\) and (C\(_6\)H\(_9\)C\(_2\)H\(_4\)NH\(_3\))\(_2\)Cu(Cl\(_{1-x}\)Br\(_x\))\(_4\) systems. (C\(_{12}\)H\(_{25}\)NH\(_3\))\(_2\)Cu(Cl\(_{1-x}\)Br\(_x\))\(_4\) systems show uniform crystalline phase for all the compositions 0 \(\leq x \leq 1\), whereas (C\(_6\)H\(_9\)C\(_2\)H\(_4\)NH\(_3\))\(_2\)Cu(Cl\(_{1-x}\)Br\(_x\))\(_4\) exhibit binary crystalline phase for the composition 0 \(\leq x \leq 1\) through the splitting of (00\(_l\)) diffraction peaks. The optical properties are primarily determined by the metal-halogen network of the 2D-IO hybrids. Raman modes are related to the buckling of distorted CuX\(_6\) (X = Cl or Br) octahedral in both of the 2D-IO systems. The Raman vibration frequencies show red-shift by the replacement of higher electronegative Cl atoms with lower electronegative Br atoms due to the reduced bonding strength of Cu-X vibrations. The vibrations related to asymmetric (1582 cm\(^{-1}\)) and symmetric (1490 cm\(^{-1}\)) deformation of NH\(_3\)-X bands also systematically redshift towards lower wavenumbers with the increasing Br/Cl ratio in both types of systems. The optical absorption of 2D-IO systems is nearly independent of the organic part and show a systematic shift in the optical features including the band-edge as a function of increasing Br-content.

EN09.06.13
Exploring Photoinduced Dielectric Polarization in Organic-Inorganic Halide Perovskites Yixuan Dou, Miaosheng Wang, Jia Zhang, Hengxing Xu and Bin Hu; The University of Tennessee, Knoxville, United States

Hybrid organic-inorganic perovskites (HOIPs) possess the possibilities of enabling photoinduced dielectric polarization. Photoinduced dielectric polarization plays an important role on suppressing the charge recombination,
facilitating charge transport, and even polarizing excited states, which are critically important to the development of optoelectronic functionalities in HOIPs. However, it is difficult to realize whether photoinduced polarization contains an electrical polarization within the dipolar polarization regime in HOIPs due to lacking the mechanism of coupling dipolar and electric polarization. This issue originates from mobile ions in HOIPs, which results in the difficulty of detecting dielectric polarization. Here, we use capacitance-voltage (C-V) measurement to probe the photoinduced dipolar polarization and then confirm it by the magneto-capacitance measurement. The capacitance-voltage (C-V) detect the dipolar polarization by applying a low alternating bias of 50 mV while the mobile ions are continuously drifted by gradually scanning the bias from -0.1 V to 1.5 V. In this manner, continuously drifted ions cannot respond to the low alternating bias, enabling the detection of photoinduced electrical polarization in dipolar polarization regime. Then, to confirm the photoinduced dipolar polarization, magneto-capacitance was used to solely detect the dipolar polarization at 1 MHz in HOIPs (MA$_x$FA$_{1-x}$PbI$_3$, x in the range of 0-0.75) under photoexcitation. Magneto-capacitance measurement is a signature tool to exclude the effects of mobile ions (i.e. surface polarization) as mobile ions do not respond to magnetic fields. It was found that the photoexcitation can substantially increase the magneto-capacitance amplitude, confirming that the photoexcitation indeed induces dipolar polarization in HOIPs. In summary, our studies provide a fundamental understanding of photoinduced dipolar polarization effects on the optoelectronic functionalities of HOIPs.

EN09.06.14

CsPbBr$_3$ Nanocrystals are Responsible for the Green Emission in Two-Dimensional CsPb$_2$Br$_5$ Chong Wang$^{1,2}$, Yanan Wang$^{2,3}$, Xinghua Su$^{2,4}$, Viktor G. Hadjiev$^5$, Shenyu Dai$^{5,2}$, Zhaojun Qin$^{2,2}$, Hector A. Calderon Benavides$^6$, Yizhou Ni$^2$, Qiang Li$^2$, Jie Jiao$^2$, Md Kamrul Alam$^2$, Haiyan Wang$^7$, Francisco C. Robles-Hernandez$^2$, Yan Yao$^2$, Shuo Chen$^2$, Qingkai Yu$^2$, Guoying Feng$^5$, Zhiming Wang$^9$ and Jiming Bao$^2$; 1Yunnan University, China; 2University of Houston, United States; 3University of Electronic Science and Technology of China, China; 4Chang'an University, China; 5Sichuan University, China; 6Instituto Politecnico Nacional, Mexico; 7Purdue University, United States; 8Texas State University, United States

Two-dimensional highly luminescent CsPb$_2$Br$_5$ has been considered as a promising candidate for optoelectronic applications in recent years due to its stability at various ambient conditions. CsPb$_2$Br$_5$ can be synthesized [1,2] as a green photo-luminescence (PL) emissive material as well as PL-inactive one. This is in part the reason for the controversial results on the band gap and origin of PL reported by different groups [3]. In this work, we present the results of a complex approach to resolve the PL puzzle using the same-spot Raman-PL probe at ambient and high pressure environments. Our study reveals that CsPbBr$_3$ nanocrystals are the origin of the green emission in CsPb$_2$Br$_5$ [4]. The Raman-PL spectra under hydrostatic pressure have ruled out the alternative theory of defect states such as Br vacancies. The pressure-dependent absorption shows that the bandgap of CsPb$_2$Br$_5$ is 0.3-0.4 eV higher than those typically reported. It remains nearly constant with pressure up to 2 GPa in accordance with our DFT calculations [4-6]. We further prove that CsPbBr$_3$:X$_y$ (X = Cl or I) is also responsible for the PL of CsPb$_2$Br$_5$:X$_y$ [4]. Our results open up new opportunities to understand and develop highly efficient inorganic lead halide optoelectronic devices.


EN09.06.15

Photoexcitation Tunable Magnetization at Hybrid Perovskite/ Ferromagnet Interface Revealed by Polarized Neutron Reflectometry Studies Miaosheng Wang$^4$, Hengxing Xu$^4$, Haile Ambaye$^2$, Jong K. Keum$^2$, Valeria Lauter$^2$ and Bin Hu$^1$; 1University of Tennessee, Knoxville, United States; 2Oak Ridge National Laboratory, United States

Hybrid lead halide perovskites are emerging semiconductors which have demonstrated extraordinary performance on photovoltaic and light-emitting devices. Meanwhile, the potential of perovskites for spin-related optoelectronics has just begun to raise up due to the strong spin-orbital coupling (SOC) for efficient spin manipulation by using
optical methods and relatively long spin coherence lifetime for spin-related optoelectronic properties to occur. However, traditional investigations on spintronic devices based on semiconductor/ferromagnet heterojunctions mainly focus on the spin injection and spin transport. The understanding of the magnetism properties at the perovskite/ferromagnet interface remains unclear. By using the depth-sensitive polarized neutron reflectometry studies, we have found that a circularly polarized photoexcitation induces a magnetization into the surface of perovskite (MAPbBr$_3$) film underneath of ferromagnetic Co layer at room temperature. On contrast, a linearly polarized light does not generate any detectable magnetization within the perovskite surface in the MAPbBr$_3$/Co sample during the polarized neutron reflectometry measurement. This observation provides an evidence to show optically induced magnetization on the perovskite surface in contact with Co surface through spin-polarized excited states. Furthermore, the perovskite/Co interface demonstrates a magneto-capacitance phenomenon, indicating that the electrical polarization on perovskite surface is coupled with magnetic polarization on the Co surface. The observed magnetization indicates that circularly polarized light-generated spin states in hybrid perovskite layer can directly interact with ferromagnet Co through electric-magnetic coupling, leading to an optically induced magnetization.

EN09.06.16
Polarizing Light-Emitting States in High-Performance Perovskite LEDs Jiajun Qin$^{1,2}$; $^1$Linkoping University, Sweden; $^2$Fudan University, China

Organic inorganic hybrid perovskites are superior candidates towards EL pumped lasing device, based on their excellent optical gain property and high dielectric constant. However, it is rather challenging due to the low carrier density under electrical operation condition, which requires extremely low threshold for realizing coherent interaction of excited states. Here, we found that, when nanometer-size small grains are used to passivate micrometer-size large grains in perovskite (MAPbBr$_3$) films, the light-emitting states essentially become linearly polarized in the direction of applied electrical field during EL operation. The EL output from the large-grain component in the mixed large/small grains slowly become linearly polarized with the time constant up to 10 seconds at constant bias in electrical field direction in the ITO/PEDOT:PSS/ MAPbBr$_3$/Bphen:PMMA/LiF(0.7 nm)/Ag device. This observation indicates that the light-emitting states in large-grain component with low bandgap gradually become electrically polarized during EL operation. Simultaneously, the EL intensity is progressively increasing with similar time scale at constant bias, showing a self-passivation of grain boundary defects occurring at the interfaces between large and small grains within mixed large/small grains under the influence of electric field. Combining these two phenomena leads to a hypothesis that the self-passivation of grain boundary defects provides the necessary condition to enable the electrically induced polarization of light-emitting states in large-grain component located in mixed large/small grains. This hypothesis is verified by the critical observation: when the grain boundary defects are further decreased by continuously decreasing the size of small grains shown by photoluminescence studies, the electrically induced polarization of light-emitting states in large-grain component is largely increased from 19 % to 29 % in the MAPbBr$_3$ LEDs prepared with mixed large/small grains. Clearly, mixing large/small grains presents an important method to realize electrically induced polarization of light-emitting states in high-performance MAPbBr$_3$ LEDs.

EN09.06.17
Nanoscale 3D Printing of Perovskites Mojun Chen$^1$, Jihyuk Yang$^1$, Zhenyu Wang$^1$, Zaoyi Xu$^1$, Heekwon Lee$^1$, Hyeonseok Lee$^1$, Shien Ping Feng$^1$, Jaejeon Pyo$^2$, Seung Kwon Seol$^2$ and Ji Tae Kim$^1$; $^1$The University of Hong Kong, China; $^2$Korea Electrotechnology Research Institute, Korea (the Republic of)

Winning high performance materials is the most important challenges in modern 3D printing technology. The excellent material properties and low-cost production of organic-inorganic metal halide perovskites make them promising building blocks for fully integrated optoelectronics devices$^{1,2}$. The practical realization of perovskite devices necessitates a high-precision control over the shape, composition and crystallinity. Many clever nanofabrication methods$^{1-5}$ have been devised to shape perovskites, however, it is still limited to in-plane and low aspect ratio with simple forms. To satisfy the demands for cutting-edge optoelectronics$^{6-8}$ with freeform circuitry and high integration density, we developed a nano-precision three-dimensional (3D) printing for organic-inorganic metal halide perovskites. The 3D printing method uses a femtoliter ink meniscus to guide evaporation-induced crystallization in mid-air, fabricating freestanding 3D perovskite nanostructures with a preferred crystal orientation. Stretching the ink meniscus with pulling process enables on-demand control of the nanostructure's diameter and
hollowness, leading to an unprecedented tubular-solid transition. By varying the pulling direction, we successfully demonstrated a layer-by-layer stacking of perovskite nanostructures with programmed shapes and positions. In this talk, we will present our results and discuss the prospects of our work for potential applications in customized, freeform optoelectronics.

References:

EN09.06.18

**Magneto-Optical Properties of Dilute Magnetic Lead-Halide Perovskite Semiconductors**

Timo Neumann and Felix Deschler; University of Cambridge, United Kingdom

Dilute magnetic semiconductors (DMS) constitute a material class which combines semiconducting properties with long-range magnetic order by introducing a substantial amount of magnetic dopants with unpaired spins to an otherwise non-magnetic host semiconductor. Fully inorganic DMS have been known for decades and advanced material processing techniques have enabled control over spin injection and the control of magnetism by electric fields and currents, yet only at cryogenic temperatures.

Due to their outstanding optoelectronic properties and high defect tolerance, organo-metal halide perovskites provide an ideal system for efficient magnetic doping. We induce long-range magnetic order in lead-halide perovskite by partially substituting lead with manganese and copper, using simple solution and solid state processing techniques. We perform temperature and magnetic field dependent magnetometry to characterise the magnetic ordering mechanisms of the material system. Polarisation-dependent, low temperature magneto-photoluminescence measurements reveal coupling between localised magnetic impurities and optically excited charge carriers, towards optical control of spin-states.

EN09.06.20

**Facet-Dependent Negative Light-Poling Effect on Organo-Lead Halide Perovskite**

Kijoon Bang¹, Taehoon Kim², Ki Tae Park², Young Ho Chu², Mansoo Choi¹² and YunSeog Lee²; ¹Global Frontier Centers for Multiscale Energy System, Korea (the Republic of); ²Seoul National University, Korea (the Republic of)

Organo-lead halide perovskite is promising candidate material class for various optoelectronic applications including solar cells due to excellent charge transport properties and defect tolerance. Although its record high efficiency is reaching 24.2%, understanding of its photo-physical properties and operating mechanism of solar cell still needs further investigations. In particular, abnormal built-in potential across illuminated MAPbI₃ perovskite surface has been reported by a number of studies, and ion migration and lattice poling have been suggested as possible origins. However, investigations on polycrystalline perovskite thin-films often possess limitations on correlating internal charge separation mechanism with lattice structure due to the high degree of structural defects as well as an uncontrollable crystal orientation.

In this study, single-crystal perovskite is investigated to provide single domain which enable facet-dependent characterization of the charge behavior such as change in electrical polarization. We scrutinize the aspect of facets of the single-crystal perovskite by employing Kelvin probe force microscopy. Simultaneous changes in surface potential in response to illumination and transient pulsing are measured and analyzed quantitatively. On (100) and
(112) plane, light induced poling effect inversely affects potential as fermi level is shifted under light. We also quantify the relation between the magnitude of the poling and angle of MA-I bond from the surface measured. Absence of electrical polarization effect perpendicular to (110) plane manifests MA-I bonds are realigned when light is shed upon. Finally, growth of MaPbI3 (110) plane on crystalline substrate is suggested to enhance the structural stability against illumination as well as optoelectronic properties.

EN09.06.21
Investigation of Formamidinium Lead Iodide Perovskite Nanocrystal Synthesis Kinetics Using Droplet-Based Microfluidics and Real-Time Fluorescence Lifetime Analysis

Julie Probst1, Stavros Stavrakis1, Maksym V. Kovalenko1,2 and Andrew J. deMello1; 1ETH Zurich, Switzerland; 2Empa – Swiss Federal Laboratories for Materials Science and Technology, Switzerland

A fundamental understanding of the nucleation and growth processes involved in synthesis of lead halide perovskite nanocrystals (NCs) is unrealized, due to the rapidity of the associated reaction kinetics. Accordingly, an ability to probe such processes on timescales below 100 ms is required. Microfluidic systems integrating real-time optical detection modules enable such observations, and thus are preferred over traditional flask-based environments. Indeed, microfluidic reactors have been used for the controlled synthesis of a variety of nanoscale materials, allowing the fast and efficient exploration of the lead halide perovskite NCs reaction parameter space. More specifically, droplet-based microfluidic systems offer many advantages over classical flask-based synthesis methods through the precise control of reagent concentrations, reaction times and temperatures. Herein, we describe an optofluidic platform for the real-time monitoring of the fast nucleation and growth kinetics associated with the formation of formamidinium lead iodide perovskite (FAPbI3) NCs on μs - ms timescales. This platform integrates in-line photoluminescence (PL) and time-correlated single photon counting (TCSPC) modules, for extraction of intensity, spectral and fluorescence decaytime information during nucleation and growth. The high temporal resolution of the platform enables facile monitoring of early time processes, with deadtimes as small as 3 ms. Real-time assessment of NC fluorescence decaytime kinetics at early times during nucleation provides additional contrast to conventional time-integrated fluorescence emission measurements. The experimental set-up consists of two parts: a microfluidic platform for fast droplet generation and precise temperature control, and an integrated optical detection system, allowing both optically-sectioned TCSPC and PL measurements. The optical properties of the early time FAPbI3 NCs were investigated at room temperature by conducting time-dependent analyses between 3 and 280 ms. As the reaction progresses, we observe that the PL peak shifts to the red, with the emission intensity increasing dramatically over the first 300 ms. This confirms that the kinetics governing NC nucleation and growth are indeed very fast, and thus access to early reaction times is critical. The evolution of fluorescence decays with reaction time indicates equally fast reaction kinetics, with a progression towards longer lifetimes. We also investigated the effect of reaction temperatures (up to 60°C) on the PL spectra and decays associated with early-time NCs, whilst keeping all the other experimental conditions constant. An increase in temperature resulted in a faster and further red shift in the photoluminescence maximum, corresponding to larger NCs being formed at higher temperatures. Remarkably, data show for the first time the observation of transient FAPbI3 NCs species emitting at 558 nm, well below the reported value (790nm) for fully-grown FAPbI3 NCs. In summary, we report a novel platform for early-stage, in-line characterization of the nucleation and growth of FAPbI3 NCs using droplet-based microfluidics. We believe that this platform will allow for a deeper understanding of the fast reaction kinetics associated with perovskite NC synthesis, and for superior engineering of the optical and electronic properties of these materials.

References


EN09.06.22
Spatially Resolved Carrier Dynamics at MAPbBr3 Single Crystal-Electrode Interface

Mahshid Ahmadi1, Liam Collins2, Katherine N. Higgins3, Eric Lukosi3 and Sergei Kalinin3; 1University of Tennessee, United States; 2Oak Ridge National Laboratory, United States; 3The University of Tennessee, United States

Beyond the admirable photovoltaic properties, the unique opto-electrical properties of organic-inorganic halide
Perovskites (OIH) combined with their relatively low-cost production, have made this class of materials a great candidate in photodetectors$^1$, LEDs$^2$, and radiation sensors$^3$. The remarkable progress has driven accelerated efforts to further improve the performance and stability of these materials. However, the phenomenological applications have greatly outpaced the fundamental understanding of the physical processes which govern the material’s electronic behavior. Key among those are at the electrode interface$^4, 5$. Exploiting the coupled electronic and ionic properties of these materials requires exquisite control over the electrode contact region. Development of strategies for realizing reliable contacts have been key to the success of semiconductor device fabrication, whereas this challenge is magnified for materials with mixed ionic and electronic carriers like OIHs. In addition, we have shown that OIHs consist of volatile elements like halides, which can react with the metallic electrode leading to the interfacial doping$^6$. Charge injection at electrode-OIHs interface may induce interfacial trapped states and recombination regions leading to unfavorable effect on charge collection efficiency,$^7, 8$ induce electrochemical reactions and result in interfacial degradation$^6, 8$. Research has shown that the onset of electrochemical reactions and degradation in OIH devices under long term operating conditions is at the electrode interface$^5$. Recently, we demonstrated that the triple phase boundary between electrode, bulk, and environment can affect the charge transport properties of MAPbBr$_3$ devices$^9$.

The lack of understanding stems largely from the lack of appropriate tools to capture the electrochemical dynamics on the length scales of the local inhomogeneities and time scales over which the coupled dynamics take place. We implemented time resolved Kelvin probe force microscopy (tr-KPFM) to explore the spatial and temporal charge dynamics at MAPbBr$_3$ devices$^{10, 11}$. Here, the temporal dynamics of the electric field and charge distribution at the electrode interface is visualized by tr-KPFM mapping. The results demonstrate an interplay of several phenomena, including charge injection, recombination and ion migration, leading to an unbalanced charge dynamic in MAPbBr$_3$-Au interface under forward and reverse biases, explaining the origin of the current-voltage hysteresis in these devices. We contrast the bias assisted charge dynamics under both illuminated and dark conditions, providing a comprehensive picture of overall carrier dynamics and interface properties in MAPbBr$_3$ with lateral Au electrodes. Remarkably, illumination leads to formation of a wider space charge region due to accumulation of negative charges (electrons and halide ions) at the positive electrode, which can effectively screen the external electric field leading to lower charge collection efficiency. The results suggest that the choice of contact or interfacial engineering can control the performance of OIH devices without requiring modification of the material’s bulk properties.


EN09.06.24
First Principle Modeling of CsPbBr$_3$-CuI Interfaces for Light Emitting Applications

Eric W. Welch and Alex Zakhidov; Texas State University, United States

The interface between CsPbBr$_3$ and CuI is studied using density functional theory and band offset calculations to explore the most likely atomic configuration and charge redistribution as a function of the number of atomic layers. The surface and interface energies for the (100) surfaces are calculated for the two terminations in CsPbBr$_3$ (CsBr and PbBr$_2$ termination) and CuI (Cu and I termination) using the bond cleaving method; eight unique interfaces exist between CsPbBr$_3$ and CuI. PbBr$_2$ on Cu termination with Br bonded to Cu and PbBr$_2$ on I termination with Pb bonded to I are found to be the low energy interfaces. The potential barrier between the layers decreases as the system increases from 7 to 9 atomic layers showing a type I band offset with a gradient pointing from CuI into CsPbBr$_3$. This indicates the potential for thin film CuI as a charge transport layer for CsPbBr$_3$ active layer devices.

EN09.06.25
Enhanced Charge Transfer Modulation at Perovskite Quantum Dot/Oxide Interface Mediated by Solvent
Polarity Engineering Shijie Zhan, Bo Hou and Jong Min Kim; University of Cambridge, United Kingdom

Inorganic perovskite quantum dots (QDs), especially CsPbX3 (X=Cl, Br, I), have been intensively studied in solar cells, LEDs and photodetectors due to their high photoluminescence (PL) quantum yield, strong absorption cross section, optical tunability and improved stability [1, 2]. Phototransistors, which are fabricated via hybridizing perovskite QDs, have been reported to have high responsivity and detectivity [3, 4]. However, perovskite QDs passivated with oleic acid (OA) ligands make it difficult to have efficient charge transport from QDs to the channel material in a phototransistor, which results in large hysteresis and low signal to noise ratio (SNR). In this work, charge transfer at the interface of CsPbBr3 QDs and Indium gallium zinc oxide (IGZO) was studied based on the platform of QD/IGZO phototransistors. By systematically controlling the displacement of OA in the CsPbBr3 film mediated by solvent polarity engineering, the performance of QD/IGZO phototransistors were remarkably improved. The responsivity of the QD/IGZO phototransistors were enhanced to 8 times larger than the reference samples. The SNR was also boosted from 1 magnitude to more than 6 magnitude. These performance improvements indicate the charge transfer enhancement at the CsPbBr3/IGZO interface, which was further confirmed through the stationary and time resolved PL analysis associated with exciton quenching dynamics.


EN09.06.26 Interplay between Resistive Switching Performance and Interlayer Spacing in Layered Perovskites So-Yeon Kim, June-Mo Yang, Eun-Suk Choi and Nam-Gyu Park; Sungkyunkwan University, Korea (the Republic of)

We report here effect of interlayer spacing in 2-dimensional (2D) layered perovskites (LPs) of [C₆H₅(CH₂)ₙNH₃]₂PbI₄ (anilinium (An) for n = 0, benzylammonium (BzA) for n = 1 and phenylethylammonium (PEA) for n = 2) on resistive switching performance. Interlayer spacing was increased from 6.98 Å to 13.29 Å for (An)₂PbI₄, 14.20 Å for (BzA)₂PbI₄ and 15.92 Å for (PEA)₂PbI₄ as chain length was increased as revealed by X-ray diffraction (XRD), where monolayer of organic cation is intercalated between inorganic PbI₄₂⁻ layers. Memristor devices were fabricated with the structure of Ag/ PMMA (polymetylmethacrylate)/ LP/ Pt. All these samples showed bipolar switching behavior, where the devices underwent the abrupt SET process near +0.2 V and the gradual RESET process within -0.5 V. Devices were operated by ohmic conduction in low resistance state (LRS, ON state) and hopping conduction in high resistance state (HRS, OFF state). ON/OFF ratio, which means the ratio of LRS (ON state) to HRS (OFF state), was increased from 10⁶ to 10⁸ as interlayer spacing was enlarged due to gradual increase in resistance at HRS, associated with insulating properties enhanced with interlayer. Although endurance and retention were slightly improved from 1.3×10⁶ cycles and 2×10⁶ s for (An)₂PbI₄ device to 2.2×10⁷ cycles and 5.5×10⁶ s for (PEA)₂PbI₄ device, this negligible increment was related to intralayer filament formation pathway.

EN09.06.27 Phase Transition Induced Carrier Mass Enhancement in 2D Perovskites Revealed by High Magnetic Field Optical Spectroscopy Michal Baranowski1,2, Szymon Zelewski2, Mikael Kepenekian3, Joanna Urban1, Alessandro Surrente1, Duncan Maude1, Agnieszka Kuc4, Edward Booker5, Samuel D. Stranks5 and Paulina Plochocka1; 1Laboratoire National des Champs Magnétiques Intenses, France; 2Wroclaw University of Science and Technology, Poland; 3Univ Rennes, ENSCR, INSA, France; 4Helmholtz-Zentrum Dresden-Rossendorf, Germany; 5Cavendish Laboratory, United Kingdom

Organic–inorganic halide perovskites have become the “next big thing” in emerging semiconductor materials, with their unprecedented rapid development and successful application in high-performance photovoltaics. Yet, their inherent instabilities, notably in the presence of moisture, remain a crucial challenge for these materials. This has focused the interest of the scientific community on perovskite derivatives such as 2D perovskites. These materials...
are significantly more stable and possess a higher tunability of their properties significantly expanding the field of their application from energy harvesting through LEDs to single material white light emitters. The variety of possible ways to tune the optical properties of 2D perovskites is their huge advantage, while at the same time, the mutual dependence between different tuning parameters hinder our fundamental understanding of their properties. In this work we attempt to address this issue for (C$_{n}$H$_{2n+1}$NH$_{3}$)$_{2}$PbI$_{4}$ (with n=4,6,8,10,12) by means of optical spectroscopy in magnetic field up to 67T. Our experimental results, supported by DFT calculations, clearly demonstrate that the reduced mass of the exciton increases by around 30% in the low temperature phase. This is reflected by a 2-3 fold decrease of the diamagnetic coefficient. Our studies show that the effective mass which is essential parameter for optoelectronic device operation can be tuned by the variation of organic spacers and/or moderate cooling achievable using Peltier coolers. In addition, we show that often observed complex features of absorption and transmission spectra track each other in magnetic field providing strong evidence for the phonon replica nature of the observed side bands.

EN09.06.28
High-Performance Solution-Processed Organo-Metal Halide Perovskite Resistive Memory Devices in Cross-Point Array Structure Keehoon Kang, Heebeom Ahn, Younggul Song, Woocheol Lee, Junwoo Kim, Youngrok Kim, Daekyoung Yoo and Takhee Lee; Seoul National University, Korea (the Republic of)

Ion migration has been one of the most important effects to be considered for organo-lead halide perovskite optoelectronic devices since it can significantly affect the long-term device stability and performance [1]. On the other hand, the mobile nature of the ionic defects in perovskite materials has opened up possibility for implementing new device functionalities such as neuromorphic and memory devices. Especially, resistive memory devices based on organo-metal halide perovskite materials have recently shown outstanding performances; a low-voltage operation enabled by an ease of ion migration and a high ON/OFF ratio which are essential for realizing low-power consumption memory. In this presentation, we report unipolar resistive memory devices in a cross-point array architecture made by using a non-halide lead source to deposit perovskite films via a simple single-step spin-coating method [2]. Our perovskite memory devices achieved a high ON/OFF ratio up to 10$^{6}$with a relatively low operation, a large endurance, and long retention times. In addition, we discuss a potential resistive switching mechanism for our perovskite memory devices which exhibit a unique unipolar (non-polar) resistive switching unlike the previously reported perovskite memory devices. Furthermore, a direct demonstration of one-diode-one-resistor scheme using our cross-point perovskite memory devices achieved a selective operation of memory cells connected via external diodes. These results, combined with a high-yield device fabrication based on solution-process demonstrated here, will contribute towards developing low-cost and high-density practical perovskite memory devices.

Reference

SESSION EN09.07/EN10.08: Joint Session: Physics of Perovskite Materials
Session Chairs: Joseph Berry, Tzung-Fang Guo, Bin Hu and Tae-Woo Lee
Wednesday Morning, December 4, 2019
Sheraton, 2nd Floor, Constitution B

8:00 AM *EN09/07.01/EN10.08.01
Exciton Properties in Individual Lead Halide Perovskite Nanocrystals Brahim Lounis; University of Bordeaux, France

Lead halide perovskites have emerged as promising new semiconductor materials for high-efficiency photovoltaics, light-emitting applications and quantum optical technologies. Their luminescence properties are governed by the formation and radiative recombination of bound electron-hole pairs known as excitons, whose bright or dark character of the ground state remains unknown and debated [1, 2]. While symmetry analysis predicts a singlet non-emissive ground exciton topped with a bright exciton triplet, it has been predicted that the Rashba effect may reverse the bright and dark level ordering.
Spectroscopically resolved emission from single lead halide perovskite nanocrystals at cryogenic temperatures provides unique insight into physical processes that occur within these materials. At low temperatures the emission spectra collapse to narrow lines revealing a rich spectroscopic landscape and unexpected properties, completely hidden at the ensemble level and in bulk materials.

In this talk, I will discuss how magneto-photoluminescence spectroscopy provides a direct spectroscopic signature of the dark exciton emission of single lead halide perovskite nanocrystals [3]. The dark singlet is located several millielectronvolts below the bright triplet, in fair agreement with an estimation of the long-range electron hole exchange interaction. Nevertheless, these perovskites display an intense luminescence because of an extremely reduced bright-to-dark phonon-assisted relaxation [4]. Resonant photoluminescence excitation spectroscopy allows the determination of the optical coherence lifetimes in these nanocrystals and to assess their suitability as sources of indistinguishable single photons [5].

References:

8:30 AM *EN09.07.02/EN10.08.02
Charge-Carrier Recombination and Photon Recycling in Bulk and Quasi-2D Metal Halide Perovskites Laura Herz; University of Oxford, United Kingdom

Organic-inorganic metal halide perovskites have emerged as attractive materials for solar cells with power-conversion efficiencies now exceeding 23%. As these devices are approaching the Shockley-Queisser limit, bimolecular (band-to-band) recombination will dominate the charge-carrier losses, with trap-mediated charge recombination becoming less prominent.

We show that in methylammonium lead triiodide perovskite, bimolecular recombination can be fully explained as the inverse of absorption,[1] and exhibits a dynamic that is heavily influenced by photon reabsorption inside the material.[2,3] Such photon recycling is shown to slow charge losses from thin hybrid perovskite films, depending on light out-coupling.[2] Interestingly, for thin films comprising a quasi-two-dimensional (2D) perovskite region interfaced with a 3D MAPbI₃ perovskite layer the blue-shifted emission originating from quasi-2D regions overlaps significantly with the absorption spectrum of the 3D perovskite, allowing for highly effective “heterogeneous photon recycling”. We show that this combination fully compensates for the adverse effects of electronic confinement, yielding quasi-2D perovskites with highly efficient charge transporting properties.[3]

In addition, we investigate optoelectronic properties of mixed tin-lead iodide and mixed iodide-bromide lead perovskites. We show how band-gap bowing in tin-lead perovskites is compatible with a mechanism arising from bond bending to accommodate the random placement of unevenly sized lead and tin ions.[4] While tin-rich compositions exhibit fast, mono-exponential recombination that is almost temperature-independent, in accordance with high levels of electrical doping,[4,5] lead-rich compositions show slower, stretched-exponential charge-carrier recombination that is strongly temperature-dependent, in accordance with a multiphonon assisted process. Finally, in the context of silicon-perovskite tandem cells, we discuss the mechanisms underlying detrimental halide segregation in mixed iodide-bromide lead perovskites with desirable electronic band gaps near 1.75 eV.[6]


9:00 AM EN09.07.03/EN10.08.03
Photoluminescence Mechanisms in MAPbBr3 Films with Controlled Crystal Size Natalie Banerji; University of Bern, Switzerland

Organo-lead halide perovskites are excellent candidates for applications in light emitting diodes (LEDs). Methylammonium lead bromide (MAPbBr3) is the most investigated perovskite for visible perovskite LEDs, but its use is still limited by a low photoluminescence quantum yield (PLQY). Efforts to increase the PLQY of this material mainly consist in fine-tuning the morphology and reducing the grain size of the polycrystalline perovskite to the micro- and nanoscale. However, the origins of the increased PLQY with reduced crystal size remain unclear. Here we elucidate the physical processes underlying the light emission of MAPbBr3 thin films using time-resolved spectroscopy.1 A systematic correlation between the enhanced PL properties and the reduction of the crystal size, achieved by using different additives during solution-processing, is observed. The co-existence of free carriers and excitons at low excitation densities is shown in as-cast polycrystalline MAPbBr3 (crystal size of the order of few μm), while only excitons are present at high excitation densities. Using the Burstein-Moss and Saha models, important quantities such as the exciton binding energy, the reduced exciton effective mass and the trap density are estimated. We then explain the increased PLQY upon crystal size reduction by the presence of a bright exclusively excitonic population even at low excitation densities, together with reduced surface trapping thanks to passivation by the additives.


9:15 AM EN09.07.04/EN10.08.04
Ultrafast Electronic Sub-Gap State Dynamics and Exciton Coupling in Hybrid Metal-Halide Perovskites
Franco Camargo1, Tetsuhiko Nagahara1, Sascha Feldmann2, Richard H. Friend2, Giulio Cerrulo1 and Felix Deschler3; 1Politecnico di Milano, Italy; 2University of Cambridge, United Kingdom; 3Technische Universität München, Germany

Metal-halide perovskites show excellent properties for photovoltaic and optoelectronic applications, with power conversion efficiencies of solar cell and LEDs now exceeding 20%. This is unexpected, because these polycrystalline, solution-processed materials are likely to contain a significant density of defects compared to melt-grown semiconductors. Yet, typical effects from defects, such as strong absorption below the bandgap, low open circuit voltage in devices and dominant non-radiative recombination were not observed. In this contribution, we investigate thin films of metal-halide perovskites CH3NH3PbX3 (X = Br,I) with multidimensional optical spectroscopy to resolve the dynamics of band and defect states on ultrafast timescales. We report an unexpected coupling between the band transitions and a continuum of sub-bandgap states, which we report to extend at least 350 meV below the band edge. We explain the comparatively large bleach signal of these dark sub-bandgap states, compared to the levels detected in linear absorption, with oscillator strength borrowing from the band-edge transition. Our results imply that, upon valence to conduction band excitation, the sub-gap states are instantaneously bleached by the presence of charges in the band for the duration of the carrier lifetime and conversely, that almost dark sub-bandgap states can be populated by light excitation. Our findings provide fundamental insights into the photophysical origin of the exceptional defect tolerance of hybrid perovskites materials.

9:30 AM BREAK
10:00 AM EN09.08.01/EN10.09.01
Molecular Engineering of Two-Dimensional Organic-Inorganic Hybrid Perovskites
Letian Dou and Yao Gao;
Purdue University, United States

Semiconductor quantum wells and superlattices, which are usually fabricated through metal-organic chemical vapor deposition or molecular beam epitaxy, are key building blocks in modern optoelectronics. The ability to simultaneously realize defect-free epitaxial growth and to individually fine-tune the chemical composition and band structure of each layer is essential for achieving the desired performance. Such structures are challenging to realize using organic or hybrid materials because of the difficulty of controlling the materials growth. In this talk, I will present a molecular approach to the synthesis of high-quality organic-inorganic hybrid perovskite quantum wells through incorporating widely tunable organic semiconducting building blocks. By introducing sterically tailored groups into the molecular motif, the strong self-aggregation of the conjugated organic molecules can be suppressed, and single crystalline organic-perovskite hybrid quantum wells (down to one mono-layer thick) and superlattices can be easily obtained via one-step solution-processing. Energy transfer and charge transfer between adjacent organic and inorganic layers are extremely fast and efficient, owing to the atomically-flat interface and ultra-small interlayer distance. The 2D hybrid perovskite superlattices are surprisingly stable, due to the protection of the bulky hydrophobic organic groups. The molecularly engineered 2D semiconductors are promising candidates for use in next-generation nanoelectronics, optoelectronics, and photonics.

10:15 AM EN09.08.02/EN10.09.02
Nanoscale and Bulk Perovskite Single-Crystals—Surface Engineering for Efficient LEDs, Photodetectors and Solar Cells
Osman M. Bakr;
KAUST, Saudi Arabia

In colloidal nanocrystal form, lead halide perovskites possess high photoluminescence quantum yields, while in bulk single-crystal form they exhibit long charge-carrier diffusion lengths. However, without proper strategies to diminish crystal surface defects and manage surface quality, the desired characteristics of perovskites cannot be effectively exploited for photovoltaic and optoelectronic devices. Here I discuss novel strategies to passivate the surface defects and improve the surface quality of perovskite nanocrystals and bulk single-crystals, enabling the fabrication of efficient devices. We demonstrate the passivation of CsPbX$_3$-type nanocrystals with molecular ligands and metal dopants leading to stable near-unity quantum yield emitters, as well as efficient blue and red light-emitting diodes (LEDs). We also show the importance of designing crystal growth conditions, such as solvent, temperature, and substrate in order to grow bulk single-crystals with low-defect densities and good surface quality. Depending on the composition, MAPbX$_3$-type single crystals grown (tens of microns thick) under optimal conditions were used to realize: a) very sensitive visible-blind UV-photodetectors with nanosecond response time; and b) single-crystal solar cells with >21% power conversion efficiency. Unlike thin film polycrystalline solar cells, efficient cells with a grain-free single-crystal absorber are an ideal unobstructed system for investigating the device physics and chemistry of perovskites.

10:45 AM EN09.08.03/EN10.09.03
Teaching Halide Double Perovskites to Absorb Sunlight
Adam Slavney$^1$, Bridget Connor$^1$, Kurt Lindquist$^1$, Stephanie Mack$^2$, Linn Leppert$^3$, Jeffrey Neaton$^4$ and Hemamala Karunadasa$^1$; $^1$Stanford University, United States; $^2$University of California, Berkeley, United States; $^3$University of Bayreuth, Germany; $^4$Lawrence Berkeley National Laboratory, United States

Halide perovskites exhibit remarkable properties as solar-cell absorbers, featuring both direct bandgaps suitable for sunlight absorption and long-lived charge carriers beneficial for charge extraction. However, the intrinsic instabilities and high toxicity of these water-soluble lead salts may impede the commercialization of this technology. Notably, even the origin of the materials' superior photophysical properties remains unclear, underscoring the importance of synthesizing and studying functional analogs of the lead perovskites. However, most stable materials...
studied as analogs have displayed weak sunlight absorption and short carrier lifetimes.

We recently introduced halide double perovskites, which can accommodate a much greater range of metals, as solar absorbers. Armed with this substitutional flexibility, we have explored alternative metals that can be incorporated into the perovskite lattice. Studying the electronic differences between the lead perovskites and lead-free double perovskites has shown us how to synthetically tune double perovskites to efficiently absorb sunlight. I will share our understanding of how to manipulate the symmetry and energy of the bandgap transition in these materials through i) dilute impurity alloying, ii) stoichiometric metal substitution, and iii) dimensional reduction. Our recent studies have led us to double perovskites with very similar properties to the lead perovskites, with small bandgaps and long-lived carriers. I will further present a pen-and-paper method for both understanding and predicting halide double perovskite band structures based on orbital symmetry arguments.

11:15 AM EN09.08.04/EN10.09.04
A-Site Cation Composition Effects in Organic-Inorganic Metal Halide Perovskite Quantum Dots—Crystallographic Phase and Particle Ordering Julian A. Vigil1,2, Michael F. Toney2 and Joseph Luther3;
1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States; 3National Renewable Energy Laboratory, United States

Hybrid organic-inorganic metal halide perovskites have demonstrated remarkable properties for thin-film solar absorbers and optoelectronics, including their ease of preparation, compositional tunability, defect tolerance and high charge-carrier mobilities. The promise of these materials has also motivated the development of modified bulk and nanoscale perovskites, including reduced-dimensional perovskites (2D, 1D) and quantum dots (QDs), with emergent optoelectronic properties. Perovskite QDs, in addition to a tunable band gap and high photoluminescence quantum yield, are of interest due to unique physical and structural phenomena such as the stabilization of metastable crystallographic phases. Luther et al. reported the stabilization of the high temperature, low-band gap cubic perovskite phase of CsPbI3 at room temperature in small QD particles via colloidal synthesis (Swarnkar et al. Science 2016, 354, 6308, 92). In addition, alloying of these CsPbI3 QDs with FAPbI3 (yielding Cs1–xFAXbxPbI3) by a simple cation exchange approach allows for access to the full compositional range (i.e. x = 0–1), unlike thin-film fabrication and direct synthesis of bulk Cs1–xFAXbxPbI3 (Hazarika et al. ACS Nano 2018, 12, 10327).

Herein, we report on structural studies of Cs1–xFAXbxPbI3 QD films by synchrotron X-ray techniques. 15-nm Cs1–xFAXbxPbI3 QDs (x = 0, 0.5) were deposited from colloidal solution, by both drop- and spin-casting methods, and investigated by grazing incidence small-angle and wide-angle X-ray scattering (GISAXS/GIWAXS). GIWAXS patterns indicate coherent particle ordering on the substrate for single-layer spin-coated films, while the subsequent ligand exchange and particle overcoating (2–5 layers) leads to reorganization and isotropic ordering of the particles. In addition, drop-casting and slow evaporation of the solvent from the colloidal solution also results in isotropic ordering. Interestingly, the diffraction patterns show evidence of distortion from the originally reported cubic perovskite phase, with significant tetragonal (Cs0.5FA0.5PbI3) and orthorhombic (CsPbI3) character. The distortion and phase contributions across the full range of alloyed Cs1–xFAXbxPbI3 QDs will be reported and discussed.

11:30 AM EN09.08.05/EN10.09.05
Highly Efficient Hybrid Perovskite Nanoparticle Light-Emitting Diodes Using Mixed Cation Young-Hoon Kim1, Sungjin Kim1, Jinwoo Park1, Seung-Hyun Jo1, Hengxing Xu2, Yonghee Lee1, Laura Martínez-Sarti3, Henk J. Bolink3, Young-Woon Kim1, Bin Hu2 and Tae-Woo Lee1; 1Seoul National University, Korea (the Republic of); 2The University of Tennessee, Knoxville, United States; 3Universidad de Valencia, Spain

Hybrid perovskite nanoparticles (PeNPs) have significant potential to be used in perovskite light-emitting diodes (PeLEDs) because of their high photoluminescence quantum efficiency and, facile color tunability and synthesis. However, the highest electroluminescence efficiencies of PeLEDs based on hybrid PeNPs are still much lower than those of PeLEDs based on hybrid perovskite bulk films and all-inorganic PeNPs. Here, we suggest a strategy to improve the electroluminescence efficiency of PeLEDs based on hybrid PeNPs. We passivate the defect states of PeNPs by introducing large organic cation into the formamidinium lead bromide nanocrystals. Based on this high quality PeNPs, we were able to fabricate efficient PeLEDs. Our work provides a promising way to improve luminescent efficiency of the PeLEDs based on hybrid PeNPs.

11:45 AM EN09.08.06/EN10.09.06
Surface Chemistry of Colloidal Cesium Lead Halides Perovskite Nanocrystals and Its Impact on the Characteristics of Blue and Green Perovskite LEDs

Maryna Bodnarchuk; Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Colloidal organic/inorganic lead halide perovskite nanocrystals (NCs) are considered promising blue and green narrow-band emitters for the next-generation light-emitting diodes. High photoluminescence efficiencies are attained in these materials without epitaxial overcoating of the NC surfaces for electronic passivation of the surface states [1]. The major practical bottleneck of these materials relates to their labile surface chemistry. In particular, typically used long chain capping ligands are problematic due to their dynamic and loose binding as well as their highly insulating nature. We have recently rationalized the typical observation of a degraded luminescence upon aging or the luminescence recovery upon post-synthesis surface treatments using a simple surface-structure model, supported by DFT calculations [2]. Healing of the surface trap states requires restoration of all damaged PbX6 octahedra and establishing a stable outer ligand shell. Restoration of such a structure, seen as an increase in the luminescence quantum efficiency to 90-100% and improvement in the overall robustness of CsPbBr3 NCs, was attained using a facile post-synthetic treatment with a PbBr2+DDAB (didodecyldimethylammonium bromide) mixture. In our most recent work [3], we have used DDAB as a sole ligand directly in the synthesis of perovskite NCs. We then used such NCs in LEDs and demonstrate high external quantum efficiencies of up to 3.6% in blue region (460nm) and 10% in the green region (520 nm).

3. Y. Shynkarenko, M. Bodnarchuk et al. submitted

SESSION EN09.09: Thin-Film Formation, Meso- and Nanoscale Structuring
Session Chairs: Samuel Stranks and Yuanyuan Zhou
Wednesday Afternoon, December 4, 2019
Sheraton, 2nd Floor, Constitution B

1:30 PM *EN09.09.01
Resonant Infrared, Matrix-Assisted Pulsed Laser Evaporation—Enabling Hybrid Perovskite Thin Films for Optoelectronics
Adrienne D. Stiff-Roberts, Enrique T. Burraza and Niara Wright; Duke University, United States

Hybrid perovskites with the ability to control spin, charge, and light could establish a new semiconductor technology that is especially useful for optoelectronic devices. While CH3NH3PbI3 (methylammonium lead triiodide, or MAPbI) easily can be solution-processed, the same is not true for hybrid perovskites comprising larger, more complex organic molecules that have incompatible solubility with metal halides. Alternatively, vapor-phase deposition of organic precursors can introduce degradation and make stoichiometric deposition with inorganic precursors more difficult. However, resonant infrared, matrix-assisted pulsed laser evaporation (RIR-MAPLE), a versatile thin-film deposition technique that features aspects of both solution-based and vapor-phase deposition, enables a wide variety of hybrid perovskite thin films that can be difficult to achieve otherwise.

RIR-MAPLE is a variation of pulsed laser deposition that uses a low-energy laser (2.94μm Er:YAG) to vaporize a frozen target matrix (polyalcohol) by resonant absorption in hydroxyl bonds. Hybrid perovskite precursors are dissolved in the target (comprising a mixture of the polyalcohol matrix and polar solvent), released by the matrix vaporization, and gently transferred to the substrate intact. This technique preserves the organic precursor material that is responsible for unique optical properties and enables stoichiometric growth based on the target composition. In addition, by removing solvent via dynamic vacuum throughout the deposition, RIR-MAPLE prevents significant incorporation of solvent in the film. Furthermore, RIR-MAPLE uses very small amounts of each precursor to deposit thin films with thicknesses comparable to other established methods. Thus, the gentle transfer of precursor materials and greater control of precursor delivery have enabled the growth of bulk (3D) [1,2] and layered (2D) [3] hybrid perovskites, including those with larger organic molecules.

This talk will review the development of RIR-MAPLE growth of hybrid perovskite thin films, demonstrating
application to 3D MAPbI and 2D hybrid perovskites (such as oligothiophene- and phenethylammonium-based metal halide perovskites). The research focus is to understand the formation of perovskite films based on precursor delivery from the RIR-MAPLE target. Materials characterization (including X-ray diffraction, atomic force microscopy, scanning electron microscopy, grazing-incidence wide-angle X-ray scattering, and UV-visible absorbance/photoluminescence spectroscopy) will be reported for a variety of RIR-MAPLE growth conditions and material systems.

We gratefully acknowledge support from the Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE), an Energy Frontier Research Center funded by the Office of Basic Energy Sciences, Office of Science within the US Department of Energy.

References:

2:00 PM EN09.09.02
Growth and Formation of Perovskite Structures—Insights Gained through In Situ Synchrotron-Based X-Ray Scattering
M Ibrahim Dar; University of Cambridge, United Kingdom

Over the last decade, the research on perovskite solar cells has been intensively pursued, not only for their many technological applications especially in photonics and optoelectronics but also for their very interesting photophysical properties. The fabrication strategies, which lead to the realization of record power-conversion efficiencies exceeding 24%, involve solution-based deposition approaches. Given the inherent complexity of solution-based bottom-up approaches, it has been extremely challenging to scale-up the promising deposition strategies, owing to the issues associated with uncontrolled growth of the perovskite structures. Therefore, to achieve a good reproducibility and to extend the existing knowledge for the applications of perovskite materials, it is of key importance to gain a fundamental understanding of the mechanism of growth and formation of perovskite structures. Moreover, the enticing optoelectronic properties of perovskites are found to be subervient to the growth, and formation of their structures. Fundamentally, the texture of perovskite films depends on the nucleation and growth and to study these processes, x-ray diffraction (XRD) is undoubtedly the technique of choice. Towards this end, we have investigated the formation of various solution processed perovskite systems using in situ Synchrotron-based x-ray scattering techniques, including grazing incidence wide angle x-ray scattering, grazing incidence x-ray diffraction, and X-ray reflectivity. In my presentation, the fundamental insights gained through structural characterization and their correlation with the efficiency of devices will be discussed.

References
2) Y. Liu, S.Akin, .., M. Ibrahim Dar*, M. Grätzel; Ultra-Hydrophobic 3D/2D Fluoroarene Bilayer-Based Water-Resistant Perovskite Solar Cells with Efficiencies Exceeding 22%. Science Advances, 2019, 5, eaaw2543, DOI: 10.1126/sciadv.aaw2543
4) N. Arora,† M. Ibrahim Dar,‡*, A. Hinderhofer, N. Pellet, F. Schreiber, S. M. Zakeeruddin, M. Grätzel Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20%. Science 2017, 358, 768-771. DOI: 10.1126/science.aam5655

2:15 PM EN09.09.03
Interfacial Effects During Rapid Lamination within MAPbI3 Thin Films and Solar Cells
Wiley A. Dunlap-Shohl, Tianyang Li and David B. Mitzi; Duke University, United States

Although hybrid halide perovskite solar cells (PSCs) have recently reached record efficiency among thin film
photovoltaic technologies, stability of these devices remains a pressing problem for commercialization. Lamination processes represent an attractive means of fabricating PSCs due to their self-encapsulating nature and compatibility with high-throughput manufacturing methods. These techniques often involve high temperature and pressure, which represents an underexplored region of perovskite processing parameter space. In this work, we investigate the behavior of the archetypal halide perovskite, methylammonium lead iodide (MAPbI₃), under elevated temperatures and pressures. We also characterize the interactions of MAPbI₃ with the commonly used electron and hole transport layers (ETL and HTL) SnO₂ and NiOₓ, and find that the latter is particularly susceptible to detrimental interactions at temperatures not far above those commonly used in ordinary perovskite film deposition techniques, with deleterious effects on device performance. SnO₂ can also evince reactions with the perovskite precursor methylammonium iodide, but is more robust than NiOₓ. Applying the above knowledge, we investigate a laminated bifacial device fabrication strategy that mitigates intrinsic and interface-related threats to the perovskite absorber, and report that such devices can reach power conversion efficiencies of >12%. These results not only advance the state of the art in laminated PSCs, but also reveal heretofore unknown interactions in commonplace device architectures that should be taken into account when developing device fabrication schemes.

2:30 PM BREAK

3:30 PM *EN09.09.04
Understanding Solvent-Precursor Interactions and Reactions in Halide Perovskite Solutions Lynn Loo; Princeton University, United States

Hybrid organic-inorganic perovskites (HOIPs) formed from organoammonium iodide and lead iodide precursor solutions are promising materials for photovoltaic applications. While lead polyiodide and lead-solvent complexes formed in solution are intermediates for HOIP crystallization, the influence of solvent choice upon the formation of such intermediates is not well understood. In this talk, I will highlight two examples in which solution chemistries can drastically impact solid-state structural development, and consequently, performance of solar cells that incorporate these films. In the first example, I will show how the formation of lead polyiodides in the precursor solutions is correlated with the basicity of the processing solvent (quantified by Gutmann’s donor number, Dₙ). Solvents with low Dₙ exhibit a strong propensity to form lead polyhalides. We infer that such solvents interact weakly with the lead salt precursor. These solvents favor the precipitation of HOIP single crystals from solution. Conversely, high-Dₙ solvents suppress the formation of lead polyiodides, indicative of strong lead-solvent coordination. Such solvents support the formation of stable precursor solutions for HOIP thin-film processing and may be added in fractional quantities to tune the basicity of the processing solvent. The tunability introduced by high-Dₙ additives provides finer control over perovskite crystallization, post-deposition processability, and the morphology of HOIP active layers for photovoltaic applications. In the second example, I will highlight undesirable side reactions that take place between DMSO, a common Lewis base additive for perovskite processing, with perovskite precursors. We identified two distinct reaction pathways by which dimethylammonium and ammonium are produced as a result of reactions between DMSO and methyammonium cation; contrary to previous reports in the literature, these reactions need not be catalyzed by the presence of formic acid. The presence of these impurities alter the stoichiometry of the precursor solution, and when incorporated in the solid state alters the perovskite structure and optoelectronic properties.

4:00 PM EN09.09.05
Effect of the Integration of a Self-Assembled Monolayer in Perovskite Solar Cell on Passivation and Extraction Olivier Fournier¹,², Claire Darin Bapaume³,², Davina Messou²,⁴, José Alvarez⁵, Laurent Lombet²,³, Muriel Boutevry⁴,², Philip Schulz²,³, Nathanaelle Schneider³,² and Jean Rousset¹,²; ¹EDF R&D, France; ²IPVF, Institut Photovoltaïque d'Ile-de-France, France; ³CNRS, Institut Photovoltaïque d'Ile-de-France, UMR 9006, France; ⁴Institut Lavoisier de Versailles (ILV), Université de Versailles Saint-Quentin en Yvelines, Université Paris-Saclay CNRS, France; ⁵GeePs, CNRS, CentraleSupelec, Université Paris-Sud, Université Paris-Saclay, Sorbonne Université-UPMC Université Paris 06, France

Since 2009, organic inorganic hybrid perovskite materials have appeared as a game changer among the thin films technologies for photovoltaic (PV) purposes. The absorber displays valuable features such as a direct tunable band gap, a high absorption coefficient, good carrier diffusion lengths and an ambipolar conductivity. This accounts for the impressive breakthroughs experienced with this technology which achieved 24.2% power conversion efficiency in 2019 [1].
Yet, the classic architecture for perovskite solar cells (PSCs) consisting of a bilayer of compact and mesoporous TiO₂ (electron transport layer – ETL), perovskite (absorber) and Spiro-OMeTAD (hole transport layer) suffers from various instabilities and from hysteretic behaviors in the J-V characteristic. The defects at the ETL/perovskite interface have been pointed out as a major cause of these features, and a lot of effort is put into interface engineering to sort this out [2]. A common way to work on this issue is to change the nature of the extraction layer, using novel organic (C₆₀-derivatives …) or inorganic (ZnO, SnO₂ …) ETLs. Another complementary approach is to stack interfacial layers with thickness no more than a few nanometers to passivate the defects and tune energy levels at the interface.

Here, we propose a cell architecture using metal oxides as ETL coated with self-assembled monolayers (SAMs) deposited by solution process. The deposition is performed on TiO₂ and ZnO substrates, deposited by spray pyrolysis and atomic layer deposition respectively: after careful cleaning, the substrates are immersed in a solution containing the organic molecules where the formation of the SAM occurs. The functionalized film is obtained after rinsing. Various molecules which differ by their anchoring group (phosphonic acid, carboxylic acid), spacer (alkyl chain, benzyl) or functionalization group (-NH₂, -halide …) are considered. The choice of the acid function influences the grafting of the molecule onto the metal oxide. The Lewis base is used to passivate interfacial defects by curing under-coordinated lead at the interface. Substitution groups on the molecule allow to tune its dipole moment ranging from negative to positive values along the anchoring group-functionalizing group axis. Once the molecule is grafted, it modifies the oxide work function, allowing for a control on band alignment between the oxide and the perovskite. On the one hand, contact angle, x-ray photoemission spectroscopy, Fourier transform infrared spectroscopy and Kelvin probe measurements are used to assess the deposition of the molecular layers and to probe the quality of the films along with their chemical and optoelectrical properties. On the other hand, the effect of the surface modification on the growth of the overlaying perovskite and on the interface are extracted from scanning electron microscopy. The use of wide field time-resolved and spectrally resolved photoluminescence imaging also gives access to precious information regarding the quality of the perovskite films grown on top of these novel layers. The extraction abilities of such architectures are assessed using an appropriate model taking into account the drift-diffusion equation under various fluxes and interfaces with different properties. The integration of such interfacial layers in full devices will also be discussed.

References
References:

4:30 PM EN09.09.07
Highly Sensitive Photodetection by Photomultiplying Halide Perovskite Nanoparticles with a Europium Complex Interfacial Layer Ayumi Ishii1,2 and Tsutomu Miyasaka1; 1Toin University of Yokohama, Japan; 2JST, Japan

Highly sensitive photodetection with large amplified photocurrent (gain) has been generally achieved by photoelectron emission or avalanche effect in inorganic photodetectors such as Si and GaAs, which needs a sufficiently strong external electric field (~100 V). Here, we demonstrate a high-gain and low-voltage photodetector with an organic-inorganic hybrid structure composed of perovskite nanoparticles as visible light absorber embedded at the interface between an organic compound coordinating Europium (Eu-terpy complex) and TiO2 mesoporous film. The devise achieves significantly high incident photon to current efficiency of 290,000% (gain value of 2900) with the highest level of responsivity up to 1289 A/W even under low applied bias -0.5 V and low irradiation light (< 1 mW/cm2), which is more than four orders of magnitude larger than those of inorganic photodetectors. Such high performance of the detector is caused by photomultiplication phenomena at the specific interface composed of the perovskite nanoparticles and Eu complex molecular layers. The perovskite nanoparticles are excited by visible light irradiation, and their electrons transfer to the conduction band of TiO2 under the applied reverse bias, whereas the holes are trapped at the interface between perovskite and Eu complex layers. The trapped holes are accumulated at the interface between perovskite and Eu-terpy complex, which results in buildup of a high electric field at the interface. Finally, a large external tunneling injection of electrons occurs from the Ag electrode, and the incident photon to current efficiency of the device exceeds 105% even under low applied bias -0.5 V. As found here, the devices made with thick perovskite films show slow response to light and therefore, the nanoparticle-based structure or significantly thin layer (<5 nm) of perovskite absorber is critical for achieving high responsivity and large amplified photocurrent.

4:45 PM EN09.09.08
Mechanism of Additive-Assisted Room-Temperature-Processing of Perovskite Thin Films Revealed by In Situ X-Ray Scattering Maged A. Abdelsamie1, Qiwei Han2, Tianyang Li2, Volker Blum2, David B. Mitzi2 and Michael F. Toney1; 1Stanford University, United States; 2Duke University, United States

Perovskite solar cells (PSCs) have attracted enormous attention due to their potential for low-cost fabrication photovoltaic devices on flexible or rigid substrates. While many approaches have been used to control perovskite formation, thermal annealing has been a typical procedure for the state-of-the-art perovskite solar cells, giving rise to additional costs and challenges for applying perovskites in flexible and/or tandem photovoltaics. Recently, thiocyanate containing additives, such as MASCN, have been shown to be candidates for highly efficient room-temperature perovskite processing. [1] Nevertheless, the mechanisms of perovskite formation and crystallization pathways involved in MASCN-additive-processing approach are unclear. Using time-resolved grazing incidence wide-angle x-ray scattering (GIWAXS), we investigate the perovskite formation in situ during spin coating and the subsequent drying process, aiming at revealing the mechanisms of additive-assisted-perovskite-formation.

Time-resolved monitoring of the perovskite thin film formation process reveals the formation of precursor phases on the route of perovskite formation, whereas perovskite formation is dominated by a sol-gel process. Our findings reveal that the nature of the precursor phase and their formation/dissociation dynamics have an impact on the extent of nucleation and growth of perovskite phase affecting the microstructure of the perovskite film. We show that a DMSO-precursor phase is obtained in the as-cast film for the MASCN-free films, whereas an additional (presently unidentified) phase is obtained when adding MASCN to the precursor solution. The latter precursor phase is less stable than the DMSO precursor phase and dissociates shortly upon applying N2 flow on the film leading to fast room-temperature conversion to perovskite. Moreover, MASCN aids in the dissociation of DMSO-precursor phase which decays faster with the presence of MASCN in the wet film. The combination of two precursors with fast and slow decay rates may contribute to the formation of micron-sized perovskite crystals, through seeding perovskite nuclei combined with the slow growth of the perovskite phase. Understanding the mechanism of room-temperature-additive-processing will pave the way for more facile control of perovskite formation, while the use of N2 flow...
provides the suitability for forming perovskite directly on roll-to-roll processing at room temperature without the need for subsequent separate steps.


SESSION EN09.10: Poster Session III: Fundamental Materials Properties and Advanced Characterization of Halide Perovskites III
Session Chair: Laura Schelhas
Wednesday Afternoon, December 4, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EN09.10.01
Pulsed Terahertz Emission from Solution-Processed Lead Iodide Perovskite Films Carlito Jr Ponseca1, Feng Wang1, Arunas Krotkus2 and Feng Gao1; 1Linköping University, Sweden; 2Center for Science for Physical Sciences and Technology, Lithuania

We report pulsed terahertz (THz) emission from solution-processed metal halide perovskite films. The obtained THz electric field from MAPbI3 is just one order of magnitude lower than p-InAs, one of the most efficient semiconductor THz emitters, while for FAPbI3, it is only 5 times lower. The pulsed THz emission is enabled by a unique combination of efficient charge separation, high carrier mobilities, and more importantly the presence of surface defects. The mechanism of generation was identified by investigating the dependence of the THz electric field amplitude on surface defect densities, excess charge carriers, excitation intensity and energy, temperature and external electric field. We also show for the first time THz emission from a curved surface, which is not possible for any crystalline semiconductor and paves the way to focus high-intensity sources. These results represent a possible new direction for perovskite optoelectronics, and for THz emission spectroscopy as a complementary tool in investigating surface defects on metal halide perovskites, of fundamental importance in the optimization of solar cells and light-emitting diodes.

EN09.10.02
Modification of the Electronic Properties of Lead Halide Perovskite Films by Low Energy Ion Irradiation Hironori Ogata, Tomoaki Nishimura, Ryusuke Umeda, Kazunori Ito, Masato Gocho, Toshiya Kobayashi and Yuki Fukazawa; Hosei University, Japan

Perovskite solar cells are an important photovoltaic technology with high efficiencies exceeding 20% due to their optimal band gap, large absorption coefficient, and high charge mobilities. One of these challenges is the understanding and control of their defect structures because perovskite compounds are relatively soft ionic crystals and ions are migrating in the crystals relatively low activation energy.

In this study, we have investigated the effect of low energy ion irradiation to both all inorganic and organic-inorganic lead halide perovskite films on the structure, morphology optoelectronic properties and photovoltaic properties systematically. Several kinds of halogen and hydrogen ion beam irradiations on the perovskite thin film was performed by using a tandem type ion accelerator with changing acceleration voltages and irradiation time. Detailed experimental results will be reported on the conference.

References:

EN09.10.03
Using Ion-Selective Membranes to Study Mobile Cations in Hybrid Organic-Inorganic Perovskite Emily C. Smith, Christie L. Ellis, Hamza Javad, Blaise G. Arden and Dhandapani Venkataraman; University of Massachusetts Amherst, United States

We used an ion selective membrane in conjunction with electrochemical impedance spectroscopy (EIS) to measure
ion transport in methylammonium lead triiodide (MAPbI₃) powder. We placed a methylammonium selective layer in between the active material and the electrode in EIS studies and found evidence of ion transport with a millisecond (ms) time constant under continuous illumination. These values are consistent with reported values of ionic conduction in thin-film perovskite solar cells. Electrospray ionization mass spectrometry (ESI-MS) revealed direct chemical evidence of methylammonium diffusion into the ion selective layer. We found no experimental evidence indicating the mobility of lead ions or protons, suggesting that methylammonium is the only mobile cation under illumination in MAPbI₃.

EN09.10.05
Coalescence Effect of CsPbBr₃ and CsPbI₃ Quantum Dots on Nanostructured Transition Metal Oxide Surface
Cynthia Rivaldo-Gomez and Jose A. Souza; Federal University of ABC, Brazil

One of the greatest interests of nanotechnology is the growth of semiconducting materials based on self-assembly of inorganic nanostructures. A facile technique consists to induce a simple cooperative interaction between nanoscale constituents and obtain larger assemblies. In this work, we will report the formation of three-dimensional nanostructures formed from perovskite CsPbBr₃ and CsPbI₃ quantum dots (QDs) by droplet evaporation method after deposited on planar oxide substrates. The colloidal solutions of CsPbBr₃ and CsPbI₃ QDs were synthesized via hot injection method. The UV-vis absorption spectrum of the QDs shows optical band gap energy of 2.4 eV and 2.1 eV for CsPbBr₃ and CsPbI₃, respectively. XRD measurements revealed that both CsPbBr₃ and CsPbI₃ QDs have an orthorhombic crystal phase at room temperature. The nanostructured oxide surface of both ZnO and TiO₂ were obtained by thermal oxidation process at high temperature 250 °C and 1020°C, respectively. The toluene solution containing monodisperse QDs was deposited (dropwise fashion) on the surface of both nanostructured ZnO and TiO₂ rutile substrates and evaporated in air at room temperature. On TiO₂ surface, different morphologies from nanocubes (edge length ~293 nm) when decorated with CsPbBr₃ NCs to microbelts (thickness ~500 nm and length ~20um) with CsPbI₃ QDs have been observed by controlling the quantum dots concentration. On the ZnO surface it was formed nanoparalelepiped (edge length 320 nm) and broom-like nanostructures (212 nm) of CsPbBr₃. We discuss our results by considering that the driven forces of quantum dots coalescence during solvent evaporation are lateral capillary meniscus inducing mass transport at the colloidal solution/oxide substrate interface.

EN09.10.06
Correlation between Structure and X-Ray Absorption Spectroscopy of Two-Dimensional Organic-Inorganic Hybrid Halide Perovskites
Jisook Hong, David Prendergast and Liang Z. Tan; Lawrence Berkeley National Laboratory, United States

There has been a recent surge of studies on organic-inorganic hybrid perovskites (OIHPs) as promising candidates for photovoltaic materials due to their high photovoltaic performance and low synthesis costs. Nevertheless, their vulnerability to moisture, light, and heat is preventing them from being used in practice. It was suggested that the stability issues can be partially solved by using two-dimensional (2D) OIHPs. However, unanswered questions on dynamical structural fluctuations of 2D OIHPs make it difficult to predict other physical properties theoretically. In this study, we explore energetically favored and entropically stabilized local structures of 2D OIHPs using \textit{ab-initio} calculations. Furthermore, we provide simulated core-level spectroscopic properties as a means to validate their atomic-scale structure, and explore additional electronic/optical properties of 2D OIHPs depending on their structural details and dynamics at finite temperature.

EN09.10.07
Ionically Driven Equilibrium Space Charge Effect—A Paradigm Change for Lead Halide Perovskite Interfaces
Gee Yeong Kim, Alessandro Senocrate, Davide Moia and Joachim Maier; Max Planck Institute for Solid State Research, Germany

Methylammonium lead iodide (MAPI) is currently in the focus of photovoltaic research not only because of high conversion efficiencies but also because of various intriguing physical-chemical properties. Here we show that equilibrium space charge effects at MAPI/TiO₂ and MAPI/Al₂O₃ interfaces are formed as a consequence of ionic excess charges, which is a totally novel view point in the photovoltaic community and of great relevance for the performance. For the analysis, we will apply a generalized picture that considers the equilibrium distribution of both ionic and electronic carriers [1-3]. These are attributed to a positive ionic excess charge at the interface, most probably due to Pb₂⁺ adsorption. We give clear conductivity experiments on MAPI-Al₂O₃ and MAPI-TiO₂.
composites as well as on MAPI thin-films on Al₂O₃ substrates with different thickness [4]. There is a positive ionic 
interfacial charge that leads to the equilibrium space charge potential. Zeta potential and surface analysis 
measurements identify Pb²⁺ adsorption at the oxide interface as reason for the space charge potential of above 0.5 V. 
The so-formed field leads to a local depletion of holes and iodine vacancies, but an accumulation of conduction band 
electrons. This work provides not only a novel view on such interfaces, but may enable a novel approach of interface 
engineering as well as a better understanding of the behavior in mesoporous systems.

EN09.10.08
Ultrafast Carrier Transport Dynamics In Situ Perovskite Films and Crystals Kanishka Kobbekaduwa¹, Shreetu 
Shrestha², Exian Liu¹, Pan P. Adhikari¹, Aniruddha Pan¹, Catalina Marinescu¹, Wanyi Nie² and Jianbo Gao¹; 
¹Clemson University, United States; ²Los Alamos National Laboratory, United States

Perovskite semiconductors including films and crystals are emerging materials that have wide ranging applications 
in the field of optoelectronics due to unique properties such as solution-processing, flexibility on substrates, and 
ambient environment processing. Although the ultrafast photophysics dynamics of carriers has been studied using 
ultrafast optical spectroscopies for the past few years, understanding its charge carrier dynamics in-situ devices has 
been a main challenge. Upon photon excitation, the photogenerated carriers carry out recombination, trapping, and 
transport in the range of several picoseconds to nanoseconds. Therefore, traditional photoconductivity measurement 
approaches such as time-of-light photoconductivity, photo charge extraction by linearly increasing voltage (CELIV) 
have temporal limitations towards understanding the carrier transport dynamics due to their low time resolution of a 
couple of nanoseconds.

In this work, we use ultrafast photocurrent spectroscopy (with sub-30 picosecond time resolution) to address the 
fundamental photophysics dynamics in-situ perovskite thin-films and crystal photoconductive devices, such as 
carrier photogeneration, recombination, transport, trapping and de-trapping. We investigate the photocurrent 
dependence with temperature, electrical field, and intensity. In addition to extracting the carrier mobility, lifetime 
and trapping level, we map out the evolution of carrier dynamics in the temporal range from sub-30 picoseconds to 1 
microsecond.

EN09.10.09
Electrochromic Phase Transition in Sn-Based Mixed Halide Perovskite Ryan Hawks, Zhizhong Chen and Jian 
Shi; Rensselaer Polytechnic Institute, United States

Smart photovoltaic windows are a green technology that allow for adjustable transparency and electrical power 
generation from solar energy. Halide perovskites have been observed to exhibit thermochromic behavior which, if 
modified, can be utilized in this technology. Cesium tin iodide/ bromide serves as a non-toxic potential candidate for 
this device as the intrinsic materials are heavily doped with Sn⁴⁺ which can boost current density under relatively 
small voltage. In this work, both the thermochromic and electrochromic phenomenon in cesium tin iodide/ bromide 
thin films are being explored. The thin films are synthesized from solution using a doctor blade method onto an 
ITO/glass slide and are capped with polydimethylsiloxane to prevent oxidation. Thermochromic behavior is verified 
by directly heating the film and observing a visible change in color, denoting a phase transformation. The film and 
all phases are characterized using X-ray diffraction. The electrochromic phenomenon caused by joule heating is 
studied as a function of applied bias and current density. The understanding of the thermochromic and 
electrochromic phenomenon in the halide perovskite thin film will allow for the development of devices in which 
the performance and stability can be measured.

EN09.10.10
2D Ferroelectric Halide Perovskite Films Yang Hu, Esther A. Wertz and Jian Shi; Rensselaer Polytechnic 
Institute, United States

The non-trivial coupling of ferroelectricity and photovoltaic properties makes ferroelectric semiconductors an 
interesting material system for both fundamental study and technological application. Ferroelectric organic- 
inorganic halide perovskite has low band gap, high charge carrier mobility, and large polarization density, and hence 
is a good candidate for studying photo-ferroelectricity. By solution method, we successfully prepare one 
ferroelectric halide perovskite, (Cyclohexanemethylamine)PbBr₄, which is also epitaxially grown on mica substrate 
by chemical vapor deposition method. We apply X-ray diffraction to characterize the crystal structure and steady 
state photoluminescence to probe the optical properties. Second harmonic generation is used to prove the inversion
symmetry breaking, and PE loop and switchable photo diode effect are characterized by transport studies. The work suggests a new class of thin film photo-ferroelectric materials which could be useful for future energy and memory devices.

**EN09.10.11**
**Large-Area Ultrahigh-Performance Digital Imaging Assembly Using High-Quality Perovskite Single Crystals**

Yucheng Liu¹, Yunxia Zhang¹, Zhou Yang¹ and Shengzhong (Frank) Liu¹,²; ¹Shaanxi Normal University, China; ²Chinese Academy of Sciences, China

Single crystalline perovskites exhibit high optical absorption, long carrier lifetime, large carrier mobility, low trap-state-density and high environmental stability. As large single-crystalline silicon wafers have revolutionized many industries ranging from solar cells to household electronics including computers and cell phones, it is envisioned that the availability of large perovskite single-crystalline will revolutionize its broad applications in photovoltaics, lasers, photodetectors, LEDs, etc. Recently, by fine-tuning the crystal nucleation and growth process, a low temperature gradient crystallization (LTGC) method is developed to grow high-quality perovskite CH₃NH₃PbBr₃ single crystals with high carrier mobility of 81 ± 5 cm² V⁻¹ s⁻¹, long carrier lifetime of 899 ± 127 ns and ultralow trap state density of 6.2 ± 2.7 × 10⁹ cm⁻³. In fact, they are better than perovskite single crystals reported in prior work: their application in photosensors gives superior detectivity as high as ~10¹³ Jones as well as remarkable water resistance and long-term environmental stability. Meanwhile, the response time is as small as 40 μs, ~3 orders of magnitude faster than their thin film devices. Furthermore, a large-area (~1300 mm²) imaging assembly composed of a 729-pixel sensor array is designed and constructed, showing excellent imaging capability thanks to its superior quality and uniformity. This work opens a new possibility to use the large high-quality perovskite single-crystal-based devices for more advanced imaging sensors. Even though the minimum width of each electrode is only 40 μm in the present example, limited by the linewidth of the shadow mask used in our lab for evaporation. However, common fabrication techniques, such as the nanoimprint lithography and electron beam exposure used in the present day fab, will offer much higher resolution in electrode fabrication.

**EN09.10.12**
**Broad Emission and Electron-Phonon Coupling in Multilayered Two-Dimensional Lead Iodide Perovskites Shown by Temperature-Dependent Photoluminescence**

Watcharaphol Paritmongkol¹,¹, Nabeel Dahod¹, Alexia Stollmann¹, Nannan Mao¹,¹, Charles Settens¹, Shao-Liang Zheng² and William Tisdale¹; ¹Massachusetts Institute of Technology, United States; ²Harvard University, United States

We report the temperature-dependent photoluminescence of multi-layered 2D lead iodide perovskites (2D LHPs) with varying quantum-well thicknesses (n = 2-4), A-site cations (methylammonium and formamidinium), and organic spacers (butylammonium, hexylammonium, and phenethylammonium). In general, new features of broad emission emerge at low temperature, and linewidth broadening as well as shifts in peak positions were observed in all samples. In particular, we found that broad emission from self-trapped excitons and trap states can coexist, although they were primarily found in bromide/chloride and iodide 2D LHPs respectively. Moreover, increasing quantum-well thicknesses leads to the suppression of the broad emission. We then analyzed the broad emission with out-of-plane distortion of Pb-(μ-I)-Pb angle and electron-phonon coupling. The electron-phonon interactions obtained from temperature-dependent linewidths and peak shifts show that both optical phonon energies and coupling efficiencies decrease with increasing quantum-well thicknesses. This finding supports the proposed behaviors of self-trapped excitons, and explains why the broad emission is mainly observed in thin 2D LHPs.

**EN09.10.13**
**Giant Oscillator Strength Transitions in Two-Dimensional CsPbBr₃ Nanoplatelets and Nanoribbons**

Daniel Rossi¹,², Jinwoo Cheon³ and Dong Hee Son²; ¹Institute for Basic Science, Korea (the Republic of); ²Texas A&M, United States

Two-dimensional semiconductor nanocrystals with a few unit-cell thicknesses have attracted much attention as highly desirable materials for photonic applications such as in lasing due to their narrow linewidth, low Auger decay probability and potential of significantly increasing the transition dipole strength upon cooling. In particular, the enhancement of the transition dipole at low temperature via giant oscillator strength transition (GOST) effect is unique to 2-dimensional semiconductor structures that relates to the coherent expansion of the exciton wavefunction in space. In this work, we investigated 2-dimensional CsPbBr₃ nanocrystals’ capability to exhibit enhanced
transition dipole by systematically studying the temperature dependent absorption and time-resolved fluorescence spectra of CsPbBr₃ nanoribbons and nanoplatelets of varying thickness. To obtain reliable spectroscopic data, we first developed the synthetic procedure producing CsPbBr₃ nanoribbons with high ensemble uniformity of the size and morphology, which exhibit high quantum yield (> 60%). These nanoribbons were stable under laser excitation in vacuum environment exhibiting stable and well-defined fluorescence spectra determined by thickness. From temperature dependent absorption and time resolved fluorescence emission measurements, we observe the GOST effect in nanoribbons and nanoplatelets, manifesting a larger absorption cross-section as well as decreased fluorescence lifetimes. For example, in 3 unit cell-thick nanoribbons the fluorescence lifetime decreases from ~3 ns at 300 K to below 10 ps at 60 K without changing the fluorescence quantum yield significantly. This behavior is similar to that observed in 2 nm thick CdSe platelets where the fluorescence lifetime reaches 150 ps at similar temperatures. These results indicate that few unit cell-thick lead halide perovskite 2-dimensional structures can be superior to their II-VI counterparts where large oscillator strengths are desirable.

EN09.10.15
Wavelength Tunable Circular Dichroism of Chiral 2D Organic Inorganic Hybrid Perovskite Sunihl Ma¹, Jihoon Ahn¹, Ji-Young Kim², Ji-hoon Kyhm³, Jung Ah Lim⁴, Wooseok Yang⁵, Nicholas A. Kotov² and Jooho Moon¹; ¹Yonsei University, Korea (the Republic of); ²University of Michigan–Ann Arbor, United States; ³Dongguk University, Korea (the Republic of); ⁴Korea Institute of Science and Technology, Korea (the Republic of)

Because 2D organic inorganic hybrid perovskites (OIHP) exhibit desirable optoelectrical properties such as high absorption coefficient, strong quantum confinement effect and highly tunable bandgap, 2D OIHP is considered as promising semiconductors for next generation optoelectronic devices. Additionally, many researches have reported that incorporation of chiral organic cation into the 2D OIHP lattices triggers another intriguing property of OIHP, which is defined as different optical response to left-handed and right-handed light. However, to increase the possibility to develop workable devices such as chiral light emitting diode (LED), wavelength tunability of chiroptical response should be guaranteed. In this study, to obtain wide wavelength tunability of chiroptical phenomenon, chemical composition engineering of 2D OIHP is carried out. Varying the mixing ratio of iodide and bromide anion in (S- or R-C₆H₅CH₂(CH₃)NH₃)₂PbI₄(1-x)Br₄x basically modifies band gap of chiral OIHP, leading to a shift of circular dichroism (CD) signal from 495 nm to 474 nm. It is also found that abrupt crystalline structure transition occurs and CD signal disappears when the 2D organic inorganic hybrid perovskite is transformed to bromide-determinant phase. To obtain material having CD at the wavelength range lower than 474 nm, S- or R-C₁₂H₇CH₂(CH₃)NH₃ with larger spacer group can be adopted. Thereby CD signal can further blue-shift to around 375 nm. Circularly polarized photoluminescence (PL) from our chiral 2D perovskite over a broad wavelength range at 70 K is also confirmed. Such a wide wavelength tunability of chiroptical property will advance the realization of color tunable circularly polarized light-emitting OIHPs.

EN09.10.16
Single-Step Synthesis of Dual Phase Bright Blue-Green Emitting Lead Halide Perovskite Nanocrystal Thin Films Harshita Bhatia, Julian A. Steele, Cristina Martin, Masoumeh Keshavarz, Guillermo Solís Fernández, Hai'feng Yuan, Guillaume Fleury, Jelle Hendrix, Maarten Roeffaers, Johan Hofkens and Elke Debroye; KU Leuven, Belgium

Metal trihalide perovskites are rapidly redefining the landscape of solid-state semiconductors utilized as active medium in photovoltaics and in light generation. Within this materials space, organic-inorganic hybrid formamidinium lead bromide (FAPbBr₃) has arisen as a promising candidate for efferent light emitting devices, due to its capacity for sharp and bright green light emissions (530 nm). Herein we have applied a facile single-step ligand-mediated method for phase-controlled synthesis of FAPbBr₃ cube- and rod-shaped nanocrystals (NCs), starting from different ratios of precursor agents. Examining their structural and optoelectronic properties – using a combination of synchrotron X-ray diffraction, X-ray spectroscopy, scanning electron microscopy and steady-state and time-resolved photoluminescence (PL) – we reveal the two NC types to fundamentally differ. While the cube-shaped NCs exhibit properties aligning with that of bulk FAPbBr₃, the nanorods exhibit a two-phase microstructure and the co-existence of both a typical cubic perovskite structure alongside the formation of a new low-symmetry monoclinic phase (P2/m). Further, the two-phase nanorods display a bright dual PL emission (peaks centered near 490 nm and 530 nm) and complex luminescence dynamics, properties characteristic of quasi-2D perovskites. The two phase nanorods generation can be assigned to the proton exchange in the presence of excess of FA⁺ during the synthesis.
The Role of Temperature and Concentration on the Morphology of CH₃NH₃PbI₃ and CsPbI₃ Perovskites
Ariany Bonadio, Leonardo Oliveira and Jose A. Souza; Federal University of ABC, Brazil

Halide perovskites have attracted great attention due to their excellent photovoltaic performance. Many growth methods have been developed to prepare these compounds with different morphologies. The identification of their crystal growth mechanism is crucial for understanding their fundamental chemical and physical properties. In this work, we have observed the formation of CH₃NH₃PbI₃ microcuboids and CsPbI₃ microwires via solvothermal method using lead iodide (PbI₂), methylamine (CH₃NH₂) or cesium acetate (CsOAc) as precursors and hydroiodic acid (HI) in isopropyl alcohol solution. We have systematically changed the solution temperature and PbI₂ concentration during the synthesis process. X-Ray diffraction shows that both CH₃NH₃PbI₃ and CsPbI₃ have high crystallinity belonging to the tetragonal (I4/mcm space group) and orthorhombic (Pnma space group) crystal phase, respectively. We have observed that the CH₃NH₃PbI₃ morphology is synthesis parameter dependent changing from small irregular particles to very regular polyhedral shape. We have also observed the presence of hollow spaces and/or hopper-type morphology at high temperature and concentration. CsPbI₃ perovskites present microwire morphology which also depends on synthesis parameter. UV-Vis absorption measurement indicated a band gap energy around 1.5 eV and 2.7 eV for CH₃NH₃PbI₃ and CsPbI₃ samples, respectively. We observed that the optical band gap energy for both compounds is synthesis parameter independent. We discuss the change in the morphology based on Wulff construction.

The Unexpected Role of Composition in Perovskite Diffusion
Kristopher Williams¹, Makhsud Saidaminov², Mingyang Wei², Andrew Johnston², Rafael Quintero-Bermudez², Andrew Proppe², Yi Hou², Grant Walters², Shana O. Kelley², William Tisdale¹ and Edward H. Sargent²; ¹Massachusetts Institute of Technology, United States; ²University of Toronto, Canada

The optimization of perovskite (typically ABX₃) for photovoltaic (PV) performance through mixed cations (A = Cs, methylammonium (MA), and formamidinum (FA)) and halides (X = Br and I) has led to engineered materials comprising six (AjBkC₁-j-kPbXzY₃-z) or more components. The role each of these components plays in increasing the PV performance is not yet well understood.

Here, we use transient photoluminescence microscopy to study the diffusion of carriers in single crystals and thin films for a variety of perovskite compositions (MAPbI₃, CsFAPbBrI, and CsMAFAPbBrI) in order to understand the effects of composition. Unexpectedly, the diffusion of carriers in single crystals was observed to be independent of the perovskite composition. When cast into thin films, however, the same materials showed a marked difference in diffusion constants and lengths. Along with angle-dependent and energy dispersive x-ray data, we determined that the limited transport in some compositions was caused by inhomogeneous crystallization at the grain boundaries. Those compositions containing methylammonium had consistent mixed-halide content across grains, while non-MA-containing compositions showed a gradient in the halide mixture, with higher Br content—and thus a larger bandgap—at the surface of film grains. Such a potential barrier inhibits the movement of carriers from grain to grain and thus their ability to reach electrical contacts.

This work reveals that compositional tuning of perovskites for PV performance has more to do with controlling grain boundary gradients than increasing transport within the bulk material. While most high-performance PV cells contain MA, we show it may be possible to produce high performance PV cells from desirable non-MA perovskites. Theoretical composition yields show current crystallization schemes favor narrow gradients in MA-containing materials, though solvent systems could be engineered to produce homogenous grains in films without the need for MA incorporation.

How Halide Perovskites Relieve Heteroepitaxial Stress?
Eitan Oksenberg¹, Eva L. Unger² and Ernesto Joselevich³; ¹FOM Institute AMOLF, Netherlands; ²Helmholtz-Zentrum Berlin, Germany; ³Weizmann Institute of Science, Israel

Ordered arrays of stable, single-crystal cesium lead bromide (CsPbBr₃) nanowires can be used to study fundamental properties of halide perovskites in a well-defined and simple one-dimensional model system. Specifically, we use
multiple spectroscopy techniques and correlate them with state-of-the-art electron microscopy methods, to reveal, with atomic resolution, large and continuous lattice rotations due to heteroepitaxial stress and lattice relaxation. We show that the lattice distortions give rise to bandgap modulations that are the dominant contributors to an anomalous size-dependent emission spectral shift well beyond the quantum confinement regime. Understanding the lattice behavior in strained perovskite and its effect on the optoelectronic properties of these dynamic materials, from the atomic scale up, is essential to evaluate their performance limits and fundamentals of charge carrier dynamics.

EN09.10.20
On the Interpretation of AC Response Analysis in Metal Halide Perovskite Solar Cells

Rasha A. Awni, Zhaoning Song, Chongwen Li, Cong Chen, Xinxing Yin, Mohammed Razooqi, Xiaoming Wang and Yanfa Yan; The University of Toledo, United States

Perovskite solar cells (PSCs) have emerged as a very promising solar cell technology due to the rapid increase of the power conversion efficiency (PCE). Further improvement in the device efficiency is limited by understanding the device working mechanism that still under debate. Herein, we propose and demonstrate how the interfaces at perovskite/charge selective layer (CSL) play major role. We have employed capacitance/impedance based techniques to understand the AC response, combined with the application of DC potential, and its implications in charge re-distribution in an operating device upon relatively low temperatures. We show that the lateral interfaces can be identified directly through an accurate determining of the equivalent circuit model which fits the capacitance/impedance spectra perfectly at different conditions. Resistance and/or capacitance circuit elements are time independent that cannot describe the large capacitance at low frequencies. However, introducing a time dependent component is necessary to describe the observed transient current behavior that is responsible for the hysteresis in the current–voltage curves. We perform current–voltage and capacitance–frequency simulations to confirm the role of time dependent component. This study provides an important progress in characterizing the electronic and ionic defect properties of perovskite devices.

EN09.10.21
Low Defect Density in Tin-Based Perovskite Crystals for High-Performance Photodetector

Qishun Yao, Binghan Li, Zihao Zhu and Qixi Mi; ShanghaiTech, China

In an effort to explore lead-free perovskite semiconductors, we recently reported [1] all-inorganic CsSnBr3 to have excellent semiconducting properties and thermal stability that are comparable or superior to those of CH3NH3PbI3. However, tin-based perovskites are prone to oxidation and formation of defect states. In this work, CsSnBr3 crystals with shiny and crack-free surfaces were grown by the Bridgman method, and the CsSnBr3 crystal boules were cut and polished into plates. Hall measurements revealed p-type carrier concentrations of 10^{12}–10^{14} cm^{-3} and carrier mobilities around 2×10^{1} cm^{2} V^{-1} s^{-1}, indicating low defect densities in the CsSnBr3 crystals. We further fabricated a 1-mm-thick CsSnBr3 plate into a photodetector with the device structure Al / TQB / CsSnBr3 / Au, where TQB is an organic electron transport material. Without an external bias, the photodetector is responsive to the entire visible spectral range, reaching a peak quantum efficiency of 7% at 700 nm. [2] This functional CsSnBr3 photodetector clarifies undue concerns about bulk defects in this material, and suggests its broader applications in X-ray photodetectors, solar cells, and other optoelectronic devices.

References

SESSION EN09.11: Composition Tuning in Perovskites—Alloys, Low-Dimensional Structures and Lead-Free Compounds
Session Chairs: Michael Irwin and Ivan Mora-Sero
Thursday Morning, December 5, 2019
Sheraton, 2nd Floor, Constitution B

8:00 AM EN09.11.01
Unraveling Charge Carrier Dynamics in Perovskite Solar Cells Using Bias-Dependent Time-Resolved
Photoluminescence Esma Ugur, Jafar I. Khan, Mingcong Wang, Erkan Aydin, Stefaan De Wolf and Frederic Laquai; King Abdullah University of Science and Technology, Saudi Arabia

Their unique optical and electronic properties make metal halide perovskites very attractive for photovoltaic and other optoelectronic applications. Meanwhile, the power conversion efficiency (PCE) of metal halide perovskite solar cells (PSCs) has reached more than 24%. Despite this impressive progress for solution-processed photovoltaic devices, performances of the PSCs are still limited by the open-circuit voltage (V_{oc}) and fill factor (FF) which are both controlled by the charge carrier dynamics. Thus, understanding the intrinsic limitations of these materials and the working mechanism of solar cells is vital to push the device efficiencies closer to the radiative Shockley-Queisser limit. Time-resolved optical spectroscopy of perovskite thin films and perovskite/charge transport layer interfaces allows identifying the photophysical processes in the absence of electric fields. On the other hand, bias-dependent photoluminescence on devices allows distinguishing between two competing processes: field-induced spatial charge separation and nonradiative charge recombination. Here, we study how the photoluminescence intensity and radiative decay in n-i-p PSC devices change when applying an external bias. We performed bias-dependent time-resolved photoluminescence (TR-PL) measurements at room-temperature in vacuo to reduce environmentally-induced and temperature-dependent photophysical changes during the PL measurements. We observe a gradual decrease of the PL intensity at V > V_{oc}. On the other hand, for V < V_{oc} no change of the PL is observed compared to the unbiased device. We will discuss how interface engineering using 2D perovskites with different cations alters charge carrier dynamics of PSCs under external bias.

8:15 AM *EN09.11.02
Interplay of Symmetry, Phonons, Electronic States and Excitons in Low Dimension Perovskites and Nanostructures Jacky Even; INSA, France

The presentation will describe some of the recent experimental and theoretical results for various classes of layered halide perovskites. Basic symmetry analysis of their electronic states will be proposed introducing simplified layered structures and compared to the case of 3D bulk materials and colloidal quantum dots (QD). The exciton fine structure, electron-phonon interactions, quantum and dielectric confinement effects will be further analyzed. The presentation will address the ongoing debate about the nature of the exciton ground state in perovskite QD.

8:45 AM *EN09.11.03
Exciton Recombination and Annihilation in Pure-Phase Phenylethylammonium Based 2D-Layered Hybrid Perovskite Crystals Emmanuelle Deleporte1, Géraud Delport1, Gabriel Chehade1, Ferdinand Lédée1, Hiba Diab1, Gaëlle Trippé-Allard1, Jacky Even2, Jean-Sébastien Lauret1 and Damien Garrot3; 1ENS Paris-Saclay, France; 2INSA-Rennes, France; 3UVSQ, France

Over the past few years, organic-inorganic halide 3D perovskites were found to present remarkable optoelectronic properties. A great attention has been paid to perovskite thin films, as an ideal building block for PV and LED devices. On the other hand, the study of single crystals has proven necessary to unveil some of the intrinsic properties of these semiconductors [1,2]. While the 2D-layered perovskites, forming self-assembled natural quantum well structures where the perovskite layer is separated by large organic cations, have been known for decades, they are attracting growing interest, for their strong photoluminescence properties, their chemical versatility and their low sensitivity to external degradation mechanisms due to UV light and moisture. Due to the quantum and dielectric confinements, 2D-layered perovskites exhibit high oscillator strengths and robust excitons, making them particularly relevant for light-emitting devices, and in the past, several works have been done to demonstrate the strong coupling regime at room temperature between excitons and photon modes in vertical microcavities [3,4] or in the distributed feedback geometry [5], or between excitons and plasmons [6]. More recently, 2D perovskites have proved to be interesting also for photovoltaics with efficiencies around 15 % and a better stability than their 3D counterpart [7]. Nevertheless, many of the fundamental photophysics properties of these 2D-layered perovskites, in particular the recombination dynamics of the excitons, remain to understood.

Pure-phase monocrystalline thin films of Ruddlesden-Popper phenylethylammonium-based 2D-layered perovskites of formula (C_{6}H_{5}C_{2}H_{4}NH_{3})_{2}(CH_{3}NH_{3})_{n-1}Pb_{n}I_{3n+1} are produced using the “Anti-solvent Vapor assisted Capping Crystallization” method [8]. The exciton recombination dynamics of the phases n = 1, 2, 3, 4 is investigated using time-resolved micro-photoluminescence (PL) in a large range of power excitation. The PL dynamics is highly dependant of the fluence due to the competing effect of traps saturation and exciton-exciton annihilation. At low
fluence, emission mechanism is excitonic, dominated by defect-assisted recombination. At high fluence, the dynamics is dominated by exciton-exciton annihilation, the order of magnitude of the annihilation rate is evaluated.

References:

Acknowledgements:
The project leading to this application has received funding from the European Union’s Horizon 2020 programme, through a FET Open research and innovation action under grant agreement No 687008, and from Agence Nationale de la Recherche within the project EMIPERO.

9:15 AM EN09.11.04
Uniaxial Expansion of the 2D Ruddlesden-Popper Perovskite Family for Improved Environmental Stability
Ioannis Spanopoulos1, Ido Hadar1, Weijun Ke1, Qing Tu1, Michelle Chen1, Hsinhan Tsai2, Yihui He1, Gajendra Shekhawat1, Vinayak Dravid1, Michael Wasielewski2, Aditya D. Mohite3, Constantinos Stoumpos1 and Mercouri G. Kanatzidis1; 1Northwestern University, United States; 2Los Alamos National Laboratory, United States; 3Rice University, United States

The unique hybrid nature of 2D Ruddlesden-Popper (R-P) perovskites has bestowed upon them not only tunability of their electronic properties but also high-performance electronic devices with improved environmental stability as compared to their 3D analogs. However, there is limited information about their inherent heat, light and air stability, and how different parameters such the inorganic layer number and length of organic spacer molecule affect stability. To gain deeper understanding on the matter we have expanded the family of 2D R-P perovskites, by utilizing pentylamine (PA)$_2$(MA)$_{n-1}$PbnI$_{3n+1}$ (n = 1-6, PA = CH$_3$(CH$_2$)$_4$NH$_3^+$, C$_5$) and hexylamine (HA)$_2$(MA)$_{n-1}$PbnI$_{3n+1}$ (n = 1-4, HA = CH$_3$(CH$_2$)$_5$NH$_3^+$, C$_6$) as the organic spacer molecules between the inorganic slabs, creating two new series of layered materials in single crystal form, for up to n = 6 and 4 layers, respectively.[1] The increase in the length of the organic spacer molecules does not affect their optical properties, however it has a pronounced effect on the air, heat and light stability of the fabricated thin films. We fabricated films on various substrates, and performed extensive environmental stability tests, evaluating their air, heat and light stability, both with and without encapsulation. Multiparameter, invaluable information was extracted from these studies, which showed that for the same number of layers the PA based materials, exhibited improved heat, light and air stability (e.g. stable for 450 days in air), as compared to BA, HA and 3D analogues. Furthermore, we verified for the first time that hybrid halide perovskites are inherently heat and light stable in the absence of moisture, a most critical finding for their potential commercialization. Lastly, evaluation of the out of plane mechanical properties of the corresponding materials showed that their soft and flexible nature can be compared to the current commercially available polymer substrates (e.g. PMMA), rendering them suitable for fabricating flexible and wearable electronic devices, expanding their utilization beyond photovoltaic applications.

References

9:30 AM EN09.11.05
Using Nonlinear Absorption to Reveal Hidden Carrier Dynamics in Lead-Halide Perovskites
Thomas Winkler1;2, Sean Bourelle1, Angus Mathieson1 and Felix Deschler3;1, 2University of Cambridge, United Kingdom; 3University of Kassel, Germany; 1Technical University of Munich, Germany
While the stimulated emission of light was postulated by Albert Einstein over 100 years ago, its nonlinear counterpart has only been observed in a handful of experiments so far. We recently discovered that nonlinear coherent amplification of an ultraviolet femtosecond laser pulse can occur in a piece of optically excited sapphire [1]. The nonlinear, two-photon stimulated emission holds promises for laser technologies, microscopy and laser-spectroscopy as it is inherently nonlinear, providing temporal/spatial focusing and control over selection rules.

Here, we discuss our recent experimental efforts to expand the nonlinear stimulated emission from the ultraviolet into the infrared regime. To that extent, we utilize novel lead-halide layered (2D) and bulk (3D) metal-halide perovskite semiconductors, which demonstrated promising properties for photovoltaic and optoelectronic devices [2,3]. With band gap energies in the visible spectrum and long carrier lifetimes, they are an ideal sample system to explore two-photon stimulated emission in an ultrafast pump-probe experiment.

We will also discuss, how we utilize the special selection rules in nonlinear absorption and emission to reveal population and carrier dynamics of dark states in 2D and 3D perovskites. By performing ultrafast linear- and circular polarized pump-probe measurements in the single and two-photon regime, we resolve the dynamics of bright and dark states separately.


9:45 AM EN09.11.06 Complexities of Contact Potential Difference Measurements on Metal Halide Perovskite Surfaces Fengyu Zhang1, Florian Ullrich2, Scott Silver1, Ross Kerner1, Barry P. Rand1 and Antoine Kahn1; 1Princeton University, United States; 2Technische Universitat Darmstadt, Germany

Understanding the electronic structure of metal halide perovskite (MHP) surfaces and interfaces is of considerable interest for the development of MHP based devices. A number of techniques, including ultraviolet and X-ray photoemission spectroscopy (UPS, XPS), contact potential difference (CPD) measurements, and Kelvin probe force microscopy (KPFM), have been applied to gather information on these surfaces and interfaces.[1-2] However, standard photoemission spectroscopy, such as UPS and XPS, only probes the top few nm of the film and cannot distinguish between flat bands and band bending occurring over several tens of nanometers. Furthermore, photoemission can induce non-equilibrium conditions of surface photovoltage (SPV) and unwanted band-flattening, providing distorted information on the equilibrium position of the Fermi level. Therefore, contactless, non-invasive, and non-destructive, Kelvin probe (KP) based CPD measurements serve as an important complementary technique to sort out some of these issues.[3] CPD measurements in the dark and under illumination (SPV measurements) provide valuable information on work function changes caused by the generation of electron-hole pairs near the surface/interface and on charging and discharging of surface/interface defect states upon illumination. Yet, CPD measurements can also be skewed and lead to erroneous results owing to changes in chemical composition and electronic structure of the surface under illumination.[4-5] Obtaining accurate SPV signals can therefore be challenging when working on perovskite surfaces, which are sensitive to, and degrade under, irradiation. Care must be taken to distinguish SPV signal and reversible band flattening as a result of photo-excitation, which occurs over short time scales (μs), from the long-term changes in surface work function due to surface reorganization or changes in stoichiometry (irreversible, or slowly reversible over hours), e.g., when the perovskite film surface undergoes degradation and decomposition during the CPD or SPV measurement. We present here a vacuum-based study[5] of the surface potential and response to illumination of two different types of perovskite films, methylammonium lead bromide (MAPbBr3) and the 2D Ruddlesden–Popper phase butylammonium lead iodide (BA2PbI4, n = 1), using KP-based CPD and SPV measurements. We show that supra-band gap illumination of both MAPbBr3 and BA2PbI4 leads to halide loss from the surface of the material, accompanied by a contamination-induced modification of the KP work function.[6] If undetected, this can lead to misinterpretations of the MHP surface potential. Repetitive calibration of the tip work function with HOPG is necessary to ensure reliable results. In contrast to MAPbBr3, BA2PbI4 exhibits a significant SPV corresponding to a partial flattening of an upward surface band bending. Our results illustrate the effectiveness of the Kelvin probe-based technique in providing complementary information on the energetics of perovskite surfaces and the necessity to monitor the work function of the probe to avoid erroneous conclusions when working on these materials.
10:30 AM *EN09.11.07

Novel Low-Dimensional Tin and Antimony Halide Compounds and Their Unconventional Applications

Maksym V. Kovalenko1,2; 1ETH Zurich, Switzerland; 2Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The spatial localization of charge carriers to promote the formation of bound excitons and concomitantly enhance radiative recombination has long been a goal for luminescent semiconductors. Zero-dimensional materials structurally impose carrier localization and result in the formation of so-called self-trapped excitons. We present fully inorganic, perovskite-derived zero-dimensional SnII material Cs4SnBr6 and a general series of Cs4-xAxBr6-yIy (A=Rb, K; x≤1, y≤1) that exhibit room-temperature broadband photoluminescence centered with quantum yields (QYs) of 10-20 % [1]. The emission peak of these materials ranges from 500 nm to 620 nm. We also present the synthesis, the structure as well as electronic and optical properties of a family of hybrid one- and two-dimensional tin (II) bromide compounds comprising guanidinium [G, C(NH2)3+] and mixed cesium-guanidinium cations: G2SnBr4, CsGSnBr4, and Cs2GSn2Br7 [2]. G2SnBr4 has a one-dimensional structure that consists of chains of corner-shared [SnBr5]2- square pyramids and G cations situated in-between the chains. G2SnBr4 is a luminescent phase with a broad emission band resulting from trapped excitonic states. In addition, we will discuss similar antimony-based compounds [3], which benefit from higher chemical robustness as compared to 0D Sn halides.

We will also present several unconventional applications of such metal halide luminophores, which harness molecular-like, moderately fast and single exponential radiative recombination kinetics. In particular, we show that the strong temperature dependence of the photoluminescence of low-dimensional tin-halides is ideally suited for remote thermography and thermal imaging [4]. The lifetimes values can be varied over several orders of magnitude by adjusting the temperature (up to 20 ns °C-1) and the sensitive range spans up to one hundred centigrade, and is tunable from -100 to 110 degC going from [C(NH2)3]2SnBr4 to Cs4SnBr6 and (C4N2H14I)4SnI6. Through the implementation of cost-effective hardware for fluorescence lifetime imaging, based on time-of-flight technology, these thermoluminophores have been used to record thermographic videos with high spatial and thermal resolution.

References:
2. O. Nazarenko et al., 2019, 31, 2121–2129
fabrication of targets with perovskite phase and their effect on the final perovskite thin film formation. The effect of PLD deposition parameters, including laser energy, fluence and frequency, as well as the system background pressure, will be discussed and linked to the structural – optoelectronic properties of the films. This work represents an important step forward in the development of controlled growth and future scalability of halide perovskites for efficient optoelectronic devices.

11:15 AM EN09.11.09
Low-Dimensional Hybrid Perovskites Containing an Organic Cation with an Extended Conjugated System
Dirk J. Vanderzande1,2, Wouter Van Gompel1, Roald Herckens1, Laurence Lutsen2, Martijn Mertens1 and Paul-Henry Denis1; 1University of Hasselt, Belgium; 2imec, Belgium

Organic-inorganic hybrid perovskites allow for creating a wide variety of structures: from a 3D structure using small organic building blocks to essentially 2D layered structures using larger organic building blocks. This opens an avenue towards a quite new class of organic-inorganic nano-composites in which the inorganic perovskite sheet acts as a template for the self-assembly of organic chromophores confined between the sheets of the inorganic layer. Consequently, an organization can be obtained for the organic chromophores that resemble the order observed in a single crystal. The number of inorganic sheets can easily be tuned by changing the stoichiometry of the organic small and large building blocks. In this way, a fluent transition of electro-optical properties can be achieved of the inorganic part from confined 2D structures to strongly delocalized quasi-3D structures. We will discuss the structures obtained so far.

The use of carbazole ammonium salts in 2D hybrid perovskites leads to materials for solar cells with enhanced photoconductivity and stronger resistance toward moisture yielding solar cells with strongly enhanced stability compared to the 3D MAPI perovskite material [1].

Also, the use of pyrene ammonium salts to synthesize 2D hybrid perovskites has been explored and initial results on the structure and optoelectronic properties will be discussed. Transitions between 1D and 2D structures were observed by specific modification of the stoichiometry of the components and also in function of temperature [2]. In combination with the introduction of extra secondary interactions in the organic layer, a material is obtained with an exceptionally low bandgap. This was realized by intercalating strong electron acceptor molecules (e.g. TCNQ and TCNB) in the organic layer. The pyrene chromophore acting as a donor together with TCNQ leads to the formation of an organic charge transfer complex between the inorganic sheets [3, 4].

In more recent work we are exploring mono tethered oligo-thiophene ammonium salts as building blocks for low dimensional hybrid perovskites. In this way, a new group of truly organic-inorganic hybrid materials is disclosed with possibly new applications for thin film electronics.


11:30 AM EN09.11.10
Computational Design of Perovskites—The Case of Ba2AgIO6, a Low Band-Gap Solution Processable Oxide Double Perovskite
George Volonakis, Nobuya Sakai, Henry J. Snaith and Feliciano Giustino; University of Oxford, United Kingdom

Over the last seven years we have witnessed the rise of lead-halide perovskites for optoelectronic applications such as photovoltaics, sensors and light-emitting diodes. Well before that, oxide perovskites have been extensively investigated and are today pivotal in many technological applications. Yet, a rational connection between these two important classes of materials is missing. In this talk, we will employ a computational design strategy to explore this missing link and demonstrate that for each halide perovskite there are several lookalike oxide perovskites with similar optoelectronic properties. As a proof of concept, we will also report on the synthesis of Ba2AgIO6, the oxide
analog of Cs₂InAgCl₆.
We will begin by showcasing recent efforts towards new materials that do not contain Pb, for which computational
design approaches from first-principles have been extensively successful and revealed another class of compounds;
the so-called halide double perovskites. Five inorganic crystals have been since synthesized and characterized;
Cs₂Bi₄AgCl₆, Cs₂Bi₄AgBr₆, Cs₂Sb₄AgCl₆, Cs₂Sb₄AgBr₆, and Cs₂In₄AgCl₆. Among these, Cs₂Bi₄AgBr₆ has the narrower
indirect band gap of 1.9 eV, and Cs₂In₄AgCl₆ is the only direct band gap semiconductor, yet with a large gap of 3.3
eV. All of them exhibit low carrier effective masses and consequently, are prominent candidates for opto-electronic
applications such as photovoltaics, light-emitting devices, sensors, and photo-catalysts. We will outline the
computational design strategy that lead to the synthesis of these compounds, and particularly focus on the insights
we can get from first-principles calculations in order to facilitate the synthesis, improve their opto-electronic
properties and the in-silico identification of compounds with properties that are similar to the lead-halide
perovskites. This rational design approach allows us to further develop a universal analogy concept that can be used
to identify analogs between oxide and halide perovskites. This new concept of analogs led us to identify a new oxide
double perovskite semiconductor, Ba₂AgIO₆, which exhibits an electronic band structure remarkably similar to that
of our recently discovered halide double perovskite Cs₂AgInCl₆ but with a band gap in the visible range at 1.9 eV.
We report the successful synthesis of Ba₂AgIO₆ by solution processes and we perform crystallographic and optical
characterization. We show that Ba₂AgIO₆ and Cs₂AgInCl₆ are both analogs of the well-known transparent conductor
BaSnO₃, but the significantly lower band-gap of Ba₂AgIO₆ makes this new compound much more promising for
oxide-based optoelectronics and for novel monolithic halide/oxide devices.

[1] Patent WO 2017/037448 Al (2015); G. Volonakis et al., JPCR 7 1254 (2016); G. Volonakis et al., JPCR 8 772
(2017); G. Volonakis, and F. Giustino APL 112 243901 (2018)

11:45 AM EN09.11.11
Twin Domains in CH₃NH₃PbI₃ Thin Layers as a Strain Relaxation Mechanism—The Ferroelasticity of Halide
Perovskites Aicha Asma Medjahed1, Pia Dally2, Tao Zhou3, Noella Lemaitre2, Stephane Cros2, Solenn Breson2,
David Djurado1, Peter Reiss1 and Stephanie Pouget4; 1CEA Grenoble/IRIG/SyMMES, France; 2CEA-LITEN/DTS/SMPV/LMPO, France; 3ESRF, France; 4CEA-Grenoble/IRIG/MEM, France

Over the past ten years, a steep rise in the efficiency of metal halide perovskite solar cells has been observed. With
the technological giant leap comes an impressive number of synthetic routes that lead to crystalline thin films used
in devices. In the case of MAPbI₃ (MA = CH₃NH₃), using chlorinated precursors has attracted high interest as the
morphological, structural and electronic properties of the resulting layers are improved when using PbCl₂ as a lead
source. The absence of chlorine in the final perovskite layer has been explained by the large ionic radii difference
between chlorine and iodine, making alloy formation impossible. However, halide exchange between MAPbI₃ and
MAPbCl₃ has already been observed when exposing MAPbI₃ (MAPbCl₃) to a MACl (MAI) solution, without any
alloying and despite the large lattice parameter mismatch (6.275 Å and 5.66 Å for MAPbI₃ and MAPbCl₃
respectively, in the cubic phase).

Here, the structure and microstructure of MAPbI₃ thin layers synthesized from PbCl₂ and MAI precursors and
optimized for devices in terms of efficiency and aging are studied. X-ray diffraction (XRD) measurement at room
temperature on these layers surprisingly reveal the presence of MAPbCl₃ phase in the film and a double texturation
along [hh0] and [00l] MAIPI directions. By in-situ XRD study of the annealing process, we unravel the role of
MAPbCl₃ as a crystallization intermediate for MAPbI₃ thin film. Three stages are observed: for the first one,
MAPbCl₃ and MAPbI₃ coexist in the layer, the intensity of the former decreasing in favor of the latter, and the
MAPbI₃ cell being under an important and increasing compressive strain (up to 0.55%). The second stage is
characterized by the formation of PbI₂, MAPbI₃ degradation phase, as a mechanism to partially relax the strain.
During the last stage, MAPbCl₃ disappears and MAPbI₃ strain is suddenly released, with no further evolution of
degradation phase. When completely removing the chlorinated phase from the layer through careful annealing, PbI₂
cannot be avoided but the double texture is no longer observed at room temperature. This two-fold texture is the
signature of twin domains present in the MAPbI₃ crystallites. Considering the ferroelastic behavior of MAPbI₃
which supposes that the response to an external strain is a structural perturbation, the twin domains find their origin
in the strain caused by the coexistence of MAPbI₃ and MAPbCl₃ in the layer. To gain further insight into the
relation between the strain levels and the twin domains, we studied the behavior upon temperature of the two
population of crystallites in layers presenting different levels of strain.
In summary, we identified one crystallization path of MAPbI₃ thin layers through ionic exchange and we characterized the strain in the layer induced by this process. We report here the XRD signature of the ferroelastic character of MAPbI₃ that have been documented only by local probes so far. Through in-situ and temperature dependent measurements, we unraveled the direct correlation between strain and twin domains.

SESSION EN09.12: Defect Science, Ion Migration and Polarization
Session Chairs: Laurent Lombez and Omer Yaffe
Thursday Afternoon, December 5, 2019
Sheraton, 2nd Floor, Constitution B

1:30 PM *EN09.12.01
Ion and Electron Conductivity in Hybrid Perovskites in Bulk and at Interfaces Joachim Maier; Max Planck Institute for Solid State Research, Germany

The measurement of ionic and electronic conductivities and their dependencies on the control parameters (stoichiometry, doping level, temperature) are discussed in terms of defect diagrams. The major stoichiometric parameter is the iodine partial pressure that has a significant influence on the properties. As far as the dopants are concerned, extrinsic (Na, oxygen) and native frozen defects are considered [1,2].

While these results show far-reaching similarities to typical oxide perovskites, the finding that under illumination not only the electronic but also the ionic conductivity is greatly enhanced, is surprising. The relevance of this effect on photo-degradation but also on photo-demixing in perovskite mixtures is set out [3].

In addition to bulk properties, interfacial effects are investigated in the light of mixed conductivity. It is shown that the space charge effects at MAPI/Al₂O₃ and MAPI/TiO₂ interfaces are determined by ionic excess charges rather than electronically dominated. Such phenomena are well studied in the case of mixed conductivity and ionically conducting solids (nanoionics) [4], but provide a paradigm change in understanding and probably also in designing relevant photoactive interfaces.

References

2:00 PM *EN09.12.02
Ion Migration and Operational Stability of Perovskite Solar Cells Qing Zhao; Peking University, China

The large amount of ionic bonds in the perovskite and the distorted lattice structure make the material possess a large number of mobile ions, and the migration of these ions is considered to be the main cause of device instability. The effect of ionic transport on the physical properties of CH₃NH₃PbI₃ perovskite films was investigated by using an in-situ fluorescence imaging system under light and electric field. It was found that prolonged ion migration can cause irreversible changes in perovskites with a large number of defect states near the electrodes, indicated by quenched fluorescence. With higher humidity (> 30%RH), ion migration is enhanced, even lead to morphology change of the film. It indicates that water molecules facilitate the ion migration in perovskites, which may explain the moisture-related burn-in degradation in perovskite solar cells. To quantitatively study the ion migration in perovskites and the effect of composition, moisture and light, perovskites were tested under different light intensity and temperatures using a cryogenic system. The electronic conductivity and the ionic conductivity are extracted via Galvanostatic and IV scanning measurement. The temperature-dependent relationship of the conductivity is summarized and analyzed. Further, the electronic and ionic transport properties of the material can be obtained by using Arrenhenius equation fitting, e.g. energy level of defects, carrier scattering mode and activation energy of ion migration. The corresponding results are as follows: light and water molecules can reduce the activation energy of ion migration by several times, and the substitution of organic cations by inorganic cations (Cs⁺) can greatly inhibit ion migration, especially under light; we demonstrated a solution-processed CsPbI₃Br solar cell can exhibit tremendous improvement on long-term operational stability under continuous steady-state operation, showing 1500
h operational stability under continuous light illumination at MPP tracking. The excellent long-term stability of CsPbI2Br indicets the importance Cs+ in the inhibition of ion migration in perovskite solar cells.

Ion migration behavior in mixed cation hybrid perovskite film is systemically investigated. Phase segregation and ion migration is identified in CsFAMA system by a combination of in situ photoluminescence scan and Galvanostatic measurement. Near the anode/cathode side, visible PL red/blue shift can be observed under synergetic effect of light and electric field. The Phase segregation was found to be correlated with the halide migration in the film. To combine the high efficiency of CsFAMA and the high stability of inorganic CsPbX3, we put forward a new structure to construct a CsPbBr3-clusters passivated perovskite film. In this structure, CsPbBr3 forms as cluster, suppresses ion migration and passivates CsFAMA grains. CsFAMA films with 3% mol of CsPbBr3 additive demonstrate enhanced PL lifetime, decreased defect state density, larger activation energy of ion migration, and suppressed phase segregation. As a result, the passivated PSCs exhibit around 20% stabilized power conversion efficiency without ‘burn-in’ exponential decay, with a champion open circuit voltage of 1.2 V for 1.62 eV bandgap perovksite. Furthermore, the target device achieves significantly extended long-term operational stability by remaining 90% of the initial efficiency after 500 h continuous operation under maximum power point (MPP) and light illumination. More importantly, under both continuous full-sun illumination, MPP operation and thermal stress (65 °C), the passivated planar type PSCs using TiO2 as electron transport layer and Spiro-OMeTAD as hole transport layer demonstrate a 125 h device lifetime (T80).

2:30 PM EN09.12.03
Identifying Degradation Mechanisms at Oxide and Noble Metal Interfaces in Halide Perovskite Devices Ross Kerner1,2 and Barry P. Rand1; 1Princeton University, United States; 2National Renewable Energy Laboratory, United States

While an ITO/MAPbI3/Au or ITO/FAPbI3/Au device appears uncomplicated, the degradation mechanisms are non-trivial to fully elucidate. In this study, we identify defect mediated, thermal and voltage-induced degradation reactions between the acid salts methylammonium and formamidinium at the ITO/perovskite interface that are exacerbated by O2-plasma treatments relative to UV-ozone. Thermally induced reactions catalyzed by the perovskite/Au interface are also discussed. Moreover, we systematically deconstruct electrically stressed devices to characterize cathodic and anodic electrochemical reactions at both the ITO and Au electrodes within a voltage window of -1.5 to 1.5 V. For example, the acidic etching of ITO can be cathodically induced near room temperature influencing impurities, electronic properties, and stability. At the Au electrode, exceeding a threshold voltage can anodically oxidize iodide to produce a small amount of triiodide which serves as an excellent lixiviant to facilitate the dissolution of Au as AuI or [AuI2]- species, transport these species through the perovskite layer, and electroplate neutral Au at the cathode. Our results illustrate that, for a single device, a variety of degradation pathways are possible with the dominant mechanism highly dependent on the specific temperature and bias regime as well as detailing how device stability can be affected by processing, reverse bias, and bias history. Finally, we believe our observations and approach to be pedagogical for experimental design aiming to uncover degradation mechanisms in more highly engineered perovskite devices.

2:45 PM EN09.12.04
Equivalent Circuit Modeling of Hybrid Perovskite Interfaces and Implications for Device Physics Davide Moia1,2, Ilario Gelmetti3,4, Phil Calado1, Alessandro Senocrate2, Gee Yeong Kim2, Jenny Nelson1, Joachim Maier2 and Piers Barnes1; 1Imperial College London, United Kingdom; 2Max Planck Institute for Solid State Research, Germany; 3Universitat Rovira i Virgili, Spain; 4Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology, Spain

Clarifying the connection between the mixed ionic-electronic conducting properties and the observed huge capacitive/inductive behavior and current-voltage hysteresis in hybrid perovskites based devices is critical to the advance of the field. Here, we discuss the observation that changes in electronic charge transfer processes, such as recombination, at interfaces of hybrid perovskite solar cells due to mobile ion redistribution can give rise to apparent capacitive behavior.[1,2] This capacitive effect differs from the chemical capacitance, which accounts for bulk polarization effects, and traditionally describes the capacitive behavior of mixed conductors.[3,4] It is also not simply associated with an accumulation or depletion of charges in the active layer, and cannot therefore be adequately described with a conventional capacitor. We identify the bipolar transistor as a most appropriate circuit element to reproduce analytically the observation of ionically-gated electron transfer at interfaces. We include transistors into an equivalent circuit model that couples ionic and electronic carrier dynamics[1]. We propose that
the huge capacitive and/or inductive behavior[5] observed for thin film perovskite solar cells is best described by electronic currents that are in fact an amplified version of the ionic current. The resulting model yields good fits to the experimental impedance spectra and can reproduce large perturbation transient measurements such as hysteretic current-voltage characteristics.[6] Since the model emphasizes the importance of ionic transport in the perovskite layer and of the space-charge behavior at interfaces in these devices, we perform an electrode material and thickness dependence analysis of perovskite devices. Our results help elucidating the space charge situation at perovskite/metal interfaces and clarify the relative contributions of chemical capacitance and of interfacial ionically-gated electronic charge transfer to the capacitive behavior of hybrid perovskite based devices.

References


3:00 PM BREAK

3:30 PM *EN09.12.05

**Suppressing Defects in Perovskites for Highly Efficient Tandem Solar Cells**

Kai Zhu; National Renewable Energy Laboratory, United States

Perovskite solar cells (PSCs) have become a competitive photovoltaic (PV) technology with rapid progress of efficiencies reaching above 24% for single-junction devices. The bandgap tunability through perovskite composition engineering is attractive for developing ultrahigh-efficiency tandem solar cells, including perovskite/perovskite, perovskite/silicon, or perovskite/thin-film absorber (e.g., CIGS). In this talk, I will discuss our recent progress on suppressing defects in perovskites covering both the wide-bandgap (~1.7–1.8 eV) and low-bandgap (~1.2–1.3 eV) perovskite compositions. For wide-bandgap PSCs, the challenge is to reduce the voltage deficit, which requires strategies for suppressing defect density. For low-bandgap PSCs based on Sn–Pb mixed perovskite films, key challenges lie at both the material and device levels. The high defect density associated with oxidation of Sn2+ to Sn4+ and formation of Sn vacancies significantly limits carrier lifetime and charge collection. I will discuss these challenges and show our recent progress on the general approaches to reduce defect density in perovskites for both low- and wide-bandgap perovskite films. The precursor chemistry and growth conditions affect significantly the physical and optoelectronic properties of perovskites. Applications of perovskite absorbers in highly efficient tandem devices will be discussed.

4:00 PM *EN09.12.06

**Dependence of Resistive Switching Performance on Composition Engineering of One-Dimensional Imidazolium Lead Iodide**

Eun-Suk Choi, June-Mo Yang, Seul-Gi Kim, So-Yeon Kim and Nam-Gyu Park; Sungkyunkwan University, Korea (the Republic of)

Demand for high-density memory semiconductors, which are essential to build large capacity for artificial intelligence and the Internet of Things, has been increasing day by day. PbI2 based resistive switching memories have been proposed as one of next generation memories because of low operating voltage, high on/off ratio and possibility of multi-level storage as nonvolatile memory. We report here resistive switching memory characteristics of imidazolium lead iodide depending on molar ratio of PbI2 to imidazolium iodide (ImI). It also proved experimentally and computationally to show the optimum performance for structural reason at any ratio composition. The stoichiometric composition results in hexagonal structure of (ImI)PbI3 which has molar ratio of PbI2:ImI = 1:1 analyzed by X-ray diffraction. The structure forms one-dimensional face-sharing [PbI3] chain.
Bipolar resistive switching characteristics having forming process are observed regardless of mixing ratio at low SET/RESET operating voltage of 0.2V and -0.2V, respectively. ON/OFF ratio is increased from $10^6$ to $10^9$ as ImI content is increased due to the increased HRS associated with pronounced insulating characteristics by ImI. Whereas, the stoichiometric (ImI)PbI$_3$ exhibits 5 times longer endurance ($10^3$) and one order of magnitude longer retention time ($10^4$ s) as compared to other compositions. Multilevel data storage also appeared by changing the compliance current. Conduction mechanism is investigated I-V measurement depending on temperature. Low resistance state (LRS) and high resistance state (HRS) are associated with Ohmic conduction and Schottky conduction, respectively. Density functional theory (DFT) calculation shows that defect formation energy of iodine vacancy is estimated to be low indicating that (ImI)PbI$_3$ has enough concentration of iodide vacancy for the filament formation and Further energy barrier calculations reveal that iodide migration preferentially occurs along 1-dimensional [234] crystallographic direction rather than interlayer [130] direction with lower energy. A good performance of (ImI)PbI$_3$-based memristor is thus related to the low defect formation energy of iodide vacancy and the preferential growth of the filament along 1-dimensional chain. These results suggest that (ImI)PbI$_3$-based memristor is potential candidate for next-generation memory application.

4:15 PM EN09.12.07
New, Lead-Free, Polar Oxynitride Semiconductors with Band Gaps Spanning the Visible Spectrum Steven T. Hartman, Arashdeep S. Thind and Rohan Mishra; Washington University in St. Louis, United States

Lead-halide perovskites have emerged as a new class of high-performance semiconductors with applications in solar cells, solid-state lighting, and photocatalysis. Some of their excellent properties, including high charge carrier mobility and defect-tolerance, can be attributed to the presence of the heavy-metal lead with Pb 6s$^2$ states at the band edge. However, lead-halide perovskites suffer from stability issues due to the generally weaker metal-halide bonds when compared to metal nitrides and oxides, which are more robust. On the other hand, metal oxides and nitrides typically have large band gaps that make them unattractive for solar energy harvesting and visible-light optoelectronics.

In this work, we will present new, stable quaternary oxynitrides, designed using first-principles density-functional-theory calculations, with predicted band gaps ranging from 1.6 to 3.3 eV, spanning the entire visible spectrum, that can act as alternatives to lead-halide perovskites. These semiconductors were predicted from a high-throughput computational search of the expansive $ABO_{3-x}N_x$ composition space, where A and B are inorganic cations, with B being a p-block metal with its s-states at either the valence or conduction band edge of the resulting compound. Several of these oxynitrides are on the convex hull of competing phases, indicating thermodynamic stability against decomposition, while others are slightly metastable. Their band structures feature a very disperse conduction band, similar to many transparent conducting oxides. The smaller electronegativity of nitrogen with respect to oxygen reduces the band gap substantially compared to oxides. In addition, some of these new compounds have a ferroelectric polarization as high as 16 μC/cm$^2$. The spontaneous polarization in such semiconductors can be expected to efficiently separate electrons and holes, leading to improved efficiency in solar cells.

The combination of a narrow, tunable band gap, high electron mobility, and ferroelectric polarization in one material would allow for several exciting applications. For example, the ferroelectric BiFeO$_3$ is known to show the bulk photovoltaic effect, but with poor power conversion efficiency and low current density due to a combination of wide band gap and low electron mobility. The new polar oxynitrides, presented here, are expected to overcome these challenges.

4:30 PM EN09.12.08
Ferroic-Ionic Effects on Photovoltaic Hybrid Organic-Inorganic Perovskites Yongtao Liu$^{1,2}$, Liam Collins$^3$, Anton V. Ievlev$^1$, Alex Belianinov$^1$, Stephen Jesse$^1$, Kai Xiao$^1$, Mahshid Ahmadi$^1$, Bin Hu$^2$, Sergei Kalinin$^1$ and Olga S. Ovchinnikova$^1$; 1Oak Ridge National Laboratory, United States; 2The University of Tennessee, Knoxville, United States

Despite the remarkable performance of hybrid organic-inorganic perovskites (HOIPs) in solar cell, light emission, and photodetector, it remains to require further advances in fundamental understandings of HOIPs photophysics. Recently, the discovery of ferroic twin domains in HOIPs has initiated contentious discussion on the ferroic nature of HOIPs. Given the interconnected nature of defect chemistry, ionic states, and ferroic properties, the effects of ferroic domains on the optoelectronic properties of HOIPs can no longer be ignored. Ferroelectric polarization— which has yet to be unambiguously established despite considerable effects to do so—is thought to facilitate the dissociation of photoinduced electron-hole pairs, benefitting photovoltaic action. Alternate to ferroelectricity,
ferroelasticity was also proposed in these materials. Here, we systematically studied the piezoelectric response of multiple CH$_3$NH$_3$PbI$_3$ thin films that exhibit twin domains and have different crystallographic planes parallel to the substrate. In doing so, we demonstrate that the piezoelectric contrast between twin domains along studied orientations is below 1 pm/V. Therefore, the ferroelectricity (if there is) along these orientations is < 1 pm/V. By applying electric biases, we find that the domain changes are governed by ion redistribution and structural deformation under electric biases. This indicates that the biases induced domain evolution in these materials is different from classical ferroelectric materials, where the ferroelectric polarization switching is the major driver. The ion redistribution and structural variation point to the potential effects of twin domains on solar cell operation. In addition, we for the first time reveal the photoluminescence (PL) variations in CH$_3$NH$_3$PbI$_3$ twin domains, indicating the different optoelectronic properties between domains. Density functional theory (DFT) simulation further indicates that the photogenerated electrons and holes show preferential distributions in the ferroelastic twin domains due to strain and chemical inhomogeneity between domains. In turn, this preferential charge distribution results in different lattice strain, alternating the behaviors of the ferroelastic twin domains in CH$_3$NH$_3$PbI$_3$. In-situ X-ray diffraction and band excitation piezoresponse force microscopy (BE-PFM) measurements present experimental evidence of the interaction between charge carriers and ferroelastic twin domains. This work provides an in-depth understanding of the effects of twin domains on optoelectronic properties of HOIPs, which are helpful for further improving the optoelectronic performance of HOIPs.

4:45 PM EN09.12.09
Giant Isotope Effect on Phonon Dispersion and Thermal Conductivity in Methylammonium Lead Iodide Perovskite Mahshid Ahmadi$^1$, Kunlun Hong$^2$, Panchao Yin$^2$, Songxue Chi$^3$, Yao Cai$^3$, Luke Daemen$^2$, Raphael Hermann$^2$, Hsin Wang$^2$, Andrew May$^2$, Mark Asta$^3$ and Michael Manley$^2$; 1University of Tennessee, United States; 2Oak Ridge National Laboratory, United States; 3University of California, Berkeley, United States

Organic-inorganic halide perovskites (OIHPs) are strong candidates for high-performance low-cost solar energy, light emission and detection applications$^{1,3}$. Despite extensive research, they remain far from well understood, particularly the role of phonons and organic molecule dynamics on the optoelectronic properties. It is known that there is a strong coupling between the dynamics of cation off-centering/orientation in the cage of octahedral and the inorganic framework tilting$^{4,5}$ but a full accounting of how this impacts thermal transport and the long-charge carrier lifetimes that help enable high power conversion efficiencies$^6$ is still elusive. A hot-phonon bottleneck effect has been shown to significantly extend the cooling time of hot charge carriers in OIHPs, which thermalize first through carrier-optic-phonon scattering, followed by optic phonon decay to acoustic phonons, and finally to the thermal conduction. To better understand the fundamental physics of these processes, it is informative to adjust the lattice dynamics independent of electronics by changing isotopes. In this work, we make use of the large 2:1 mass ratio of deuterium to hydrogen to alter the hydrogen-related dynamical modes of the organic molecules. Even though deuteration does not change the overall mass density of the lattice significantly, we find using neutron scattering that deuteration results in a large 20-50% softening in the longitudinal acoustic (LA) phonons near zone boundaries$^7$. This softening of the LA phonon occurs as the liberation modes of NH$_3$ and CH$_3$ soften and push down on the zone boundary LA phonons via mode anticrossing. This anticrossing behavior demonstrates that there is strong coupling between these hydrogen-controlled molecular modes and the LA phonons. The observed zone boundary softening of the LA phonons causes a significant fraction of the LA-phonon density of states to have a reduced group velocity$^8$ owing to a decrease in the propagation velocities of the LA phonons caused by the phonon softening. Finally, we use first-principles calculations to show that light- or X-ray-induced lattice expansions/distortions$^{11,12}$ associated with improved performance produce relatively small changes to these phonons, indicating that previous x-ray measurements$^3$ are not strongly biased by the probe and that these phonon properties are likely retained under operating conditions. Our findings highlight the importance of phonon-molecular mode interactions in organometallic halide perovskites and suggest a route to enhance hot-carrier properties by tuning the hot-phonon bottleneck.

EN09.13.01
Improvement in Printable Mesoscopic Perovskite Solar Cells via Thinner Spacer Layer
Qifei Wang¹² and Hongwei Han¹²; ¹Huazhong University of Science and Technology, China; ²Wuhan National Laboratory for Optoelectronics, China

In recent years, the perovskite solar cells (PSCs) based on printable triple mesoscopic structure develop rapidly showing a certified power conversion efficiency (PCE) of 15.6% for the lab-scale device, 10.4% for 100 cm² and an AM 1.5 sunlight stability of over 10000 h.

The mesoporous ZrO₂ (mp-ZrO₂) layer plays an important role in separating the mesoporous TiO₂ (mp-TiO₂) and the carbon layer, whose thickness closely relates to the open-circuit voltage (VOC) and PCE. However, thicker mp-ZrO₂ layer needs more perovskite solution to fill in and causes problems in the cost and reproducibility of devices.

To reduce the thickness of the mp-ZrO₂ layer, two directions can be taken into account. One is to select a more insulating material to replace ZrO₂. The other one is to modify the TiO₂ with proper materials to decrease the recombination between the TiO₂ and the carbon layer. Herein, we choose Al₂O₃ as a modification material on TiO₂. Through simple spraying pyrolysis method, a thin layer of Al₂O₃ is deposited on the surface of the TiO₂ layer. The insert of Al₂O₃ does not change the pore-filling situation or the crystallization of perovskite in the mesoporous scaffold, but accelerates the injection of electrons and reduces the recombination of light-induced carriers. For the thickness of ZrO₂ layer decreases with the help of Al₂O₃, the usage of solvent and PbI₂ is also reduced, which could protect the environment and are benefit for human's health. The modified TiO₂ makes the device both more cost-efficiently and environment-friendly. We support modifying TiO₂ with Al₂O₃ through spraying pyrolysis method improves the performance of devices in all aspects and reduces the usage of raw materials, which would make sense in the commercialization of printable mesoscopic PSCs.

EN09.13.02
Influence of Quantum Confinement and Charge Transport Layers on Hybrid Perovskite Carrier Dynamics through THz Emission Spectroscopy
Kyle Virgil, Jina Lee, Qin Yang, Griffin Mead, Geoffrey Blake and Harry A. Atwater; California Institute of Technology, United States

Designing hybrid perovskite optoelectronics which are simultaneously robust, scalable, and highly efficient relies on characterizing their intrinsic charge transport phenomena. We present investigations into picosecond carrier dynamics of sub-micron thick halide perovskite films in the terahertz (THz, or far-infrared) regime. Terahertz emission spectroscopy (TES) is employed to discern the influence of perovskite quantum confinement and electron/ hole transport layers on photocurrent generation. Notably, we observe THz emission from a range of 2D halide perovskites. Emission was observed down to “n=1” perovskite layer architectures like butylammonium lead iodide (BA₂PbI₄). These results suggest significant photo-Dember charge separation within 2D perovskite layers, brought upon by a difference in excited electron-hole mobilities. Using this response, we can interrogate carrier dynamics.
dynamics within the 2D perovskite planes and near interfaces with typical charge transport layers like PCBM, Spiro-OMeTAD, TiO2, etc. Comparing material parameters extracted from systematically varied THz emission spectra allows us to further analyze the relationship between photoexcited carrier transport and local perovskite environment. This work offers non-traditional insights to help guide the rapid development of perovskite solar cells, and strengthens our foundational knowledge of hybrid perovskite materials. Cohesively optimizing perovskite potential through diverse scientific frontiers is necessary to achieve the revolutionary energy technology of our future.

**EN09.13.03**

*Ultrafast Carrier Dynamics of Thin-Film Perovskite Solar Cells*  
*Exian Liu¹, Kanishka Kobbekaduwa¹, Pan P. Adhikari¹, Kai Zhu² and Jianbo Gao¹; ¹Clemson University, United States; ²National Renewable Energy Laboratory, United States*

Despite notable achievements of perovskite solar cells have been made for efficiency improvement by optimizing the device structure, and film morphology and structure, the fundamental photophysics of perovskite solar cell, especially the photoexcited carrier dynamic process including relaxation, transport, recombination, and trapping remains unclear. Most studies on solar cell physics were carried out with steady-state measurements, while its ultrafast carrier dynamics has not been demonstrated so far.  

Aim to elucidate ultrafast carrier dynamics *in-situ* solar cells with more than 20 % power conversion efficiency, in this talk, we present the carrier dynamics *in-situ* organic-inorganic halide perovskite solar cell using ultrafast photocurrent spectroscopy with sub-40 picosecond time. With comprehensive investigation on temperature-dependent, voltage-dependent and laser power-dependent photocurrent of this solar cell, we elucidate the photoexcited carrier relaxation and recombination process from sub-40 picosecond to microsecond. This study establishes the novel characterization approach for *in-situ* solar cells, in addition to addressing the fundamental desirable questions including carrier lifetime, mobility, trap density, and carrier transport mechanisms.

**EN09.13.04**

*Tailoring Structural Disorder and Crystal Orientation in 2D Perovskite Thin Films for High-Efficiency Optoelectronics*  
*Siraj Sidhik¹, Wenbin Li¹, Austin Fehr¹, Yafei Wang¹, Mercouri G. Kanatzidis², Jacky Even³, Jean-Christophe Blancon¹ and Aditya D. Mohite¹; ¹Rice University, United States; ²Northwestern University, United States; ³Univ. Rennes, France*

Two-dimensional (2D) halide perovskites are solution-processed hybrid organic-inorganic materials with unique structure and photo-physical properties, which has led to several proof-of-concept high efficiency optoelectronic devices such as photovoltaics and light emitting devices with technologically relevant stability. Despite several 2D perovskite crystals of different phase and composition have been synthetized, only a few have been successfully integrated into efficient and stable optoelectronic devices. The main challenges consist in both reducing the amount of structural disorder (i.e. a single 2D perovskite phase and high degree of orientation of the crystalline grains) and optimizing the 2D layer orientation for directional transport. More precisely, the designprinciples for controlling the phase purity, orientation and crystallinity of 2D perovskite thin film needs to be established. In this work, we propose a systematic approach to understand and control the phase purity, crystallinity and orientation of 2D perovskites of different phase (Ruddlesden-Popper, Dion-Jacobson and Alternating Cation) and varying perovskite thickness. Our approach consists in fabricating the thin films with different 2D perovskites using solvent engineering strategies, and subsequently performing correlated structural (GIWAXS) and physical (optical and electrical) characterization of the films to determine their degree of purity, orientation and crystallinity. Finally, we demonstrate proof-of-concept optoelectronic devices that validate these findings and pave the path for tuning the structure and properties of 2D perovskite thinfilms for low cost, high efficiency and stable devices.

**EN09.13.06**

*The Working Principle of Hybrid Perovskite Single Crystal Detector for Gamma-Ray Photon Counting*  
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Gamma-ray spectroscopy that quantifies the gamma-ray energies is a critical technology used in many disciplines such as astrophysics, nuclear material detection and medical diagnosis. Recently, organic-inorganic lead halide
Optically Switchable Photoelectron Injection from Perovskite Nanorods for Wavelength-Distinguishable UV

Perovskite materials have received intense interest as solid state gamma ray detectors owing to their intrinsic properties such as high effective atomic number, low defect density and excellent transport property. Specifically, chlorine-doped methylammonium lead tribromide (MAPbBr$_3$-Cl) and methylammonium lead triiodide (MAPbI$_3$) single crystals have shown energy resolutions of about 10% for various gamma ray energies from 60 keV ($^{241}$Am) to 662 keV ($^{137}$Cs). [1, 2] While those demonstrations are highly promising, the device operational mechanism of the hybrid perovskite detectors are greatly under explored, and the electrical pulses generated from the gamma-ray photon are not well understood which are essential for further detector optimization and construction of gamma-ray spectra.

Here we report the working mechanism of solid-state gamma-ray detectors made from MAPbBr$_3$-Cl single crystals. Specifically, we build devices with high or low work function contacts that collect only p-type (holes) or n-type carriers (electrons). Detailed device characteristics reveal that the main source of the dark noise in MAPbBr$_3$-Cl crystals originates from the thermally injected electrons from the impurity to the conduction band edge. As a result, only p-type device can observe clear gamma-ray induced electrical pulses from several radioactive sources with different amplitudes that correspond to gamma-ray photons at various energies. In addition, we discover the unusually long rise time (100 micron second) of pulses at room temperature can be greatly reduced at lower temperature. This suggests the long rise time arises from the slow structural dynamics under bias, such as interfacial ion migration. Our study reveals the operational mechanism and paves the way for material optimizations to improve the performance of hybrid perovskite-based gamma-ray detector.


Optically Switchable Photoelectron Injection from Perovskite Nanorods for Wavelength-Distinguishable UV Photodetector

Ultraviolet (UV) radiation has given rise to high-speed, wide-coverage and non-line-of-sight wireless optical communications due to its small susceptibility to solar background interference and flexibility of transmitter/receiver orientations such as pointing, acquisition and tracking. For a wireless UV communication, function generator produces pattern-controlled electrical signals that contain characteristic information on the intensity and on-off frequency of UV lights, which are emitted by transmitter and subsequently detected by receiver to realize the relay of information. Moreover, UV radiations with different wavelengths are employed in communication systems so as to enable bidirectional and high-capacity optical transmission, where large distinction between UV wavelengths is demanded for minimized inter-channel interference. Therefore, developing a photodetector that can accurately identify UV intensity variation, while simultaneously distinguishing UV photons in different wavelengths is highly desirable for acquiring and decoding the information embedded in UV carriers. Owing to the suitable bandgaps and superior charge transport properties, lead halide perovskites (e.g. MAPbCl$_3$, CsPbCl$_3$, FAPbI$_3$) have realized high-performance UV photodetectors. Nonetheless, such photodetectors were never able to differentiate UV photons with different energies due to indiscriminate, unidirectional transport of photogenerated charge carriers in 1) prototypical p-in photodiode structures, 2) lateral photoconductor structures with external voltage biases, and 3) devices utilizing metal electrodes with much discrepant work functions for guided carrier migration. In addition, photodetectors need to be sufficiently sensitive to accurately detect UV photons with temporally varying flux based on superior photoelectronic properties (e.g. large free carrier density, high mobility), since optical information can also be ciphered in the oscillating intensities. As such, it is intriguing both at scientific and technological levels to develop UV photodetector that permits multidirectional carrier transport in perovskite materials with radically improved optoelectronic properties, so as to observe perturbed photocurrent responses and to eventually elucidate the energies and intensities of UV photons. Here, with the presence of LiCl additive in formamidinium chloride (FACl) solution, as-grown LiCl:FAPbCl nanorods demonstrated greatly enhanced crystallinity and UV photoresponse as compared to pristine FAPbCl nanostructures without LiCl additive. Most importantly, LiCl:FAPbCl nanorod film exhibits unprecedented distinguishability to UV lights with different energies and oscillating intensities, via unipolar/bipolar and periodically oscillating photocurrents. This work could advance the fundamental understanding of photoinduced...
carrier processes in halide perovskites and facilitate the development of novel UV-based optical communications.

EN09.13.08
Template Stripping of Perovskite Thin Films for Dry Interfacing and Surface Structuring

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Metal-organic halide perovskites, with the chemical formula CH$_3$NH$_3$PbX$_3$ (X = I, Br, Cl), benefit from unique material properties that include continuous band-gap tunability, high carrier mobility, low non-radiative carrier recombination rates, and simple deposition approaches.1-3 Thanks to these advantages, perovskite thin-film devices are promising candidates for photovoltaic and light-emitting technologies.4 To facilitate the integration of perovskite thin films into such optoelectronic device architectures, a need exist for simple and efficient fabrication methods. Here we present a template-stripping technique to produce ultra-flat and flexible perovskite thin films.5 Spin-coated CH$_3$NH$_3$PbBr$_3$ perovskite thin films can be mechanically cleaved from a silicon template using an epoxy adhesive to expose ultra-flat perovskite surfaces with root-mean-square roughness down to 2.7 nm. The flatness and flexibility of these films enable new processing strategies based on dry interfacing. To demonstrate this, we interface perovskite thin films with plasmonic hole arrays. Through the interaction of the perovskite film with surface plasmon polaritons at the perovskite-metal interface, we are able to obtain a six-fold enhancement of the outcoupling of the perovskite film’s emission in the out-of-plane direction. In addition, by using prepatterned silicon templates, we show that our template-stripping method can produce structured perovskite surfaces with micrometer-sized structures.

Based on these demonstrations, we envision that our template-stripping approach can be utilized for the straightforward integration of perovskite materials into optoelectronic devices.

References

EN09.13.09
Role of Temperature and Antisolvent in Rapid Single Crystal Growth Using Inverse Temperature Crystallization

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Perovskite (ABX$_3$) materials show remarkable solar cells power conversion efficiency (PCE) of ~22% in past years.1 The applications of perovskite material have spread into different areas such as optoelectronic devices, LEDs, Lasers, X-ray detectors.2 The perovskite detector based on single crystal have been mostly used single-crystal grown by inverse temperature crystallization method. Perovskite (ABX$_3$) material has demonstrated extraordinary optoelectronic properties in polycrystalline thin films as well as in single crystals. Among various method of methyl ammonium lead iodide (MAPbI$_3$) perovskite single crystal growth, the inverse temperature crystallization has been proven to be the best in terms of crystal growth and optoelectronic properties.

In this work, the mechanism of MAPbI$_3$ single crystal growth have been studied via changing the three parameters such as growth temperature, precursor composition and anti-solvent. After varying these parameters, we got success in growing a single crystal of 1 cm at room temperature (RT). The acetonitrile (ACN) which acts as an anti-solvent in the precursor solution influences the temperature of crystallization. Besides this, ACN is also improving the solubility of MAI in GBL solvent and its presence affect the growth of crystals. The optimized ACN concentration provides adequate nucleation density to form a crystal. The higher amount of ACN concentration is unfavourable for single crystal growth because it enhances the concentration of nucleation sites. In RT crystal nucleation the availability of active ions tenability is required, which is obtained by adding more ACN and increase the solution molarity (M). Further increase in ACN concentration leads to the formation of several nucleation sites, which retards the single crystal growth. By optimizing the ACN concentration and other parameters, we got a meta-saturation state which helped in the growth of single crystal at RT.
The crystal growth striations were observed at a higher temperature (HT). The striations were absent in the RT case. The variation in growth rate between the consecutive layers is the cause behind striation formation. The heat dissipated by the previous layer opposed the flow of ions, which helped in the formation of the consecutive layers. This phenomenon is also affected by the growth rate. Finally, conventional crystals were synthesized successfully at different temperatures ranging from high to room temperature. These RT crystals showed significantly similar structural and photophysical properties as compared to the crystals grown at higher temperatures.

Reference:
1. www.nrel.gov/pv/assets/images/efficiency-chart.png

EN09.13.10
Electronic Stability of Lead Halide Perovskites Studied via Time Resolved Microwave Conductivity Min Ji Hong and John G. Labram; Oregon State University, United States

Photovoltaic devices based on Lead Halide Perovskites (LHPs) have drawn significant attention due to their outstanding performance in optoelectronic devices. Despite being processable from solution at low temperature, perovskite solar cells have demonstrated certified power conversion efficiencies (PCE's) in excess of those of polycrystalline silicon. However, LHPs exhibit poor stability under ambient environmental conditions and hence restrict commercialization for a long-term use. As the material's electronic properties (mobility and carrier lifetime in particular) are directly related to the device performance, developing an extensive understanding of the stability of optoelectronic properties is crucial for future applications.

Several previous studies have investigated the stability of LHP based devices in air. However almost all studies of electronic properties are carried out via electronic devices, and hence include the implicit encapsulation electrodes and transport layers provide.

In this work, we present electronic properties of solution processed hybride halide perovskite thin films studied via Time Resolved Microwave Conductivity (TRMC) under two different conditions: (1) Extended exposure to elevated temperatures and (2) Extented exposure to ambient (air) conditions. TRMC is a technique enabling direct evaluation of a material's mobility without any contacts, and in the absence of interfacial effects. This study enables us to make unambiguous statements on material stability in these compounds, which could be highly informative for LHP-based optoelectronic applications.

EN09.13.11
Phase Engineering in 2D Ruddlesden–Popper Perovskite Solar Cells Shuang Yu1, Yajie Yan1, Kaibo Zheng2 and Ziqi Liang1; 1Fudan University, China; 2Technical University of Denmark, Denmark

Recently, two-dimensional (2D) Ruddlesden–Popper (RP) perovskites have attracted broad attention for the excellent moisture resistance and tailorable composition.[1] However, compared with the 3D perovskite, the quantum confinement effect restrains interphase exciton splitting and charge transport owing to the incorporation of an insulating organic spacer layer. Meanwhile, randomly oriented 2D octahedral sheets inside thin film greatly hinder the charge carrier transfer along the vertical direction of the photovoltaic device. Phase engineering in 2D RP perovskites may offer a promising avenue to these obstacles.[2] Our recent studies have revealed that spontaneously generated 3D phases within 2D perovskite grain boundary not only promote the exciton splitting at the interface of 2D phases but also provide an additional channel for charge transport in device. These 3D phases can be introduced by two different approaches\(^\text{\textdagger}\): either the molecular design of organic spacer or the optimization of perovskite thin film processing.

Firstly, we employed the shorter branched isobutylamine (iso-BA) to replace linear n-butylamine (n-BA) and generate two aliphatic systems of \((n\text{-BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}\) and \((\text{iso-BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}\) 2D perovskites \((n = 4)\). It was found that the iso-BA 2D perovskite exhibit remarkably enhanced optical absorption and crystallinity along with preferably aligned orientation than n-BA analogue.[3] The resulting solar cells exhibit high PCEs of 10.63% and 8.82% with hot-casting and room-temperature processing, respectively. Transient transport studies establish the formation of 3D phases in iso-2D perovskite, which in turn accelerates charge/energy transfer and reduces charge accumulation caused by the unbalanced transfer rate, thereby significantly increasing the PCE.[4]
Second, among aromatic organic spacer based 2D perovskite system, we introduced S-bearing thiophene-2-ethylamine (TEA) to displace phenylethylamine (PEA). The intensive interaction between S and Pb atom not only stabilizes 2D inorganic lattices but also disrupts their long-range ordering which distorts the lattices and creates the nucleation sites for the formation of 3D phases. As a result, the best cell based on (TEA)2(MA)3Pb4I13 yield a prominent stable PCE of 11.2% without any photocurrent hysteresis. Importantly, the unencapsulated device display excellent ambient stability by preserving 80% efficiency after 270 h storage in air with 60 ± 5% relative humidity at 25 °C.

Third, by utilization of NH4Cl additive and DMSO solvent, we demonstrate their favorable synergistic effects on 2D (PEA)2(MA)3Pb4I13 perovskites fabricated at room temperature, which enable to passivate trap states within 3D phase (NH4Cl) and promote the 2D/3D inter-phase charge transfer (DMSO). The optimal cell delivers an impressive PCE (n = 4) of 13.41% with eliminated hysteresis. These findings highlight the importance of 3D phase engineering to modulate the charge carrier dynamics and improve optoelectronic properties of 2D RP perovskites, which offer an effective approach toward commercialized perovskite solar cells with high efficiency and excellent stability.

Reference

EN09.13.12
Improvement of Film Quality of Solvent-Supported EDTA-Blended SnO2 Based Planar Perovskite Solar Cell in Low Temperature Process Jihyun Kim, Hye Ri Jung, Bich Phuong Nguyen, Yeon Soo Kim and William Jo; Ewha Womans University, Korea (the Republic of)

In recent years, SnO2, which is an electron-selective layer (ESL) of a planar-type perovskite solar cell (PSC), has attracted attention as a promising substance. While SnO2 has many advantages, SnO2 films contain surface defects that can degrade electronic properties by trapping charge carriers. Herein, we fabricate n-i-p planar-type PSCs with ethylene diamine tetraacetic acid (EDTA)-blended SnO2 (E-SnO2) ESL and investigate the effect of selecting a mixture of solvent, on the solar-cell performance is discussed. We gain better crystallinity, uniform morphologies, higher carrier mobility and enhanced interfacial quality of PSCs with solvent-mixed E-SnO2 ESL compared to traditional SnO2 ESL. The electrical properties of PSCs based on solvent-mixed E-SnO2 ESL using Kelvin probe force microscopy (KPFM) and a conductive atomic force microscope (c-AFM) are examined and the work function and local current of the surface are measured. We also investigate the potential distribution of the cross-sectional area of PSCs. By using KPFM, we can compare the band structure and explain the carrier transport mechanism between the solvent-mixed E-SnO2 ESL and the PSC interface. These photovoltaic performances, optical and electronical properties offer the potential to improve device operation by optimizing solvent-mixed E-SnO2 ESL quality.

EN09.13.13
Preparation of Halide-Dependent Perovskite Heterostructure for Advanced Interface with Exfoliated MoS2 and WS2 Hye Ri Jung and William Jo; Ewha Womans University, Korea (the Republic of)

Heterostructure consist of organolead halide perovskite and 2D transition metal dichalcogenides (TMDs) was reported to exploit as a high-performance photodetector and a stable perovskite solar cell. TMDs assisted the effective carrier transfer in the interfaces with its high charge mobility and facilitated well aligned band structure for providing the advanced device design. In that point, fabrication and investigation of the charge transport mechanism and the band alignment in various heterostructures is significant for understanding the interfacial properties between the halide-dependent perovskites and TMDs. We fabricated the heterostructure with exfoliated MoS2 and WS2 with organolead lead halide perovskites, and conductive atomic force microscopy was used thereafter to display the electrical contacts of the heterostructure. Photocurrent also enhanced in the heterostructures by enhanced charge
transport in the interface. Furthermore, Kelvin probe force microscopy was conducted to demonstrate the band alignment in the different type of heterojunction. We propose the efficient heterostructure from the charge transport mechanism and the band structure in the various junctions depending on the halide-dependent perovskites and TMDs.

EN09.13.14
CVD Patterning of Lead Iodide Thin Film and Hybrid Perovskite Conversion Geemin Kim, Sol An, Myungwoong Kim and Naechul Shin; Inha University, Korea (the Republic of)

Organic-inorganic hybrid perovskites (OIHPs), i.e., such as methylammonium lead iodide perovskites (CH$_3$NH$_3$PbI$_3$) have demonstrated distinguished optoelectronic properties for a variety of applications including photovoltaics (PV), light emitting diodes (LED), and photodetectors, etc. To this end, solution-based crystallization of OIHPs has been widely employed to prepare perovskite thin films desired for the device fabrication process. Attracted interests due to their enormous potential in photovoltaics (PV) application, such as Solar cell, light emitting diodes (LED), and photodetectors. Most applications are based on the polycrystalline thin film which synthesized via dissolution & recrystallization in organic solvent. However, it has limitations such as irregular morphologies with randomly oriented grains, which cause large grain boundaries which deteriorate carrier lifetime and diffusion length. Despite the versatility of solution-based synthesis, however, the as-prepared perovskite films exhibit relatively irregular surface roughness implying the existence of randomly-oriented crystal domains and large density of grain boundaries, which ultimately reduce the device performance and lifetime. Moreover, the device fabrication based on the typical “top-down” lithography remains difficult to apply due to the general instability of OIHPs to the solvents involved in the process. However, it has limitations such as irregular morphologies with randomly oriented grains, which cause large grain boundaries which deteriorate carrier lifetime and diffusion length.

In this study, we report the CVD patterning of lead iodide (PbI$_2$) thin films on a micro-scale pre-patterned Si substrate by P(NBOC-r-GMA) polymer, followed by conversion into CH$_3$NH$_3$PbI$_3$ using methylammonium iodide (CH$_3$NH$_3$I) vapor. Detailed analysis of PbI$_2$ film growth on the polymer patterns suggests that the surface energy difference between polymer and Si promotes the selective deposition of PbI$_2$ precursor onto hydrophilic Si surface with a uniform thickness of about 100 nm. We observe the formation of [0001]-oriented PbI$_2$ nanoplatelets are preferred on Si surface, and the selectivity and surface coverage of patterned PbI$_2$ thin films can be controlled via modulation of growth temperature. The patterned PbI$_2$ films maintain their morphology after perovskite conversion by virtue of vapor-solid intercalation. We also demonstrate photodetector arrays based on the patterned CH$_3$NH$_3$PbI$_3$ crystalline thin films and confirm the potential for the various optoelectronic applications. Our results highlight the advantage of CVD patterning of perovskite materials in large scale production for various optoelectronic applications.

EN09.13.15
Spatially Extended Gap States Induced Up-Conversion Photoluminescence Xixiang Zhu$^1$, Hengxing Xu$^1$, Yongtao Liu$^{1,2}$, Jia Zhang$^1$, Miaoqang Wang$^1$, Ilia Ivanov$^1$, Olga S. Ovchinnikova$^1$ and Bin Hu$^1$; $^1$University of Tennessee, United States; $^2$Oak Ridge National Laboratory, United States

Quasi-2D Ruddlesden-Popper perovskites have demonstrated interesting optical properties in down-conversion regime. In our work, we found the infrared-to-visible up-conversion photoluminescence (PL) peaked at 521 nm occurring in quasi-2D perovskite [(PEA)$_n$(MA)$_{4-n}$Pb$_5$Br$_{16}$ with n = 5] films by using infrared CW 980 nm laser beam to excite the gap states at room temperature. With increasing the CW laser intensity, the up-conversion PL intensity is almost quadratically increased with the power dependence factor of 1.7. This presents an evidence to show that the up-conversion PL is essentially a two-photon process occurring through the gap states. Furthermore, the two-photon up-conversion PL shows a strong dependence of n value in the 2D perovskites. As lowering the n value, the up-conversion PL signal is dramatically decreased, becoming negligible when the n value is lower than 3. Simultaneously, the gap states are non-detectable in optical absorption when n < 3. This verifies that the gap states are indeed responsible for generating the two-photon up-conversion PL. Moreover, it was found that the two-photon up-conversion PL shows an appreciable dependence of magnetic field through spin mixing mechanism. This provides direct evidence that the gap states are essentially spatially extended states to enhance two-photon up-conversion PL in 2D perovskites.

EN09.13.16
Surface Passivation, Thermal Stability and Temperature-Dependent Photoluminescence of CH$_3$NH$_3$PbI$_3$ and
**Double Perovskite Cs₂AgBiBr₆ Nanocrystals**

Yangning Zhang, Cherrelle J. Thomas and Brian A. Korgel; University of Texas at Austin, United States

CH₃NH₃PbI₃ (MAPI) nanocrystals with tetragonal crystal structure and cuboidal shape terminated by (110) and (002) facets and double perovskite Cs₂AgBiBr₆ nanocrystals with cubic double perovskite crystal structure and cuboidal shape terminated by {001} facets were synthesized. Oleylamine and oleic acid are used in the synthesis of both nanocrystals and their interactions with the nanocrystal surfaces were studied and compared using ¹H nuclear magnetic resonance (¹H NMR) spectroscopy and nuclear Overhauser effect (NOESY) spectroscopy. Oleylamine and oleic acid both cap the MAPI nanocrystals, while only oleylamine bonds to Cs₂AgBiBr₆. In the synthesis of Cs₂AgBiBr₆ nanocrystals, oleic acid promotes the ionic metathesis reaction, but does not serve as a capping ligand. It could be substituted with diisoctylphosphinic acid to produce nanocrystals with similar size, cuboidal shape, uniformity, cubic double perovskite crystal structure, and optical properties. Superlattices of MAPI and Cs₂AgBiBr₆ nanocrystals were assembled and studied with grazing incidence small- and wide-angle X-ray scattering (GISAXS and GIWAXS) with *in situ* heating. MAPI nanocrystals undergo a tetragonal-to-cubic phase transition at 55-60°C similar to bulk films and begin to degrade at 90°C, when PbI₂ begins to form. Both hexagonal and rhombohedral phases of PbI₂ are observed as thermal degradation products. *In situ* photoluminescence (PL) shows that the emission energy increases with increasing temperature and decreases in intensity. In contrast, the PL peak wavelength of Cs₂AgBiBr₆ nanocrystals does not change with increasing temperature. Also, GISAXS and GIWAXS showed that Cs₂AgBiBr₆ nanocrystals are more stable, up to 250°C. At this temperature, the nanocrystals sinter, but the Cs₂AgBiBr₆ crystal orientation remains the same on the substrate.

**EN09.13.17**

*Revealing the Origin of Luminescence Center in 0D Cs₄PbBr₆ Perovskite* Zhaojun Qin¹,², Shenyu Dai³,², Viktor G. Hadjiev²,², Chong Wang⁶,², Lingxi Ouyang⁴,², Lixin Xie²,², Yizhou Ni²,², Chunzheng Wu¹,², Guang Yang²,², Shuo Chen²,², Liangzi Deng²,², Qingkai Yu¹, C. W. Chu²,²,⁶, Guoying Feng¹ and Jiming Bao²,²; ¹University of Electronic Science and Technology of China, China; ²University of Houston, United States; ³Sichuan University, China; ⁴Yunnan University, China; ⁵Texas State University, United States; ⁶Lawrence Berkeley National Laboratory, United States

As a zero-dimensional all-inorganic perovskite with excellent optical properties, Cs₄PbBr₆ has attracted considerable attention as well as intensive debates, especially two opposing mechanisms of its highly efficient green photoluminescence (PL): embedded CsPbBr₃ nanocrystals versus intrinsic Br vacancy states. Here, we provide sensitive but noninvasive methods that can identify CsPbBr₃ nanocrystal inclusions in Cs₄PbBr₆ as dominant green PL source in this compound. We first synthesized both green PL emissive and non-emissive Cs₄PbBr₆, obtained the complete Raman spectrum of Cs₄PbBr₆ and assigned all Raman bands based on density functional theory simulations. We then used correlated Raman-PL as a passive structure-property method to identify the difference between emissive and non-emissive Cs₄PbBr₆ and revealed the existence of CsPbBr₃ nanocrystals in emissive Cs₄PbBr₆. Finally, we used molecular dynamics simulations based on density functional theory. The resolution of this long-lasting controversy paves the way for device applications of low-dimensional perovskites, and our comprehensive optical technique integrating structure-property with dynamic response can be applied to other materials to understand their luminescence centers.

**EN09.13.18**

*Impact of Nuclear Disorder on the Urbach Energy in Halide Perovskites* Christian Gehrmann and David Egger; Technische Universität München, Germany

Halide perovskites (HaPs) are intriguing optoelectronic materials and promising candidates for efficient solar-cell devices. In particular, HaPs exhibit small Urbach energies and sharp optical absorption edges allowing for efficient collection of sunlight in thin-film photovoltaic devices. On the other hand, HaPs also exhibit complex nuclear dynamics and structural effects, including anharmonicity and disorder, which is unusual for efficient optoelectronic materials. Moreover, since small Urbach energies indicate a low amount of disorder, the aforementioned optoelectronic properties are difficult to rationalize. Using first-principles methods, we study the disorder potential induced for electronic states in various paradigmatic HaPs. To account for the complex nuclear motions at elevated temperatures, we used molecular dynamics simulations based on density functional theory. With this approach, we take into account anharmonicity in the lattice dynamics to all orders in the Taylor expansion of the crystal potential. We find that correlations in the disorder potential are dynamically confined to atomic distances, and that the massive
nuclear motions of A-site and X-site ions dynamically shortens them. This length-scale of the correlations in the disorder is similar to the one reported for usual inorganic semiconductors, and we show that the dynamic shortening of the disorder leads to favorable distributions of band edge energies. We conclude that sharp optical absorption edges and small Urbach energies, which are highly desired properties of any solar absorber material, are enabled by this dynamic mechanism.

EN09.13.19
Self-Patterned CsPbBr₃ Nanocrystals for High-Performance Optoelectronics Bin Xin and Iman Roqan; King Abdullah University of Science and Technology, Saudi Arabia

All-inorganic lead halide perovskites are promising materials for many optoelectronic applications. However, two issues that arise during device fabrication hinder their practical use, namely inadequate continuity of coated inorganic perovskite films across large areas and inability to integrate these films with traditional photolithography due to poor adhesion to wafers. Herein, for the first time, to address these issues, we show a room-temperature synthesis process employed to produce of CsPbBr₃ perovskite nanocrystals with two-dimensional (2D) nanosheet features. Due to the unique properties of these 2D nanocrystals, including the “self-assembly” characteristic, and “double solvent evaporation induced self-patterning” strategy are used to generate high-quality patterned thin films in selected areas automatically after-drop-casting, enabling fabrication of high-performance devices without using complex and expensive fabrication processing techniques. The films are free from micron size cracks. In a proof-of-concept experiment, photodetector arrays are used to demonstrate the superior properties of such films. We provide evidence of both high responsivity (9.04 A/W) and high stability across large areas. The photodetectors fabricated on flexible substrate exhibit outstanding photo-response stability. Advanced optical and structural studies reveal the possible mechanism. Our simple and cost-effective method paves the way for the next-generation nanotechnology based on high-performance, cost-effective optoelectronic devices.

EN09.13.20
First-Principles Theory Investigation on Structural and Photoelectronic Properties of Formamidinium Lead Halide Perovskites Yang Zhao; Huazhong University of Science & Technology, China

Formamidinium lead halide perovskites have attracted wide attention as photoelectronic conversion materials due to the high photoelectronic conversion efficiency (PCE), low cost and simple synthetic process. The structural, electronic and optical properties of mixed formamidinium lead halide perovskites FAPbIₓClₓ₋ₓ (FA = NH₂CH=NH₂⁺, x = 0 ~ 3) have been investigated by the first-principles theory. Our results show that FA cations lie along [001] direction in the trigonal FAPbX₃ (X = Cl, Br, I). However, the direction is slightly shifted owing to the distortion of PbX₆ (X = Cl, I) octahedrons in the mixed FAPbIₓClₓ₋ₓ. The Pb—I bond distances (0.315 ~ 0.334 nm) are larger than Pb—Cl bond distances (0.282 ~ 0.302 nm). With the increase of I/Cl ratio, the lattice parameters and volumes of FAPbIₓClₓ₋ₓ increase. The FA cations play a crucial role in balancing the crystal structure, but they do not participate into the process of frontier orbital transition directly. They just play the role of charge donors to contribute ca. 0.76 e to PbI₃ framework. FAPbIₓClₓ₋ₓ are direct band-gap semiconductors, with the direct bandgap nature at Z (0, 0, 0.5) symmetry point. The valence band maximum (VBM) is composed of antibonding orbitals of I 5p (Cl 3p) and a few Pb 6s orbitals, and the conduction band minimum (CBM) is composed of Pb 6p orbital. There exists a combined covalent and ionic bonding mechanism between Pb and I (Cl) ions. As the I/Cl ratio increases, the band gaps decrease and the absorption spectra are red shifted. FAPbI₃ has an ideal band gap of 1.53 eV. It exhibits the superior absorption spectrum especially in the range of 300 nm to 500 nm, which elucidates that FAPbI₃ has great potential as the photoelectronic conversion material. Our results could provide theoretical guidance for the experimental design and synthesis of perovskite solar cells.

EN09.13.22
Investigation of Electrode Electrochemical Reactions in CH₃NH₃PbBr₃ Perovskite Single-Crystal Field-Effect Transistors Junzhan Wang; University of Cambridge, United Kingdom

Optoelectronic devices based on metal halide perovskites, including solar cells and light-emitting diodes, have attracted tremendous research attention globally in the last decade. Due to their potential to achieve high carrier
mobilities, organic-inorganic hybrid perovskite materials can enable high-performance, solution-processed field-effect transistors (FETs) for next-generation, low-cost, flexible electronic circuits and displays. However, the performance of perovskite FETs is hampered predominantly by device instabilities, whose origin remains poorly understood. Here, perovskite single crystal FETs based on methylammonium lead bromide are studied and device instabilities due to electrochemical reactions at the interface between the perovskite and gold source-drain top contacts are investigated. Despite forming the contacts by a gentle, soft lamination method, evidence is found that even at such “ideal” interfaces, a defective, intermixed layer is formed at the interface upon biasing of the device. Using a bottom-contact, bottom-gate architecture, it is shown that it is possible to minimize such a reaction through a chemical modification of the electrodes, and this enables fabrication of perovskite single crystal FETs with high mobility of up to ≈15 cm² V⁻¹ s⁻¹ at 80 K. This work addresses one of the key challenges toward the realization of high-performance solution-processed perovskite FETs.

Reference:

EN09.13.23
Raman Scattering Obtained from Laser Excitation of MAPbI₃ Single Crystal Hagit Aviv, Tal Ben Uliel and Yaakov R. Tischler; Bar-Ilan University, Israel

Finding renewable energy sources is of paramount importance to meet the increasing global energy demand whilst minimizing the impact on the environment. The research community has focused on solar energy as it is endlessly available, and have ranked the methylammonium lead iodide (MAPbI₃) as the most promising candidate amongst perovskite solar cells. Despite its high efficiency, the MAPbI₃ is sensitive to humidity, light, and temperature, its instability affects primarily on the crystalline structure and eventually leads to degradation. Three crystalline structures are known for this material, orthorhombic, tetragonal, and cubic which exist in different temperatures. Here we report on several processes detected from laser excitation of MAPbI₃ single crystal at ambient conditions. A phase transition from tetragonal to cubic phase was induced by excitation of over 15 mW laser power. The phases were characterized by LF-Raman and PL, taken simultaneously with the increase of exciting laser power and the spectral changes were assigned to the structural differences. In addition, Raman stimulation of iodine vapors signal was observed, those vapors were generated from the core of the focus wherein the highest temperature lead to degradation. The stimulated Raman phenomenon was enabled due to the unique properties of the MAPbI₃ single crystal and revealed viability to use this material for additional applications in other research fields.

EN09.13.24
Why Introducing MA⁺ Cations in Mixed Halide Perovskites Matters—An Atomistic Perspective Giuseppe Fisicaro, Antonino La Magna, Alessandra Alberti, Emanuele Smecca, Giovanni Mannino and Ioannis Deretzis; CNR Institute for Microelectronics and Microsystems, Italy

Mixed halide perovskites containing a compositional mixture of formamidinium (FA⁺) and methylammonium (MA⁺) ions are the actual standard for obtaining record-efficiency perovskite solar cells. Although the compositional tuning that brings to optimal performance of the devices has been largely established, little is understood on the role of even small quantities of the MA⁺ ions in boosting the efficiencies of primarily FA⁺-based hybrid perovskite solar cells. In this study, we use Car-Parrinello molecular dynamics in large supercells containing different ratios of FA⁺ and MA⁺ ions. Our analysis shows that the introduction of MA⁺ cations in the perovskite crystal reduces the orientational disorder of the FA⁺ cations and leads to a lowering of the vibrational intensity of the inorganic lattice. The charge asymmetry of the MA⁺ cation within the inorganic cage plays a key role for such ordering process, as it accelerates the reorganization of the organic molecules towards energetically more favorable configurations. Such structural/vibrational optimization facilitates the transport of the photogenerated carries and, in conjunction with the higher thermal stability of FA⁺-based perovskites, it should be at the origin of the enhanced photovoltaic properties of mixed FA⁺-MA⁺ perovskites.

EN09.13.25
Machine Learning of Electrochemical Reactions at the Metal-Hybrid Perovskite Interfaces from Voltage Dependent Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) Data Katherine N. Higgins¹, Matthias Lorenz², Maxim Ziatdinov², Rama Vasudavan², Liam Collins², Anton V. Ievlev², Olga S. Ovchinnikova², Sergei Kalinin² and Mahshid Ahmadi¹; ¹University of Tennessee, Knoxville, United States; ²Oak Ridge National Laboratory
Laboratory, United States

Electrochemical reactivity at the hybrid perovskite interfaces remains one of the most complex phenomena affecting their applications, both via stability of hybrid perovskite structures and via enabling novel functionalities such as sensing [1, 2]. However, exploration of these phenomena is severely limited by the intrinsic complexity of the hybrid perovskite electrochemistry [3, 4], presence of multiple mobile ionic species, and possible role of the environmental species at the triple-phase junctions [5]. Here we report the in-situ studies of electrochemistry of hybrid perovskite-metal interface via time- and voltage-resolved time of flight secondary ion mass spectrometry (ToF-SIMS) measurements of lateral perovskite heterostructures. ToF-SIMS data allows visualizing lateral chemical composition along the surface and its time evolution with light and bias. The machine learning workflow combining Hough transform and non-negative matrix factorization is developed to extract the salient features of associated chemical changes. These data are further compared to the time-resolved Kelvin Probe Force Microscopy measurements. Furthermore, the non-negative tensor decomposition is used to separate the time- and voltage-dynamics in the multidimensional data sets. Our in-situ characterizations provide a comprehensive information on the chemical nature of moving species, ion accumulation, and interfacial electrochemical reactions.


SESSION EN09.14: Emerging Properties and Frontier Phenomena of Halide Perovskites
Session Chairs: Natalie Banerji and Philip Schulz
Friday Morning, December 6, 2019
Hynes, Level 2, Room 206

8:00 AM EN09.14.01
Puzzling Perovskite Photoconductivity Dynamics Revealed by Scanned Probe Measurements of Electric Force Gradients, Dissipation and Impedance Spectra John A. Marohn1, Ali M. Tirmzi1, Ryan P. Dwyer1, Rachael Cohn1, Jeffrey A. Christians2, David T. Moore2, Fangyuan Jiang2, Jake Precht2, Rajiv Giridharagopal2 and David S. Ginger2; 1Cornell University, United States; 2National Renewable Energy Laboratory, United States; 3University of Washington, United States

We recently undertook a rigorous treatment of the interaction of a charged cantilever with an electrically conductive sample having significant sample impedance. The results were surprising. Starting from an electromechanical model of the cantilever-sample interaction, we used Lagrangian mechanics to derive coupled equations of motion for the cantilever position and charge [1]. Using this approach we derived equations describing the cantilever frequency shift and friction observed in Kelvin-probe and electric-force microscopy experiments. A key player in our theory is the transfer function describing the voltage drop across the tip-sample gap; this transfer function depends on the tip-sample capacitance and the complex sample impedance (i.e., sample capacitance and resistance). Our central new finding is that the cantilever frequency and dissipation measure the real and imaginary parts, respectively, of this transfer function. We show how scanned-probe, broadband local dielectric spectroscopy measurements enable us to characterize the local sample impedance. Our new treatment enables us to clearly understand, for the first time, how both sample capacitance and resistance contribute to the frequency shift and dissipation observed in electrical scanned-probe microscope experiments. We have used these insights to study light-induced conductivity and capacitance in a series of 3D perovskite [2,3] and 2D [4] perovskite and organic photovoltaic films as a function of time, temperature, and substrate. Many, though not all, of the perovskite samples show a conductivity which rises...
promptly upon illumination and recovers slowly in the dark. This recovery shows an activated temperature
dependence with a large activation consistent with ion or vacancy motion. These findings are generally consistent
with the Kim-Maier picture that light creates vacancies [5].

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Resolved Electrical Scanning Probe Microscopy of Layered Perovskites Reveals Spatial Variations in Photoinduced
Ionic and Electronic Carrier Motion. ACS Nano 2019, 13(3):2812-2821, doi: 10.1021/acsnano.8b08390

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10.1038/s41563-018-0038-0

8:15 AM EN09.14.02
Excitonic Properties of Lead Halide Perovskites under Weak Magnetic Field—Implication of Strong Exciton-
Phonon Coupling Yasuhiro Yamada1, Hirofumi Mino1, Kenichi Oto1 and Yoshihiko Kanemitsu2; 1Chiba
University, Japan; 2Kyoto University, Japan

Lead halide perovskites APbX3 [A = Cs+, CH3NH3+ (MA+), and CH(NH2)2+; X = I−, Br−, and Cl−] have attracted
attention both from the viewpoint of fundamental physics and device applications such as solar cells and light-
emitting devices because of their unique optoelectronic properties. To clarify the origin of the advanced features of
this class of materials, we have so far studied the photoresponses of lead halide perovskite thin films, single crystals,
and perovskite-based devices, revealing unique carrier recombination dynamics.1-5) In addition, the recent researches
have suggested the polaron formation is the key mechanism for the unique nature of halide perovskites. However,
the impact of electron-phonon interaction on the band-edge optical properties are still under discussion.
Magneto-reflectance spectroscopy is one of the most powerful tools to derive the band-edge optical parameters of
semiconductors including exciton binding energy, reduced mass, effective dielectric constant, etc. However,
previous magneto-optical studies on lead halide perovskites have estimated the exciton binding energies by
employing extremely strong pulsed magnetic fields exceeding 100 T. This approach was difficult for the accurate
determination of exciton binding energy at zero magnetic field. Moreover, previous theoretical works have suggest
that special attention is needed for the excitonic properties under strong magnetic field in the case of strong exciton-
phonon interaction. Therefore, the measurements with high-quality crystals under weak magnetic fields are essential
for an accurate estimation.

In this work, we performed high-sensitivity measurements using circular dichroism of reflectance at low
temperatures (1.5 K) under relatively weak magnetic fields (< 7T), where the cyclotron energy is sufficiently small
compared with the LO phonon energy and exciton binding energy. We successfully observed the higher-order
exciton states (1s, 2s, and 3s) of a MAPbBr3 single crystal, which enabled us to determine exciton binding energy
accurately. The estimated exciton binding energy is much smaller than that of previous work under strong field. In
the presentation, we will discuss the discrepancy between the data of low- and strong magnetic field in conjunction
with the strong exciton-phonon interaction. Also, the results of different halide perovskites will be compared.

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Final Program 1/13/2020 941
Non-Radiative Recombination in Metal Halide Perovskites—Thin Films vs Bulk Crystals

Martin Ledinsky1, Ales Vlk1, Zdenek Remes1, Jan Valenta2, Tereza Schonfeldova1, Jakub Holovsky1,3, Zdenka Hajkova1, Lucie Landova1,3, Erkan Aydin4, Stefaan De Wolf4 and Antonin Fejfar1; 1Institute of Physics AS CR, Czechia; 2Charles University, Faculty of Mathematics and Physics, Czechia; 3Faculty of Electrical Engineering, Czech Technical University in Prague, Czechia; 4King Abdullah University of Science and Technology (KAUST), Saudi Arabia

Metal-halide perovskites show many interesting properties important for its use in optoelectronic devices, such as solar cells. One of the prime characteristics is their very low deep defect density, leading to relatively low non-radiative losses. This is directly translates into a high density of photo-generated carriers in these films resulting in a very high open-circuit voltage ($V_{OC}$).1 However, although excellent power conversion efficiencies (PCEs) have been reported (>24%), the remaining $V_{OC}$ losses are an open challenge to maximize the PCE. To reveal the correlation between electronic quality and the perovskite solar cells we report here on a set of spectroscopic measurements.

First, we probed the temperature dependence of the absorption spectra of methylammonium lead iodide and bromide (CH$_3$NH$_3$PbI$_3$/Br$_3$), both for films and bulk crystals. We extracted the Urbach energy, $E_0$, as the reciprocal value of the slope of the absorption at the band edge, when plotted in a logarithmic scale. Its value depends on the material disorder and generally correlates well with the loss in $V_{OC}$ of optimized cells, compared to their bandgap.2,3 We found a strong decrease in $E_0$ upon cooling, accompanied by a slow decrease in their optical band gap energy. Values measured for films and bulk crystals were highly comparable, indicating bulk-like properties of perovskite films.

Next, from the theoretical $E_0$ temperature dependence, we obtained the average energy of electronically active phonon states to be about 100 cm$^{-1}$, which implicates that the dynamic disorder of halide perovskite films and single crystals is mainly caused by cage vibrations.4 We were able to calculate the density of active static defects in perovskites from the temperature dependence as well. Its value is very low for all characterized materials in comparison with other materials used for solar cells, including bulk monocrystal semiconductors like GaAs or crystalline silicon. Thin methylammonium lead iodide films doped by Cs and/or Rb reveal an even lower deep defect density, which is in agreement with the overall superior properties of finalized cell based on these materials.

Finally, we found a strong correlation between the $V_{OC}$ deficiency of finalized solar cells and $E_0$ measured by PL spectroscopy. We will show these results in combination with measurements of the quantum yield PL efficiency and correlate these with non-radiative $V_{OC}$ losses in the solar cell. These results will help to establish more practical efficiency limits of perovskite solar cells by taking into account the $E_0$, not only the Shockley-Queisser radiative based limit, which considers just the bandgap of active material.

References


Direct X-Ray Detection by Stable and Radiation Hard Perovskite Thin Films

Beatrice Fraboni1,2, Andrea Ciavatti1,2, Laura Basiricò1,2, Satyaprasad P. Senanayak1 and Henning Sirringhaus3; 1University of Bologna, Italy; 2INFN, Italy; 3University of Cambridge, United Kingdom
The demand for large area high-energy radiation detection systems combining high sensitivity and low-cost fabrication, has pushed the research in the last ten years to develop and design both novel materials and device geometries. Despite organic semiconductors have attracted a great attention, their low atomic number strongly limits the high-energy radiation absorption and, blending the organic solution with high Z nanoparticles is necessary to maximize their radiation absorption. Hybrid organic-inorganic perovskites have been recently proposed as alternative materials for X- and γ-photon direct detection, thanks to their high Z atoms, combined with high charge mobility.

In this work we report on thin film X-ray detectors made of solution processed Cesium-containing triple cation perovskite, namely Cs0.05(MA0.17FA0.78)Pb(I0.8Br0.2)3 (CsFAMA), where cesium (Cs) has added to mixed organic cations (methylammonium (MA) and formamidinium CH3(NH2)2 (FA)) and mixed halides (I and Br). We demonstrate how X-ray detectors based on solution processed CsFAMA film possess a high sensitivity, with values up to 80 µC mGy⁻¹ cm⁻³ in short-circuit conditions, and up to 380 µC Gy⁻¹ cm⁻² when operated under low (i.e. 4V) bias conditions: two orders of magnitude higher than previously reported perovskite thin films and comparable to perovskite single-crystal at 50V operating bias [1]. We performed radiation hardness tests and verified that the detectors are still properly working after receiving a total dose of 10 Gy in few minutes. Indeed, the combination of thin films and long carrier diffusion length allows in perovskites the efficient collection of photogenerated charges, even in presence of defects or radiation-induced traps, resulting in a higher radiation tolerance than thicker films and single crystals. Finally, we characterized perovskites thin films with enhanced stability in air. Remarkably, the electrical performance of the final detectors is still unaffected after 50 days of storage in air, with degradation of X-ray sensitivity limited to 15%.

In the light of the above discussed state-of-the-art, we reckon that thin film perovskite devices: i) surpass the state-of-the-art performance of inorganic large area detectors (a-Se and poly-CZT); ii) can overcome the scalability limitation of thick layers and single crystals; iii) allow to envisage battery-operated wearable detectors thanks to their low voltage operation. Our studies confirm the great potential of perovskite thin films devices (e.g. solar cells and X-ray detectors) for space application, where light-weight, large area, mechanical flexibility and radiation hardness are crucial features.


9:00 AM EN09.14.05
Revealing the Dynamics of Synthesis and Structure-Property Evolution of Hybrid Metal Halide Perovskites via Multi-Modal In Situ Probes Tze-Bin Song¹, Shambhavi Pratap², Nobumichi Tamura¹ and Carolin M. Sutter-Fella¹; ¹Lawrence Berkeley National Laboratory, United States; ²Technical University of Munich, Germany

The field of metal halide perovskites is moving towards more and more complex compositions enabling improved device performance and stability. Most of the improvements however, were achieved through empirical optimization of processing conditions. Fast and complex chemical reactions lead to significant variations in material properties. Precise control over device performance requires a better understanding and active control over synthetic parameters, thus in situ monitoring of evolving properties can help identify synthesis and structure-property relationships.

We study metal halide perovskite synthesis via multi-modal in situ characterization combining synchrotron diffraction, photoluminescence, infrared and optical imaging to shed light on evolving material properties. Using this approach, we are able to identify different formation paths determined by the nature of the chemical precursor, including the precursor phase transition to perovskite phase and direct perovskite formation from molecular building blocks. Moreover, we find that final film morphology is determined in the first seconds of annealing and can be related to crystalline precursor phases. This new multi-modal platform enables simultaneous optical as well as structural characterization already during spin coat deposition of multicomponent precursors and antisolvents, thus allows new insights into the complex dynamics related to perovskite formation.

9:15 AM *EN09.14.06
Anharmonic Semiconductors—Lessons Learned from Halide Perovskites Omer Yaffe; Weizmann Institute, Israel

In semiconductor physics, the dielectric response, charge carrier mobility and other electronic material properties at finite temperatures, are always treated within the framework of the harmonic approximation. This approach is very
successful in capturing the properties of tetrahedrally bonded semiconductors such as silicon and GaAs.

In my talk, I will show that halide perovskites are fundamentally different due to their strongly anharmonic lattice dynamics. Large amplitude, local polar fluctuations induced by lattice anharmonicity localize the electronic states and enhance the screening of electric charge within the material. In other words, halide perovskites behave more like a liquid than a crystalline solid. I will also discuss the implications of these findings on other families of semiconductors such as organic and rock-salt semiconductors.

9:45 AM BREAK

10:15 AM EN09.14.07
Investigations on Perovskite Materials and Solar Cells by Surface Science and Advanced Characterization
Yabing Qi; Okinawa Institute of Science and Technology, Japan

Metal halide perovskite solar cell research keep progressing on various fronts. My group at OIST uses surface science and advanced characterization to obtain fundamental understanding about perovskite materials and solar cells. The research focus in the field has been shifting from power conversion efficiencies to stability and upscalability. In this talk, I will present our research progress on degradation mechanisms of perovskite materials, development of strategies to improve stability of perovskite materials and devices, upscalable fabrication of perovskite solar cells and modules, and surface science understanding of perovskite materials and stability.

10:45 AM EN09.14.08
Energy Level Tuning of Perovskite Layers for Efficient Integrated Perovskite/Bulk Heterojunction Solar Cells
Matyas Daboczi¹, Jinhyun Kim¹, Jinho Lee¹,², Chieh-Ting Lin¹, Hongkyu Kang², Yi-Chun Chin¹, Gabseok Seo¹, Stoichko D. Dimitrov³, Martyn McLachlan¹, Kwanghee Lee³, James R. Durrant¹,³ and Ji-Seon Kim¹; ¹Imperial College London, United Kingdom; ²Gwangju Institute of Science and Technology, Korea (the Republic of); ³Swansea University, United Kingdom

Interfacial energy level alignment between the constituent layers of a solar cell is critical in order to avoid photogenerated charge carrier losses and hence to achieve high device efficiency¹. In this presentation we focus on the integrated perovskite/bulk heterojunction solar cell (referred to here as the integrated cell), which applies a small bandgap organic semiconductor based bulk heterojunction (BHJ) blend on top of a larger bandgap perovskite layer in order to harvest both the visible and near-infrared part of the solar spectrum²,³. We reach a high power conversion efficiency (PCE) of 17.7%, however this is lower than the 19.2% (calculated based on the increase in short circuit current), which is due to decreased fill factor in the integrated cell compared to the reference perovskite device. We show that the origin of such losses is the presence of a 250 meV energetic barrier at the perovskite/BHJ interface leading to undesired charge carrier accumulation and recombination. A possible strategy to overcome this limitation is to shift the energy levels of either the perovskite or the BHJ layer. We will demonstrate how this can be achieved by small compositional change of the perovskite layer. We will show two promising ways to tune the valence and conduction band edges of the widely used methylammonium lead iodide (MAPI) photoactive layer. First, by incorporating tin and bromide ions into MAPI, shifting the valence band edge between -5.4 and -5.0 eV and the conduction band edge between -3.8 and -3.5 eV is achieved. Applying only 15% tin and 30% bromide leads to a perovskite layer with the same bandgap (1.6 eV) as MAPI but with more than 200 meV shallower energy levels.

Second, we will show that that a similar shift (100-200 meV) towards shallower energy levels can also be achieved by the simple incorporation of only 12.5% bromide into MAPI. Despite the increased bandgap (1.65 eV) the best single-junction devices with such mixed halide system can reach PCE of 19.2% in single-junction devices. Surface photovoltage and energy level measurements show that the origin of such improvement is the shallower Fermi level in the developed mixed halide perovskite, which changes the interfacial band bending and by that helps hole extraction in the device. We will show that both of the developed perovskite layers with energy levels shifted shallower by around 200 meV compared to MAPI can be applied in the integrated perovskite/bulk heterojunction solar cell in order to improve on their efficiency.

Our results give an invaluable tool to increase the performance of perovskite based integrated devices through improved interfacial energy level alignment, which tool can also be applied in any perovskite multi-junction devices.

References:

**11:00 AM EN09.14.09**

**New Deposition Route for Formamidinium Lead Iodide (FAPbI3) Perovskite Nanocrystals**

Dylan Amelot¹, Nadine Witkowski¹, Emmanuel Lhuillier¹, Alberto Calloni², Gianlorenzo Bussetti², Herve Cruguel¹ and Sebastien Royer¹; ¹Institut des nanosciences de Paris, France; ²Dipartimento di fisica, Politecnico Milano, Italy

Lead halide perovskite (LHP) have received a lot of attention over the past decade, notably due to the unprecedented evolution of LHP solar cells leading to efficiency up to more than 20% in only a few years. Recently, a new approach based on colloidal perovskite nanocrystals (PNC) of CsPbI₃ led to great improvements for nanocrystal-based solar cells[1]. A tremendous amount of work has been done over the past few years to better understand the electronic/excitonic structure, optoelectronic properties and degradation mechanisms and new surface chemistry tools are being developed[2-4]. However, there is still a lack of a clear, unified picture of the different mechanisms that limit the efficiency of the devices, whether at the material level or at the interfaces in device, or on how to address these limitations. There is also room for improvement of the transport properties of PNC films through more tailored surface chemistry treatments. A more standardized approach of film preparation and characterization could lead to better understanding the limitations of PNC devices and improving their overall efficiency.

At Institut des Nanosciences de Paris, we recently synthesized formamidinium (FA) lead iodide (FAPbI₃) nanocrystals, which have the smallest band gap of the LHP nanocrystal family (around 1.6 eV), ideal for photovoltaic applications and which show better stability than their Cesium-based counterparts. Characterizations using X-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), X-ray photoemission (XPS) and transport measurements on spin-coated films will be presented. These measurements allowed us to deduce the crystalline structure and inorganic stoichiometry of these nanocrystals, in agreement with literature. We also report on a ligand exchange procedure, using a process previously developed for CsPbI₃ [5], to enhance carrier transport in films. Valence band photoemission (UPS) combined with Inverse photoemission (IPES) measurements have been conducted in collaboration with a team at Politecnico Milano, suggesting that FAPI is a near intrinsic semiconductor with a weak n-type character. We are also developing a new route of film deposition that consists in spraying the nanocrystals in vacuum. We will present preliminary characterizations of the obtained films showing good agreement with spin-coated ones. This new deposition technique would allow for unprecedented in-situ measurements on these PNC as for instance studying the interfaces in devices or films under stresses such as radiation, temperature, oxygen or humidity.


**11:15 AM EN09.14.10**

**Peculiarities in the Emission and Absorption Properties of Cs₂AgBiBr₆ Double Perovskite Crystal**

Michal Baranowski¹,³, Szymon Zelewski³, Joanna Urban¹, Agnieszka Kuc¹, Laura Schade⁴, Roger Johnson⁴, Markus Dollmann⁴, Pabitra Nayak⁴, Henry J. Snaith¹, Paolo Radealli⁴, Robert Kudrawiec², Robin Nicholas⁴ and Paulina Plochocka¹; ¹Laboratoire National des Champs Magnétiques Intenses, UPR 3228, CNRS-UGA-UPS-INSA, France; ²Wroclaw University of Science and Technology, Poland; ³Helmholtz-Zentrum Dresden-Rossendorf, Germany; ⁴University of Oxford, Clarendon Laboratory, United Kingdom

Double perovskite crystals such as Cs₂AgBiBr₆ have appeared as a potential answer to inherent instability and toxicity of classic hybrid organics-inorganic led-halide perovskites. In their structure Pb²⁺ cation is substituted by pair of cations with formal oxidation states +1 and +3 forming so-called “double perovskite” with general formula
A\textsuperscript{+1}\textsubscript{2}B\textsuperscript{+1}\textsuperscript{2}X\textsubscript{6}. Band structure calculations show that many of the double perovskite compounds have a band gap in the range promising for solar cell applications and some of the possible compounds have already been synthesized corroborating theoretical predictions. So far Cs\textsubscript{2}AgBiBr\textsubscript{6} has been the most intensively studied representative of double perovskite family. Theoretical calculations predict that the fundamental band gap of Cs\textsubscript{2}AgBiBr\textsubscript{6} has an indirect nature but surprisingly the photoluminescence emission can be easily observed from this compound. In this work we show that overall picture of the emission form Cs\textsubscript{2}AgBiBr\textsubscript{6} might be far more complicated than indirect band to band emission. Using a combination of photoluminescence (PL), photoluminescence excitation (PLE) and absorption studies we show that the PL emission in Cs\textsubscript{2}AgBiBr\textsubscript{6} is dominated by a strong electron-phonon interaction. Our experimental results indicate that the emission from this material is related to a color center (or self-trapped exciton) rather than a band-to-band transition. The resonant excitation of this center results in a strong enhancement of PL emission demonstrating the competition between the nonradiative recombination paths related to the indirect bandgap and color center emission. Crucially, we show that the significant PL broadening together with the large Stokes shift between emission and PLE maximum can be well explained using Franck-Condon model indicating a strong electron-phonon coupling characterized by a relatively large Huang-Rhys factor ~12. In addition, the nontrivial nature of the PL emission in Cs\textsubscript{2}AgBiBr\textsubscript{6} is revealed by magnetic field studies. Surprisingly, the PL exhibits an unexpected red shift and decrease of its intensity with increasing magnetic field. Such behavior is extremely atypical for semiconductors, where usually a blue shift and increase of intensity of the emission line is observed at high magnetic fields as a consequence of the squeezing of the exciton wave function by magnetic field. Moreover, the PL shift in magnetic field depends on temperature and systematically decreases as the temperature increase from 4K to 100K. These results suggest that there remain many open questions concerning the exact nature of PL emission in these fascinating compounds.

11:30 AM EN09.14.11
Uncovering the Energy Level Alignment at a 2D/3D Perovskite Interface Scott Silver and Antoine Kahn; Princeton University, United States

Metal halide perovskite (MHP) solar cells have garnered significant attention over the past six years for their high efficiency and low processing costs. However, their relatively poor environmental stability remains as one of the preeminent challenges impeding their widespread proliferation. One increasingly popular method for improving the stability of these materials and devices is to cap the 3D MHP layer with a layer of a higher stability 2D Ruddlesden-Popper phase perovskite.\cite{1,2} These 2D-capped devices have demonstrated success in improving device lifetimes with minimal reduction in efficiency, yet the energy level alignment at these 2D/3D interfaces has not been measured directly and remains largely unknown. In this study, we fabricate an interface between the 3D methylammonium lead iodide (MAPbI\textsubscript{3}) and the 2D butylammonium lead iodide (BA\textsubscript{2}PbI\textsubscript{4}) using a butylamine post-treatment technique investigated in the literature\cite{3} and probe the ionization energy and electron affinity of the resulting film as well as the valence and conduction band offsets at the interface using ultraviolet and inverse photoelectron spectroscopy, respectively. The resulting energy diagram indicates a type I heterojunction with little if any charge transfer between the two layers. The BA\textsubscript{2}PbI\textsubscript{4}\cite{4} layer acts as a small barrier for the extraction of electrons and a larger barrier for holes. Design guidelines for optimizing the 2D/3D interface in future work will be discussed.

References:

11:45 AM EN09.14.12
Band Alignment and Photoinduced Charge Transfer in CsPbBr\textsubscript{3}-CdSe Nanoplatelet Hybrids Coupled by Molecular Linkers Swayandipta Dey\textsuperscript{1}, Hagai Cohen\textsuperscript{1}, Iddo Pinkas\textsuperscript{1}, Hong Lin\textsuperscript{2}, Miri Kazes\textsuperscript{1} and Dan Oron\textsuperscript{1};\textsuperscript{1}Weizmann Institute of Science, Israel;\textsuperscript{2}Tsinghua University, China

Controllable interface characteristics are demonstrated at the nanoscale, using two types of semiconducting nanoparticles with nearly identical optical band gaps, CsPbBr\textsubscript{3} nanocrystals, and CdSe nanoplatelets, capped with
bifunctional molecular linkers. By exploiting chemical recognition of the capping molecules, the two types of nanoparticles are brought into mutual contact, thus initiating spontaneous charge transfer and the formation of a strong junction field. Depending on the choice of capping molecules, the magnitude of the latter field is shown to vary in a broad range, corresponding to an interface potential step as large as circa 1 eV. The band diagram of the system, as well as the emergence of photo-induced charge transfer processes across the interface, are studied here by means of optical and photoelectron based spectroscopies. Our results propose an interesting template for generating and harnessing internal built-in fields in heterogeneous nanocrystal solids where two disparate systems coupled by short molecular linkers form an analog of nano p-n junctions with the built-in field depending on the nature of the interface.

SESSION EN09.15: Structure and Morphology—Microscopic Imaging, Tomography and Grain Boundaries
Session Chairs: Emmanuelle Deleporte and Yuanyuan Zhou
Friday Afternoon, December 6, 2019
Hynes, Level 2, Room 206

1:30 PM *EN09.15.01
Tomographic Atomic Force Microscopy Reveals 3D Interconnected Network of Efficient Charge Transfer Channels at Grain Boundaries in Polycrystalline MAPbI3 Thin Films Jingfeng Song,1 Yuanyuan Zhou,2 Michael Martin,1 Andrew Levin,1 Moishe Azoff-Slifstein,1 Nitin P. Padture2 and Bryan D. Huey1; 1University of Connecticut, United States; 2School of Engineering, United States

Hybrid perovskite solar cells based on methylammonium lead triiodide (MAPbI3) are of tremendous scientific and technological interest, with power conversion efficiencies already beyond 22%. Typically, the MAPbI3 thin films for planar solar cells are polycrystalline, with average grain sizes ranging from 100 nm to a few microns. Due to the correspondingly high interfacial area, it is thus imperative to characterize and understand the role of grain boundaries in the photo-generated carrier transport for MAPbI3 thin films. As with many photovoltaics, these interfaces may prove critical to the future design and optimization of high efficiency and reliability MAPbI3 devices. Accordingly, we demonstrate the first fully-3D photo-generated carrier mapping throughout polycrystalline MAPbI3 thin films via Tomographic Atomic Force Microscopy (TAFM). These results unambiguously identify for conventionally prepared polycrystalline MAPbI3 that the grain boundaries act as highly interconnected 2D conductive channels, including photoconductivities up to 4 times greater than the adjacent bulk. The conclusions are also supported by co-located I/V, I/intensity, surface potential, and topographic mapping.

2:00 PM EN09.15.02
Thermal Properties of Highly Oriented All-Inorganic CsPbX3 (X=Br, Cl) Perovskite Films—Dependence on Halide, Dimensionality and Crystal-Phase Tobias Haeger,1 Maximilian Wilmes,1 Johannes Bahre,1 Neda Pourdavoud, Stefan Zaeferrer, Ralf Heiderhoff and Thomas Riedl; 1University of Wuppertal, Germany; 2Max-Planck-Institut für Eisenforschung GmbH, Germany

Thermal management in hybrid and all-inorganic halide perovskite devices is expected to be of outstanding importance for the performance and reliability of solar cells, light-emitting diodes, and lasers, because both lifetime and performance are influenced by temperature or temperature gradients. Aside from hybrid halide perovskites, where the A-site cation is organic, the interest in all-inorganic perovskites is continuously increasing, as they provide a higher stability compared to their hybrid analogues. As thermal conductivities, thermal diffusivities, and heat capacities of these perovskites are typically low, their experimental assessment is extremely challenging [1-3].

Here, local thermal transport studies on all-inorganic cesium lead-halide based perovskite thin films, with Cl, Br as halides (X), will be presented. Re-crystallized CsPbX3 and CsPb2X5 layers were realized by the application of a planar hot pressing (PHP), previously developed by us [4,5]. Highly 100 oriented films are confirmed by X-ray diffraction (XRD) and electron backscattered diffraction (EBSD) analysis. Furthermore, we evidence a coexistence of grains consisting of the 3D phase (CsPbX3) and the 2D phase (CsPb2X5) depending on the preparation conditions of pristine layers [6]. Extended quantitative thermal conductivity measurements without the need of elaborate sample preparation are performed applying an advanced 3ω-technique in the frequency domain using our Scanning
Near-field Thermal Microscope [3]. We simultaneously map the topography, thermal conductivity (e.g. CsPbBr$_3$ and CsPb$_2$Br$_5$: 0.43 W/mK and 0.33 W/mK, respectively), thermal diffusivity (both 0.3 mm$^2$/s), and the volumetric thermal capacity (1.3 J/(cm$^3$K) and 1.1 J/(cm$^3$K)) with a high spatial resolution of typically 100 nm to understand the thermal properties in dependence of the dimensionality of the perovskite material. For comparison and as a reference, their single crystalline analogues, which are grown by anti-solvent vapour crystallisation, have been studied. In addition to heat transport analyses in dependence of the halide and dimensionality, the influence of temperature-dependent phase-transitions (e.g. 3D CsPbBr$_3$: orthorhombic - tetragonal - cubic) on the thermal properties are analysed the behaviour near the phase-transition is discussed in detail.

Our results demonstrate, that thermal management in all-inorganic halide perovskite devices will be a serious challenge and requires particular attention.


2:15 PM EN09.15.03
Enhanced Charge Transport by Incorporating Formamidinium and Cesium Cations for Two-Dimensional Perovskite Solar Cells Fei Zhang and Kai Zhu; National Renewable Energy Laboratory, United States

Organic-inorganic hybrid two-dimensional (2D) perovskites (n≤5) have recently attracted significant attention due to their promising stability and optoelectronic properties. Normally, 2D perovskites contain a mono cation (e.g., methylammonium (MA$^+$) or formamidinium (FA$^+$)). Here, we report for the first time on fabricating 2D perovskites (n=5) with mixed cations of MA$^+$, FA$^+$, and cesium (Cs$^+$). The use of these triple cations leads to the formation of a smooth, compact surface morphology with larger grain size and fewer grain boundaries compared to the conventional MA-based counterpart. The resulting perovskite also exhibits longer carrier lifetime and higher conductivity in triple-cation 2D perovskite solar cells (PSCs). The power conversion efficiency (PCE) of 2D PSCs with triple cations was enhanced by more than 80% (from 7.80% to 14.23%) compared to PSCs fabricated with a mono cation; the PCE is also higher than that of PSCs based on binary-cation (MA$^+$-FA$^+$ or MA$^+$-Cs$^+$) 2D structures.

2:30 PM EN09.15.04
Understanding Charge Separation and Recombination in your Own Perovskite Solar Cell with an Open-Access-Online Platform to Swiftly Compute Your Device Band Diagram Luca Bertoluzzi$^1$, Kevin A. Bush$^1$, Jixian Xu$^2$, Caleb C. Boyd$^{1,2}$, Rohit Prasanna$^{1,2}$, Brian O'Regan$^1$, Michael D. McGehee$^2$ and Nicholas Rolston$^1$; $^1$Stanford University, United States; $^2$National Renewable Energy Laboratory, United States; $^3$Sunlight Scientific, United States

Single junction perovskite solar cells have now achieved efficiencies exceeding 24% and silicon-perovskite tandem solar cells are outperforming single junction silicon devices. The path to achieve the last remaining efficiency percentiles to reach the Shockley-Queisser limit for single junction devices requires to understand the main limiting processes that hinder device performance.

One of the crucial parameters that control device performance is the photogenerated-carrier separation. Efficient charge separation can be achieved by understanding and controlling the electric potential distribution. In perovskite solar cells, the electric potential profile is controlled by mobile halide vacancies that migrate and accumulate at the contacts in response to an applied potential. The potential distribution is dependent on the vacancy concentration. Therefore, it is crucial to quantify the mobile vacancy concentration to understand the electric potential distribution in a perovskite device.

In this talk, we will first show how to measure and calculate the vacancy concentration and provide concentration values for a range of perovskite compositions and contacts. We will then briefly show how to easily simulate the band diagram of one’s own perovskite solar cell with an online-open-access platform we developed.$^1$ We will conclude this talk by discussing some important examples showing the role of the illumination side, the mobile ion
Metal halide perovskite materials exhibit exceptional performance characteristics for low-cost optoelectronic applications. Though widely considered defect tolerant materials, perovskites still exhibit a sizeable density of deep sub-gap non-radiative trap states, which create local variations in photoluminescence [1] that fundamentally limit device performance. These trap states have also been associated with light-induced halide segregation in mixed halide perovskite compositions [2] and local strain [3], both of which can detrimentally impact device stability [4]. Understanding the nature of these traps will be critical to ultimately eliminate losses and yield devices operating at their theoretical performance limits with optimal stability. We recently used local photoemission electron microscopy (PEEM) to directly visualize the deep trap sites, revealing spatially heterogeneous nanoscale clusters.

In this talk we detail a low-dose, high resolution and multi modal approach to determine 1) the physical origins of these deep trap states 2) their effect on the electronic properties of (Cs0.05FA0.78MA0.17)Pb(I0.83Br0.17)3 thin films and 3) their association with sub-grain crystallographic boundaries. By combining scanning electron and synchrotron X-Ray microscopy techniques with PEEM measurements we reveal that there are distinct structural and compositional fingerprints associated with the generation of these trap sites. In addition, our scanning electron diffraction measurements achieve a spatial resolution of 4nm with an accumulated electron dose of only ~6 e/Å² (over an order of magnitude lower than established tolerable dose limits for metal halide perovskites). We will also explore how this combination of high-resolution and low accumulated dose provides new insights into the pristine crystallography of these materials on the nanoscale; thus helping to answer ongoing open questions such as ‘what truly defines a grain?’ and ‘are grain boundaries beneficial or detrimental to performance’? References

3:00 PM BREAK

3:30 PM EN09.15.06
Shifting the Thermodynamics of Polymorph Transitions in Metal-Halide Perovskites via Nanoconfinement
Xiaoqing Kong and Stephanie Lee; Stevens Institute of Technology, United States

Metal-halide perovskites undergo multiple temperature-dependent polymorph transitions, generally with the smallest bandgap phases thermodynamically favored only at elevated temperatures. We present nanoconfinement as a strategy to shift the thermodynamics of polymorph transitions in order to stabilize high-performance metal-halide perovskites against temperature-induced polymorph transitions and humidity-induced degradation. Specifically, when crystal sizes are reduced to the sub-micron length scale, the surface free energy contribution to the total Gibbs free energy of the crystals becomes increasingly important. By exploiting the dependence of the surface free energy on the symmetry of the crystal structure, it is possible to shift polymorph transitions to lower temperatures under nanoconfinement compared to the bulk. For methylammonium lead iodide (MAPbI₃) crystals confined in anodized surfaces.
aluminum oxide (AAO) templates with pore sizes ranging from 20 – 250 nm, the cubic polymorph was found to be stable at temperatures above 200 K, compared to 330 K for the bulk. Similarly, nanoconfined γ-CsPbI₃ formed at 370 K in AAO templates, compared to 448 K in the bulk phase and was stable to temperatures as low as 4 K once formed. Such stability afforded the extraction of phonon energies of CsPbI₃ from temperature-dependent photoluminescence spectra. Furthermore, these nanoconfined crystals exhibit excellent stability against humidity-induced degradation, with no change in their X-ray diffraction patterns over a period of at least two years upon storage in air.

3:45 PM EN09.15.07
Investigation of S-Donor Solvents for Processing Hybrid Organic-Inorganic Perovskites Joseph C. Hamill¹, Oluwaseun Romiluyi², Sara Thomas¹, Fengyu Zhang¹, Xiaoming Zhao¹, Michael F. Toney¹, Jeffrey Schwartz¹, Antoine Kahn¹, Paulette Clancy⁴ and Lynn Loo¹; ¹Princeton University, United States; ²Cornell University, United States; ³Stanford Synchrotron Radiation Lightsource, United States; ⁴Johns Hopkins University, United States

Lewis base solvents, such as dimethylsulfoxide (DMSO), that strongly coordinate with Pb²⁺ are commonly added to hybrid organic-inorganic perovskite (HOIP) precursor solutions to improve thin-film morphology and subsequent photovoltaic (PV) performance. Although nearly all previous studies of precursor solution chemistry have focused on oxygen-donor solvents as Lewis base additives, we expect “softer,” sulfur-donor solvents to coordinate more strongly with Pb²⁺, a borderline-soft Lewis acid. To confirm this hypothesis, we performed extended X-ray absorption fine structure (EXAFS) spectroscopy at the Pb L₃ absorption edge to probe the coordination environment of Pb²⁺ in solutions comprising mixtures of S- and O-donor solvents. Of the S- and O-donor solvent pairs examined, the S-donor solvent consistently outcompetes its O-donor structural analog for coordination sites around Pb²⁺. In the specific comparison between N-methyl-2-pyrrolidone thione (NMPT) and N-methylpyrrolidone (NMP), density-functional theory calculations indicate that NMPT coordination with Pb²⁺ is favored by 10 kcal/mol relative to NMP coordination with Pb²⁺. Similar to the addition of DMSO to precursor solutions, the incorporation of NMPT in fractional quantities provides morphological control of the perovskite film. Unlike DMSO, however, we found NMPT to be stable against undesired transmethylation or disproportionation reactions with methylammonium [1]. Consequentially, films processed with NMPT exhibit no sub-gap electronic states near the valence band edge, in contrast with films prepared using DMSO. We thus believe NMPT merits serious consideration as a solution additive for producing stable HOIP precursor solutions and high-quality HOIP thin films.


4:00 PM EN09.15.08
Advanced Photo-Hall Characterization to Unravel the Impact of PbI₂ Passivation in MAPbI₃ Julie Euvrard¹, Oki Gunawan² and David B. Mitzi¹; ¹Duke University, United States; ²IBM T. J. Watson Research Center, United States

Metal-Halide perovskite-based solar cells have shown a remarkable rise in performance in less than a decade with power conversion efficiencies now exceeding 23%. Recent literature provides a constant stream of new recipes and processing techniques, leading to improved power conversion efficiencies although often with limited detailed understanding of the mechanism for performance improvement. In particular, additive engineering and stoichiometric variations are widely studied to optimize the performances of the solar cells.[1,2] However, the underlying impact of additives and stoichiometry on transport and recombination properties are only little understood. In this study, we take advantage of a newly developed advanced characterization technique using a highly sensitive Hall-effect measurement performed at variable light intensity.[3,4] This new carrier-resolved photo-Hall technique gives access to both majority and minority carriers properties (n, p, µn and µp). In addition, carrier recombination lifetime τ and diffusion length Ld can be extracted with this technique using light intensities comparable to 1 sun. Importantly, all parameters can be extracted using the same sample and at the same light intensity level. We use the new technique to explore the impact of excess PbI₂ in MAPbI₃ precursor solution (MA: methylammonium), which has been suggested to improve solar cell efficiency through defect passivation at the grain boundaries.[5-7] Samples with similar grain sizes are compared to follow the evolution of transport and recombination properties of the perovskite film with and without the addition of excess PbI₂. We show that excess PbI₂ has a negligible impact on carrier density, conductivity and mobility, while it significantly improves the lifetime by one order of magnitude (from ~1 ns to ~20 ns). Combined with SEM images, these results suggest that
extra PbI₂ effectively passivates deep traps at the MAPbI₃ grain boundaries. Therefore, this study offers an in-depth analysis of the MAPbI₃ properties using an important new characterization technique and supports the passivation role of extra PbI₂.


4:15 PM EN09.15.09
The Role of Metal-Semiconductor Interface in Hybrid Perovskite Devices for High-Performance Solid-State Detector
Shreetu Shrestha1, Hsinhan Tsai1, Kasun Fernando1, Fangze Liu1, Yusheng Lei2, Michael Yoho1, Sheng Xu2, Kevin Baldwin1, Sergei Tretiak1, Duc Vo1 and Wanyi Nie1; 1Los Alamos National Laboratory, United States; 2University of California, San Diego, United States

Hybrid perovskites have emerged as excellent semiconductors enabling efficient opto-electronic devices such as solar cells, light emitting diodes, lasers as well as radiation detectors with performances approaching state-of-the-art. Apart from the intrinsic properties of the semiconductor, interfaces are critical to make a superior device. Hence, understanding the nature of the interface between metal contacts and perovskite is essential to further advance device performance, especially in low power detection applications (i.e. single photon detection mode) where a clean interface with minimized dark recombination is required.

Here, we use scanning photocurrent microscopy (SPCM) on lateral methylammonium lead triiodide (MAPbI) thin film device with commonly used high work function metal and low work function metal contacts to investigate perovskite-metal interfaces. By comparing the spatially resolved photocurrent maps of devices with Au (high work-function metal) to Ti (low work-function metal), we find that a Schottky barrier exists in both cases and the barrier is higher for the Ti/perovskite junction resulting in a lower photocurrent. Our results also suggest that the MAPbI thin films used in this study have a surface work function higher than Au indicating the presence of doping or band bending near the surface. From the decay of the photocurrent profile near the metal contacts, we estimate charge carrier diffusion length to be 9 ± 2 µm. Using this knowledge, we successfully demonstrate a single crystal MAPbI gamma ray detector from which sharp gamma-ray induced pulses are observed. This is benefitted from the clean interface built with high work function metal that blocks the dark current and extracts photo-generated carriers. Our study indicates that the interface plays a significant role especially in solid state detector operating at low flux photon counting mode.

4:30 PM EN09.15.10
Halide Perovskites with a Cesium Layer—Work Function Variation and a Model of Photo- and Thermal-Field Emission
Kevin L. Jensen1, Daniel Finkenstadt2, Andrew Shabaev1, Sam Lambrakos1, Matthew Critchley2, Sina Lewis1, Amanda Neukirch2, Nathan Moody3 and Sergei Tretiak4; 1U.S. Naval Research Laboratory, United States; 2U. S. Naval Academy, United States; 3The Ohio State University, United States; 4Los Alamos National Laboratory, United States

Halide perovskites have been extensively studied and show promise for a variety of optoelectronic application, e.g., satellites, energy conversion technologies, medical imaging, and in particular, photocathode materials for x-ray Free Electron Lasers (x-FEL’s) and photo-detectors. A thin layer of cesium (Cs) on pure inorganic perovskites, particularly CsPbBr₃ and CsPbI₃, has been shown to significantly improve their photocathode performance [1], primarily because the Cs coating significantly reduces the work function from ~4 eV to between 1.8 - 2.3 eV, depending on surface termination, crystal face, and degree of sub-monolayer coverage. In the present work, we shall: (i) combine findings from Density Functional Theory (DFT) with a phenomenological model developed by Gyftopoulos and Levine to predict the reduction in work function in relation to Cs coverage. (ii) describe the variation in work function Φ as a function of submonolayer coverage θ, (iii) explore the relationship between
emitted charge and work function variation using a thermal-field-photoemission model for which the transmission probability is evaluated using a novel approach to finding the Gamow tunneling factor for Schottky barriers, and (iv) demonstrate the performance of the new thermal-field and photoemission methods of evaluating current density compared to exact transfer matrix approaches (TMA) for the evaluation of transmission probability (methods which are applicable to photocathodes as well as thermal-field emitters in general).


SYMPOSIUM EN10

Emerging Light-Emitting Materials and Devices—Perovskite Emitters, Quantum Dots and Other Low-Dimensional Nanoscale Emitters
December 2 - December 6, 2019

Symposium Organizers
Hanwei Gao, Florida State University
Maksym Kovalenko, ETH Zurich
Tae-Woo Lee, Seoul National University
Jiangeng Xue, University of Florida

Symposium Support
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* Invited Paper

SESSION EN10.01: Low-Dimensional Perovskite/QD Emitting Materials and their Optical Phenomena
Session Chairs: Maksym Kovalenko and Tae-Woo Lee
Monday Morning, December 2, 2019
Sheraton, 2nd Floor, Back Bay D

8:00 AM EN10.01.01
Tuning the Transition Dipole Moment of CsPbBr3 Nanoplatelets for Improved Light Outcoupling of Blue Light-Emitting Diodes Tassilo Naujoks1, Thomas Morgenstern1, Carola Lampe2, Matthew Jurow2, Yi Liu2, Alexander S. Urban2 and Wolfgang Bruetting1; 1University of Augsburg, Germany; 2Ludwig-Maximilians-Universität München, Germany; 3Lawrence Berkeley National Laboratory, United States

The unique optical properties of lead halide perovskites have drawn significant attention towards their application in light emitting devices (LEDs) in recent years. While quantum yield, emission wavelength and stability are already in the focus of many research groups, the orientation of the emissive transition dipoles has rarely been investigated. As known from other thin film applications such as organic LEDs, this quantity can severely affect the light outcoupling of the device and thereby limit the external quantum efficiency.

In this work, we investigate CsPbBr3 nanoplatelets of variable thickness and determine the orientation of their transition dipole moments from thin film radiation pattern analysis. We then apply optical simulations to elucidate the performance limits of perovskite based blue LEDs in prototypical device architectures.

As was already shown, the transition dipole moment (TDM) of CsPbBr3 nanocrystals can be tuned from preferentially vertical in nanocubes to horizontal in ultra-thin nanoplatelets [1, 2]. At the same time, quantum
confinement renders the emission color from green to deep blue. Here, we use a systematic thickness variation from 2 to 6 monolayer thick nanoplatelets to study the tunability of the TDM orientation and the concomitant color shift. We find that with increasingly beneficial horizontal orientation, the outcoupling efficiency increases to values close to 30%. However, since the photoluminescence quantum efficiency degrades considerably for decreasing thickness [3], the overall maximum device efficiency does not significantly improve beyond 20%. Thus, for the currently available material sets we can conclude that while for nanocubes the non-ideal orientation limits device performance, devices with nanoplatelets are limited by non-optimal PLQYs. Nevertheless, our results reveal very promising new efficiency limits for solution-processed light emitting diodes: Solution-processed, highly efficient deep-blue LEDs, with strong horizontal TDM orientation made of CsPbBr3 nanoplatelets are in reach.


8:15 AM EN10.01.02
Interplay between Broadband and Narrow Photoluminescence in 2D Ruddlesden-Popper Perovskites Ido Hadar1, Ioannis Spanopoulos1, Peijun Guo2, Richard Schaller1,2 and Mercouri G. Kanatzidis1; 1Northwestern University, United States; 2Argonne National Laboratory, United States

2D Ruddlesden-Popper perovskites (2D R-P), are an emerging group of materials that derive from the rapidly growing family of organic-inorganic perovskites. The 2D R-P are formed by the addition of an organic cation to the 3D perovskite, which acts as a spacer and forces the perovskite layers to separate, offering an additional knob to tune the material’s properties. In general, the 2D R-P shows significantly improved stability in comparison to the 3D perovskites and the colloidal nano-perovskites, making these materials appealing for various optoelectronic applications, such as photovoltaic devices and light emitting diodes. An interesting aspect arises from 2D R-P’s versatile structure is the ability to control their photoluminescence properties (PL). Depending on the exact structure and composition, the 2D R-P may show narrow excitonic PL, tunable by quantum confinement effects, low energy emission related to edge states and for some specific structures broadband ‘white’ emission. The latter case is specifically desired as it shows fairly high PL quantum yield and offers a simple path toward devices. Yet, the exact physical origin for the wide emission and the materials’ criteria for obtaining it are still not fully resolved. Experimentally, it was found that perovskite structures exhibiting complex connectivity and strong distortion are more prone to show broadband emission, but there is no clear model of why. The current models explaining the wide emission are focused on study the kinetics between the excitonic states (leading to narrow emission) and the low energy states (leading to broadband PL).

In order to better understand the underlying structural and physical mechanism for the broadband emission, a material that shows a clear transition between the narrow and broadband emission will be beneficial. We found that the simple single layer 2D Ruddlesden-Popper perovskite – (CH3(CH2)3NH3)2PbI4 – can show such transition from narrow PL at room temperature to broadband PL at low temperature. This transition relates to a phase transition from the slightly distorted room temperature structure to a significantly distorted phase below 200 K. At lower temperatures the distortion becomes larger, leading to stronger broadband emission, and at even lower temperatures it becomes weaker in correlation with the previously published kinetic model. By studying additional single layer 2D R-P samples, with longer organic cations as the spacer groups, we further change the distortion and formulate a more general model for the narrow to broadband PL transition. This study enables us to gain a better understanding of how the octahedra distortion in perovskites activate the low energy emissive states and lead to broadband emission and give some simple design rules to rationally approach the synthesis of such materials.

8:30 AM EN10.01.03
Physical Dynamics in Soft Lattice Halide Perovskites Lina Quan1,2 and Peidong Yang1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

Recently, lead halide perovskite materials have introduced a new paradigm for semiconducting materials. The controlled synthesis, detailed structural analysis, optical, and electronic properties are of great fundamental interest.
A high degree of ionic bonding character in perovskites gives rise to higher coordination environments, and significant structural disorder; the collective result is a family of “easy to make, easy to break” materials that are highly dynamic and readily reconfigurable. Particularly, highly ionic perovskite materials exhibit exceptional photophysical and optoelectronic properties even with significant electron-phonon coupling and structural disorder, motivating an investigation into the origins of these outstanding properties. This talk will focus on the research scope from simple ABX₃ inorganic halide perovskite towards other more complex halide perovskites and understand their structures and lattice dynamics. We develop the advanced synthetic methodology of perovskite nanostructures with desired size, composition, and optical properties, including colloidal, solution-phase and vapor-phase approaches. We anticipate rich phase transformation behaviors and rich electronic structures in such complex halide perovskites. Moreover, the phase transition and soft ionic lattice dynamics in such materials were demonstrated in detail using time- and spatially-resolved spectroscopy techniques.

9:00 AM *EN10.01.04
Luminescent Low Dimensional Metal Halide Perovskites and Hybrids Biwu Ma; Florida State University, United States

Organic-inorganic metal halide hybrids, including ABX₃ metal halide perovskites, are an emerging class of functional materials with exceptional structural and property tunability. During the last decade, remarkable progress has been made in using solution processable metal halide perovskites as active materials for optoelectronic devices, including photovoltaic cells (PVs), light emitting diodes (LEDs), photodetectors, and lasers, for their excellent optical and electronic properties. By controlling the morphological dimensionality, low dimensional metal halide perovskites, including 2D nanolealets, 1D nanowires, and 0D quantum dots, have been developed to exhibit distinct properties from their bulk counterparts, due to quantum size effects. For instance, the emission of CsPbBr₃ nanocrystals can be tuned from green for nanocrystals with sizes of larger than the exciton bohr radius (~ 7 nm), to blue for quantum dots, nanowires, nanolealets, and hollow nanocrystals with strong quantum confinement. Besides ABX₃ perovskites, organic metal halide hybrids, containing the same building blocks of metal halide octahedra (BX₆), can be assembled with low dimensional structures at the molecular level, i.e. single crystalline bulk assemblies of metal halides with 2D, quasi-2D, corrugated-2D, 1D, corrugated-1D, and 0D structures. Due to the strong quantum confinement and site isolation, these low dimensional metal halide hybrids at the molecular level exhibit remarkable and unique properties that are significantly different from those of ABX₃ perovskites. For instance, broadband white emissions have been achieved in single crystalline bulk assemblies of 1D metal halide wires and tubes; and near-unity photoluminescence quantum efficiency has been realized for a number of 0D organic metal halide hybrids containing various metal halide species or clusters. In this talk, I will discuss our recent efforts on the development and study of highly luminescent low dimensional metal halide perovskites and hybrids, from synthetic control to device integration.

9:30 AM BREAK

10:00 AM *EN10.01.05
Excitons, Phonons and Excited State Dynamics in Low-Dimensional Halide Perovskites William Tisdale; Massachusetts Institute of Technology, United States

Hybrid organic-inorganic halide perovskites are a newly rediscovered class of solution-processable semiconductor materials with surprisingly promising optoelectronic performance. When fabricated in a nanostructured form – either as layered 2D quantum wells or colloidal nanocrystals – hybrid perovskite nanomaterials exhibit a combination of interesting properties revealing both quantum mechanical and classical composite effects. In this talk, I will discuss the thermal, electronic, and excitonic properties of hybrid perovskite nanomaterials as a function of composition, structure, and temperature – and what these experimental observations tell us about the interactions between the organic and inorganic subphases of this interesting class of materials.

10:30 AM *EN10.01.06
Advances in Reduced-Dimensional Solution-Processed Light Emitters Edward H. Sargent; University of Toronto, Canada

I will discuss progress in the realization of electrically-driven optical sources (LEDs) based on reduced-dimensional materials. I will discuss perovskites, quantum dots, and hybrids of the two.
Multiexciton Interactions in Cesium Lead Halide Perovskite Nanocrystals
Katherine Shulenberger1, Matthew N. Ashner1, Seung Kyun Ha1, Franziska Krieg2,3, Nathan D. Klein1, Hendrik Utzat1, Maksym V. Kovalenko2,3, William Tisdale1 and Moungi G. Bawendi1; 1Massachusetts Institute of Technology, United States; 2ETH Zürich, Switzerland; 3Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Cesium lead halide perovskite nanocrystals have recently emerged as a promising material system for a number of lighting and lasing applications due to their extensive color tunability, high photoluminescence quantum yield, and relatively narrow emission linewidths. Furthermore, these materials exhibit relatively low-threshold optical gain. If perovskite nanomaterials are to meet this potential in light emission applications, it is crucial to have a comprehensive understanding of the properties – not just under low-flux excitation – but under high-flux, device relevant conditions as well. We have thoroughly investigated the properties of the doubly excited state (“biexciton”) in CsPbBr3 nanocrystals utilizing time- and spectrally-resolved ensemble photoluminescence, flux-dependent transient absorption spectroscopy, and single nanocrystal second- and third-order photon correlation measurements. Our results demonstrate that the biexciton state has a negligible and even slightly repulsive interaction energy. Furthermore, the dynamics of the biexciton state are much more rapid than what would be predicted by established statistical scaling models, providing insight into the processes which dominate multiexciton emission.

Exploiting the Moisture Assisted Passivation of Organo-Metal Hybrid Perovskite Nanocrystals
Huanyu Zhou, Jinwoo Park, Yeongjun Lee, Joo Sung Kim and Tae-Woo Lee; Seoul National University, Korea (the Republic of)

Organometal hybrid perovskites nanocrystals (PeNCs) with ABX3 structure (A=small organic cations, B=Pb and X=halides) have been widely adopted as the emitters owing to their superior optical properties, quantum efficiency and the tunable photoluminescence wavelength with high color purity. However, due to the dynamic electrostatic interaction between ligands and the quantum dots and the existence of surface defects, such PeNCs normally suffer from poor stability issues. In this study, PeNCs are dispersed in the polymer matrix and the stability of the PeNC is enhanced due to the compatibility of the polymer matrix with the ligand. In addition, we realize that with the controlled diffusion of moisture through the polymer matrix into PeNCs, the PL intensity increases by 125% after immersing in water for 2 months, which is induced by the surface passivation of PeNCs through the recrystallization process. Our work provides a fundamental approach to improve the stability of PeNCs against the environment with controlled diffusion of moisture and oxygen through the polymer matrix.

Reference

Recent Developments in Nanocrystal Quantum Dot Lasing—From Novel Concepts to Novel Devices
Victor I. Klimov; Los Alamos National Laboratory, United States

Colloidal semiconductor quantum dots (QDs) are attractive materials for realizing highly flexible, solution-processable optical gain media with readily tunable operational wavelengths [1,2]. However, QDs are difficult to use in lasing due to extremely short optical gain lifetimes limited by nonradiative Auger recombination [3,4]. This, in particular, is a serious obstacle for realizing cw optically and electrically pumped lasing devices. Recently, we have explored several approaches for mitigating the problem of Auger decay by taking advantage of a new generation of core/multi-shell QDs with a radially graded composition that allow for considerable (nearly complete) suppression of Auger recombination [5,6]. Using these specially engineered QDs, we have been able to realize optical gain with direct-current electrical pumping [7], which has been a long-standing goal in the field of colloidal nanostructures. Further, we applies these dots to practically demonstrated the viability of a ‘zero-threshold-optical-gain’ concept using not neutral but negatively charged particles wherein the pre-existing electrons block either partially or completely ground-state absorption [8]. Such charged QDs are optical-gain-ready without excitation, which allows us to reduce the lasing threshold to record-low values that are well below a fundamental single-exciton-per-dot limit. Most recently, we have developed QD devices that operate as both an electroluminescent (EL) structure and a low-
threshold, single-mode optically pumped laser. These devices feature a distributed feedback resonator integrated into a bottom electrode of a p-i-n multilayered stack. By carefully engineering a refractive-index profile across the device, we have been able to demonstrate excellent lasing behavior even with a very thin active region, which comprises only three monolayers of the QDs. These ultrathin devices can be pumped electrically and exhibit strong EL with good efficiency ‘roll-off’ characteristics. All of these recent developments demonstrate a considerable promise of colloidal QDs for implementing solution-processable optically and electrically pumped laser devices operating across a wide range of wavelengths.


SESSION EN10.02: Perovskite and QD Emitting Materials
Session Chairs: Maksym Kovalenko and Tae-Woo Lee
Monday Afternoon, December 2, 2019
Sheraton, 2nd Floor, Back Bay D

1:30 PM *EN10.02.01
Light-Induced Structural Transitions in Layered 2D Perovskites Aditya D. Mohite; Rice University, United States

Organic-inorganic (hybrid) perovskite have recently emerged as a new semiconductor platform for next generation optoelectronics devices. These perovskite solids feature weak bonds between their organic and inorganic building blocks, which results in an intrinsic softness and dynamics disorder of the lattice and an acute sensitivity to external stimuli. For example, our recent work demonstrated that continuous sunlight illumination leads to a uniform expansion of the perovskite lattice, which impact the optoelectronic properties of the three-dimensional (3D) perovskites. In particular, this effect is beneficial as it helps cure electronics impurities and lowers energetic barriers near the surface/interface. Here, we present comprehensive in-situ studies of light and electrical field induced structural dynamics of in layered two-dimensional (2D) hybrid perovskites. We correlate the changes in the structure of the 2D perovskite to modification of both the physical properties and the figures of merit in solar cells and light emitting devices. We propose a new microscopic model to explain the evolution of the structure and optoelectronic properties under external stimuli. These results demonstrate that structural characterization of hybrid perovskite under external perturbation is key in unraveling the fundamental physics of these materials.

2:00 PM *EN10.02.02
2D Heterostructures of Ruddlesden–Popper (RP) Layer Halide Perovskites and Their Optoelectronic Applications Song Jin; University of Wisconsin-Madison, United States

The remarkable solar performance of lead halide perovskites can be attributed to their excellent physical properties that present many mysteries, challenges, as well as opportunities. Better control over the crystal growth of these fascinating materials and fabrication of heterostructures using two-dimensional (2D) Ruddlesden–Popper layered metal halide perovskites with different bandgaps would open up opportunities for exploring new properties and
device applications. I will first briefly summarize our results on the solution and vapor-phase growth of single crystal halides and lead halides (APbX₃). Then I will focus my discussion on the growth of multi-layered multi-colored vertical heterostructures of 2D Ruddlesden–Popper (RP) layered lead iodide perovskites with defined n phases and atomically sharp interfaces, in which the long chain ammonium ligands serve as the barriers to prevent ion migration across the junctions. We have further developed the controlled growth of large area nanosheets of RP perovskite phases with varying n values and different anions and well defined vertical heterostructures of these phases. These heterostructures were used to study the carrier transfer mechanisms between different RP phases and as building blocks for optoelectronic devices. High performance room temperature lasing with broad tunability of emission was also demonstrated with single-crystal APbX₃ perovskite nanowires. The excellent properties of these single-crystal perovskite nanostructures of diverse families of perovskite materials with different cations, anions, and dimensionality make them ideal for fundamental physical studies of carrier transport and decay mechanisms, and for enabling high performance lasers, LEDs, and other optoelectronic applications.

2:30 PM EN10.02.03
Proton-Transfer-Induced 3D/2D Hybrid Perovskite for Stable Light-Emitting Diodes Joo Sung Kim¹, Hobeom Kim¹, Jung-Min Heo¹, Mingyuan Pei², In-Hyeok Park³, Zhun Liu⁴, Hyung Joong Yun⁵, Min-Ho Park¹, Su-Hun Jeong¹, Young-Hoon Kim¹, Jinwoo Park¹, Lijun Zhang², Hoichang Yang², Hyun-Myung Jang³, Kian Ping Loh⁶, Nam-Gyu Park⁶ and Tae-Woo Lee¹; ¹Seoul National University, Korea (the Republic of); ²Inha University, Korea (the Republic of); ³National University of Singapore, Singapore; ⁴Jilin University, China; ⁵Korea Basic Science Institute (KBSI), Korea (the Republic of); ⁶Sungkyunkwan University, Korea (the Republic of)

Metal halide perovskites (MHPs) has been considered as promising materials in the field of light-emitting diodes (LEDs), owing to their advantages on light emission such as extremely high color purity (full width at half maximum ≈ 20 nm at room temperature), high photoluminescence quantum efficiency > 90%, easily tunable bandgap and low material cost.¹ In addition, the efficiency of perovskite light-emitting diodes (PeLEDs) based on three-dimensional (3D) polycrystalline perovskites has been greatly increased despite the short period of research.²–⁴ However, the short lifetime during the operation has been a key challenge to be overcome for their practical applications.⁵ The most critical factor is the ion migration in perovskites, which can seriously degrade the crystal structure and luminescent efficiency during device operation, especially for PeLEDs because of the required high bias voltage for device operation.

Here, we demonstrate proton-transfer-induced 3D/2D hybrid perovskite that was obtained by adding a small amount of neutral amine instead of alkyl ammonium halide salt. Proton transfer from organic ammonium precursor to neutral amine in additive/perovskite composition enabled crystallization of 2D perovskite on the surfaces of 3D perovskite grains without destroying the 3D phase. In this study, we almost removed overshoot of luminance over time and highly extended the lifetime of PeLEDs by more than 20 times by developing a 3D/2D hybrid perovskite emitter; the 2D perovskite passivates the trap sites of 3D perovskite and blocks possible pathways of ion migration. We also identified the mechanism of remarkably suppressed luminance overshooting and significant lifetime extension by blocking ion migration in PeLEDs. Our work provides promising guidelines to improve the stability of PeLEDs with the exact explanation on degradation mechanism assisted by the ion migration in perovskite.

Reference

2:45 PM EN10.02.04
Inter-Triplet Coherences in Perovskite Nanocrystals Diogo B. Almeida1,2, Albert Liu2, Luiz G. Bonato1, Gabriel Nagamine1, Ana F. Nogueira1, Steven Cundiff2 and Lazaro Padilha1; 1Universidade Estadual de Campinas, Brazil; 2University of Michigan, United States

Currently, all inorganic CsPbX3 perovskite nanocrystals are among the most investigated semiconductor nanostructures due to their set of unique optical properties, which includes high emission quantum efficiency, tolerance to surface defects, and broadband tunability while maintaining narrow emission spectra. Fast emission lifetime (up to one order of magnitude faster than CdSe based nanomaterials at room temperature) is yet another relevant property of this class of nanomaterials, which is due to the fact that, different from other nanostructures, the band edge is defined by a bright triplet state. This triplet exciton fine structure is still not well explored and further understanding is necessary to turn these unique properties of perovskite NCs useful for optoelectronic application. However, accessing the ultrafast temporal evolution and the coherent dynamics of those states is difficult due to the inhomogeneous broadening. Here, we will show that we can get around this inhomogeneous broadening by using multi-dimensional coherent spectroscopy (MDCS), and access relevant information regarding the triplet fine structure.

In our experiment, we investigate, at cryogenics temperatures, an ensemble of CsPbI3 quantum dots with side lengths of 8.7 ± 2.6 nm. Using a sequence of three ultrafast laser pulses, with specified relative polarization, we resonantly excite different triplet coherences. For co-linearly polarized laser pulses, we observe a strong central emission peak, with a zero-phonon line of about 0.12 meV (FWHM), and two weaker ones positioned about 0.30 meV apart from the main peak, and nearly as broad as the center one. While the central peak is attributed to the absorption and emission from the ground level to same excited state \( \Psi_i \), the side band are related to the absorption and emission involving the ground state and \( \Psi_x \) and \( \Psi_y \), through coherent coupling. When we rotate the polarization of the second pulse to be perpendicular to the two others, the central peak disappears, while the side peaks at 0.30 meV becomes weaker and a broader peak, with linewidth of nearly 0.87 meV, and about 1.60 meV apart from the center, emerges becoming the most intense one. Those peaks are related to the absorption and emission involving the ground state and \( \Psi_i \) and \( \Psi_z \). We do not observe, in any configuration coherences between \( \Psi_x \) and \( \Psi_z \), which suggests that the dipole moment corresponding to \( \Psi_y \) is much stronger than for the other two. From the inter-triplet coherences we can infer that the coherence time for each one of the triplet levels is \( T_{2x} = 5.68 \) ps, \( T_{2y} = 5.32 \) ps, and \( T_{2z} = 0.76 \) ps. In addition to these, our data indicates that the triplet state splitting is size dependent and, by temperature dependence studies, we show that the inter-triplet coherence is only weakly dependent on the temperature up to about 50K.

3:00 PM BREAK

3:30 PM *EN10.02.05
Lead Halide Perovskite Quantum Dots: A Source of Quantum Light? Moungi G. Bawendi; Massachusetts Institute of Technology, United States

The development of practical optical quantum technologies requires the reproducible and scalable production of single quantum emitters with long optical coherence times that can be readily integrated with devices. We have recently demonstrated the potential for chemically-made, colloidal lead halide perovskite (CsPbX3, X=Cl, Br, I) quantum dots (PQDs), to be single emitters of quantum light. Using Photon-Correlation Fourier spectroscopy (PCFS) at low temperatures, we found that PQDs exhibit long optical coherence times and small exciton fine-structure splittings. The long coherence (80 ps) and short radiative emission lifetimes (210 ps) render the PQD emission linewidth near the Fourier transform limit. Moreover, we show that spectral diffusion is dramatically reduced compared to other colloidal quantum dots and that the majority (50-80%) of photons are emitted coherently. This fraction of coherent photons is already comparable to silicon vacancy centers in diamond, which are common emitters in quantum photonics. Our results suggest that, while all other colloidal quantum dot materials suffer from prohibitively incoherent emission, PQDs can be explored as sources of indistinguishable single photons that can be processed from solution onto virtually any substrate and coupled with hybrid nano-photonic components like waveguides or plasmonic gap cavities.

4:00 PM *EN10.02.06
Temperature Dependence of Radiative Decay Time in Perovskite Nanocrystals Alexander L. Efros; U.S. Naval Research Laboratory, United States
Single photon super-radiance is a way to move the radiative decay time into the sub-nanosecond time regime. Single photon super-radiance was introduced by Dicke, who demonstrated that single photon spontaneous emission of N coherently excited atoms occurs N times faster than the spontaneous emission rate of a single atom, \( t_0 \); in other words the single photon super-radiative decay time: \( t_{SR} = t_0 / N \). Single photon super-radiance has been observed recently in inorganic CsPbX₃ (X=Cl,Br,I) perovskite nanocrystals (NCs) at liquid hydrogen temperatures. Sub-nanosecond radiative decay time of weakly bound excitons can be also understood in terms of the phenomenon known as giant oscillator strength (GOS). GOS was introduced initially to explain the excitation spectra of shallow impurities. Despite relatively small concentration, these impurities are observed as narrow sharp lines with intensities comparable to the intensity of the exciton line in the band edge absorption spectrum. It was predicted theoretically that exciton weakly confined in a spherical NC, which radius \( a \) is much larger than the exciton radius \( a_{ex} \), is characterized by GOS which strength, \( f_{NC} = f_0 (a'/a_{ex})^3 \), where \( f_0 \) is the exciton oscillator strength. The single photon super-radiance connected with GOS of NCs observed generally at liquid helium temperatures shows unusual and counter-intuitive increase of the radiative decay time with temperature. We demonstrate that the unusual behavior of the radiative decay time observed in perovskite NCs is connected with the thermal population of upper optically forbidden exciton states and with phonon-induced admixture between these states and the ground exciton level, which reduces GOS of the ground exciton state. The latter mixing process is dominant at low temperatures and leads to formation of an exciton-phonon polaron.


4:30 PM *EN10.02.07

**Environmentally Friendly Quantum Dots for Display Applications** Eunjoo Jang; SAIT, Korea (the Republic of)

Ever since the physics of quantum dot (QD) was discovered, much research effort has been carried out for more than 30 years, and lots of applications adopting QDs have been proposed. Especially, wide color gamut displays using QDs as active light emitting materials have drawn much attention. And, the QD-based consumer displays such as LED TVs, tablets, and special monitors are now on the market. They provide best color gamut, reasonable power efficiency, and affordable price showing superior competitive edge to OLED technology. However, there used to be issues and argues using Cadmium containing materials in practical consumer devices. In spite of the European RoHS Exemptions, we needed to be aware the environmental risk of producing large quantity of Cd-containing materials and using them in the consumer electronics. Samsung has dedicated to develop more environmentally friendly InP based QDs that showed considerably high efficiency and saturated color spectrum compared to the Cd-containing materials. The structure of Cd-free QD was specially tailored for display applications and the synthetic process was optimized to produce reliable materials in commercial scales. In order to improve the efficiency and stability of the QDs in the devices operating under severe atmosphere, specific composite materials were designed and the fabrication process was optimized. From 2015, Samsung has released Cd-free QD adopted UHD TV for major product line-up which show the best color gamut among the current displays. Now we are trying to expand this established Cd-free QD technology as a material platform and make additional breakthroughs in wider optoelectronic applications. Also, we are trying to understand the fundamental properties of defect states of InP QDs via density functional simulation and spectroscopic analyses.
Quantum dots are semiconductor nanocrystals whose size can be tuned to control their optical absorption and emission properties. When excited electrically or optically, a spatially confined electron-hole pair (exciton) is generated. The quantum dot’s emission wavelength can be changed through the confinement effect by tuning the quantum dot to be the size of the exciton’s Bohr radius or smaller. Due to their bulk bandgap, CdSe quantum dots are tunable across the entire visible spectrum. Quantum dots can also simultaneously sustain multiple excitations, which can result in two bound excitons (biexcitons), three bound excitons (triexcitons), or more. Multiexcitons have lower quantum yields than single excitons due to the addition of nonradiative Auger recombination and are typically generated under higher flux conditions, due to the Poissonian absorption statistics of quantum dots. The dynamics and recombination pathways of triexcitons specifically are not well understood and therefore their efficiency is not well optimized in quantum dot devices. Previous theoretical studies show that triexcitons in CdSe quantum dots occupy two angular momentum states of the band-edge 1S-like state (filling the 1S-like state) and one spin state of the higher-energy, 1P-like state. Furthermore, previous work in our group predicted that triexciton emission is dominated by band-edge S-like recombination rather than the P-like recombination, but not definitively proven. We utilize time-correlated single photon counting (TCSPC) with a four spectrally-filtered single-photon counting detectors to detect 1S-like and 1P-like emission from the triexciton state. We demonstrate that almost all triexciton emission occurs from band-edge S-like recombination, indicating that multiexciton interactions drastically reduce the emission rate from the P-like state. These results provide a crucial step to improving the efficiency of nanocrystal materials in device relevant conditions.
method to deposit perovskite films with good film morphology. What is more, the thickness of vacuum-evaporated films could be precisely controlled compared with that of solution-processed ones. Herein, we first demonstrated organic-inorganic hybridized 2D perovskite thin film as light emitting layer via evaporation method. Base on our characterization, we got 2D nanoflake structure perovskite crystals with small crystal size. The one-dimensional confined structure not only can significantly improve electron-hole injection, but also can enhance luminescence efficiency due to quantum confinement. The planar device EQE boost to 4.8% with luminance about 11000cd/m² after constructing the 2D structure. In addition, larger device size by 1.5cm*2cm were also demonstrated, which shows potential in large area display.

**EN10.03.04**

**Slot-Die Coating of Formamidinium Lead Bromide Nanocrystals for Large-Area Perovskite Light Emitting Diodes**

Alasdair A. Brown1,2,3, Xin Yu Chin3, Suan Hui Pu1, Ju Nie Tey2, Bahulayan Damodaran3, Liudi Jiang1, Subodh G. Mhaisalkar3,3 and Nripan Mathews3,3; 1University of Southampton, United Kingdom; 2Agency for Science, Technology and Research, Singapore; 3Nanyang Technological University, Singapore

Metal halide perovskites (MHPs) have recently demonstrated exceptional promise as emissive materials for light-emitting applications. They exhibit remarkable colour purity and high photoluminescence quantum yield (PLQY), tuneable across the visible spectrum. As a result, prototype small-area light-emitting diodes (LEDs) with external quantum efficiencies (EQE) exceeding 20 % have been achieved. A significant attraction of MHPs is their inherent compatibility with solution-processing. Considering also the low cost of the precursor materials, MHPs have the potential to facilitate cost-effective, high throughput roll-to-roll (R2R) LED fabrication on flexible substrates. Despite the potential, there have been very few reports of large-area perovskite LEDs realized through scalable deposition techniques; the vast majority still rely on spin-coating. Spin-coating places an inherent limitation on scalability; as each substrate must be coated separately it is unsuitable for desirable continuous processing. Slot-die coating provides an attractive alternative. It is a straight-forward continuous process, suitable for R2R deposition. Furthermore, the volume of excess solution required is fixed, thus material wastage for large-scale deposition processes would become almost negligible. This is in stark contrast with spin-coating, where most of the solution is ejected from the substrate.

The applicability of slot-die coating for light-emitting diode fabrication has been demonstrated extensively for organic light-emitting diodes, establishing the capability of the technique to reproducibly deposit films of around 40 nm. Recently, Prakasam et al. achieved the first slot-die coated LEDs by directing N₂ gas flow onto wet films to induce fast gas-assisted crystallization of MAPbBr₃. They obtained modest current efficiency (CE) of 2.6 cd A⁻¹ for 4.46 cm² active area devices, which were slot-die coated as a 230 cm² strip. Similar methods have been reported several times for slot-die coating of bulk perovskite films for solar cells, where crystallization control is also a challenging issue.[14]

MHP nanocrystals (NCs) provide a simpler alternative. As the perovskite phase has already been crystallized prior to film deposition, the NC ink can be slot-die coated without additional provisions. Thus, the development and optimization of a slot-die coating process for MHP NCs would provide a versatile large-area deposition method, demonstrating a significant advancement of perovskite LED scalability. Herein, we report the fabrication of slot-die coated LEDs from our FAPbBr₃ NCs. The slot-die coating parameters were optimised to obtain full surface coverage over an active area measuring 16 cm². Maximum external quantum efficiency (EQE) of 7.26 % (CE = 31.9 cd A⁻¹) and maximum luminance of 1428 cd m⁻² were achieved. To the best of our knowledge, both of these values are the highest reported for perovskite LEDs fabricated using a fully scalable deposition technique. These results represent a significant enhancement of the scalability of perovskite light-emitting diodes towards future commercial viability.


**EN10.03.05**

**Synthesis and Photophysical Properties of Diamine Intercalated Hybrid Layered Perovskites**

Rounak A. Naphade and Osman M. Bakr; King Abdullah University of Science and Technology, Saudi Arabia

Hybrid perovskite materials have expanded their scope of interest to a wide research community owing to their desirable photo-physical properties, which made them useful for opto-electronic applications. Low-dimensional hybrid perovskites, in particular, have been the subject of intensive research as of late due to the ease of tuning of
Here in this work, we present the case of the ethylene diammonium cation as an intercalating agent for forming a 1D layered lead halide perovskite framework. We show that the addition of mono-ammonium bromide salt (up to 20 mol %) during the crystal growth enables the manipulation of the crystal’s framework from 1D to 2D-stair-case like perovskite. The ethylene diammonium cation along with water molecules stabilize this stair-case like crystal framework. The ethylene diammonium cation acts simultaneously as an inter-layer cation as well as a cation filling the in between adjacent voids of octahedrons. This mono-ammonium bromide salt incorporation in the single crystals shows simultaneous broadband and narrow emission depending on the excitation source. With a combination of structural, spectroscopic, and Density functional theory (DFT) approaches we investigate the origin of dual emission from single crystals of this layered perovskite. Our findings suggest that self-trapped excitons and the presence of water molecules inside the crystal lattice control the dual emission from these crystal systems.

EN10.03.06
Increasing Photoluminescence Quantum Yield by Nano-Photonic Design of Quantum-Confined Halide Perovskite Nanowire Arrays Daquan Zhang, Qianpeng Zhang, Yu Fu, Leilei Gu and Zhiyong Fan; The Hong Kong University of Science and Technology, Hong Kong

High photoluminescence quantum yield (PLQY) is required to reach optimal performance in solar cells, lasers and light-emitting diodes (LEDs). Typically, PLQY can be increased by improving the material quality to reduce the non-radiative recombination rate. It is in principle equally effective to improve the optical design by nanostructuring a material to increase light out-coupling efficiency and introduce quantum confinement, both of which can increase the radiative recombination rate. However, increased surface recombination typically minimizes nanostructure gains in PLQY. Here a template guided vapor phase growth of perovskite nanowire (NW) arrays with unprecedented control of NW diameter from the bulk (250 nm) to the quantum-confined regime (5.7 nm) is demonstrated, while simultaneously providing a low surface recombination velocity of 18 cm s^{-1}. This enables an obvious PLQY enhancement from 0.33% up to 42.6% for MAPbI_{3} quantum wires, and up to ~90% for MAPbBr_{3} quantum wires, exclusively using nanophotonic design, which will be promising for LEDs applications with high external quantum efficiency (EQE). The simple extension of this technique to a wide variety of semiconductors and the ultra-high density of vertical QWs may also provide interesting opportunities in quantum transport, electronics and memory devices in the future.

EN10.03.07
Understanding the Trade Off Between Efficiency and Stability in Perovskite Light-Emitting Diodes with Bulky Ammonium Cations Jonathan Warby, Bernard Wenger, Olivia J. Ashton, Ashley Marshall and Henry J. Snaith; University of Oxford, United Kingdom

Recently metal halide perovskite light emitting diodes (LEDs) have been reported with high efficiencies, most often made by in situ generation of nanocrystals in a film or the formation of quantum well hetero-structures. In both cases, bulky ammonium cations are used which greatly improve the optoelectronic properties of the perovskite by direct chemical passivation, increased dielectric confinement and carrier funnelling, all which encourage efficient radiative bimolecular recombination.

However, the operational stability of these devices is poor with even the state of the art only able to function for a few hours. More often than not, this stability is overlooked in favour of achieving high efficiency, but this now needs to be urgently addressed.

In this work we investigate the influence of the bulky ammonium cation on the stability of CsPbBr_{3} based perovskite LEDs. Upon addition of these molecules into precursor solutions we observe an increase in external quantum efficiency of four orders of magnitude. Despite this excellent improvement in efficiency we also demonstrate that the optimised LEDs are far less stable than those made without the additive. Through optical and structural characterisation we elucidate the reason for this drop in stability and provide an insight into alternative strategies for obtaining both high efficiency and stable LEDs.

EN10.03.08
Dissected Mechanism of Elastic Mechnoluminescence in ZnS:Mn Microparticles Implies the Possibility of Nanoscale Stress Sensor Maria Mukhina1, Jason Tresback1, Justin Ondry2, Austin Akey1, Paul Alivisatos2 and Nancy Kleckner1; 1Harvard University, United States; 2University of California, Berkeley, United States
Elastic mechanoluminescent (ML) materials convert energy of reversible elastic mechanical deformation into optical emission. ZnS:Mn stands out among thousands of ML compounds due to one of the lowest reported thresholds for ML appearance in the range 0.6 - 1 MPa = 0.6 - 1 pN/nm² [1]. Material which is capable of reversible mechanoluminescence at such low pressure range is perfect candidate for nanoscale stress sensor demanded in many technological and biomedical applications. However, further development of ML-based technologies is stalled due to the limited understanding of mechanisms underlying appearance of elastic ML.

We use a new approach to study microscopic characteristics of low force elastic mechanoluminescence in single ZnS:Mn microparticles. It employs the combination of a micropositioner for force application and the Perfect Focus System (PFS) of a Nikon Ti2 widefield microscope to track pressure and ML from single microparticles which are 0.5 - 5 µm in size. We demonstrate that ML in ZnS:Mn is fully endogenous, non-destructive and reversible physical process. Furthermore, analysis of time-resolved microscopic images of ML patterns reveals striation, which does not overlap with analogous features seen in the photoexcited emission of the same particle. It implies that microparticle’s volume is heterogeneous in terms of ML, and certain microscopic structures within the volume are more effective ML emitters. We use Transmission Electron Microscopy (TEM), Focused Ion Beam (FIB) and Kelvin Probe Force Microscopy (KPFM) techniques to show that ZnS:Mn microparticles contain high concentration of zinc blende (ZB)/wurtzite (WZ) stacking faults with electrically charged interphase boundaries.

We propose a new mechanism of elastic mechanoluminescence in ZnS:Mn which relates its structural and mechanoluminescent properties and explains very low threshold for ML appearance. This mechanism relies on the presence of stacking faults and concomitant built-in electric fields which produce a saw-tooth like potential profile inside the crystal. In the faulted crystal, the electron density is shifted towards the positively charged interfaces of the stacking faults in order to compensate for the built-in fields. It leaves the negatively charged interfaces unscreened. Hence, the electrons and holes trapped at the oppositely charged interfaces serve as a source for ML photons. Application of mechanical stress induces an onset of piezoelectric field which is locally enhanced at the electron-depleted interfaces. The carriers trapped at the interfaces gain an excess energy and recombine either immediately or at the moment of the stress release. The local enhancement of the piezoelectric field provides the explanation for extremely low pressures (as low as 240 kPa) which are sufficient for ML excitation in ZnS:Mn. Based on the new model, the ML structural unit comprises two segments of one crystal phase separated by the inclusion of the other phase. Based on our TEM data, it can be scaled down to less than 30 nm what, along with the low threshold for ML appearance, makes ZnS:Mn a perfect candidate for nanoscale force sensor.


EN10.03.09
ZnO/Graphene Oxide Hybrid Quantum Dots-Based Deep-Blue Light-Emitting Diodes Won Kook Choi¹, Hong Hee Kim¹,² and Yeonju Lee¹,²; ¹Korea Institute of Science and Technology (KIST), Korea (the Republic of); ²Yonsei University, Korea (the Republic of)

Currently, much research interest related to achieving white emission has refocused on quantumdots (QD)-LEDs based on fluorescent semiconducting nanoparticles consisting of 10-100 atoms. QD-LEDs have a good color rendering index (CRI), high quantum efficiency, high purity, and narrow emission spectra due to the quantum confinement effect and the size-dependent tunability of the bandgap. Nevertheless, the development of Cd-free non-hazardous as well as In-free cost-effective QDs has become essential and is encouraging intensive research for future optoelectronic devices. Oxide semiconductors are appropriate as eco-friendly materials to produce white light if the visible light emission caused by the electron transition between the defect energy levels of interstitials or vacancies existing in the bandgap is effectively exploited. II-VI ZnO is one among such strong candidates. In general, the PL spectrum of ZnO is characterized by two features, near band edge (NBE) emission in the UV region and defect-related blue, green, yellow, and orange-red emissions in the visible region. Even though the origin of defect-related visible emission have not been manifestively revealed, Defects depending on the excitation wavelength (λex) related to the emissions of green, yellow, and orange-red from ZnO QDs are completely inhibited by removing oxygen vacancies via the hybridization of Zn interstitials with anti-bonding O-states of graphene oxide (GO) QDs. This also leadsto only λex independent violet-purple-blue (V-P-B) emissive ZnO-GO QDs with a high photoluminescence quantum yield (PLQY) of 92%. White-light emission with CIE (0.32, 0.34) from PL QD-LEDs
is realized using a mixture of ZnO and ZnO-GO QDs excited by a UV LEDs chip. ZnO-GO QD-based deep-blue LEDs with luminance of ca 2,000 cd/m², a luminous efficacy (LE) of more than 2.5 cd/A, and external quantum efficiency (EQE) of about 3% with CIE (0.16, 0.11) are also successfully achieved.

EN10.03.10
Tuning the Carriers Localization in CdS/CdSe/CdS Quantum Dots for an Efficient Amplified Spontaneous Emission Process
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Quantum dots (QDs) have emerged as a promising material to be applied in the next generation of lasers. The possibility of controlling its emission color by size, added to its facile synthesis stimulated intense research in this field in the last years¹. However, there is still many challenges that need to be overcome to make this material competitive with current technologies. Among them, we can highlight the ones related to increase its output efficiency under long term optical or electrical pumping. An important strategy to reach this goal is to build heterostructures, such as core/shell or core/alloy/shell QDs². In this way, it is possible to increase both its absorption cross section and decrease losses due to, for example, non-radioactive Auger recombination. However, increased lattice mismatch in large shell structures drastically decreases their photoluminescence quantum yield (PLQY) due to the creation of interfacial defects. A novel class of heterostructured nanomaterial, called spherical quantum well (SQW), composed by an internal CdS seed, followed by an intermediary emissive layer of CdSe and an outer CdS shell can reduce the crystalline strain between the shell and the emissive layer, allowing for structures that combine high absorption cross section and near unity PL quantum yield³. Here, we investigate the performance of this new class of nanomaterial for lasing applications, by studying their multi-exciton dynamics and amplified spontaneous emission (ASE) threshold. From time resolved photoluminescence studies, we show that the multi-exciton Auger recombination rate is highly reduced in this nanostructure. Varying the shell and well sizes, we report Auger lifetimes from 0.3 to 1.4 ns across samples for positive trions, meanwhile for the negative ones, the lifetime varied from 1.5 to 8.0 ns. Inspired on these characteristics, the size dependence of the ASE properties on SQWs were studied. From that, we show that the ASE threshold decreases as the nanoparticle volume increases, because of the higher cross section, reaching 50 μJ/cm² for the biggest sample. However, considering the average of dots needed to generate ASE, this trend is inverse, going from 1.30 for the smallest particle to 2.35 for the biggest. To understand this phenomenon, the bi-exciton binding energy of the samples were investigated. From that, we show that the reason for this is a transition from an attractive bi-exciton interaction regime to a repulsive one, as the shell thickness increases. To conclude, the unique set of properties presented by SQW brings new insights to overcome current challenges on the application of QD in new laser technologies. Additionally, the ideas presented here can be expanded to other kinds of compositions, making this structure suitable to different kind of lightening emission applications, such as in LEDs and luminescent solar concentrators.


EN10.03.11
Investigation of the Spacer Effects on Emitting Properties of the Ruddlesden-Popper Phase Br-Based Perovskites
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Recently, perovskite light emitting diodes (LEDs) has been attracting great attention as a next-generation LED that can replace existing OLED and QLED. However, methylammonium lead halide (MLH) perovskite is not applicable to LED devices due to its low moisture stability. Quasi-2D perovskites (PEA₂(MA₃₋₁PbBr₃₊₁ has been reported to enhance the photoluminescence (PL) and water-stability compared to conventional MLH 3D perovskite (MAPbBr₃). However, the development of conventional ruddlesden-popper phase perovskites has been only focused on red and
green emission region. In this regard, herein we tried to tailor the emission range of Br-based quasi-2D perovskite from green to blue region by integrating organic cation spacer. As the candidates for spacer, selected aromatic (phenylethylammonium (PEA), benzyltrimethylammonium (BTA)) and aliphatic cations (isopropylammonium (IPA), n-propylammonium (nPA)) were employed by controlling the relative concentration ratio. As a result, the PL intensities and the emission wavelength of the new class of quasi-2D perovskites, BTA and nPA-based perovskites, showed deep-blue emissions at 475 nm, with the uniform and well-structured surface coverage. In addition, The PL intensity of blue perovskite thin film was on par with that of green one ((PEA)2(MA)n-1PbnBr3n+1). By controlling the ratio of BTA and nPA, we could fine-tune the wavelength of the PL wavelength from 610 nm (green) to 475 nm (blue) systematically (with 7 nm intervals). Based on our dimensionality-controlled perovskites, the blue-emissive Q-2D perovskite LED showed low turn-on voltage (less than 4 V) with high-current density (42 mA/cm²). The protocol and strategy established in this study can be exploited to enhance high level electron quantum efficiency (EQE) and luminance.

EN10.03.12
Multi-Emissions from Calcined Oyster Shells Yu Ying Su; National Tsing Hua University, Taiwan

Calcined oyster shells contain an abundant number of color centers arising from Ca and O vacancies. Emissions occur at both 20K and 300K with intensity much greater than reported data on carbon supported ZnO nanocrystals. Optical transitions proceed through three-body mechanisms where nonradiative processes involve transverse acoustical and optical phonons. Oxides obtained from suppliers show a low profile of emission, attributed to water absorption that causes charge transfer and weakens spin-orbital coupling.

EN10.03.13
Photon Upconversion from Near Infrared to Blue Light with TIPS-Anthracene as an Efficient Triplet-Triplet Annihilator Naoyuki Nishimura1,2, Victor Gray1,3, Zhilong Zhang1 and Akshay Rao1; 1University of Cambridge, United Kingdom; 2Asahi Kasei Co, Japan; 3Uppsala University, Sweden

Photon upconversion (PUC) via triplet-triplet annihilation (TTA) is an attractive means for solar energy concentration, bio-imaging, and photochemical reaction, such as photoinduced drug delivery. In particular, generation of blue light (< 500 nm) via upconversion is important, because blue light is required for most photochemical reactions, as well as photocatalytic water splitting to produce hydrogen, since most materials with the efficient quantum yield for photocalytic water splitting can harvest only photons with energy above 500 nm. On the other hand, utilizing near infrared (NIR) photons is crucial for applications such as bio-imaging and drug delivery, as the window for high transparency of biological tissue lies in the NIR region (700 - 900 nm). Thus, PUC from NIR to blue would be beneficial to many emerging applications. As the difference in energy between blue and NIR photons is large (e.g., 470 nm: 2.64 eV and 800 nm: 1.55 eV), a reduction of energy loss in PUC process, leading to larger anti-Stokes shift (\( \text{PUC emission energy} - \text{excitation energy} \)), is also important. However, there has been no report, to the best of our knowledge, of a material with an anti-Stokes shift greater than 1.0 eV that also has a linear excitation intensity dependency (slope 1 for the PUC process). One of the keys to reduce loss in energy for PUC is to minimize the driving force of TTA process (difference in energy between 2T1 and S1 of TTA material). Reports of annihilators fluorophores which can accept low-energy triplets (< 1.55 eV) and generate blue light have so far mainly focused on 9,10-Bis(phenylethynyl)anthracene (BPEA) and perylene derivatives. However, these materials function with low efficiency of TTA and/or require large driving force for TTA. There is a clear need for PUC materials with a large anti-Stokes shift as well as efficient PUC from NIR to blue.

Here, we demonstrate efficient PUC converting from NIR energy to blue photons using the commercially available material 9,10-Bis[(triisopropylsilyl)ethynyl]anthracene (TIPS-Ac) as an efficient TTA material despite a low driving energy for the TTA process (< 0.32eV). When TIPS-Ac was sensitized with Pd(II) meso-Tetraphenyl Tetrabenzoporphine (PdTPBP), a generates triplets via intersystem crossing, the PUC photoluminescence quantum yield with excitation at 635 nm was 27 ± 0.5 % with a TTA efficiency of 77 ± 3 %. Combining TIPS-Ac with Pt(II) meso-Tetrphenyl Tetrabenzoporphine (PtTPBP), where we show directly generates triplet via NIR excitation at 785nm, the PUC achieved an anti-Stokes shift of 1.03 eV with a linear excitation intensity dependency. Therefore, there is a clear need for PUC materials with a large anti-Stokes shift as well as efficient PUC from NIR to blue.
EN10.03.14

Visualizing the Soft Ionic Lattice in Spatially Resolved Emissive Halide Perovskite Nanowire Heterojunctions

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Lead-halide perovskites are a family of semiconductor materials with excellent optoelectronic properties ideally suited for various light-emitting applications beyond solar cells. Particularly, inorganic perovskites CsPbX3 nanostructures are drawing increasing research interests because of their better stability and prior properties. Comparing to conventional semiconductors, these halide perovskites present a unique soft and dynamical ionic lattice. Owing to facile ion migration, anion exchange chemistry was demonstrated in CsPbX3 nanostructures with high PLQY throughout the exchange reaction process. Via developing a novel localized anion exchange method, we demonstrate spatially resolved multi-color CsPbX3 nanowire heterojunctions. These perovskite heterojunctions show tunable photoluminescence over the entire visible spectrum with high resolution down to about 500 nm, which can represent key building blocks for high-resolution displays. Moreover, the intrinsic solid-solid anion interdiffusion dynamics can be visualized in these perovskite heterojunction nanowires through photoluminescence techniques. Besides, there are rich structural phase transitions in the inorganic perovskites. The non-perovskite phase with a large bandgap and poor photoactivity can be thermally-driven transformed into a meta-stable perovskite phase with a decreasing bandgap and excellent optical properties. Using in situ nanoscale cathodoluminescence (CL) microscopy, we can directly visualize the transition dynamics from a non-perovskite to a perovskite phase in single-crystal CsPbX3 nanowires and resolve nanoscale nucleation and growth in the transient two-phase junctions. The reverse transition from perovskite phase to the non-perovskite phase can be further realized with moisture which introduces halide vacancy in the crystal lattice and lowers the kinetic barrier. These fundamental understandings can offer insightful guidelines for engineering the perovskite nanomaterials with novel functional devices.

EN10.03.15

Dynamic Control of Nanoparticle Deposition—Additive Manufacturing with Atmospheric Pressure Plasma

Alexander Ho and Rebecca Anthony; Michigan State University, United States

Additive manufacturing has become a well-established manufacturing style for a range of metals and polymers. An exciting new area is the extension of additive manufacturing to include nanoscale semiconductors, which exhibit interesting properties that can differ from their bulk counterparts. Plasmas have found considerable use in the synthesis of nanoparticles due to their wide operation range which effectively accommodates the tunable properties of nanoparticles. Atmospheric pressure plasmas allow for the miniaturization of reactors easing the integration of the reactors into additive manufacturing systems that rely on an aerosol jets for deposition. Presented here is our work on the additive manufacturing of silicon nanoparticle layers synthesized at atmospheric pressure with a nonthermal plasma. We generated a plasma with a 13.56 MHz RF power supply inside a glass capillary tube between two external ring electrodes. A silane precursor gas together with an argon background gas were flown to the reactor for the synthesis of silicon nanoparticles, with tunable size depending on gas flowrates. The plasma reactor was mounted to a programmable and motorized gantry responsible for driving the reactor through predetermined patterns in all three spatial dimensions. While we achieved sub-millimeter linewidths with aerodynamic focusing using a tapered capillary, we also seek to
exploit the innate nanoparticle charging properties of the plasma synthesis method to modify the deposition. Charge accumulation on the nanoparticles from the plasma and a high voltage power supply were used to control the linewidth of the deposition through electrostatic forces. Through this process we achieved even narrower linewidths, with thicknesses up to and exceeding 100µm as dictated by the dwell time of the reactor. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) indicated that the particle crystallinity and size can be altered in-process via controlling the supplied power and gas flowrates, translating to a dynamic control over nanoparticle properties as we deposit the predetermined patterns. Fourier-transform infrared spectroscopy (FTIR) revealed a stable surface with oxygen-and nitrogen-containing compounds passivating the Si nanoparticle surfaces; this along with the amorphous region present at the edges of crystalline nanoparticles indicates the presence of an oxynitride shell. Photoluminescence of the nanoparticles was observed at a wavelength of 705 nm upon excitation with UV radiation. The ability to synthesize and deposit the nanoparticles with property tunability in-process points to the promise of this approach for additive manufacturing using plasmas.

EN10.03.16
Synthesized High Member of All Inorganic Two-Dimensional Ruddlesden-Popper Single Halogen Perovskite Nanocrystals Cheng-Chieh Lin¹, Shao-Ku Huang², Di-Yan Wang², Cheng-Yen Wen², Chia-Chun Chen³ and Chun-Wei Chen¹,²
¹Taiwan International Graduate Program, and National Taiwan University, Taiwan; ²National Taiwan University, Taiwan; ³Tunghai University, Taiwan; ⁴National Taiwan Normal University, Taiwan

A new model all-inorganic Ruddlesden-Popper phases perovskite (AIRPP) Csn⁺₁BnX3n⁺₁ (n = 1, 2, …) exhibits a more stable crystal structure in the ambient atmosphere and provides a unique quantum well structure separated by inorganic spacer (AX, A= Cs⁺ X= Cl⁻, Br⁻ and I⁻). However, a mixed halide AIRPP Cs₂PbI₂Cl₂ exhibited a large band gap and display strong UV-light response in photodetectors. Therefore, it is still very important topic developing single halide red (R), green (G) and blue (B) emissions with tunable optical properties in visible light range. In this study, we demonstrated phase stable quasi-2D all-inorganic Ruddlesden-Popper phases perovskite (AIRPP) Csn⁺₁PbₓBr3n⁺₁ nanosheets (n=3, 4) with single halide stabilized by additional stronger bounding surface ligand octadecanedioic acid (ODA). The pure phase of quasi-2D AIRPP nanosheets are confirmed by STEM, HR-TEM images and XRD measurements. The different n thickness and layer structure are also identified by density functional theory (DFT). From the optical characterization, the bandgap of Csn⁺₁PbₓBr3n⁺₁ nanosheets (n=3) was found to be ~2.7eV with photoluminescence quantum yield (PLQY) exceeding 40%. The film of Csn⁺₁PbₓBr3n⁺₁ nanosheets (n=3) also displays strong visible light response at a wavelength of 460nm. Moreover, these series of single halide AIRPP exhibited long-term stability over three months in ambient condition.

EN10.03.17
Properties of Ion Gel-Based Flexible Electro-Chemiluminescence Full-Color Display Do-kyun Kwon, Jong-Woo Kim and Jae-Min Myoung; Yonsei University, Korea (the Republic of)

Electro-chemiluminescence (ECL) displays using electrochemical reaction are attracting attention owing to their remarkable advantages, such as simple structure, ultra-thinning, and use of electrodes without work function limitations. However, despite these advantages of ECL displays, a significant limitation still exists, which is the simultaneous realization of red (R), green (G), and blue (B) emissions with excellent emission characteristics. Related studies reported so far have succeeded in improving the individual emission characteristics of R, G, and B ECL display, but have not implemented all colors simultaneously. In order to implement next-generation displays, it is necessary to improve the B emission characteristics and simultaneously realize emission of the three primary colors of R, G, and B.

In this study, ion gel-based flexible ECL full-color display has been successfully demonstrated by overcoming the limitations of simultaneous implementation of R, G, and B emissions. The ECL display was implemented using Ru(bpy)₃(PF₆)₂, [Ir(Fppy)₂(dmb)][PF₆] and FlrMepic corresponding to R, G, and B emissions, respectively. In particular, to achieve improved B ECL displays, the blended blue (BB) ECL display was designed using a mixed-metal chelate coreactant system with mixing of G and B luminophores. The BB ECL display shows significantly improved properties in terms of the operating voltage, luminance, and stability. Furthermore, even after dynamic bending tests of 5000 cycles at a radius of curvature of 10 mm, the flexible ECL display shows stable emission properties. The optical and electrochemical properties of ECL gels were measured using a PL measurement system and a cyclic voltamogram measurement. To confirm the emission of the ECL display, the AC voltage generated by the function/arbitrary waveform generator was used. The EL spectra, luminance, and color coordinates were observed using an EL measurement system and chroma meter.
Keywords: electro-chemiluminescence, ion gel, mixed-metal chelate system, multi-color implementation, flexible display.

EN10.03.18
Facile Room-Temperature Synthesis of Stable Lead Halide Perovskite Nanoplatelets by Ligand-Assisted Reprecipitation Seung Kyun Ha, Catherine M. Mauck and William Tisdale; Massachusetts Institute of Technology, United States

Colloidal lead halide perovskite nanocrystals, which are solution-processable, color-pure, tunable and highly luminescent, are newly arising semiconductor nanomaterials for light-emitting applications. And among nanocrystals with various geometries, quantum- and dielectric-confined two-dimensional colloidal lead halide perovskite nanoplatelet is one of the most favorable candidates for the next-generation light-emitting applications. In this work, we demonstrate a facile room-temperature synthesis of colloidal perovskite nanoplatelet (Chemical formula: \( \text{L}_2[\text{ABX}_3]_{n-1}\text{BX}_4 \), L: organic alkylammonium ligands, A: methylammonium or formamidinium, B: lead, X: bromide and iodide, \( n \): number of [BX\(_6\)]\(^4\)-octahedral layers in the direction of nanoplatelet thickness) via ligand-assisted reprecipitation. We also show that the band gap of the nanoplatelets can be continuously tuned throughout the visible range by halide composition engineering. Then it is further demonstrated that various organic species can be incorporated as surface-capping ligands without any major modifications in the synthetic protocols, opening up the possibility of optimizing the surface chemistry for various applications. Then we focus on the stability of deep-blue luminescent (\( \lambda_{\text{max}} = 437 \text{ nm} \)) nanoplatelet species, which is essential for achieving wide color gamut, and systematically investigate the factors that affect the photostability\(^1\). Photobleaching is found to be coming from intrinsic instability of the perovskite nanoplatelet lattice against UV irradiation, while moisture triggers the transformation of nanoplatelets into thicker, less-confined structures. It is further shown that the substitution of methylammonium for formamidinium and the addition of excess alkylammonium bromide ligands can effectively enhance both the photo- and ambient stability of the nanoplatelets. And lastly, we demonstrate stable color-pure deep-blue luminescence from the dropcasted film of methylammonium lead bromide nanoplatelets.


EN10.03.19
Colloidal Core/Shell Heterovalent Heterostructures for Highly Luminescent Cd-Free Nanocrystals Byeong Guk Jeong\(^1\), Jun Hyuk Chang\(^2\), Donghyo Hahn\(^2\), Hyeonjun Lee\(^3\), Doh C. Lee\(^3\) and Wan Ki Bae\(^1\); \(^1\)Sungkyunkwan University, Korea (the Republic of); \(^2\)Seoul National University, Korea (the Republic of); \(^3\)Korea Advanced Institute of Science and Technology, Korea (the Republic of)

We represent comparative study on core/shell heterostructure nanocrystals based on III-V/II-VI semiconductor with InP/Zinc chalcogenide geometry that show high photoluminescence quantum yield (>80\%) with narrow emission linewidth (~45 nm). We compared the optical properties of nanocrystals with different interfacial geometries before growth of zinc chalcogenide shell. The comparative studies based on spectroscopic analysis and elemental analysis by XPS and ICP-OES reveals that non-radiative traps in the InP nanocrystals are effectively suppressed by controlled interface and surface. Controlled interface of InP/zinc chalcogenide nanocrystal produce energetically favorable interface without net charge, which is called "neutral interface", to successfully confine the electron and hole wavefunction into the InP nanocrystals. Therefore, the III-V/II-VI heterovalent heterostructures show high PL QY of InP based core/shell heterostructures.

EN10.03.20
Properties of Phase-Stabilized Mixed-Cation Perovskite with Hydrophilic Polymer for Red Light-Emitting Diode Do Hoon Kim, Yun Cheol Kim and Jae-Min Myoung; Yonsei Univ, Korea (the Republic of)

The ionic crystals of perovskites have been widely investigated for application in light-emitting devices (LEDs) due to their adjustable optical bandgap by changing the composition of the halide anions. However, small ion size of Cs\(^+\) in inorganic perovskite causes poor crystallinity and small exciton binding energy owing to the inherent defects present in the bulk perovskite hinders the luminescence efficiency of perovskite LEDs (PeLEDs). Moreover, a cesium lead iodide (CsPbI\(_3\)) which is studied as an emitter of red PeLED is not only required to be heat-treated at a
high temperature of 200 °C for phase stabilization but also vulnerable to oxygen and moisture in the air. So, in order to improve the crystallinity and prevent the phase separation of perovskite, it is preferable to use mixture of Cs⁺ and methylammonium (MA) or formamidinium (FA) cation. Furthermore, by adding hydrophilic polymer into the perovskite precursor, the crystal size can be reduced. So, a flat and uniform perovskite film can be formed, leading to decrease of non-radiative defects and leakage current. The phase-stabilized mixed-cation perovskite with hydrophilic polymer not only improve the crystallinity of the perovskite structure but also prevent the phase separation of perovskite.

In this study, to improve the crystallinity and prevent the phase separation of perovskite, CsxMA1-xPbI3 films were fabricated as mixed-cation perovskite by adding methylammonium iodide (MAI) and poly(2-ethyl-2-oxazoline) (PEOXA) as a hydrophilic polymer into the CsPbI3 precursor. The optimized CsxMA1-xPbI3-PEOXA film deposited on poly-TPD showed a uniform surface coverage with a crystal size and thickness of 28.7 nm and 114.2 nm, respectively, and exhibited a strong electroluminescence peak centered at 662 nm. Furthermore, CsxMA1-xPbI3-PEOXA-based red PeLED showed stable device performance at 24 °C under 20.3% relative humidity for 3 days. Therefore, it is believed that the PeLED with a CsxMA1-xPbI3-PEOXA film can be a good candidate for red light-emitting PeLEDs.

EN10.03.21
**Efficient Iridium Phosphorescent Materials for Green Light Emitting Diodes**
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The design and exploration of high stable organic luminescent materials with high luminous efficiency has become an important research area in the frontier of chemistry and materials science. Iridium complexes are one of the best phosphorescent materials. This project aims to synthesize a new "3+2+1" dentate coordination type of luminescent iridium complex, allowing the introduction of a specific ligand in a controlled way, controlling the luminescence properties of iridium complex through appropriate selection of ligand. Finally, a green emissive iridium complex has been synthesized, and the photophysical studies reveals it display a structured emission bands at 474 and 500 nm. These complexes display structural stability at ambient temperatures and quantum yields greater than 30%. In addition to the study of physical properties, we cast this green phosphorescent material as phosphor powders on a 460 nm blue chip to form light-emitting diodes. It was found that the LED has realized pure green emitting and the Commission Internationale Ed l’Eclairage coordinate of the fabricated green LEDs was (0.3,0.6), Moreover, the green LEDs displayed luminous efficiency of 5 lm/W under an injection current of 30 mA.

EN10.03.22
**Improved Green Perovskite EL Performance through New Polymer HTL Based on Carbazole**
Seokwoo Kang, Sunwoo Park and Jongwook Park; Kyung Hee University, Korea (the Republic of)

In conventional organic light emitting diode (OLED) as well as perovskite light emitting diode (PeLED) device, polyvinyl carbazole (PVK) and Poly-TPD have been widely used as a hole transporting layer (HTL) in the past. However, PVK and Poly-TPD have disadvantage in terms of soluble property limitation during stacked-soluble process device preparation. So, more research is needed in terms of materials to apply these materials to perovskite devices. Therefore, we synthesized new polymer HTL material, PBCZCZ for PeLED device. It has non-soluble property to general solvent after thermal treatment and curing process. For the surface analysis of PBCZCZ and PVK, contact angle and AFM analysis were carried out. Contact angle of PBCZCZ is about 5 ° lower than that (76 °) of PVK, and AFM analysis shows similar surface roughness. Also, we found that PBCZCZ achieves much higher mobility than PVK. The structure of PBCZCZ is that two new functional groups are added to the carbazole group. The device configuration is ITO/PEDOT:PSS(40nm)/PBCZCZ(15nm)/CsPbBr3/TPBi(30nm)/LiF(1nm)/Al(100nm). When new polymer HTL material were used, it showed high luminance efficiency of 34.81 cd/A and EQE of 4.01%.

EN10.03.23
**Room Temperature Synthesis of Cesium and Formamidinium Lead Bromide Nanocrystals via Phosphine-Based Chemistry**
Filip Ambroz, Thomas J. Macdonald and Ivan P. Parkin; University College London, United Kingdom

Room temperature (RT) synthesis of perovskite nanocrystals (NCs) is typically achieved employing a ligand-assisted reprecipitation (LARP) method that is compared to the hot-injection (HI) approach cost effective and
industrially friendly. However, the method has many drawbacks that can hinder large scale production of NCs. In this work, we report an amine and an oleic acid free synthesis of lead bromide perovskite NCs using a combination of trioctylphosphine oxide (TOPO) and diisooctylphosphinic acid (TMPPA) ligands. The alternative combination of ligands allows us to synthesize NCs at room temperature (RT) and in air using industrially friendly solvents. We show how our approach can be used to synthesize fully inorganic, CsPbBr$_3$ NCs and hybrid organic-inorganic FAPbBr$_3$ (FA = formamidinium) NCs with the PL emission (fwhm ≈20 nm) between 530 – 535 nm which is in line with the Rec. 2020 color standards. Moreover, using spectroscopy techniques we investigated ligand interactions with the NC surfaces and find that the ligands used in this study are bond via a Pb-O-P bond. In addition, we show that compared to a typically used ligand combination of carboxylic acid and amines, phosphine ligands can be easier removed from the NC surfaces.

EN10.03.24
Anion Exchange Blue Perovskite Quantum Dots LED with Metal Halide

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Lead halide perovskite (CsPbX$_3$, X = Cl, Br, I) quantum dots (QDs) have great potential for light-emitting devices (LED) owing to their high color purity and ease of solution processability$^{[1-3]}$. The mix-halide perovskite QDs can be controlled their emission wavelength, CsPb(Cl/Br)$_3$ for blue region by adjustment halide composition. Here, we demonstrate anion-exchange blue perovskite QDs CsPb(Cl/Br)$_3$ from pristine CsPbBr$_3$ using metal chloride. CsPbBr$_3$ was synthesized by the general hot-injection method. The metal chloride was added into CsPbBr$_3$ solution. The anion-exchange CsPb(Br/Cl)$_3$ exhibit a strong blue-shift in their of photoluminescence (PL) spectrum and UV-vis absorption spectra. The PL peaks of the anion-exchange blue perovskite exhibited a blue-shift from 508 nm (pristine) to 470 nm owing to the replacement of Br$^-$ anions by Cl$^-$ anions in the perovskite QDs. Furthermore, the anion-exchange blue perovskite in toluene dispersion exhibited high PLQYs of about 90%. To investigate the reason for increase of PLQY, we performed X-ray photoelectron spectroscopy (XPS). We found the presence of anion defects causing non-radiative recombination in the pristine CsPbBr$_3$. On the other hand, anion defects were suppressed in the anion-exchange blue perovskite. Blue CsPb(Cl/Br)$_3$ LED with anion exchange showed external quantum efficiency (EQE) of over 1%.


SESSION EN10.04: Physics of Perovskite Light-Emitting Materials and Devices
Session Chairs: Hanwei Gao and Bin Hu
Tuesday Morning, December 3, 2019
Sheraton, 2nd Floor, Back Bay D

8:15 AM EN10.04.01
Quantum-Confined Stark Effect of Lead Halide Perovskite Quantum Dots in a Mixed Dimensional van der Waals Heterostructure

Chitrareema Chakraborty$^{1,2}$, Hendrik Uitzat$^2$, Cheng Peng$^2$, Matthias Ginterseder$^2$, Mouni G. Bawendi$^2$ and Dirk Englund$^2$; $^1$Harvard University, United States; $^2$Massachusetts Institute of Technology, United States

The discovery of a myriad of two-dimensional (2D) materials has triggered enormous efforts to integrate distinct monolayers into van der Waals heterostructure for integrated nano-photronics and optoelectronics devices. Mixed dimensional (0D-2D) heterostructures have been previously studied only in relevance to interface charge transport, energy transfer, and photosensitization. In this work, we leverage on mixed dimensional van der Waals heterostructure and fabricate a vertical field-effect device using a combination of 2D and 3D materials to demonstrate quantum-confined Stark effect (QCSE) in highly luminescent perovskite-based (Cesium lead bromide, CsPbBr$_3$) colloidal quantum dots (QDs) with strong excitonic properties. Quantum-confined Stark effect (QCSE) is a basic feature of semiconductor nanostructures that characterizes the change in optical response on applying an electric field perpendicular to the structure.
In our device, few layers of h-BN (hexagonal boron nitride) and monolayer graphene serve as the dielectric and electrical contacts respectively. The QDs are deposited in the center of the heterostructure. We study the photoluminescence (PL) from the perovskite quantum dots embedded within the heterostructure at 4K. Application of a DC voltage in pre-determined step leads to a shift in the PL emission energy. This shift can be reversed by sweeping the voltage back to zero. The maximum observed energy shift is about 30 meV. The spectral shift is also accompanied by a change in intensity and linewidth of the QD which is the hallmark of the QCSE.

In conclusion, we have demonstrated QCSE in perovskite-based CsPbBr3 QDs by embedding them in a vertically stacked van der Waals heterostructure. Using 2D materials for QCSE based modulators makes it highly flexible and easy to integrate with any existing device. In future, such device concept can be used to resonantly tune the transition of a QD for strong coupling with another local emitter or a nano-cavity mode. Further, active feedback from such devices can also reduce slow spectral diffusion in QDs.

8:30 AM *EN10.04.02
Ferroelectric Polaron in Lead Halide Perovskites Xiaoyang Zhu; Columbia University, United States

Lead halide perovskites have been demonstrated as high performance materials in solar cells and light-emitting devices. These materials are characterized by coherent band transport expected from crystalline semiconductors, but dielectric responses and phonon dynamics typical of liquids. Here we explain the essential physics in this class of materials based on their dielectric functions and dynamic symmetry breaking on nano scales. We show that the dielectric function in the THz region may lead to dynamic and local ordering of polar nano domains by an extra electron or hole, resulting a quasiparticle which we call a ferroelectric large polaron, a concept similar to solvation in chemistry. The collective nature of polarization in a ferroelectric large polaron may give rise to order(s)-of-magnitude larger reduction in the Coulomb potential. We develop Fourier transform coherent phonon spectroscopy to directly probe the energetics and local phonon responses of ferroelectric polarons. The ferroelectric polaron may explain the defect tolerance and low recombination rates of charge carriers in lead halide perovskites, as well as providing a design principle of the “perfect” semiconductor for solar cells.

9:00 AM EN10.04.03
Coherent Single-Photon Emission from Colloidal Lead Halide Perovskite Quantum Dots Hendrik Utzat1, Weiwei Sun1, Alexander Kaplan1, Franziska Krieg2, Matthias Ginterseder1, Boris Spokoyny1, Nathan D. Klein1, Katherine Shulenberger1, Collin Perkinson1, Maksym V. Kovalenko2 and Moungi G. Bawendi1; 1Massachusetts Institute of Technology, United States; 2ETH Zürich, Switzerland

Chemically prepared colloidal semiconductor quantum dots have long been proposed as scalable and color-tunable single emitters in quantum optics, but they have typically suffered from prohibitively incoherent emission. We now demonstrate that individual colloidal lead halide perovskite quantum dots (PQDs) display highly efficient single photon emission with optical coherence times as long as 80 ps, an appreciable fraction of their 210 ps radiative lifetimes [1]. These measurements suggest that PQDs should be explored as building blocks in sources of indistinguishable single photons and entangled photon pairs. Our results present a starting point for the rational design of lead halide perovskite-based quantum emitters with fast emission, wide spectral-tunability, scalable production, and which benefit from the hybrid-integration with nano-photonic components that has been demonstrated for colloidal materials.


9:15 AM EN10.04.04
Rational Strategies to Obtain High Quantum Yields in Perovskite Materials for Light-Harnessing and Light-Emitting Application Neha Arora, M Ibrahim Dar and Richard H. Friend; University of Cambridge, United Kingdom

The extraordinary optoelectronic properties of metal halide perovskite semiconductors allowed the development of highly-efficient light-harnessing and light-emitting diodes based on this new generation of functional semiconductor materials. The outstanding power-conversion efficiencies shown by perovskite solar cells (PSCs) and remarkable external quantum efficiency displayed by perovskite-based light-emitting devices (PeLEDs) are realized, respectively, due to low photovoltage deficits and relatively high photoluminescence quantum yields. Therefore, it has become very important to investigate the causation of high photoluminescence quantum yields,
which translate into low-voltage losses in PSCs, and high external quantum efficiencies of PeLEDs. In my presentation, I will discuss the fabrication of high-performance mixed-cation perovskite-based LEDs and solar cells with an active layer based on a new composition. The improved external quantum efficiencies and photovoltages are obtained by improving the optoelectronic quality of the active layer, optimizing the charge extraction layers, and tuning the interfacial properties which in turn boosts the photoluminescence quantum efficiency, reducing the non-radiative recombination loss and thus enabling balance charge injection. The causation of high internal and external quantum efficiencies and photovoltage was investigated using various structural (Synchrotron-based x-ray scattering), morphological and spectroscopic (photothermal deflection absorption spectroscopy, photoluminescence quantum yield measurements, time-integrated and time-resolved photoluminescence) characterization techniques. The detailed insights gained through these various techniques will be discussed.

References


9:30 AM BREAK

10:00 AM *EN10.04.05
Mechanisms of Efficient Light Emission in Metal Halide Perovskites Yanfa Yan and Xiaoming Wang; University of Toledo, United States

Metal halide perovskites have been attracting great attention during the past few years as emerging optoelectronic materials in solar cells and light emitting devices (LEDs). Perovskite LEDs include both narrowband single color light emission and broadband white light emission. Recently, broadband white-light emission has been observed in one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) organic-inorganic lead halide perovskites. In addition to the broadband feature, the photoluminescence (PL) spectra of these materials show a massive Stokes shift compared to the corresponding absorption onset. The bandwidths of PL spectra are related to the strength of electron-phonon coupling. While it is weak in narrow band emission, it is strong in broadband emission forming self-trapped excitons (STEs). Interestingly, it has been observed in only certain three-dimensional and low-dimensional metal halide perovskites. In this talk, we will show by density-functional theory calculation that multiple STE structures exist in each perovskite exhibiting broadband emission. However, only the STE with Jahn-Teller like octahedral distortion is mainly responsible for the observed broadband emission, though it may not be the lowest energy structure. Both narrowband and broadband emission can be very efficient, which is attributed to the unique defect properties in metal halide perovskites, i.e., the dominant defects only create shallow levels in the bandgap.

10:30 AM *EN10.04.06
Cooling, Scattering and Recombination—The Role of the Material Quality for the Physics of Tin Halide Perovskites Maria Antonietta Loi; University of Groningen, Netherlands

Tin-based perovskites have long remained a side topic in current perovskite opto-electronic research. With the recent efficiency improvement in thin film solar cells [1] and the observation of a long hot carrier cooling time in formamidinium tin iodide (FASnI3) [2], a thorough understanding of the material's photophysics becomes a pressing matter. Since pronounced background doping can easily obscure the actual material properties, it is of paramount importance to understand how different processing conditions affect the observed behavior. Using photoluminescence spectroscopy, we therefore investigated thin films of FASnI3 fabricated through different protocols. We show that hot carrier relaxation occurs much faster in highly p-doped films due to carrier-carrier scattering. From high quality thin films, we extract the longitudinal optical phonon energy and the electron-phonon...
coupling constant, which are fundamental to understand carrier cooling. Importantly, high quality films allow for the observation of a previously unreported state of microsecond lifetime at lower energy in FASnI3, that has important consequences for the discussion of long-lived emission features in the field of metal halide perovskites.


11:00 AM EN10.04.07
Nanolaser Optimization through Statistical Optoelectronic Analysis Juan A. Alanis1, Patrick Parkinson1, Chennupati Jagadish2, and Hoe Tan2; 1The University of Manchester, United Kingdom; 2The Australian National University, Australia

Due to their characteristic elongated shape and reflective end-facets, semiconductor nanowires can be used as Fabry-Perot resonators to fabricate nanolasers. As a way of studying the key elements for lasing operation in these devices, we have developed and successfully employed a large scale optical technique to study interwire functional inhomogeneity. Taking advantage of this novel method we are able to locate and optically study a large number of nanolasers by Photoluminescence (Figure 1). Through a statistical comparison, different parameters such as nanowire length, material inhomogeneity, lasing wavelength etc. are correlated to identify which mechanisms contribute to low-power lasing. We discuss two applications of this approach; nanowires with multi-quantum-well GaAs/AlGaAs active region [1], and p-doped GaAs nanowires [2].

Taking advantage of a large scale optical technique, we have identified key parameters which would improve optoelectronic efficiency and potentially decrease the spread in performance of semiconductor nanowires. Also, we were able to find the best performing nanowire for single device applications. This approach is of industrial value, as well as providing identification of best operating nanolasers for the fabrication of devices for fundamental study.


11:15 AM EN10.04.08
Spin-Polarised Exciton Exchange Splitting and Luminescence Dynamics in Hybrid Metal-Halide Perovskites Ravichandran Shivanna1, Sean Bourelle1, Satyaprasad P. Senanayak1, Alexander Gillett1, Richard H. Friend1 and Felix Deschler2; 1University of Cambridge, United Kingdom; 2Technische Universität München, Germany

Excitons are the dominant photo-excited species in 2D layered perovskites and the early-time photoexcited species in 3D bulk metal-halide perovskites. Strong spin orbit coupling in these materials enables optical excitation of excitonic states with a defined total angular momentum and the generation of circularly-polarised emission from polarised spin-states. Here, we use circularly-polarised broadband transient absorption and luminescence spectroscopy to study spin-dependent exciton interactions and radiative recombination in the two-dimensional (2D) Ruddlesden-Popper perovskites (BA)3(MA/FA/Cs)2Pb3I11 and 3D bulk MAPbBr3. We spectrally resolve an ultrafast dynamic circular dichroism in the optical response that we discuss to arise from a photoinduced polarisation in the electronic state total angular momentum quantum number. We show that the optically-active states are split in energy via spin-dependent exchange interactions between excitons following photoexcitation, giving rise to shifts in the luminescence spectrum. We report that the room temperature exciton spin lifetimes in 2D metal-halide perovskites increases at low carrier densities, which we discuss as a spin scattering mechanism through Elliott-Yafet processes. Detailed analysis of the initial depolarisation kinetics indicate that the rate of carrier spin relaxation is reduced following the formation of ground state exciton from which luminescence occurs. Our results provide a fundamental picture of the role of exciton-exciton interactions in determining room temperature spin lifetimes and luminescence polarisation, highlighting the potential of hybrid perovskites for applications in spin-polarised light-emitting devices.
11:30 AM EN10.04.09  
Manipulating Exciton Dynamics in Colloidal Cd$_{1-x}$Mn$_x$Se Quantum Dots via Tunable Spin-Exchange Interactions  
Ho Jin$^{1,2}$ and Victor I. Klimov$^1$; $^1$Los Alamos National Laboratory, United States; $^2$The University of New Mexico, United States

Strong quantum confinement unique to colloidal semiconductor quantum dots (QDs) significantly enhances spin exchange interactions between band carriers and Mn dopants. In this case, a single exciton can exert an effective exchange field of a few tesla on the embedded magnetic dopants, which leads to the formation of zero-dimensional magnetic polarons.$^{1,2}$ The strong spin exchange also enables extremely fast energy transfer between the excited Mn ion and the QD exciton which allows one to effectively manipulate nonequilibrium ‘hot’ carriers prior to their relaxation into the band-edge levels.$^3$ This process can also be utilized to generate hot electrons with weak cw optical excitation.$^4$

Mn-doped CdSe QDs represent attractive structures for studies of the effect of resonant versus off-resonant exchange interactions on photoexcited electronic dynamics in a coupled host-semiconductor/magnetic-ion system. However, a colloidal synthesis of high quality Cd$_{1-x}$Mn$_x$Se QDs is still challenging. Among existing synthetic methods, the diffusion doping yields simultaneously the highest Mn$^{2+}$ content and good size uniformity.$^5$ This methods exploits a gradient between Mn$^{2+}$ chemical potentials in the solution and the QD phases for making incorporation of magnetic ions into QDs thermodynamically favorable. In the present study, we aim to improve the Mn diffusion doping method by controlling the chemical potentials of Cd$^{2+}$ in solution. In particular, during the initial synthesis of CdSe QDs, we use secondary phosphines for increasing the nucleation rate and thereby improving the consumption of the Cd precursor. This helps form a pure MnSe shell on top of the CdSe cores upon introduction of a Mn source without producing a Cd$_{1-x}$Mn$_x$Se alloyed layer. This leads to the improved monodispersity of the resulting doped particles as indicated by the reduction of the absorption peak widening to less than 7 meV instead of >20 meV observed for the previous syntheses.$^5$ Further, the removal of excess Cd from the reaction mixture by post-treatment with oleic acid accelerates incorporation of Mn$^{2+}$ into the CdSe lattice by facilitating creation of Cd vacancies due to diffusion of Cd ions towards the QD surface. As a result of fast Mn incorporation, we can induce a 100-meV shift of the absorption edge in just 5 min of the reaction, which is ~50 times faster than for the previously reported procedures.$^5$ This new method allows us to tune the QD band gap by 600 meV, which is accompanied by the dramatic change in the strength of the sp-d exchange coupling between the magnetic dopants and the semiconductor host. By applying CdS shelling to the doped structures, we boost their room-temperature emission efficiencies to more than 60%. By varying the QD size and the level of Mn doping, we observe a strong effect of tunable exchange interactions on electronic dynamics on a wide range of time scales from hundreds of femtoseconds to hundreds of nanoseconds.


11:45 AM EN10.04.10  
Time-Resolved Luminescence Spectroscopy of Light-Emitting Materials on Different Time Scales Combined with Spatial Resolution  
Eugeny Ermilov, Volker Bushmann, Christian Oelsner, Frank Birke, Felix Koberling, Matthias Patting, Marcus Sackrow, Michael Wahl and Rainer Erdmann; Picoquant GmbH, Germany

Luminescence properties of novel light-emitting materials are determined by the architecture and function of the respective devices and directly relate to the physical and chemical nature and quality of these materials. The understanding of photophysical processes as well as structure-property relationship of the new classes of light emitting materials are important steps toward the optimization of their properties to emit specific light for practical applications in different devices.

Time-resolved fluorescence spectroscopy is a modern and most valuable tool to investigate excited state dynamics in molecules, complexes, or semiconductors, which affect the light emitting properties of materials. This type of measurement technique became more and more popular in many scientific fields, including chemistry, biology, physics, as well as in life, materials or environmental sciences and is the ideal method for measuring also weak luminescence.
The combination of time-resolved luminescence spectroscopy with microscopic techniques is without doubt a highly modern and powerful kind of material investigation. Advantages of both techniques are combined in a variable, precise and powerful kind to investigate the photoinduced photophysical processes as well as structural properties of novel light-emitting materials.

Here we will demonstrate the performance of a spectrometer-microscope assembly for characterization and analysis of different light-emitting materials (e.g., halide perovskite, quantum dots and organic-inorganic nanomaterials) in terms of time resolution, ability to measure long decays (e.g., phosphorescence, delayed fluorescence) and record time-gated spectra using laser drivers with burst capabilities. Further more we present different kind of hardware as well as handling optimization for a combination of a state of the art photoluminescence spectrometer with a confocal upright microscope for steady-state, anisotropy, and time-resolved measurements. With this we give prove, that this multi-dimensional approach can be easily and successfully used to exploited investigations of e.g. photoinduced charge carrier dynamics in these materials and its correlation with the localized inhomogeneities and defect sites. Furthermore, surface effects, energy transfer transfer processes as well as the influence of dopants, impurities and defect sites on the luminescence properties of emitters will be discussed.

SESSION EN10.05: Synthesis of Perovskite Nanoparticles for Light-Emitting Devices
Session Chairs: Maksym Kovalenko and Tae-Woo Lee
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Back Bay D

1:30 PM EN10.05.01
Synthesis of Lead-Free Perovskite Quantum Dots for Solar Cell and Lighting Applications
Zeying Chen1,2, Pravakar P. Rajbhandari1,2 and Tara P. Dhakal1,2; 1Center for Autonomous Solar Power, United States; 2Binghamton University, The State University of New York, United States
Metal halide perovskites have received remarkable attention as perovskite photovoltaic (PV) devices. These have already achieved unprecedented higher power conversion efficiency (PCE of 24%) approaching silicon-based PV (PCE of 27%). However, these outstanding optical efficiencies can only be realized by lead-based perovskites and the devices are chemically unstable in air and moisture. Therefore, the key to the large-scale production of perovskite-based solar cell will come down to address their “toxicity” and instability problems. In our research, we are taking up the challenge to replace lead with nontoxic or less toxic element, Sn, and partially or even completely substitute Sn with Ge. For stability, mostly inorganic elements will be chosen. In addition, synthesis of quantum dot (QD) of these materials with water-resistant shell encapsulation to further stabilize the perovskite material will be investigated. The QDs will be synthesized with varying size and compositions to cover the whole UV-VIS spectrum.

1:45 PM EN10.05.02
High-Efficiency Printed Metal Halide Perovskite Nanoparticle Light-Emitting Diodes
Jinwoo Park1, Young-Hoon Kim1, Hengxing Xu2, Yonghee Lee1, Joo Sung Kim1, Sungjin Kim1, Su-Hun Jeong1, Min-Ho Park1, Young-Woon Kim1, Bin Hu2 and Tae-Woo Lee1; 1Seoul National University, Korea (the Republic of); 2The University of Tennessee, Knoxville, United States
We demonstrated bar-coating followed by a fast solvent evaporation process to yield uniform, fully-covered and thickness-controllable films of metal halide perovskite (MHP) nanoparticles (NPs). Based on optimized device structure with uniformly printed MHP NPs, highly efficient perovskite light-emitting diodes (PeLEDs) were achieved. Large-area and active-matrix PeLEDs were also demonstrated. We also analyze the ion-migration and non-radiative recombination pathways in NP films by measuring capacitance, transient electroluminescence and magnetic-field dependent characteristics of NP based PeLEDs and NP films. This work provides a promising way to toward development of MHP emitters in large-scale industrial displays and solid-state lighting, and suggests analysis methods that can be useful for other perovskite optoelectronic devices.

2:00 PM EN10.05.03
Enhanced Stability of Colloidal Quantum Dots by Shell Encapsulation Enabled by Cross-Linkable Polymeric Ligands
Jaewan Ko and Joona Bang; Korea University, Korea (the Republic of)

Endowing quantum dots (QDs) with robustness and durability has been one of the most important areas of research in this field, since the major limitations of QDs in practical applications are their thermal and oxidative instabilities. In this work, we propose a facile and effective passivation method to enhance the photochemical stability of QDs by structurally designing polymeric double shell network of thiol-terminated poly(methyl methacrylate-\textit{b}-glycidyl methacrylate) (P(MMA-\textit{b}-GMA)-SH) block copolymers ligated to QDs. To achieve this, the cross-linking reaction of GMA epoxides in PGMA block was conducted using Lewis acid catalyst under an ambient environment in order not to affect the photophysical properties of pristine QDs, which provides QDs with robust double layers consisting of highly weatherable and transparent PMMA outer-shell and oxidation-protective crosslinked inner-shell. Consequently, the resulting QDs surrounded by crosslinked double shell layers exhibited exceptional tolerance to heat and oxidants when dispersed in organic solvents or QD-nanocomposite films, as evidently corroborated under various harsh conditions with respect to temperature and oxidant species. In addition, it was shown that the outer polymer brush can provide the miscibility of resulting QDs with host polymer matrix to fabricate a well-defined QD-nanocomposite films via cost-effective solution process. The present approach not only provides simple yet effective chemical means to enhance the thermochemical stability of QDs, but also offers a promising platform for the hybridization of QDs with polymeric materials for developing flexible light-emitting or light-harvesting devices.

2:15 PM EN10.05.04
Highlighting Challenges of Oleate-Capped Formamidinium Lead Bromide Perovskite Nanocrystals
Olivia J. Ashton, Ashley Marshall, Jonathan Warby, Bernard Wenger and Henry J. Snaith; University of Oxford, United Kingdom

Studies conducted on the stability of perovskite nanocrystals have begun to aid understanding of how to handle these emerging materials. Through extensive experimental and computational studies, a consensus has emerged in the community surrounding the crucial nature of the surface of the nanocrystals and the complex, dynamic ligand shell around them. Different ligands have been shown to both improve photoluminescence quantum yield to near unity, and bolster stability to washing and colloidal lifetimes. The binding groups of the ligands and their introduction in the synthesis or as a post-treatment have been highlighted time and again.

To date these impressive developments have mostly focused on cesium lead bromide, CsPbBr\textsubscript{3}. The perovskite family extends its compositional range in both the cation and anion sites, and the translation of successes is not straightforward. In this work, we investigate the fabrication of formamidinium lead bromide, FAPbBr\textsubscript{3}, via a phosphine oxide assisted synthesis and the challenges faced when applying lessons learnt from the all inorganic perovskite to this system. Through nuclear magnetic resonance spectroscopy coupled with optical characterisation we demonstrate the influence of the labile formamidinium protons on the surface chemistry of the nanocrystals and how this in turn changes their stability, structural integrity and affects the reaction pathway in the formation of these nanocrystals compared to their inorganic counterpart.

2:30 PM EN10.05.05
Light Emitting Diodes Based on Colloidal Quantum Dots with Ultrahigh Current Densities Exceeding 1,000 A per cm\textsuperscript{2}
Heeyoung Jung\textsuperscript{1}, Young-Shin Park\textsuperscript{1,2}, Jaehoon Lim\textsuperscript{1,3} and Victor I. Klimov\textsuperscript{1}; \textsuperscript{1}Los Alamos National Laboratory, United States; \textsuperscript{2}The University of New Mexico, United States; \textsuperscript{3}Ajou University, Korea (the Republic of)

Colloidal semiconductor quantum dots (QDs) have great potential as optical gain media for realizing solution processable lasers with readily tunable emission wavelengths. A present challenge in this area is the demonstration of electrically pumped lasing devices. Recent advances towards this goal include the realization of optical gain with direct current (d.c.) electrical pumping [1], the demonstration of high brightness QD light emission diodes (LEDs) [2], and the development of effective strategies for tackling the efficiency ‘droop’ problem [3]. Next tasks include pushing current densities to \textasciitilde100 A cm\textsuperscript{-2} (or above) levels and incorporation of an optical resonator into a QD-LED device. Here, we address the first of these challenges by practically demonstrating pulsed QD-LEDs that achieve ultrahigh current densities exceeding 1,000 A cm\textsuperscript{-2}. This allows us to inject more than 10 excitons per dot and thereby realize population inversion of both the ground-state (1S) and the excited-state (1P) transitions. This demonstration exploits continuously graded QDs (cg-QDs) embedded into a ‘current focusing’ \textit{p-i-n} LED [1].
actuated using short-pulse electrical bias. As we demonstrated previously, cg-QDs exhibit strong suppression of nonradiative Auger decay [1, 4], which is essential for achieving highly emissive multie exciton states. These dots are integrated into an inverted p-i-n LED with hybrid (inorganic/organic) charge transport layers. An interlayer of an insulating material with a narrow (~50 μm) gap is deposited on top of the QDs to limit the injection area and thereby increase current density (J). Using this approach, we achieve J of ~50 A cm⁻² with d.c. current excitation. We able to push current density to ~600 A cm⁻² using 5 μs voltage pulses, and increase it further to >1,000 A cm⁻² with 1 μs pulses. Using these ultrahigh current densities, we are able to realize an unusual electroluminescence (EL) regime when the intensity of the 1P band exceeds that of the 1S emission. Based on the quantitative analysis of the EL spectra and comparison with optically excited photoluminescence, we conclude that using electrical pumping we are able to excite at least 10 (and potentially >20) excitons per dots. Such excitation levels greatly exceed the thresholds for both 1S and 1P optical gain. Importantly, these extremely high current densities are realized using a fairly thick active medium comprising up to 4 QD monolayers. We further demonstrate that the layers of this thickness are capable of lasing if combined with optimized distributed feedback cavities. Not only these results prove the feasibility of electrically pumped lasing with colloidal QDs but they also suggest that the goal of practically realizing such devices is within close reach.


2:45 PM EN10.05.06
**Mechanistic Investigation of Alkanethiol Treatment of Colloidal CsPbX₃ Nanocrystals** Kenneth R. Graham, Md Aslam Uddin, Justin K. Mobley, Abdullah Masud, Tuo Liu, Rosemary Calabro, Doo Young Kim and Christopher I. Richards; University of Kentucky, United States

Metal halide perovskite nanocrystals (NCs) are promising materials for use in optoelectronics. However, further improvements in stability, reproducibility, and photoluminescence quantum yield (ΦPL) are essential for enabling commercial applications. Inadequate surface passivation is a major cause of instability, irreproducibility, and low ΦPL. We find that post-synthetic treatment with alkanethiols reproducibly yields stable NCs with near unity ΦPL for a range of synthetic conditions and varying initial ΦPL of the as-synthesized NCs. A mechanistic investigation shows that thiol addition leads to thioether formation via the thiol-ene reaction with octadecene, oleic acid, and oleylamine. Both thioliates and thioethers are suspected to bind to undercoordinated Pb atoms on the NC surfaces, and the surface binding and ΦPL increases can be rapidly accelerated through exposure to blue or UV light. Furthermore, we show that metallic Pb nanoparticles appear in many batches of synthesized CsPbBr₃ NCs and that dodecanethiol addition eliminates these metallic Pb particles. Applying similar alkanethiol treatment to thin films processed with varying Cs:Pb or methylammonium:Pb stoichiometry we find that alkanethiols only bind to the film surfaces when a significant excess of PbX₃ is included in the processing solution.

3:00 PM BREAK

**SESSION EN10.06: Physics, Analysis, and Processing of Perovskite Emitters and Their Devices**
Session Chairs: Hanwei Gao and Zhi Kuang Tan
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Back Bay D

3:30 PM *EN10.06.01
**Probing the Bias-Induced Interfacial Characteristics of MAPbBr₃ Perovskite LEDs** Tzung-Fang Guo, Aswaghosh Loganathan and Teng Lam Shen; National Cheng Kung University, Taiwan
The interfacial phenomenon in the case of MAPbBr$_3$-based organic-inorganic hybrid light-emitting diode (LEDs) depends upon the existence of vacant sites that enable electric-field driven ion migration which in turn causes detrimental effect on the device efficiency. A clear deeper knowledge of the fundamental interfacial mechanism in hybrid LEDs that is dependent on the material properties must be essentially brought in focus so as to improve the optoelectronic properties.

In this present study, we have attempted to bring out this interfacial phenomenal occurrences using Admittance Spectroscopy and demonstrate the fundamental mechanism in such perovskite LED and further establish a method to tune the interfacial kinetics by appropriate passivation of perovskite layer by additive engineering. Defect passivation via additive engineering improved the LED device performance incredibly evidenced by the lowering of built-in potential ($V_{bi}$) indicating faster light turn-on and reduced interface potential revealing better interfacial charge injection behavior. Moreover, the current-voltage (I-V) hysteresis behavior speculated to be arising due to ion migration is suppressed. Carrier dynamics is altered by enhancing the carrier injection due to improved interfacial conduction and noticeable change from inductive behavior to capacitive behavior due to increased carrier density. The DC bias dependences of characteristic times and carrier distribution are analyzed to understand the complex kinetic behavior of hybrid LED as it is composed of both organic and inorganic components. This clear understanding of the interfacial kinetics and carrier dynamics will enable materials scientists to establish strategic design to overcome the existing disadvantages in near future and improve the optoelectronic functionalities and properties.

4:00 PM EN10.06.02

Exciton Fine Structure of CsPbBr$_3$ Perovskite Quantum Dots—A First-Principles Study Oleksandr Voznyy$^{1,2}$ and Kamalpreet Singh$^{1,2}$; 1University of Toronto Scarborough, Canada; 2University of Toronto, Canada

Cesium lead halide perovskite nanocrystals are a highly attractive class of materials for coherent light emission, with implications for lasing, light-emitting diodes, and quantum computing. Fine-tuning their properties for the above applications requires an exact understanding of their exciton fine structure, in particular, spacing and polarization of their triplet and singlet states. Experimental reports have been controversial, implicating that the Rashba effect may be inducing an inversion in the order of bright and dark states.

To aid in the resolution of this debate, we performed an investigation of the fine structure of the triplet emission properties in these materials. Using the wave functions generated via DFT calculations including spin-orbit coupling for cubic, orthorhombic and tetragonal cesium lead halide perovskite nanocrystals of ~3 nm in diameter, we further augmented them with Coulomb coupling between the exciton configurations, to resolve the absorption and emission fine structure in a configuration interaction method.

We anticipate our work will aid in the resolution of the debated emission fine structure of CsPbBr$_3$ nanocrystals and thereafter allow for the development of bright materials for optoelectronics.

4:15 PM EN10.06.03

A New Tool to Probe Local Photophysical Properties in Passivated Perovskite Nanoplatelets for Light-Emitting Devices Miguel Anaya, Kyle Frohna, Javad Shamsi, Kangyu Ji, Krzysztof Galkowski and Samuel D. Stranks; University of Cambridge, United Kingdom

Confined versions of metal-halide perovskites have emerged over the past years as a versatile class of semiconductors for high-performance optoelectronic devices.[1] Despite their unique properties, this family of perovskites has however been observed to display photo-instability, especially when emitting in the blue region of the electromagnetic spectrum. Moreover, the use of ligands to mitigate agglomeration and the large density of surface defects in the material hamper charge carrier injection and radiative recombination and thus their definitive integration in real-world devices.[2,3]

In this talk, we will present a detailed photophysical characterisation of blue emitting CsPbBr$_3$ perovskite nanoplatelets (NPLs) in which a controlled Br- and light-based passivation strategy is employed to improve both their optical and electrical properties. In this regard, we will introduce a new powerful technique with which we can extract the Urbach energy, absorptance, quasi-Fermi level splitting and photoluminescence quantum efficiency (PLQE) values in the materials at the nanoscale by hyperspectral wide-field imaging. The observations reveal microscale heterogeneities in the pristine NPLs films that are remarkably suppressed in the treated samples. Furthermore, the optoelectronic quality of this blue emitters is boosted by means of a high PLQE surpassing 50%
and an important reduction of surface defects. Interestingly, our approach allows us to achieve fine control over the work function (as revealed by Kelvin Probe) of the systems. Finally, we fabricate LEDs based on the most efficient materials and obtain maps at the diffraction limit scale demonstrating homogeneous external quantum efficiencies close to 0.3% at 460nm, which match those at the macroscale.[4]


4:30 PM EN10.06.04
Real-Time Investigation of Colloidal Quantum Dot Self-Assembly During Blade-Coating Ahmad R. Kirmani1, James Z. Fan2, Edward H. Sargent2 and Lee Richter1; 1National Institute of Standards and Technology, United States; 2University of Toronto, Canada

Colloidal quantum dots (CQDs) have been intensely pursued for applications in flexible light-emitting displays and photovoltaics. Self-assembly of CQDs into long-range ordered 3D superlattices (SL) leads to emergence of new optical and electronic properties and offers to extend their benefits portfolio beyond those afforded by size-confinement. Technological viability of these structures requires their controlled fabrication using scalable coating methods. In this study, we explore lead sulfide (PbS) CQD self-assembly during blade-coating using time-resolved X-ray scattering and optical interferometry. Blade-coating is an established prototyping tool for slot-die coating. We monitor the nucleation and subsequent evolution of the CQD SLs during the ink-to-film transformation. A rich structural diversity is observed when tuning the CQD size, concentration, solvent and substrate temperature. SLs are found to nucleate very early in the coating stage from an FCC phase at the solvent-air interface during which the individual CQDs are randomly oriented. As the solvent nears complete evaporation, the system enters a transition stage where the FCC SL contracts and morphs into a final, dry BCC phase due to ligand packing frustration. This transition is marked by an orientational ordering of the CQDs that grows stronger with the CQD size. We also observe SL twinning during coating of the largest: 8 nm diameter CQDs. This study develops a fundamental understanding of and provides design rules for fabricating and tailoring self-assembled CQD solids via scalable coating.

4:45 PM EN10.06.05
High-Resolution Patterning and Tandem Processing Achievable for Quantum Dots Films Crosslinked with Photoinduced-Ligand Binding Agents Moon Sung Kang and Jeehye Yang; Sogang University, Korea (the Republic of)

To fully exploit the excellent luminescence characteristics of quantum dots (QDs), researches on EL displays based on QDs have been actively conducted. To achieve this, a multi-color QD patterning technology must be established. Processing and patterning of quantum dots involve a solution-based technique, unlike the organic light emitting materials which are typically deposited through evaporation-based technique. The applicability of QDs to various solution process allows one to carry out their deposition over a large-scale at low cost, but it also causes a problem of dissolving the bottom layer if the secondary layer is applied by solution process consecutively. To avoid this problem, several QD patterning techniques have been developed, such as inkjet printing and microcontact printing. Here we report a simple way to obtain high-resolution patterns of InP QDs using a chemical crosslinker (bis-perfluorophenyl azide) that can bind to ligands surrounding the QD surface to form a bridging network upon exposure to UV, which is referred to as the photoinduced-ligand binding agents (PiLBA). Due to the chemical durability of the cross-linked QDs, non-crosslinked portions can be etched chemically to form high resolution (<3 μm) patterns of QDs. Multi-color patterns can also be stacked laterally or vertically by repeating the same solution process (see images below). The EL characteristics of the cross-linked QDs varied systematically with the loading of the PiLBA. The simple strategy converting the QD films to be photo-resistive will make significant impact enabling the production of high-resolution, high-throughput, full-color EL displays based on QDs intensively explored in the community.
EN10.07.01
White Electroluminescence Devices with Double Emitting Layers Employing Red Quantum Dots and Blue Organic Phosphorescent Molecules
Jiwan Kim and Aram Moon; Kyonggi University, Korea (the Republic of)

Colloidal quantum dots (QDs) which are nano-sized semiconductors, have special properties such as easy emission tunability, high color purity and solution processability. With the commercial potential of QD-based displays being confirmed, quantum dot light-emitting diodes (QLEDs) have attracted attention as next generation display technology.

Over the past several decades, many groups have studied about the core / shell structure of QDs, charge transport layers and the charge balance to improve the efficiency and lifetime of QLEDs. The performance of QLEDs has dramatically improved through the studies, but it is only limited to monochromatic QLEDs. Therefore, for commercialization of full color QLEDs, studies on white emitting QLEDs should be conducted.

Herein, we fabricated white standard structured electroluminescence (EL) devices with double emitting layers (EMLs) using red QDs and blue organic phosphorescent molecules. The double EMLs were formed by stacking blue organic molecules EML directly on the red QDs EML.

Recently, organic light-emitting diodes (OLEDs) structure with the QD color filters has received huge attention in the display industry mainly applying QD to the color converting layer. This structure is different with our white QLEDs, but a blue OLEDs is commonly used between two structures. In this study, we used bis[2-(4,6-difluorophenyl)pyridinato-C2,N]iridium(III) (FIrpic) as the blue emitting organic materials. By using FIrpic, which has a broad emission spectrum, white emission with relatively high color rendering index (CRI) was obtained with less materials, only single QDs EML and organic EML.

When the applied voltage was more than 7 V, the red and blue peaks appeared simultaneously from the EMLs. Commission Internationale de l'Eclairage graph shows that the color coordinate shifts from the red region to the white region as the voltage increases. At an applied voltage of 12 V, the device exhibited a maximum luminance of 4,619 cd/m², a peak current efficiency of 2.17 cd/A and the high CRI of 66.

Our unique QLEDs with double EMLs shows the potential for white EL devices using less materials. Therefore, this result is expected to contribute to the development of practical full color display beyond OLEDs in the near future.

EN10.07.02
Mn-doped Lead Halide Perovskite Nanocrystals with High Luminescence and Application for Light-Emitting Diodes
Zhuo Chen, Lvming Dong, Hanchuan Tang and Jianfeng Zang; Huazhong University of Science and Technology, China

All-inorganic halide perovskites (CsPbX₃, X=Cl, Br and I) have emerged as one of the most prominent materials in the application of photoelectric devices due to remarkable properties such as high photoluminescence quantum yields and tunable emitting color, but toxic Pb is not environment-friendly. Therefore, the effort to develop lead-free all-inorganic perovskite QDs becomes inevitable. Herein, we report a simply, atmospheric synthesis approach for incorporating manganese (Mn) ions into cesium lead halide (CsPbX₃) perovskite quantum dots (QDs) with high luminescence and stability. Different Mn-to-Pb feed ratios are explored to study the influence on the intensity of two emission peaks, around 400 nm and 600 nm, respectively, and the optimum luminescence up to 65% is achieved.

The optical properties of as-prepared nanocrystals remain consistent even after several months. Besides, we obtain high luminescence Mn-doped blue perovskite nanocrystals and the stability has been greatly improved in comparison to those pure blue perovskite nanocrystals. Both the orange and white light-emitting diodes (LEDs) are obtained by directly employing the as-prepared CsPbₓMn₁₋ₓCl₃ QDs as color conversion materials on a commercially available 365 nm GaN LED chip and combining the orange nanocrystals with the Mn-doped blue perovskite nanocrystals on a UV LED. The excellent optical properties of the CsPbₓMn₁₋ₓCl₃ QDs offer great potential for the application of high
performance flexible displays on composite polymer substrates.

**EN10.07.03**

**Atomistic Defect States as Quantum Emitters in Monolayer MoS\(_2\)**

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Quantum light sources in solid-state systems are of major interest as a basic ingredient for integrated quantum device technologies. The ability to tailor quantum emission through deterministic defect engineering is of growing importance for realizing scalable quantum architectures. However, a major difficulty is that defects need to be positioned site-selectively within the solid. In this work this is overcome by controllably irradiating single-layer MoS\(_2\) using a sub-nm focused helium ion beam to deterministically create defects. Subsequent encapsulation of the ion bombarded MoS\(_2\) flake with high-quality hBN reveals spectrally narrow emission lines that produce photons at optical wavelengths in an energy window of one to two hundred meV below the neutral 2D exciton of MoS\(_2\).

Based on ab-initio calculations we interpret these emission lines as stemming from the recombination of highly localized electron-hole complexes at defect states generated by the helium ion bombardment. Using a many-body approach for dephasing due to electron phonon emission, we quantify the spatial extension of the emission centers and compare them to the results of the ab-initio calculation. [1]


**EN10.07.04**

**Flexible Electrochromic Displays with Subpixelated Ion Gel-Based Viologens by Multiple Patterning**

Jong-Woo Kim, Do-kyun Kwon and Jae-Min Myoung; Yonsei University, Korea (the Republic of)

Electrochemical devices have attracted attention as display materials owing to their properties such as simple structure, low-power driving, and variety of electrodes irrespective of work function. Among the electrochemical materials, electrochromic materials which exhibit reversible color change by redox reactions have been used in the field of smart windows, mirrors, displays, and sensors. To utilize electrochromic materials for active-matrix display applications, an electrochromic display (ECD) requires simultaneous implementation of various colors and a fine-pixelation process.

In this study, flexible ECDs with simultaneously implementable subpixelated-EC gels by sequential multiple patterning were successfully demonstrated. Ionic liquid-based EC gels of monoheptyl-viologen, diheptyl-viologen (DHV), and diphenyl-viologen (DPV) were used to create the colors of ECDs: magenta, blue, and green, respectively. Especially, to realize an improved green color, DHV–DPV composite gels were synthesized. Three EC gels exhibited stable properties without degradation during repetitive operation. The subpixelation process for multicolored-flexible ECDs was designed to facilitate both easy fabrication and rapid operation with various patterns at low cost. The subpixelated EC gels using a film mask could be implemented to a minimum size of 200 \(\mu\)m. Furthermore, the subpixelated flexible ECDs exhibited high durability even after 1000 cycles of mechanical bending tests at a bending radius of 10 mm. The surface characteristics of the EC materials were confirmed by optical microscopy, and the optical characteristics were analyzed by using a UV-vis spectrometer. The redox potential of the EC gel was confirmed by cyclic voltammetry using a potentiostat. After fabrication of patterned-ECD on a flexible substrate, the analyses of optical properties and reliability test were conducted according to the applied voltage.

Keywords: viologen, ion gel, patterning, electrochromic display, flexible

**EN10.07.05**

**Mapping Plasmon-Enhanced Upconversion Fluorescence Near Au nanodisks**

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Strategies for controlling and enhancing the fluorescence of molecules and nanocrystals have been the subject of intense research in the past decades [1-3]. This trend is motivated by the need to develop new highly sensitive biosensors, and by the possibility to improve optoelectronic devices like light emitting diodes and solar cells. Here, we present a study of upconversion fluorescence enhancement effects near Au nanodisks by scanning near-field optical microscopy. The enhancement and localization of light near the metallic structures are directly visualized by using a single Er/Yb-codoped fluorescent nanocrystal [4,5] glued at the end of a sharp scanning tip. Excitation was achieved in a transmission mode by a linearly polarized laser diode (\(\lambda = 975\) nm) focused in the tip-sample region. Fluorescence was detected in the visible range after the absorption of two photons by up-conversion. In general, the fluorescence enhancement pattern presents two lobes aligned in the direction of the incident polarization direction, but the intensity amount and the details of the enhancement distribution strongly depend on the nanodisk size. The observed patterns are in good agreement with the near-field maps calculated by finite-difference time-domain method, both in two and three dimensions above the structures. The relationship between the far-field optical response of the nanostructures and the achieved enhancement is also analyzed. [6]


EN10.07.06
Characteristics of Violet Light-Emitting Diodes Fabricated Using p-CuI Film/n-MgZnO Quantum Dot Heterojunction Sung-Doo Baek and Jae-Min Myoung; Yonsei University, Korea (the Republic of)

Solid-state lighting based on GaN and related compounds has been successfully developed and commercialized over the last few decades. Until recently, many researches have been attempted to discover new kinds of inorganic semiconductor candidates for next-generation light-emitting diodes (LEDs) that can replace GaN. Among those, ZnO has attracted much attention as a representative candidate due to its various advantages such as a wide direct transition band gap (~3.37 eV) with a large exciton binding energy (~60 meV), low-cost production, and harmlessness to the human body. However, it is challenging to obtain p-type ZnO due to native donor defect of oxygen vacancy in the ZnO lattice, thereby achieving ZnO p-n homojunction is a difficult task. To overcome this problem, many studies have been conducted on p-n heterojunction LEDs using n-type ZnO with other p-type semiconductors.

In this study, CuI possessing a direct transition band gap (~2.95 eV) with a large exciton binding energy (~58 eV) has been adopted as a p-type material for ZnO heterojunction LEDs. As an n-type material, MgZnO quantum dot (QD) which has much wider band gap than ZnO was used. Moreover, the size reduction of MgZnO QDs was observed, causing the band gap widening of MgZnO by the quantum confinement effect. The wider band gap of MgZnO can effectively suppress excess electron injection from cathode to the p-CuI layer, enhancing the electron-hole recombination efficiency by charge balance between electrons and holes. The CuI film was obtained by iodination process of Cu metal film deposited on ITO-coated glasses and the n-Mg\(_x\)Zn\(_{1-x}\)O QDs were separately synthesized by low-temperature solution process. The p-n heterojunction was formed by spin-coating of the synthesized n-MgZnO QDs on the CuI film. The morphology of the obtained p-CuI film and n-MgZnO QD were confirmed by scanning electron microscope and transmission electron microscope, respectively. Optical characteristics of each layer were evaluated by photoluminescence and UV-Vis-NIR spectroscopy. The Mg content of MgZnO QDs was examined by X-ray photoelectron spectra analysis. Finally, the electrical and optical characteristics of the fabricated LED were evaluated by current-voltage measurement, electroluminescence measurement with light emission images.

EN10.07.07
Wirelessly Operated Wearable Micro Light-Emitting Diodes on a Fabric Seung Hyung Lee, Han Eol Lee, Jung Ho Shin and Keon Jae Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

In the era of hyper-connection, wearable displays are attracting attention as a two-way communication method. Although there have been several demonstrations of displays on clothes, the problem of high power consumption
still remained. In this work, we present wirelessly operated wearable micro light-emitting diodes (WμLEDs) fabricated on a fabric. The stability of the WμLEDs was investigated under harsh conditions like high temperature and humidity, mechanical deformation and sunlight, which means that the WμLEDs can be used for outdoor applications. Furthermore, a passive-matrix WμLEDs device was successfully demonstrated which emitted bright red light.

**EN10.07.08**

**Deep Red to Near Infrared Emitting Iridium Complex for Solution-Processable Phosphorescent OLEDs with Substituents Engineering** Sungjin Park, Seyeong Lim, Taehyun Kim and Taiho Park; POSTECH, Korea (the Republic of)

The emerging future engineering technology such as dark-vision displays and photobiomodulation light therapy has induced an enormous demand for the design of highly efficient, flexible, stable, and low-cost deep-red emitting luminophores. Herein, six new deep-red and near infra-red (650–800 nm) emissive iridium(III) complexes have been designed and synthesized, variation on cyclometalating (benzo[b]thiophen-2-yl)quinoline main ligand and picolinate, β-diketonate ancillary ligands. The structures and distorted octahedral coordination motifs of six iridium complexes were analyzed by single-crystal X-ray diffraction analysis. Herein, four iridium complexes were developed with electron donating or withdrawing substituents anchored on the quinoline moiety of (benzo[b]thiophen-2-yl)quinoline cyclometalating ligands. With single-crystal X-ray diffraction analysis, exact coordination geometry, intermolecular interactions were identified. In addition, deep study on the effect of the ancillary ligands on the excited-state process was carried out and the results were compared with reference compounds containing thenoyltrifluoroacetylacetone in place of the picolinate ancillary ligand. The picolinate ancillary ligand has rigid nature and high triplet energy level which induces a robust deep-red emission while the triplet spin density population and flexible deformation of β-diketonate ancillary ligand resulted an excited-state geometrical deformation, yielding unfavorable, nonradiative pathways. Therefore, iridium complexes which uses the picolinate as ancillary ligand show excellent emission efficiencies (Φ<sub>PL</sub> = 0.48 and 0.37, respectively) and were effectively employed as deep-red dopants in organic light-emitting diodes, constructed via a solution-processed approach. The unoptimized synthesized iridium complexes based devices with various doping ratios performed maximum external quantum efficiency values of 5.03% and 3.41%, respectively.

**EN10.07.09**

**Thiol Ligand Exchange—Enhanced UV-Visible Photostability of CsPbI<sub>3</sub> Perovskite Quantum Dots Synthesis and Polymer Film Application** Yongjin Kim, Seungmin Baek and Sang-Wook Kim; Ajou University, Korea (the Republic of)

PeQDs show high quantum yields (QYs) of 40–90% with a narrow full-width-at-half-maximum (FWHM) of 20–45 nm. The narrow FWHM results in a wide color gamut, making PeQDs attractive as promising materials for optoelectronic applications such as light emitting diodes (LEDs), photodetector and lasers. However, perovskite structures suffer from serious stability problems due to their ionic characteristics. Among the PeQDs, red-emitting CsPbI<sub>3</sub> QDs with the α-phase structure are particularly unstable and it is difficult to maintain the structural stability of these species under light, moisture, or heat conditions because iodine has a large ionic radius, weak ionic bonds, and low stability. synthesizing the perovskite quantum dots, oleic acid(OA) and oleylamine(OLA) are often used as capping ligands. However, it is difficult to stabilize the ionic perovskite due to weak surface binding, thus optical properties are easily degraded. Herein, we report highly photo-stable CsPbI<sub>3</sub> perovskite quantum dots after ligand exchange with thiol (-SH, X-type ligand). The success of ligand exchange from OA and OLA to thiol could be stabilize the structure. Because thiols can attach to the surface of CsPbI<sub>3</sub> due to their high affinity for Pb<sup>2+</sup>, thereby stabilizing CsPbI<sub>3</sub>. Also, the α-phase structure could be maintained and the photoluminescence (PL) could be persisted for an extended period. As a result, structure stability and optical properties (Quantum Yields) were improved. Furthermore, the synthesized CsPbI<sub>3</sub> PeQDs showed that the photo-stability was highly improved under UV(365nm) irradiation. The PL intensity of thiol-uncapped CsPbI<sub>3</sub> decreased sharply for 12 hours, while thiol-capped CsPbI<sub>3</sub> QDs maintained their PL for 120 hours. For LCD color filter application, perovskite film was prepared using PeQDs and cyclo olefin copolymer (COC). The thiol-treated PeQD films improved their stability compared with the untreated PeQD films under irradiation with a 15 volt back-light unit (BLU). Due to the reason, it is predicted that it will be suitable for use as a color filter for LCD.

**EN10.07.10**
Improving the Grain Growth for High-Performance Inorganic Perovskite Solar Cells

Dongliang Bai; Shaanxi Normal University, China

Perovskite have received extensive attention due to their unique crystal structure, high extinction coefficient, high carrier mobility, and long carrier migration distance. However, organic-inorganic hybrid perovskites are sensitive to light and heat, and are easily decomposed in the presence of light and heat. In view of the photosensitivity and heat sensitivity of organic-inorganic hybrid perovskite batteries, inorganic perovskites with excellent stability in light and heat have been favored. However, the efficiency of inorganic perovskite solar cells is low. In this paper, the quality of the film is improved by doping the inorganic perovskite, and the thickness of the perovskite layer is increased by appropriate temperature treatment of the inorganic perovskite solution to improve the efficiency of the inorganic perovskite solar cell and the stability. The following work:

The first part is that the manganese ions insert into the inorganic perovskite. Studies have shown that the incorporation of manganese ions significantly increases the crystallites and reduces the defects of the film. The efficiency of CsPbBrI$_2$ inorganic perovskite solar cells based on 2% MnCl$_2$ doping is 13.47%, and the average grain size is up to 1200 nm, which significantly reduces the defects of inorganic perovskite films, and the stability of device has been greatly improved. The device maintains an efficiency of over 90% for 30 days under low humidity conditions and exhibits excellent stability.

The second part increases the thickness of the inorganic perovskite film by heating the inorganic perovskite solution at a suitable temperature without adversely affecting the film quality. After heating the inorganic perovskite solution at 100 degrees for 5 minutes, the film thickness was thickened from 165 nm to 195 nm, and the current density was greatly improved. The efficiency of the CsPbBrI$_2$ inorganic perovskite solar cell was 14.81%, The device maintains an efficiency of over 90% for 30 days under low humidity conditions and exhibits excellent stability.

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EN10.07.11

Highly Efficient Metal Halide Perovskite Light-Emitting Diodes Combining Plasmonic Nanomesh Electrodes and Nanophotonic Substrates

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Metal halide perovskites have emerged as promising materials for light-emitting diodes (LEDs), due to high color purity, tunable bandgap, high luminescence efficiency, and solution processability. The external quantum efficiency (EQE) of green perovskite LEDs has been boosted up to more than 20%, via strategies of compositional engineering, interfacial engineering, defect passivation, and crystal grain confinement, but the value is still far behind that of the commercial organic LEDs. A primary restriction of the EQE is the total internal reflection within the planar perovskite waveguide, due to the large refractive index contrast between the perovskite layer and the surrounding carrier transport layers; and the current efficiency is limited by non-radiative energy loss attributable to electrode quenching.

Here we propose an approach of embedding plasmonic nanomesh electrodes onto nanophotonic fused silica substrates to increase the device efficiency via their synergistic effect. On one hand, the current efficiency is improved when the plasmonic nanomesh electrode not only serve as transparent electrodes with small sheet resistance, but also offer localized surface plasmonic resonance to enhance spontaneous emission rate and realize electrode quenching control. On the other hand, 2D nanopillars of fused silica substrates confine the perovskite to the complementary nanostructure, and EQE is increased by light extraction enhancement through the perovskite “antenna”. FDTD Simulations are applied to optimize the 2D nanostructure (period, duty cycle, and depth) for the highest EQE with the adopted material system.

EN10.07.12

Nanophotonic Engineering for Perovskite Light-Emitting Diodes Performance Enhancement

Qianpeng Zhang, Daquan Zhang, Yu Fu and Zhiyong Fan; The Hong Kong University of Science and Technology, Hong Kong

Perovskite light-emitting diodes (LEDs) have developed very fast in the past five years, and the external quantum efficiency (EQE) higher than 20 percent has already been achieved. However, two issues remain. One is the light extraction issue; another is the stability issue. Perovskite LEDS with photoluminescent quantum yield (PLQY) higher than 80% have already been reported, but the planar structure device shows 20% closing to the limit. It means the light extraction is the next step to further enhance the EQEs of perovskite LEDs. In this work, we used nanophotonic substrate to improve the light extraction efficiency to 73% and achieved 17.5% EQE for
methylammonium lead bromide (MAPbBr₃) perovskite LED, which is enhanced twice compared to the planar device. The proposed nanophotonic substrate consists of two parts, namely nanodomes as couplers and photonic crystals as optical antennas. With a geometrical design, we found out the optimal geometry was one-micron pitch and 400 nm diameter for the photonic crystals. As for the stability issue, we fabricated LED devices with perovskite nanowires (NWs) embedded in anodic alumina membrane (AAM), and the AAM prevent the water molecule diffusion on the lateral direction. With the AAM protection of perovskite NWs, the T50 of our devices had been improved from 13 mins to 37 mins with the peak luminance more than 10,000 cd m⁻². Moreover, the NWs showed enhanced field emission and could achieve 16% EQE with the cesium lead bromide (CsPbBr₃) perovskite LED. Our work demonstrates the strength of nanophotonic engineering for perovskite performance enhancement in both efficiency and stability.

EN10.07.13
Polymer-Encapsulated Perovskite Nanocrystals—Fabrication and Optical Properties Carola Lampe, Verena A. Hintermayr, Maximilian Löw, Janina Römer, Willem Vanderlinden, Moritz Gramlich, Hyowon Jeong, Anton X. Böhm, Cornelia Sattler, Bert Nickel, Theobald Lohmüller and Alexander S. Urban; Ludwig-Maximilians-Universität München, Germany

Halide perovskite nanocrystals (NCs) have shown impressive advances, exhibiting optical properties that outpace conventional semiconductor NCs, such as near-unity quantum yields and ultrafast radiative decay rates. Herein, we present a block copolymer-templated synthesis for perovskite NCs providing a drastically enhanced stability. The polymer spontaneously forms micelles which act both as nanoreactors and as a protective shell. Encapsulated by this polymer shell, the NCs display strong stability against water degradation and ion migration. Heterostructures of encapsulated MAPI and MAPBr NC layers exhibiting efficient Förster resonance energy transfer (FRET), revealing a strategy for optoelectronic integration. Furthermore, we study the encapsulated NCs via single-particle spectroscopy and investigate the temperature dependence of the optoelectronic properties.

EN10.07.14
Colloidal Synthesis of Ni-Doped Cs₂AgInCl₆ Double Halide Perovskites Nabasindhu Das¹,²; ¹Indian Institute of Technology Roorkee, India; ²Indian Institute of Science, India

Over the last few years, there has been a steep growth in the study of lead halide perovskites, and due to their attractive optoelectronic properties, they have been incorporated into a number of devices like solar cells, lasers etc. However, due to the presence of lead as an environmentally unsustainable component and being toxic in nature, studies have been done to find alternative solutions to replace lead with other elements. Research has been done to partially dope these halide perovskites with Sn²⁺ and Ge²⁺, however these elements suffer from immediate oxidation to their respective +4 states. In the meanwhile, to obtain lead-free halide perovskites, recent studies have focussed on replacing two divalent ‘Pb²⁺’ cations with one monovalent and trivalent cation, generating quaternary A₂M⁺M³⁺X₆ compounds, which maintains the 3-D perovskite crystal structure as well as the charge neutrality. However, the problems in double perovskite structures are low photoluminescence (PL) emission and limited power efficiency (~ 2.2 %). This has further motivated the research groups around the world to search for direct-bandgap double perovskites, and a number of stable direct band gap perovskites have been computationally found to be stable. Bulk Cs₂AgInCl₆ has been synthesised by various groups having a direct band-gap of ~ 3.3 eV and a long carrier lifetime (~ 6 µs) and exhibit excellent stability to moisture, light and heat due to the presence of inorganic cation. Recently, L. Manna et. al. have doped nanocrystals of Cs₂AgInCl₆ with Mn²⁺ owing to the enhanced optical properties and observed a red-shift in the emission spectra.[1] Limited solubility of precursors in solvents causes a problem of solution processing in double perovskite synthesis. Herein, to solve the above problems we have undergone the synthesis of Cs₂AgInCl₆ nanocrystals by a simple colloidal hot-injection approach and further dope them with Ni to elevate their optical properties.

In this approach chloride salts of Ag and In were mixed in octadecene and size distribution control was done by injecting oleylamine and oleic acid as ligands. Nanocrystals were finally precipitated by injecting hot Cs oleate solution and the colloidal solution was re-dispersed in hexane post centrifugation and washing of the nanocrystals. 0.1 % and 0.3% Ni was doped by adding nickel chloride to the initial solution. The nanocrystals showed white photoluminescence under a UV lamp. STEM-EDS analysis was used to determine the Ni concentration in the doped nanocrystals. HRTEM micrographs of Ni-doped Cs₂AgInCl₆ nanocrystals that due to the inclusion of Ni ions, there was no disruption in the crystalline nature and no defects were formed. Optical properties were determined by UV-
vis spectrometry and PL spectrometry. There was a weak PL emission (PLQY ~ 1.6 %). Absorption onset of both doped and undoped nanocrystals was at ~ 350 nm with a strong increase in the absorbance at 272 nm. Undoped nanocrystals showed an emission peak at 560 nm that was consistent with earlier reported results of Cs2AgInCl6 NCs in the quantum confinement regime. In the Ni-doped nanocrystals, a blue shift in the emission spectra was observed with the emission peak at 490 - 470 nm, the extent of the blue shift depending on the Ni dopant concentration. Studies were done to determine the stability of as-synthesized nanocrystals and were found to be stable in air for at least a week with no change in the photoluminescence by the naked eye. Further studies to understand the behaviour of Ni2+ ions in the environment of the host matrix can be done by ESR spectroscopy which can shed light on the observed blue shift in the emission spectra of the doped samples. In conclusion, we have shown a colloidal route to synthesise Ni-doped Cs2AgInCl6 that gives phase-pure stable NCs in the air with increased bandgap.

References

EN10.07.15
**Inducing the Formation of Perovskite Nanoplatelets Using SnX4 Salts as Halide Precursors** Luiz G. Bonato, Raphael F. Moral, Gabriel Nagamine, José C. Germino, Arthur A. de Oliveira, Douglas S. da Silva, Fernando Galembeck, Lazaro Padilha and Ana F. Nogueira; State University of Campinas, Brazil

Lead halide perovskite nanocrystals (APbX3) are among the most exciting materials of the last 5 years due to their outstanding optoelectronic properties. These materials present narrow emission peaks and low trap state density. In cube-shaped perovskite nanocrystals, excitons are typically in weak quantum confinement regime, showing low size-dependence of the excitonic peak position as observed in the absorbance spectrum.1 Contrarily, the so-called 2D perovskite nanocrystals exhibit strong quantum confinement effects due to their limited thickness (just a few monolayers), resulting in absorption and photoluminescence (PL) excitonic transitions strongly dependent on the thickness of the nanocrystals,2 turning them promising materials for tunable optoelectronic applications.2 Therefore, the development of synthetic protocols to grow more stable and with higher control over the perovskite nanoplatelets (PNPL’s) thickness, is highly desirable. But to do this, it is crucial to gain insight into the mechanism that leads to the formation of PNPs.

In this work, we describe the formation of PNPs induced by the use of SnX4 (X = Cl, Br, and I) salts as the halide source through a new protocol, inspired by two distinct methods reported by Protesescu et al.3 and by our group.4 All spectral features corresponding to highly confined excitons (i.e., sharp excitonic absorption and emission) can be directly related to the 2D morphology of PNPs, which is confirmed by Transmission Electron Microscopy images. Besides that, the utilization of 1H-NMR and FTIR techniques helped to elucidate the nature of the disturbance in the acid-base equilibrium between oleic acid and oleylamine, caused by the Sn4+ cations. Our data suggest that the formation of Sn-oleylamine complexes is the cause of such disturbance, increasing the ratio [oleic acid]/[oleylamine], which was observed by the displacement in chemical shift of 1H-α to the amine group toward higher values. Such displacement can be assigned to a high concentration of oleylammonium species, increasing the ratio [oleylammonium]/[Cs+], favoring the formation of PNPs even at high temperatures, as supported by our results.

REFERENCES
Recently halide double perovskites have shown promise as phosphors for light emission applications such as white light phosphor converted LED applications. Here we report on halide double perovksite Cs2NaBiCl6 doped with Mn2+ ions resulting in an orange emitting compound under UV light. Optical measurements indicate an absorption profile comprised of localized Bi3+ 6s2 to 6s16p1 transitions. These isolated absorption processes lead to efficient energy transfer to Mn2+ sites leading to emission from the 4T1g to 6A1g transition. Unlike other reported Mn2+ double perovskite hosts, the zero dimensional electronic structure of Cs2NaBiCl6 surprisingly yields enhanced energy transfer to emissive sites. Compositions are analyzed via a variety of techniques such as XRD, UV-vis diffuse reflectance, photoluminescence, thermogravimetric analysis, and electron paramagnetic resonance. Through careful control of synthetic parameters single crystals with Br- partially substituting for Cl- are stabilized via hydrothermal methods. By relaxing the crystal field around absorbing Bi3+ sites, excitation peaks shifted to lower energies, closer to that of commercial blue LEDs. Tailoring of photoluminescent properties demonstrates the potential of double perovskite phosphors by tuning optical properties through chemical substitution. Routes to further improve this system as well as to extend these models to other double perovskite systems are discussed.

8:00 AM *(EN10.08.01/EN09.07.01

Exciton Properties in Individual Lead Halide Perovskite Nanocrystals

Brahim Lounis: University of Bordeaux, France

Lead halide perovskites have emerged as promising new semiconductor materials for high-efficiency photovoltaics, light-emitting applications and quantum optical technologies. Their luminescence properties are governed by the formation and radiative recombination of bound electron-hole pairs known as excitons, whose bright or dark character of the ground state remains unknown and debated [1, 2]. While symmetry analysis predicts a singlet non-emissive ground exciton topped with a bright exciton triplet, it has been predicted that the Rashba effect may reverse the bright and dark level ordering.

Spectroscopically resolved emission from single lead halide perovskite nanocrystals at cryogenic temperatures provides unique insight into physical processes that occur within these materials. At low temperatures the emission spectra collapse to narrow lines revealing a rich spectroscopic landscape and unexpected properties, completely hidden at the ensemble level and in bulk materials.

In this talk, I will discuss how magneto-photoluminescence spectroscopy provides a direct spectroscopic signature of the dark exciton emission of single lead halide perovskite nanocrystals [3]. The dark singlet is located several millielectronvolts below the bright triplet, in fair agreement with an estimation of the long-range electron hole exchange interaction. Nevertheless, these perovskites display an intense luminescence because of an extremely reduced bright-to-dark phonon-assisted relaxation [4]. Resonant photoluminescence excitation spectroscopy allows the determination of the optical coherence lifetimes in these nanocrystals and to assess their suitability as sources of indistinguishable single photons [5].

References:


May 2019.

8:30 AM *EN10.08.02/EN09.07.02
Charge-Carrier Recombination and Photon Recycling in Bulk and Quasi-2D Metal Halide Perovskites Laura Herz; University of Oxford, United Kingdom

Organic-inorganic metal halide perovskites have emerged as attractive materials for solar cells with power-conversion efficiencies now exceeding 23%. As these devices are approaching the Shockley-Queisser limit, bimolecular (band-to-band) recombination will dominate the charge-carrier losses, with trap-mediated charge recombination becoming less prominent.

We show that in methylammonium lead triiodide perovskite, bimolecular recombination can be fully explained as the inverse of absorption,[1] and exhibits a dynamic that is heavily influenced by photon reabsorption inside the material.[2,3] Such photon recycling is shown to slow charge losses from thin hybrid perovskite films, depending on light out-coupling.[2] Interestingly, for thin films comprising a quasi-two-dimensional (2D) perovskite region interfaced with a 3D MAPbI3 perovskite layer the blue-shifted emission originating from quasi-2D regions overlaps significantly with the absorption spectrum of the 3D perovskite, allowing for highly effective “heterogeneous photon recycling”. We show that this combination fully compensates for the adverse effects of electronic confinement, yielding quasi-2D perovskites with highly efficient charge transporting properties.[3]

In addition, we investigate optoelectronic properties of mixed tin-lead iodide and mixed iodide-bromide lead perovskites. We show how band-gap bowing in tin-lead perovskites is compatible with a mechanism arising from bond bending to accommodate the random placement of unevenly sized lead and tin ions.[4] While tin-rich compositions exhibit fast, mono-exponential recombination that is almost temperature-independent, in accordance with high levels of electrical doping,[4,5] lead-rich compositions show slower, stretched-exponential charge-carrier recombination that is strongly temperature-dependent, in accordance with a multiphonon assisted process. Finally, in the context of silicon-perovskite tandem cells, we discuss the mechanisms underlying detrimental halide segregation in mixed iodide-bromide lead perovskites with desirable electronic band gaps near 1.75eV.[6]


9:00 AM EN10.08.03/EN09.07.03
Photoluminescence Mechanisms in MAPbBr3 Films with Controlled Crystal Size Natalie Banerji; University of Bern, Switzerland

Organo-lead halide perovskites are excellent candidates for applications in light emitting diodes (LEDs). Methylammonium lead bromide (MAPbBr3) is the most investigated perovskite for visible perovskite LEDs, but its use is still limited by a low photoluminescence quantum yield (PLQY). Efforts to increase the PLQY of this material mainly consist in fine-tuning the morphology and reducing the grain size of the polycrystalline perovskite to the micro- and nanoscale. However, the origins of the increased PLQY with reduced crystal size remain unclear. Here we elucidate the physical processes underlying the light emission of MAPbBr3 thin films using time-resolved
A systematic correlation between the enhanced PL properties and the reduction of the crystal size, achieved by using different additives during solution-processing, is observed. The co-existence of free carriers and excitons at low excitation densities is shown in as-cast polycrystalline MAPbBr\(_3\) (crystal size of the order of few \(\mu\)m), while only excitons are present at high excitation densities. Using the Burstein-Moss and Saha models, important quantities such as the exciton binding energy, the reduced exciton effective mass and the trap density are estimated. We then explain the increased PLQY upon crystal size reduction by the presence of a bright exclusively exitonic population even at low excitation densities, together with reduced surface trapping thanks to passivation by the additives.


9:15 AM EN10.08.04/EN09.07.04
Ultrafast Electronic Sub-Gap State Dynamics and Exciton Coupling in Hybrid Metal-Halide Perovskites
Franco Camargo\(^1\), Tetsuhiko Nagahara\(^1\), Sascha Feldmann\(^2\), Richard H. Friend\(^2\), Giulio Cerrulo\(^1\) and Felix Deschler\(^1\); \(^1\)Politecnico di Milano, Italy; \(^2\)University of Cambridge, United Kingdom; \(^3\)Technische Universität München, Germany

Metal-halide perovskites show excellent properties for photovoltaic and optoelectronic applications, with power conversion efficiencies of solar cell and LEDs now exceeding 20%. This is unexpected, because these polycrystalline, solution-processed materials are likely to contain a significant density of defects compared to melt-grown semiconductors. Yet, typical effects from defects, such as strong absorption below the bandgap, low open circuit voltage in devices and dominant non-radiative recombination were not observed. In this contribution, we investigate thin films of metal-halide perovskites CH\(_3\)NH\(_3\)PbX\(_3\) (X = Br,I) with multidimensional optical spectroscopy to resolve the dynamics of band and defect states on ultrafast timescales. We report an unexpected coupling between the band transitions and a continuum of sub-bandgap states, which we report to extend at least 350 meV below the band edge. We explain the comparatively large bleach signal of these dark sub-bandgap states, compared to the levels detected in linear absorption, with oscillator strength borrowing from the band-edge transition. Our results imply that, upon valence to conduction band excitation, the sub-gap states are instantaneously bleached by the presence of charges in the band for the duration of the carrier lifetime and conversely, that almost dark sub-bandgap states can be populated by light excitation. Our findings provide fundamental insights into the photophysical origin of the exceptional defect tolerance of hybrid perovskites materials.

9:30 AM BREAK
and single crystalline organic-perovskite hybrid quantum wells (down to one mono-layer thick) and superlattices can be easily obtained via one-step solution-processing. Energy transfer and charge transfer between adjacent organic and inorganic layers are extremely fast and efficient, owing to the atomically-flat interface and ultra-small interlayer distance. The 2D hybrid perovskite superlattices are surprisingly stable, due to the protection of the bulky hydrophobic organic groups. The molecularly engineered 2D semiconductors are promising candidates for use in next-generation nanoelectronics, optoelectronics, and photonics.

10:15 AM *EN10.09/EN09.08.02
Nanoscale and Bulk Perovskite Single-Crystals—Surface Engineering for Efficient LEDs, Photodetectors and Solar Cells Osman M. Bakr; KAUST, Saudi Arabia

In colloidal nanocrystal form, lead halide perovskites possess high photoluminescence quantum yields, while in bulk single-crystal form they exhibit long charge-carrier diffusion lengths. However, without proper strategies to diminish crystal surface defects and manage surface quality, the desired characteristics of perovskites cannot be effectively exploited for photovoltaic and optoelectronic devices. Here I discuss novel strategies to passivate the surface defects and improve the surface quality of perovskite nanocrystals and bulk single-crystals, enabling the fabrication of efficient devices. We demonstrate the passivation of CsPbX$_3$-type nanocrystals with molecular ligands and metal dopants leading to stable near-unity quantum yield emitters, as well as efficient blue and red light-emitting diodes (LEDs). We also show the importance of designing crystal growth conditions, such as solvent, temperature, and substrate in order to grow bulk single-crystals with low-defect densities and good surface quality. Depending on the composition, MAPbX$_3$-type single crystals grown (tens of microns thick) under optimal conditions were used to realize: a) very sensitive visible-blind UV-photodetectors with nanosecond response time; and b) single-crystal solar cells with >21% power conversion efficiency. Unlike thin film polycrystalline solar cells, efficient cells with a grain-free single-crystal absorber are an ideal unobstructed system for investigating the device physics and chemistry of perovskites.

10:45 AM *EN10.09/EN09.08.03
Teaching Halide Double Perovskites to Absorb Sunlight Adam Slavney$^1$, Bridget Connor$^1$, Kurt Lindquist$^1$, Stephanie Mack$^2$, Linn Leppert$^3$, Jeffrey Neaton$^4$ and Hemamala Karunadasa$^1$; $^1$Stanford University, United States; $^2$University of California, Berkeley, United States; $^3$University of Bayreuth, Germany; $^4$Lawrence Berkeley National Laboratory, United States

Halide perovskites exhibit remarkable properties as solar-cell absorbers, featuring both direct bandgaps suitable for sunlight absorption and long-lived charge carriers beneficial for charge extraction. However, the intrinsic instabilities and high toxicity of these water-soluble lead salts may impede the commercialization of this technology. Notably, even the origin of the materials' superior photophysical properties remains unclear, underscoring the importance of synthesizing and studying functional analogs of the lead perovskites. However, most stable materials studied as analogs have displayed weak sunlight absorption and short carrier lifetimes.

We recently introduced halide double perovskites, which can accommodate a much greater range of metals, as solar absorbers. Armed with this substitutional flexibility, we have explored alternative metals that can be incorporated into the perovskite lattice. Studying the electronic differences between the lead perovskites and lead-free double perovskites has shown us how to synthetically tune double perovskites to efficiently absorb sunlight. I will share our understanding of how to manipulate the symmetry and energy of the bandgap transition in these materials through i) dilute impurity alloying, ii) stoichiometric metal substitution, and iii) dimensional reduction. Our recent studies have led us to double perovskites with very similar properties to the lead perovskites, with small bandgaps and long-lived carriers. I will further present a pen-and-paper method for both understanding and predicting halide double perovskite band structures based on orbital symmetry arguments.

11:15 AM EN10.09/EN09.08.04
A-Site Cation Composition Effects in Organic-Inorganic Metal Halide Perovskite Quantum Dots—Crystallographic Phase and Particle Ordering Julian A. Vigil$^{1,2}$, Michael F. Toney$^2$ and Joseph Luther$^3$; $^1$Stanford University, United States; $^2$SLAC National Accelerator Laboratory, United States; $^3$National Renewable Energy Laboratory, United States
Hybrid organic-inorganic metal halide perovskites have demonstrated remarkable properties for thin-film solar absorbers and optoelectronics, including their ease of preparation, compositional tunability, defect tolerance and high charge-carrier mobilities. The promise of these materials has also motivated the development of modified bulk and nanoscale perovskites, including reduced-dimensional perovskites (2D, 1D) and quantum dots (QDs), with emergent optoelectronic properties. Perovskite QDs, in addition to a tunable band gap and high photoluminescence quantum yield, are of interest due to unique physical and structural phenomena such as the stabilization of metastable crystallographic phases. Luther et al. reported the stabilization of the high temperature, low-band gap cubic perovskite phase of CsPbI$_3$ at room temperature in small QD particles via colloidal synthesis (Swarmkar et al. Science 2016, 354, 6308, 92). In addition, alloying of these CsPbI$_3$ QDs with FAPbI$_3$ (yielding Cs$_{1-x}$FA$_x$PbI$_3$) by a simple cation exchange approach allows for access to the full compositional range (i.e. $x = 0–1$), unlike thin-film fabrication and direct synthesis of bulk Cs$_{1-x}$FA$_x$PbI$_3$ (Hazari et al. ACS Nano 2018, 12, 10327).

Herein, we report on structural studies of Cs$_{1-x}$FA$_x$PbI$_3$ QD films by synchrotron X-ray techniques. 15-nm Cs$_{1-x}$FA$_x$PbI$_3$ QDs ($x = 0, 0.5$) were deposited from colloidal solution, by both drop- and spin-casting methods, and investigated by grazing incidence small-angle and wide-angle X-ray scattering (GISAXS/GIWAXS). GIWAXS patterns indicate coherent particle ordering on the substrate for single-layer spin-coated films, while the subsequent ligand exchange and particle overcoating (2–5 layers) leads to reorganization and isotropic ordering of the particles. In addition, drop-casting and slow evaporation of the solvent from the colloidal solution also results in isotropic ordering. Interestingly, the diffraction patterns show evidence of distortion from the originally reported cubic perovskite phase, with significant tetragonal ($Cs_0.5FA_0.5PbI_3$) and orthorhombic ($CsPbI_3$) character. The distortion and phase contributions across the full range of alloyed Cs$_{1-x}$FA$_x$PbI$_3$ QDs will be reported and discussed.

11:30 AM EN10.09/EN09.08.05
Highly Efficient Hybrid Perovskite Nanoparticle Light-Emitting Diodes Using Mixed Cation Young-Hoon Kim¹, Sungjin Kim¹, Jinwoo Park¹, Seung-Hyun Jo¹, Hengxing Xu², Yonghee Lee¹, Laura Martinez-Sarti³, Henk J. Bolink³, Young-Woon Kim¹, Bin Hu¹ and Tae-Woo Lee¹; ¹Seoul National University, Korea (the Republic of); ²The University of Tennessee, Knoxville, United States; ³Universidad de Valencia, Spain

Hybrid perovskite nanoparticles (PeNPs) have significant potential to be used in perovskite light-emitting diodes (PeLEDs) because of their high photoluminescence quantum efficiency and, facile color tunability and synthesis. However, the highest electroluminescence efficiencies of PeLEDs based on hybrid PeNPs are still much lower than those of PeLEDs based on hybrid perovskite bulk films and all-inorganic PeNPs. Here, we suggest a strategy to improve the electroluminescence efficiency of PeLEDs based on hybrid PeNPs. We passivate the defect states of PeNPs by introducing large organic cation into the formamidinium lead bromide nanocrystals. Based on this high quality PeNPs, we were able to fabricate efficient PeLEDs. Our work provides a promising way to improve luminescence efficiency of the PeLEDs based on hybrid PeNPs.

11:45 AM EN10.09/EN09.08.06
Surface Chemistry of Colloidal Cesium Lead Halides Perovskite Nanocrystals and Its Impact on the Characteristics of Blue and Green Perovskite LEDs Maryna Bodnarchuk; Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Colloidal organic/inorganic lead halide perovskite nanocrystals (NCs) are considered promising blue and green narrow-band emitters for the next-generation light-emitting diodes. High photoluminescence efficiencies are attained in these materials without epitaxial overcoating of the NC surfaces for electronic passivation of the surface states [1]. The major practical bottleneck of these materials relates to their labile surface chemistry. In particular, typically used ling chain capping ligands are problematic due to their dynamic and loose binding as well as their highly insulating nature. We have recently rationalized the typical observation of a degraded luminescence upon aging or the luminescence recovery upon post-synthesis surface treatments using a simple surface-structure model, supported by DFT calculations [2]. Healing of the surface trap states requires restoration of all damaged PbX$_6$ octahedra and establishing a stable outer ligand shell. Restoration of such a structure, seen as an increase in the luminescence quantum efficiency to 90-100% and improvement in the overall robustness of CsPbBr$_3$ NCs, was attained using a facile post-synthetic treatment with a PbBr$_2$+DDAB (didodecyldimethylammonium bromimde) mixture. In our most recent work [3], we have used DDAB as a sole ligand directly in the synthesis of perovskite NCs. We then used such NCs in LEDs and demonstrate high external quantum efficiencies of up to 3.6% in blue region (460nm) and 10% in the green region (520 nm).

SESSION EN10.10: Engineering of Perovskite Composition and Emitting Devices
Session Chairs: Tzung-Fang Guo and Yanfa Yan
Wednesday Afternoon, December 4, 2019
Sheraton, 2nd Floor, Back Bay D

1:30 PM *EN10.10.01
High Performance Perovskite Light-Emitting Devices for Displays and Advanced Applications Zhi Kuang Tan; National University of Singapore, Singapore

The efficiency of electroluminescent perovskite devices have increased rapidly from 0.76% in earlier works to above 20% in recent reports. Such high performance, coupled with excellent spectral qualities and easy manufacturability have captured the attention of the academic and commercial communities. In this talk, we will discuss some physical principles behind device efficiency enhancement, and report our new strategies in improving the uniformity and robustness of perovskite light-emitting diodes. We will also report our recent activities in the deployment of luminescent perovskites in color-enhanced displays and other advanced consumer product applications.

2:00 PM EN10.10.02
Fabrication of High-Performance Perovskite Optoelectronic Devices Zhanhua Wei; Huaqiao University, China

Metal halide perovskite materials are an emerging class of solution-processed semiconductors with considerable potential for use in optoelectronic devices. For example, light-emitting diodes (LEDs) based on these materials could see application in flat-panel displays and solid-state lighting, owing to their potential to be made at low cost via facile solution processing, and could to provide tunable colors and narrow emission line widths at high photoluminescence quantum yields. However, the highest reported external quantum efficiencies of green- and red-light-emitting perovskite LEDs are around 14% and 12%, respectively—still well behind the performance of organic LEDs and inorganic quantum dot LEDs. Here we describe visible-light-emitting perovskite LEDs that surpass the quantum efficiency milestone of 20%. This achievement stems from a new strategy for managing the compositional distribution in the device—an approach that simultaneously provides high luminescence and balanced charge injection. Specifically, we mixed a presynthesized CsPbBr$_3$ perovskite with a MABr additive (where MA is CH$_3$NH$_3$), the differing solubilities of which yield sequential crystallization into a CsPbBr$_3$/MABr quasi-core/shell structure. The MABr shell passivates the nonradiative defects that would otherwise be present in CsPbBr$_3$ crystals, boosting the photoluminescence quantum efficiency, while the MABr capping layer enables balanced charge injection. The resulting 20.3% external quantum efficiency represents a substantial step towards the practical application of perovskite LEDs in lighting and display [1].

Moreover, we will show some research progress of perovskite LEDs with colorful emission, solar cells and other photonic applications in our lab.

References

2:15 PM EN10.10.03
High-Intensity CsPbBr$_3$ Perovskite LED using Poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) as Hole Transport and Electron-Blocking Layer Gintautas Simkus1,2, Pascal Pfeiffer2, Simon Sanders2, Dominik Stümmler2, Aliénor Wagner1, Andrei Vescan1, Holger Kalisch1 and Michael Heuken1,2; 1AIXTRON SE, Germany; 2RWTH Aachen University, Germany
In the last years, metal halide perovskites have attracted great attention as promising materials for light-emitting diodes (LED), owing to their excellent optical and electronic properties such as high charge-carrier mobility, narrow emission spectra and easily tunable colors [1,2,3]. The highest external quantum efficiencies of CsPbBr$_3$ LED recently exceeded 20 % [4]. Efficiencies were enhanced mainly by suppressing non-radiative recombination and establishing improved charge balance. The most efficient LED utilize hole-transport layers (HTL) of either a hydrophilic organic co-polymer (PEDOT:PSS) or an inorganic oxide (NiO$_x$), ensuring beneficial wetting properties for perovskite formation [5]. Despite a huge variety of organic hole-transport materials, the polar solvents required for perovskite synthesis narrow their choice leaving PEDOT:PSS as one of the few remaining options. However, PEDOT:PSS is lacking sufficient electron-blocking properties in electron-rich CsPbBr$_3$-based LED structures. Consequently, an additional blocking layer is required to achieve optimum charge balance as a prerequisite for high luminous efficiency.

In this work, we employ the hydrophobic hole-transporting polymer poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine)) (PTAA) as HTL. PTAA exhibits a high LUMO value of 1.8 eV [6], ensuring the desired electron-blocking properties. Thus, the requirement for an additional blocking layer is eliminated, simplifying the LED fabrication process. This HTL was examined in LED structures with a configuration of glass/ ITO (100 nm)/PTAA (10 nm)/ CsPbBr$_3$ (60 nm)/(2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)) (TPBi) (30 nm)/ LiF (1 nm)/Al (100 nm). In this stack, PTAA and CsPbBr$_3$ were deposited from solutions (PTAA – 3 mg/ml in toluene; CsPbBr$_3$ – 12 wt% of precursor solids PbBr$_2$ and CsBr with a molar ratio of 1:1.7 in dimethyl sulfoxide) by spin-coating in purified N$_2$ atmosphere (H$_2$O < 1 ppm, O$_2$ < 1 ppm). TPBi was selected as electron transport layer which also acts as a hole-blocking layer due to its deep HOMO level of 6.2 eV [7]. This combined with the PTAA electron blocking ability ensures superior carrier as well as exciton confinement in the emissive perovskite layer. The hydrophobicity of the PTAA surface was reduced by a short exposure to remote N$_2$ plasma, which allowed the formation of a dense CsPbBr$_3$ film from solution on top. The room temperature photoluminescence spectra of pure CsPbBr$_3$ layer (without any additives for grain passivation and trap density minimization) exhibited a saturated color ($\lambda_{\text{max}} = 520$ nm) with a FWHM of 18 nm indicating a low degree of energetic disorder. The fabricated LED yielded high current densities exceeding 200 mA/cm$^2$, a turn-on voltage of 2.9 V, bright emission of 10,000 cd/m$^2$ and stable EQE (external quantum efficiency) of 1.5 %. The LED performance could be improved considerably by employing molecular pinning to enhance the morphology of CsPbBr$_3$ layers which leads to suppressed non-radiative recombination at interfaces and perovskite grain boundaries [8].

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2:30 PM BREAK

SESSION EN10.11: Surface and Defect Passivation in Perovskite Light-Emitting Devices
Session Chairs: Tae-Woo Lee and Zhi Kuang Tan
Wednesday Afternoon, December 4, 2019
Sheraton, 2nd Floor, Back Bay D

3:30 PM *EN10.11.01
Defect Passivation of Perovskite Layers for Efficient Perovskite Light-Emitting Diodes Myoung Hoon Song$^1$, Seungjin Lee$^1$, Chung Hyeon Chang$^1$, Jong Hyun Park$^1$, Eui Dae Jung$^1$ and Han Young Woo$^2$; $^1$Ulsan National Institute of Science and Technology, Korea (the Republic of); $^2$Korea University, Korea (the Republic of)
The organic-inorganic hybrid perovskite materials have been studied extensively owing to their excellent optical and electrical characteristics that enable a remarkable enhancement of device efficiency in light-emitting diodes (LEDs) and solar cells. High film quality of perovskite is necessary to develop highly efficient and stable perovskite optoelectronic devices. However, defect sites such as voids, pinholes, grain boundaries and under-coordinated ions, creating a large number of undesired electronic trap sites can exist in solution-processed perovskite films. Here, we observe the significant beneficial effects on the efficiency and long-term stability of perovskite light-emitting diodes (PeLEDs) through passivating the defect sites of perovskite layers.

4:00 PM *EN10.11.02
Surface Passivation and Stability of Metal Halide Perovskite LEDs Barry P. Rand; Princeton University, United States

Hybrid organic-inorganic halide perovskite materials are of considerable interest for optoelectronics. We will discuss our approach to surface passivation using an excess solution stoichiometry of organoammonium so as to maintain an ammonium terminated surface in films that consist of nanoscale crystallites. Proper passivation allows for enhanced quantum yield and stable mixed halide stoichiometries. In another aspect, we have determined that metal halide perovskites not only feature ionic motion but are also considerably redox active and heat sensitive, and are looking to understand how redox chemistry, and ionic processes more generally, dictate material and device physics and degradation.

4:30 PM EN10.11.03
Dual Passivation of Both Lead and Halide Defects for Perovskite Light Emitting Diodes with External Quantum Efficiency Exceeding 20% Zhengguo Xiao, Zhibin Fang and Wenjing Chen; University of Science and Technology of China, China

Organic-inorganic hybrid perovskites are very promising for light emitting diodes (LEDs) due to their high color purity, tunable emission wavelength, and balanced electron and hole conduction etc. The optoelectronic properties of hybrid perovskite have shown to be very tolerant to defects, which has been demonstrated in solution processed perovskite photovoltaics. However, both lead and halide defects have been shown to be a big problem for solution processed perovskite LEDs (PeLEDs) with nanometer-sized crystallites. The defects cause obvious non-radiative recombination and short operation stability.

In this talk, we will report the molecular design of additives for dual passivation of both lead and halide defects in perovskites. We synthesized 4-fluoro-phenylmethylammonium-trifluoroacetate (FPMATFA) using a simple solution process. The C=O bond in TFA group can coordinate with lead and passivate the lead defects, while the organoammonium cations, FPMA+, can coordinate with halide and passivate halide defects. In addition, the bulky FPMA group can constrain the grain growth of 3D perovskite, which enhances electron-hole capture rates and radiative recombination rate. As a result, we achieved a decent external quantum efficiency of 20.9% for formamidinium/cesium based PeLEDs. What’s more, the operation lifetime of PeLEDs is also greatly improved due to the low trap density in the perovskite film.

4:45 PM EN10.11.04
A Room Temperature Synthesis of Highly Robust Phosphonate-Capped Cesium Lead Bromide Perovskite Nanocrystals with Near-Unity Photoluminescence Quantum Yield Alasdair A. Brown1,2,3, Thomas J. Hooper1, Xin Yu Chin1, Parth Vashishtha3,3, Suan Hui Pu1, Bahulayan Damodaran2, Ju Nie Tey1, Liudi Jiang1, Subodh G. Mhaisalkar3,3 and Nripan Mathews3,3; 1University of Southampton, United Kingdom; 2Agency for Science, Technology and Research, Singapore; 3Nanyang Technological University, Singapore

Over the last 5 years, the performance of perovskite nanocrystal-based light-emitting diodes (LEDs) has improved dramatically, achieving external quantum efficiencies (EQEs) which are comparable with their chalcogenide counterparts. Crucially, perovskite nanocrystals (NCs) can be synthesised with straightforward wet chemistry techniques under ambient conditions, in stark contrast to the high temperature, inert gas environment necessary for chalcogenide core-shell structures. All-inorganic cesium lead bromide (CsPbBr3) NCs are particularly promising, as they exhibit much better thermal and environmental stability than formamidinium (FA) or methylammonium (MA) based perovskites. However, the colloidal stability of CsPbBr3 NCs remains poor, which severely restricts any future application in optoelectronics.
The stability of perovskite nanocrystals is strongly reliant on surface chemistry. It is vital that the ligands bound to the nanocrystals can both passivate deleterious defects and form a robust attachment to the surface. Ligands that do not adhere strongly to the nanocrystals are prone to desorption, leading to agglomeration and rapid degradation of their initially exceptional luminescence. Until recently, labile carboxylic acid and alkylamine ligands were almost universally employed for CsPbBr$_3$ nanostructures. However, it has been shown that the dynamic binding equilibrium they establish limits both the colloidal and device stability. Phosphonic acids have since emerged as a promising alternative. A hot-injection synthesis of CsPbBr$_3$ NCs capped by octylphosphonic acid (OPA) ligands enabled LEDs with an EQE of 6.5 % and half-lifetime of over 30 mins. In contrast to the standard ligands, phosphonic acids have been shown to bind irreversibly to lead sites, thus indicating their high potential for stability enhancement. We sought to elucidate the underlying surface chemistry of phosphonic acid binding to CsPbBr$_3$ NCs. Through a ligand exchange approach, we revealed that OPA binds as the monoionic phosphonate, such that P=O and P−OH functionalities remain free. Most importantly, 2D $^1$H−$^{31}$P solid-state NMR demonstrated that these functionalities allow extensive inter-ligand hydrogen bonding, such that the nanocrystals are passivated by an interconnected octylphosphonate network. Based on the discovery of this phenomenon, we devised a direct room temperature, open-air synthesis of CsPbBr$_3$ NCs passivated by an octylphosphonate network. Trioctylphosphine oxide (TOPO) aided the dissolution of PbBr$_2$ and OPA in toluene, such that the injection of cesium octanoate immediately formed highly luminescent green-emitting nanocrystals. Post-synthetic treatment with didodecyldimethylammonium bromide (DDAB) provided DDA$^+$ ligands that bind to surface bromide, increasing the solubility, while the excess Br$^-$ filled any gaps in the octylphosphonate network. This approach proved exceptionally effective; even after 3 purification cycles with methyl acetate, a photoluminescent quantum yield (PLQY) of 95 % was retained. Thus we have successfully developed an ambient, room temperature synthesis of robust near-perfect CsPbBr$_3$ nanocrystals. We anticipate that this method will improve the viability of these nanocrystals for high performance optoelectronic applications.


EN10.12.03
Pulsed Laser Synthesis and Tuning Optical Properties of High Quantum Yield Nitrogen Doped Graphene Quantum Dots
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The graphene quantum dots (GQDs), a zero-dimensional graphene quantum structure, have triggered an intense research worldwide. GQDs possess unique optical, chemical and physical properties as compared to conventional quantum dots (QDs), such as low toxicity, biocompatibility, optical stability, chemical inertness, high photostability and good water-solubility and therefore hold great application potential in biomedical, optoelectronics and energy storage devices. The doping of GQDs with heteroatoms is one of the most effective ways to tune their photoluminescence emission and to increase quantum yield. In this study, we developed a novel approach to synthesize high-quality Nitrogen-doped graphene quantum dots (N-GQDs) with high quantum yield, via irradiation of s-triazene in a solution with benzene by using pulsed laser. The TEM, HRTEM, XPS, XRD, Raman spectroscopy and FTIR were carried out to observe the morphology, size distribution, crystalline structure and to prove successful doping of GQDs with nitrogen atoms. To observe optical properties of as synthesized N-GQDs, the UV-vis and
Photoluminescence measurements were carried out. The as-synthesized NGQDs exhibit high quality crystalline structure of graphene with an average size of about 3.7 nm. A high quantum yield was exhibited by the obtained N-GQDs as compare to the pristine GQDs. The obtained N-GQDs with oxygen-rich functional groups exhibit a strong emission. These outcomes result in an ample opportunity for the biomedical and optoelectronic applications.

EN10.12.04
Highly Processable and Thermally Stable Perovskite Nanocrystals Embedded in Ceramic Matrix by Aerosol Deposition
Chaeyeon Son, Sunghoon Kim and Sang-Wook Kim; Ajou University, Korea (the Republic of)

Inorganic perovskite structure has emerged as optoelectronic materials as possessing advantageous optical properties for display applications used in a polymer-encapsulated form. However, insulating polymers acting as a host matrix are generally vulnerable to thermal stresses, so that softening distortion or deterioration occurs in thermoplastic polymers (generally over 150 °C). So, we develop nanostructured CsPbBr3/Al2O3 composite film by aerosol deposition (AD). At first, CsPbBr3/Al2O3 composite powders are synthesized by the recrystallization of CsBr and PbBr2 ionic salts onto the surface of Al2O3 particles and have bright and saturated green emission. Next, the composite powder supported on submicron α-Al2O3 particles is effectively changed to a film-type by aerosol deposition (AD). AD, which is based on shock-loading solidification caused by countless collisions of fine ceramic particles, has many advantages for perovskite NCs, which operate at room temperature, in a vacuum system to minimize the exposure of oxygen and moisture and under an eco-friendly condition of the nonsolvent process. The ceramic composite film show high long-term stability at 150 °C for over 20 days, a pure green spectrum with a narrow full width at half maximum (522 nm and FWHM of 17 nm) and an absolute photoluminescence quantum yield of 8%–15%. General inorganic film have difficulty in flexibility and pattern. But, the films deposited by AD can be used as down-converting material for LCD backlight with a wide area of 89.2% in REC. Furthermore, it can be applied to a variety of display fields, such as high flexible chemical composite films, multilayer films, patterning of surfaces for an advanced color filter array, and deposition on protected substrates toward diverse display fields.

EN10.12.05
Core-Shell Perovskite Microcrystals
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Lead halide perovskites (LHPs) are promising optoelectronic materials, but with ionic bonding characteristics, LHPs disassemble readily in any polar solvents. This structural instability, together with dynamic lattice disorder, has prohibited the crystalline coating of LHPs using polar precursors. Here, we report a sonochemistry-based technique to synthesize poly-norepinephrine (pNE)-coated CsPbBr3 microcrystals. The colloidal core-shell-type CsPbBr3 microcrystals were synthesized in a polar solvent without any surfactants. High-resolution X-ray photoelectric spectroscopy suggests that the electronegative catechol group of the pNE forms Lewis acid-base adducts with under-coordinated Pb atoms. This passivation reduces surface defects, decreases hysteresis, and increases optical gain. Density functional theory (DFT) supported these observations. Furthermore, the pNE coating serves as diffusion-blocking layers, increasing the lifetime of LHPs in water by 1000-fold. This allowed us to observe lasing from a single core-shell perovskite micro-particle in water. The pNE coating also enabled us to use conventional reactions to functionalize perovskite microcrystals, for example, with fluorescent proteins and plasmonic nanoparticles. This work may open a new avenue towards environment-stable and multifunctional perovskite laser particles.

EN10.12.06
Identifying and Reducing Interfacial Losses to Enhance Color-Pure Electroluminescence in Blue-Emitting Perovskite Nanoplatelet Light-Emitting Diodes
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Perovskite nanoplatelets (NPLs) hold great promise for light-emitting applications, having achieved high photoluminescence quantum efficiencies (PLQEs) approaching unity in the blue wavelength range, where other metal-halide perovskites have typically been ineffective. However, the external quantum efficiencies (EQEs) of
blue-emitting NPl light-emitting diodes (LEDs) have typical values of 0.1% or below. In this work, we show that the performance of NPl LEDs is primarily hindered by a poor electronic interface between the emitter and hole-injector. Through Kelvin Probe and X-ray photoemission spectroscopy measurements, we reveal that the NPls have remarkably deep ionization potentials (≥6.5 eV), leading to large barriers for hole injection, as well as substantial non-radiative decay at the emitter/hole-injector interface. We find that an effective way to reduce these non-radiative losses is by using poly(triarylamine) interlayers, which lead to an increase in the EQE of the blue (464 nm emission wavelength) and sky-blue (489 nm emission wavelength) LEDs to 0.3% and 0.55% respectively. The EQEs of these devices are two orders of magnitude higher than the control devices without the poly(triarylamine) interlayer, and we elucidate the role of these interlayers through detailed spectroscopic and single-carrier device measurements. Our work also identifies the key challenges for further improvements in efficiency [1].

References

EN10.12.07
X-Ray and Neutron Scattering Studies of Colloidal Nanocrystal Quantum Dots and Their Ligands Michael P. Weir1, Daniel Toolan1, Neil C. Greenham2, Richard H. Friend2, Akshay Rao2, Anthony Ryan1 and Richard Jones1;
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Understanding the structure of the nanocrystal cores and stabilizing ligands in colloid quantum dots presents unique set of challenges that are ideally suited to study using X-ray and neutron scattering (SAXS and SANS) techniques. There is a large electron density difference between the metal chalcogenide (e.g. lead sulfide, PbS) nanocrystal core and most organic materials. This includes the native ligands present from synthesis (typically oleic acid, OA) and solvents or polymeric matrices where present. This provides an excellent contrast scenario for studying the shape, size, distribution and packing of QD cores using SAXS either in transmission or in grazing incidence (GISAXS) while dispersed or packed in various media. Similarly, with the potential for multiple isotopic contrasts (e.g. using deuterated solvents or ligands), SANS measurements are highly sensitive to the structure of ligands and other molecules adsorbed on the QD surface and to the correlations and packing of the QD cores.

In this presentation, we explore as a case study the characterisation of PbS-OA quantum dots and their functionalisation by exchange with ligands of varying chemistry, including a variety of carboxyl-terminated small molecules. For as-synthesized QD, SAXS allows a rough estimation of OA present in the given solution and an upper bound on the amount that is bound to the PbS cores, whilst some may remain in solution. Solution SANS measurements, utilising contrast variation, can then be used to determine the thickness and density of the OA shell. In combination, SAXS and SANS are therefore also well suited to the study of ligand exchange processes. Using SAXS as a pre-characterisation, SANS resolves the changes in ligand shell scattering length density, which are related back to changes in coverage and packing density and to the degree of native ligand, if any, that is still present. This presentation follows the structural changes that occur during various ligand exchange procedures and discusses some of the self-assembling structures that emerge.

EN10.12.08
Single-Step Production and Controlled Heteroatom Doping of Photoluminescent Graphene Quantum Dots through Laser Ablation in Liquid Rosemary L. Calabro, Dong-Sheng Yang and Doo Young Kim; University of Kentucky, United States

Graphene quantum dots (GQDs) are promising for a number of applications including catalysis, sensing, imaging, and photovoltaics. The advantages of GQDs over traditional inorganic quantum dots include (i) a cheap and large-scale synthesis with abundant carbon sources, (ii) excellent biocompatibility and environmental friendliness, and (iii) a high photodynamic index. One promising approach to tune the emission of GQDs and to enhance photoluminescence quantum yield (PLQY) is the incorporation of heteroatoms such as N, B, P, or S into the aromatic backbone of GQDs. Furthermore, the incorporation of heteroatoms into high-surface-area GQDs can develop highly active electrocatalysts and sensory materials. Traditional methods to produce GQDs require the use of harsh chemicals, long reaction times, and tedious purification steps and allows limited control over the functional groups in the produced GQDs. This presentation will report our recent progress in developing the synthetic technique of laser ablation in liquid (LAL) as a promising alternative method to prepare GQDs. LAL allows for fast production, use of fewer chemicals, simple purification, fewer byproducts, higher production yields, and improved
control of the product by precise tuning of laser ablation parameters. We have successfully developed LAL to produce N-doped GQDs from carbon nano-onions in aqueous solutions containing three nitrogen precursors (ammonia, ethylenediamine, and pyridine). The choice of nitrogen precursor molecule allowed for the tuning of both the overall nitrogen content as well as the distribution of nitrogen-related functional groups present in the produced GQDs. The variation of LAL parameters and nitrogen precursors enabled us to tailor photoluminescence (PL) spectral properties and PL lifetimes. We have found that high concentrations of amine groups tend to red shift the emission and exhibit shorter PL lifetimes whereas pyridinic groups caused a blue shift in the emission and exhibited longer PL lifetimes. Additionally, the PL properties of these GQDs was highly dependent on the nitrogen-related functional groups while band gap emission was mainly non-radiative. This presentation will also report the promising electrochemical features of these N-doped GQDs since they demonstrated high activity for the conversion of oxygen to hydrogen peroxide, an important chemical in many industrial applications. LAL was then employed to dope GQDs with other heteroatoms including B, P, and S that further tuned the PL properties and expanded potential applications.

EN10.12.09
Improving Color Purity in Thermally Activated Delayed Fluorescence Emitters Ramin Ansari, Wenhao Shao, Seong Jun Yoon, Jinsang Kim and John Kieffer; University of Michigan, United States

We explore the key factors that determine the emission bandwidth of thermally activated delayed fluorescence (TADF) emitters combining computational and experimental methods of investigation. TADF is one approach to achieve high internal quantum efficiencies (IQEs) in metal-free organic light emitting diode (OLED). In TADF the first triplet (T1) to first singlet (S1) reverse intersystem crossing (ISC) is promoted by configuring molecules in an electron donor-acceptor (D-A) alternation, so as to exhibit a small energy gap (DEST) between S1 and T1 levels. This allows for non-radiative triplet states to up-convert to radiative singlet states and fluoresce. However, the donor-acceptor strategy may result in molecular conformations that produce broad emission spectral bands (FWHM = 70-100 nm). Despite reports suggesting that suppressing D-A dihedral rotation can reduce the emission bandwidth, the actual reason behind the narrower-band emission is not well understood. Our results suggest that the intrinsic TADF emission bandwidth is mainly controlled by the charge transfer character, and that molecular space restriction or rotation have minimal effects. Our results can be used to design molecular organic alternatives with sharp emissions for LED applications.

EN10.12.10
Internal Contact Electrification Lights Up Electroluminescent Phosphors in ‘Phosphor–Polymer’ Elastic Composites—A New Strategy for Converting Mechanical Energy into Light Gyudong Lee, Seongkyu Song, Younghoon Kim, Soon Moon Jeong and Sung Jun Lim; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

Mechanoluminescence (ML) is a light emission induced by mechanical action applied to a solid material. This phenomenon has been known for a long time and observed from numerous materials in our daily life. However, unlike photoluminescence or electroluminescence, ML had received little attention as a light-emitting technology because most of previously known ML processes are one-time momentary light emission events which require irreparable deformation of materials like breaking or tearing. Then, in 2013, Jeong et al. [1] reported a unique ML phenomenon that an elastic composite, which is phosphor micropowders (Cu or Mn doped ZnS) embedded in a stretchable polymer (PDMS), exhibits unprecedentedly bright and unwearying ML under repeated (~10^5 times) elastic stresses like stretching, bending, or pressing. This groundbreaking discovery has led to the development of many distinctive ML-based light-emitting technologies such as wind-driven full-color display, handwriting recognition, or magnetic-induced luminescence.

Despite the applications are being continuously expanded, the mechanism of this unique elastic ML process has remained unknown. Most of the previous models relied on a special piezoluminescent characteristic of doped ZnS phosphors called ‘self-recovery’ effect. However, none could fully explain the incomparably high brightness and durability of the new elastic ML. In this presentation, we will introduce a set of experimental evidences that this elastic ML is due to the characteristics of the phosphor alone but due to the interaction between the phosphor and the elastic polymer substrate. Especially, our findings claim that the interface between the phosphor and the elastic polymer plays the most essential role. We demonstrate that this elastic ML can be completely switched on and off depending on the combination between the compositions of phosphor’s surface coating layer and elastic polymer, and the combination that switches on the elastic ML is the one that maximizes the contact electrification at
their interface. We also show that such interface-driven ML is not working with common piezoluminescent materials but only working with high quality electroluminescent phosphors like doped ZnS. These findings strongly suggest that the elastic composite ML is in fact a lighting up process of electroluminescent phosphors by the internal microscale contact electrification at the phosphor–polymer interface. Moreover, our conclusion implies that this can be further developed as a general strategy for designing new composite materials using various nanoscale luminescent materials that can efficiently convert mechanical energy into lights.


**EN10.12.11**

Flexible and Stretchable LEDs with Silica Coated Cesium Lead Halide Perovskite Nanocrystals through APTES Treatment Sangyeop Lee, Sanghyun Jeon, Ho Kun Woo and Soong Ju Oh; Korea University, Korea (the Republic of)

Currently, cesium lead halide perovskite(CsPbX3 X = Cl, Br, I) nanocrystals (NCs) have been attracted enormous attention for optoelectronics materials due to their prominent optical properties such as excellent color reproducibility and high photoluminescence quantum yield (PLQY). Herein, we demonstrate a simple coating process of perovskite NCs by adding (3-Aminopropyl) triethoxysilane (APTES) with precursor to fabricate stretchable and flexible light emitting diode (LED). The chemical, optical, and structural properties of perovskite NCs without and with APTES treatments. It was demonstrated that APTES treatment successfully creates silica shell, which improves the stability of perovskite NCs by passivating their surface. As a result, silica coated perovskite can be embedded in polymer matrix without any degradation structure and luminescence efficiency. By embedding NC in PDMS, we fabricated stretchable color filters showing high color reproducibility and remaining high luminescence, stretchable LEDs with mixture of PDMS/Cu-doped ZnS and silica coated perovskite NCs, with improved durability and stability.

**EN10.12.12**

Inkjet Printed Metal Halide Perovskite for Light-Emitting Diodes—From Bulk Perovskite To Perovskite Nanoparticles Hyeon-Dong Lee1, Huanyu Zhou1, Hui Jae Choi2, Sungjin Kim1, Young-Hoon Kim1, Byung Doo Chin1 and Tae-Woo Lee1; 1Seoul National University, Korea (the Republic of); 2Dankook University, Korea (the Republic of); 3NREL, United States

Metal-halide perovskites (hereafter, perovskite) are promising materials for a light emitter of light-emitting diodes (LED) based on their narrow emission spectrum and the easy bandgap tunability. In the top-down approach using the perovskite dissolved in polar solvent such as dimethyl sulfoxide (DMSO), the growth mechanism can be easily controlled by using various additives and applying solvents, so small grain size with strong exciton confinement can be easily achieved. As the bottom-up approach, perovskite nanoparticles synthesized with passivating ligand have high photoluminescence quantum efficiency (PLQE) due to the strong exciton confinement. Both methods are promising way to develop the highly efficient PeLEDs, but these have been mainly studied by spin-coating process. Spin-coating process is a good process to easily control the morphology of perovskite film but is not suitable for fine patterned microarrays that meet criteria of high-definition display.

In this work, we induced an inkjet manipulated approach for fine patterned perovskite microarrays. Combining with a high viscosity co-solvent, the outward capillary flow as the cause of ring stains can be suppressed. Also, adding the additive into the perovskite ink, we modulated a crystal growth mechanism of perovskite ink, and finally obtained perovskite microarrays with perfect morphologies. With these results, we provide insight on how to fabricate perovskite microarrays for efficient PeLEDs.

**EN10.12.13**

Tailoring Size and Dimensionality (0D/1D/2D) of Cesium Lead Halide Perovskite Nanocrystals through Immiscible Polar Solvent Assisted Post Synthetic Oriented Attachment Sanghyun Jeon, Junhyuk Ahn, Ho Kun Woo and Soong Ju Oh; Korea University, Korea (the Republic of)

Herein, we demonstrate the post-synthesis engineering methods to precisely control size and dimensionality (0D/1D/2D) of as-synthesized all-inorganic cesium lead halide perovskite (CsPbBr3) nanocrystals (NCs). We investigate the chemical effects of polar solvents properties such as immiscibility, polarity, and boiling point on the surface of NCs as well as structural and optical properties. By appropriately utilizing the properties of solvent, the
effect of polar solvent could be indirectly and mildly conveyed to the NCs making them lose their ligands and attached with proximal NCs without destruction. Based on our observation, we developed “Immiscible solvent phase mixing” method to induce epitaxial growth of CsPbBr$_3$ NC. The size of NCs can be easily tailored by controlling the engineering time. Taking advantage of the minimal effect of mild solvent, we also developed liquid-air interface self-assembly method to systematically control the dimensionality. At the interface, NCs could be horizontally assembled and grown into large area, single crystalline nanowire (1D) and nanoplate (2D) via the oriented attachment process. Finally, we discussed the origin of non-destructive epitaxial growth phenomenon with suggested model system.

**EN10.12.14**
**Doped Two-Dimensional Perovskites for Light Emitting Applications** Daniele Cortecchia, Wojciech Mroz, Tetiana Borzda, Giulia Folpini, Rosaria Brescia, Luca Leoncino and Annamaria Petrozza; Istituto Italiano di Tecnologia, Italy

Metal halide perovskites are gaining increasing interest for their light emitting properties and have become attractive for a wide range of optoelectronic devices such as light emitting diodes (LEDs), light emitting field-effect transistors (LE-FETs), lasers and scintillators. [1] While high efficiencies have been reached with 3D dimensional perovskites, the research community keeps exploring alternative structures to boost the luminescence yield and increase the material’s tunability. In particular, the increased structural flexibility has revived great interest in low dimensional perovskites. [2] Here, the possibility to increase the exciton binding energy by spatial and dielectric confinement is believed to be beneficial to improve the radiative recombination efficiency. However, with the exception of multidimensional perovskites of the Ruddlesden-Popper series where luminescence is strongly enhanced due to energy funneling effects, the quantum yield of single-layered 2D perovskite films remains low (<3%). This is likely due to detrimental trap-assisted recombination, and has so far hampered their effective integration into electroluminescent devices.

To overcome such issues and improve the emission properties of 2D perovskites, here we identify two synthetic and defect engineering strategies, [3] one involving the use of photoactive organic cations (such as 1-naphthylmetylammonium) and one based on metallic doping involving the use of transition metals (e.g. Mn$^{2+}$) and lanthanides (e.g. Eu$^{3+}$, Yb$^{3+}$). [4] While both strategies allow the tuning of perovskite luminescence from the visible down to the near infrared region (NIR), we find that highly efficient energy transfer from the perovskite to the metallic ion can be achieved in case of inorganic doping, provided that a suitable energy level alignment of the host-guest system is realized. In particular, by using temperature-dependent and time-resolved spectroscopy, we demonstrate that the presence of Mn$^{2+}$ ions allows to overcome the funneling of the photoexcited species in inefficient recombination pathways (e.g. permanent traps) thus improving the photoluminescence quantum yield beyond 20% in perovskite films. Finally, we provide a proof-of-concept demonstration of the electroluminescence properties of such doped-systems in light emitting diodes. [3]

Our work shows the potential of the doping strategy for the tuning and enhancement of the perovskite’s luminescence properties and further stimulates the investigation of a broader range of host/guest systems.


**EN10.12.15**
**Rational Design of Multicolor Lanthanide-Based Upconversion Nanocrystals** Sanyang Han and Akshay Rao; University of Cambridge, United Kingdom

Meeting the high demand for lanthanide-doped luminescent nanocrystals across a broad range of fields hinges upon the development of a robust synthetic protocol that provides rapid, just-in-time nanocrystal preparation. However, to date, almost all lanthanide-doped luminescent nanomaterials have relied on direct synthesis requiring stringent controls over crystal nucleation and growth at elevated temperatures. Here we demonstrate the use of a cation exchange strategy for expeditiously accessing large classes of such nanocrystals. By combining the process of cation exchange with energy migration, the luminescence properties of the nanocrystals can be easily tuned while preserving the size, morphology, and crystal phase of the initial nanocrystal template. This post-synthesis strategy
enables to achieve, for the first time, upconversion luminescence in Ce\(^{3+}\) and Mn\(^{2+}\)-activated hexagonal-phased nanocrystals, opening a gateway towards applications ranging from chemical sensing, biological imaging to anti-counterfeiting.

**EN10.12.16**

**Lattice Anchoring Stabilizes Solution-Processed Semiconductors**

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The stability of solution-processed semiconductors remains an important area for improvement on their path to wider deployment. Inorganic caesium lead halide perovskites have a bandgap well suited to tandem solar cells but suffer from an undesired phase transition near room temperature. Colloidal quantum dots (CQDs) are structurally robust materials prized for their size-tunable bandgap; however, they also require further advances in stability because they are prone to aggregation and surface oxidization at high temperatures as a consequence of incomplete surface passivation. Here we report 'lattice-anchored' hybrid materials that combine caesium lead halide perovskites with lead chalcogenide CQDs, in which lattice matching between the two materials contributes to a stability exceeding that of the constituents. We find that CQDs keep the perovskite in its desired cubic phase, suppressing the transition to the undesired lattice-mismatched phases. The stability of the CQD-anchored perovskite in air is enhanced by an order of magnitude compared with pristine perovskite, and the material remains stable for more than six months at ambient conditions (25 degrees Celsius and about 30 per cent humidity) and more than five hours at 200 degrees Celsius. The perovskite prevents oxidation of the CQD surfaces and reduces the agglomeration of the nanoparticles at 100 degrees Celsius by a factor of five compared with CQD controls. The matrix-protected CQDs show a photoluminescence quantum efficiency of 30 per cent for a CQD solid emitting at infrared wavelengths. The lattice-anchored CQD:perovskite solid exhibits a doubling in charge carrier mobility as a result of a reduced energy barrier for carrier hopping compared with the pure CQD solid. These benefits have potential uses in solution-processed optoelectronic devices.


**EN10.12.17**

**Direct Synthesis of CsPbBr\(_3\) Nanocrystal-Polymer Composite Films by UV Curable Prepolymer through Room Temperature Reprecipitation Method**

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Wook Hyun Kim

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Recently, all-inorganic metal halide perovskite nanocrystals (PeNCs) with a general formula CsPbX\(_3\) (X=Cl\(^-\), Br\(^-\), I\(^-\)) have been extensively studied for optoelectronic applications such as solar cells, light-emitting diodes (LEDs), photodetectors, and lasers due to their tunable bandgap, high photoluminescence (PL) quantum yield, long charge diffusion length, high absorption efficiency, and low-cost solution processability. The bandgap energies and PL spectra can be easily tuned over the entire visible spectral region of 410 ~ 700 nm through a halide anion exchange process. Additionally, PeNCs exhibited a narrow PL linewidths and high stability against heat and light, so they are widely studied as next-generation LED materials. [1,2] However, the instability of PeNCs to water or polar solvents due to their ionic bonding property is a major obstacle to their device applications. Several studies have been conducted on the encapsulation of PeNCs using silica or polymer materials such as polyhedral oligomeric silsesquioxane (POSS), mesoporous silica, tetramethylorthosilicat (TMOS), and polyvinylpyrrolidone (PVP). [3-5]

In this study, we describe the introduction of encapsulation by modified ligand-assisted reprecipitation (LARP) method in which the perovskite precursor salts solution is dropped directly into the UV curable prepolymers solution at room temperature. It is confirmed that PeNCs encapsulated by UV cured polymer have excellent moisture stability. We will present the data of UV-Vis absorption, PL, and XRD measurement of PeNCs-polymer composite films in detail. This work provides a simple and robust method for the preparation of stable and bright PeNC films that can applicable for water-stable and highly efficient wide color gamut LED displays or other optoelectronic devices.

Giant Modal Gain Coefficients in Colloidal Nanoplatelets

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In recent years, colloidal II-VI nanoplatelets have become promising gain media for lasers offering properties superior than those of the conventional nanocrystals. Using the nanoplatelets, thresholds for amplified spontaneous emission were lowered to a few $\mu$J/cm$^2$ with gain lifetimes reaching up to 0.5 ns. In addition, early reports pointed out that modal gain coefficients in the nanoplatelets can be large. However, limits of the modal gain, which are important for practical laser applications, have not been understood nor elucidated to date. Here, we systematically investigate modal gain coefficients in CdSe nanoplatelets by performing variable stripe length measurements as a function of optical pump intensity. We find that modal gain coefficients in the CdSe nanoplatelets at room temperature reach a remarkable level of 6,600 cm$^{-1}$ with a material gain up to 15,300 cm$^{-1}$. The modal gain coefficient measured in the CdSe nanoplatelets is the largest among any other gain media at room temperature, and the material gain coefficient is on par with the best reports using epitaxially-grown quantum wells. We find that giant modal gain coefficients are ubiquitous to the CdSe nanoplatelet family as confirmed by samples having different vertical thicknesses and lateral sizes. The large gain coefficients of the nanoplatelets indicate that gain-active species, i.e., biexcitons, are highly persistent even under high pumping levels. Therefore, nonradiative processes including Auger recombination do not rapidly deplete biexcitons in the nanoplatelets as they do in typical quantum dots, overcoming an important bottleneck against achieving efficient lasing in colloidal semiconductors.

A Micro-Spherical Metal-Dielectric Plasmonic Platform for Strong Light Absorption and Emission

Seok Joon Kwon; Korea Institute of Science & Technology, Korea (the Republic of)

Micro-scale structured dielectric substrate have been widely employed for platforms for photonic devices such as photodetectors, photovoltaic devices, and light emitters. When the platforms are integrated with metallic nanostructures, they can also work as plasmonic platform supporting strong near-field in a form of surface plasmonic resonance (SPR) or gap plasmonic resonance (GPR). In the present study, we developed a plasmonic structure composed of dielectric micro-sphere which are coated with metallic nanoparticles. Due to the spherical shape, the structure exhibited strong absorption behavior in a wide range of visible (Vis) and near infrared (NIR) spectrum. The strong absorption was found to be due to strong resonance in the structure resulting from Fabry-Perot spherical cavity resonance and extended optical path length derived by metallic nanoparticles on the surface. As well as the strong absorption, the plasmonic structure also exhibited strong light emission properties in Vis spectrum. In particular, we observed whispering gallery mode (WGM) resonance-derived facilitated light emission, which was experimentally checked by upconversion nanoparticles (UCNPs) on the surface of the structure. When aligned in a form of micro lattice, the plasmonic micro-spheres also exhibited additional advantages in light emission such as wide viewing-angle and higher haze efficiency, which are promising in developing NIR-to-Vis light emission film.

Optical Gain Modulation of a Colloidal Quantum Dot Film in an Electrical Device

Junhong Yu, Sushant Shendre, Weon-kyu Koh, Baiquan Liu, Songyan Hou, Chathuranga Hettiarachchi, Savas Delikanli, Pedro H.
In view of optical gain application, colloidal quantum dots (CQDs) are suffering from band-edge state degeneracy which requires multiple-exciton to achieve population inversion. However, fast and efficient Auger process in the CQDs containing multiple-exciton increases the lasing threshold and limits the gain lifetime. Here, by applying the electric field to the quasi type-II CQDs (CdSe/CdS/ZnS core/shell/shell) embedded in the Sawyer−Tower circuit, we have demonstrated tunable amplified spontaneous emission (ASE) threshold in a long-sought practical device where the CQDs sandwiched between two dielectric layers retain their high quantum efficiency as in parent solution (quantum yield of > 70%). Singly-charged CQDs help building up population inversion due to pre-existing electrons while strongly enhanced Auger recombination in multiple-charged CQDs (i.e., doubly charged exciton) stymies the optical amplification. This approach allows us to fine-tune and achieve the optimal charging level to utilize the advantages of singly charged CQDs and reduce the adverse effect of doubly charged CQDs.

In addition to demonstrating tunable optical gain experimentally, we also developed a kinetic equation model to systematically analyze the electric field dependent light amplification behavior systematically. The kinetic model not only confirms our experimental results but also presents to be a reliable tool for accessing the requirements of the charging level to achieve nearly zero-threshold gain in CQDs. The implications, then, to potential applications of our robust and environment-undependable tuning method are broad, from controlling exciton recombination dynamics to continuous wave (CW) or possibly electrically pumped CQD lasers.

**EN10.12.22**

**Continuous-Wave Pumped Biexciton Emission in Copper-Doped Colloidal Quantum Wells** Junhong Yu¹, Manoj Sharma¹, Mingjie Li¹, Pedro H. Martinez¹, Savas Delikanli², Ashma Sharma¹, Yemliha Altintas², Chathuranga Hettiarachchi¹, Tze Chien Sum¹, Hilmi Volkan Demir¹,² and Cuong Dang¹; ¹Nanyang Technological University, Singapore; ²Bilkent University, Turkey

In atomically thin transition metal dichalcogenides (TMDs), biexcitons have sparked an unprecedented research enthusiasm since the first observation by Heinz and colleagues (Nature Phys. 11, 477–481, 2015). While TMDs are still suffering from synthesis cost, upscaling capability and quantum efficiency, colloidal nanomaterials can be an appealing complement to TMDs for biexciton sources. The specific hurdles and problems in demonstrating radiative, sustained biexcitons at room temperature in colloidal nanomaterials were earlier investigated by other groups: Klimov, Sargent, Moreels and others. Specific examples of major technical hurdles were manifested through: i) the efficient Auger recombination in multiple-carrier and quantum-confined environment, leading to ultrafast deactivation the high-order correlated excitonic states; ii) relatively small biexciton binding energy, which is comparable to the thermal energy at room temperature and much smaller than the inhomogeneous broadening of exciton emission, causing the biexciton emission only be resolved/observed at cryogenic condition.

Here, by doping the CdSe colloidal quantum wells with transition metal ions (copper) to create a new Coulomb interaction environment for band-edge excitonic resonance, we have reached and showed proof of sustained, well-resolved biexciton emission in a long-sought “all solution processable regime” enabling the easy integration of potential quantum emitters into almost any optoelectronic quantum architectures. Suppressed Auger loss in 1D quantum confinement and reduced Coulomb screening assisted by dopant-host interaction enables a biexciton binding energy of ~64 meV, a factor of 2 greater than the values reported in other colloidal nanomaterials and comparable to the value reported in TMDs. The biexcitons are robust, optically and mechanically in ways that have no parallel in the reported literature in terms of colloidal nanomaterials.

**EN10.12.23**

**Uniformly Dispersed Colloidal Quantum Dots in Conductive Polymer for High-Sensitivity and Ultra-Fast Infrared Photodetectors** Yifan Dong¹,²; ¹China University of Geosciences, China; ²The Chinese University of Hong Kong, Hong Kong

Near-to-mid-infrared (IR) photodetection technologies have the potential to revolutionize the infrastructures of surveillance and manufacturing by enabling military or civil night vision, environmental gas monitoring, and chemical spectroscopic analysis. However, current commercial IR photodetectors, particularly those with beyond 2000 nm spectral response, rely on expensive and size-limited epitaxial growth processes that are not compatible with silicon wafer technologies. Colloidal HgTe quantum dots (QDs), with a spectral response spanning almost the
entire near-to-mid-IR range, are a promising material candidate for the new generation photodetectors. However, at room temperature, the HgTe QD based photodetectors exhibit rather low specific detectivity of less than 109 Jones (or cm Hz1/2 W−1 in SI units); therefore, HgTe QD based photodetectors have to work at low temperatures to reduce dark currents and obtain better detecting performance. This requires the use of large cooling systems, which leads to a huge increase in the cost and limitation of the application, making it difficult to achieve miniaturized photodetection systems for portable imagers, spectrometers and sensor network applications. The limitations of HgTe QD based photodetectors intrinsically rise from the fact that HgTe QDs have low charge transfer properties and poor colloidal stability in ambient air condition. Combining HgTe QDs with a stable and highly conductive matrix, forming hybrid IR photodetectors is very promising to mitigate the limitations, as the conductive media can help with the facilitating charge transport mobility, providing great mechanical and chemical stabilities, and the HgTe QDs can act as the light absorber for sensing. P3HT, a well-established conjugated conductive polymer with excellent electronic properties, compatible band gaps and great mechanical and chemical stabilities, is an ideal candidate for the matrix material. However, achieving a controllable bicontinuous percolation network and a well-defined interface between QDs and the polymer matrix remains challenging, as it is very difficult to disperse high-density HgTe QDs uniform into P3HT matrix without aggregation, as it’s critical to tune the interface properties between HgTe and P3HT with efficient electron-hole separation and uniform phase distribution.

Here, we demonstrate for the first time a facile method to synthesize and control the nanoscale morphology and interfacial properties of poly(3-hexylthiophene) (P3HT) matrix and HgTe QDs hybrids using chemical grafting and ligand exchange methods. Solvent-assisted chemical grafting and ligand exchange were used to control the interface of P3HT/HgTe nanohybrids and the HgTe QD interparticle distance, respectively. It’s demonstrated that the formation of an interpenetrating and percolating P3HT/HgTe network gives rise to efficient charge separation and charge transport, significantly improving photovoltaic performance, which is promising for high-performance and low-cost IR photodetector applications.

EN10.12.24
Improved Stability and Performance of All Inorganic Perovskite Quantum Dots by Mixing Rubidium Cation and Fabrication of Their Full-Color Film with Wide Color Gamut
Seungmin Baek and Sang-Wook Kim; Ajou University, Korea (the Republic of)

In recent years, perovskite quantum dots (PeQDs) have received a lot of attention for many application. however, PeQDs were particularly unstable and the optical properties were readily degraded because of its structural instability. To overcomes these problems, We synthesized perovskite using new cations. Mixed-cation Cs0.4Rb0.6PbX3 (X = Cl, Br, I) perovskite quantum dots (PeQDs) are developed and show high quantum yields of 93% and 86% for green and blue wavelengths, respectively. The stability is significantly improved under heat, UV, and water aging conditions. We also fabricated the film by applying cyclic olefin copolymer to perovskite for the first time. The films have a wide color gamut covering up to 104.15% of the BT.2020-defined color space, with the white light color coordinates of (0.33, 0.32), luminance of 68.86 Cd/m2, and correlated color temperature of 5299 K at 20 mA

EN10.12.25
Efficient Light Emitting Diode Achieved by Using Mixed 2D/3D Perovskites and Manipulating Charge-Injection Balance
Weiming Qiu1,2, Azhar Fakharuddin1,3, Jielin Yan1,3, Guillaume Croes1,2, Robert Gehlhaar1, Andrey Kadashchuk4, Vidmantas Gulbinas5, Hongzheng Chen3 and Paul Heremans1,2; 1imec, Belgium; 2KU Leuven, Belgium; 3Zhejiang University, China; 4National Academy of Sciences of Ukraine, Ukraine; 5Center for Physical Sciences and Technology, Lithuania

Mixed 2D/3D perovskite films with self-assembled quantum wells have significantly improved the performance of perovskite light emitting diodes (PeLEDs). In this work, such films are fabricated through a two-step interdiffusion method that is widely employed in processing of perovskite solar cells, however, remains rarely explored for PeLEDs. Mixed 2D/3D perovskites based on FAPbBr3 and (MAPb(I/Br)3, with the incorporation of large-cation ligands, are fabricated for green and near-infrared emission, respectively. We systematically studied the processing condition on the morphology and optoelectronic properties of the resulting perovskite films. Moreover, with pumped-probe measurements, we also provide insight on how the charge dynamics change when tuning 3D perovskite to a mixed 2D/3D one, which significantly improves the radiative recombination. The PeLEDs based on two-step fabricated mixed 2D/3D perovskites show maximum external quantum efficiency (EQE) of 7.36% (green) and over 16% (near-infrared), which are significantly higher than PeLEDs using the corresponding 3D perovskites.
Finally, we present the importance of balanced charge injection on improving EQE roll-off as well as device stability. The electron injection is tuned systematically by doping the electron transport layer, reaching a balanced electron and hole injection at optimal condition. We achieve EQE > 10% beyond 100 mA/cm² and a remarkable half lifetime beyond 40 h at 10 mA/cm² for the optimized device with balanced injection.

**EN10.12.26**

**Uniformity Enhancement of Photo-Luminescent Quantum Dots Dispersed in Liquid Crystalline Matrix for Emissive Displays**

_Sujie Kang, Sin-Hyung Lee and Sin-Doo Lee; Seoul National Univ, Korea (the Republic of)

Quantum dots (QDs) have emerged as one of the most promising semiconducting nanoparticles (NPs) for high-performance information displays due to their tunability of the emission wavelength, narrow full width at half maximum (FWHM), and high quantum efficiency. In the QD-based displays, the uniform dispersion of the QDs is one of the critical issues to achieve the emission uniformity over the entire area of an individual pixel and to suppress the aggregation-induced quenching. In general, the QDs can be dispersed in a variety of host media such as organic semiconductor materials and cross-linkable polymers (hereafter referred to the QD hybridization). In the direct color conversion by the photo-luminescent (PL) QD hybridization, the color purity and the PL intensity of the QDs are limited due to the localized aggregation of the QDs in the host matrix. Thus, it remains a challenge to produce highly uniform dispersion of the QDs for the high color purity and the high PL intensity in well-defined patterns.

In this work, we developed a simple and effective method of achieving the uniform QD hybridization with the molecular field effect of the host matrix on the dispersion of the QDs. In order to utilize the molecular field effect, a reactive mesogen (RM), which exhibits the liquid crystal (LC) properties and can be photo-polymerized, was used as the host matrix. Two types of the QD hybrid films were prepared depending on whether the polymerized RM matrix was aligned or not. A solution of red QDs (with the peak wavelength of 620 nm), dissolved in the homogeneous RM solution, was spin-coated on a glass substrate with or without the homogeneous alignment and then photo-polymerized under the ultraviolet (UV) exposure. The RMs aligned along the homogeneous direction indeed suppressed the aggregation of the QDs due to the high degree of the molecular ordering of the RMs through the photo-polymerization. Based on the 3-dimensional emission profiles, probing using the confocal microscopy, in the ordered QD hybrid film, the mean peak-to-peak distance between two adjacent emission sites was found to be about 60 nm and the FWHM was comparable to the radius of an individual QD (about 40 nm). In contrast, in the non-ordered RM film, the FWHM was quite arbitrary and the distance between two emission sites was random due to the aggregation of the QDs. Note that the intensity of the emission spectrum of the ordered QD hybrid film increased with increasing the weight concentration of QDs. The aggregation of the QDs appeared at about 2 wt. % of the QDs.

We examined the electro-optical properties of the PL-based QD display consisted of the ordered QD hybrid patterns, a light modulator, and an excitation light source. A simple vertically aligned LC cell was fabricated as the light modulator. The blue LED with the peak wavelength of 455 nm was used as the excitation light. The QD hybrid film was patterned by the UV exposure through a photomask, followed by the removal of the un-polymerized region. The same process for red QDs was repeated for green QDs (the peak wavelength of 530 nm). For the blue patterns, the dummy regions containing blue absorbers were used for balancing the intensity. As the applied voltage increased, the intensity of the emission spectrum of the QDs increased according to the change in the phase retardation which converts the polarization state of the excitation light. This leads directly to the modulation of the emission spectra of the QDs with the color gamut extended to 82 % of the BT. 2020 standard. Our approach will provide a useful guideline to produce the QD hybridization for emissive displays with high color purity.

This work was supported in part by Samsung Display Co. and BK21 Plus Program funded by Ministry of Education of Korea.

**EN10.12.27**

**Improving Thermal Stability of Core/Shell Quantum Dots Using Block Copolymer Protective Layer**

_Geon Yeong Kim, Eugene N. Cho and Yeon Sik Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Application of semiconductor nanocrystals increased over the years in fields such as solar cells, sensors, light-emitting diodes and electronics. Particularly, a form of nanocrystal known as quantum dots (QDs) has gained interest with the recent development in displays. With easy color tunability, high color purity, and high quantum yield, QDs has been selected as the candidate for next-generation displays. Because of use commercially, there is a
movement for shifting the materials composition from Cd-based to Cd-free core shell QDs such as InP/ZnS. However, these attractive initial properties are difficult to maintain when undergoing fabrication and long-term operation. This is especially the case for processing QDs at elevated temperatures. During thermal processing of QDs for display application, the quantum efficiency suffers a substantial loss. From the electronic process standpoint, the loss is due to carrier ejection to trap states or electron-hole pair ejection. In addition, the materials composition and structure can vary upon thermal processing due to phenomena such as particle sintering, Ostwald ripening, or surface composition change. Furthermore, oxidation of the shell can influence the quantum yield to decrease more than 50% as well as cause blue or red shift of the photoluminescence spectra.

In order to prevent degradation from thermal processing, we believe the key is to create a protective layer for the QD. Here, we utilize block copolymer (BCP) to act as a protective layer through micelle formation. The QDs were loaded into the core of the block copolymer micelles, using self-assembly property of block copolymer. The micelle core wraps around the QD expecting to hold ligands in place while the micelle corona gives additional protection of the QD from the surrounding environment. This will provide a two-way protective layer to the Cd-free core-shell QD preventing outer shell of the QD from ligand detachment and oxidation. The block copolymer protective layer is expected to improve the thermal stability and retain PL of 90% after post thermal treatment.

Reference

SESSION EN10.13: Physics and Lasing Properties of Nanoscale Emitters
Session Chairs: Hanwei Gao and Jiangeng Xue
Thursday Morning, December 5, 2019
Sheraton, 2nd Floor, Back Bay D

8:00 AM *EN10.13.01
Room Temperature Optical Properties of Single Perovskite Quantum Dots Gabriele Raino1,2, Annelies Landuyt1,2, Franziska Krieg1,2, Caterina Bernasconi1,2, Stefan Ochsenbein1,2, Dmitry Dirin1,2, Maryna Bodnarchuk1,2 and Maksym V. Kovalenko1,2; 1ETH Zürich, Switzerland; 2Empa – Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Lead-halide perovskite APbX₃ (A=Cs or organic cation; X=Cl, Br, I) nanocrystals (NCs) are subject of intense research due to their exceptional properties as both classical¹ and quantum light sources.²⁻⁴ Many challenges often faced with this material class concern the long-term optical stability, a serious intrinsic issue connected with the labile and polar crystal structure of APbX₃ compounds. When conducting spectroscopy at a single particle level, due to the highly enhanced contaminants (e.g., water molecules, oxygen) over NC ratio, deterioration of NC optical properties occurs within tens of seconds, with typically used excitation power densities (1-100 W/cm²), and in ambient conditions.

Here,⁵ we demonstrate that choosing a suitable polymer matrix is of paramount importance for obtaining stable spectra from a single NC and for suppressing the dynamic photoluminescence (PL) blueshift. In particular, polystyrene (PS), the most hydrophobic amongst four tested polymers, leads to the best optical stability, one-to-two orders of magnitude higher than that obtained with poly-(methyl methacrylate) (PMMA), a common polymeric encapsulant containing polar ester groups. Molecular mechanics simulations based on a force-field approximation corroborate the hypothesis that PS affords for a denser molecular packing at the NC surface. These findings underscore the often-neglected role of the sample preparation methodologies for the assessment of the optical properties of perovskite NCs at a single particle level and guide the further design of robust single photon sources operating at room temperature.

References:
The best perovskite LEDs have external quantum efficiencies that approach or even exceed the limit expected from classical models of optical outcoupling with perfect internal quantum efficiency. I will discuss how light is transferred from trapped modes to outcoupled modes in these devices, presenting measurements of laterally resolved electroluminescence and photoluminescence that can distinguish between scattering and other mechanisms. We find an important contribution from photon recycling, where trapped photons are absorbed in the emissive layer and re-emitted, giving another chance to enter an outcoupled mode. I will discuss the effects of parasitic absorption in non-emissive electrode layers, and will present measurements on new geometries which further enhance optical outcoupling.

Low-Threshold Upconverting Microlasers via Controlled Assembly of lanthanide-Doped Nanoparticles

Energy looping Lanthanide-doped nanoparticles were introduced recently as an attractive gain medium for continuous-wave upconverted lasing. A useful architecture for constructing microlasers with these materials involves their adsorption onto dielectric microbeads that support stable whispering gallery mode (WGM) resonances. Despite recent advances in upconverting nanoparticle microlasers, improvement in resonators’ sizes, lasing threshold and reliable processability is needed for their utilization in different imaging, sensing and photonics applications. Our previously reported microsphere resonators exhibited a broad distribution of lasing thresholds and processing variability which limit their practical applications. In this work, a more complete understanding of the nanoparticles’ deposition process, and the structural factors that determine efficient lasing was achieved. We demonstrate using correlative microscopy that the quality of WGMs is significantly influenced by structural characteristics of the beads’ coating layer of nanoparticles, such as thickness and surface roughness. With this understanding, superior lasing was achieved following delicate control over the self-assembly of nanoparticles on the microcavity’s surface. We show that 5-µm microspheres with controlled sub-monolayer UCNP coatings exhibit 25-fold lower laser thresholds (1.7 kW/cm²) and 30-fold lower variability compared to the lowest threshold UCNP lasers. WGMs are observed in the upconversion spectra for microspheres as small as 3 µm, for which optical losses had previously prevented observation. These advances will enable the fabrication of more efficient upconverting lasers for imaging, sensing, and actuation in optically complex environments.

Widely Tunable Laser from Mixed-Halide Perovskites and Optical Amplification from Functional Perovskite Light-Emitting Diodes

Solution-processed perovskite semiconductors have emerged as efficient light emitters due to their bandgap tunability, high color purity, and favorable optical gain. Recently, optically pumped lasers from perovskite thin films have been demonstrated in various feedback configurations under either pulsed or continuous-wave excitation. However, unlike colloidal quantum dots or organic materials, the reports of lasing have been confined to either the green or near infrared spectral range, lacking red-emitting lasing due to undesirable halide phase separation. Through proper selection of self-assembled bulky ligand additives and the use of a cesium-mixed cation in the mixed-halide perovskite composition, we are able to suppress phase separation. In this study, we demonstrate widely tunable distributed feedback (DFB) lasers operating at room temperature. Our optimized mixed-halide perovskite films were prepared on quartz gratings and achieve single-mode lasing across the green and near infrared with a pump threshold of 4 µJ/cm² and full-width-half-maximum of 0.65 nm under pulsed optical excitation. The laser
devices were stable and robust so that the lasing emission lasted for more than 40 hours (~ $10^4$ laser pulses) under sustained excitation. Despite extensive research and progress on perovskite-based light-emitting diodes (LEDs) and lasers, realization of electrically driven solution-processed perovskite laser devices still remains elusive due to several barriers such as required high threshold current density, robust transport layers, and thermal management. Recently we have shown that hybrid perovskite LEDs can operate at the high current density regime (up to 620 A/cm$^2$) with no pronounced non-radiative Auger recombination. Further investigations enabled us to achieve amplified spontaneous emission from a typical perovskite LED structure, where the active layer is sandwiched by organic transport films. Methylammonium lead iodide perovskite with nanometer-sized crystallites have been optimized to provide high optical gain coefficient (~ 500 cm$^{-1}$), verified by a variable-stripe-length measurement. Then, second-order DFB Bragg gratings were patterned directly on indium tin oxide, acting as both transparent electrode and optical feedback structure. From this LED device architecture, we achieve single-mode DFB lasing with a threshold of 7 µJ/cm$^2$ and full-width-half-maximum of less than 1.0 nm through pulsed optical excitation. At the same time, this device was able to operate as an LED under direct current drive with a maximum external quantum efficiency (EQE) of 0.7%. In particular, the peak EQE occurred at a current density of 1.3 A/cm$^2$. Extrapolating from our previous work, these results suggest that operation at pulsed current densities of a few kA/cm$^2$ is achievable, putting the goal of electrically stimulated lasing within reach.

9:30 AM BREAK

10:00 AM *EN10.13.05
Controlling Orbit-Orbit Interaction in Hybrid Perovskites through Managing Grain Formation towards Amplified Spontaneous Emission

Bin Hu; University of Tennessee, United States

Organic-inorganic hybrid perovskites in polycrystalline films have demonstrated efficient amplified spontaneous emission (ASE). Essentially, amplified spontaneous emission can be enabled by initiating the cooperative interaction between light-emitting states. Here, we consider the orbit-orbit interaction that can occur through short-range and long-range interaction channels. Specifically, the short-range and long-range orbit-orbit interactions are occurred through magnetic dipole-dipole interaction and polarization-polarization interactions, fundamentally influencing the interaction between light-emitting states. In this study, we intentionally tuned the orbit-orbit interaction between short-range and long-range channels and simultaneously study the length scale of light-emitting states by using magneto-ASE measurements during ASE characterizations in polycrystalline perovskite (MAPbBr$_3$) films where the grain formation are effectively managed. Interestingly, by concurrently inducing fast and slow crystallization upon mixing two precursor solutions ( PbBr$_2$ + MABr and Pb(Ac)$_2$*3H$_2$O + MABr), the polycrystalline perovskite films can be prepared with large grains of micrometers attached with small grains of nanometers, leading to self-doping effects. In this situation, the small and large grains functions as doping agents and light-emitting centers, respectively. Especially, the self-doping realized by attaching small grains to the surfaces of large grains provides a unique method to tune the orbit-orbit interaction between short-range and long-range channels. As a consequently, cooperative spatially extended states can be formed, leading to low-threshold ASE. This presentation will discuss the tuning of orbit-orbit interaction towards generating cooperative spatially extended states by managing grain formation for generating ASE in organic-inorganic hybrid perovskites.

10:30 AM EN10.13.06
Spectral Linebroadening of CdSe Nanoplatelets and Quantum Dots for Light Emitting Devices
Johanna van der Bok, Bas Salzmann, Daphne Dekker, Matt Peerlings and Andries Meijerink; Utrecht University, Netherlands

There is need for efficient narrow band red and green luminescent materials for white light LEDs and LED-based display backlights to improve the energy efficiency and color gamut. Recently CdSe and InP semiconductor nanoparticles (known as quantum dots, QDs) were introduced in displays (e.g. Samsung QLED TV) because of their high efficiency and relatively narrow emission bands. A promising alternative for these QDs are CdSe nanoplatelets (2D NPLs) because of their narrower spectral linewidth compared to 0D and 1D confined nanostructures[1]. To enhance the quantum yield, stability and to tune the emission towards the red, a CdS or ZnS shell is grown around the NPLs. Unfortunately, core-shell NPLs do not exhibit the same narrow spectral linewidth. The difference in spectral width for core and core-shell NPLs has been explained by a difference in electron-phonon coupling after shell growth [2]. Here we aim to obtain insight in the origin of the difference in spectral width for core and core-shell NPLs. We investigated the temperature dependent line broadening of CdSe QDs, NPLs and core-shell NPLs.
Measurements were performed over a wide temperature range, between 4 and 423K and included measurements at elevated temperatures which are relevant for practical application in displays and white light LEDs but are usually neglected.

The line broadening studies reveal that homogeneous line broadening is similar for the various systems studied (core and core-shell NPLs and QDs). Homogeneous line broadening was found to be size dependent and small QDs (2.5nm diameter) showed a noticeably stronger homogenous broadening compared to the other systems. The significantly narrower band emission of core NPLs is explained by strongly reduced inhomogeneous broadening compared to core-shell NPLs and QDs. The larger spectral linewidth of CdSe core-shell NPLs is not due to an increase in homogeneous broadening caused by differences in electron-phonon coupling as previously suggested. Instead it is caused by an increased inhomogeneous linewidth after growth of the CdS or ZnS shell, probably related to inhomogeneities of the shell and exciton emission originating from different regions in the core-shell NPLs where the local electronic structure and bandgap are affected by variations in the shell thickness. This is supported by the recent improvements in synthesis procedures for core-shell NPLs which show less inhomogeneous broadening [3].

The present observations show that the spectral linewidth of NPL-heterostructure emission can be improved and is not caused by stronger exciton-phonon coupling due to the shell material. This makes green emitting core-crown NPLs and red emitting core-shell NPLs promising candidates for narrow band emitters in future displays and LEDs. Extending measurements to a regime that matches the operating temperature for the emitters in commercial applications (displays, white light LEDs) is rarely done but highly relevant. Our measurements up to 150 °C show a continuing increase in line width for both QD and NPL emission while the NPL emission line width remains narrower: ∼34 nm for green emitting QDs and ∼15 nm for green emitting NPLs at 150 °C. The significantly narrower emission bands for CdSe NPLs at device operating temperatures give the NPLs a clear advantage and make these emitters competitive with narrow band phosphors which have ∼20-30 nm spectral bandwidths in the green-red spectral region.


10:45 AM EN10.13.07
Design Rules for One-Step Seeded Growth of Nanocrystal Heterostructures Emory Chan¹, Haoran Yang², Leslie Hamachi³ and Iva Reza³; ¹Lawrence Berkeley National Laboratory, United States; ²Lawrence Berkeley National Lab, United States; ³Columbia University, United States

Quantum dot heterostructures such as core@shell nanocrystals are used as light-emitting materials for applications such as biological imaging, lasers, displays, and solid-state lighting. The inorganic shells of these materials, which confine excitons and chemically passivate these materials, are typically grown on seed nanocrystals through continuous or layer-by-layer methods, which are tedious and time-consuming. Here, we present design rules for more scalable reactions in which uniform shells are grown on CdSe quantum dots in a single step. We leverage high-throughput synthesis along with a custom library of precursors with tunable reactivity to develop a comprehensive understanding of the role of precursor reactivity, ligands, and temperature in these one-step seeded growth reactions. These experiments reveal a narrow region of experimental parameter space that promotes the uniform, purely heterogeneous growth of shell material on the seed particles. This “ideal growth” regime is sandwiched between opposing regimes that lead to secondary nucleation or ripening during growth. Coupled with kinetic simulations, these experiments reveal that precursor reaction rate and monomer solubility determine the balance between secondary nucleation and ripening. Therefore, accelerating the rate of shell growth through the use of more reactive precursors must be accompanied by a precise increase in ligand concentration in order to maintain uniform shell growth. These design rules will be critical for the predictable growth of complex, multi-shell architectures used to engineer band gaps and mediate multi-excitonic processes in high-efficiency quantum dot optoelectronic devices.

11:00 AM EN10.13.08
Single Exciton Gain and Stimulated Emission from Robust Doped PbS CQD Films at Room Temperature Sotirios Christodoulou¹, Iñigo Ramírez¹, Andreas Othonos², Alberto Figureira¹, Mariona Dalmases¹, Onur Ozdemir³, Santanu Pradhan¹, Grigorios Itskos² and Gerasimos Konstantatos¹; ¹ICFO - Institut de Ciencies Fotoniques, Spain; ²University of Cyprus, Cyprus
The last two decades CdSe-based colloidal quantum dots (CQDs) and most recently perovskite nanocrystals have been under the spotlight for lasing application as exhibit excellent optoelectronic properties such as high photoluminescence quantum yield (PLQY), optical stability and wide emission tunability. Already, CQD technology has delivered ultra-low lasing and stimulated emission thresholds even with continuous wave excitation (CW). Nevertheless, the research has centred in UV-Vis while very few examples has been shown in the low energy part of the electromagnetic spectrum.

On the other hand, light sources (lasers) in NIR is still the last piece missing for the realization of silicon Photonics (CMOS), while photodetectors and modulateors on Si have been already demonstrated. Apart from silicon photonics, the realization of low-cost, solution-processed materials with gain across the telecommunication window is of paramount importance for expanding the optical fiber data capacity beyond the limit of currently used Er-doped amplifiers. The realization of low-threshold and high gain amplified spontaneous emission (ASE) with high degree of tunability across the telecom band has not been achieved yet. The reason behind this challenge has been the high degeneracy of states in infrared CQDs over that of visible CQDs (twofold degeneracy of CdSe over eight-fold degeneracy for PbS-chalcogenides).

To tackle the high degeneracy of the PbS CQD we developed a doping scheme, which allow us heavily dope the PbS CQD filling with electron the conduction band. Both theoretical simulations (DFT) and experimental results (UPS) confirm that the Iodine substitution promotes the shift of the fermi energy (EF) over the conduction band (CB) while via size careful size selection of the CQD we can fine-tune the doping strength. Absorption spectra of the doped PbS CQD films shows a bleach of the band-edge transition according to the doping efficiency, while it is completely bleached when the CB is fully filled with 8 electrons. The doped PbS films are stable for months under ambient conditions while is the first demonstration permanent robust doping in conductive films.

Photothermal threshold quantum yield (PTQY) is a calorimetric technique, incorporating a photothermal deflection spectrometer and a photoluminescence spectrometer to simultaneously and precisely monitor the average amount of heat energy (non-radiative) and light energy (radiative) given off as a result of each incident pump photon. By
removing the need to directly quantify spectral radiance, with sufficient sampling, PTQY can achieve a theoretical precision of 0.02%, an improvement of multiple orders of magnitude in precision over conventional integrating sphere approaches. PTQY was previously applied by our groups to measure near unity CdSe:CdS quantum dots, measuring a peak PLQY of 99.6 ± 0.2% at an optimal CdS shell thickness. We will report on efforts to extend PTQY to study additional near unity nanoscale emitters, including halide perovskite nanoparticles, which can also achieve near unity PLQY, and have promising optoelectronic applications as single-photon sources or in optical refrigeration. Ultrahigh precision PLQY measurements are required to validate such utility. Furthermore, by validating that nanoscale emitters are operating near their thermodynamic limits, we will present how this technique can be applied to more directly quantify the impact of defects on photophysical properties.


11:30 AM EN10.13.10
Nanoscale Core-Shell Hyperbolic Structure—An Emerging Platform to Trigger Laser Action from Light-Emitting Materials
Hung-I Lin, Kanchan Yadav, Kun-Ching Shen, Chun-Che Wang, Ting-Jia Chang, Monika Kataria, Golam Haider, Pradip Kumar Roy, Yit-Tsong Chen and Yang-Fang Chen; National Taiwan University, Taiwan

Enhancing the light-matter interaction from low-dimensional nanoscale emitters has been attracted tremendous attentions for displays and optoelectronic devices. To achieve this goal, traditional methods have been used the plasmonic materials due to reshaping density of states (DOS) and tailing the light emission. However, the main drawbacks of the plasmonic materials are the propagation loss and narrowband resonance, which remains challenging to provide a broadband DOS to explore its functionality. Here, we develop a novel nanoscale core-shell hyperbolic structure with an extremely pronounced coupling effect inside the multishell (Au/SiO₂) nanoscale composite. Then, a giant localized electromagnetic wave of surface plasmon resonance is formed, causing a pronounced out-coupling effect than the plasmonic materials. To integrate the emerging light-emitting material, we mixed the nanoscale core-shell hyperbolic structure mixed with DCJTB dye molecules to measure the lasing spectra. DCJTB dye molecule, a kind of organic laser dye, has been used for solar-concentrator application. The lasing threshold is ultralow of ~42 μJ/cm², which was excited by a 374 nm pulsed diode laser. There is no laser action can be observed for the plasmonic-based Au nanoparticle at the low pumping power density.

Confirmed by simulation results, the nanoscale core-shell hyperbolic structure has achieved ~320 times higher scattering efficiency as compared with the plasmonic-based Au nanoparticle. Besides, the simulated mode volume is ~208 times smaller than the same components of multilayer structure, demonstrating that the nanoscale core-shell hyperbolic structure is able to strongly confine the energy, reduce propagation loss, then a tremendous feedback is formed to trigger the laser action. We believe that the nanoscale core-shell hyperbolic structure steps a great advance in lasing action from nanoscale materials, highly energy conversion efficiency for solar cells, and broadband absorption of optoelectronic devices applications.

Acknowledgments
This work was financially supported by the "Advanced Research Center for Green Materials Science and Technology" from The Featured Area Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (107L9006) and the Ministry of Science and Technology in Taiwan (MOST 107-3017-F-002-001).
Thursday Afternoon, December 5, 2019
Sheraton, 2nd Floor, Back Bay D

1:30 PM *EN10.14.01
Trion Dynamics in Perovskite Nanocrystals Yoshihiko Kanemitsu; Kyoto University, Japan

Metal halide perovskite nanocrystals (NCs) are a new class of semiconductor materials with excellent optical properties. These NCs are anticipated for use in light-emitting devices, because they exhibit high luminescence efficiencies at room temperature and their emission wavelengths can be easily controlled by the halogen composition and/or the NC size. In general, the trion, which is a stable state consisting of one electron–hole pair (exciton) and one excess charge, plays a crucial role in the optical responses of NCs. Trions usually cause photoluminescence intermittency, reduce the luminescence yield, and can also affect the threshold for optical gain. Thus, a deep understanding of the trion dynamics in NCs is important for development of NC-based light-emitting devices.

In this work, we analyze the dynamics of trions in perovskite NCs at room temperature. We studied their dynamics by means of single dot spectroscopy, femtosecond transient absorption spectroscopy, and Z-scan measurements [1-3]. Our results show that the biexciton Auger rate evaluated from femtosecond transient absorption spectroscopy can be expressed as the sum of the Auger rates of positive and negative trions obtained by single dot spectroscopy [4]. We further investigated the excitation fluence dependence of the trion generation. The trion generation in NCs under weak photoexcitation can be controlled by surface modification [5]. Under strong photoexcitation, the intrinsic nonradiative Auger recombination of biexcitons causes ionization of the perovskite NCs and trion generation. An important practical aspect is that the chemical modification of perovskites enables suppression of trion generation in light-emitting devices [6]. We discuss the trion dynamics in perovskite NCs and the mechanism of ionization of perovskite NCs.

Part of this work was supported by JST-CREST (JPMJCR16N3).

2:00 PM *EN10.14.02
Carrier Dynamics in Halide Perovskite Nanocrystal Assemblies Jochen Feldmann; Ludwig-Maximilians-Universität (LMU), Germany

I will report on the optical properties of metal halide perovskite nano-platelets with controllable thickness down to one monolayer [1]. Pronounced quantum confinement effects, large excitonic binding energies and comparably high radiative recombination rates have been found, all depending on the number of monolayers present in the respective nano-platelets. Ultrafast optical experiments provide insight into characteristic charge carrier and spin relaxation scenarios in 2D perovskites [3]. Finally, the assembly of halide perovskite nanocrystals into ordered supercrystals [3,4] and the exchange of ligands lead to remarkable changes of their optical properties.


2:30 PM EN10.14.03
Improving Upconversion Performance of Colloidal Quantum Dot Nanostructures through Heterostructure Engineering Jill Cleveland, Tory Welsch, Eric Chen, Christopher Milleville, Kyle Lennon, Jing Zhang, James Bork,
Photon upconversion is a process in which two or more low-energy photons are sequentially absorbed in a material resulting in the emission of a higher-energy photon. Photon upconversion has a wide range of potential applications including optoelectronic devices, biotechnology, and solar energy harvesting. Semiconductor nanoparticles have recently emerged as a promising platform for upconversion due to the tunability of their absorption and emission wavelengths through control of particle shape, size, and composition. Additionally, semiconductors have inherently broadband absorption, capturing essentially all photons with energy above their bandgap, which is an important feature for solar energy harvesting applications. Previously our group developed a kinetic rate model and demonstrated upconversion could enhance solar cell performance beyond the Shockley-Queisser limit by providing additional above bandgap illumination from an upconversion layer located behind the cell. We have also demonstrated near-infrared (NIR)-to-visible upconversion photoluminescence in CdSe(Te)/CdS/CdSe core/rod/emitter colloidal quantum dot (QD) nanostructures under continuous wave illumination at solar relevant fluxes. While we and others have demonstrated the feasibility of using semiconductor nanostructures for upconversion, the reported efficiencies are rather low. We recently demonstrated that principles of semiconductor heterostructure engineering can be employed to achieve a factor of 100 improvement in upconversion efficiency. For example, by carefully controlling the core QD composition and introducing a gradient within the nanorod, we reduce nonradiative recombination rates and improve carrier transfer through the nanostructure, resulting in higher upconversion efficiency. We will report on the design, synthesis, and photophysical characterization via ultrafast and time-integrated optical spectroscopy of a range of such structures. We will describe further improvements in upconversion performance that could be realized by employing new colloidal synthesis techniques to optimize our current structures and introducing new particle shapes and elemental compositions.

2:45 PM EN10.14.04
The Room-Temperature Electrical Generation of a Single Exciton in a Single Colloidal Quantum Dot
Yunzhou Deng; Zhejiang University, China

The electrical generation of emissive excited states is at the heart of electroluminescent (EL) devices. The emissive excited state for colloidal quantum dots (QDs), a class of high-efficient and color-pure luminescent materials, is described as an exciton, i.e. a bound electron-hole pair. Recently, QD-based EL devices demonstrated distinctive performances at both single-dot and ensemble levels. However, the underlying mechanism associated with the electrical generation of excitons in QDs has yet to be clarified. Here we use the recently developed single-dot EL devices as a model system to identify the elementary steps responsible for the electrical generation of a single exciton confined in an isolated QD.

A new experimental technique, namely, optically probing a single emitter under electrical injection, was developed. We repetitively excited a single QD under constant electrical biases by a pulsed laser, enabling optically probing of all possible states associated with the single-dot EL. According to transient PL results, we identified the intermediate negatively-charged state (QD-) by the characteristic lifetime of the negatively-charged trion (X-). In addition, the occurrence of the intermediate QD- was verified by the red-shifted spectrum of the single QD measured under simultaneous optical and electrical excitation. The identification of the intermediate state suggested that the electrical generation of a single exciton in the single QD followed a deterministic pathway comprised of the prior electron injection and the succeeding hole injection. Quantitatively, the rate coefficient for hole-injection into a negatively-charged QD, which was substantially greater than that for hole-injection into a neutral QD, was determined to be comparable to that for electron-injection into QD.

This work provides a unique microscopic picture of the electrical generation of single excitons in single QDs at room-temperature. Our findings implicate the vital role of the long-lived intermediate QD- in boosting charge balance of single-photon EL devices and shall bring new insights into operation mechanisms of state-of-the-art QLEDs.

3:00 PM BREAK
3:30 PM *EN10.15.01

In Situ Fabricated Perovskite Quantum Dots for Display Applications

Haizheng Zhong; Beijing Inst of Technology, China

Perovskite quantum dots (QDs) are now emerging as low-cost alternative emitters for display applications. Very recently, we developed the in-situ fabrication of hybrid perovskite QDs embedded composite films (PQDCF) with high transparency, superior photoluminescence emission and additional processing benefits for down-shifting applications. The potential use of PQDCF as color converters in LCD backlights was successfully demonstrated, showing bright potential in display technology. Moreover, we further explored the electroluminescence devices based in-situ fabricated perovskite QDs. The enhancing role of ligand-assisted reprecipitation (LARP) process was illustrated, providing uniform FAPbX3 (X=Br, Cl, I) perovskite QDs films with photoluminescence quantum yield up to 78%. The electroluminescence devices with a maximum external quantum efficiency (EQE) of 16.3% and 15.8% were achieved, showing the promising to achieve high efficiency. In all, the in-situ fabrication strategy provides very convenient route for display technology.

4:00 PM *EN10.15.02

III-V Colloidal Nanocrystals for Optoelectronic Applications

Sohee Jeong; Sungkyunkwan University (SKKU), Korea (the Republic of)

Recently, InP colloidal nanocrystals draw immense attention because of their successful debut in the display market and many researches in the field focus on improving the optical properties via various synthetic scheme. Still, understanding on synthetic mechanism, surface chemistry of III-V colloidal nanocrystals is limited which results in inferior optical properties with poorer stability when compared to Cd or Pb based colloidal nanocrystals. Here, I plan to discuss the chemical and physical properties of III-V nanocrystals based on their rather covalent bonding nature. Further, approaches to enhancing optical properties via chemically passivate deeper trap states from dangling bonds based on microscopic understanding on covalent surfaces will be shared.

4:30 PM *EN10.15.03

Unraveling the Origin of Operational Instability of Quantum Dot Based Light-Emitting Diodes

Jun Hyuk Chang1, Kookheon Char1 and Wan Ki Bae2; 1Seoul National University, Korea (the Republic of); 2Sungkyunkwan University, Korea (the Republic of)

Quantum dot (QD) based light-emitting diodes (QLEDs) are promising candidate for next generation display. For practical use of QLEDs, guaranteed operational stability at desired brightness is essential. Yet understanding the origin of operational instability of QLEDs is lagging behind. In this presentation, I explain the origins for the operational instability of QLEDs. The electrical characterization of QLEDs and spectroscopic analysis on the QD emissive layer within devices indicates two main mechanisms for the device degradation. The first is the luminance efficiency drop of the QD emissive layer in the running devices due to the accumulation of excess electrons in QDs, which escalates the possibility of non-radiative Auger recombination processes in QDs. The other is the electron leakage toward hole transport layers (HTLs) that accompanies irreversible physical damage to the HTL by creating non-radiative recombination centers. These processes are distinguishable in terms of the timescale and the reversibility, but both stem from a single origin, the disparity between electron versus hole injection rates into QDs. Ground on this experiment result, I offer rational guidelines that promise the realization of high performance QLEDs with proven operational stability.

4:45 PM *EN10.15.04

Role of Cationic Ligands on Surface Passivation of Cesium Lead Bromide Nanocrystals

Lucy Yoon and Joshua Choi; University of Virginia, United States

A demand for more saturated color display, longer lifespan, improved economic viability, and optimal luminescence efficiency is rapidly growing in optoelectronic industries. Metal halide perovskite has been a rising candidate as our next generation semiconducting material due to the following: widely tunable bandgaps, exceptional efficiency, and
relatively facile and inexpensive fabrication processes. Inorganic cesium lead halide perovskite (CsPbX₃) nanocrystals, in particular, have emerged as an ideal option for practical application due to their high performance and intrinsic stability. Nanocrystals have challenges associated with major charge recombination sites on the surfaces. In order to overcome this problem, surface ligands can be employed to passivate charge traps. Ionic salts, given an advantage of ionic nature of perovskite, are effective at passivating either or both cationic and anionic defect sites. However, systematic understanding of the surface chemistry with the ionic salt ligands is still lacking. Here we present our study on the nature of cation and anion pairs on the efficacy of CsPbX₃ nanocrystal surface passivation. Based on a combination of optical spectroscopy, density functional theory calculations, device fabrication and testing, we show that the specific combinations of cations and anions result in superior charge trap passivation efficacy due to their different binding interactions and steric effects.

EN10.16.01
A New Approach to Fabricate Three-Dimensional GaN LEDs for Effective Light Energy Conversion
Youngshik Cho, Min Soo Jeon, Hanmin Jang, Heung Soo Lee and Dong Rip Kim; Hanyang University, Korea (the Republic of)

Herein, we experimentally demonstrate the successful fabrication of three-dimensional (3D) gallium nitride on silicon (GaN-on-Si) light-emitting diodes (LEDs) using 3D Si micro-scale structures on which multiple facets of {111} crystal planes are formed for effective light energy conversion. Hetero-epitaxial integration of GaN LED layers over 3D Si micro-scale structures by metal organic chemical vapor deposition not only forms continuous GaN layers on top of Si, but also achieves excellent crystal quality of GaN layer due to the effective release of the strain energy by the faceted structures of Si. Our GaN layers formed on 3D Si structures have threading dislocation densities (TDD) comparable to the GaN grown over the sapphire substrates. In addition, the formed GaN layers have unique 3D morphology favorable to the enhanced light emitting characteristics, while they exhibit broadband, multi-color emission characteristics due to the anisotropic formation of multiple quantum well (MQW) layers in the 3D structures, leading to realize full-color light emitters. While utilizing the advantages of 3D micro-scale structures, our approach to create GaN-on-Si LED with effective light energy conversion characteristics can be utilized to realize high performance optoelectronic devices for diverse applications.

Acknowledgement
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EN10.16.02
Enhanced Electroluminescence Intensity Using Voltage Waveform Control in Alternative-Current Driven Organic Light-Emitting Diode
Byeong-gon Kim, Duck-Kyu Lim, Jun-Chan Choi and Hak-Rin Kim; Kyungpook National University, Korea (the Republic of)

In this work, we introduce an asymmetric voltage waveform to operate the AC-driven organic light emitting devices (OLEDs) for an increased amount of exciton generation. The device structure is the substrate/indium tin oxide electrode / polyimide / poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) with carbon nanotube (CNT) / aluminum (Al) electrode. In our proposed asymmetric structure, two types of charge carriers are injected from Al electrodes according to the electric field conditions. The energy barrier of hole injection from Al electrodes can be reduced by introducing CNT dispersion into the poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) layer. The holes injected through the CNT path accumulate on the PI/PFO interface and the excitons are created in the inverted field conditions. The hole injection barrier has lower CNT (0.7 eV) energy barrier than PFO's highest occupied molecular orbital energy
level injection barrier (1.5 eV). Therefore, the holes accumulate at the PFO/PI interface using the CNT paths. The electrons are injected into the lowest unoccupied molecular orbital energy level injection barrier (1.5 eV) of the PFO at the Al electrode. In this structure, the electrons have the mobility of PFO and the holes have the mobility of CNT. Holes are injected along the CNT channel during a positive cycle. At the same time, the charge carriers are generated in the CNT and the generated electrons generate weak light inside the PFO layer together with holes injected through the CNT. Weak light is generated due to the low density of electrons generated in the CNT during the positive cycle. The holes generated from the CNTs move to the PFO/PI interface and accumulate together with the holes injected through the electrodes. In the negative cycle, electrons can be injected and transported following the PFO paths. The injected electrons recombine with the holes generated by the electric field in the CNT, and the generated electrons and injected electrons move toward the PFO/PI interface. When the opposite polarity is applied, holes in the PFO/PI interface rapidly move toward the Al electrode. Since the hole mobility of CNT is much faster than the electron mobility of PFO, injected electrons and accumulated holes form excitons near the Al electrode. The hole mobility of CNTs is much faster than the electron mobility of PFOs of around 10^{-5} cm^2/Vs. Therefore, when a negative cycle is initiated, the holes at the PFO/PI interface recombine with the electrons injected near the Al electrode or rapidly escape through the electrode. More accumulated holes are needed to increase the amount of excitons that emit in combination with injected electrons. Therefore, if the positive cycle is longer than the negative cycle, the number of holes accumulated increases, and the probability of recombination the injected electrons and accumulated holes increases.

In our experiment, at the same operating voltage (40 V) and frequency (600 kHz) conditions, the electroluminescence (EL) intensities can be higher or lower according to the asymmetric waveform than that operated in conventional symmetric waveform, where the relative total EL intensities are 1.7:1:0.8 for samples operated at the waveforms having the relative polarity duration ratios.

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EN10.16.03
3D Bromide Hybrid Perovskite–Based Microcavity for Large Surface and Low-Cost Polaritonic Applications
Paul Bouteyre1, Hai Son Nguyen2, Jean-Sébastien Lauret1, Gaëlle Trippé-Allard1, Géraud Delport1, Ferdinand Lédée1, Hiba Diab1, Ali Belarouci2, Christian Seassal2, Damien Garrot3, Fabien Bretenaker1 and Emmanuelle Deleporte1; 1Laboratoire Aimé Cotton, CNRS, ENS Paris-Saclay, Université Paris-Saclay, France; 2Université de Lyon, Institut des Nanotechnologies de Lyon - INL, UMR CNRS 5270, CNRS, France; 3Groupe d’Etude de la Matière Condensée, Université de Versailles Saint Quentin En Yvelines, Université Paris-Saclay, France

Since a couple of years, the hybrid organic-inorganic perovskites CH$_3$NH$_3$PbX$_3$, with X a halogen (I, Br, Cl), have emerged in the framework of photovoltaics and for light-emitting devices such as electroluminescent diodes and lasers. One of the main advantages of these materials is that they can be low-temperature and solution processed. Thus they can be deposited in large surface, which is suitable for wide-scale wafers and devices, with a low cost.

We consider here a one-dimensional planar microcavity containing a large-surface (1 cm$^2$) spin-coated CH$_3$NH$_3$PbBr$_3$ thin film as the optically active material. We choose this hybrid perovskite, emitting in the green range, to address the problem of the green gap for lasers and LEDs. We demonstrate the strong coupling regime between the photon mode of the Fabry-Perot cavity and the excitonic mode of the perovskite at room temperature even with a low-quality factor of the order of 100 [1]. This leads to the formation of the so-called polaritons, which are a linear and coherent superposition of the exciton and photon states.

Up to now, the strong coupling regime with 3D halide perovskites has been obtained for bromine or chlorine-based nano/micro-platelets or nano/micro-wires. The observation of polaritons in a spin-coated microcavity is particularly significant because it opens the route to new large surface and low-cost optoelectronic devices based on polaritonic effects, operating at room temperature and compatible with electrical injection. Indeed, all-optical logical devices on a single chip constitute the perspective of polaritons at room temperature: a large-area device is required to propagate the encoded information in the polaritonic flow across macroscopic distance.

This work has been financially supported by the National French Agency for Research, in the framework of the projects EMIPERO and POPEYE. The work of P. Bouteyre is supported by the Direction Générale de l’Armement (DGA).
References


EN10.16.04
From Photoluminescent Nanoparticle Powders to Ceramics—Process induced Barium Distribution between Particle Volume, Surfaces and Interfaces of MgO Nanocrystals Oliver Diwald, Thomas Schwab, Hasan Razouq, Gregor Zickler and Matthias Niedermaier; University of Salzburg, Austria

The rational design of nanoparticle based oxide ceramics is an important prerequisite for both, materials chemistry and physics and the manufacture of advanced materials with unprecedented optical properties.[1] Moreover, the search for suitable luminescent materials of sufficient availability, low cost and biocompatibility is of great scientific and economic interest. A possible approach to substitute currently used rare earth materials or heavy metals in optical applications, which feature luminescent properties in the visible range of light is the use of highly dispersed alkaline earth oxides (MgO, CaO, SrO and BaO). The emission properties of ionic surface dopants and segregated metal oxide clusters originate from surface exciton annihilation at low coordinated surface sites.[2]

In this study, a hybrid chemical vapour synthesis approach was used to incorporate impurity ions, such as Ba(2+), into the nanocrystalline MgO host lattice within the Mg-combustion flame.[3] Subsequent vacuum annealing promotes ion diffusion within the non-equilibrium solids, leads to particle reorganization and, ultimately, to the surface and interface decoration of the MgO nanocrystals with nanometer-sized photoluminescent BaO segregates. Structure characterization work performed with the help of X-ray diffraction and Transmission Electron Microscopy (TEM) revealed Ba-concentration dependent trends in nanoparticle growth. Moreover, annealing provides means to control impurity localization [3] and to trigger Ba-segregation within the MgO nanocrystals, as studied with Energy Dispersive X-ray Spectroscopy (EDX). The surface functionalization of the MgO nanoparticles leads to significant changes of the optical properties, showing BaO specific absorption bands (Ultraviolet-Visible-Spectroscopy) and both, a strong increase and a shift of the materials’ photoemission properties into the range of visible light (Photoluminescence).

After powder consolidation the controlled manipulation of impurity ions affects composition, energetics and, thus, the optical properties of constituent grains and grain boundaries. The here established understanding of impurity segregation including the important influence of surrounding atmospheres during processing was employed to functionalize the intergranular regions inside alkaline earth oxide nanoparticle derived ceramics. We tracked characteristic photoluminescence emission features that are specific to the surface excitonic properties of highly dispersed alkaline earth oxide ions and clusters as a diagnostic tool [2] and found that the properties could have been retained during consolidation and sintering.


EN10.16.05
Citric-Acid-Based Carbon Dots with Luminescence Quantum Yields > 50%—Spectral Tuning of the Luminescence by Ligand Exchange and pH Adjustment Florian Meierhofer1,1, Frank Dissinger2, Florian Weigert1, Siegfried Waldvogel2, Ute Resch-Genger1 and Tobias Voss1,1; 1Braunschweig University of Technology, Germany; 2Johannes Gutenberg University, Germany; 1Braunschweig University of Technology, Germany; 1Federal Institute for Materials Research and Testing, Germany

We report the synthesis and characterization of carbon nanodots (CDs) with high quantum yield (η>50%) and tailored optical absorption as well as emission properties. A well-described protocol with polyethyleneimine (PEI) as amine precursor is used as a reference to a new CD system which is stabilized by aromatic 2,3-diaminopyridine (DAP) molecules instead. The DAP stabilizer is installed in order to red-shift the absorption peak of the n-π* electron transition allowing efficient radiative recombination and light emission. Size, shape, and chemical composition of the samples are determined by (HR)TEM, EDX and FTIR-spectroscopy. Optical parameters are investigated using UV-VIS, PL and QY measurements. Several parameters such as concentration, excitation wavelength and pH are studied. Zeta-potential analysis indicate that pH-induced (de-)protonation processes of functional moieties directly affect the n-π* energy bands. This results in unique pH-dependent absorption and emission characteristics which are discussed on the specific chemical composition of each CD system.
Quantum Efficient Semiconducting Nanocrystal and Passivation Layer for Optimal Opto-Electronic Application

Taliya Gunawansa, Sangram K. Pradhan, Messaoud Bahoura, Jacob Strimaitis and Wagneci Hawley; Norfolk State University, United States

Photoluminescent colloidal quantum dots (QDs) have been enhancing a plethora opto-electronic devices including photodetectors, light-emitting diodes, displays, and solar cells. Incorporating quantum dots into the hetero-junction solar cell process has yielded significant increases in efficiency. A highly favored, cost and time efficient fabrication method of producing optimal tunable quantum dots is a one pot microwave irradiation technique. Water soluble cadmium telluride (CdTe) quantum dots are suitable for hetero-junction solar cells due to their high band-gap photoluminescence quantum efficiencies and mono-exponential exciton decays. Additionally, quantum dot enhanced photo-electrochemical (PEC) solar cells have yielded higher efficiency in charge generation amid the photoanode and electrolyte interface. Various characterization techniques were used to observe the opto-electronic properties of the CdTe QDs: photoluminescence spectroscopy (PL), ultraviolet-visible spectroscopy (UV-VIS), and transmission electron microscopy (TEM). Furthermore, the leakage current, capacitance, and frequency dispersion measurement show the stable performance of our CdTe QDs/Zn NPs hetero-junction solar cell.

Multi-Exciton Interactions and Size—An Interplay for Efficient Two-Photon Induced Gain in Perovskite Quantum Dots

Gabriel Nagamine, Jaqueline O. Rocha, Luiz G. Bonato, Ana F. Nogueira, Carlos H. Brito Cruz and Lazaro Padilha; Universidade Estadual de Campinas, Brazil

Lead bromide perovskite quantum dots (PQDs) have emerged recently as a promising material for lighting applications. Among its properties, we can highlight the defect tolerant structure, which allows for highly emissive nanoparticles, with photoluminescence quantum yield typically higher than 70%, for core only nanoparticles. Also, its facile synthesis opened the perspective for a scalable production for the application of future technologies. Additionally to that, two intriguing properties have been reported recently on the literature: ultra-low amplified spontaneous emission (ASE) threshold (typically in the order of 5-20 μJ/cm²)¹ and an extremely large two-photon absorption cross section (typically in the order of 10⁵ GM)². Although these properties are highly desirable for the application of PQDs in many optical systems, there is still no comprehensive study about the physical mechanism responsible for them. Here, we perform a systematic size dependence study of the two-photon absorption and threshold for two-photon induced ASE of PQDs to investigate the physical origin of these properties³. For the two-photon absorption studies, we analyzed PQDs nanoparticles with sizes ranging from 7.4 ± 0.8 to 12.5 ± 1.5 nm. From that, we report a 2PA cross section at 1.55 eV (transition at 3.1 eV) ranging from 2x10⁵ GM to 7x10⁵ GM. These values are almost one order of magnitude higher than for other visible emitting quantum dots such as CdSe and CdTe. However, by comparing the nanoparticles size, we show that this is just a matter of volume, and not due to any particular strong transition oscillator strength. We also performed size dependent two-photon excited ASE (2PA-ASE) studies on the PQDs. From that, we obtained that the 2PA-ASE threshold in terms of the fluence tends to be higher for the smallest samples, due to the reduced 2PA cross section. However, if we consider the threshold in terms of the average of excitons needed to generate ASE, the observed trend is the opposite, on which the biggest samples present the highest thresholds. In order to understand this unexpected behavior, the bi-exciton binding energies of the PQDs were investigated. From that, we observe a strong anti-correlation between the average of excitons needed to generate ASE and the bi-exciton binding energy, which goes from 41 to 61 meV. This indicates that the strong Coulombic interactions in PQDs are responsible for a red shift on the ASE energy, which causes a significant reduction on the reabsorption losses. This enables ASE with an average of excitons per dot of 0.73 for the smallest nanoparticles, which makes PQDs one of the most promising materials for future applications in the field of lasers.

EN10.16.08
First-Principles Study on the Fundamental Limit in the Homogeneous Linewidth of CdSe Quantum Dot
Sungwoo Kang\(^1\), Youngho Kang\(^2\) and Seungwu Han\(^1\); \(^1\)Seoul National University, Korea (the Republic of); \(^2\)Korea Institute of Materials Science, Korea (the Republic of)

For decades, the quantum dot has been studied as an important class of tunable light emitters with narrow emission linewidths. Although the development of synthetic method has reduced the linewidth contributed from the inhomogeneity in size and shape (inhomogeneous linewidth), the linewidth of single-particle (homogeneous linewidth) still exists because of exciton-phonon coupling, exciton fine structure, and spectral diffusion. It is widely accepted that the main contribution of the homogeneous linewidth is exciton-phonon coupling (~90%), followed by exciton fine structure (~10%). In this study, we develop a theoretical method to calculate the contribution of exciton-phonon coupling in the homogeneous linewidth of quantum dots. Ground-state electronic structure and phonon properties of the quantum dot are studied by density functional theory (DFT) calculations, and excited state is described by delta-DFT framework. Huang-Rhys factor is obtained by projecting structural distortion of exciton structure to phonon mode, and the luminescence spectra is calculated using the parallel approximation. As a model system, we investigate the luminescence linewidth of CdSe quantum dot with various size and structures such as tetrahedron, sphere, and spheroid. Our results are compared with recent experiments that identified the homogeneous linewidths by phonon-correlation Fourier spectroscopy and 2-dimensional electron spectroscopy.

EN10.16.09
Near Infrared Light Emitter of Single-Walled Carbon Nanotubes with Local Functionalization Using Bis-aryldiazonium Modifiers
Tomohiro Shiraki, Boda Yu, Naotoshi Nakashima and Tsuyohiko Fujigaya; Kyushu University, Japan

Single-walled carbon nanotubes (SWNTs) with semiconducting features emit photoluminescence (PL) in near infrared (NIR) regions. The NIR PL generates through a radiative relaxation process of exciton that is a bound electron-hole pair produced by photo-excitation of the tubes. Owing to their unique one dimensional nanostructures, the exciton is stable at room temperature and migrates through the one-dimensional structure.[1] As a new method to utilize the mobile excitons for PL enhancement, defect doping to SWNTs by local chemical functionalization is recently gathering great attention. The locally functionalized SWNTs (lf-SWNTs) show additional PL (\(E_{11}\)) with red-shifted wavelengths and enhanced quantum yields compared to original PL (\(E_{11}\)) of pristine SWNTs.[2-11] Therein, the local functionalization of the tubes creates emissive sites whose electronic structures are modified, giving narrower bandgap and exciton trapping features. Interestingly, the modifier molecules are found to be a key tool to modulate PL of lf-SWNTs. For example, we achieved largely red-shifted PL (\(E_{11}\)) generation over 100 nm-shifts than typical \(E_{11}\) PL by functionalization based on a proximal doping technique.[7] Here, we report chemical functionalization for such longer wavelength PL generation and wavelength tuning based on molecular structure design of the modifiers. Firstly, we synthesized bis-aryldiazonium modifiers (bAs) that have two reactive aryldiazonium groups connected with a methylene linker. In order to achieve wavelength tuning of \(E_{11}\) PL, the linker effects were examined by changing the connected positons on the aryl groups (para and \(m\)bAs for meta) and the length of methylene chains.[11] For local functionalization, SWNTs were solubilized in a D\(_2\)O solution containing sodium dodecyl sulfate (SDS), and then reacted with the synthesized bAs through diazonium chemistry. In PL spectra of the obtained lf-SWNTs (lf-SWNTs-pbA and lf-SWNTs-\(m\)bA), PL peaks appeared at 1245 nm and 1257 nm, respectively when the linker of five methylene units was used. Those were assigned to \(E_{11}\) PL that were observed in longer wavelength regions than \(E_{11}\) PL of mono-aryl functionalized lf-SWNTs (ca. 1140 nm). When the linker lengths of bAs were changed, it’s found that the shorter linkers induced longer wavelength PL. Namely, the methylene chain length is a factor for wavelength tuning of \(E_{11}\) PL. In addition, the lf-SWNTs-\(m\)bA showed larger spectral shifting behavior in the linker length-dependent \(E_{11}\) wavelength compared to the lf-SWNTs-pbA. Thus, the molecular design of the bis-aryldiazonium modifiers provides a wavelength modulation technique for \(E_{11}\) PL, which would develop new types of NIR PL nanomaterials applicable to bio-imaging/sensing and telecommunication devices. Details and other functionalization methods will be discussed at the meeting.


**EN10.16.10**

**Chemical Origin of Visible and Near-Infrared Photoluminescence from Graphite-Derived Carbon Dots**

Yoonsang Park¹ and Woosung Kwon²; ¹Pohang University of Science and Technology, Korea (the Republic of); ²Sookmyung Women’s University, Korea (the Republic of)

Carbon dots (CDs) have unique photoluminescence (PL) properties arising from their surface functional groups and carbon core. However, unclear microscopic origin of the visible and near-infrared PL from CDs hinders attempts toward energy modification and limits their practical use. Here, we investigate the chemical origin of the visible and near-infrared PL of graphite-derived CDs (gCDs) by manipulating their chemical structures via reduction and deprotonation. The relation between chemical and PL changes resulting from these modifications are thoroughly investigated. Using time-resolved spectroscopy, we establish the roles of functional groups and carbon cores in excitation of the energy states responsible for the visible and near-infrared PL. We find that oxidized sp³ carbon matrix and small sp² carbon clusters are responsible for resonantly excited and slightly tunable emission in the visible and the near-infrared, respectively.

**EN10.16.12**

**Highly Efficient AlGaN Deep Ultraviolet Light-Emitting Diodes with Localized Surface Plasmon Resonance by 40 nm Al Nanoparticles Array Using Block Copolymer Self-Assembly**

Gyeongwon Ha and Jin Kon Kim; Pohang University of Science and Technology, Korea (the Republic of)

AlGaN-based deep ultraviolet(DUV) light-emitting diodes(LED) have ability for sterilization, air/water purification, medical treatment and so on. However, most of DUV leds have low external quantum efficiency due to inherent problem such as low internal quantum efficiency and light extraction efficiency. These factors limit their practical applications. Here, We present a remarkable enhancement in AlGaN light-emitting diodes (LEDs) through the coupling of localized surface plasmon (LSP) mediated by a high density array of Al nanoparticle (NP). The array of Al NP with the optimum resonance diameter of ~ 40 nm for 285 nm DUV emission has been achieved by utilizing block copolymer self-assembly. The internal quantum efficiency is increased by 57.7% owing to the reduced radiative recombination lifetime mediated by LSP. As a consequence, the AlGaN DUV LEDs with the array of Al NP show the enhanced electroluminescence by 33.7% with comparable electrical properties to the reference devices.

**EN10.16.13**

**New Sulfide Precursor with Tunable Decomposition by Lewis Base for Controlled Shell Deposition on Quantum Dot Cores**

Joonhyuck Park and Hee-Sun Han; University of Illinois at Urbana Champaign, United States

Deposition of high quality, tailored shell is a key to achieve the optimal optical properties of quantum dots (QDs) such as high quantum yield, suppressed blinking and fluorescence stability. Commonly used sulfide precursors for shell deposition include bis(trimethylsilyl) sulfide (TMS₂S), thioureas and alkylthiols. Shell deposition is mostly achieved by slow injection of these precursors into a reaction pot containing QD cores at elevated temperature. For these precursors, the decomposition rate of precursors is only controlled by reaction temperature. As reaction temperature also governs the reactivity of the quantum dot surface, it is hard to independently tune the reactivity of precursors without affecting the instability of nanocrystals. Here, we present a new sulfide precursor whose decomposition rate depends on the structure and basicity of added Lewis base. We have studied the decomposition rate of the new precursors with various Lewis base molecules using variable temperature nuclear magnetic resonance spectroscopy and a dip probe that monitors absorption during shell growth. In this talk, I will introduce a new shell deposition method using this new precursor and Lewis base molecules that yields high quality shell.

**EN10.16.14**

**Enhanced Efficiency of InP Quantum Dot Light-Emitting Diodes by Metal Doped ZnO Electron Transport Layer**

Jaeyoul Kim¹, Byeong Guk Jeong², Wan Ki Bae² and Jeonghun Kwak¹; ¹Seoul National University, Korea
Quantum dot (QD) light-emitting diodes (QLEDs) have been gaining much attraction in the display and lighting industry due to their superb characteristics such as size-dependent bandgap tunability, narrow emission spectra, and low cost solution process. Although cadmium (Cd) QLEDs show excellent device performance, the toxicity is a serious concern for applications. Among eco-friendly QD materials, indium phosphide (InP) QDs are the most promising candidate for developing high-performance displays with a wide color gamut. However, the performance of InP QLEDs is still far behind compared to Cd QLEDs. In this work, we demonstrate that the efficiency of InP QLEDs are greatly improved by adopting metal-doped ZnO nanoparticle as an electron transport layer (ETL). By optimizing the Al doping concentration, we achieved a higher performance, in terms of the peak external quantum efficiency (EQE) of 3.62% compared to the device with an undoped ZnO nanoparticle of 1.81%. Systematic analysis on the optical and electrical properties of the metal-doped ZnO films was carried out to understand the underlying mechanism for the improved device performance. Compared to the undoped ZnO film, the Al doped ZnO film has enhanced electron mobility and reduced energy barrier for the electron injection into the InP QD emissive layer. We believe that the analysis based on the metal-doped ZnO will give further insight into improving and understanding InP QLEDs.

**EN10.16.15**

**Doping InP Quantum Dots with Cu⁺ Slows Down Hot Electron Cooling**

Paul T. Prins¹, Pieter Geiregat², Dirk A. Spruijt¹, Freddy T. Rabouw¹, Celso de Mello Donega¹ and Daniel Vannmaekelbergh¹; ¹Debye Institute for Nanomaterials Science, Netherlands; ²Physics and Chemistry of Nanostructures Group, Belgium

Nonresonant excitation of colloidal quantum dots (QDs) creates hot carriers that subsequently cool down to the band edges or are trapped in localized states. Carrier cooling and trapping typically happens on timescales from femtoseconds to picoseconds, orders of magnitude faster than the nanosecond to microsecond timescales of radiative recombination. Understanding cooling and trapping is relevant for (hot) carrier extraction in photovoltaics and to increase the luminescence output of QDs used as phosphor.

We investigate carrier cooling and trapping in InP QDs with a ZnSe₁₋ₓSₓ shell. Undoped QDs are compared to Cu⁺-doped QDs, where the Cu⁺ ion serves as a designed hole trap. Using pump probe transient absorption spectroscopy with femtosecond time resolution, we are able to monitor the population of electrons in the conduction band. Our comparative study shows that hot electron cooling is almost an order of magnitude slower in the Cu⁺-doped QDs than in the undoped QDs. We ascribe this to rapid hole trapping on the Cu⁺ ion. This confirms the model in which hot electron cooling goes via an Auger-like process, where the hot electron transfers its excess energy to the hole which subsequently relaxes by phonon coupling. In our Cu⁺-doped QDs the hole is trapped on a Cu⁺ ion on sub-picosecond timescales, so the Auger cooling pathway is unavailable to the hot electron. Instead it must cool down via another, slower, pathway, most likely by coupling to high-energy vibrations at the surface of the QDs. This must also mean that hole trapping on the Cu⁺ ion is faster than the Auger cooling timescale of the undoped QDs, which is of the order of 300 fs. Our results provide insight in the behaviour of hot electrons and holes in the short time period after excitation of both Cu⁺-doped and undoped InP QDs.

**EN10.16.16**

**Fast Electron Transfer from Colloidal PbS Nanosheets to TiO₂**

Shashini M. Premathilaka, Yiteng Tang, Tharaka M. Weeraddana and Liangfeng Sun; Bowling Green State University, United States

Colloidal PbS nanosheets are an emerging two-dimensional material for infrared applications. In contrast to the zero-dimensional quantum dot, the anisotropic structure of the nanosheet provides an additional parameter to tune its properties. In this structure, it is possible to independently tune the energy gap (through the thickness) and the other properties (through the lateral size). The other properties include the exciton oscillator strength, the exciton-exciton interaction, and the electronic coupling of the nanosheet with other materials. All of them are important in optoelectronic applications.

The strong coupling between the nanosheet and an electron-accepting material - TiO₂ - enables a fast electron transfer, favoring charge extraction for photovoltaic devices. Our time-resolved photoluminescence spectroscopy results show that it takes less than one nanosecond for the electron to transfer from PbS nanosheets to TiO₂ in a solution. It is about one thousand times faster than the electron transfer from PbS quantum dots to TiO₂ in the same
experimental condition.

**EN10.16.17**

**Synthesis and Photoluminescence Properties of Upconverting Nanomaterials Produced through Laser Ablation in Liquid**

Rosemary L. Calabro, Priya Karna, Dong-Sheng Yang and Doo Young Kim; University of Kentucky, United States

Upconverting nanomaterials are promising in several applications including bioimaging, sensing, photodynamic therapy, drug delivery, photovoltaics, and security. Specifically, NaYF₄ co-doped with Yb³⁺ as a photosensitizer and Er³⁺ as an activator is suitable for biological applications because Yb³⁺ can be excited by photons at 980 nm which have a long-penetration distance in biological tissues. Following the laser excitation of Yb³⁺, photoexcitation energy is transferred multiple times to Er³⁺ from Yb³⁺ before Er³⁺ emits both red and green photons. The overall upconversion efficiency of NaYF₄:Yb³⁺/Er³⁺ is highly affected by the phase with hexagonal (β) phase allowing for much better efficiency than cubic (α) phase. One major challenge in making upconverting nanomaterials feasible for biological applications is to synthesize highly performing β-phase upconverters with good solubility in water. Traditional methods, such as solvothermal synthesis, fall short with limitations including toxic side products, poor solubility in water, high reaction temperatures, long reaction times, and poor control of phase and morphology. Additionally, the conditions required to produce the preferred β-phase may cause damage to capping agents. This presentation will address our novel approach of laser ablation in liquid as a promising alternative for upconverting nanomaterial synthesis. The laser ablation in liquid allows a fast production, fewer chemicals, fewer byproducts, and control over the product by tuning the laser parameters. NaYF₄:Yb³⁺/Er³⁺ targets are prepared by coprecipitation, and then are pressed into a pellet and annealed to convert to β-phase. This is followed by 532 nm pulsed nanosecond laser irradiation of the pellet in either water or in aqueous solutions containing capping agents including citric acid, polyethylene glycol, ascorbic acid, or albumin. The laser irradiation induces formation of smaller particles that are stable in water. The size of the particles can be controlled by the laser fluence and the solubility can be tuned by the choice of capping agents in the liquid during laser ablation. Additionally, the samples produced through laser ablation show improved β-to-α ratios when compared to the annealed pellets. Laser ablation in liquid allows for direct capping of upconverting nanomaterials and the laser conditions can be tuned to prevent damage to the capping agent in solution. Finally, time correlated single photon counting analysis revealed that NaYF₄:Yb³⁺/Er³⁺ samples with capping agents showed longer photoluminescent lifetimes in both the green and red regions due to protection from surface quenching by the capping agent.

**EN10.16.18**

**Enhancing Phosphorescence in Metal-Free Organic Phosphors by Synergistically Combining Contributing Factors**

Ramin Ansari, Jinsang Kim and John Kieffer; University of Michigan, United States

In traditional metal containing phosphors, spin-orbit coupling (SOC) caused by a heavy atom effect of the metal, enhances the intersystem crossing between the first singlet (S₁) and triplet (T₁) states, which results in phosphorescence. Room-temperature phosphorescence (RTP) from metal-free organic phosphors is preferable for applications such as bio-imaging by eliminating toxicities of the standard metal complexes. However, the development of RTP from metal-free organic systems is challenging due to inefficient SOC for lack of heavy atoms. A common strategy to promote SOC for metal-free phosphors involves carbonyl groups that generate π* states. ISC from S₀ (ππ*) to T₁ (ππ*) is allowed according to the El Sayed rule. Furthermore, we have shown that intramolecular halogen effect can dramatically enhance RTP. Inspired by these results, we combine species exhibiting a heavy atom effect, molecular groups obeying El-Sayed rule, and intramolecular halogen bonding to synergistically enhance RTP. Our organic phosphors contain selenium, which is not toxic, bromine, and carbonyl groups. Our experimental and theoretical findings provide useful design guidelines for room-temperature organic phosphors with bio-imaging and sensing applications.

**EN10.16.19**

**Broadband White Emission in Cs₂AgIn₁₋ₓBiₓCl₆ Phosphors**

Matthew Gray and Patrick Woodward; The Ohio State University, United States

Here we report on the photoluminescent properties of the lead-free double perovskite solid solution Cs₂AgIn₁₋ₓBiₓCl₆. The In³⁺ end-member, Cs₂AgInCl₆, is a direct gap semiconductor that absorbs UV light (λ < 350 nm) and shows little to no photoluminescence. Incorporation of Bi³⁺ leads to a strong sub-band gap absorption that peaks in
the near UV (~360 nm) and extends into the visible (λ > 390 nm). This absorption, which is thought to originate from localized 6s2 → 6s1p1 transitions on Bi3+ ions, is split by a Jahn–Teller distortion of the excited state. In-rich samples (0.0 < x < 0.5) show strong photoluminescence that is attributed to radiative decay of self-trapped excitons, with a broad emission peak of significant intensity from 450 to 750 nm. The color of the emitted light is best described as white to yellow-white (CCT = 3119 K), due to the extreme breadth, FWHM ≈ 217(2) nm, of the emission peak. The excitation spectrum extends out to 450 nm for samples near x = 0.25, while the photoluminescent quantum yield (PLQY) reaches a maximum of 39 ± 3% in the x = 0.167 sample. The combination of highly efficient broadband photoluminescence that can be driven by visible photons (λ > 390 nm) emitted from a Ga1-xInxN LED is attractive for solid state lighting applications.

**EN10.16.20**

**High-Efficiency UV Light-Emitting Diodes Based on Catalyst-Free Gd-ZnO Nanotube Array Grown on p-GaN**

Norah Alwadai, Idris Ajia, Bilal Janjua, Boon Ooi and Iman S. Roqan; King Abdullah University of Science and Technology, Saudi Arabia

We report on the successful growth of a high-quality homogenous, hexagonal, well-defined, and vertical n-ZnO nanotube (NT) array on p-GaN films without catalyst or seeding, using pulsed laser deposition to fabricate high-efficiency ZnO NTs/GaN-based UV light emitting diodes (LEDs). The ZnO NTs were in-situ doped with gadolinium (Gd) (0.2 wt%) to increase the donor density and assisting in NT growth. Micro-photoluminescence (micro-PL) measurements reveal that our LEDs show an intense bandedge emission without a defect band. Our findings demonstrate for the first time a novel fabrication method for an electrically pumped Gd-doped ZnO NTs/GaN-based LED operating in the UV range, with a high internal quantum efficiency (> 65%). Scanning transmission electron microscope (STEM) reveal that Gd dopants in the PLD target create in-situ discrete Gd nanolayer (~ 1 nm). No efficiency droop effect is observed at high carrier injection rates, which can be due to the high binding energy of ZnO bound excitons and a negligible Auger recombination. PL measurements and time-resolved PL (TRPL) carrier dynamics investigations indicate that, at room temperature, the LED emission is dominated significantly by the radiative recombination process, confirming that a superior cost-effective UV LED structure can be obtained, with potential application in the large-scale device production.

**EN10.16.21**

**Dynamic Etching and Functionalization of Germanium Nanocrystals for Tunable Photoluminescence**

Shuang Cui, Robert Tenent, Gregory Pach, Nathan Neale and Lance Wheeler; National Renewable Energy Lab, United States

The narrow bulk band gap and large exciton Bohr radius of germanium (Ge) make it an attractive material as a low-toxicity replacement for II-VI and IV-VI semiconductor nanocrystals (NCs) in applications such as optoelectronics, biological imaging, and lithium-ion batteries. NC photoluminescence (PL) is dependent on precise control over the NC size and surface chemistry. NC size is experimentally varied using precursor chemistry and reaction times during Ge NCs synthesis. Here we report a post-synthetic method to simultaneously functionalize the Ge NCs surface and etch Ge NCs to a desired size. UV-Visible absorbance and PL spectroscopy showed quantum confinement effects and strong emission with no dependence on the excitation wavelength. At 7 nm, the PL emission of Ge NCs is blue-shifted from the bulk Ge value of 0.67 to 1.44 eV. Bandgap emission due to quantum confinement is shifted to higher energies of 1.68 and 1.85 eV as etching time is increased. Fine control over the size and surface passivation in one step renders ease fabrication of Ge NCs.

**EN10.16.22**

**The Effect of Molecular Conformations on The Photophysics of External Stimuli-Responsive Organic Emitters—Thermally Activated Delayed Fluorescence vs Room-Temperature Phosphorescence**

Youhei Takeda¹ and Przemyslaw Data²; ¹Osaka University, Japan; ²Silesian University of Technology, Poland

We have developed an organic emitter that displays external stimuli-responsive emission colors ranging from yellow to orange, based on the structure of twisted donor-acceptor-donor (D-A-D) triad comprising of dibenzo[a,j]phenazine as the acceptor and phenothiazine as the conformationally-flexible donors (Chemical Science, 2017, 8, 2677). The D-A-D triad also shows orange thermally activated delayed fluorescence (TADF) in CBP host matrix, and the OLED devices fabricated with the D-A-D emitter nicely shows a high external quantum yield up to ca.17%. More recently, we have revealed that the stimuli-responsive emission color-change is based on the
conformational change at the phenothiazine unit by time-resolved spectroscopy in the film (Journal of Materials Chemistry C, 2019, 7, 6616), where the thermally activated delayed fluorescence and room-temperature phosphorescence processes compete with each other. In this presentation, the effect of conformation of the molecule on emission properties will be discussed.

**EN10.16.23**
Integration of Uponconversion Nanoparticles and Core-Shell Meta-Structure—An Efficient Platform towards Efficient Uponconversion Efficiency

Yu Ting Huang, Ting-Jia Chang, Kanchan Yadav, Hung-I Lin, Monika Kataria, Chun-Che Wang, Yit-Tsong Chen and Yang-Fang Chen; National Taiwan University, Taiwan

Enhancing the quantum efficiency and tailoring the density of states (DOS) of upconversion nanoparticles (UCNPs) have been attracted tremendous attentions due to the applications range from bio-imaging to solar battery under the excitation of near-infrared light source. Plasmonic materials, such as noble nanoparticles or metal-like materials, have been widely used to achieve these goals. However, the intrinsic loss of plasmonic materials limit themselves play the dominant roles for broader applications. Previous results mainly focused on a relatively high pumping power density (MW/cm²) to excite the emission of UCNPs, which are too large for in-vivo imaging usage. Therefore, the demand of reducing pumping power density to achieve efficient quantum efficiency is urgently emerging.

Here, we provide a first integration of UCNPs and core-shell hyperbolic meta-structure, which allows us to drastically reduced the pumping power density (~0.1 kW/cm²) to achieve a giant emission from UCNPs for more than 20 times. This core-shell hyperbolic meta-structure is composed of the core material, SiO₂, with radius of 3 nm and alternative multishells, Au (5 nm)/SiO₂ (3 nm)/Au (5 nm). A continuous coupling effect in between the multishells is created, a pronounced energy is subsequently out-coupled to enhance the emission of UCNPs. As confirmed by the simulation results, the core-shell hyperbolic meta-structure increases the DOS, confines the energy with a higher ability, and transmits these energy to the decorated UCNPs rather than being annihilated. This unique characteristic makes the emission of UCNPs only require ultra-low power of excitation light with an extremely enlarged emission intensity. Our research provides an excellent alternative for the design of hyperbolic meta-structure and offers a new platform for the enhancement of upconversion efficiency, which is very useful for the realization of practical applications in many areas.

**Acknowledgments**
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**EN10.16.24**
Pulsed Laser Synthesis and Superparamagnetic Properties of Metal-Free Nitrogen Doped Graphene Quantum Dots

Muhammad Shehzad Sultan¹, Vladimir I. Makarov¹, Muhammad Sajjad², Brad Weiner¹ and Gerardo Morell¹; ¹University of Puerto Rico - Rio Piedras, United States; ²Austin Peay State University, United States

In this study, we developed a novel approach to synthesize high-quality metal-free Nitrogen-doped graphene quantum dots (N-GQDs) with high quantum yield, via irradiation of s-triazene in a solution with benzene by using pulsed laser. The TEM, HRTEM, XPS, XRD, Raman spectroscopy and FTIR were carried out to observe the morphology, size distribution, crystalline structure and to prove successful doping of GQDs with nitrogen atoms. Furthermore, for the first time, to our knowledge, their magnetic properties were investigated. The results indicate that N-GQDs exhibit superparamagnetic behavior. The specific size, shape and zigzag edge structure of N-GQDs were considered to explain the origin of the observed magnetism. The magnetization dependence led to estimating the N-GQD material magnetic permeability for different ambient temperatures. From the zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements, carried out at 50 Oe magnetic field strength, we estimated the blocking temperature $T_B$ to be around 300 K. Based on the experimental data analysis, the magnetic permeability, number of correlated spins per single N-GQD, and number density of superparamagnetic N-GQD per gram of material were estimated. The excellent superparamagnetic properties together with optical properties manifested by N-GQDs have the potential to lead to high performance biomedical applications.
Development of Solution-Processable Blue OLEDs Based on Thermally Activated Delayed Fluorescence (TADF) with Spiroacridine Donor

Chul Woong Joo, Nam Sung Cho, Jaehyun Moon, Seung-Youl Kang, Seong-Deok Ahn, Yun Hi Kim, Jonghee Lee and Hyunkoo Lee; ETRI, Korea (the Republic of); Gyeongsang National University, Korea (the Republic of); Hanbat National University, Korea (the Republic of)

Solution-processed Organic Light-Emitting Diodes (OLEDs) have attracted great attention as a device for application in large-size OLEDs because of simple fabrication process and easy scalability of the solution process. However, the device performances of the solution-processed OLEDs are still inferior to those of vacuum-deposited OLEDs and further improvement of the device performances of solution-processed OLEDs is required. In this work, high-efficiency solution-processed blue organic light-emitting diodes (OLEDs) were developed using two thermally activated delayed fluorescence (TADF) aromatic molecules, 10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)-2,5-dimethylphenyl)-10H-spiro[acridine-9,9'-fluorene] (TXSA) and 10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-methylphenyl)-10H-spiro[acridine-9,9'-fluorene] (TTSA), composed of spiroacridine donor and triazine acceptor units. As a result, the blue OLEDs based on two novel TADF molecules exhibited remarkable electroluminescence with a high quantum efficiency of 14.9% and current efficiency of 29.3 cd/A. Our results demonstrate that TXSA and TTSA TADF molecules are prospective materials to fabricate high-performance solution-processed blue OLEDs with a simple device structure. Detailed device performances using TADF molecules will be presented in the presentation.

Current Transport Mechanism and Photodetection in Graphene Quantum Dot/GaN Schottky Contacts

Bhishma Pandit and Jaehee Cho; Chonbuk National Univ, Korea (the Republic of)

Graphene, as a typical 2-dimensional material, becomes a promising material due to its excellent electrical and thermal conductivity, flexibility, and high transparency. While the semi-metallic property of graphene limits the compatibility with the optoelectronic devices, graphene quantum dot (GQD) facilitates its implementation for various optoelectronic devices, enabling multifunctionality in sensing and emitting devices, because the quantum size effect provides the way to tune the energy bandgap of graphene. In this regard, understanding the current transport mechanism between GQD and semiconductor materials is obviously fundamental to explore.

In this study, we investigated the contacts of GQD formed on a n-type GaN semiconductor. Blue-luminescent GQDs (QD size < 15 nm) prepared by the hydrothermal method were sprayed on a GaN wafer and the electrical and optical properties of the fabricated contacts were measured. The GQD/GaN contacts showed rectifying behavior with a typical Schottky barrier height of 0.64 eV. The spectral photoresponse and temporal response of the GQD/GaN contact revealed that the responsivity shows a sharp increase for the wavelength shorter than 375 nm. Furthermore, the metal–semiconductor–metal (MSM) photodiode with interdigitated GQD contacts on n-type GaN was fabricated, which provides the lower dark current in comparison with the GQD/GaN Schottky diode. The responsivity of the MSM photodiode was remarkably improved with increasing the annealing temperature (up to 800 °C), showing good photoresponse in the ultraviolet (UV) region.


Three-Dimensional Whispering Gallery Mode Laser from AlInGaN-Based Rolled-Up Microcavity

Yufeng Li, Peng Hu, Xilin Su and Feng Yun; Shaanxi Provincial Key Laboratory of Photonics & Information Technology, Xi’an Jiaotong University, China; Solid-State Lighting Engineering Research Center, Xi’an Jiaotong University, China

Microcavities with whispering gallery modes (WGM), usually formed by two dimensional (2D) circular structures, are significant elements in integrated optics, quantum information and topological photonics. We report three-dimensional (3D) WGM from rolled-up microdisks and microtubes consisting of strain-released AlInGaN multiple quantum wells structure membranes. For the rolled-up microdisk, despite the ultrathin and deformed cavity laser, the
2D WGM shows a reasonably high quality factor (~1300) and exhibits single mode lasing in vertical direction due to the anisotropic feature of the rolled-up disk. For the microtube cavity, a highly polarized stimulated emission was achieved at a low threshold of 415 kW/cm². A high spontaneous emission factor $\beta$ of 0.46 was obtained due to large cavity confinement factor of 25.1% achieved by large refractive index contrast between the membrane and the ambient air. Our results suggest promising and practical pathways for achieving novel microcavities lasing with III-Nitride material system for on-chip application.

EN10.16.28

Intraband Mid- and Long-Wave Infrared PbS Colloidal Quantum Dots Photodetectors Enabled by Robust Heavy Doping

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Photodetection in the mid and long-wave infrared (MWIR, LWIR) is of paramount importance for applications in night-vision, medical diagnosis, astronomy, environmental pollution monitoring, spectroscopy, and telecommunications. However, commercial infrared detectors are costly due to their epitaxial growth methods and complex non-monolithic integration with CMOS technology. Moreover, their performance is optimized upon cooling adding further complexity to their integration, power consumption, and miniaturization. The possibility of exploiting low-energy intraband transitions make colloidal quantum dots (CQD) an attractive low-cost alternative to expensive low bandgap materials for infrared applications. Unfortunately, fabrication of quantum dots exhibiting intraband absorption is technologically constrained by the requirement of controlled heavy doping, which has limited, so far, MWIR and LWIR CQD detectors to mercury-based materials. We have developed a robust doping strategy for PbS quantum dot solid-state films that allows harvesting of mid- and long-wave infrared radiation, well beyond the reach of PbS even in its bulk form. Our doping method leads to simultaneous interband bleach and an increase of intraband absorption. We show doping to be stable under ambient conditions for up to 2 months; therefore allowing, for the first time, to realize intraband PbS CQD photodetectors for energies below the bulk bandgap, in the 5-9 µm range. We also show that the doping is stable at low temperatures, which allows them to be used in sensitive photodetectors and other potential applications such as bolometers.

EN10.16.29

Broadband White-Light Emission from Supramolecular Piperazinium-Based Lead Halide Perovskites Linked by Hydrogen Bonds

Mi Hee Jung; Sejong University, Korea (the Republic of)

We demonstrate white-light emission using lead halide perovskites: (pip)$_2$PbBr$_6$ (pip = piperazine), (pip)$_2$Pb$_4$Cl$_{12}$, (1mpz)$_2$PbBr$_6$ (1mpz = 1-methylpiperazine), and (2,5-dmpz)$_0.5$PbBr$_3$ 2((CH$_3$)$_2$SO) (2,5-dmpz = trans 2,5-dimethylpiperazine, abbreviated as (2,5-dmpz)$_0.5$PbBr$_3$), in which the inorganic frameworks were connected by piperazinium dications through hydrogen bond, forming a three-dimensional supramolecular network. From single-crystal X-ray diffraction measurements and Raman spectroscopy, we identified the crystal structures and local environmental vibrational mode in the inorganic framework, finding that (pip)$_2$PbBr$_6$ crystallized in the centrosymmetric orthorhombic space group Pnnm, whereas (pip)$_2$Pb$_4$Cl$_{12}$ crystallized in the trigonal/rhombohedral space group R3. The zero-dimensional (1mpz)$_2$PbBr$_6$ structure crystallized in the centrosymmetric monoclinic space group P2/n, whereas the [PbBr$_6$]$^{4-}$ octahedral was separated by 1-methylpiperazine dication. The (2,5-dmpz)$_0.5$PbBr$_3$ 2((CH$_3$)$_2$SO) contained a half cation, which was completed by inversion symmetry, along with two dimethyl sulfoxide solvent molecules that crystallized in the monoclinic space group P2$_1$/c. Among the perovskites, (2,5-dmpz)$_0.5$PbBr$_3$ 2((CH$_3$)$_2$SO) exhibited the longest carrier lifetime (42 ns), the lowest band gap (2.34 eV), and the highest photoluminescence quantum yield (58.02%). This is because it is a 1D corner-sharing structure and has the localized electronic states near to the conduction band minimum, which contributes to high photoluminescence quantum yield and white-light emission.

EN10.16.30

General Synthetic Route to High-Quality Colloidal III–V Semiconductor Quantum Dots Based on Pnictogen Chlorides

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The synthesis of colloidal III–V quantum dots (QDs), particularly of the arsenides and antimonides, has been limited...
by the lack of stable and available group V precursors. In this work, we exploit accessible InCl₃- and pnictogen 
chloride-oleylamine as precursors to synthesize III–V QDs. Through coreduction reactions of the precursors, we 
achieve size- and stoichiometry-tunable binary InAs and InSb as well as ternary alloy InAsₓSbx QDs. On the basis 
of structural, analytical, optical, and electrical characterization of the QDs and their thin-film assemblies, we study 
the effects of alloying on their particle formation and optoelectronic properties. We introduce a hydrazine-free 
hybrid ligand-exchange process to improve carrier transport in III–V QD thin films and realize InAs QD field-effect 
transistors with electron mobility > 5 cm²/(V s). We demonstrate that III–V QD thin films are promising candidate 
materials for infrared devices and show InAsₓSbx QD photoconductors with superior short-wavelength infrared 
(SWIR) photoresponse than those of the binary QD devices.

EN10.16.31
Decoding Fluorophore X—Characterization of a Novel, Non-Blinking, Single Photon Source Nicole Cogan¹, Zoran Ristanovic², Michel Orrit² and Todd Krauss¹; ¹University of Rochester, United States; ²Leiden University, Netherlands

Quantum light-matter interfaces are at the heart of quantum optics and solid-state approaches to quantum 
information science. In particular, single photon sources are highly desirable for photonic quantum sciences, such as 
quantum communication and quantum cryptography, in order to ensure physical security and protect information 
travelling over channels. Novel single photon sources are rare because they must satisfy a very strict set of criteria: 
the photons from such a source must be indistinguishable with an arbitrary high repetition rate, have near zero 
probability of multiple photon emission, and should operate at room temperature. An ideal single photon source 
should also emit photons deterministically at arbitrary times, or “on demand”.

We have discovered a potentially new single-photon source, denoted here as Fluorophore X. Single molecules of 
Fluorophore X exhibit a distinct three-peak photoluminescence (PL) spectrum centered at 610 nm, reminiscent of an 
organic dye. However, unlike a typical dye, the PL from Fluorophore X is extremely bright and robust, with a 
brightness comparable to small diameter CdSe nanocrystal quantum dots. PL from single molecules of Fluorophore 
X has a constant intensity (i.e. are nonblinking) with the ability to remain “on” for several minutes before turning 
“off”. This behavior is also quite different from traditional fluorophores, which typically photobleach quickly and/or 
exhibit fluorescence blinking. Notably, Fluorophore X exhibits photon antibunching at room temperature, with a 
g²(0) < 0.21. Interestingly, while Fluorophore X was originally observed over 20 years ago using single-molecule 
PL spectroscopy, in the intervening two decades it has been repeatedly misidentified as either an organic dye, a 
colloidal semiconductor or oxide nanoparticle, or as an “impurity” in various solvents, polymers, dyes, and 
substrates. In an important breakthrough, we have developed a simple method to synthesize and purify Fluorophore 
X in relatively large concentrations, which has enabled acquisition of the first ensemble PL, photoluminescence 
excitation (PLE), and absorption spectra of this molecule, at 300 K and at 10 K. While the PL spectrum and PL 
lifetime (few ns) are similar to a molecular dye, the unusually small Stokes shift of 10 nm (at ~ 600 nm) between 
absorption and PL spectra as well as the outstanding single molecule PL photostability suggest that Fluorophore X 
also has similarities to inorganic emitters. In fact, no small molecule is known to exhibit all these properties, making 
the structure and composition of this new and exciting single-photon source completely unknown. In that regard, in 
addition to the photophysical characterization of Fluorophore X, we will present NMR and mass spectrometry data 
that will shed important light on its molecular composition and structure.

EN10.16.32
Photoluminescence of High-Quality and Biocompatible Graphene Quantum Dots Synthesized by Hydrogen-Assisted Vacuum Pyrolysis of Silicon Carbide for Bioimaging Application Naeun Lee, Heonyong Jeong, Sang Yoon Lee, Jung Woo Kim, Hyung San Lim and Sung Oh Cho; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Graphene quantum dots (GQDs) which are composed of few layers graphene have superior characteristics such as 
large surface area, tunable photoluminescence. Using these characteristics, GQDs are used for bio-imaging, 
biosensing, and drug delivery. Various methods have been developed to synthesize GQDs, however conventional 
methods have some disadvantages such as using harmful chemicals and complicated process. Thus, a facile method 
to produce biocompatible GQDs with simple synthesis process is a major challenge. Herein, a facile route to high-
quality and luminescent GQDs based on hydrogen-assisted pyrolysis of silicon carbide (SiC) without use of harmful 
chemicals are developed. In pyrolysis of SiC, the morphologies of both graphene and SiC surface are significantly
affected by the annealing conditions, particularly the etching rate of Si and C atoms on the SiC surface. In this study, the GQDs were created on the bumpy structure of SiC by controlling the etching rate of Si and C atoms at high temperature. Annealing temperature in study was raised up to 1500°C and maintained for 30 minutes. Fabricated GQDs was detached from the substrate using ethanol and prepared GQD solutions were centrifuged to eliminate large particles detached from the substrates.

The average size of fabricated GQDs were measured to be 2.58 nm and GQDs were composed of few layers graphene. Synthesized GQDs are proven to have highly-ordered crystalline structure by HRTEM and Raman spectra. In Raman spectra, the D to G peak intensity ratio of the GQDs is 0.79 and this value means comparatively high crystallinity. Especially, sharp 2D band were observed in the Raman spectra. X-ray photoelectron spectra and Fourier transform infrared spectra support the high purity of GQDs and suggest the hydrogen termination of GQDs. Moreover, the size of the GQDs could be controlled by adjusting the annealing temperature. As the annealing temperature increases, average size of GQDs was reduced. Synthetic mechanism of GQDs are explained by removal rate of Si and C atoms. When SiC is heated at high temperature in a vacuum, the Si atoms on surface are rapidly removed. Therefore, the surface becomes bumpy and the remained C atoms rearranged to graphene. However, a small amounts of hydrogen in the furnace etch C atoms on surface, interfering with growth, resulting in nano-sized graphene domains are produced. Thus, the GQD are formed on a rough SiC surface.

UV-vis absorption spectra of the high-quality GQDs showed the 2 peaks located at 262 and 327nm. Absorption band at 262nm is originated from a π-π* transition of aromatic C=C bond and the other band at 327 nm are reported in other researches about GQDs. GQDs aqueous solution exhibited the strong PL signals and excitation-independent PL behavior. Furthermore, 3 emission peaks located at 360, 382 and 400 nm were observed in the spectra. The PL excitation (PLE) spectrum of the GQDs showed two broad peaks centered at 290 and 343 nm. The energy difference between these two PLE peaks is comparable to that between the two UV absorption peaks centered at 262 and 327 nm. It is assumed that the photoluminescence of GQDs are attributed to intrinsic emission.

High-quality GQDs exhibited an excellent biocompatibility in living cells. Cell viability test of high-quality GQDs were performed on hepatocytes. Treatments of cells with GQDs for 48 hours at various doses did not significantly affect cell viability in comparison to the control. The microscopic observation revealed that hepatocytes treated with GQDs retained normal cellular morphology. The low cytotoxicity of high-quality GQDs is attributed to the use of no any harmful chemicals in the synthetic process and high-purity. Collectively, these results strongly suggest that high-quality GQDs exhibited the clear PL spectra and excellent biocompatibility with low cytotoxicity. Therefore, high-quality GQDs synthesized by this method are more suitable in the bioimaging fields than existing.

**EN10.16.33**

**Efficient Upconversion Films for Si-Based Photodetectors**

Nidhi Dua, Sandeep Kumar and Madhusudan Singh; Indian Institute of Technology Delhi, India

Production of new materials for near-infrared (NIR) sensing and hyperspectral imaging based on Si-devices with a mature design and process technology is desirable. Efficient harvesting of unutilized infrared photons can also be used to enhance the sensitivity and efficiency of Si-based solar cells and detectors. Upconversion materials absorb multiple infrared (IR) photons and emit a single visible photon obeying energy conservation. Previous results have established the vital importance of obtaining hexagonal phase in the NaYF₄: Yb(18%), Er(2%) system. Doping with Gd(15%) results in a completely hexagonal phase with no minor cubic peaks observed in X-ray diffraction(Rigaku Miniflex benchtop X-ray diffractometer). It is important to establish minimal process conditions needed to achieve an annealed product with the highest photoluminescence efficiency. Fixing anneal time at 24 hours under ambient atmosphere, we find that after annealing at 400°C, a mixed-phase appears. Above 500°C, cubic phase dominates over the hexagonal phase, with a corresponding reduction in photoluminescence efficiency observed with 785 nm (intensity ~ 557 mW/cm²) excitation. A colorimetric change in upconverted emission from green (400°C, 539 nm), to red (500°C, 655 nm and 675 nm) is observed with a change in annealing temperature. This signifies that the mixed and cubic phase favors the red emission whereas the hexagonal phase favors the green emission. High-resolution transmission electron microscopy (HRTEM) (FEI TecnaiTF20, 200kV) scans reveal the formation of agglomerated particle clusters upon deposition from a suspension (in ethanol) at all annealing temperatures though spherical particles (~22 nm) can be observed for synthesized temperatures. Morphology of nanoparticles intrinsically changes from spherical to rod-shaped nanostructures in materials annealed at 500°C. Work is ongoing on the functionalization of these nanoparticles to reduce possible effects of concentration quenching, and to produce printable inks. These findings are expected to establish important composition and annealing process steps for the production of efficient upconversion materials and to develop a process for fabrication of low-cost near-infrared detectors.
EN10.16.34
Pressureless Sintering of $\text{M}_2\text{Si}_5\text{N}_8\text{Eu}^{2+}$ ($\text{M}=\text{Ba, Sr}$) Phosphor Ceramic Using MgO, CaO Additives Effect as Sintering Aids Jeong Woo Lee; Korea Polytechnic University, Korea (the Republic of)

$\text{M}_2\text{Si}_5\text{N}_8\text{Eu}^{2+}$ ($\text{M}=\text{Ba, Sr}$) phosphor shows excellent thermal quenching characteristic and a wide wavelength range of spectrum (580–620 nm) from yellow to amber according to Ba and Sr molar ratios, which is used for automotive amber LED light sources.

In this study, the phosphor with various Sr compositions were synthesized by heat-treatment at 1,600°C for 8 h. The fabrication of $\text{M}_2\text{Si}_5\text{N}_8\text{Eu}^{2+}$($\text{M}=\text{Ba, Sr}$) phosphor ceramic plate (PCP) was carried out by dry ball milling phosphor with MgO and CaO as sintering aid. The mixture was compressed into a pellet using uniaxially pressed with a 10 mm round pellet shaped and treated again through cold isostatic pressing (CIP) at 200 MPa for 10 min. These green bodies were pressureless sintered at 1550 – 1650 °C for 4 h under a mixed gas atmosphere of 95% N2+5% H2 to compare density and optical properties. The density of the sintered samples were measured by an Archimedes method and scanning electron microscope (SEM) image. Moreover, the microstructure of sample with EDS analysis of different grains and grain boundaries were observed using a transmission electron microscopy (TEM). The crystal structure was analyzed by an X-ray diffraction system (XRD) with CuKα radiation. When the molar concentration of Sr was 0.2 mol, the wavelength shows 600 nm optical characteristics suited to amber LED. As a result, when the ratio of MgO and CaO using the sintering preparation was 70: 30 ratio, the mixture add with 7 wt% shows the density of 4.318 g/cm3 to exhibit excellent sintering density. These sintered PCPs have excellent effect as adaptive optical characteristics for using an amber light for automotive LED applications.

EN10.16.35
InGaGaN Honeycomb Lattice Nanocolummun LEDs Gyo Imamura1, Keigo Yoshida2, Akihiro Ueno2, Keiji Takimoto1, Rie Togashi1, Ichirou Nomura1, Tomohiro Yamaguchi2, Tohrui Honda2 and Katsumi Kishino1; 1Sophia University, Japan; 2Kogakuin University, Japan

The emission efficiency InGaGaN-based visible LEDs dramatically deteriorates with increasing the wavelength from green to red, because of the lower radiative recombination rate as well as the worsening crystal quality as the InGaN content increases. On the other hand, bottom-up grown InGaGaN nanocolumns (NCs), which possess columnar nanocrystals with diameters ($D$) of typically 30-300nm, exhibit excellent nanocrystal effects such as dislocation-free, 1) lattice strain relaxation and no generation of misfit dislocations at the InGaN/GaN hetero-interfaces. The nanocrystal effects are advantageous for improving the red-emitting InGaGaN NC arrays, demonstrating a high internal quantum efficiency (IQE) of 20% at 600 nm. 2) At the same time, the enhanced photoluminescence intensity at 600 nm via surface plasmon and exciton coupling was observed improving the IQE. 3) The plasmonic effect is effectively introduced in NC LEDs, by depositing the plasmonic metals on the sidewall of the NC LEDs, close to the InGaN active layer, and do not conflicting with the current injection scheme. However, for InGaN NC triangle-lattice array, the spacing between NCs is ordinarily less than 50 nm, which makes the deposition of plasmonic metals on the sidewall difficult. In this study, we investigate novel InGaGaN NC honeycomb-lattice arrays, in which the NCs were arranged in the geometry of a honeycomb. The honeycomb-lattice arrays possess airspaces inside honeycomb structures, revealing the sidewalls of NCs. It is, therefore easy to deposit plasmonic metals on the NC sidewalls, which enables a fabrication of plasmonic NC LEDs. The period of the honeycomb-lattice array ($L'$) is defined by the distance between adjacent honeycomb structure centers. In the experiment, different InGaGaN honeycomb-lattice arrays with 150×150 μm² area were prepared on the same substrate changing $L'$ from 160 to 300 nm, employing the Ti-mask selective area growth (SAG) of RF plasma assisted molecular beam epitaxy. In the SAG, Si-doped n-type GaN were grown on Ti-mask patterned GaN template, preparing GaN NCs at the nanohole mask openings. On the GaN NCs, InGaN active layers were prepared, followed by the growth of Mg-doped p type GaN/AlGaN superlattice (SL) cladding layers. Finally, p-GaN contact layers were grown on the top of NCs. The height of NCs was approximately 800 nm. Beautifully arranged NC honeycomb-lattice arrays were obtained for $L'$ from 160 to 300 nm. The nanocolumn diameter increased with increasing $L'$, the corresponding $D$ were from 123 to 255 nm. Note that the InGaN honeycomb-lattice arrays without p-GaN/AlGaN SL cladding were evaluated by photoluminescence (PL) measurement, observing the PL peak wavelengths of 643 (red) and 577 nm (yellow) for $L'$ of 300 and 230 nm, respectively. Using the pn-junction NC honeycomb arrays (different sample), we made the process to form p and n type electrodes fabricating the InGaN
honeycomb-lattice NC LEDs. To suppress the leakage current, SOG was embedded at the spacing between NCs and the tops of NCs were exposed by a chemical etching. A thin Ni/Al contact layer was deposited on them, followed by the deposition thick ITO transparent electrode of 300 nm thickness. Finally, Ti/Al/Pt/Au metal electrodes of 30 nm diameter were prepared at the center of the 150×150 μm² NC top surface. The emission characteristics were evaluated under the direct current injection. When the injection current was 25 mA, a honeycomb-lattice NC LED with L'=300 nm exhibited the emission spectrum with the peak wavelength of 600 nm (orange emission). This is the first demonstration of InGaN-based honeycomb-lattice NC LEDs suitable for the plasmonic LED structure.

Reference

EN10.16.36
Stability and Doping of Lead-Free Double Perovskite Nanocrystals Yehonadav Bekenstein; Technion–Israel Institute of Technology, Israel

Replacing lead in halide perovskites is of great interest due to concerns about stability and toxicity. Recently, lead free double perovskites in which the unit cell is doubled, and two divalent lead cations are substituted by a combination of mono- and trivalent cations have been synthesized as bulk single crystals and as thin films. Here, we study stability and optical properties of all-inorganic cesium silver (I) bismuth (III) and silver (I) Indium (III) halide nanocrystals with the double perovskite crystal structure. The cube shaped nanocrystals are monodisperse in size with typical side lengths of 8 to 15 nm. The absorption spectrum of the nanocrystals presents a sharp peak, which we assign to a direct bismuth s-p transition and not to a quantum confined excitonic transition. In the case of indium nanocrystals Na+ doping increases the emission which is generally very brad and weak. Using spectroscopy combined with high resolution transmission electron microscopy (TEM) based elemental analysis, we conduct stoichiometric studies at the single nanocrystal level as well as decomposition assays in solution and observe that Ag⁺ diffusion and coalescence is one of the pathways by which this material degrades. Drying the nanocrystals leads to self-assembly into ordered nanocrystal solids, and these exhibit less degradation than nanocrystals in solution. Our results demonstrate that Cs₂AgBiX₆ (X = Cl, Br) nanocrystals are a useful model system to study structure-function relationships in the search for stable non-toxic halide perovskites.

EN10.16.37
Metal–Organic Frameworks as Environment-Friendly White Light Emitters Muhammad Usman, Maximillian Chibuike and Tatiana Timofeeva; New Mexico Highlands University, United States

Replacing the traditional lighting source with white light-emitting diodes (WLEDs) could take a significant bite out of global energy consumption. According to US department of energy, 29% reduction in energy consumption will be achieved by 2025 by replacing current lighting sources with LEDs. In order to resolve the energy crisis and to address the environmental concerns, designing WLED is highly desirable but isn't completely benign or budget friendly. To help reduce the environmental footprint and cost of these lights, we have designed a continuous broadband WLED based on metal-organic framework (MOF). Advantage of MOF-based LED is that alkaline earth metal is used in designing the luminescent material which is more environmental-friendly as compared with commonly used lanthanides. Its continuous emission spectrum resembles the spectrum of ordinary sun light and hence, emits a white light similar to natural light. In addition, the continuous broadband white light originates from a single component; hence the cost of production is much lower than the current technologies. The recent developments to use MOFs as white light emitter will be presented. Our design of this natural light emitter device with advantageous features will open new perspectives for developing environmentally friendly, human-friendly, and energy-saving solid-state lighting materials.

EN10.16.38
Methylammonium Lead Halide Nanocrystals for Efficient and Color Pure Red-LEDs Yasser H. Hassan¹, Jong Hyun Park², Aditya Sadhanala¹, Bo Ram Lee², Richard H. Friend³ and Henry J. Snaith¹; ¹University of Oxford, Canada; ²Ulsan National Institute of Science and Technology (UNIST), Korea (the Republic of); ³University of Cambridge, United Kingdom

Recent advances in the synthesis of methylammonium lead halide perovskite nanocrystals (NCs) bringing them to
the forefront of promising candidates for light-emitting diodes, due to their potential for bandgap tunability through chemical composition, and high luminescence efficiency in the red emission window region. Nevertheless, achieving an effective red electroluminescence emission with bandgap stability is still an ongoing challenge for perovskites. Specifically, mixed halide (doping lead iodide perovskite with bromide ion) is a traditional approach to tune the bandgap to the effective red region; however, photoinduced ion segregation leads to bandgap instabilities. Here, we report highly efficient mixed halide perovskite NCs-based light-emitting devices (PeNCs-LEDs) with high color purity in the red emission window. We study the mechanism behind the instability in these NCs by using X-ray diffraction, in-situ photoluminescence, photothermal deflection spectroscopy, and femtosecond transient absorption measurements. Furthermore, we also present ways to stabilize the emission to obtain highly efficient perovskite NCs-based light-emitting devices. Our work represents a significant advance in augmenting mixed halide perovskites’ both bandgap instabilities and parasitic non-radiative losses in perovskites and thus alleviate the limits in red-perovskite-based light-emitting diodes.

8:30 AM EN10.17.01
Epitaxial Germanium-Tin Nanowires for Nanoscale mid-IR Emitters Michael Seifner¹, Alain Dijkstra², Jos Haverkort² and Sven Barth³,¹; ¹Vienna University of Technology, Austria; ²Eindhoven University of Technology, Netherlands; ³Goethe University Frankfurt, Germany

Germanium can be converted into a purely group IV-based direct bandgap material by alloying with >~9 at% Sn requiring to overcome the solubility limit of < 1 at%. Conventional approaches will not lead to the desired metastable compound and alternative synthesis strategies using kinetically controlled, low temperature growth conditions have to be established. To date, notable photoluminescence in Ge₁₋ₓSnₓ nanostructures is only observed in exceptional cases, mostly limited to the low temperature regime (~100 K) or in an energy range close to elemental Ge nanostructures and not in the IR-regime expected by the nominal composition. This contribution will demonstrate that metallic Sn can be used as both nucleation seed and source for the formation of single crystalline Ge₀.₈₁Sn₀.₁₉ nanowires via a CVD approach. These nanostructures are epitaxially grown on Ge (111) substrates in high yield. Moreover, a clear difference in composition and morphological structure evolution of micro- to nanoscale objects can be observed. STEM-EDX elemental mapping is used to determine the Sn content, while TEM confirms the single crystalline nature of the obtained products. The temperature and laser power dependent photoluminescence analyses verify the formation of a direct band gap material with emission in the mid-infrared region. The emission signal matches the expected energy for unstrained Ge₀.₈₁Sn₀.₁₉ material (e.g. band gap of 0.3 eV at room temperature) and illustrates excellent crystal quality of the nanowires samples. This is the first demonstration of room temperature photoluminescence in Ge₁₋ₓSnₓ nanowires and the optical properties are comparable to the best examples described for thin film samples of this metastable alloy. These materials with band gaps in the mid-IR hold promise in applications such as thermal imaging as well as photodetection and could be used as building blocks for group IV-based mid- to near-IR photonics.


8:45 AM EN10.17.02
Brighter Colloidal PbS Nanosheets as an Infrared Emitter Yiteng Tang, Shashini M. Premathilaka, Tharaka M. Weeraddana, Liangfeng Sun and Antara Antu; Bowling Green State University, United States

As the counterpart of colloidal two-dimensional visible-light emitters, colloidal lead-sulfide nanosheets are the
emerging efficient infrared light emitters with a tunable wavelength covering the whole fiber-optical communication band. Due to the lack of active surfaces such as \{111\} facets, the PbS nanosheets exhibit more efficient and stable optical properties than PbS quantum dots. Our experimental results show that colloidal PbS nanosheets dispersed in an organic solvent can achieve over 60% photoluminescence quantum yield at the wavelength around 1200 nm, exceeding the well-passivated colloidal PbS quantum dots emitting at the same wavelength.

In contrast to PbS quantum dots, the loss of the photoluminescence efficiency is greatly reduced when the PbS nanosheets are transferred from a solution phase to a solid film. The photoluminescence quantum yield of the PbS-nanosheet film reduces to 1/3 of the original nanosheets in solution, instead of around 1/10 as in the case of quantum dots. Thus a photoluminescence quantum yield \( \sim 20\% \) can still be achieved in a film of PbS-nanosheets. After coupling the PbS nanosheet film with a commercial green LED, we have fabricated an infrared LED with a down-conversion efficiency of about 13%.

The photophysics study of this infrared emitter demonstrates its excellent properties. A very narrow photoluminescence emission linewidth (~ 66 meV) has been achieved in the nanosheets even at room temperature. Meanwhile, we observed a sharp optical absorption peak near the band edge. This is the first demonstration of the exciton peak from colloidal PbS nanosheets, proving the existence of excitons in this extended two-dimensional material with a large dielectric constant.

9:00 AM EN10.17.03

(110)-Oriented 2D Halide (X = I, Br, Cl) Perovskites Templated by Small Cyclic Diammonium Cation with White-Light Emission Xiaotong Li\(^1\), Peijun Guo\(^2\), Mikael Kepenekian\(^3\), Ido Hader\(^1\), Claudine Katan\(^3\), Jacky Even\(^4\), Konstantinos Stoumpos\(^5\), Richard Schaller\(^2\) and Mercouri G. Kanatzidis\(^1\); \(^1\)Northwestern University, United States; \(^2\)Argonne National Laboratory, United States; \(^3\)Institut des Sciences Chimiques de Rennes, France; \(^4\)FOTON, France; \(^5\)University of Crete, Greece

Two-dimensional (2D) halide perovskites are emerging light-emitting materials because of their high tunability and outstanding physical properties. Besides the narrow-band emission that provide high color-purity, broad-band white-light emission that originates from self-trapped excitons (STE) in the highly distorted structures is also an intriguing field. The (110)-oriented 2D perovskites are generally distorted and believed to be good candidates for white-light emitting. Here, we report that 3-aminopyrrolidinium (3APr) is a cation which permits the formation of (110)-oriented 2D perovskites for all three halides, in the form of (3APr)\( \text{PbX}_4 \) (X = I, Br, Cl). Structural characterization by single-crystal X-ray diffraction reveals that the distortion of the inorganic part is influenced by the stereocchemical conformation of the cation between the perovskite layers. The high level of distortion results in the emergence of white-light emission, rarely seen in iodide perovskites, as well as the bromide and chloride isostructural analogues, which provides perfect platform to compare the broad emission mechanism for all three halides. The bromide and chloride perovskites show longer lifetimes and higher color rendering index (CRI) (83 and 85), relevant to solid-state lighting. The mechanism as studied by temperature-dependent PL suggests that a different STE mechanism is responsible for the observed broad-band emission for each halide. The detrapping energy is the highest for the chloride compound where the broad-band emission dominates even at low temperature. Comparative studies of white-light emission for all three isostructural halide perovskites as a set may advance the understanding of the mechanism for white-light emission in 2D perovskites.

9:15 AM EN10.17.04

Hybrid-Typed Perovskite Quantum Dots White LEDs for Wide Color Gamut Display Chieh-Yu Kang, Chih-Hao Lin, Chun-Lin Tsai, Chin-Wei Sher, Po-Tsung Lee and Hao-Chung Kuo; National Chiao Tung University, Taiwan

The main advantage of QDs-based WLEDs (quantum dots-based white light emitting diodes) over conventional WLED is high color purity with low cost production. Although there are several ways like QLEDs, QD film in LCD to apply QDs for next generation display, QDs-based WLEDs still have several superior potentials. Compared to QLEDs, they have higher efficiency and better reliability. This design requires fewer quantities of QDs to reach target color point which attributes to reduce cost hugely. Despite of great interest in QDs-based WLEDs, the major two issues that limits the practical applications are their instability and anion-exchange reaction when different QDs mixing together. It is important to develop a suitable packaging type to overcome the anion-exchange reaction in order to get long term stability.

Therefore, we proposed a hybrid-typed structure with blue LED pumping liquid green 518 nm PQD and red 630 nm PQD film. The liquid green PQD is on the top of red PQD film. Compared to the structure using green and red PQD
film (41 lm/W), this hybrid structure owned higher efficiency (51 lm/W) for PQD LEDs. It also showed outstanding color gamut that can be reached to 122 % of NTSC standard and 91 % of Rec. 2020 at a correlated color temperature (CCT) of 5516 K. The thermal resistance of hybrid-typed structure is better than the solid type structure. The device temperature vs current was measured. It shows that for hybrid-typed PQD WLED, the operating temperature will not increase too much with current increasing. The temperature gap between hybrid-typed and solid-typed PQD WLEDs is very big, which is about 15 Celsius degree. This characteristic resulted to better reliability performance at 200 hrs (12% decay).

However, the luminous efficiency and reliability performance is still not good enough to catch up conventional WLEDs' spec. We found that the drop of light intensity comes from the red QD. Thus, to improve this situation, we replaced the red QD to K$_2$SiF$_6$:Mn$^{4+}$ (KSF) for hybrid-typed structure in order to get higher efficiency and reliability without the decrease of color gamut. The light performances of hybrid type using liquid green PQD and 630 nm KSF mixed with silicone was measured. The luminous efficiency can reach to 85lm/W at 10 mA driving and wide color gamut can still be kept (122 % of NTSC and 91 % of Rec. 2020). The reliability results of this hybrid-typed PQD WLEDs have been tested. The light intensity only decays by 6 % at 1000 hours. In this study, we demonstrate that the hybrid-typed PQD WLED has the higher luminous efficiency (85 lm/W) compared to the solid-typed structure and good wide color gamut performance (123 % of NTSC and 92 % of Rec. 2020) and better reliability result show that hybrid-typed structure is one of the choice for next generation display.

9:30 AM EN10.17.05
Quantum Dot Based Flexible Full Color Micro-LED Display Lu Hing Hu, Jae Yong Choi, Sumin Hwangbo and Jong-Hyun Ahn; Yonsei University, Korea (the Republic of)

Gallium Nitride (GaN) based blue light emitting diode (LED) is definitely an emerging technology which already grabbed attention from various fields, including indoor and outdoor lighting systems, displays, and medical devices because of its excellent quality of light illumination. GaN LEDs in micrometer scale can be driven at higher current densities and give promising energy efficiency in light emission. [1] The outstanding performance of micro-LEDs have attracted many researches that study the potential applications of micro-LEDs. [2, 3]

In this report, we have studied method to realize full color RGB micro-LED display by patterning quantum dots (QD) on GaN micro-LED, which will convert blue light into either red or green light. We developed QD-PR that can be photolithographically patterned in micro scale using conventional method. By mixing high refractive index nanoparticles, TiO$_2$ as scattering enhancers into the QD-PR, the light output intensity can be improved and standard RGB can be achieved. In addition, in order to realize flexible micro-LED display, micro-LED array is released from Si substrate by wet etching process and then transferred onto ultrathin plastic substrate. Finally, flexible RGB micro-LED display was demonstrated.

References


9:45 AM BREAK

SESSION EN10.18: Characterization of Nanocrystals and Physics of Pervoskite Devices
Session Chairs: Sohee Jeong and Haizheng Zhong
Friday Morning, December 6, 2019
Hynes, Level 2, Room 208
How Magic-Sized Clusters Grow—Insights from Experiments
Aniket Sandip Mule, Sergio Mazzotti, Aurelio Rossinelli, Simon F. Solari, Marianne Aellen and David J. Norris; Optical Materials Engineering Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, Switzerland

Magic-sized clusters (MSCs) are semiconductor nanocrystals that have well-defined structural and optoelectronic properties. These clusters are believed to grow in discrete steps from one “magic” size to the next. However, even after decades of study, the nanocrystal community does not have a detailed understanding of why “magic” sizes exist and how they grow. This is due in part to the challenges in their experimental investigation, e.g. due to their small size they can be difficult to isolate and image via electron microscopy. Here, we work to overcome these issues by developing a synthetic protocol that yields MSCs up to larger length scales. These particles can be isolated and purified easily using size-selective precipitation. We then analyse a series of these MSCs using a combination of optical (absorption, photoluminescence, and photoluminescence excitation) and structural characterisation (XRD, NMR, and TEM). The comparison of these results with previous reports suggests that the particles exhibit tetrahedral shapes. Based on our observations, we propose an atomistic model that explains the growth of MSCs and rationalizes the existence of their precise structures. This work improves our understanding of nanocrystal growth and could help expand the library of available MSCs.

How Magic-Sized Clusters Grow—A Microscopic Theory
Sergio Mazzotti, Aniket Sandip Mule and David J. Norris; ETH Zurich, Switzerland

Magic-sized clusters (MSCs) are small semiconductor nanocrystals with well-defined structures and characteristic optoelectronic properties. Only a few “magic” sizes with superior thermodynamic stability are believed to exist. They have been shown to grow sequentially, meaning that one “magic” size transitions directly to the next. However, the origin of their stability and the mechanism that determines their growth remain puzzling. Our experiments, in line with previous reports, suggest that MSCs are tetrahedral in shape. Based on these findings, we present a microscopic model that rationalizes their stability and growth. By combining classical nucleation theory and the tetrahedral shape of MSCs, our model explains why MSCs correspond to local minima in a free-energy landscape and why they grow sequentially. Our model can help find other crystalline materials exhibiting the same “magic” growth behavior.

Halide Perovskites—Is it All about the Interfaces?
Philip Schulz; CNRS IPVF, France

The established paradigm, that functionality and performance of a semiconductor device is critically linked to the design of the interfaces in the device, has been a major working hypothesis to access the full potential of halide perovskite (HaP)-based optoelectronics, including photovoltaics and light-emitting diodes. As an example, the rapid improvements in the performance and stability of HaP solar cells mainly originates from careful interfacial design principles and a dedicated interface layout [1]. Despite these successes, many basic physical and chemical properties of HaP thin film and crystal surfaces and at the interface to adjacent layers, e.g. carrier injection layers in the case of perovskite emitters, have been difficult to access. These challenges arise as many key parameters, such as the energy level alignment between transport layer and emitter, are convoluted with the interface chemistry of the multi-component HaP semiconductor.

In my talk, I will present how we employ surface sensitive methods, with a focus on photoelectron (PES) and X-ray spectroscopies, to measure electronic properties, energetics and chemistry at the interface between perovskite films and transport or buffer layers. In particularly PES is used to determine the energy level alignment at the interface. Yet, we face severe challenges to generalize the trends from these observations as the complex chemistry between HaP layer and adjacent semiconductor often lies at the root of the observed interfacial alignment processes and band bending [2]. Furthermore, I will give examples for typical pitfalls that occur, when characterizing HaP surfaces and interfaces with PES methods. Most importantly, beam damages effects have been identified as the perovskite layers can exhibit distinct signs of degradation under vacuum conditions and concomitant irradiation with high-energy photons. However, while we generally intend to avoid these transient effects in our measurements, we can extract additional physical and chemical parameters from the evolution of energy level positions and stoichiometry during
the PES measurements with direct implications on the material stability and degradation pathways [3]. In the second half of my talk, I will discuss the use of these methods to access the effects of surface treatment and interfacial design routes for HaP quantum dot thin films. We demonstrated that treating the surface of CsPbI3 based quantum films with a formamidinium iodide solution led to improved device characteristics of perovskite quantum dot solar cells [4]. By using PES and X-ray absorption spectroscopy techniques, we were able to identify that the surface treatment can be employed for a targeted ligand exchange, opening up a broad application space of these treatments for perovskite quantum dot based light emitting devices [5].


SESSION EN10.19: Synthesis of Inorganic Nanomaterials
Session Chairs: Sohee Jeong and Haizheng Zhong
Friday Afternoon, December 6, 2019
Hynes, Level 2, Room 208

1:45 PM EN10.19.02
Top-Emitting Quantum Dot Light-Emitting Diodes Based on InP Quantum Dots Taesoo Lee, Donghyo Hahm, Kyunghwan Kim and Jeonghun Kwak; Seoul National University, Korea (the Republic of) Cd-free quantum dot (QD) light-emitting diodes (QLEDs) such as InP QLEDs are now being actively researched for the substitute of environmentally toxic Cd-based QLEDs. We can classify the InP QLEDs based on the direction of emission, which are the bottom emission QLEDs (BQLEDs) emitting light through the substrate electrode and the top emission QLEDs (TQLEDs) emitting light through the top transparent electrode. The TQLEDs have several advantages for their use in display devices, such as high aperture ratios and efficient light extraction. In this work, we fabricated InP-based BQLEDs and TQLEDs and compared their optical and electrical characteristics. The TQLEDs showed better optical properties than BQLEDs because the outcoupling through the thin, top transparent silver anode in the TQLEDs was much higher than that through the indium tin oxide (ITO) in the BQLEDs. As a result, the maximum luminance of the TQLEDs was 29300 cd/m², which is 4 times higher than that of the BQLEDs (7400 cd/m²). The full width at half maximum of the electroluminescence (EL) spectrum was also narrowed down from 41 nm of the BQLEDs to 37 nm of the TQLEDs owing to the microcavity effect. The maximum current efficiency of the TQLEDs (9.7 cd/A) was increased by 1.4-fold compared to that of the BQLEDs (6.9 cd/A). Detailed performance and analysis on the TQLEDs and BQLEDs based on InP QDs will be presented.

2:00 PM EN10.19.03
Controlling Intermediates in the Two-Step Growth of PbS Nanocrystals Philippe B. Green, Philip Sohn, Christian J. Imperiale and Mark W. Wilson; University of Toronto, Canada
Advancing the synthesis of PbS nanocrystals for infrared optoelectronic applications requires improved mechanistic understanding of the growth process. Here we demonstrate that the nucleation of PbS nanocrystals is preceded by the formation of a distinct cluster intermediate. This intermediate is characterized by a reproducible red emission spectrum (λpeak: 740 nm) that exhibits a large Stokes shift (hv>300meV). Having revealed a two-step growth mechanism, we explore the manipulation of the cluster reaction lifetime to control nanocrystal growth kinetics. We demonstrate that the addition of diglyme (diethylene glycol dimethyl ether) gives straightforward control of PbS nanocrystal size. This occurs because diglyme accelerates cluster agglomeration, which reduces the number of nascent nanocrystals and results in a larger average size at completion. Further, the shortened cluster reaction lifetime minimizes the duration of the nucleation period, permitting the synthesis of nanocrystals with ensemble
linewidths comparable to leading literature reports at lower reaction temperatures. In sum, we report that the nucleation and growth of PbS nanocrystals proceeds via a two-step mechanism involving a cluster intermediate, and open the door to the use of process additives to tune reaction kinetics and tailor the synthesis of this critical infrared-active nanostructured material.

2:15 PM *EN10.19.04
Towards Ultra-Stable Indium Phosphide Quantum Dots David Wegner, Anass Benayad, Delphine Boutry, Marie Carriere and Peter Reiss; CEA, France

Colloidal semiconductor nanocrystals (quantum dots) possess unique optical properties, which make them attractive emitters for diverse applications in optoelectronic devices and biomedical imaging. During their life cycle, aging of quantum dots can lead to their dissolution and induce high toxicity due to the release of toxic chemical compounds. In this context, InP-based QDs have been proposed as less hazardous alternative to widely studied CdSe-based QDs. To enhance the photoluminescence quantum yield (PLQY) and (photo-)stability, InP QDs are generally capped with a Zn(Se,S) gradient shell. ZnSe acts as a “lattice adapter” due to its lower lattice mismatch with the InP core, while the external ZnS layer(s) are chemically more inert than ZnSe. We demonstrate that this type of shell alone does not provide sufficient stability, neither under controlled ageing conditions in a climatic chamber nor in biological environment. As shown by EXAFS, ageing led to dissociation of In-P and Zn-S/Zn-Se bonds, and to complexation of In and Zn ions with carboxylate and/or phosphate moieties. Moreover, these degradation products exhibited, in contrast to the pristine QDs, significant cytotoxic effects.

To improve the stability, further growth of additional shells on top of the gradient shell was performed, namely an intermediate ZnS shell and an outer alumina shell. In the case of this core / triple shell system continuous irradiation did not induce any chemical modifications detectable by means of XPS. To the contrary, in the case of the core / single shell system with the gradient shell degradation of the ZnS outer layer and oxidation of the In(Zn)P core occurred. These effects were also at the origin of a marked decrease of the PL intensity and a hypsochromic shift of the PL maximum. In summary, the overgrowth of InP-based core/shell QDs with an inert alumina shell leads to strongly enhanced chemical stability without impacting the PLQY. The formation of toxic degradation products under ageing conditions can thus be avoided.

2:45 PM EN10.19.05
Two-Colour Fluorescence Intermittency Spectroscopy—Shedding Light on Blinking in Nanocrystals Minhal Hasham and Mark W. Wilson; University of Toronto, Canada

Colloidal quantum dots (QDs) exhibit narrow emission across the visible and NIR spectrum, and reproducible wet-chemical syntheses produce QDs with size-tunable electronic properties. While already employed in LEDs, solar cells, and biomedical imaging, QDs suffer from photoluminescence intermittency (blinking)\(^1\), which is associated with irreversible photochemical damage\(^2\). The spectroscopic manifestation of blinking is clear—even under continuous above-bandgap excitation, emission from QDs will randomly switch between ON and OFF states, with both states lacking well-defined average lifetimes due to probability distributions that are power-law distributed over many orders of magnitude. However, it has remained challenging for spectroscopic evidence to distinguish between the variety of proposed mechanisms. Here, motivated by previous demonstrations of emission recovery from QD ensembles in the dark\(^3\), we employ a two-colour experiment to modulate the lifetime of the OFF states of QDs. By optically interacting with the OFF state, its lifetime was expected to be truncated at shorter timescales than the minutes/hours observed for thermal recovery at room temperature. However, we did not observe the expected light-driven recovery, even due to local heating. Thus, we consider that the optical cross-section of the dominant OFF state must be small compared to a control experiment using the excited-state absorption of Mn-doped ZnSe QDs\(^4\).

This result is surprising in light of previous thermal recovery kinetics, as the weak oscillator strength is consistent with an OFF state that is different than typical band-edge carriers. By shedding light on the spatial and energetic nature of the state(s) involved in blinking, we will guide modifications to synthetic procedures which produce non-blinking quantum dots, resulting in enhanced long-term photostability.

3:30 PM EN10.20.01
Recrystallized All-Inorganic Lead Halide Perovskite Thin-Films Show Low-Threshold Stimulated Emission and Lasing at Room Temperature
Neda Pourdavoud¹, Tobias Haeger¹, Andre Mayer¹, Manuel Runkel¹, Piotr Cegielski², Ivan Shutko¹, Anna Lena Giesecke², Ouacef Charfi³, Ralf Heiderhoff³, Stefan Zaefferer³, Max Lemme², David Becker-Koch⁵, Yana Vaynzof², Hella-Christin Scheer¹, Wolfgang Kowalsky³, Patrick Görrn¹ and Thomas Riedl¹; ¹Wuppertal University, Germany; ²AMO GmbH, Germany; ³Technical University of Braunschweig, Germany; ⁴Max Planck Institut für Eisenforschung, Germany; ⁵Heidelberg University, Germany

Aside from their remarkable success in photovoltaics, metal-halide perovskites are also highly promising as light emitters. For lasers, perovskites currently seed a new promise for the realization of electrically operated laser diodes that can be prepared from solution at low temperatures on virtually any substrate. The marriage of perovskite active materials with silicon (nitride) photonics holds promise to unlock substantial progress in the field of integrated optoelectronics.

As MA-based organic-inorganic halide perovskites lack intrinsic stability, all-inorganic perovskites, such as cesium lead halides, are particularly promising.

However, most attempts to use thin-films of CsPbX₃ for light emission only led to disappointing results with very low photoluminescence quantum yields (PL-QY) and amplified spontaneous emission (ASE) in CsPbX₃ thin-films has only been achieved at cryogenic temperatures. The poor performance at higher temperatures has been attributed to non-radiative recombination associated with a high number of defects. Unlike the case of thin films, CsPbX₃ nanoparticles (size < 10 nm) or nano-rods showed a high PL-QY and exhibited ASE at room temperature. These results nurtured the paradigm that for efficient light emission from lead halide perovskites at room temperature, one needs to confine the charge carriers/excitons on the nanometer scale to prevent their migration to non-radiative defects.

Here, we present results that challenge this paradigm. We demonstrate thin films of cesium lead bromide, which show a high photoluminescence quantum yield of 68% and ASE at room temperature with low threshold. The continuous films (~ 100% coverage of the substrate) are composed of large crystals with micrometer lateral extension. Our layers result from originally rough as-deposited layers, that were recrystallized by thermal imprint.[1,2] Using these layers, we demonstrate the first cesium-lead bromide thin-film distributed feedback (DFB) and vertical cavity surface emitting lasers (VCSELs) with ultra-low threshold at room-temperature. These results nurture the paradigm that for efficient light emission from lead halide perovskites at room temperature, one needs to confine the charge carriers/excitons on the nanometer scale to prevent their migration to non-radiative defects.

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3:45 PM EN10.20.02
Environmentally Stable Room Temperature Continuous Wave Lasing in Two-Dimensional Photonic Crystal Polycarbonate Perovskite Composite
Jiyoung Moon¹, Masoud Alahbakhshi¹, Abouzar Gharajeh¹, Ross E. Haroldson¹, Sunah Kwon², Zhitong Li¹, Roberta Hawkins¹, Moon J. Kim¹, Walter Hu¹, Anvar Zakhidov¹,² and Qing Gu¹; ¹University of Texas at Dallas, United States; ²ITMO University, Russian Federation
Organic-inorganic perovskites have emerged as a promising laser gain medium due to its high quantum efficiency, balanced ambipolar charge transfer characteristics, strong light absorption, and long carrier lifetime. Various types of perovskite laser have been reported since the first demonstration of amplified spontaneous emission (ASE) from perovskite in 2014 [1]. Synthesis of nanowire or microdisk cavity, or spin-coating of perovskite thin film on pre-patterned structure have been the common method of making perovskite lasers. These devices are mostly tested under pulsed pumping and/or at cryogenic temperature due to their high lasing thresholds. Because of device self-heating at high pump power, their operation under continuous wave (CW) pumping at room temperature is hindered. One way to achieve CW room temperature operation is to reduce lasing threshold by directly patterning the perovskite into a high Q cavity with large mode confinement. However, perovskite’s sensitivity in polar solvents, high temperature and high-electron energy makes direct patterning using conventional lithography challenging. Previously, we showed that direct patterning of perovskite is possible with nanoimprint lithography (NIL), and demonstrated CW lasing with 13W/cm² threshold from a MAPbI₃ distributed feedback cavity at room temperature [2]. However, lasing only sustained for ~250s when operated around lasing threshold.

To achieve stable lasing behavior, in addition to designing for even higher Q cavities to further reduce operational power, we introduce multiplex strategies that include morphological, structural, and interfacial engineering of perovskite thin film. With these considerations, we demonstrate for the first time, over 90 minute-long green CW lasing with 9.4W/cm² threshold from polycarbonate MAPbBr₃ composite in a two-dimensional photonic crystal (2D PhC) cavity without any substrate cooling. This demonstration highlights (i) synergistic effect of high crystallinity of material, high Q cavity, and defect passivation (ii) facile, high output, and controllable fabrication method which can be applied to other types of perovskite and is closely aligned with what industry seeks for mass production (iii) ultra-low lasing threshold and long lasing stability at CW room temperature, making electrically pumped perovskite laser diode look promising.


4:00 PM OPEN DISCUSSION

4:15 PM EN10.20.04
Efficient Light Emitter by Scalable InGaN Nanowire Photonic Crystal Roksana Rashid¹ and Zetian Mi¹,²;
¹McGill University, Canada; ²University of Michigan–Ann Arbor, United States

To the urge for efficient semiconductor light emitters operating in the green gap, we’ve demonstrated InGaN nanowire photonic crystals, including dot-in-nanowires, nanotriangles, and nanorectangles with precisely controlled size, spacing, and morphology, and further establishes that bottom-up InGaN photonic crystals can exhibit highly efficient and stable emission. The formation of stable and scalable band edge modes in defect-free InGaN nanowire photonic crystals is directly measured by cathodoluminescence studies. The luminescence emission, in terms of both the peak position (λ ≈ 505 nm) and spectral linewidths (full-width-half-maximum ≈ 12 nm), remains virtually invariant in the temperature range of 5–300 K and under excitation densities of 29 W cm⁻² to 17.5 kW cm⁻². To the best of our knowledge, this is the first demonstration of the absence of Varshni and quantum-confined Stark effects in wurtzite InGaN light emitters—factors that contribute significantly to the efficiency droop and device instability under high-power operation. Such distinct emission properties of InGaN photonic crystals stem directly from the strong Purcell effect, due to efficient coupling of the spontaneous emission to the highly stable and scalable band-edge modes of InGaN photonic crystals, and are ideally suited for uncooled, high-efficiency light-emitting-diode operation.

4:30 PM EN10.20.05
Design of Novel Deep Ultra-Violet AC-Driven Electroluminescence Devices Based on Boron Nitride Nano-Materials Weiqiang Yuan, Thushan Wickramasinghe and Wojciech M. Jadwisienczak; Ohio University, United States
In this paper we study the prospect of using the hexagonal BN (h-BN) quantum dots and 2D nanosheets for generating deep ultraviolet (UV-C) emission by impact excitation and impact ionization. Our objective was to design and model alternating current driven thin electroluminescence devices (ACTEL) and alternating current driven powder electroluminescence devices (ACPEL) based on h-BN having different nano-morphologies. The recent efforts in developing dc-driven III-nitrides-based deep UV-photonic devices focused on band gap engineering of epitaxially grown heterostructures. Alternatively, one can consider developing UV-C light sources operating on principles of hot electrons impact excitation processes in h-BN material. We have shown by considering the lucky drift model and the Born Approximation (impact excitation cross section) for high field electronic transport in a single h-BN layer, when considering both ballistic and drift modes, that the electroluminescence (EL) efficiency of the ACTEL device is 0.04% when biased at 110 V. The low EL efficiency is primarily due to the long distance (~5 µm) secondary electrons need to pass between subsequent collisions in the h-BN matrix to gain sufficient energy required for electron-hole pair generation. This decreases the likelihood of an electron encountering a second collision after already being subjected to one collision within a single layer of the phosphor, significantly reducing the efficiency. To overcome this issue new ACPEL devices made of alternating h-BN phosphor-insulator layer pairs stacked together was considered. The focus was on selecting insulator material and optimizing the layers thicknesses to promote transport in ACPEL devices via ballistic mode primarily. In such a case primary electrons moving in the BN phosphor layer (ballistic mode) after encountering a collision, enter into a subsequent dielectric layer where they are reaccelerated before entering the next BN phosphor layer. The process is repeated through the ACPEL stack resulting in an efficiency enhancement as compared to a single h-BN layer ACTEL device. In the presentation we will demonstrate using COMSOL Multiphysics and analytical calculations that by taking into account the BN morphology (nano-poly-crystalline vs. single crystal) and the device structure (h-BN phosphor layer thickness, insulator layer parameters, number of layers pairs in the stack) the calculated ACPEL device emission efficiency can be as high as 20%.

**SYMPOSIUM EN11**

**TUTORIAL: Silicon Photovoltaics—Device Concepts, Materials and Interfaces Engineering, Fabrication, Testing and Applications**
December 1 - December 1, 2019

* Invited Paper

**TUTORIAL**

Silicon Photovoltaics—Device Concepts, Materials and Interfaces Engineering, Fabrication, Testing and Applications

Sunday Afternoon, December 1, 2019
Hynes, Level 2, Room 205

Silicon and related thin films are applied widely in solar cells and other electronic devices. This comprehensive tutorial will introduce the processing methods, material properties, fundamental nature of interfaces and device engineering concepts. In Part 1 the design rules of solar cells will be discussed. In Part 2 the processing & properties of all materials and interfaces in a crystalline silicon solar cells will be reviewed. In part 3, the wide variety of high efficient crystalline silicon device architectures including their fundamental approaches to reduce the optical and
electrical losses will be presented. In part 4, the design schemes for modules, the characterization methods for performance and reliability, photovoltaic applications and its role in the energy transition will be discussed.

1:30 PM
**Device Physics of Solar Cells** Arno H. M. Smets; Delft University of Technology

The important optical, electrical and thermodynamic design rules that determine both the losses and performance of the photovoltaic devices will be discussed. A description based on balancing photo-generation with recombination gives simple insight into the operation of all modern solar cells.

2:15 PM
**Processing and Properties of Crystalline Silicon and Supporting Layers and the Nature of Their Interfaces** Arno H. M. Smets; Delft University of Technology

Processing of crystalline silicon and supporting layers like passivating materials (SiO2, Al2O3, SiNx, a-Si) are presented. The dependence of the material and interface properties on impurities, doping, crystal orientation, interstitials, defects, chemical and electrical passivation will be discussed.

3:00 PM BREAK

3:30 PM
**Device Architectures for High Efficient Crystalline Silicon Solar Cells** Arno H. M. Smets; Delft University of Technology

The wide variety of crystalline silicon device architectures including their fundamental approaches to reduce the optical and electrical losses will be surveyed. This overview will include Al Back Surface Field solar cells, Partial Back Contact (PERC) solar cells, heterojunction junction solar cells (HJ/HIT), interdigitated back contact (IBC), tunnel oxide passivated contact (TOPCon), bifacial solar cells and hybrid multi-junction PV concepts.

4:15 PM
**From Crystalline Silicon Cells to Reliable Modules: Characterization, Application and the Role of Photovoltaics in the Energy Transition** Arno H. M. Smets; Delft University of Technology

The different module interconnection and encapsulation schemes will be introduced. A short introduction on the important characterization tools for cells and modules will be given. Finally, residential up to large-scale utility applications and the role of crystalline silicon in the energy transition will be discussed.

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**SYMPOSIUM EN11**

Silicon for Photovoltaics  
December 2 - December 5, 2019  

**Symposium Organizers**  
Stefaan De Wolf, King Abdullah University of Science and Technology  
Kaining Ding, Research Center Juelich  
Takuya Matsui, National Institute of Advanced Industrial Science and Technology  
David Young, National Renewable Energy Laboratory  

**Symposium Support**  
Bronze
Direct Observation of Dopants in Commercial Textured Silicon Heterojunction Solar Cells by Atom Probe Tomography

Yasuo Shimizu¹, Bin Han¹, Naoki Ebisawa¹, Yoshinari Ichihashi², Taiki Hashiguchi², Hirotaka Katayama², Mitsuhito Matsumoto², Akira Terakawa², Koji Inoue¹ and Yasuyoshi Nagai¹

¹Tohoku University, Japan; ²Panasonic Corporation, Japan

Silicon heterojunction (SHJ) solar cells [1], composed of a stack of thin intrinsic/doped amorphous layers, have been extensively developed towards high conversion efficiency photovoltaic property, which has been already employed in industrial production. Though a theoretical calculation demonstrates that the intrinsic limit of its efficiency reaches ~29% [2], the layer structures in actual SHJ devices still leave to be improved. The fabrication processing, such as doping methods, is considered for achieving ideal layer formation controlled with precise dopant concentration. In general, SIMS is used as a reliable analysis technique for obtaining the elemental profiles along the depth direction of the layers grown on flat substrates, which enables to determine an optimal doping condition. However, the elemental profiles on the pyramid surfaces in SHJ is unknown due to well-known dimensional limitation in the conventional analytical experiment. Therefore, it is a challenging issue to clarify how we effectively introduce the dopants in the pyramid surfaces determined by accurate characterization in commercial SHJ devices. Laser-assisted atom probe tomography (APT) has been proven useful for visualizing elemental distributions in Si-based device structures [3]. APT has a potential to directly detect the dopants and draw the concentration profiles perpendicular to the pyramid surface thanks to a site-specific lift-out by focused ion beam (FIB) technique. In this work, we established an experimental success in analyzing pyramid surface area less than 2×2 μm² dimension. In order to introduce B atoms into amorphous layers, we compared the elemental distributions of n-type layer doped by two kinds of doping molecules; (CH₃)₃B and B₂H₆.

After forming textured surface by alkali solution, intrinsic amorphous Si thin layer was grown by using plasma chemical vapor deposition, followed by B doped layer formation using (CH₃)₃B or B₂H₆. Finally, ~100 nm-thick of indium tin oxide as a transparent conducting layer was deposited on top. For APT specimen preparation, FIB apparatus equipped with SEM was used. A local electrode atom probe (LEAP4000XHR, CAMECA) equipped with a 355 nm wavelength pulsed laser was employed for APT analysis. Based on the atom maps including thin intrinsic/doped amorphous layers, we found that the amount of carbon, as a residual contaminant, doped by (CH₃)₃B is higher than that by B₂H₆. Furthermore, a large amount of hydrogen was directly observed in the amorphous layers, which may affect the photovoltaic property. The atom maps around the intrinsic/doped amorphous layers will also be presented.

This work was supported in part by NEDO (New Energy and Industrial Technology Development Organization) under METI (Ministry of Economy, Trade and Industry).


Ultrathin Silicon Oxide and p⁺-poly-Si Passivation for High-Efficiency c-Si Solar Cells

Xueqi Guo¹, Yuheng Zheng¹, Zhe Rui¹, Qing Yang¹, Zhixue Wang¹, Mingdun Liao¹, Chunhui Shou¹, Jie Yang¹, Xinyu Zhang², Qi Wang², Hao Jin², Baojie Yan² and Jichun Ye³

¹University of Shanghai for Science and Technology, China; ²Ningbo Institute of Materials Technologies and Engineering, China; ³Ningbo University, China

Ultrathin Silicon Oxide and p⁺-poly-Si Passivation for High-Efficiency c-Si Solar Cells

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¹University of Shanghai for Science and Technology, China; ²Ningbo Institute of Materials Technologies and Engineering, China; ³Ningbo University, China
As an emerging technology, the surface passivation with an ultrathin silicon oxide and highly doped poly-Si stack has attracted a great attention because of the outstanding passivation quality. The carrier transport through the ultrathin SiOx was originally proposed through quantum tunneling, and therefore it was named as tunnel oxide passivated contact (TOPCon) [1] although the transport through pin-holes has been identified as the transport path in some cases [2]. The highest laboratory solar cell efficiencies of 25.7% and 24.4% were achieved with n-type and p-type FZ c-Si wafers, respectively [3,4], and a large-area cell efficiency of 22.8% was achieved with n-type CZ c-Si wafer using an industrial capable fabrication process [5], demonstrating the potential in the efficiency improvement of solar panels. However, most of the poly-Si passivation layers are doped with P to form an n-TOPCon structure for high quality passivation. From the industrial application point of view, p-type poly-Si as the passivation and contact layer (p-TOPCon) is highly desired in the solar cell manufacturing, especially for upgrading the current PERC lines. In this contribution, we report our recent progresses in the research and development of high quality p-TOPCon, where the ultrathin SiOx layer is made by chemical oxidization in high temperature HNO3, plasma assisted N2O oxidization, and thermal oxidization; and the p-poly-Si layer is made by PECVD with in-situ doping. We find that the SiOx made by the thermal oxidization performs better than those made by the other methods, with which a supper passivation using the p-TOPCon on n-type solar grade CZ c-Si wafers is achieved with iVoc of 729 mV, effective carrier lifetime (τeff) of 2.5 ms at 1×10^{15} cm^{-3} carrier density, and saturated recombination current density (J0) of 13 pA/cm^2. XPS analysis shows that the thermally oxidized film has a higher oxidization quality with a ratio of Si4+ chemical bonding configuration than those made by the other methods. In addition, the thermally oxidized SiOx layer reduces the B aggregation in the SiOx layer and the B diffusion into the c-Si wafer effectively as measured by ECV. We also investigated the PECVD a-Si:H deposition as well as various hydrogenation processes after the high temperature crystallization and their influences on the passivation quality. We find a wide PECVD process window for achieving high-quality passivation and an innovative hydrogenation method using water vapor annealing for improving the passivation quality effectively. We will also report the solar cell results with the p-TOPCon contact.


9:45 AM BREAK

10:15 AM *EN11.01.03
High Performance Semi-Transparent Si-Based Carrier-Selective Passivating Contacts for c-Si Solar Cells Manufactured at Different Thermal Budgets
Olindo Isabella; Delft University of Technology, Netherlands

Silicon solar cells based on PERC architecture [1][2] have become the new industrial standard beyond the Al-BSF architecture [3]. To aim at higher efficiencies, research is on innovative architectures based on carrier-selective passivating contacts (CSPCs) for quenching recombination mechanisms at contact interfaces. Focussing on Si-based CSPCs, low thermal budget heterojunction (HTJ) cells and high thermal budget TOPCon-like cells have achieved record efficiency values ~26% in both front/back-contacted (FBC) [4] [5] and interdigitated back-contacted (IBC) [6] [7] configurations. However, these architectures are challenging from upscaling stand point; thus, leaner and cost-effective processes that can enable efficiencies between 24% and 25% on large area are industrially appealing. In this contribution, we first review the opto-electrical properties and passivation quality of in-house developed semi-transparent CSPCs based on silicon alloyed with oxygen or carbon and manufactured at different thermal budgets. Then, starting from standard FBC cell configuration and recognizing the inherent parasitic optical losses due to Si-based CSPCs, we monitor the evolution of short-circuit current density in simple-process FBC and IBC devices endowed with our semi-transparent CSPCs.

In case of low thermal budget CSPCs compatible with HTJ architecture, we have developed and optimized n-type and p-type nc-SiOx:H layers, which concurrently exhibit wide band gap, optimal crystallinity fraction and low activation energy (E_{a-n} = 46.6 meV and E_{a-p} = 89.6 meV). These properties make our nc-SiOx:H layers excellent candidates for ideal carrier transport [8]. When employed in a double-side textured cell precursor based on 280-μm thick n-type FZ c-Si wafer, our nc-SiOx:H layers enable iVoc = 735 mV and iFF = 86.85% with τ_{eff} > 10 ms at also Δn < 10^{15} cm^{-3}. Rear junction devices based on such type of precursors, completed with sputtered ITO and Ag-based
screen-printed contacts, present efficiencies in excess of 21% with $J_{SC} = 39.1 \text{ mA/cm}^2$ for cell area of 7.84 cm$^2$ [9]. While further back-end optimization is needed to demonstrate higher efficiencies, this material system can boost the efficiency of FBC HTJ devices well beyond the current 25.1% efficiency record [4].

Passing to high thermal budget CSPCs, we have studied, as function of thickness, a wide range of poly-Si(Ox)(Cx) material systems by means of LPCVD (i.e. double-sided) or PECVD (i.e. single-sided) routes with ex-situ (implantation, diffusion) or in-situ doping and on flat or textured interfaces. Even though we have realized textured poly-Si CSPCs with thickness down to 6 nm (n-type poly-Si, $V_{OC} = 728$ mV, $J_0 = 6.5 \text{ fA/cm}^2$), our best n-type (p-type) CSPCs are flat 35-nm (20-nm) thick poly-SiO$_x$ layers, which exhibit $iV_{OC}$ up to 740 (716 mV) and $J_0$ down to 3 (11) fA/cm$^2$. These layers, similarly to poly-Si$_x$ layers [10], can be more transparent than poly-Si counterparts. As such, we have introduced polyO$_x$-polyO$_x$ FBC devices [11][12], which could yield 21.5% for cell area of 1 cm$^2$, by slightly improving the $V_{OC}$ of our poly-poly FBC standard devices ($V_{OC} = 691$ mV vs $V_{OC} = 682$ mV) and massively enhancing the $J_{SC}$ ($J_{SC} = 40.7 \text{ mA/cm}^2$ vs $J_{SC} = 38.1 \text{ mA/cm}^2$) without the use of any dual anti-reflective coating (DARC). To further augment the $J_{SC}$, we have devised a simple-process IBC poly-Si architecture, that exhibits $J_{SC:DARC} = 42.2 \text{ mA/cm}^2$ [13] with 23% for cell area of 2 cm$^2$ [14].

PO-SiOₓ on flat c-Si, an iVoc equal to 711 mV is obtained. By increasing the N₂O plasma treatment time, the iVoc increases to 723 mV. With the same process conditions, n-type poly-SiOₓ CSPC on textured c-Si gives 710 mV. The p-type poly-SiOₓ CSPC with PO-SiOₓ is also under development by optimizing the N₂O plasma condition and the high-temperature annealing process. In this case, preliminary results indicate an iVoc equal to 668 mV for flat layers.

Poly-SiOₓ – poly-SiOₓ FBC cell, featuring wet-chemical SiOₓ on both sides, textured n-type poly-SiOₓ at the front side and flat p-type poly-SiOₓ at the rear side, performs an efficiency of 21.5% with Voc = 691 mV, FF = 76.4%. The replacement of wet-chemical SiOₓ with PO-SiOₓ is ongoing, for which a higher FF and similar Voc at cell level are expected, leading to a cell efficiency well above 21.5%. Results will be presented at the conference.


11:00 AM EN11.01.05
Insights into the Gettering and Passivation Phenomena in Doped Poly-Silicon Passivating Contacts in Si-Photovoltaics by Atom Probe Tomography Apurv Yadav1, Di Yan2, Wenjie Yang2, Keita Nomoto1, Daniel Macdonald2 and Simon Ringer1; 1The University of Sydney, Australia; 2The Australian National University, Australia

We summarize our recent findings on the properties of doped poly-Si structures for solar cell applications in terms of their impurity gettering effects (iron); through analysis of 3D elemental distribution profiles of, phosphorus /and boron (diffused dopants), undoped poly-Si (control) and implanted iron (impurity). Doped poly-Si films with an underlying interfacial oxide layer have been shown to enable high efficiency silicon solar cells, due to their excellent electrical contact and surface passivating effects , and also because they possess very strong gettering properties (>99.9% metal (Fe- impurity) removal from the bulk) without compromising its passivating qualities.

Our study uses atom probe microscopy to determine the 3D distribution of elements to explore the phenomenon of gettering by poly-Si based layers. We investigate the role of dopants, oxygen, grain-boundaries and, interfaces, and observe if trends in the elemental distributions play a role in impurity gettering. This study is performed in conjunction with transmission electron microscopy (TEM) to facilitate atom probe reconstruction and support atom probe tomography (APT) analysis.

Our results indicated the gettering properties of poly-Si layers differ based on the dopants present (phosphorus vs boron) and are enhanced 1. in the presence of dopants (compared to undoped contacts), 2. at interfaces and 3. in the presence of oxygen.

The potential implications of these findings are in designing passivating contacts with enhanced gettering and passivating qualities. This will support the development of new solar cell processes for higher efficiency silicon solar cells at lower costs.

11:15 AM EN11.01.06
The Role of Defects for Charge Collection in c-Si HTJ Solar Cells Paul Procel, Aurora Saez-Armenteros, Carlos Ruiz-Tobon, Luana Mazzarella, Yifeng Zhao, Can Han, Guangtao Yang, Olindo Isabella and Miro Zeman; Technical University Delft, Netherlands

Defects in semiconductors are typically involved in performance degradation of photovoltaic devices in terms of recombination mechanisms and light instability [1-2]. Defects basically act as available energy states that can capture or emit charge inside the layer itself or to other materials/systems. In case of hydrogenated amorphous silicon (a-Si:H), these defects are related to non-periodic variations of the lattice potential, known as band tail energy states. These defects feature two state conditions: (i) neutral when empty or (ii) charged when occupied. Similarly, sub-gap electronic states close to mid-gap energy are defects in the form of dangling bond states [1]. The
latter defects are dominant for recombination mechanisms at room temperature and they show amphoteric nature, which means that they exhibit three different states of charge. Altogether, these energy states build a complex configuration for charge collection that is not fully understood yet.

By means of rigorous TCAD modelling [3], we hereby discuss the role of the energy states for charge collection in silicon heterojunction (HTJ) solar cells inside contact stacks, namely intrinsic a-Si:H/doped n-type or p-type a-Si:H / transparent conductive oxide (TCO). Specifically, we investigate the different nature and properties of defects which affect recombination mechanisms for charge transfer, also known as trap-assisted tunneling (TAT). Furthermore, we correlate these mechanisms to solar cell external parameters for pursuing more efficient device.

We observe that TAT processes are not dominant in case of energy alignment of occupied states and available states within contact stack system. In presence of a proper energy alignment, field/thermionic emission and band-to-band processes from and to hetero-interfaces are dominant. In fact, such events are more efficient, as they do not exhibit any energy loss in terms of elastic transitions between energy states. On the other hand, TAT transitions are evident in the absence of energy states alignment and imply energy variation. Accordingly, we analyze the individual material properties that evidence TAT processes. Interestingly, such conditions are fulfilled only for positive charge collection while TAT is not apparent for negative charge collection. The electronic properties, ruling the aforementioned energy alignment, are associated to the Fermi-energy of each individual layer forming the heterojunction contact: p-type a-Si:H activation energy ($E_{a,p}$) and TCO carrier concentration ($N_{TCO}$). Therefore, we performed numerical calculations to evaluate charge transport in terms of fill factor (FF) within reasonable ranges of $E_a$ and $N_{TCO}$ values. From our modelling results, we observed four different intervals featuring different charge collection processes:

a) $35 < E_{a,p} < 260 \text{meV}$ and $1 \times 10^{20} < N_{TCO} < 1 \times 10^{21} \text{cm}^{-3}$: Elastichange transitions (FF>85%)

b) $260 < E_{a,p} < 430 \text{meV}$ and $1 \times 10^{20} < N_{TCO} < 1 \times 10^{21} \text{cm}^{-3}$: TAT based on dangling bond states (80%<FF<85%)

c) $35 < E_{a,p} < 260 \text{meV}$ and $1 \times 10^{19} < N_{TCO} < 1 \times 10^{20} \text{cm}^{-3}$: TAT based on valence band tail states (55%<FF<80%)

d) $260 < E_{a,p} < 430 \text{meV}$ and $1 \times 10^{19} < N_{TCO} < 1 \times 10^{20} \text{cm}^{-3}$: TAT based on dangling bond states (60%<FF<80%). Note that here the energy variation within TAT intervals is larger than b).

We identified that defects featuring energy close to Fermi-energy (i) work more effectively on TAT processes and (ii) are closer than 10nm to the p-type a-Si:H/TCO interface (tunneling distance). In particular, TAT based on dangling bond states is more efficient than TAT based on tail states. Such a difference is ascribed to the initial dynamics (from neutral state) of recombination based on amphoteric states, that is able to capture positive charge from c-Si or negative charge from TCO, whereas tail states only allow to capture positive charge from c-Si.


11:30 AM EN11.01.07
Investigations of and Solutions for Contamination Mechanisms of Intrinsic poly-Si Gap Contamination in SiOx. Passivated Interdigitated Back Contact Silicon Solar Cells Matthew B. Hartenstein1,2, William Nemeth2, Vincenzo LaSalvia2, Steven Harvey2, Matthew Page2, David L. Young2, Paul Stradins2 and Sumit Agarwal1;
1Colorado School of Mines, United States; 2National Renewable Energy Laboratory, United States

We demonstrate a new, purely mechanical mask alignment technique for dopant patterning of interdigitated back contact solar cells (IBC's) monocrystalline silicon (c-Si) solar cells. This technique uses ceramic pins to hold the mask and substrate tightly together for dopant deposition using plasma- enhanced chemical vapor deposition (PECVD). Problems associated with this dopant patterning step are investigated and solutions are developed for each. IBC silicon solar cells are the current record holders for silicon photovoltaic efficiencies based on various contacting structures [1]. Additionally, passivated contact schemes involving heavily doped polycrystalline silicon on silicon oxide (poly-Si/SiOx) have been demonstrated on both two-sided architectures [2][3] and IBC architectures [4][5][6], achieving efficiencies over 25%. These poly-Si/SiOx IBCs have been demonstrated with oxides of ~2.2 nm thickness to great success. Many groups have achieved high efficiencies on IBCs with these 2.2 nm passivating oxides by patterning the back-side dopants using photolithographic techniques, ion implantation, or laser doping, but these processes are undesirable due to their complexity, potential damage to the cell or cost. However, IBC solar cells have not yet been demonstrated using the ~1.5 nm tunneling oxide passivated contact structure fully contacted with doped polycrystalline silicon (poly-Si) fingers separated by intrinsic poly-Si. We investigate factors that are critical for the performance of IBC solar cells based on these tunneling oxide poly-Si passivated contacts. Because many of the above-mentioned dopant patterning techniques have led to fabrication complications, we have chosen to pattern the back side using masked PECVD of doped hydrogenated amorphous silicon (a-Si:H). Although this is a
simpler process, there are a few troubles which can occur. During patterning of doped lines using direct deposition through a shadow mask, we show using time-of-flight secondary ion mass spectrometry (TOF-SIMS) that the intrinsic polyc-Si gap becomes contaminated with dopants, leading to shunting. Two possible contamination mechanisms during high-temperature crystallization annealing are investigated. Using controlled experiments in a crystallization tube furnace, it is shown that dopants can desorb from the surface of the doped a-Si:H and transfer through the gas phase to be adsorbed onto the intrinsic gap and diffuse inward to contaminate the intrinsic gap. Mitigation strategies are developed for each of these contamination mechanisms to minimize shunt losses, confirmed using conductivity measurements. Dopant migration during PECVD is mitigated through a partial etch back of the a-Si:H surface to clear the intrinsic gap of dopants before crystallization. Gas phase transfer is mitigated by addition of a barrier between the doped a-Si:H and the gas phase, either with a capping layer or by annealing in an oxygen ambient which forms a surface layer of SiOx, etched away by further processing. Complete IBC cells fabricated using these processing strategies will be presented at the conference. Improved IBC manufacture techniques will reduce the cost of such high efficiency cells and modules, promoting the expanded use of solar energy.

References
are on par with standard PV wafers regarding the electronic quality.

2:00 PM EN11.02.02
Investigating the Practical Efficiency Limits of Solar Cells by Using Thin CZ-Quality Substrates André Augusto, Pradeep Balaji, Joseph Karas, Richard King and Stuart Bowden; Arizona State University, United States

Different silicon solar cells technologies have surpassed or are close to surpassing 26% efficiency. Dielectric oxides and amorphous silicon-based layers combined with minimal metal/silicon contact areas were responsible for reducing the surface saturation current density below 3 fAcm⁻². At open circuit, for passivating contact solar cells, the recombination is mostly fundamental (Auger and radiative), representing near 80% of the total recombination. At the maximum power injection, the fundamental recombination fraction drops to less than 50% as the surface recombination and SRH bulk step in. As a result, to further increase the performance is paramount to reduce the bulk dependence and secure proper surface passivation. Bulk dependence can be mitigated either by improving the bulk quality or by reducing the wafer thickness. We demonstrate for commercial relevant high-quality CZ wafers, thinner wafers and surface saturation current densities 10 times lower than the present state-of-the-art, are required to further increase the efficiency and narrow the gap towards the fundamental limit. For an n-type SRH bulk lifetime of 10 ms and a resistivity of 3 Ohm.cm, the optimum substrate thickness range is between 40 to 60 μm. By optimizing the thin layer of a-Si:H (<7nm) we have accomplished surface saturation currents below 1 fAcm⁻² across multiple substrates thicknesses, reaching effective minority carrier lifetimes over 2.2 ms and implied open-circuit voltages of 765 mV on 40 μm-thin n-type CZ substrates after ip/in a-Si:H stack deposition. We use thinner wafers as testbed to optimize the thin intrinsic a-Si:H layer, as the effective minority carrier lifetime response to surface passivation increases inversely with the substrate thickness, and bulk recombination becomes less predominant in the final make-up of the lifetime, particularly at maximum power injection. We manufactured screen-printed silicon heterojunction solar cells on free-standing 40 μm-thin CZ-wafers with efficiencies close to 21%. In these cells the screen-printing layout needs to be optimized, and further gains in current and fill factor are expected in the coming months. These results were a direct consequence of an extreme good surface passivation and improved generation current provided by an antireflective bi-layer thin-ITO/SiO₂. The antireflective bi-layer increased the current density in 1.2 mAcm⁻² from our baseline antireflecting coating, mostly by mitigating the parasitic absorption via thinner ITO front layer.

2:15 PM EN11.02.03
Performance of Silicon Solar Cells Using Very High Resistivity Substrates André Augusto, Apoorva Srinivasa, Richard King and Stuart Bowden; Arizona State University, United States

Today’s highest-efficiency solar cells typically operate near the threshold between low-level and high-level injection. It is not well understood if pushing further into a regime in which the cell operating point is solidly in high level injection at all times of the day has further benefits for initial solar cell performance, for reducing degradation rates, or for controlling the charge state and diffusivity of impurities that determine recombination in the bulk. In this work we explore the potential advantages of using very high resistivity n- and p-type, to manufacture high performance solar cells. Analytical modeling indicates that high resistivity substrates (10 Ωcm - >10k Ωcm) are required to have bulk Shockley-Read-Hall lifetimes in the millisecond range to outperform wafers with standard resistivities (< 10 Ωcm). Additionally, for resistivities over 10 Ω.cm, efficiencies show to be weakly dependent of the bulk resistivity. These results if experimental verified, can lead to more affordable ingot manufacturing, by lessening the requirements of dopants homogeneity along the ingot. We successfully passivated both n- and p-type substrates using i-a-Si:H, obtaining surface saturation current densities comfortable below 10 fAcm⁻² and effective minority-carrier lifetimes over 2 ms at maximum power injection over the entire range of bulk resistivities (3 Ωcm - >10k Ωcm). For very high resistivity wafers (15k Ωcm) effective minority-carrier lifetimes over 10 ms were measured for both n- and p-type substrates. At moment we are manufacturing and characterizing solar cells and passivated samples, both p- and n-type over a wide range of temperatures (up to 80 °C) and injections. Preliminary results on silicon heterojunction solar cells indicate similar performance behavior for different light intensities regardless the base resistivity of the substrate.

2:30 PM EN11.02.04
Progress in the Fabrication of Liquid Phase Crystallized Silicon Solar Cells Hassan Ali¹, Frank Pennartz¹, Nelli Hambach¹, Friedhelm Finger¹, Wolfhard Beyer¹, Daniel Amkreutz², Maurice Nuys³ and Stefan Haas¹;¹Forschungszentrum Jülich, Germany; ²Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany
Liquid phase crystallization (LPC) technology offers an alternative solution to the established wafer-based solar cells. It is a kerfless fabrication method that promises high efficiency solar cells on large-sized glass substrates. Recently, a conversion efficiency of 14.2% for back contacted 13 µm thick silicon on glass was demonstrated [1]. In this technology, amorphous or nano-crystalline silicon films prepared by various fabrication methods are used. In our work, we focus on films deposited by plasma-enhanced chemical vapor deposition (PECVD) due to its industrial relevance and easy integration into large-scale manufacturing. The standard layer stack for PECVD-based LPC solar cell consists of a multifunctional SiOx/SiN/SiOx (ONO) interlayer directly deposited on the glass followed by a 5-10 µm thick amorphous silicon (a-Si:H) precursor layer and finally a SiOx capping layer to promote the wettability of the film during crystallization. To drive out the hydrogen from the standard a-Si:H layer, the whole stack goes through a 2-day oven annealing (RT to 550 °C) process before crystallization by an 808 nm line-shaped continuous wave (CW) laser source. Without this hydrogen removal, the material delaminates during crystallization [2]. Unfortunately, this slow annealing process increases the manufacturing time.

In our contribution, we sum up our recent progress in the fabrication of the LPC layer stack and present an alternative solution to further reduce the manufacturing time of LPC cells. To reduce the annealing time, a porous material with interconnected voids was realized [3]. This allowed to rapidly anneal the a-Si:H precursor layer within 30 minutes (under ambient or nitrogen atmosphere) up to 550°C and drive out the hydrogen without material delamination, thus decreasing the manufacturing time and heating cost drastically. We examined this hypothesis by introducing artificial vents into dense films for the H effusion, which usually delaminate during the 30-minute rapid annealing process. With these vents, the film stabilizes depending on the distance between the vents. Furthermore, the LPC process induces strong thermal-induced stress which may lead to glass cracking. Profilometry was implemented to evaluate the radius of surface curvature and Stoney's equation was used to quantify the mechanical stress before and after laser crystallization. To lower the thermal-induced stress, laser scan speed was optimized to decrease the thermal gradient between layers of mismatching thermal expansion coefficients [4]. As a result, we were able to achieve (using porous precursor material) crack-free crystallized poly-crystalline silicon with grain diameters of several µm and grain lengths of several mm. Also, the crystallization was made possible without the need for a capping layer.

In conclusion, we were able to get rid of the capping layer fabrication step and significantly decrease the annealing time. Hence, we present a high-throughput approach for future up-scaling of liquid phase crystallization technology.

**Keywords:** Liquid phase crystallization, Amorphous silicon, Rapid annealing, Hydrogen effusion, Thermal-induced stress

**References**


2:45 PM BREAK

3:15 PM *EN11.02.05*

**Smart Stack Technology for Si-Based Tandem Solar Cells**

Hidenori Mizuno, Kikuo Makita, Hitoshi Sai, Takuya Matsui, Tetsuhiko Miyadera, Takeshi Tayagaki, Toshimitsu Mochizuki, Ryuji Oshima, Takeyoshi Sugaya and Hidetaka Takato; National Institute of Advanced Industrial Science and Technology (AIST), Japan

Developing strategies towards Si-based tandem solar cells has gained considerable attention in the photovoltaic research community to prepare for the future demand of higher-efficiency solar cells. In this respect, we have proposed “smart stack” technology, an approach using metal nanoparticle arrays to bond dissimilar semiconductor materials both electrically and optically. Such functional metal nanoparticle arrays can be readily available by a method known as block copolymer nanolithography. Using Pd or Cu nanoparticle arrays, for example, we have fabricated triple-junction tandem cells comprising of InGaP/GaAs top cells and crystalline Si (c-Si) bottom cells. Through the fine tuning of the InGaP/GaAs cells as well as the introduction of advanced c-Si cell technologies (such as tunneling oxide passivated contact or heterojunction), efficiencies of over 30% have been recently realized. Other than InGaP/GaAs top cells, lead halide perovskites are of great interest, and efforts to demonstrate perovskite/c-Si
tandem by the smart stack technology is also actively ongoing. This presentation overviews the concept, process, and device performances of the smart stack technology, including some of recent attempts.

3:45 PM EN11.02.06

Efficiency Potential and Application of Singlet Fission Enhanced Silicon Solar Cells Benjamin Daiber1, Koen v.d. Hoven1, Moritz H. Futscher1, Joris Bodin1, Alyssa v.d. Boom2, Sidharam Pujari2 and Bruno Ehrler1; 1AMOLF, Netherlands; 2Wageningen University, Netherlands

Silicon is the dominating solar cell material, therefore add-ons on the silicon solar cell that can improve the power conversion efficiency are urgently needed. In certain organic materials singlet fission generates two triplet (spin 1) excitons from one singlet (spin 0) exciton. If the triplet excitons are harvested in the silicon solar cell the efficiency could be dramatically increased, as we show. There are different transfer pathways between the organic singlet fission material and silicon. We have simulated the achievable efficiency for each transfer path with realistic assumptions such as a singlet fission quantum efficiency of 1.7 (1.7 e-h pairs per high energy photon), a transmission loss of 5%, and different entropy gains of the Singlet Fission process.

Even with these realistic assumptions, the efficiency of a silicon/singlet fission solar cell can be as high as 34% when combined with the current record silicon solar cell of 27%. We found that dissociating the triplet excitons at the interface leads to a large potential efficiency gain because a triplet energy lower than the silicon bandgap still leads to charge generation, and allows for high current generation. We also find that current singlet fission materials do not absorb light strongly enough, motivating sensitization schemes. A direct triplet exciton transfer shows lower overall efficiencies because the energy level requirements are more strict, however the solar cell architecture is more elegant since there are no additional contacts needed. Finally, we compare the singlet fission/silicon solar cells to the efficiency potential of perovskite/silicon tandem solar cells. We find that tandem cells are particularly beneficial for a silicon base cell with low efficiency, while a highly efficient silicon solar cells benefits less from the perovskite top cell. In contrast, the efficiency gain from the singlet fission layer is almost constant for all silicon base cells, and for highly efficient silicon cells would clearly outperform a high-efficiency perovskite top cell.

We also fabricated Silicon solar cells with a top layer of tetracene. The silicon base cell are back-contacted, so we can HF-etch the silicon solar cell from one side to have direct access to the Silicon <111> sides of pyramidal textured silicon. Through measuring the photocurrent under a magnetic field we can differentiate between the photocurrent contribution of singlet and triplet excitons. A newly improved magnetic field dependent photocurrent setup allows us to measure current changes in the order of 0.01% and is a vital tool for a precise attribution of the origin of the photocurrent. We find that after deposition of the tetracene layer we see an injection of singlets or photons into silicon, but after aging the solar cell we see evidence for triplet transfer. The characteristic Merrifield curve (photocurrent as function of applied magnetic field ) inverts, which suggest the injection of triplet excitons from tetracene into silicon. This behavior can be observed for and tetracene-silicon solar cells that have been aged for five days in air or six weeks encapsulated in nitrogen atmosphere. We discuss a changing orientation of the tetracene molecules over time and a thin layer of silicon dioxide growing between tetracene and silicon. A better understanding of the energy transfer processes at the interface will be important for future device applications.

4:00 PM EN11.02.07

Electron Paramagnetic Resonance Study of Sodium Guests in Silicon Clathrate—A Cage-Like Crystalline Silicon Allotrope Yinan Liu1, William K. Schenken1, Ahmad A. Majid1, Lakshmi Krishna1, Timothy A. Strobel2, Reuben T. Collins1, P C. Taylor1 and Carolyn A. Koh1; 1Colorado School of Mines, United States; 2Carnegie Institute of Washington, United States

Si clathrates are cage-like, crystalline Si allotropes with potentially exciting optoelectronic properties. Room temperature and atmospheric pressure metastable clathrates are synthesized in the presence of alkali guest atoms, such as Na, which occupy the interstitial sites in the cages. Na guests, however, degenerately dope the crystals. Realizing the potential of these materials as new, crystalline Si-based, earth abundant electronic materials requires fundamental understanding of guest properties and how to control their occupancy and diffusion in the cage-like host crystal structure. Elucidation of these properties is complicated by complex interactions among the Na donors. For this reason, a detailed understanding of isolated, or nearly isolated, Na donors is critical to eventually realizing the potential of these semiconductors for electronic and opto-electronic devices.

Here, we present an EPR study of Na guests in type II Si clathrate as a function of temperature and Na concentration. Since at low temperatures a Na donor is paramagnetic, EPR hyperfine interactions allow low concentrations of Na ions to be detected while probing the interaction between ions and the Si cages. In low
temperature measurements, the EPR spectrum with ≤1 at. % of Na exhibits four hyperfine lines due to the interaction of the Na valence electron with the nuclear spin \( I=3/2 \) of Na\(^{23} \). The hyperfine coupling constant \( 13.3 \text{ mT} \) together with the atomic coupling constant for an isolated Na atom \( 31.6 \text{ mT} \) indicates that about 42% of the wave function of the paramagnetic electron resides on the Na atom and the rest resides on the surrounding Si sublattice. The type II crystal structure includes both small and large cages. At this low Na concentration, the Na is almost entirely in the large cages and a small anisotropy in the four hyperfine lines indicates it is slightly off center in the cage, as suggested by other measurements. We also identify an EPR contribution at \( g=2.005 \) which is consistent with the presence of Si dangling bonds in a highly disordered or amorphous Si phase. Identifying this line as due to dangling bonds allows a clearer identification of the other features in the clathrate spectrum.

The observation of structure from "super hyperfine" interactions of the Na valence electron with more than one magnetic nucleus provides additional insight into the properties Na as a donor in type II clathrate. Doublets surrounding each of the four Na hyperfine lines are identified, using EasySpin spectral simulations, as arising from naturally occurring Si\(^{29} \) nuclei in the surrounding Si cage. Based on the magnitude of the Si\(^{29} \) interaction, it is estimated that about half of the spin density on the Si sub-lattice extends past the confining cage. Additional fine structure is observed halfway between the strong hyperfine lines. Simulations suggest they arise from the interaction of either one or two electrons on Na\(^{23} \) nuclei \( I=3 \) in adjacent cages. This spectrum consists of 7 lines, four of which are hidden by the four strong hyperfine lines for isolated Na\(^{23} \) atom cages, with the others positioned between the hyperfine lines as observed. Interactions of electrons associated with Na\(^{23} \) atoms in adjacent cages is consistent with spin density extending beyond the confining cage. In addition to probing the nature of the Na donor in the clathrate structure, EPR provides other useful information. For example, using the integrated intensity of the Na hyperfine lines we estimate the concentration of isolated Na in samples specifically prepared to have low Na content to be \( \sim 3 \times 10^{17}/\text{cm}^3 \) which is approaching a regime where the doping is not degenerate. This work was supported by National Science Foundation Award #1810463.

4:15 PM EN11.02.08
Dopant Profile Engineering to Improve Charge Carrier Lifetime in Gold-Hyperdoped Silicon Sashini S. Dissanayake\(^1\), Philippe K. Chow\(^2\), Nikki O. Pallat\(^1\), Rhoen Fiutak\(^1\), Jeffrey M. Warrender\(^2\) and Meng-Ju Sher\(^1\);
\(^1\)Wesleyan University, United States; \(^2\)U.S. Army Combat Capabilities Development Command - Armament Center, United States

Intermediate band photovoltaics have been proposed to better utilize the solar spectrum and ‘hyperdoping’ of silicon is an effective method to realize such a material [1]. We investigate various hyperdoping methods and dopant concentration profile tailoring, to increase the charge carrier lifetime in intermediate band semiconductor materials. Hyperdoping is a well-established technique to introduce large concentrations of deep-level dopants such as heavy chalcogens and transition metals for intermediate band formation [1,2]. Various hyperdoping and annealing methods — namely, dopant ion implantation followed by pulsed laser melting (PLM) [3], or dopant ion implantation followed by flash lamp annealing (FLA)[4], or dopant thin film deposition followed by PLM [5] can produce impurity-supersaturated, single crystalline layers, which absorb sub-bandgap light. A drawback of the non-equilibrium PLM technique is inherent dopant segregation to the silicon surface [6], which leads to short charge carrier lifetimes without contributing to device performance. In this study, we investigate the extent of the surface segregation on the photocarrier lifetime using controlled etching methods as a way of removing the surface-segregated silicon surface.

We investigate the influence of the etch processing on charge carrier lifetime using terahertz (THz) spectroscopy. Optical pump THz probe spectroscopy is a non-contact photoconductivity measurement for measuring carrier lifetime with picosecond temporal resolution [7]. We focus our study of the recombination dynamics on the gold-hyperdoped silicon (Si:Au) system, prepared via thin film deposition and PLM. We find that whereas unprocessed Si:Au layers exhibit rapid recombination with a lifetime of 16 ps, CF\(_4\)-based reactive ion etching (RIE) increases the lifetime by a factor of 2, contrary to the widely-known role of RIE for increasing surface recombination. We also characterize the structural and absorption properties of the material. Additionally, we simulate the lifetime dependence on dopant concentration profile. We use these THz lifetime measurements to verify results of dopant profile engineering, to optimize materials for intermediate band photovoltaics. This study provides a material processing-based approach towards overcoming the historically-low external quantum efficiencies reported for hyperdoped Si optoelectronic devices.


Final Program 1/13/2020  1050

4:30 PM EN11.02.09
Monolithic Thin-Film Chalcogenide-Silicon Tandem Solar Cells Enabled by a Diffusion Barrier
Alireza Hajijafarassar, Filipe Martinho, Andrea Crovetto, Jorgen Schou and Ole Hansen; Technical University of Denmark, Denmark

Following the recent success of monolithically integrated Perovskite/Si tandem solar cells, there has been a surge of interest in alternative wide bandgap top-cell materials with prospects of a fully earth-abundant, stable and efficient tandem solar cell. Thin film chalcogenides such as Cu2ZnSnS4 (CZTS, 1.6 eV band gap) or Cu2BaSnS4 (CBTS, 2.0 eV band gap) could be suitable candidates. However, this class of materials has the disadvantage that generally at least one high temperature step (> 500 C) is needed during the synthesis, which could contaminate the Si bottom cell. Here, we systematically investigate the monolithic integration of CZTS and CBTS on a Si bottom solar cell. A simple double-sided Tunnel Oxide Passivated Contact (TOPCon) structure is used as bottom cell, and a thin TiN layer is selected as both a diffusion barrier and a recombination layer between the two sub-cells. We show that TiN successfully mitigates in-diffusion of CZTS elements into the c-Si bulk during the high temperature sulfurization process, and no evidence of electrically active deep Si bulk defects in samples protected by just 10 nm TiN. Post-process minority carrier lifetime in Si exceeded 1.5 ms, i.e., a promising implied open-circuit voltage (i-Voc) of 715 mV after the high temperature sulfurization. Based on these results, we demonstrate the first proof-of-concept two-terminal CZTS/Si and CBTS/Si tandem devices with a efficiencies up to 3.3%. A general implication of this study is that the growth of complex semiconductors on Si using high temperature steps is technically feasible, and can potentially lead to efficient monolithically integrated two-terminal tandem solar cells.

4:45 PM EN11.02.10
Hyperdoped Si Photodetectors with High Efficiency and Extended Infrared Response
Yining Liu1, Wenjie Yang2, Jeffrey M. Warrender3, Quentin Hudspeth1, Peter Hadchiti1, Jim Williams2, Imad Agha1 and Jay Mathews1;
1University of Dayton, United States; 2Australian National University, Australia; 3Benet Lab, United States

Supersaturated solutions of transition metal impurities in Si have been shown to create intermediate bands (IBs) between the valence and conduction bands in Si. This new IB induces sub-band gap absorption, thereby increasing the range of optical absorption in silicon further in the infrared. The extended response of this hyperdoped Si make it a promising material for photovoltaic devices. Ion implantation followed by pulsed laser melting has been demonstrated as a method to produce concentrations of impurities in Si that are well above the solid solubility limit. Recently, photodetectors fabricated from Si hyperdoped with Au or Ti have been shown to have sub bandgap responsivity, demonstrating the material’s promise for increasing the efficiency of Si solar cells beyond conventional limits.

To achieve devices that could be commercialized for PV cells or other demanding applications, hyperdoped Si must show significant optical absorption, and high quality Ohmic contacts for carrier extraction must be achieved. In this work, we fabricated Si layers hyperdoped with Au or Ti at varying thickness, measured the optical absorption enhancement relative to Si, and attempted to form Ohmic contacts to the layers. The results show significant enhancement of optical absorption by increasing the implant energy. For making Ohmic contacts to hyperdoped materials, we tried several treatments, including boron or phosphorus shallow doping, rapid thermal annealing (RTA) of contact, etching off the top metallic layer, and modifying the PLM process to suppress dopant segregation. Recipes for Ohmic contacts to each layer were demonstrated. And the low ohmic contact resistivity around 0.1 ohmcm2 can be achieved.

Prototype photodetectors were fabricated out of Au or Ti hyperdoped Si materials produced using the II-PLM
method. The devices were fabricated using the optimized Ohmic contact process to maximize the carrier extraction. The IV characterization shows a rectifying effect for the Si based junction. The detection range is extended to 2μm, well beyond the limit of typical Si photodetectors. More importantly, the external quantum efficiency in the sub-band gap region was increased by nearly two orders of magnitude over previously published work. These results represent a significant improvement in the development of a hyperdoped Si solar cell. The enhancement in optical absorption and carrier extraction should translate to a significant increase in solar cell efficiency.

SESSION EN11.03: Poster Session: Silicon for PV
Session Chairs: Stefaan De Wolf, Kaining Ding, Takuya Matsui and David Young
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EN11.03.01
ZnS,Se<sub>1-x</sub> Photovoltaic Carrier-Selective Contacts to Si—Band Offsets and Simulation-Driven Design Rebecca D. Glaudell and Harry A. Atwater; California Institute of Technology, United States

ZnS,Se<sub>1-x</sub> films are promising materials for front carrier-selective contacts in silicon photovoltaics given their wide bandgaps and low resistivities compared to amorphous silicon, with the potential to capture more photo-generated current than a traditional heterojunction with intrinsic thin layer (HIT) solar cell. We have synthesized ZnS,Se<sub>1-x</sub> films (x ranging from 0 to 1) grown on Si by molecular beam epitaxy and employed X-ray photoelectron spectroscopy and spectroscopic ellipsometry to measure band offsets of ZnS,Se<sub>1-x</sub> with respect to Si and have compared the results to Sentaurus optoelectronic simulations of photovoltaic devices incorporating ZnS,Se<sub>1-x</sub> carrier-selective contacts. Further experimentally-determined parameters, including complex refractive index and resistivity, were also included in simulations of a HIT-style cell to determine the ZnS,Se<sub>1-x</sub> top contact mole fraction x, doping level, and thickness for optimal device performance. In simulations, the highest performance ZnS,Se<sub>1-x</sub> contact is found to outperform the simulated and experimental performance of a comparable HIT cell with a- Si/ITO front contact. Experimental transport measurements for ZnS,Se<sub>1-x</sub> top contacts will be discussed.

This material is based upon work supported by the NSF and the DOE under NSF CA No. EEC-1041895, by the DOE under Award Nos. DE-EE0006335 and DE-EE0004946, and by the NSF Graduate Research Fellowship under Grant No. 1144469.

EN11.03.02
PEDOT:PSS Hole Transport Layers Deposited by Spray Coating for Silicon Solar Cells Deniz Türkay<sup>1,2</sup>, Naser Beyraghi<sup>1,2</sup>, Milad Ghasemi<sup>1,2</sup>, Konstantin Tsoi<sup>1,2</sup>, Kerem Artuk<sup>1,2</sup>, Elif Cuce<sup>1,2</sup> and Selcuk Yerci<sup>1,2,2</sup>; 1Center for Solar Energy and Applications (GÜNAM), Turkey; 2Middle East Technical University, Turkey

The low temperature budget, availability of various deposition techniques, and wide range of adjustability in physical and electrical properties makes poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) a promising candidate as an hole-transport layer (HTL) for low-cost silicon based heterojunction solar cells. However, majority of works utilizing a PEDOT:PSS layer for silicon solar cells incorporate a spin-coating process for the deposition, which in fact is not a suitable technique for mass production as it inherently requires batch processing and a large portion of the dispensed solution is wasted in the process. In this work, we spray coat PEDOT:PSS layers on silicon surfaces as an alternative and use two different equipment: an in-house built airbrush system and a commercial ultrasonic coating system. For both systems, we investigate the coating quality on mirror-polished and random pyramid textured monocrystalline wafers. We analyze the effect of sample temperature and sample-to-nozzle distance on morphological properties and on electrical performance (contact resistivity, surface saturation current density) of the deposited films. Since the optimal deposition parameters and chemical content of the PEDOT:PSS films are heavily influenced by the hydrophobicity of the silicon surface, we perform the depositions on (1) surfaces having an ultra-thin chemical oxide, and (2) surfaces that are subjected to an HF dip prior to the deposition for oxide removal. Under optimized conditions, we achieve surface saturation current densities below 30 fA/cm<sup>2</sup> and contact resistivities below 100 mΩ.cm<sup>2</sup>. Finally, to demonstrate the performance on a device level, the
films are used as HTLs at the rear side of silicon solar cells where an n-type amorphous silicon layer serves as the electron transport layer at the front side of the cell.

EN11.03.03
On the Origin of Photoresponse of Au- and Ti-Hyperdoped Si Photodiodes

Shao Qi Lim¹, Christopher Lew², Philippe K. Chow³, Brett Johnson², Jeffrey M. Warrender¹ and Jim Williams¹; ¹Australian National University, Australia; ²The University of Melbourne, Australia; ³US Army ARDEC, United States

Si-based near-and mid-infrared photodetectors have been demonstrated through the introduction of an intermediate band in the bandgap of Si by hyperdoping with deep level impurities. The potential CMOS compatibility of such materials makes it attractive to the ICT and military sectors, and could advance the realization of cheap and high-resolution infrared imaging. These materials are typically fabricated by ion implantation followed by pulsed laser melting (PLM) to achieve hyperdoping concentrations beyond the Mott limit (~10²⁰ cm⁻³).

Studies involving Te-, Se-, and S-hyperdoped Si have demonstrated optical activity up to the mid-infrared [1-2]. However, at the highest doping concentrations the material undergoes an insulator-to-metal transition, making it unfavourable for a near-infrared photodetector. On the other hand, detectors made from Si hyperdoped with transition metals that introduce deep level states closer to mid-gap of Si, such as Ti and Au, exhibit a near-infrared photoresponse with an activation energy between 0.72—0.78 eV [3-4]. However, these diodes have very low quantum efficiencies, and the reason for this is currently unclear.

In a recent study of Au-hyperdoped Si diodes [5], we observed a deep level defect at Ec-0.35 eV originating from the interaction between implantation and PLM-induced defects at concentrations as high as 10¹⁴ cm⁻³ within the device depletion layer. In this presentation we present photocurrent data from these diodes and show that the Ec-0.35 eV defect and the Au-related deep level give comparable contributions to photocurrent. Hence, our experiments suggest that the near-infrared spectral kink previously observed in both Au- and Ti-hyperdoped Si diodes is almost certainly related to the Ec-0.35 eV defect and not hyperdoping, indicating that there is an underlying problem with present photodiode structures for hyperdoped materials. In a further series of experiments, we show that the hyperdoping of Ti in Si (required for optical activity) cannot be achieved by PLM in the nanosecond regime, providing further evidence for the contribution of processing defects to the observed near-infrared absorption and photoresponse in the Si(Ti) system.


EN11.03.04
Controlling the Spacing of Silicon MW Arrays for Radial Junction Solar Cells via Microsphere Lithography

Namwoo Kim, Inchan Hwang and Kwanyong Seo; UNIST, Korea (the Republic of)

Silicon microwires (MWs) have been widely investigated for realizing the high-efficiency silicon solar cells thanks to the outstanding light absorption property and ease of the formation of the radial junction. To achieve the high-efficiency MW based radial junction solar cells, it is necessary to control the structure of MW arrays such as diameter and length of the MWs and spacing between MWs. The structure of MW arrays is generally determined by the process conditions of the optical lithography, which is the method of forming the pattern. However, the patterning process based on optical lithography reaches the fundamental diffraction limit of about 200 nm. Also, the optical lithography process uses photoresist that is harmful to the human body and requires expensive equipment and a specific place, such as a clean room.

In this presentation, we introduced a novel fabrication process of MW arrays through microsphere lithography. In general, the microsphere lithography is the technique to form hexagonally packed ordered arrays of micrometer-sized latex or silica spheres as lithography masks. The spacing between the spheres can be controlled simply by etching the uniformly arranged the microsphere arrays. Also, microsphere lithography has the advantages of low cost, large scale fabrication, and high throughput performance.

We formed a monolayer of polystyrene beads using microsphere lithography on a silicon wafer and controlled the
spacing between the beads through the oxygen plasma etching up to 100 nm. As a result, we successfully fabricated MW arrays with a dense spacing of 100 nm using polystyrene beads monolayer as an etching mask. The fabricated MWs via the microsphere lithography process exhibited an excellent light absorption of 97% at the entire wavelength region (300-1100 nm) even without anti-reflection film layer. The MW arrays with dense spacing enable the use of MWs that are shorter than that of MWs with micro-scale spacing due to the reducing of a reflective surface. Also, the reduction of the MW length has the effect of reducing the surface recombination of the carriers separated by the radial junction of the MW. Therefore, we expect the proposed microsphere lithography would be the essential process for the formation of optimized MW arrays for the high-efficiency radial junction solar cells.

EN11.03.05
Facile Annealing Strategy to Improve Surface Uniformity of Sputtered BaSi2 Films
Yilei Tian1, Ana B. Montes1,2, Olindo Isabella1 and Miro Zeman1; 1Delft University of Technology, Netherlands; 2University of Lisbon, Portugal

BaSi2 is regarded as a promising absorber material in thin-film solar cell applications, due to its excellent optical and electrical properties, including a suitable band gap (~1.3 eV), a high light absorption coefficient reaching 10⁵ cm⁻¹ for photon energy > 1.5 eV, a long minority carrier lifetime τ (~10-27 μs), and essentially elemental abundance and nontoxicity [1]. Besides molecular beam epitaxy and thermal evaporation, sputtering is an industrially applicable technique to fabricate BaSi2 thin films. However, structure transformation and property degradation due to thermal annealing process have become major concerns for obtaining high-quality BaSi2 films [2]. Herein, we present a facile annealing method to suppress the surface oxidation of sputtered BaSi2 process by employing a capping BaSi2 film, which further improves surface uniformity of BaSi2 films.

Depositions of BaSi2 thin films were done in a radio-frequency magnetron sputtering setup. Detailed deposition parameter can be found in our previous research [2]. Glass substrates were used. After the sputtering process, deposited BaSi2 films were subsequently annealed at 600 °C for 30 min in vacuo. During the annealing process, the sample was covered by the other BaSi2 film on the glass substrate, with a film facing film configuration. Raman spectra were recorded on a Renishaw InVia Raman microscope with a 633-nm laser. Raman mapping was done with a scan area of 40 × 40 μm².

Three distinct regions can be observed from the Raman mapping of the BaSi2 sample, which was partially covered by the other BaSi2 film during the annealing, including (i) a uniform region (covered by BaSi2), (ii) a transition region and (iii) a non-uniform region (exposed to the annealing environment). Five Raman peaks of BaSi2 (bands at 276 cm⁻¹, 293 cm⁻¹, 355 cm⁻¹, 376 cm⁻¹, and 486 cm⁻¹) can be found in all these three regions [3]. In addition to those peaks, a peak at 245 cm⁻¹, which might be related to the surface oxidation, and a peak at 519 cm⁻¹, which indicates the formation of Si nanocrystals (NCs), can be observed in the transition and non-uniform regions. Raman intensity maps of peak 245 cm⁻¹ show that surface oxidation mainly occurred in the exposed (non-uniform) region, and more Si NCs are also detected in this region due to the oxidation. Contrarily, the covered region presents nearly no Si NCs and oxide peaks. This suggests that surface oxidation could be effectively suppressed by covering BaSi2 films during annealing. Also, BaSi2 distributes more uniformly in the covered region according to the Raman maps of peak intensity of 486 cm⁻¹ (BaSi2). In the exposed region, a smaller width of peak at 486 cm⁻¹ can be observed, uncovering a better BaSi2 crystalline quality in the exposed region compared to the covered region. Because of the existence of capping BaSi2 layer, less heat can reach to the covered BaSi2, thus leading to a less effective crystallization.

In this annealing method, the capping BaSi2 layer might function in effect as an oxygen-eliminating agent, so that less oxygen exists between those two BaSi2 films. In our configuration, the capping BaSi2 layer is closer to the heater, which heats to a higher temperature the capping BaSi2 compared to the covered BaSi2. Hence, the residual oxygen in the annealing environment is inclined to react with the capping BaSi2 film and this suppresses the oxidation of the covered BaSi2. However, the lower temperature of covered BaSi2 in turn slightly slows down the crystallization of BaSi2. Currently, we are working on the optimization of annealing condition to improve the crystalline quality, such as increasing the temperature, prolonging the duration and adjusting the annealing atmosphere. Further characterizations are being conducted as well.

References
Enhancement in Efficiency of Solar Cells by Controlling Layers Thickness and Interfacial Layer of Directly Grown Graphene
Malik A. Rehman; Sejong, Korea (the Republic of)

Although semiconductors pn junctions and metal semiconductor Schottky junctions are considered to be constituent elements of photovoltaic and electronic devices. But after the discovery of graphene, immense interest has been developed to make graphene silicon Schottky junction solar cells. The ultrathin 0.33 nm layer of graphene has capability to absorb 2.3% of visible light. These ultrathin layers are not just used as an absorbance material, but due to its essential properties such as tunable work function it increases the Schottky barrier height and built in potential for efficient transport of charge carriers in photovoltaic devices. Recently, graphene/Si Schottky junction solar cells are extensively used to harvest solar energy but high efficiency is limited due to huge surface recombination at the interface. Moreover, during the wet transfer process; wrinkles, surface defects and impurities deteriorate the performance of device. Thus, we propose an ideal approach to directly grow the graphene on planar and textured silicon by using plasma-enhanced CVD, compatible with industrial level applications. Thus, by controlling the thickness of interfacial layer Al₂O₃ and graphene, we achieved highest efficiency. The high-k dielectric layer of Al₂O₃ blocks the electron and eventually reduces the surface recombination at the interface. However, with the optimization of graphene thickness layer, there was an improvement in the work function of graphene, likewise an enhancement in open circuit voltage. Resultantly significantly improving overall device efficiency. Additionally, with control of thickness of graphene on bare silicon, efficiency was increased from 3.6% to 5.51%. Thus, so far with interfacial layer optimized thickness, we achieved highest efficiency of 8.4%. Interestingly, with doping of nitric acid and anti-reflection polymer layer coating of PMMA efficiency is remarkably improved from 5.51% to 9.18%. However, with doping and polymer layer coating the cell stability for longer time was compromised, while, with Al₂O₃ interfacial layer solar cells have excellent stability for more than one year.

Interdigitated Back-Contact c-Si Solar Cells with Non-Conventional Selective Contacts
Benjamin Andres Pusay, Rosa Estefania Almache, Gerard Masmitja, Eloi Ros, Joaquim Puigdollers, Isidro Martin, Cristobal Voz and Pablo Rafael Ortega; University of Politecnica-Catalunya, Spain

The photovoltaic industry is mainly dominated by crystalline silicon (c-Si) based solar cells where, the contact selectivity is usually achieved by doping the wafer surfaces with phosphorus and boron atoms. Several alternatives are used in order to avoid the high temperature, furnace-based, diffusion process. Examples include silicon heterojunction using both intrinsic and doped amorphous silicon films, or the formation of p⁺ and n⁺ regions by laser-firing of doped dielectric films. Nevertheless, in both cases the use of toxic and flammable gases is required. Recently, the use of dopant-free materials based on transition metal oxides like MoOₓ and V₂Oₓ have shown excellent hole and electron selectivity. The use of TiO₂ is an attractive option to form electron-selective contacts, due to its small conduction- and large valence-band offsets (ΔEₓ ~0.05 eV, ΔEᵥ ~2.0 eV), allowing an easy electrons transport through the c-Si/TiO₂ interface while blocking the holes. The introduction of a SiO₂ interlayer at the c-Si/TiO₂ interface improves the quality of the selective contact reaching efficiencies up to 21.6%. The replacement of this high temperature (700 C) SiO₂ layer by other dielectric films deposited a low temperatures is an interesting objective. [1]

In this work we study the properties of Al₂O₃/TiO₂ stacks deposited by Atomic Layer Deposition at low temperature (125 C) as electron transport layers. The goal is to use the optimized Al₂O₃/TiO₂ stacks as selective contacts in interdigitated back-contacted (IBC) c-Si(n) solar cells. Results have confirmed surface recombination velocities below 40 cm/s with implied open circuit voltage values of 675 mV in symmetrical Al₂O₃/TiO₂ test samples. Specific contact resistance values below 3 mΩcm² are also measured. These excellent results pave the way to use these stacks as electron selective contacts on IBC solar cells, in combination with V₂Oₓ hole selective contacts. Experimental and technological details as well as first IBC solar cell results will be presented. [1] X. Yang, et al., Advanced Materials 2016, 28, 5891.

Neural Network to Determine Appropriate Thermocouple Positions in Crystal Growth Furnace
Abderahmane Boucetta1, Kentaro Kutsukake2, Hiroaki Kudo1, Tetsuya Matsumoto1, Takuto Kojima1 and Noritaka Usami1;
1Nagoya University, Japan; 2AIP, RIKEN, Japan

EN11.03.08
Neural Network to Determine Appropriate Thermocouple Positions in Crystal Growth Furnace
Abderahmane Boucetta1, Kentaro Kutsukake2, Hiroaki Kudo1, Tetsuya Matsumoto1, Takuto Kojima1 and Noritaka Usami1;
1Nagoya University, Japan; 2AIP, RIKEN, Japan
To produce high-quality silicon ingots for solar cells, good control of growth conditions such as the gas flow and the temperature distribution is required. This last has a direct effect on the growth rate, the shape of solid/liquid interface, and thermal stresses. For this concern, it is important to measure the temperatures inside the furnace and around the crucible. However, it is difficult to implement infrared thermometers in directional solidification (DS) furnaces nor installing many thermocouples (TCs) because of the limited space and the movement during the growth. The current study focuses on finding the appropriate positions to install TCs around the crucible that allow us to get the temperature distribution. Due to the presence of abundant variables such as the crucible movement and the temperature of multiple heaters, we decided to solve this issue by a combination of crystal growth simulation and machine learning. Crystal growth experiments with typical conditions were simulated using CGSim software, and the results were used as training data for machine learning. To predict temperature distribution from the limited number of TCs, we have made $2^1C_4 \times 5985$ neural network (NN) models by picking 4 TC positions out of 21 candidate positions on the crucible wall. The NN models consist of 8 inputs (3 heater temperatures: upper, middle and bottom, 4 measured TC temperatures: TC1, TC2, TC3 and TC4, and crucible position) and 21 outputs that correspond to the temperatures distribution on the crucible wall. The minimum loss was obtained at the NN model with the TC positions at 0, 1, 2 and 9 cm from the bottom of the crucible to its top. All the NN models with the ten lowest losses have the TC positions 0, 1 and 2 cm from the bottom of the crucible. This suggests the importance of measuring the temperature around the bottom of the crucible to obtain the precise temperature distribution.

**EN11.03.09**

**Boosting Silicon Solar Cell Efficiency through Upconversion-Assisted Enhanced Absorption in Near Infrared**

Nidhi Dua, Rajinder S. Deol, Mohammed S. Reza and Madhusudan Singh; Indian Institute of Technology Delhi, India

Mono- and multi-crystalline silicon-based solar cells form the bulk of global installed photovoltaic capacity (~403 GW in 2018) for commercial power generation, with a 27% cumulative annual growth rate achieved in 2018, with grid parity being achieved in an increasing number of countries. The industry has matured over the last 15 years, going from silicon shortage to solar overcapacity, which has resulted in anti-dumping duties being imposed in several countries. Power conversion efficiencies in silicon are impacted by bulk defects, contacts, solar spectrum mismatch, etc. Specifically, the absorption coefficient in silicon starts declining below $10^3$ cm$^{-1}$ above around 800nm, declining to one-tenth that value near 1000nm. Such material limitations also manifest themselves in a peak in the responsivity of silicon-based detectors. In this work, we report on the development of an upconversion-based absorber (NaYF$_4$: Yb(18%), Er(2%), Gd(15%)) operating near 980 nm used for increasing the efficiency of a commercial solar cell. The absorber was synthesized using thermal decomposition, followed by powder X-ray diffraction (PXRD) measurements which reveal a mostly hexagonal phase closely associated with high upconversion photoluminescence (PL) efficiencies. An ink composed of the product with polystyrene (PS) was formed with a loading ratio of 23% w/w in chloroform. Micro glass slides were cleaned using stepwise solvent clean, followed by a plasma ashing step, prior to spin coating with the ink to deposit a thin film. Scanning electron microscopy (SEM) scans of the deposited reveal a thickness of ~158±33 nm. Atomic force microscopy (AFM) scans reveal that the roughness of the films is approximately 31 nm. When excited with 785 nm laser light (intensity ~560 W/cm$^2$), upconversion emission at green (539 nm) and red (665 nm) is observed using a Horiba/Labram spectrometer. Upon excitation with 980 nm, however, green emission is observed with the naked eye. To test the viability of the idea, we used the coated glass slide in two measurement setups with a low-cost commercial solar cell (the slide placed on top of the solar cell): a) a 980 nm laser diode (Thorlabs, intensity ~ 450 mW/cm$^2$), b) under AM1.5G conditions with a solar simulator (Newport LCS-100). Under direct irradiance of 980 nm laser diode, we observed an enhancement of the short-circuit current ($J_{sc}$) of ~ 25% . The control device in each case was a blank uncoated glass slide placed on top of the solar cell. As expected, the enhancements were found to be somewhat lower with the solar simulator (~7.2% in $J_{sc}$). These increases are preliminary results with unoptimized films in a measurement geometry that is unlike one we envisage for deployed solar cells. We are currently engaged in verifying these initial measurements, and tuning the precise loading ratio with these upconversion absorbers to obtain higher increases in short-circuit currents, and developing films that can be deposited directly on top of the commercial solar cell to minimize incoupling losses.

**EN11.03.10**

**Theoretical Study of Tandem Solar Cell Configuration Based on Different Si Allotropes**

Rodion Belosludov and Haruhiko Morito; Institute for Materials Research, Tohoku University, Japan
The growing energy supply demanded by modern society poses challenges to scientists and engineers in that many of the currently used technologies and prospective innovations must be directed in a more sustainable way. The reduction in the use of fossil fuels and replacement with new environmentally friendly energy sources, especially renewable energy resources represents one of the present grand energy challenges. Sunlight is the most abundant free renewable energy source and crystalline silicon photovoltaics are among the leading technologies for solar power conversion. The efficiency of the solar cell mainly depends on the band gap and is limited to a maximum theoretical power conversion of ~ 31% [1]. One possible strategy to improve efficiency is to optimize the response of the photoactive materials at shorter wavelengths. The combination of high-efficiency solar cells in a tandem configuration on a Si platform using thin film III–V materials as well as perovskites has recently attracted great attention [2]. Silicon clathrates are inclusion compounds that consist of a Si cage-like framework with a direct 1.9 eV band gap and can be considered for photovoltaic applications including thin-film single-junction devices such as Si clathrate on c-Si for all-Si tandem cells.

The structural optimization and electronic properties of Si clathrates with cubic structures I (CS-I) and II (CS-II), silicon surface and Si clathrates on silicon surface have been performed using first-principles calculations within the framework of density functional theory (DFT).

The atomic optimization of Si clathrates with and without Na atoms as well as Si (001) surface were carried out. The obtained results showed that the band gap of pure Si clathrate is larger in comparison of band gap of Si surface. The present of sodium shifts the Fermi level to conduction band which indicates the importance of guest removing from clathrate framework. The reconstruction Si clathrate on c-Si surface was performed using ab-initio molecular dynamic simulations during 5 ps at 300 K. The clathrate structure remains cage-like framework after deposition of Si surface and the electronic structure of tandem configuration is changed due to removing dangling bonds on the surface. Thus, the present study revealed the possibilities for modifying the electronic and optical properties of crystalline silicon photovoltaics by deposition of thin-film Si clathrate.

REFERENCES

EN11.03.11
Effect of Buffer Layer Changing on Characteristics of the Tandem Solar Cell of Dye-Sensitized Solar Cell and Silicon Solar Cell Masaya Ando, Shinya Kato, Naoki Kishi and Tetsuo Soga; Nagoya Institute of Technology, Japan

Since the conversion efficiency of single junction silicon (Si) solar cells is close to the theoretical limit, the application of tandem solar cells with stacking order in different band gap energy (E_g) has attracted the attention. It is expected that the solar cell performance can reach around 40% efficiency by combining the silicon solar cell (E_g=1.12 eV) as the bottom layer and dye-sensitized solar cell (DSSC) based on the N719 dye (E_g=1.7 eV) as the top layer for tandem solar cell structure. In that cell, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)/PEDOT:PSS can be used as the buffer layer between the top cell and bottom cell which involved the silver (Ag) grid and passivation layer component. Although the DSSC/Si tandem solar cells have been investigated so far, there is no detailed information near the PEDOT:PSS of this tandem solar cell. Therefore, here, we studied the effect of changing in property of buffer layer containing PEDOT:PSS on the solar cell characteristics.

To make the solar cell device, firstly, we prepared the electron transport layer by depositing titaniumdioxide(acetylacetonate)/TiO_2 via spin-coating which was followed by nanoporous TiO_2 (P25) deposition via doctor blade method onto FTO glass substrate. Then, this layer was annealed at 450°C for 30 minutes and soaked in N719 dye for 18 hours to fabricate the DSSC electrode. Secondly, for Si solar cell preparation, the 80nm-thick ITO was sputtered on a pn junction Si wafer. Thereafter, Al electrode was deposited on the back surface of Si wafer by thermal evaporation method. Also, PEDOT:PSS (PH1000) layer with dimethylsulfoxide (DMSO) addition was coated on ITO by spin-coating. Finally, the performance of DSSC/Si tandem solar cell was measured by AM 1.5 solar simulator after an iodine electrolyte injection.

As a Si solar cell, a pn junction Si wafer (pn-Si) and a pn junction Si wafer with Ag grid and a passivation layer (Ag-pn-Si) were prepared. When the only PEDOT:PSS layer was deposited between the top cell and the pn-Si bottom cell, the open-circuit voltage (V_op) of tandem cell was more than 1 V, whereas the V_op of DSSC and Si solar cell before stacking were 0.6-0.7 V and 0.5 V, respectively. On the other hand, if Ag-pn-Si is introduced as a bottom cell, the device stability became poor since it is difficult to protect the electrode corrosion due to the iodine electrolyte usage. Although the only deposited ITO layer in-between the top cell and bottom cell could greatly
reduce the $V_{oc}$ up to 0.2 V, interestingly, the introduction of ITO layer under PEDOT:PSS has succeeded in electrode protection from corrosion which has improved the photovoltaic properties. Based on these results, it is noted that the improvement of buffer layer in the DSSC/Si tandem solar cell can increase the conversion efficiency of photovoltaic device. Furthermore, PEDOT:PSS film conditions on the photovoltaic properties of DSSC/Si tandem solar cell will be discussed later.

EN11.03.12  
**A Study on Circuit Modeling for Shadowing Loss Analysis of Shingled Photovoltaic Modules**  
Jisu Park, WonJe Oh and Jaehyeong Lee; Sungkyunkwan University, Korea (the Democratic People's Republic of)

In the case of the shingled solar module, the power decrease according to the shading is large because of the reduction of the cell area due to the division. Therefore, it is necessary to develop a simulation method with high accuracy according to shading ratio and type to analyze the power loss and to design a module structure that shows stable power even when shading.

Based on the measured photo I-V data, the cell strips circuit is modeled using a double diode model, and the shingled string circuit is modeled by serial connection of the electrical equivalent circuits of the cell strips according to the number of interconnection. Since the cell strips are bonded by a conductive adhesive, the cell strip circuits are connected in series via the RECA corresponding to the ECA resistance component. Next, circuit modeling for shading loss analysis of shingled strings is performed. Finally, the accuracy of shading loss analysis circuit modeling is verified by comparing simulation results with actual measured values.

Based on the accurate shading loss analysis method, the shading loss according to the module structure is analyzed by applying the bypass diode according to the serial, parallel, and parallel / parallel arrangement of the string. We then design the module structure with low shading loss by calculating the power rate in shading.

EN11.03.13  
**A Study on the Design of Solar Cell Electrode Structure for High Power Photovoltaic Module Fabrication**  
WonJe Oh, Jisu Park and Jaehyeong Lee; Sungkyunkwan University, Korea (the Republic of)

New technologies for fabricating high-power modules include a cell dividing and bonding technique. This technique divides and joins cells into a string arranged in series and parallel to produce a module. Since the bus bar structure is not visible, the effective area for absorbing light increases, and since there is no space between cells, modules with high density can be manufactured. Therefore, modules with higher output than existing modules can be manufactured in the same area. The module manufactured by the dividing and bonding technique is called a shingled PV module, and this module requires a new electrode structure for dividing and bonding. Therefore, we designed the front electrode structure suitable for the shingled PV module by calculating the power loss according to the number of cell divisions and the number of fingers. Simulation results show that the number of fingers at maximum efficiency decreases as the number of divisions increases. This is because as the number of divisions increases, the distance between the busbars becomes narrow, so that the current collection of one finger between the bus bars becomes smaller. Therefore, in order to collect the same amount of current, the interval between the fingers must be widened, which means a decrease in the number of fingers. Therefore, as the number of divisions increases, the maximum efficiency is obtained in the case where the number of fingers is small. In addition, the actual solar cell of the electrode pattern having the optimum number of fingers for each type of divided cell is manufactured and analyzed. In order to investigate the applicability of the solar cell with the designed electrode structure to the shingled PV module, we investigated the characteristics change after bonding the cells divided by the laser with the conductive adhesive.

EN11.03.14  
**Investigation of Silicon Carbide Schottky Barrier Diodes with Silicon Nitride Interface Layer**  
Hasan H. Gullu¹, Ozge Bayrakli Surucu², Makbule Terlemezoglu³,³,⁴, Seda Kayra Gullu³,⁵ and Dilber Esra Yildiz⁶; ¹Atilim University, Turkey; ²Kirsehir Ahi Evran University, Turkey; ³Middle East Technical University, Turkey; ⁴Tekirdag Namik Kemal University, Turkey; ⁵Tubitak Space Technologies Research Institute, Turkey; ⁶Hitit University, Turkey

Silicon carbide (SiC) has attracted considerable attention for photonic and electronic device applications due to inherent electrical and high thermal conductivity, indirect wide band gap, large critical breakdown electric field, high saturation electron drift velocity and high chemical stability in the use of metal-semiconductor (MS) Schottky barrier diodes (SBDs) with and without interfacial layer. It has also superior characteristics that present alternatives
to the inherent problems in the use of oxide and carbon based catalysts. In this study, a novel metal-insulator-semiconductor (MIS) diode including a silicon nitride (Si$_3$N$_4$) layer was investigated to improve SiC based MS diode. Although there are many reported work on the electrical characteristics of this kind of wide band gap semiconductor diodes under the effect of insulator layer, it is still an open research area to develop a complete understanding on contribution to the electronic characteristics. Recently, high dielectric constant materials have attracted considerable attention as an alternative interfacial layers for their photonic and electronic device applications at metal/semiconductor interface. Under this aim, the current-voltage, capacitance-voltage and conductance-voltage characteristics of MIS 4H-SiC diodes were analyzed and compared to the MS diodes. The MS heterojunction diode was fabricated by thermal evaporation of Au metal onto the n-4H SiC wafer substrate and Si$_3$N$_4$ layer was deposited into the metal/semiconductor interface by magnetron sputtering method. Forward and reverse biasing behavior of diodes were discussed according to thermionic emission with Gaussian distribution of barrier height and Schottky emission models, respectively. Device parameters as, barrier height, ideality factor, interface states, and series resistance were also calculated comparatively among these two diodes. The capacitance values for MS diode was found in decreasing behavior from ideality with crossing the certain forward bias voltage point whereas rapid increase in conductance values with the increasing voltage was observed for all fabricated diodes. Under all these works, high device performance was considerably observed from the Au/n-4H SiC diodes with Si$_3$N$_4$ interfacial insulator layer.

EN11.03.15

Defects in a-Si for Electronically-Coupled Upconverters in Silicon Solar Cells Wenjie Yang and Daniel Macdonald; Australian National University, Australia

The electronically-coupled upconverter (ECUC) is a novel concept for harvesting sub-band gap photons in silicon solar cells through the impurity photovoltaic effect [1]. Unlike conventional intermediate band approaches [2] in which mid-gap defects/impurities are introduced to the bulk of the device, this approach utilises a wider-band gap upconverter layer (e.g. a-Si) situated at the rear of a conventional Si solar cell in which the defects are contained. The band offset between the upconverter and the Si-bulk sweeps sub-band gap photocarriers generated in the upconverter into the base whilst isolating carriers generated in the base from entering the upconverter, allowing a net gain in carriers.

While a-Si ECUC layers containing ion-implantation-induced defects have been shown to absorb at sub-band gap wavelengths [3], it remains to be seen whether sub-band gap photocarriers can indeed be generated. In this work, we use a range of different implantation and post-implantation annealing conditions to control the type and concentration of defects in the a-Si. We investigate the generation of carriers in a-Si ECUC layers by measuring the band-to-band photoluminescence from both the Si substrate and the a-Si layer itself, under sub-band gap laser excitation of a few kW/cm$^2$. We also use time-resolved photoluminescence to study the recombination dynamics within the a-Si layer. Finally, we explore the possibility of incorporating other impurities into the ECUC layer to enhance its sub-band gap photoresponse.

References:

EN11.03.16

Fabrication of poly-Si Membranes Using Water-Soluble Sacrificial Sr$_3$Al$_2$O$_6$ Oxide Layers Jungkwu Kwon, Changhoon Jeong, Jungi Min and Sangwoo Ryu; Kyonggi University, Korea (the Republic of)

Recently facrication of heterostructure membranes using sacrificial layers has been widely investigated as it can be used to understand the effect of interfacial strain inside the bottom-up heterostructures. In addition, similar to 2D materials like graphene, a transfer method of a thin heterostructure membrane into other devices is simulating industrial interest. However, most of the previous works report only limited size of the membranes. In this study, we show a cost-effective way to fabricate large scale poly-Si membranes grown ona water-soluble Sr$_3$Al$_2$O$_6$ (SAO) sacrificial buffer layer. SrCO$_3$ and α-Al$_2$O$_3$ are mixed at a molar ratio of 3:1 and calcined at 1200°C to synthesize
SAO. The SAO slurry is prepared by mixing the synthesized SAO powder with PVB and ethanol, and a 10 μm-thick SAO layer is deposited on a Si wafer with a micrometer film applicator and then sintered 650°C. After the deposition of Si on top of Si on top of the SAO layer using various deposition method, the dissolution of SAO into water. XRD analysis reveals that poly-Si membranes are obtained. In order to explore the possible application to solar cells, photovoltaic properties of the poly-Si membranes such as light absorption, current density, open circuit voltage and minority carrier were examined.

EN11.03.17
Organic/Inorganic Hybrid Coatings of Silicon Solar Cell Back Sheet to Reduce Moisture Permeability
Dongwook Jung, Jungi Min, Eunjin Jang and Sangwoo Ryu; Kyonggi University, Korea (the Republic of)

Al₂O₃ is one of the widely investigated materials for preventing moisture permeation of electronic devices. However, a phase transition occurs when it is exposed to a harsh environment making a channel inside through which water can permeate. In this work, a silane-based polymer (Silamer) layer is introduced to solve this problem as Al₂O₃ is deposited on a back sheet (BS) of silicon solar cells. Al₂O₃ was deposited at 70 °C by atomic layer deposition (ALD) and Silamer was spin-coated followed by curing in low vaccum at the same temperature. During this process, the Silamer layer forms a three-dimensional SiO₂-embedded organic layer and planarizes the BS covering pin-hole defects, which reduces the moisture permeation. By adjusting the thickness and the structure of the deposited layers, Silamer (400 nm) / Al₂O₃ (40 nm) / BS is found to be the most effective for waterproofing with the lowest WVTR value through Ca tests. As it is applied to silicon solar cells, this organic/inorganic hybrid coating shows to reduce potential-induced degradation effectively which is mostly caused by ion migration through the channels formed by the moisture permeation. In addition, alternative deposition methods of Al₂O₃ other than ALD for scaling up will be discussed.

EN11.03.18
First-Principles Study in Search for Stable Dopants in Hyperdoped Silicon for Infrared Photoresponse
Naheed Ferdous and Elif Ertekin; University of Illinois at Urbana-Champaign, United States

Silicon (Si) based solar energy conversion systems have a large variety of applications, including photovoltaics, photodiodes and photodetectors. The conversion efficiency depends on the absorption of incoming solar energy. Unfortunately, photoresponse of Si is limited by its band gap (1.12 eV) that does not allow absorption below visible wavelength of sunlight. For effective solar energy conversion to electrical signal, enhanced photoresponse has been achieved by doping silicon beyond its solid solubility limit. The highly non-equilibrium supersaturation process is known as hyperdoping that includes ion implantation followed by pulsed laser melting and rapid resolidification. The high concentration of dopants modifies the optoelectronic properties of Si by forming defect levels within the forbidden band gap, but it comes with a price of metastability. Most recently gold (Au) has gained renewed interest as an impurity in Si that is intentionally introduced to extend optical absorption towards infrared region. However, experimental evidence showed that upon thermal relaxation, the absorption suddenly drops down. This suggests that the solubility and stability of dopants in Si are equally important as infrared absorption. Therefore, a systematic study is essential to identify possible dopants that have either high solubility or low diffusivity so that it becomes kinetically trapped during thermal relaxation and preserves the high optical absorption. In this work, we use first-principles density functional theory (DFT) to obtain the possible defect configurations of candidate dopants in Si. Primarily late 3d transition metals are chosen as they provide defect levels in the middle of the band gap of Si and are promised to provide infrared absorption. Among them, manganese (Mn), cobalt (Co) and silver (Ag) are chosen from optical point of view. On the other hand, from the solubility point of view, nickel (Ni) and copper (Cu) shows better solubility (1 and 2 orders of magnitude higher) than Au, which are group IB materials. Further, we analyze the optical absorption of possible equilibrium defect configurations in conjunction with their solubility. Finally, we discuss how diffusivity can play a role during thermal relaxation and consequently on optical absorption.
High-Volume Production of Ultra-Low-Cost Silicon Absorber Materials Manufactured via Kerfless Direct Wafer® Process

Adam Lorenz, Jasmin Hofstetter, Ralf Jonczyk, Ray Fraser, John Linton and Ali Ersen; 1366 Technologies Inc., United States

As the PV industry strives toward terawatt scale, addressing the last remaining cost centers of the crystalline silicon value chain is essential to achieving the extremely low levelized cost of electricity (LCOE) required to drive solar's adoption. To date, improvements within the value chain have focused primarily on cost reduction, with most technical contributions happening on the surface of the material, at the cell level. New fabrication methods have emerged that change this dynamic and allow for significant strides in both cost reduction and technical advancements with the absorber materials themselves.

Alternative absorber fabrication methods such as the Direct Wafer process are synergistic with lower cost and higher absorption, as well as more efficient energy usage. In Direct Wafer manufacturing, which has reached high-volume production, wafers are grown one-by-one directly from a small reservoir of molten silicon in a high-purity growth environment. Direct access to the wafer-forming surface and the molten silicon reservoir allow modifications of individual wafer properties, customized for a given cell architecture. Efficiency parity with high-performance cast multi-crystalline wafers has been demonstrated on a PERC production line at 20.5% average efficiency. This discussion will also demonstrate that Direct Wafer technology is synergistic for use with future cell architectures such as TOPCon that are insensitive to bulk resistivity and require high minority carrier lifetime or device architectures such as tandem which necessitate a low-cost base material with bandgap suited for long wavelength absorption.

The high-purity growth environment of the Direct Wafer process limits the introduction of dopant impurities into the feedstock and allows high bulk resistivity beyond 100 Ω-cm. Since wafers are also grown one-by-one, bulk resistivity can also be easily tuned and targeted around virtually any resistivity. This allows for a much tighter distribution than what is possible in ingot-based wafers where resistivity distribution is governed by solid-liquid segregation leading to a wide range of resistivities along the ingot height.

The low impurity concentration in Direct Wafer product is also reflected in the high effective lifetime that can be achieved. Electron lifetime in Direct Wafer product increases with increasing resistivity and effective lifetime >1 ms have been validated. Advanced cell architectures like PERT and TOPCon cells require lifetimes of milliseconds to achieve their efficiency entitlement and leverage potential LCOE advantages despite increased cell production cost. Currently, mostly high-cost n-type mono-crystalline wafers are used for advanced cell architectures because of higher lifetime in n-type silicon. With Direct Wafer product, there is considerable potential to accelerate the adoption of higher efficiency device architectures as low-cost, high-resistivity Direct Wafer product replaces the more expensive n-type mono wafer.

Advanced, low-cost wafer manufacturing also provides a course to cost effective tandem cell fabrication. The technical roadmap for the Direct Wafer process provides for a cost of just $0.12 per wafer through a combination of ~1.5g/W silicon utilization and lower non-silicon conversion costs than current ingot-sawn wafers. This base, combined with low-cost cell processing tailored for long wavelength absorption at lower current, makes an economically favorable candidate for realizing commercial tandem modules that exceeds the performance of today’s best single-junction silicon modules at a lower total cost/watt.

An inherent high-purity growth environment and unique features distinguish Direct Wafer technology from standard sawn wafers. The benefits of a more efficient approach to fabrication coupled with the ability to access the raw material at the melt level present an opportunity to leverage low-cost wafer technology with numerous future advanced cell architectures.

Investigation of the Role of Hydrogen in Light- and Elevated Temperature-Induced Degradation in p-Type Silicon through Intentionally Inducing Defects with Tabula Rasa

Abigail R. Meyer1,2, Vincenzo LaSalvia2, William Nemeth2, Matthew Page2, David L. Young2, Paul Stradins2 and Sumit Agarwal1; 1Colorado School of...
Currently, the photovoltaic (PV) market is dominated by boron-doped, or $p$-type, silicon (Si) solar cells. More specifically, the Si PV market is moving from a more traditional architecture, the aluminum back surface field (Al-BSF) solar cell to a more advance structure, the passivated emitter rear contact (PERC) solar cell. The PERC cell features exceptional surface passivation and therefore, higher efficiencies compared to the Al-BSF. However, with the surface no longer limiting the PERC cell, bulk lifetime becomes increasingly more important to raise efficiencies. One source of recombination within the PERC Si bulk is light and elevated temperature induced degradation (LeTID) where cells and modules experience a decline in minority carrier lifetime when exposed to illumination at elevated temperatures. LeTID was discovered only ~5 years ago and therefore, the degradation and regeneration mechanism, along with the defect structure, are unknown. A preliminary solution to LeTID has been discovered [1] but requires intense illumination and high temperatures and can take ~15 hours to complete. In order for $p$-PERC cells to continue to dominate the PV market, we must ensure their efficiencies rise and remain stable throughout their time in the field.

LeTID can result in a ~10% relative efficiency loss of $p$-PERC solar modules over their lifetime in the field [2]. The defect which causes LeTID is thought to be hydrogen, and more specifically, related to the over hydrogenation of cells during the firing process to create contacts. Many empirical studies have been conducted to link hydrogen to LeTID, but no atomistic studies have been brought forward to solidify this hypothesis. In this work, we aim to study the role of hydrogen in LeTID by intentionally inducing defects in boron-doped float zone ($p$-FZ) silicon (Si) and therefore, manipulating the amount of hydrogen that is held in the Si bulk after fast firing. We hypothesize that by allowing the Si bulk to hold more hydrogen, samples will experience increased degradation caused by LeTID compared to samples without intentionally induced defects.

References
stability. Furthermore, they have shown specific colors owing to the colors of polymers or dyes. To address this issue, some researchers have been developed near infrared (NIR)-absorbing STSCs to fabricate neutral-color STSCs like that of glass. However, NIR-absorbing STSCs have been shown very low PCE under 1% until now. Accordingly, a different approach is required to develop STSCs with neutral color, high PCE, and long-term stability.

As a method to develop new-concept neutral-color STSCs with high PCE and stability, crystalline silicon (c-Si) based STSCs can be considered. c-Si would be one of the best candidates to develop STSCs because conventional c-Si solar cells are known to exhibit high PCE and long-term stability compared to other solar cells. However, the development of c-Si based STSCs is extremely challenging due to the opaque characteristic of c-Si wafers with thicknesses of 200 µm. To fabricate STSCs using c-Si, thinning of c-Si has been considered as a method to increase transparency. However, as the absorption of long-wavelength light is extremely limited in thin films, their application to solar cells is not suitable. In addition, a thin c-Si film has a particular color because of absorption spectrum cutoffs in the visible light wavelength range.

In this presentation, we show a novel approach to develop neutral-color transparent c-Si solar cells. First of all, we have developed a neutral-color transparent c-Si substrate using a 200-µm thick c-Si wafer, which is known to be opaque. Transparent c-Si substrates were fabricated by placing hole-shaped light transmission windows on a bare c-Si wafer. These windows were designed to enable the transmission of all incident visible light through the substrate, resulting in a colorless substrate. In addition, the spacing between the holes was appropriately selected by considering the minimum angle of resolution for humans to ensure that the individual transmission windows are not visible to the human eye. A light absorption area was also designed on the substrate to efficiently absorb incident light of the spectral range between 300 nm and 1100 nm. The transmittance of the transparent c-Si substrate was systematically tuned from 20% to 50% under the full solar spectrum. The STSCs fabricated with the substrate exhibit a PCE of up to 12.2%, with $J_{sc} = 29.2$ mA/cm²; $V_{oc} = 588$ mV; and $FF = 71.1\%$ with a transmittance of 20%. The cell performance of the transparent c-Si solar cells is higher than those of other neutral-color semi-transparent solar cells reported thus far. Hence, our novel c-Si STSCs presents a unique opportunity to develop next-generation neutral-color STSCs which would satisfy high efficiency as well as high stability. Furthermore, we believe that this study makes a significant contribution to not only photovoltaics fields but also various transparent optoelectronics.
etch process is the protection of the passivation layer during the patterning, which eliminates a wet cleaning step and an additional deposition of the intrinsic a-Si:H layer. We report for this simplified process flow the best device with 22.7% efficiency (22.4% average efficiency and area of 2x2 cm²) and a $V_{OC}$ of 728 mV demonstrating high-quality passivation.

Second, we discuss the challenges of interconnecting IBC cells, notably connecting opposite cell polarities in the same plane with selective isolation and the necessity to use low-temperature processing. To develop an industrially relevant technology, low-cost and simplicity are essential but unmet requirements by current solutions. To overcome this challenge, we introduce the 3D woven interconnection concept based on standard module materials. Polymer encapsulant is interwoven with low-temperature solder-coated metal ribbons to form a three-dimensional woven fabric. The encapsulant provides the electrical insulation between ribbons of opposite polarity. Part of the ribbons electrically interconnect neighboring cells while ribbons in a perpendicular direction connect the cell metallization to the cell-to-cell ribbon, hence creating a two-level metallization. Additionally, the co-development of the materials and the lamination process enables a combined soldering and module lamination in one process step and within the limits of industrial laminators. We will demonstrate the adaptation of this technology to bifacial IBC cells as well as to busbarless cell design. We report on the properties of the interconnect in single-cell and mini-modules demonstrating < rel. 2% FF loss, Rsh> 7MΩ in isolation tests and showcase its stability in over 400 thermal cycles.

Third, we present our latest development in perovskite device stacks focusing on $\text{Cs}_{0.15} \text{(CH}_3\text{N}_2)_{0.85} \text{Pb(I}_{0.71} \text{Br}_{0.29})_3$ (CsFAPbIBr) as a photo-stable mixed-halide with a wide bandgap (1.72 eV). We show that the key to achieving high $V_{OC}$ is the careful control of perovskite-hole transport layer interface. Through effective interface passivation, we fabricate 1.72 eV mixed-halide perovskite solar cells with a $V_{OC}$ deficit as low as 0.5 V. We demonstrate in single junction semi-transparent perovskite devices with efficiencies of 11.7% without passivation and 13.8% with Al$_2$O$_3$ passivation layer in small area devices. This device also maintains an average transmittance of 90% in the wavelength range of 700 – 1200 nm making it an ideal top cell in 2 or 4-terminal tandem devices, which consequently contributes to a record 27.1% efficient perovskite/IBC c-Si tandem cell (area: 0.13 cm²), and 25.3% efficiency for 4 cm² perovskite minimodule on 4 cm² c-Si IBC cell. In the end, we will also report on upscaling of perovskite modules up to 30x30 cm² area.

10:45 AM EN11.05.02
Investigating the Contact Mechanism for Screen-Printable Ag/Cu Paste in the Si Solar Cell Using Microstructural, Optical and Electrical Analyses Keming Ren, Ye Tang, Yong Zhang and Abasifreke Ebong; University North Carolina at Charlotte, United States

The cost of photovoltaic electricity hinges on the metallization of the Si solar cells, which dominate today’s commercial cells. In a bid to further reduce the cost of the metallization, one of the feasible methods is to use cheaper metals to replace the dominant screen-printed Ag metal contacts, which account for the most cost of the metallization. Among all the metals, Cu is considered as an excellent potential alternative due to its similar conductivity (1.7 μΩ-cm for copper, 1.6 μΩ-cm for silver) but ~90 times less cost. However, Cu is known to diffuse into Si at high temperature, leading to shunt the junction and reduce the minority carrier lifetime in the cell. Thus, researchers have used plated Ni/Cu in which Ni acts as a barrier through NiSi formation to block Cu from diffusing into Si. But, because of the involving processing steps and reliability issues, this technology is not adopted. Since screen-printing technology is high-throughput and simple to manufacture solar cells, the most cost-effective method is, therefore, replacing the Ag or part of the Ag in the paste by Cu. But this method puts a strict requirement to the nature of the paste, in particular, that prevents the Cu from diffusing into Si during the high-temperature sintering of the contacts. Thus, it is important to investigate the microstructural (SEM, TEM), optical (Raman Spectroscopy) and electrical (conducting AFM) properties of the Ag/Cu/Si interface through one-step atmospherical firing process and thus to understand the contact mechanism of the Ag/Cu paste. This work, therefore, reports on the microstructural analyses (SEM, TEM) of the Ag/Cu/Si interface, supported by the Raman Spectroscopy and the conductive AFM. The preliminary studies showed that there was no evidence of Cu diffusion into the Si and Cu was found only in the reformed glass after high-temperature sintering. The conductive AFM revealed the contact mechanism was through the Ag crystallites grown in the Si. The electrical output parameters of the solar cell corroborated the microstructural, optical and electrical analyses.

11:00 AM EN11.05.03
Performance and Stability of Monofacial and Bifacial PERC Silicon Cells, with Comparison to Al-BSF
Jennifer Braid, Eric Schneller, Menghong Wang, Alan Curran, Jiqi Liu, Nick Bosco, Jennifer L. Carter, Raymond Weiser, Laura Bruckman, Bryan D. Huey, Kristopher Davis, Jean-Nicolas Jaubert and Roger H. French; 1Case Western Reserve University, United States; 2University of Central Florida, United States; 3National Renewable Energy Laboratory, United States; 4University of Connecticut, United States; 5Canadian Solar, Inc., China

Passivated emitter and rear contact (PERC) silicon photovoltaic cells comprise over 50% of all solar cells manufactured in 2019, and are expected to completely replace traditional aluminum back surface field (Al-BSF) cells by 2023. In addition to higher power yield due to reduced recombination at the rear contact, PERC cells can easily be manufactured with monofacial or bifacial architectures. However, the additional passivating dielectric layer in PERC cells, as well as the reduced rear-side metallization in bifacial cells, calls into question the long-term durability of this technology versus the established Al-BSF cell.

Here we compare the performance of monofacial and bifacial PERC cells, benchmarking against Al-BSF, both as bare cells, and in minimodules through damp heat exposure. Cells are characterized with illuminated I-V curve tracing, Suns-Voc, and electroluminescence, as well as photoluminescence and spatially resolved external quantum efficiency. Cell fragments are also investigated with photoconductive atomic force microscopy.

In this work, we show that PERC cells have greater stability through damp heat exposure than Al-BSF. Bifacial PERC cells also show surprisingly high mechanical durability compared with full rear side aluminized cells. Al-BSF cells show greater corrosion and resulting resistive losses than PERC cells when encapsulated with EVA. Performance loss due to additional degradation modes are also quantified. Comparison of electroluminescence and photoluminescence images of mini-modules, as well as external quantum efficiency measurements, reveal the underlying degradation mechanisms for each cell type. These results are confirmed with photoconductive atomic force microscopy, with which electrical properties of the cell including Voc and Isc are mapped cross-sectionally to study operational changes of the degraded cell.

11:15 AM EN11.05.04
Modified Laser-Fired Contact Process for Efficient PERC Solar Cells Inho Kim, Jae Myeong Choi and Beomsic Jung; Korea Institute of Science and Technology, Korea (the Republic of)

A laser-fired contact (LFC) process is one of the techniques for making local electrical contacts at the rear side of PERC (passivated emitter and rear cell) solar cells. In the LFC process, opening of the passivated dielectric layers and alloying of Si and Al need to be made in a single step laser process. For this reason, the LFC process is accompanied by the loss of Al and the laser damage to the Si wafer. In this study, we present a novel multi-step LFC process combining the conventional LFC and laser induced forward transfer (LIFT) processes. The modified LFC scheme we proposed consists of three steps: (1) opening of the passivation layers and partial alloying of Al-Si, (2) additional deposition of Al on the local contact holes, (3) post laser firing of the transferred Al. Applying the modified LFC process to the PERC cells, we demonstrate the effective recombination velocity of the laser processed wafers can be remarkably reduced while maintaining the low contact resistance. The best of the PERC solar cell with the modified LFC process exhibited 20.5% of an efficiency while the conventional LFC cell showed 18.6%. The efficiency gains of the modified LFC PERC cells was largely contributed by the enhanced open circuit voltage (Voc) and fill factor (FF).

11:30 AM *EN11.05.05
Metallization Pastes for n-Type Solar Cell Mass Production toward >23% Efficiency Qijie Guo, Guangyao Jin, Mia Li, Fangqing Guo, Bingfei Cao, Youyong Xu and Paul D. VerNooy; DuPont, United States

Significant growth of n-type solar cell with passivated contact technology is expected in the coming few years. However, whether it will become the mainstream technology to replace the dominant position of p-type in the market will be subject to the total cost of ownership improvement throughout the whole value chain engagement. Today p-PERC cell efficiency is approaching 22.5%; n-type needs to demonstrate >23% efficiency with good yield and cost to be competitive. Passivated contact is a key technology for n-type in the drive for higher efficiency, however, metallization pastes specially developed for passivated contact is needed to achieve performance and cost competitiveness in mass production. DuPontTM, a leading innovator in metallization technology for Si solar cells, is developing a total package metallization solution for n-type passivated contact structure to help our customers stay ahead in this next wave of high efficiency technology upgrade after PERC. A new generation Solamet® PV3Nx with improved performance on contacting ultra-lightly doped boron emitter and an upgraded PVD2x busbar paste
were developed to be suitable for both double printing and dual printing applications. In addition, an innovative formulation was developed to minimize the recombination loss on thin polycrystalline silicon film for rear side metallization. Overall, we believe innovations in metallization technology will lead to a potential efficiency of >23% for n-type in mass production.

SESSION EN11.06: Other Topics of Interest
Session Chairs: Qijie Guo, Adam Lorenz, Takuya Matsui and Eszter Voroshazi
Tuesday Afternoon, December 3, 2019
Sheraton, 3rd Floor, Fairfax B

1:30 PM *EN11.06.01
Solar Fuel Production Using Combined Silicon-Based Photovoltaic-Electrochemical Systems—Challenges for Efficiency, Stability and Up-Scaling Friedhelm Finger, Vladimir Smirnov and Katharina Welter; Forschungszentrum Juelich, Germany

Preparing chemical fuels from natural resources by using renewable energies and thereby replacing the fossil fuel exploitation with all its detrimental consequences is and will be a major research activity and challenge now and in the near future.

One approach which already receives considerable attention is the generation of hydrogen from water via electrolysis using solar cells as a power source. We have been concerned with this concept: an integrated photovoltaic (PV) - electrochemical (EC) device feasible for stand-alone operation under sunlight illumination, yielding high solar-to-hydrogen (STH) conversion efficiencies, using preferably natural abundant and non-toxic materials and having an up-scalable technology.

As solar cell material we have chosen thin film silicon (hydrogenated amorphous and microcrystalline silicon). The thin film silicon approach has the unique features of i) an easy vertical and lateral integration of multi-junction cells which allows for tuning of the required output voltage while making very efficient use of the solar spectrum, ii) an already established scalable production technology, and iii) earth-abundant and non-toxic photovoltaic base materials.

Alternatively, we have investigated series connected crystalline silicon wafer based solar cells.

We will show and compare the performance of PV-EC coupled systems with STH conversion efficiencies of close to 10% and 14% for thin film and crystalline silicon solar cells, respectively, and demonstrate the development and up-scaling of related PV-EC cassette systems including the preparation of earth abundant based catalyst materials.

The results can be used to discuss the concept of a closely coupled PV-EC system vs. “wired” systems where a photovoltaic module is connected to a possibly locally remote electrolyzer, and to estimate annual hydrogen production for typical outdoor illumination conditions.

2:00 PM EN11.06.02
Overview of Si Tandem Solar Cells and Approaches to PV-Powered Vehicle Applications Masafumi Yamaguchi1, Kan-Hua Lee1, Kenji Araki1, Nobuaki Kojima1, Yoshiho Ohshita1, Taizo Masuda2 and Akinori Satou2; 1Toyota Technological Institute, Japan; 2Toyota Motor Co., Japan

Development of high-efficiency solar cell modules and new application fields are significant for further development of PV (photovoltaics) and the creation of new clean energy infrastructure based on PV. Especially, Si tandem solar cells such as III-V/Si, chalcogenide/Si, and perovskite/Si tandem cells are desirable for high-efficiency and low-cost cells. We surveyed the progress of heterogeneous Si tandem solar cells and analyzed the prospects of their conversion efficiencies by estimating ERE (external radiative efficiency) as a measure of non-radiative recombination loss. Although 35.9% efficiency under 1-sun has been demonstrated with InGaP/GaAs/Si 3-junction tandem cell, 41% efficiency will be realized with the 3-junction Si tandem solar cells by improving ERE from 3% to
Regarding 2-junction Si tandem cells, 32.8% and 28% have been achieved with GaAs/Si and perovskite/Si tandem cells, respectively. The 2-junction Si tandem cells have an efficiency potential of 35% by realizing 20% ERE. The authors have demonstrated 28.2% with mechanically stacked InGaP/GaAs/Si tandem solar cell. Most recently, Sharp has also achieved 33.0% efficiency with 3.604cm² InGaP/GaAs/Si 3-junction solar cells by using the mechanical stack.

High-efficiency and low-cost solar cells such as Si tandem cells have great potential for PV as a vital energy source in mobility application where the installation area is limited. The NEDO established a “PV-Powered Vehicle Strategy Committee” for investigating the potential for contributing to reducing CO₂ emissions in the transport sector by installing high-efficiency solar cells on automobiles. According to the IRENA’s and NEDO’s reports, new broader PV market with more than 10GW and 50GW in 2030 and 2050, respectively are expected to be established. Cumulative PV capacity for PV-powered vehicles will be 50GW and 0.4TW in 2030 and 2050, respectively. According to statistics by the Ministry of Japan, 2/3 of the family car runs less than 30 km per day in Japan. Namely, the average annual energy that is needed to the light-weight family car powered by sunlight will be 642 kWh/year. 642 kWh/year is not an incredible value as well as a promising because the use of more than 30 % of high-efficiency PV enables the society that majority of the family cars run by the sun and without supplying fuel. Thus, we are developing high-efficiency and low-cost solar cells and modules for automobile applications.

Approaches on automobile application by using III-V/Si tandem, partial concentration, and static low concentration and so forth are also presented. Because of the space limitation, it should be a high-efficiency panel. III-V/Si tandem cells are one candidate. The CPV (concentrator PV) is very attractive for saving the cost of the cell. Cars move quickly, and appearance is essential. Trackers were thought to challenge to implement. One of our choices is a static concentrator customized to the automobile. In addition to high-efficiency, low-cost, 3-dimensional curved surface, color variation and so forth are needed and thus further R&D of solar cells, and modules for automobile applications are necessary.

Although III-V cells have an extremely high conversion efficiency of up to 46.0%, which is suitable for this application, cost reduction is necessary to realize the concept. The Si tandem solar cells by combining Si and other materials such as III-V compound, II-VI compound, chalcopyrite, perovskite, and so forth are desirable for realizing super high-efficiency and low cost. Recently, Si tandem solar cells have paid considerable attention because of high-efficiency and low-cost potential.

New static low concentrators were proposed for the vehicle application. Besides, a III–V/Si partial CPV module with high diffuse sunlight transmission is studied and low concentration static III-V/Si partial CPV module with 27.3% annual efficiency for car-roof application has been developed.

2:15 PM EN11.06.03
Impedance Spectroscopy as a Tool to Characterize PID and CID in Bifacial and Standard PERC
Photovoltaics Kevin Musselman¹, Travis Yeow¹, Jing Sun², Zheng Yao² and Jean-Nicolas Jaubert²; ¹University of Waterloo, Canada; ²Canadian Solar Inc., Canada

Advancements in photovoltaic technologies are hindered by degradation mechanisms such as potential induced degradation (PID) and current-induced degradation (CID). In this work, impedance spectroscopy is used to examine passivated emitter and rear cell (PERC) silicon modules with PID and CID. A comparison between control and degraded modules is done to identify key differences in the impedance spectra and determine the extent of the degradation. CID was also examined at the cell level, where reductions in minority carrier lifetimes could be more accurately measured. The PID and CID mechanisms studied are found to induce unique changes in the impedance spectroscopy results, making them distinguishable and quantifiable. Finally, the ability to mitigate CID through the use of different silicon wafers and a current induced regeneration process was characterized by impedance spectroscopy.

2:30 PM EN11.06.04
Atomistic Structure of Si/GaAs Heterointerfaces Fabricated by Surface Activated Bonding Revealed by STEM Combined with Low-Temperature FIB
Yutaka Ohno¹, Yasuo Shimizu¹, Yasuyoshi Nagai¹, Ryotaro Aso², Naoto Kamiuchi³, Hideto Yoshida³, Jianbo Liang³ and Naoteru Shigekawa³; ¹Tohoku University, Japan; ²Osaka City University, Japan; ³Osaka University, Japan

Tandem solar cells consisting of Si and III-V compounds are one of the promising candidates for next-generation
terrestrial photovoltaic systems. Surface-activated bonding (SAB) at room temperature (RT), in which surfaces of substrates are activated before bonding by creating dangling bonds under an energetic particle bombardment in a high vacuum, is applied to form Si/GaAs heterointerfaces with a low interface electrical resistance [1], and high-efficiency InGaP/GaAs/Si triple-junction cells are demonstrated [2]. Even though the interface electrical resistance (~10^{-1} \Omega cm^2) is low enough for solar cells, it is still higher than the ideal one at defect-free heterointerfaces (~10^{-4} \Omega cm^2), presumably due to the defects introduced during SAB processes. The interface resistance varies depending on SAB conditions including energetic atom irradiation and post-bonding annealing [1]. In order to understand the origin of the resistance, atomistic structure of the hetero-interface, depending on SAB conditions, have been examined by cross-sectional transmission electron microscopy (X-TEM).

In general, X-TEM specimens with heterointerfaces, in which the bonding materials are different in etching rate, are fabricated with milling techniques using energetic ions such as focused ion beam (FIB). We have clarified that the structural and compositional properties of semiconductor homointerfaces fabricated by SAB are modified during FIB processes operated at RT, especially for wide-gap materials, and such a modification can be suppressed by FIB processes operated at -150 °C [3]. In the present work, we have therefore examined the atomic arrangement and composition at Si/GaAs heterointerfaces fabricated by SAB using X-TEM specimens fabricated by FIB milling operated at -150 °C.

Si/GaAs heterointerfaces were fabricated at RT under a SAB condition [4], with the substrates of B-doped (100) p-Si (with a carrier concentration of 2x10^{14} cm^{-3}) and Si-doped (100) n-GaAs (2x10^{16} cm^{-3}). X-TEM specimens with an as-bonded heterointerface were prepared at -150 °C by using a FIB system (FEI, Helios NanoLab600i) with a cold stage customized for the FIB system (IZUMI-TECH, IZU-TSCS004) [3]. The specimens were examined by high-angle annular dark-field (HAADF) and energy dispersive x-ray spectroscopy (EDX) analyses under scanning TEM (STEM) with a JEOL JEM-ARM200F analytical microscope.

HAADF-STEM-EDX revealed that, an amorphous layer, about 4 nm in thickness, is introduced along the as-bonded heterointerface. Most of the amorphous layer are composed of Si, and no amorphous GaAs is apparently observed, as proposed [4]. Atomic intermixing across the heterointerface, within a range of a few nm, is observed. Both Ga and As atoms penetrate into the amorphous Si layer, and the amount of Ga atoms in the layer is about two times larger in comparison with As atoms. Those excess Ga atoms, acting as p-type dopant, can improve the electrical property of the amorphous p-Si layer, that is damaged during the SAB processes. Similarly, the electrical property of the n-GaAs bonding surface can be improved via the penetration of Si atoms. Those self-restoration processes may assist the formation of low-resistance Si/GaAs heterointerfaces by SAB. We will also discuss the effect of post-bonding annealing.


2:45 PM BREAK

3:15 PM EN11.06.05
Novel IWO and IWO:h Deposited by DC Mode Sputtering for Silicon Heterojunction Solar Cells Annabel Mikosch, Weiyuan Duan, Andreas Lambertz, Friedhelm Finger and Kaining Ding; Forschungszentrum Jülich GmbH, Germany

The silicon heterojunction (SHJ) solar cell is promising for mass production of high efficiency solar cells. To date, the average SHJ solar cell conversion efficiency in mass production is well above 23%. The improvement of transparent conducting oxide (TCO) in SHJ solar cells in terms of transparency and conductivity is one of the key issues to achieve higher conversion efficiencies. The most commonly used TCO is Sn-doped indium oxide (ITO), due to its high transparency and low resistivity. Compared with ITO, W-doped indium oxide (IWO) shows higher charge carrier mobility resulting in high transparency in the near infrared (NIR) spectral range while maintaining low resistivity.\(^1\) The carrier mobility can be further increased when hydrogen is introduced during the deposition leading to hydrogenated IWO:H\(^2\). Therefore, IWO and IWO:H could be advantageous candidates for a high-efficiency SHJ solar cells.

Until now, the application of IWO and IWO:H in SHJ solar cells has been studied using soft deposition methods such as reactive plasma deposition (RPD)\(^3\) or radio-frequency (rf) mode sputtering.\(^2\) But for the mass production of
SHJ solar cells, direct current (DC) mode sputtering is commonly used as it offers high throughputs and is an established deposition technology in the optoelectronic industry. To successfully introduce the novel, high mobility TCOs into a SHJ solar cell production line the DC sputtering of IWO and IWO:H needs to be developed and investigated with respect to possible sputtering damages on the thin silicon layers of SHJ solar cells.

Here, we present our most recent work on DC sputtered IWO on SHJ solar cells. In preliminary experiments to this study we have optimized the deposition process for single layers of IWO on glass from Corning type Eagle. The resulting films exhibited high transparency (average absorption of < 2% from 400 - 1100 nm), low sheet resistance (105 Ω/sq), and carrier mobility of up to 55 cm²/Vs. The IWO films were also applied to 19 × 19 mm² SHJ solar cells increasing the short circuit current density $J_{sc}$ from 38.65 mA/cm² to 39.09 mA/cm² compared to ITO without introducing sputtering damage to the underlying solar cell. In this contribution, we extend the study of DC sputtered IWO further by introducing hydrogen to fabricate IWO:H and also apply the TCOs on full size M2 solar cells. The novel TCO layers deposited by DC sputtering will be compared to ITO with respect to contact resistance and sputtering damage to the underlying silicon layers. To our knowledge, this is the first study of DC sputtered IWO and IWO:H using an industrially relevant technique for SHJ solar cells.


3:30 PM EN11.06.06
**The Value of Efficiency**
Ian Marius Peters¹, Carlos David Rodriguez Gallegos², Sarah Sofia¹, Tonio Buonassisi¹ and Erin Looney¹; ¹Massachusetts Institute of Technology, United States; ²Solar Energy Research Institute of Singapore, Singapore

What is the value of improving the efficiency of a solar cell? In this contribution we introduce a tool to assess the value of efficiency (VOE) by analyzing the dynamic co-dependence of levelized cost of electricity (LCOE) on manufacturing cost and efficiency. Looking at historic trends we find that the allowable cost for innovation has dropped rapidly in the past and is projected to further decline in the future, but at a slower pace. This is good news for researchers, as it will ease the difficulties of hitting a moving cost target. Additionally, we find that VOE values for residential- and utility scale systems converge at different levels, indicating a stronger future diversification of these PV market segments. Similarly, we find local differences for VOE suggesting a further possible market diversification based on region. Efficiency is a much stronger driver for LCOE reductions in a handful of highly industrialized countries like the U.S., Germany, Australia or Japan than in the rest of the world. Advanced solar cell concepts like $n$-type monocrystalline PERC silicon solar cells could, hence, be economically preferable to multicrystalline silicon solar cells in these regions, but may not be the better choice in countries like China or India. Extending the analysis to more advanced concepts including tandem solar cells, we confirm previous finding that these concepts have great potential to improve LCOE for residential applications, but will likely struggle to compete on the utility market. Finally, we explore the detrimental impact of degradation, and show that competing on the basis of LCOE necessitates matching the stability of established technologies.

3:45 PM EN11.06.07
**Optimizing the Absorbing Layer Thickness of the Top Cell in 4-Terminal Gallium Arsenide-on-Silicon Tandem Solar Cells**
Riley Whitehead¹, Kaitlyn VanSan², Michael Rienäcker¹, Henning Schulte-Huxel², Robby Peibst², John Geisz¹ and Adele Tamboli¹,²; ¹National Renewable Energy Laboratory, United States; ²Colorado School of Mines, United States; ³Institute for Solar Energy Research in Hamelin, Germany

One method to improve silicon solar cell efficiency is to stack a silicon cell beneath a wide-bandgap top cell. To improve the overall tandem cell efficiency from that of silicon alone, the top cell material should have a higher spectral efficiency than silicon for the wavelengths of light within the top cell’s bandgap. GaAs is currently the material with the highest recorded cell efficiency for a single junction cell, at 29.1% efficiency. GaAs also has a theoretical and realized spectral efficiency higher than that of silicon between the wavelengths of 360-860 nm. Our team was able to exploit these GaAs attributes to obtain a record efficiency of 32.8% for a mechanically-stacked rear heterojunction (RHJ) GaAs-on-Si (GaAs/Si) tandem cell designed to operate in the 4-terminal (4T) (i.e. optically coupled but electrically independent) configuration.

The purpose of this study is to further optimize the GaAs emitter layer thickness to maximize the efficiency of the
4T GaAs//Si tandem cells. Our record 4T GaAs//Si tandem solar cell was achieved using a 2 µm GaAs emitter layer but subsequent optical modeling of the 4T GaAs//Si tandem solar cells suggests that a slightly thicker emitter could potentially lead to even better top cell efficiencies. In addition, NREL began a collaboration with ISFH that provides high-efficiency interdigitated back contact (IBC) solar cells that could further improve the tandem cell efficiencies, when used as the Si bottom cell in the 4T GaAs//Si cell.

Our un-certified current-voltage (I-V) results show an efficiency increase of 0.43% (absolute) by increasing the emitter thickness from 2.0 µm to 2.8 µm. The tandem cells are currently pending cell certification but the results for the GaAs//Si tandem cell with an emitter thickness of 2.8 µm is expected to be >32% and could potentially exceed the existing record efficiency. We will present the results of modeling the GaAs emitter thickness using modified Hovell equations that estimates the Jsc, based upon light absorption and carrier recombination. We will compare these modeled predictions to the NREL-certified I-V and external quantum efficiency (EQE) results obtained from 4T GaAs//Si tandem cells fabricated with absorber layer thicknesses varying from 1.5 to 3.5 µm. We will also compare the performance of our 4T GaAs//Si tandem cells to the record 4T GaAs//Si tandem cell efficiency of 32.8%.

4:00 PM EN11.06.08
Role of the Interlayer in Improving Passivating Contact with Atomic Layer Deposited TiOx on Crystalline Si
Takeya Mochizuki1, Kazuhiro Gotoh1, Yasuyoshi Kurokawa1, Takahisa Yamamoto1, Tomohiko Hojo2, Eiji Akiyama2 and Noritaka Usami1; 1Nagoya University, Japan; 2Tohoku University, Japan

High efficiency crystalline Si (c-Si) solar cells can be realized by employing carrier selective contacts to efficiently collect one type of photogenerated carriers by providing excellent passivation performance and low contact resistance at the heterointerface. Atomic layer deposited TiOx (ALD-TiOx) is known as one of the promising candidates for electron selective contacts owing to the small conduction band offset (<0.05 eV) and large valence band offset (>2.0 eV), which can selectively transport photogenerated electrons in c-Si while repelling holes. Passivation performance could be modified by both surface treatment of the c-Si substrate prior to deposition and post-deposition process. Therefore, it is important to understand underlying physics during the process to establish the guideline how to improve passivating contacts.

In this contribution, we report on the role of the interlayer in improving passivating contact with ALD-TiOx/c-Si, and show that formation of low-density SiOx prior to depositing TiOx is of crucial importance to improve passivation performance.

All experiments were carried out on double-side mirror-polished float-zone (Fz) grown c-Si(100) substrates. After degreasing and removing a native oxide layer, various chemical treatments were done to form SiOx interlayer with different densities. TiOx layers were deposited at 150 °C by a thermal ALD (GEMStar-6, Arradiance). The forming gas annealing were carried out in a mixed gas (3% H2 and 97% Ar) to activate the surface passivation performance. The effective minority carrier lifetime of the samples was measured by a WCT-120 lifetime tester (Sinton Instruments). For a part of samples, EEL spectra were obtained using an EEL spectrometer attached to a Cs-corrected STEM (JEM-ARM200FC, JEOL Ltd.), which was operated at 200 kV. The desorption of hydrogens was characterized by thermal desorption spectroscopy (TDS) using a quadrupole mass spectrometer with different heating rates to analyze Si-H2 bonding energies.

The effective carrier lifetime of about 1.4 ms was achieved by inserting ultra-thin SiOx interlayer formed by nitric acid at room temperature. The TEM images and EEL spectra revealed that non-stoichiometric SiOx existed for as-deposited samples and Ti contained, near-stoichiometric SiO2 was formed after post deposition annealing. This suggests that diffusion of Ti and O atoms took place during the post deposition annealing. To enhance this process, we considered that introduction of SiOx interlayer with lower density is effective. As a result, employment of so-called SC-2 solution (HCl:H2O2:H2O=1:1:5) prior to deposition of TiOx led realization of the effective lifetime of 1.7 ms. The enhanced diffusion of O from TiOx would also contribute to the reduction of the contact resistance by increasing O vacancies in the ALD-TiOx layer. Furthermore, higher Si-H2 bonding energy was confirmed by TDS, suggesting that hydrogens also play a role in improving passivation performance.

4:15 PM EN11.06.09
First Principles Modeling of Water-Induced Polymer Encapsulant Degradation in Silicon Modules
Arun Kumar Mannodi Kanakkithodi1, Rishi Kumar2, David P. Fenning2 and Maria K. Chan1; 1Argonne National Laboratory, United States; 2University of California San Diego, United States
An outstanding issue in photovoltaic modules is the accelerated degradation caused by the presence of moisture, which leads to interfacial instability, encapsulant decomposition and corrosion at contacts. Currently, experimental observation and characterization of moisture in PV modules is not trivial, which presents a major obstacle to designing high-reliability modules. First principles calculations provide a suitable way to study the ingress of water and its detrimental effect on the polymer encapsulant and on the interface between the semiconductor and the polymer. In this work, we use density functional theory (DFT) computations to model the structure, degradation mechanisms, and adhesive strength on metal surfaces of ethylene vinyl acetate (EVA), the most common polymer encapsulant used in Si PV modules. The molecular structure of EVA is modeled both as an isolated single chain and in a crystalline arrangement with closely packed chains, using a structure prediction algorithm that includes Van der Waals corrections applied to the standard DFT functional. Infrared active modes computed for the low energy EVA structures using density functional perturbation theory match well with reported experiments. The Nudged Elastic Band (NEB) method is applied to model the decomposition mechanism of EVA, with and without the presence of water, following the Norrish I and Norrish II mechanisms, leading to the formation of acetaldehyde and acetic acid, respectively. Computed energy barriers show a preference for acetic acid formation, are lower in the presence of a water solvent than in vacuum, and match well with reported experimental activation energies. The NEB computed energy barrier is further seen to be dependent on the percentage of deacetylation and the presence or absence of a catalyst, such as a proton or a hydroxyl ion. This systematic study leads to a clear picture of the hydrolysys-driven decomposition of EVA in terms of energetically favorable mechanisms, possible intermediate structures, and IR signatures of reaction products. We further model the adhesion of EVA and related polymers (including decomposition products) on surfaces of metals such as Cu and Ag, in order to determine the sticking power of the polymer encapsulant and thus the strength of the interface with and without the presence of water.

4:30 PM OPEN DISCUSSION

4:45 PM  EN11.06.11
Influence of the Dopant Gas Precursor in p-Type Nanocrystalline Silicon Layers for High Efficiency Heterojunction Solar Cells  Luca Antognini, Vincent Paratte, Jan Haschke, Christophe Ballif and Mathieu Boccard; Ecole Polytechnique Federale de Lausanne, Switzerland

While standard design of Silicon heterojunction (SHJ) uses amorphous silicon (a-Si) doped layer, switching to nanocrystalline silicon (nc-Si) is a promising route to improve efficiency [1]. One challenge to ensure a good contact is the fast nucleation of the nc-Si on the underneath intrinsic a-Si passivating layer. To promote the crystallization without damaging the passivation, a short SiH4/H2/CO2 plasma treatment was introduced prior to the p-layer deposition [2], [3] which enabled efficiencies up to 23.45% [4]. As shown by the results of p-i-n solar cells [5], clarifying the role of the boron source in SHJ is crucial for further improvement.

In this work, we compare the use of BF3 and TMB for nc-Si hole contacts. Efficiency values over 23% are obtained for both gases for the same deposition parameters, however cells using TMB-based layers yield a better FF (81.7% vs. 80.8%), whereas BF3 cells exhibit a better Jsc (40.0 mA/cm2 vs. 39.2 mA/cm2).

Symmetric stacks of c-Si(n) / a-Si(i) / nc-Si(p) / ITO address the question of the stability of the passivation along the process. We see that the implied open-circuit voltage (iVoc) is strongly reduced by the p-layer deposition for BF3, while it is not systematically changed for TMB. The ITO deposition reduces also more strongly the passivation when deposited on BF3 p-layer, reducing iVoc by ~ 30mV while it is not the case for the samples with TMB p-layer. However, annealing enables full recovery of the sputtering damage with even slight improvement (~735 mV) compared to the value before ITO deposition.

Using Spectroscopic ellipsometry, similar thicknesses were found for both dopant gases, yet with a smaller refractive index for BF3-based layers (n=2.6 vs. n=3.5 at 600 nm) and a higher optical bandgap for BF3 (E04=2.23 eV vs. 1.79 eV), which suggests a more porous layer. UV-Raman spectroscopy yields a higher crystallinity for BF3 layers than TMB (Xc = 60% v.s. Xc = 40%), confirming the structural difference of both materials. Both results are consistent with the difference in short-circuit current when used in a solar cell.

The marked difference between these materials indicates distinct optimization path that need to be unraveled. We plan to further investigate the nucleation and the doping efficiency differences by varying the dopant gas flux and
the surface pretreatment and relate them to the past results obtain from p-i-n solar cells. We will also investigate the 
contribution of carbon and fluorine via Secondary Ion Mass Spectroscopy (SIMS) to understand the effect of the 
dopant gas on the device performance to enable further efficiency improvement.

References:

SESSION EN11.07/EN08.07: Joint Session: Perovskite/Silicon Tandems
Session Chairs: Stefaan De Wolf and Kai Zhu
Wednesday Morning, December 4, 2019
Sheraton, 2nd Floor, Back Bay AB

8:30 AM *EN11.07.01/EN08.07.01
Highthroughput Fabrication of Efficient Perovskite Solar Modules and Tandem Solar Cells Jiinsong Huang;
University of North Carolina at Chapel Hill, United States

The efficiencies of small-pixel perovskite photovoltaics have increased to well above 20%, while the question is 
whether fabrication methods can be transferred to scalable manufacturing process. Here we report a method of fast 
blading large area perovskite films at an unprecedented speed of 99 millimeter-per-second or higher in ambient 
condition by tailoring solvent coordination capability. Combing volatile non-coordinating solvents to Pb2+ and low-
volatile, coordinating solvents achieves both fast drying and large perovskite grains at room temperature. The 
reproducible fabrication yields a record certified module efficiency with aperture area of 63.7 cm2. The perovskite 
modules also show a small temperature coefficient of -0.13%/°C and nearly fully recoverable efficiency after 58 
cycles of shading, much better than commercial silicon and thin film solar modules. The application of the coating 
method to perovskite/silicon tandem cells and will also be presented. We will answer the question whether the 
perovskite layers can be fabricated at the speed of silicon cells are produced in the regular production lines.

9:00 AM *EN11.07.02/EN08.07.02
Correlating the Performance of Perovskite/Silicon Tandem Solar Cells with Their Nanostructure Quentin 
Jeanne, Florent Sahli, Peter Fiala, Ricardo Z. Razera, Fan Fu, Daniel Jacobs, Chien-Jen Yang, Vincent 
Paratte, Olivier Dupre, Gizem Nogay, Brett A. Kamino, Saeid Rafizadeh, Arnaud Walter, Soo-Jin Moon, 
Adriana Paracchino, Marion Dussouillez, Bertrand Paviet-Salomon, Aicha Hessler-Wyser, Matthieu Despeisse, 
Mathieu Boccard, Sylvain Nicolay, Andrea Ingenito and Christophe Ballif; 1EPFL PV-LAB, Switzerland; 
2CSEM, Switzerland

Crystalline Si (c-Si) solar cells are driving the progression of renewable electricity generation technologies thanks to 
lowering costs and increasing efficiencies. One solution to maintain this cost-competitiveness on the long-term involves increasing efficiencies beyond the limit of c-Si by stacking a perovskite solar cell on a commercial c-Si one to form a photovoltaic tandem device. The tunable bandgap, soft processing conditions and high single-junction performance of perovskites indicate that this approach could upgrade c-Si solar cells to efficiencies >30% through a few extra process steps with low additional process costs.

For maximum photocurrent and compatibility with existing c-Si process flows, the perovskite solar cell should be deposited directly on the textured front side of the c-Si solar cell, a texture that improves light management in the c-
Si. But this pyramidal texture imposes several microfabrication challenges as the perovskite absorber is typically deposited via solution processing, and is about one order of magnitude thinner than the height of the pyramids it needs to cover. Achieving a conformal deposition of all the layers of the top cell on this pyramidal texture and hence maximum performance requires a fine control over the layer formation to avoid pinhole formation.
In that regard, electron microscopy techniques, notably analytical transmission electron microscopy (TEM), can shed some light on the device nanostructure and its dependence on processing/operation conditions, guiding the development of devices. However, the fragile nature of perovskite solar cells complicates their preparation into thin cross-sections necessary for TEM observations and their analysis with high-energy electrons. This presentation will review artifacts that may occur during TEM sample preparation and observation, elaborate several strategies to identify and mitigate them, before discussing several topics correlating nanostructure and performance of perovskite single-junction and tandem solar cells. This contribution will present how electron microscopy data coupled with other techniques provide valuable inputs to guide the development of high-efficiency (>25%) tandems featuring textured n- and p-type c-Si solar cells, notably by i) identifying optimal bottom cell contact nanostructures, ii) isolating crystallographic and chemical features enabling the recombination junction to quench shunts, iii) guiding the removal of shunts running through the perovskite absorber on textured c-Si by adapting process conditions and iv) visualizing the dewetting of charge-selective layers during the crystallization of the perovskite solar cell on certain recombination junctions. In addition, degradation pathways triggered by reverse voltages (also investigated through TEM in situ biasing experiments), during long-term operation at maximum power point at various temperatures, or during damp heat tests (85°C/85% relative humidity) will be examined. These results highlight the dynamic nature of the perovskite nanostructure (ionic migration within the absorber and into the contacts, volatilization of species, crystallographic phase change/decomposition) depending on the external stimuli and its influence on the solar cell performance.

References:
Wide-bandgap (~1.7-1.8 eV) perovskite solar cells have attracted substantial research interest in recent years due to their great potential to fabricate efficient tandem solar cells via combining with a lower bandgap (1.1-1.3 eV) absorber (e.g., Si, copper indium gallium diselenide, or low-bandgap perovskite). However, wide-bandgap perovskite solar cells usually suffer from large open circuit voltage ($V_{oc}$) deficits caused by small grain sizes and photoinduced phase segregation. We show that in addition to large grain sizes and passivated grain boundaries, controlling interface properties is critical for achieving high $V_{oc}$'s in the inverted wide-bandgap perovskite solar cells. We adopt guanidinium bromide solution to tune the effective doping and electronic properties of the surface layer of perovskite thin films, leading to the formation of a graded perovskite homojunction. The enhanced electric field at the perovskite homojunction is revealed by Kelvin probe force microscopy measurements. This advance enables an increase in the $V_{oc}$ of the inverted perovskite solar cells from an initial 1.12 V to 1.24 V. With the optimization of the device fabrication process, the champion inverted wide-bandgap cell delivers a power conversion efficiency of ~19% and sustains more than 72% of its initial efficiency after continuous illumination for 70 h without encapsulation. The improvement on performance of wide-bandgap perovskite subcells enables us to fabricate efficient and stable perovskite tandem solar cells.

The record power conversion efficiency is 28 % for perovskite-silicon tandems and 23.2 % for perovskite-perovskite tandems. One of the challenges that must be overcome to achieve efficiency greater than 30% is to reduce the voltage loss in high bandgap perovskite cells and prevent light-induced phase separation. We have found that treating the surface of perovskites can dramatically reduce the extent of light -induced phase separation, which has interesting implications for how the process occurs. We have also developed new strategies for increasing the bandgap in perovskite compounds that have modest amounts of bromine. We have been able to make semitransparent high bandgap solar cells with greater than 20% power conversion efficiency that do not suffer from light-induced phase separation. These advances in combination with improvements in the atomic layer deposition of highly impermeable metal oxide contacts enable the fabrication of highly efficient and stable tandems.
conditions but does not require lateral current extraction between the cells, which becomes challenging when scaling devices to large areas.

In this talk I will give an overview of the history of three terminal devices and discuss the wide range of possibilities to create high efficiency tandem devices from combining various top cells with Si bottom cells. I will show how TCAD models agree with simple physical models and experimental results to explain the trends in the behavior of 3T tandems.

2:00 PM EN11.08.02
Performance Comparison of III-V//Si Tandem Solar Cells in the Three-Terminal Configuration Kaitlyn VanSant1, Emily Warren2, Michael Rienäcker3, Henning Schulte-Huxel1, Robby Peibst1, John Geisz2, Paul Stradins2 and Adele Tamboli2,1; 1Colorado School of Mines, United States; 2National Renewable Energy Laboratory, United States; 3Institute for Solar Energy Research in Hamelin, United States

Multi-junction solar cells are a key pathway towards achieving higher photovoltaic efficiencies. The theoretical efficiency limit of a single-junction (1J) Si solar cell is 29.6%, whereas efficiencies >32% have already been achieved for 1J III-V top cells stacked on Si bottom cells in both the two terminal (2T) and four terminal (4T) configurations.2,3 We will present a third path towards achieving efficiencies >32% with mechanically-stacked III-V-on-Si (III-V//Si) tandem solar cells using a three terminal (3T) configuration.

The typical tandem device architectures either connect the sub-cells in series in a 2T configuration, or operate the stacked sub-cells independently, which requires four terminals (4T). Both configurations, however, have considerable drawbacks. The 2T configuration requires that the sub-cells are current matched to operate efficiently and so this narrowly constrains the choice of the sub-cell materials. The 4T configuration does not require sub-cell current matching but this design prohibits the possibility of monolithic growth and necessitates the inclusion of gridlines or a lateral conduction layer at the back of the top cell which reduces the transmission of light to the bottom cell.4

The 3T configuration is a hybrid approach devised to address the constraints of the other two. The additional contact associated with the interdigitated back contact (IBC) Si bottom cell enables extraction or injection of current which circumvents the need for current matching between the sub-cells. The 3T design does not require an intermediate grid and is potentially compatible with both mechanical stacking, if a transparent conductive adhesive (TCA) is used, or monolithic growth. Moreover, simulations predict that 3T tandem cells could achieve efficiencies over 32%, comparable to record 4T tandem cell efficiencies.3,4

We have fabricated and measured 3T mechanically-stacked III-V-on-Si (III-V//Si) tandem solar cells and will present an overview of how a 3T tandem solar cell operates. We will compare the JV and QE characteristics of a GaInP//Si tandem cell to a GaAs//Si tandem cell and analyze how the performance between these two 3T tandem solar cells differ, depending on which sub-cell is current limiting.


2:15 PM EN11.08.03
An Ambipolar Poly(Vinylidene Fluoride-co-Trifluoroethylene) Passivated Back Surface Field Layer for High Efficient Organic/Si Hybrid Solar Cells Sung Bum Kang, Myeong Hoon Jeong and Kyoung Jin Choi; Ulsan National Institute of Science and Technology, Korea (the Republic of)
The interfacial layer between semiconductor and metal cathodes in photovoltaics play a critical role in enhancing the transport of charges carriers or preventing the recombination at the interface. Here, high crystalline and self-assembled poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) thin films are shown to function as a passivation layer and also acts as back surface field layer for photovoltaic devices, simultaneously. The P(VDF-TrFE) thin films are spincoated on the bottom of n-Si surface by modified breath figure methods. After that, poly(3,4-ethylene dioxy thiophene):poly(styrene sulfonate) are formed on the top of nano-textured Si as the junction. Comparing previously reported organic / Si hybrid solar cells with this study, such devices demonstrate record-breaking photovoltaic conversion efficiency of 18.1% with electrostatic passivation and reflection of minority carriers by the induced built-in electric field. Furthermore, due to its switchable ferroelectric property, the P(VDF-TrFE) thin films can be utilized to the p-Si solar cells as passivated back surface field layers. Finite-difference time-domain simulation reveals that the electric field due to the below spontaneous polarization causes band bending of Si, reflecting minority carriers and reducing the surface recombinations of the devices.

2:30 PM BREAK

SESSION EN11.09: Defects and Photon Management
Session Chair: Kaitlyn VanSant
Wednesday Afternoon, December 4, 2019
Sheraton, 3rd Floor, Fairfax B

3:30 PM *EN11.09.01
Insights into the Intrinsic Recombination Limit of Silicon Devices Mariana I. Bertoni; Arizona State University, United States

High-efficiency solar cell devices characterized by extremely high open-circuit voltage ($V_{OC}$) values have shown that the traditional constraints imposed by extrinsic recombination processes will be eventually surpassed at some time in the foreseeable future. The accurate evaluation of Auger lifetime and its temperature-dependence are thus fundamental not only for the correct interpretation of effective carrier lifetime data, but also for the simulation of device performance, especially when these are deployed in the field, where the operating conditions can greatly vary from the standard testing conditions. In this work, we present the Auger lifetime across a range of temperatures from 300 to 500 K and a range of injection level from $5 \times 10^{14}$ to $1 \times 10^{16}$ cm$^{-3}$ showing that, in stark opposition with what generally accepted, a strong increment of the lifetime values happens at high temperatures. Based on these results, we discuss the ambipolar Auger coefficient in the high injection range and propose a parameterization for its temperature dependence in agreement with a model previously presented in literature. Finally, we evaluate the intrinsic-limited implied voltage ($iV$) within the same range of injection level and temperature, and show that the evaluated strong increment of Auger lifetime counteracts the typical drop of high-efficiency solar cells performance with high temperature.

4:00 PM EN11.09.02
Microparticle-Assisted Texturing (MPAT) Process on As-Cut Crystalline Silicon—Controllable Texture Size, Low Optical Reflectivity, Quick Formation, Extremely Low Material Loss and Toward Mass-Production Cong T. Nguyen, Keisuke Ohdaira and Hideki Matsumura; Japan Advanced Institute of Science and Technology (JAIST), Japan

Heterojunction back-contact (HBC) crystalline silicon (c-Si) solar cells with energy conversion efficiency > 26%, which reaches nearly the theoretical limit of ~30%, have been achieved, hence reducing fabrication cost becomes more and more valuable. The decreasing thickness of c-Si to < 100 µm is one of the keys since c-Si typically takes half of the total cell cost. Usually, the surface of c-Si is textured to improve sunlight confinement or efficiency. For such thin c-Si, small texture size and low amount of Si etching loss are strictly required to maintain its mechanical strength during fabrication processes. In mass-production, wet processes are preferable for lowering the cost. We have already reported a novel method, so-called microparticle-assisted texturing (MPAT) process, in which glass microparticles were mixed with conventional alkaline-based texturing chemical solutions to reduce the texture size, etching duration, and etched c-Si thickness by almost one order of magnitude. The MPAT process was applicable to
c-Si with a thickness down to 50 µm. The superiorities were attributed to that the glass microparticles with certain kinetic energy can sweep out reaction-generated hydrogen bubbles from the c-Si surface to speed up the texture formation. However, the previous work focused on only mirror-polished c-Si wafers. In this work, we studied the MPAT process on as-cut c-Si used for actual solar cell mass-production. The similar superiorities such as small texture size (< 3 µm), low optical reflectivity (R~7%) quick formation (3–5 min), and extremely low c-Si loss [< 2 µm, even smaller than the depth of the saw-damaged layer (SDL) ~ 6 µm] were revealed. In addition, we also developed a suitable wet chemical cleaning prior to surface passivation using catalytic chemical vapor deposition (Cat-CVD) silicon nitride (SiN_x)/amorphous silicon (a-Si) stacked layers. A world-record low surface recombination velocity (SRV) ~ 0.38 cm/s was achieved. Owing to the high-quality surface passivation, both SDL removal and texturing can be done by only the MPAT process within a few minutes. After coating SiN_x/a-Si, the reflectivity reaches ~ 0.4 % at minimum, and < 2% in wide wavelength 450–950 nm. Toward mass-production using the MPAT process, etching of multiple c-Si full-size wafers with a pitch of 5 mm was proved to be possible to obtain uniform textures with a yield almost 100%. Therefore, the MPAT process is almost close to the mass-production of low-cost and high-performance thin c-Si-based solar cells.

Polycrystalline silicon (poly-Si) has proven to be a game-changing material in the field of high thermal budget carrier-selective passivating contacts (CSPCs) for c-Si solar cells beyond PERC architecture. However, doped poly-Si exhibits a very high free carrier absorption (FCA), which has turned the attention of researchers towards wide bandgap materials, such as poly-SiO_x and poly-SiC_x. In these materials, the opto-electronic properties depend on oxygen and carbon alloying, respectively. To properly model the generation profile in solar cells based on poly-Si, poly-SiO_x or poly-SiC_x, CSPCs, a thorough understanding of their optical properties, especially the absorption coefficient, is essential.

As weak FCA at long wavelengths is difficult to detect using ellipsometry, we have used in this work two techniques, the absolute photothermal deflection spectroscopy (PDS) and the reflection / transmission (RT), that are sensitive enough to measure absorption values below 1%. In this way, we could obtain the absorption coefficient of n- and p-type doped poly-SiO_x and poly-SiC_x, CSPCs on quartz and on crystalline silicon (c-Si) wafer substrates, respectively, in the wavelength range between 300 nm to 2000 nm. The absorption coefficients of doped CSPCs obtained from these measurement techniques are in the same order to magnitude, albeit we observed small differences owing to the different substrates and/or the measurement techniques.

By changing the oxygen-to-silane gas ratio, \( R_{CO2} = \frac{[CO2]}{([CO2] + [SiH4])} \), and carbon-to-silane gas ratio, \( R_{CH4} = \frac{[CH4]}{([CH4] + [SiH4])} \), the optical properties of our in-house developed poly-SiO_x and poly-SiC_x layers can be obviously altered. We note a decrease in the FCA for n- and p-type doped poly-SiO_x layers in the infrared region with respect to the reference poly-Si (\( R_{CO2} = 0 \)). Among n- and p-type doped poly-SiO_x and poly-SiC_x layers, n-type doped poly-SiO_x (\( R_{CO2} = 0.83 \)) layer with a doping concentration of 1e20 cm^{-3} has the least FCA in the wavelength range between 800 nm and 1200 nm. In this respect, for the same thickness, it would be better to use n-type doped poly-SiO_x rather than n-type doped poly-SiC_x, at the back side of front/back-contacted or interdigitated back-contacted c-Si solar cell architectures.

The obtained absorption coefficient values can now be used as input to study the optical behaviour of single- and multi-junction solar cells endowed with such CSPCs. Simulations of two, three and four terminal perovskite / c-Si solar cells are ongoing and will be presented at the conference.

1 G. Yang, et al., APL, 2016.

Elimination of Shadowing Losses Using Light Trapping Metallic Electrodes Mengdi Sun and Pieter G. Kik; University of Central Florida, United States
Transparent electrodes are used in many optoelectronic devices, such as solar cells, high speed photodetectors, imaging arrays, and displays. Common materials used for transparent electrodes include conductive oxides, carbon nanotubes, graphene, and metal nanowire networks. In all current approaches a balance needs to be struck between good electrical conductivity and high optical transmission: thinner films lead to higher transmission, but lower electrical conductivity. Among the many approaches, metal nanowire electrodes provide extremely high conductivity, but introduce significant shadowing losses due to reflection and absorption.

In this presentation we numerically investigate the optical and electrical performance of silver nanowire electrodes that can virtually eliminate all shadowing losses by the metallic contacts. This is achieved through light trapping via total internal reflection at the surface of a thin dielectric cover layer. Two kinds of interdigitated electrodes are considered, using either cylindrical silver wires or triangular silver wires. It is shown that both designs can simultaneously provide high optical transparency and high electrical conductivity when using micron sized silver wires. The relative contribution of radiative and non-radiative loss is evaluated as a function of wire size, including the effect of surface plasmon polariton mediated dissipation. The performance is analyzed at high metal coverage to highlight the importance of light trapping. It is shown that 2 μm wide triangular silver wires with 25% metal coverage, embedded in a Si₃N₄ cover layer can provide a peak transparency of 98% and an average optical transmission of 93% across a broad wavelength range spanning from 400nm to 1.1μm, while offering sheet resistivity as low as 0.35Ω/sq. Reducing the wire width to 300nm reduces the light trapping efficiency of triangular electrodes by ~40%, which is quantitatively explained in terms of the angular distribution of the reflected light from isolated wires. A new figure of merit is proposed to evaluate the overall performance of light trapping transparent metallic electrodes, and it is shown that triangular electrodes progressively outperform cylindrical electrodes as the wire size increases. Methods for producing large area light trapping electrodes will be discussed.

4:45 PM EN11.09.05
Zr-Doped Indium Oxide (IZRO) Transparent Electrodes for Perovskite-Based Tandem Solar Cells Erkan Aydin¹, Michele De Bastiani¹, Xinbo Yang¹, Muhammad Sajjad¹, Faisal Aljamaan¹, Yury Smirnov², Mohamed N. Hedhili¹, Wenzhu Liu¹, Thomas G. Allen¹, Lujia Xu¹, Emmanuel Van Kerschaver¹, Monica Morales-Masis², Udo Schwingenschlögl¹ and Stefaan De Wolf¹; ¹King Abdullah University of Science and Technology, Saudi Arabia; ²University of Twente, Netherlands

Parasitic absorption in transparent electrodes is one of the main roadblocks to enable power conversion efficiencies (PCEs) for perovskite-based tandem solar cells beyond 30%. To reduce such losses and maximize light coupling, the broadband transparency of such electrodes should be improved, especially at the front of the device. Here, we show the excellent properties of Zr-doped indium oxide (IZRO) transparent electrodes for such applications, with improved near-infrared (NIR) response, compared to conventional In-doped tin oxide (ITO) electrodes. Optimized IZRO films feature a very high electron mobility (up to ~77 cm²/V.s), enabling highly infrared transparent films with very low sheet resistance (~18 Ω/sq for annealed 100 nm films). For devices, this translates in a parasitic absorption of only ~5% for IZRO within the solar spectrum (250-2500 nm range), to be compared with ~10% for commercial ITO. Fundamentally, we find that the high conductivity of annealed IZRO films is directly linked to promoted crystallinity of the indium oxide (In₂O₃) films due to Zr-doping. Overall, on four-terminal perovskite/silicon tandem device level, we obtained an absolute 3.5 mA/cm² short-circuit current improvement in silicon bottom cells by replacing commercial ITO electrodes with IZRO, resulting in improving the PCE from 23.3 to 26.2%. [1]

References
Atomic Layer Deposited Nanolayers for Silicon Photovoltaics

Bart Macco, Jimmy Melskens and Erwin Kessels; Eindhoven University of Technology, Netherlands

Thin films are ubiquitous in the preparation of crystalline silicon solar cells. With the introduction of the PERC technology also the method of atomic layer deposition (ALD) has been introduced in high volume manufacturing in photovoltaics. Currently, the technique is quickly gaining market share for the deposition of ultrathin Al₂O₃ nanolayers for rear side surface passivation. The advantages of ALD are that it is scalable, that it is well suited to prepare high quality and uniform nanolayers, and that it is a "soft" deposition technique preventing interface damage. In this presentation the state of the art of ALD for silicon photovoltaics will be discussed as well as some ongoing developments and potential new applications. This includes new materials for surface passivation, nanolayers for passivating contacts, transparent conductive oxides as well as applications of ALD for polysilicon passivating contact solar cells.

Thermally Stable Passivating Hole-Selective Contacts Using Atomic Layer Deposited Molybdenum Oxide with Thin Aluminum Oxide

Geoffrey Gregory, Zhengning Gao, Titel Jurca, Parag Banerjee and Kristopher Davis; University of Central Florida, United States

One high efficiency crystalline silicon (c-Si) solar cell that has potential to be cost-competitive with Al-BSF devices while maintaining the passivation quality of PERC structures is the silicon heterojunction. Most notably is the Heterojunction with Intrinsic Thin-layers (HIT) solar cell, which chemically passivates the surface of the c-Si with intrinsic hydrogenated amorphous silicon (a-Si:H) while allowing charge carriers to conduct through the contact. Doped a-Si:H layers then create the potential gradient necessary for carrier diffusion and charge collection to occur.

Even with its high performance and simplified fabrication process, the HIT solar cell has potential to be improved upon. The a-Si:H layers produce parasitic absorption of high energy light. Many groups have also found the a-Si:H contacts to be sensitive to annealing treatments above 200°C. This limits the processing space for the metallization step, which typically occurs at much higher temperatures.

In this work we use Atomic-Layer-Deposited (ALD) MoOₓ as a hole-selective contact to c-Si in combination with thin SiOₓ and Al₂O₃ passivation layers to study the solar cell parameters of carrier selective contacts without the use of a-Si:H. While the optical properties of MoOₓ present a significant reduction in parasitic absorption compared to a-Si:H, the temperature stability of the material is still in question. Many groups have been unable to anneal MoOₓ based contacts above 120°C without degrading the electrical properties of the contact. We show that by using a thin Ni capping layer before Al metallization, the contact remains stable up to 300°C with contact resistivities below 10 mΩ-cm². This presents significant improvements on the thermal budget of the MoOₓ processing sequence and will allow for more appropriate contact formation steps.

Using Ultraviolet Photoelectron Spectroscopy we measure a work function of 6.2 eV in our 5nm MoOₓ contact. We simulate the band-bending and hole concentration at the c-Si surface as a function of the MoOₓ contact work function and show that our films exhibit sufficient hole-selective properties. Additionally, High Resolution Transmission Electron Microscopy images show that when a thin Ni capping layer is not used prior to Al metallization, a 2-3 nm Al₂O₃ layer forms at the Al/MoOₓ interface. This insulating interlayer contributes to a large barrier to hole transport, making the Al/MoOₓ contact incompatible with high efficiency heterojunction solar cells. The Al/Ni/MoOₓ contact, however, exhibits no such interlayer. This suggests that Ni may act as a diffusion barrier to O species during solar cell fabrication.

Finally, we show that by using a thin (~1 nm) Al₂O₃ passivation layer at the MoOₓ/c-Si interface, we are able to achieve a minority carrier lifetime of over 1 ms on n-type c-Si.

TiOₓ Thin Layer as an Efficient Passivating Hole Selective Contact

Takuya Matsui¹, Martin Bivour², Martin Hermle² and Hitoshi Sai¹; ¹National Institute of Advanced Industrial Science and Technology (AIST), Japan; ²Fraunhofer Institut für Solare Energiesysteme ISE, Germany

Using Ultraviolet Photoelectron Spectroscopy we measure a work function of 6.2 eV in our 5nm MoOₓ contact. We simulate the band-bending and hole concentration at the c-Si surface as a function of the MoOₓ contact work function and show that our films exhibit sufficient hole-selective properties. Additionally, High Resolution Transmission Electron Microscopy images show that when a thin Ni capping layer is not used prior to Al metallization, a 2-3 nm Al₂O₃ layer forms at the Al/MoOₓ interface. This insulating interlayer contributes to a large barrier to hole transport, making the Al/MoOₓ contact incompatible with high efficiency heterojunction solar cells. The Al/Ni/MoOₓ contact, however, exhibits no such interlayer. This suggests that Ni may act as a diffusion barrier to O species during solar cell fabrication.

Finally, we show that by using a thin (~1 nm) Al₂O₃ passivation layer at the MoOₓ/c-Si interface, we are able to achieve a minority carrier lifetime of over 1 ms on n-type c-Si.
Recently, Yang et al. have reported 22.1% efficient c-Si solar cell by applying an atomic-layer-deposited (ALD) TiOx thin-layer as electron contact to n-type base [1]. The origin of the electron selectivity of TiOx has been ascribed to the asymmetric current flow at the (n) c-Si/TiOx interface where the conduction band offset is much lower than the valence band offset. On the other hand, we recently found that TiOx can be tuned from electron to hole selectivity by controlling the ALD condition etc. [2]. This offers an interesting possibility that TiOx can be used as a hole selective contact alternative to the widely-used p-type a-Si:H and transition-metal oxides such as MoOx, WOx and V2Ox. In this contribution, we show for the first time that TiOx thin layers can act as efficient passivating hole selective contacts.

TiOx thin layers were deposited by thermal-ALD on c-Si (FZ, 1 Ωcm, (100), planer, n-type). Firstly, carrier selectivity of the deposited TiOx was studied by measuring Voc of solar cells. To decouple the carrier selectivity from its surface passivation an intrinsic a-Si:H buffer layer was inserted between c-Si and TiOx. A standard SHJ structure of either (i-n) a-Si:H/ITO or (i-p) a-Si:H/ITO stack was formed as a counter electron or hole contact, respectively. It is found that Voc of the solar cell is 200-400 mV higher when using our TiOx as hole contact than using it as electron contact. The SPV measurement showed that the TiOx induces large band bending (~900 mV) with respect to (n) c-Si while almost no band bending is created when deposited on (p) c-Si. This implies the presence of the negative fix charge in the TiOx, which is considered as one of the origins of the observed hole selectivity of the TiOx. Furthermore, we found that the carrier selectivity of TiOx depends significantly on the work function (WF) of the capping metal (or TCO) contact. The Voc is increased monotonically with increasing the WF of the capping layer when using TiOx as hole contacts. This indicates that band bending in (n) c-Si is significantly influenced by the WF of the capping layer, as it is well-known in the MIS contact system. By using an ITO/TiOx/(i) a-Si:H stack as an emitter layer on (n) c-Si, we obtained a relatively high Voc of 650 mV. Furthermore, the TiOx is also found to act as a good passivation layer with respect to c-Si. An effective lifetime of >1 ms was obtained by depositing TiOx on (n) c-Si without a-Si:H buffer layer. By optimizing both the surface passivation and the hole selectivity of the TiOx layer, we attained solar cell efficiencies of >18%, demonstrating that TiOx has potential of working as an efficient passivating hole selective contact. We discuss the origin of the hole transport in the TiOx which contradicts to the previous transport model based on the band alignment at the TiOx/Si interface.

great attention worldwide in the last decade. In contrast to the widely investigated and commercially competitive
thin film solar cells such as CuIn_xGa_{1-x}Se_2 and CdTe, Sb_2S_3 is non-toxic and exists naturally as stibnite minerals,
with both while Sb and S are both earth abundant elements. Sb_2S_3 is a binary compound with a single phase,
consisting of linked one-dimensional ribbons. Such a ribbon structure provides a preferential pathway for electron
transfer if with along the desired orientation. Antimony sulphide has high absorption coefficient of \(\alpha > 10^5\) and a bandgap of \(~1.7eV\), making it a suitable top cell candidate for tandem
cells. In this work, we demonstrate several crucial steps to enable this application in industrial cells by looking
into the influence of texture and doping level, oxide preparation method, metal contacting and thermal stability.

Secondly, we show that the SiO_x can be prepared in many ways (RCA, LTO, UV/O_3, NAOS) which all yield good
conductivity (< 1 m\(\Omega\)cm). Therefore, if a proper tunnel contact between c-Si/SiO_x/ZnO can be made,
the ZnO could serve as a full-area passivating, antireflective and lateral transport layer on the front side of a c-Si
solar cell. In this work, we demonstrate several crucial steps to enable this application in industrial cells by looking
into the influence of texture and doping level, oxide preparation method, metal contacting and thermal stability.

Furthermore, the rapid thermal evaporation (RTE) method has been recognized as an effective and reliable method
to grow Sb_2S_3 thin films, achieving an efficiency of 3.5% with a high Voc of 710 mV when using CdS as electron
transport layer (ETL). However, the reported orientation of the Sb_2S_3 is not well controlled when deposited by the
RTE method. In this work, we report the first fabricated Sb_2S_3 thin films with vertical orientation by VTD method.
To better understand the key factor that enables the vertical growth of Sb_2S_3, we use the RTE method as a reference,
which does not create vertically aligned Sb_2S_3 crystals on a CdS buffer layer. We achieved the an efficiency of
4.73% with a high Voc of 710 mV by using the iTO/CdS/Sb_2S_3/Gold configuration via VTD method compared to
370 mV using RTE method. We propose a simple model to describe the growth process.

**11:00 AM EN11.10.07/FF05.10.07**

**Atomic-Layer-Deposited ZnO as a Full-Area Passivating, Contacting and Antireflection Layer for c-Si Solar Cells**

Bart Macco, Marc Dielen, Bas van de Loo, Jimmy Melskens and Erwin Kessels; Eindhoven University of
Technology, Netherlands

The field of c-Si photovoltaics has strongly diversified in recent years with the advent of a wide variety of novel
passivation and passivating contact materials. Recently, we have demonstrated excellent surface passivation using
stacks of ultrathin (~1.5 nm) RCA SiO_x capped with ALD ZnO/Al_2O_3, with an implied open-circuit voltage (i\(V_{oc}\)) of
725 mV on planar c-Si(n) wafers. Within this SiO_x/ZnO/Al_2O_3 stack, the RCA SiO_x enables chemical passivation, similar as in poly-Si passivating contacts. The Al_2O_3 layer on top serves as a dense capping layer: It prevents
effusion of H from the ZnO upon annealing, which is needed to hydrogenate the SiO_x.

The unique aspect of the (doped) ZnO is that it is suited as an antireflection coating (simulated \(J_{sc} \approx 41.6\) m\(\Omega\)cm\(^2\))
which is also conductive (< 1 m\(\Omega\)cm). Therefore, if a proper tunnel contact between c-Si/SiO_x/ZnO can be made,
the ZnO could serve as a full-area passivating, antireflective and lateral transport layer on the front side of a c-Si
solar cell. In this work, we demonstrate several crucial steps to enable this application in industrial cells by looking
into the influence of texture and doping level, oxide preparation method, metal contacting and thermal stability.

Firstly, we verified that the stack also passivates on textured c-Si(n) wafers (i\(V_{oc} \approx 728\) mV) and that its passivation
on \(n^+\) doped surfaces has on par with industrial SiN_x. The stack is thermally stable up to \(~550\) °C, which is
not firing-compatible, but allows for a much higher paste curing temperature than for HIT-type cells.

Secondly, we show that the SiO_x can be prepared in many ways (RCA, LTO, UV/O_3, NAOS) which all yield good
passivation. UV/O_3 however yields the best passivation and is a room-temperature, single-sided treatment which
allows for accurate control over the oxide thickness (~1.65 nm).

Thirdly, in order to be able to contact the ZnO by metal, we can selectively remove the insulating Al_2O_3 capping
layer from the ZnO after hydrogenation by a wet-etch. Interestingly, no proper tunnel contact (\(>10 \Omega\)cm\(^2\)) can be
made on 3 \(\Omega\)cm c-Si(n) wafers, whereas a “first-try” value of ~0.1 \(\Omega\)cm\(^2\) was obtained on \(n^+\) doped surfaces (100
\(\Omega/sq\)). This contact resistivity is sufficiently low to use ZnO as a “hybrid” homo/heterojunction contact on \(n^+\)
surfaces: the $n^+$ doped Si surface provides electron-selectivity and facilitates tunneling, whereas the ZnO provides full-area passivation and aids in lateral transport, potentially allowing for higher Ohmic FSFs. Ongoing work focuses on the effect of the doping levels of both the c-Si and ZnO and the integration of the ZnO on the front of a PERC-type cell.


11:15 AM EN11.10.08/FF05.10.08 Controllable Fixed Charge Densities of TiO$_2$–Based Passivation Layer in c-Si Solar Cells Dohee Kim and Jihun Oh; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Surface passivation of crystalline Si (c-Si) is a key enabler for achieving high efficiency c-Si solar cells. While an Al$_2$O$_3$ surface passivation layer grown by atomic layer deposition (ALD) is known for excellent surface passivation for p-type Si from the negative fixed charges in the Al$_2$O$_3$ layer, low refractive index of Al$_2$O$_3$ demands an additional anti-reflection coating to suppress optical reflection, which leads to extra capital cost in c-Si solar cell manufacturing. Therefore, the multi-functional passivation layer that can provide both the high level of passivation quality and optimum optical property is necessary for high efficiency and cost-effective silicon solar cells. Here, we designed the multifunctional Al-doped TiO$_2$ passivation layer using ALD single process for low cost high efficiency silicon solar cells. TiO$_2$ film grown by ALD is a promising candidate for front multifunctional passivation layer of p$^+$-emitter/n-base structure due to negative fixed charge densities and appropriate refractive index for anti-reflection coating of silicon solar cell. ALD process allows to control the composition accurately and provide excellent passivation quality with thin films. In this work, we controlled the Al concentration in TiO$_2$ film with amorphous phase from 0 to 15.5 % by adjusting the cycle ratio of Al$_2$O$_3$ to TiO$_2$ in ALD process. We then successfully demonstrated that the fixed charge densities of Al-doped TiO$_2$ passivation layer can be controlled from $-8 \times 10^{11}$ cm$^{-2}$ to $-3 \times 10^{12}$ cm$^{-2}$ by varying the amount of Al concentration. As a result, we achieved implied $V_{oc}$ up to 709 mV with 15nm thick Al-doped TiO$_2$ on n-Si by maximizing field-effect passivation. We also investigated the effect of film thickness on surface passivation quality. By Al doping in TiO$_2$ passivation layer it showed significant enhancement of passivation performance compared to TiO$_2$ film from 5 to 55 nm thickness. Al-doped TiO$_2$ film provided high level of passivation quality leading to implied $V_{oc}$ of 700 mV from 15 to 55 nm. Finally, we have conducted research to reduce the total reflectance of silicon by applying Al-doped TiO$_2$ passivation layer of which the refractive index became close to 2.3, ideal refractive index for silicon solar cell. Therefore, we successfully demonstrated that the ALD Al-doped TiO$_2$ multifunctional passivation layer is a suitable candidate for high efficient Si solar cells based on the p$^+$-emitter/n-base structure with excellent optical property and outstanding passivation characteristic.

11:30 AM *EN11.10.09/FF05.10.09 Opening up the Processing Window for Chemical Vapor Deposited Oxides over Lead-Halide Perovskite Photovoltaics to Achieve Improved Performance Ravi D. Raninga1, Robert A. Jagt1, Solene Bechu2,3, Tahmida N. Huq1, Yen-Hung Lin1,2, Zewei Li1, Muriel Bouttemy2,3, Mathieu Fregnaux2,3, Henry J. Snaith1, Richard H. Friend4, Philip Schulz2,3, Judith L. MacManus-Driscoll1 and Robert Hoye1; 1University of Cambridge, United Kingdom; 2Institut Photovoltaïc d’Île de France (IPVF), France; 3Université de Versailles Saint-Quentin en Yvelines, Université Paris-Saclay CNRS, France; 4University of Oxford, United Kingdom; 5CNRS, Institut Photovoltaïc d’Île de France (IPVF), France

The growth of oxides by atomic layer deposition (ALD) over lead-halide perovskites in solar cells is attracting increasing attention for improving environmental and mechanical stability. A wide range of materials have now been investigated, including SnO$_2$, TiO$_2$, Al-doped ZnO and zinc tin oxide. These oxide overlayers have led to unencapsulated perovskite solar cells achieving stable performance for 4500 h in ambient air. However, the range of growth temperatures that can be used to grow the oxide overlayers over the perovskite films is restricted to typical values of only 60 - 100 °C due to the low stability of the perovskites. This limits the mobility and density of the oxide films achievable. In this work, we show that we can open up the processing window of oxides grown over lead-halide perovskites by using atmospheric pressure chemical vapor deposition (AP-CVD). This technique yields oxide films with similar uniformity, density and electronic properties as ALD films at similar growth temperatures, but with orders of magnitude higher growth rates [1]. We investigate the growth of TiO$_2$ over thermally-sensitive
CH$_3$NH$_3$PbI$_3$ films. We achieve a growth rate of 1.19 ± 0.04 nm s$^{-1}$ at a deposition temperature of 150 °C, which allows 7 nm TiO$_x$ films to be grown in 6 s (compared to >30 min for ALD). We show that this rapid deposition enables TiO$_x$ to be directly grown on CH$_3$NH$_3$PbI$_3$ films without damage to the bulk or surface, as shown by our X-ray diffraction, X-ray photoemission spectroscopy and time-resolved photoluminescence measurements. Indeed, we show that the TiO$_x$ overlayers can be grown at temperatures exceeding 180 °C without a significant drop in efficiency in CH$_3$NH$_3$PbI$_3$ solar cells. These results can be generalised to triple-cation perovskite devices, as well as to AP-CVD SnO$_x$ overlayers. In particular, we show that the conformal nature of the oxide overlayers lead to perovskite devices with improved performance (reaching 19.7% for triple-cation perovskite devices using a 60 nm SnO$_x$ overlayer). Our work demonstrates AP-CVD to be a versatile technique for growing high-quality oxides over a wide range of processing conditions.

Reference

SESSION EN11.11: Passivating Contacts II
Session Chairs: Kaining Ding and David Young
Thursday Afternoon, December 5, 2019
Sheraton, 3rd Floor, Fairfax B

1:30 PM *EN11.11.01
Passivating Contacts Based on Physical Vapour Deposition Techniques for Silicon Solar Cells Di Yan, Andres Cuevas, Sieu Pheng Phang, Yimao Wan, Wenjie Yang and Daniel Macdonald; The Australian National University, Australia

Surface-passivating, carrier-selective contacts formed by heavily doped silicon films and thin interfacial oxide layers are capable of achieving high performance, leading to record efficiencies for silicon solar cells at both laboratory (25.8% TOPCon on n-type wafers and 26.1% POLO on p-type wafers) and industrial scale (24.6% by Trina Solar on 245 cm$^2$ n-type wafers). This type of passivating contact is increasingly regarded as the basis for the next generation of high performance technology for silicon solar cells. It can also constitute a baseline technology for PV research labs due to its simple implementation and excellent electrical performance. Different approaches have been explored for growing the thin interfacial oxide, depositing the silicon film, and incorporating dopants into it, most of which are based on various forms of chemical vapour deposition. In this contribution, we will present a novel approach based on physical vapour deposition. We have formed p-type passivating contacts based on PVD deposited silicon films doped in-situ with boron atoms. A low recombination current density $J_{oc} = 20$ fA/cm$^2$ and a low contact resistivity $\rho_c = 10$ mΩ-cm$^2$ have been achieved. Such a PVD-formed p-type passivating contact has been successfully implemented as full area rear hole selective contacts in p-type silicon solar cells. The best devices have reached a conversion efficiency of 23% with an open-circuit voltage of 701mV. At the same time, we are working on the development of n-type passivating contacts using a similar approach. In this presentation, we will compare the PVD approach with chemical vapour deposition approaches in terms of their fabrication processes and electrical performance. We will discuss results for PVD p-type passivating contacts and show work in progress for PVD n-type passivating contacts.

2:00 PM *EN11.11.02
Passivating Contacts Based on (Sub-)Monolayers of ALD-Oxides and the Kinetics of Thermal Bulk-Lifetime Degradation in FZ-Si Daniel Hiller; Australian National University, Australia

The first part of the talk will deal with (sub-)monolayers of ALD metal oxides, mainly Al2O3, deposited onto tunnel-SiO2. Wet-chemically grown and dry-thermally oxidized tunnel-SiO2 have a different surface termination, which leads to a different initial deposition during the first ALD-cycles. Despite the deposition of just sub-monolayers the Si-surface passivation can reach very good levels, even before a forming gas annealing, while maintaining a low contact resistivity due to tunneling through the ultra-thin layer stack. The surface passivation is explained via the formation of induced acceptor states in SiO2, which capture electrons from the dangling bonds at the Si/SiO2 interface so that these defects are electronically deactivated, while a negative fixed charge in the...
dielectric layer enables field effect passivation [1,2,3].

In the second part, the kinetics of the thermal activation as well as the annihilation of the grown-in defects in float-zone (FZ) Si wafers are studied. In the critical temperature window between approx. 400-800°C the bulk-lifetime of FZ-Si is decreased by more than 2 orders of magnitude and this degradation takes place on very short timescales. In addition to conventional furnace annealing, rapid thermal annealing (RTA) and millisecond flash lamp annealing (FLA) were studied. It will be demonstrated that also the recovery of the bulk lifetime can be achieved by thermal treatments that are much shorter and at lower temperatures than previously reported. Finally, the role of impurities detected by SIMS and their possible defect configurations (modelled by density functional theory) are discussed.


2:30 PM BREAK

3:00 PM CLOSING REMARKS AND AWARDS

**SYMPOSIUM EN12**

Structure–Function Relationships and Interfacial Processes in Organic Semiconductors for Optoelectronics

December 2 - December 6, 2019

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**SESSION EN12.01: Structure-Properties Relationships in Organic Semiconductors—Chemistry**

Session Chair: Kevin Sivula
Monday Morning, December 2, 2019
Sheraton, 2nd Floor, Back Bay C

**9:45 AM *EN12.01.01**

*Halogenated Semiconducting Polymers for Photovoltaic Conversion* Nicolas Leclerc, Narayanaswamy Kamatham, Olzhas Ibraikulov, Stéphanie Ferry, Pablo Durant, Amina Labiod, Benoit Heinrich, Thomas
Heiser3, Patrick Lévêque3 and Stéphane Méry2; 1ICPEES-CNRS, France; 2IPCMS, France; 3ICube, France

In recent years, partially fluorinated organic semiconducting polymers have aroused a considerable interest, to be used as electron-donating material in organic photovoltaic solar cells and have led to a significant increase in power conversion efficiency.[1-3] There are several reasons for this success, including:

- a planarization of the polymer skeletons via weak bonds between the fluorine atoms and the neighboring atoms and heteroatoms that improves the charge transport and the π-stacking in fluorinated polymers,
- the electro-deficient nature of the fluorine atom, which significantly stabilizes the energy levels of the frontier molecular orbitals.

For similar reasons, the chlorine atom has recently emerged as a suitable substitute for fluorine in some (macro)-molecular structures.[4] However, its larger steric size and reduced electronegativity, as compared to fluorine, is found to significantly modulate its impact.

In this communication, we propose to clarify the architectural principles that govern the properties of fluorinated and chlorinated polymers. In particular, we will discuss the evolution of the structural and optoelectronic properties of two families of organic semiconducting polymers incorporating either of these two halogens, according to their positions and numbers. Finally, through additional molecular engineering work at the level of side chains (in particular via innovative siloxane chain functionalization), we will also discuss the role of these side chains on the polymers solubility, on their orientation on the substrate as well as on their miscibility with electron-accepting materials.


10:15 AM EN12.01.02
Liquid-Crystalline and Semi-Crystalline—Understanding Structure-Function Relationships in n-Type Donor-Acceptor Copolymer Films Sabine Ludwigs; University of Stuttgart, Germany

My talk will give an overview about our recent findings on structure-function relationships of n-type donor-acceptor copolymer films based on P(NDI2OD-T2).1 On the molecular scale the role of 2,6- and 2,7-linked regioisomers in the polymer backbone for the preparation of regioregular (RR) and regioirregular (RI) systems is discussed.2 A specificity of P(NDI2OD-T2) is its strong tendency for aggregation in solution. We find that with increasing regioirregularity the overall aggregation tendency goes down which is beneficial for applications where mixing with other compounds is necessary, e.g. for organic photovoltaics or for chemical doping.

On the other hand the strong aggregation tendency of the RR system is useful for the preparation of highly anisotropic structures. On the mesoscopic scale we give new insights in the structure formation upon solution deposition.3 A morphology analysis shows that the deposited films are based on characteristic fiber morphologies where the fiber and chain directions are coinciding. The involvement of liquid-crystalline phases, in particular nematic-like preordering in highly concentrated solutions is demonstrated. Solvent vapor annealing is shown to lead to large area alignment in spherulite-like superstructures with semi-crystalline structures. Particularly nice is the applicability of blade-coating to achieve highly anisotropic films where both the bulk and the surface morphology can be determined: whereas blade-coated films after 220°C annealing give evidence for face-on orientation in the bulk with segregated stacking in polymorph Form I, 300°C annealing leads to an edge-on orientation with mixed stacking in Form II.3,4 All films have a top edge-on layer. Using these well-defined morphologies we can access detailed insights into electrochemical and chemical doping mechanisms.5,6

1) Y. M. Gross, and S. Ludwigs, P(NDI2OD-T2) Revisited – Aggregation Control as Key for High Performance n-Type Applications, Synthetic Metals 2019, 253, 73.
In this presentation we report the development of novel organic semiconductors, as well as the process engineering, for mechanically flexible transistors and circuits. Particularly, we show that "ultra-soft" polymers comprising naphthalenediimides (NDI) units co-polymerized with "rigid" and "flexible" organic units can change how charge transport is affected by mechanical stress, demonstrating that polymer backbone composition is more important than film degree of texturing. This strategy enables to reduce the elastic modulus of the semiconducting film by >2-4x while retaining good charge transport characteristics. In addition, by fabricating polymer/polymer blends by shear techniques, it provides a new avenue to enhance charge transport and achieve excellent mechanical robustness, which is further increased by modification of the film morphology. Thus, we demonstrate that these materials can enable TFT-based circuits for ultra-flexible displays and sensors on plastics. Finally, new oxide-polymer blends can be used to fabricate high-rectification and stretchable diodes via the self-assembly/phase separation properties of polymers having different surface energy.

11:15 AM EN12.01.05
NFA Molecules with an Extended Pi-Conjugated Core—Synthesis, Characterization, Photovoltaic Performances and Stability Analysis Lydia Cabau¹, Yann Kervella¹, Olivier Bardagot¹, Yatzil Avalos², Agnes Rivaton³, Carmen Ruiz Herrero³, David Duchê³, Jean Jacques Simon⁴, Pavlo Perkhun², Olivier Margeat², Christine Videlot-Ackermann², Melanie Bertrand⁴, Jörg Ackermann² and R Demadrille¹; ¹Univ. Grenoble Alpes, CEA, CNRS, IRIG, SyMMES, France; ²Aix-Marseille University, CINaM, UMR CNRS 7325, France; ³Universite Clermont Auvergne, UMR CNRS 6296, SIGMA Clermont, ICCF, France; ⁴Aix-Marseille Univ., Univ. Toulon, UMR CNRS 7334, IM2NP, France; ⁵ARMOR, Organic Photovoltaics Division, Armor Sustainable Energies (ASE), France

In the last years, non-fullerene acceptors (NFAs) have strongly burst into the field of organic photovoltaics (OPV) as alternative to fullerene derivatives. NFAs molecules not only have overcome the technical drawbacks associated to the fullerenes, but they also have made possible the increase of the efficiency over 16%¹ in single junction and over 17%² in tandem solar cells. Despite the extensive efforts made to achieve high efficiencies, more investigations are needed to further understand degradation mechanisms and hence improve their stability in order to make OPV technology a viable contender with technologies based on inorganic semiconductors for commercialization. In that context, we developed three new ITIC-like NFAs with extended p-conjugated spacers between the donor and acceptor moieties. We present the synthesis and characterization of these innovative NFAs, the performances obtained in bulk-heterojunction solar cells, in addition to a comparative study of the degradation mechanisms. The fluorination of the acceptor moiety was employed as a strategy to improve the device performance³. The organic solar cells fabricated with the new NFAs combined with PCE12 as the electron donor exhibit, power conversion efficiencies comprised between 5-6 %, as preliminary results. Noticeably, the new NFAs allowed to reach Voc over 1.1 V which is significantly higher than the Voc obtained with the reference ITIC-based devices. Interestingly, one of the new NFA demonstrates remarkable stability compared to ITIC.

In this communication, the synthetic strategies, the optoelectronic properties of the molecules, the performances in devices and the degradation mechanisms under thermal and photochemical stress will be presented and discussed.

References:
Halochromic Switch from the 1st to 2nd Near Infrared Window of Diazapentalene-Dithienosilole Copolymers
Christine Dagron-Lartigau1,2, Wissem Khelifi1,2, Hussein Awada1,2, Katarzyna Brymora1,4, Sylvie Blanc1,3, Lionel Hirsch5,4, Frederic Castet3,4 and Antoine Bousquet1,2; 1Pau University, France; 2CNRS, France; 3ISM, France; 4Bordeaux University, France; 5IMS, France

Up to now, halochromism has mostly been demonstrated on chromophores absorbing in the UV-visible range. However, research in the field of Infra-Red (IR) technologies is in strong development, driven by technological needs in military and civilian applications, such as imaging, optical communications, energy or photodetectors.[1] Also, since 50% of the solar energy falls into the IR spectral region, photovoltaic materials are under development to increase solar cells efficiency.[2] IR-materials are also synthesized for biosensing and bioimaging because IR light penetrates into tissues, the so-called “biological window”.[3] To design organic IR materials, the basic principle is to reduce the bandgap. Specifically, synthesis of electron donor–acceptor (D–A) alternating conjugated copolymers has demonstrated high potential to decrease the bandgap under 1.5 eV, leading to IR-absorbing or emitting materials.[4] For the moment, most of these organic materials showed a maximum absorption peaks falling in the first NIR optical window covering 750−1000 nm. Actually, the second NIR optical window covering 1000−1350 nm is more promising for biological applications due to its higher photothermal conversion and deeper tissue penetration.[5]

In this presentation, we will report the synthesis of a low bandgap copolymer based on the 2,5-diazapentalene (DAP) unit, derived from the diketopyrrolopyrrole (DPP) chromophore. We combine the strong acceptor DAP unit with the dithienosilole (DTS), a photostable electron donor [6] that allows the introduction of solubilizing alkyl chains onto the silicon atom. As the result of the polymerization, an IR-material was synthesized with a maximum absorption at 850 nm in chloroform solution. Upon protonation of the DAP unit with Brønsted acids or its complexation with Lewis acids, the maximum of absorption is further shifted up to 1100 nm (edge at 1500 nm) in the second NIR optical window. To the best of our knowledge, this halochromic behavior is the highest reported up to now. Using a combination of spectrophotometry, cyclic voltammetry and DFT calculations, we identified the Brønsted and Lewis adducts that are formed. We can demonstrate that this optical shift is correlated with a decrease of the copolymers bandgap associated to the decrease in the LUMO energy and enhancement of the pi-electron delocalization along the conjugated backbone, as revealed by the lowering of the bond length alternation.[7]

Acknowledgments: Agence Nationale de la Recherche (TAPIR project no. ANR–15-CE24-0024-02) and Région Nouvelle Aquitaine (TAMANOIR project no. 2016-1R10105-0007207) for their financial support. Pole Modélisation HPC facilities of the Institut des Sciences Moléculaires, co-funded by the Nouvelle Aquitaine region, as well as by the MCIA (Mésocentre de Calcul Intensif Aquitain) resources of the Université de Bordeaux and of the Université de Pau et des Pays de l’Adour for computer times.

Excellent Semiconductors Based on Tetraceno-Tetracene and Pentaceno-Pentacene—From Stable Closed-Shell to Singlet Open-Shell

Michel Frigoli1, Tanguy Jousselin-Oba1, Masashi Mamada2 and Chihaya Adachi2;
1Paris-Saclay University, France; 2Kyushu University, Japan

Designing stable open-shell organic materials through the modifications of the π-topology of molecular organic semiconductors have attracted recently considerable attention.1 However, their uses as an active layer in organic field-effect transistors (OFETs) are very limited and the obtained hole and electron charge mobilities are around 10−3 cm2 V−1 s−1.

Herein, we disclosed the synthesis of two peri-fused materials so-called tetraceno-tetracene (TT) and pentacenopentacene (PP) which have low band gap of 1.79 and 1.42 eV, respectively.2 Their ground state natures have been investigated by different experiments including steady state absorption, electron spin resonance, superconducting quantum interfering device (SQUID) and variable temperature NMR along with DFT calculations. TT and PP have closed-shell and singlet open-shell structures in their ground state, respectively, and possess high stability. Their biradical characteristics were found to be 0.50 and 0.64. The origin of the open-shell character of PP is related to the concomitant opening of two tetracenes with the recovering of two extra aromatic sextets and a small HOMO-LUMO energy gap (gap < 1.5 eV). Thanks to the high stability, thin film OFET devices could be fabricated. In TG-BC configuration PP shows remarkably high hole mobility of 1.4 cm2 V−1 s−1 while TT exhibits a hole mobility of 0.77 cm2 V−1 s−1. In configuration of BG-TC, ambipolar behaviors for both were obtained with hole and electron mobilities of 0.21 and 0.01 cm2 V−1 s−1 for PP and 0.14 and 0.006 cm2 V−1 s−1 for TT.

References

SESSION EN12.02: Structure-Properties Relationships in Organic Semiconductors—Organic Field-Effect Transistors
Session Chair: Pichaya Pattanasattayavong
Monday Afternoon, December 2, 2019
Sheraton, 2nd Floor, Back Bay C

1:45 PM *EN12.02.01
Molecular Strategies to Increase Robustness of Organic Semiconductor Thin Films for Application in Photovoltaic and Photoelectrochemical Devices
Kevin Sivula; Ecole Polytechnique Federale Lausanne, Switzerland

As organic semiconductors attract increasing attention to application in diverse fields such as bioelectronics and artificial photosynthesis, understanding and improving their robust operation in a variety of challenging environments is a critical task. In this presentation, results from our lab are highlighted including our development of a morphology control strategy using conjugation-break spacers [1], demonstration of melt-processed small-molecule OPVs [2], and investigations of covalently-linked block[3] and network polymers[4], which afford tunable charge transport and solvent tolerance—making them promising for application as charge-transport interlayers in all-solution processed devices. In addition the application of bulk-heterojunctions to artificial photosynthesis via photoelectrochemical water splitting[5] will be discussed in terms of the requirements for material stability.


2:15 PM EN12.02.02
Hybrid Field Effect Transistors (HFET) a Fully Covalent Transistor with a Pi-Conjugated Organosilica Material

Olivier Dautel1, Gilles Roche1, Guillaume Wantz2 and Joel Moreau1; 1Charles Gerhard Institute, France; 2Bordeaux INP UMR 5218, France

The use of novel organosilica materials embedding π-conjugated moieties as semiconductor into field effect transistors will be presented. For that purpose, the [1]benzothieno[3,2-b][1]benzothiophene (BTBT),1 has been chosen as π-conjugated core, first functionalized with hydroxyl groups2 and then modified with hydrolysable and cross-linkable triethoxysilyl moieties. After polycondensation, this compound forms a hybrid material composed of charge transport pathways as well as insulating layers (SiOx). However, overall, the material is found to be a semiconductor and can be incorporated into field effect transistors. Taking advantage of the solgel chemistry3 involved here, we built Hybrid Field Effect Transistors that are fully cross-linked with covalent bonds.4 Molecules are cross-linked to each other, covalently bonded to the silicon oxide dielectric and also covalently bonded to the gold electrode thanks to the use of an appropriate additional interfacial monolayer in between. This is the first report of fully covalent transistors. Those devices show impressive resilience against polar, aliphatic and aromatics solvents (even under sonication). This study opens the route towards a new class of hybrid materials to create highly robust electronic applications.

REFERENCES


2:30 PM EN12.02.03

Influence of Alkyl Side-Chain Type and Length on the Thin-Film Microstructure and OFET Performance of Naphthalene Diimide-Based Organic Semiconductors

Adam Welford1, Subashani Maniam1, Eliot Gann2, Lars Thomsen3, Steven Langford4 and Chris McNeill3; 1Monash University, Australia; 2National Institute of Standards and Technology, United States; 3Australian Nuclear Science and Technology Organisation, Australia; 4Swinburne University of Technology, Australia

The effect of side chain length and type on the microstructure and organic field-effect transistor (OFET) performance of solution-processed naphthalene diimide (NDI) thin films will be discussed. Linear side chains with four (C4), five (C5), six (C6), eight (C8) and twelve (C12) carbon atoms are studied along with a branched ethyl hexyl (EH) side chain. Interestingly, relatively high mobilities of up to ~ 0.2 cm²/Vs are achieved for short (C4) and long (C12) side chains with linear chains of intermediate length and the branched side chain producing lower mobilities. The observed mobility trends are explained in terms of the competing influence of changes in crystal packing and changes in thin film morphology with changes in side chain length. Shorter side chains produce changes in the lateral stacking of NDI units which promote higher mobility while longer side chains produce solution-processed thin films with higher film quality evidenced by larger domain sizes and lower orientational disorder. Side chain length is also found to strongly modulate the molecular orientation of the NDI core, with high edge-on orientations observed for long chains, and tilted orientations for short chains. Thin film microstructure is investigated using a range of techniques including atomic force microscopy, grazing incidence wide-angle X-ray scattering and near-edge X-ray absorption fine-structure spectroscopy.

2:45 PM BREAK
Session Chair: Paul Meredith
Monday Afternoon, December 2, 2019
Sheraton, 2nd Floor, Back Bay C

3:15 PM EN12.03.01
Molecular Design and Structure-Function Relationships in Thermally Activated Delayed Fluorescence (TADF) Materials for Applications in OLEDs Martin R. Bryce; Univ of Durham, United Kingdom

Molecules showing thermally activated delayed fluorescence (TADF) have emerged as a promising alternative to heavy-metal complexes for applications in high efficiency organic light emitting diodes (OLEDs).[1] To date the most successful TADF emitters have been designed with electron donor (D) and electron acceptor (A) units covalently linked with conjugational separation between the units. This separation can lead to a very small excited state singlet-triplet gap (ΔEST) on the order of a few meV. If ΔEST is small, a significant population of the triplet state that occupies upper vibrational levels is able to undergo reverse intersystem crossing (RISC), giving rise to delayed fluorescence. OLEDs fabricated with TADF emitters have shown impressive performances, sometimes with external efficiencies (EQE) above 30%.[2]

We will report how the efficiency of TADF can be controlled by precise molecular design of donor-acceptor linked molecules, with particular emphasis on the rigidity of the molecular framework and the dihedral angle between the donor and acceptor units. Representative building blocks include: phenothiazine, acridine and triazaangulene as donors, and dibenzothiophene-S,S-dioxide and 9,9-dimethylthioxanthene-S,S-dioxide as acceptor units. Synthesis, photophysical studies, theoretical calculations and high efficiency OLED data, including blue/deep-blue emitters will be presented, based on our on-going studies.[3-6]

References

Acknowledgements. We thank EPSRC grant EP/L02621X/1 and EU Horizon 2020 Grant Agreement No. 732103 (HyperOLED) for funding.

3:30 PM EN12.03.02
Optical Properties of TADF Materials by TDDFT Nobuhiko Akino and Yasunari Zempo; Hosei University, Japan

Organic light emitting diodes (OLEDs) have been of great interest for display and lighting applications during decades and have been increasing to be utilized in smartphone and flat-panel display due to many advantages such as self-emission, high contrast, wide viewing angle, and so on. From the OLED material point of view, improvement of emissive exciton generation probability is an important factor for higher efficiency. After the development of fluorescent materials, the phosphorescent materials have been
introduced and have shown to achieve high efficiency. On the other hand, phosphorescent materials require expensive heavy metal such as Ir and Pt. Recently, thermally activated delayed fluorescence (TADF) materials have been developed as a new class of light emitting material where triplet excitons are converted into singlet excitons without heavy metals in phosphorescent materials.[1] Theoretically, an internal quantum efficiency (IQE) of 100%, the same as for phosphorescent materials, can be expected.

In order to study the optical properties of materials, we have employed the time dependent density functional theory (TDDFT), which is one of the most prominent and widely used methods for calculating excited states of various molecules, and it is recognized as a powerful tool for studying their electronic transition. In our calculations, the real-time and real-space (RSRT) techniques are employed in solving time dependent Kohn-Sham equation by the finite difference approach [3] without using explicit bases such as plane waves and Gaussian basis. Within the framework of this approach, we can solve for the wave functions on the grid with a fixed domain, which encompasses the physical system of interests. Furthermore, we have applied the maximum entropy method (MEM) to the optical analysis of the time-series data from the real-time TDDFT. We have confirmed that the MEM technique provides higher resolution in fewer computational steps, compared to the conventional Fourier transform technique.

In this study, we have focused on the spectrum of TADF materials including materials based on DABNA[2], which has recently been studying intensively because of its narrow FWHM (full-width at half maximum) in its spectrum, that is, of its high color purity. Main focus would be to design new materials with small exchange energy required for TADF character and with good color purity, starting from the understanding of existing molecules and the effect of substituents by quantum chemical calculation. The peak emission wavelength seems to be well predicted. In the presentation, we will discuss the correlation between simulation and experiment in peak wavelength and also the spectrum shape.

REFERENCES

3:45 PM EN12.03.03
Acenes with “Butterfly Wings”—Singlet Fission in a Highly Stable Bisalkynylated Derivative of Tetrabenzoanthracene Peter Budden1, Matthias Müller2, Jan Freudenberg2, Uwe Bunz2 and Richard H. Friend1; 1University of Cambridge, United Kingdom; 2Heidelberg University, Germany

Through transient optical and magnetic field measurements we have observed clear evidence for singlet exciton fission to triplet exciton pairs in a “butterfly-shaped” acene derivative, TIPS-tetrabenzoanthracene (TTBP), that has excellent ambient stability imparted by the presence of triphenylene “wings”.

The synthesis and impressive stability of large acenes with triphenylene “wings”, including TTBP, have recently been reported. One property of acenes of great current interest is their ability to undergo singlet fission: that is for photoexcited singlet excitons to generate a pair of triplet excitons each of roughly half the energy of the singlet. The energy of these triplets could be utilised to reduce thermalisation losses in solar cells.

The core of the molecule to which the butterfly wings are attached is Trisopropylsilylthynyl-anthracene (TIPS-anthracene). The total effect of the two wings to the molecular energy levels is similar to that of extending anthracene by one regular benzene ring, i.e. TIPS-tetracene, which itself has previously been shown to undergo efficient singlet fission, albeit with poor ambient stability. Here, the triplet absorption spectrum of TTBP that we observe in transient absorption experiments is remarkably similar to that of TIPS-tetracene, indicating that the triplet exciton is concentrated on the central part of the TTBP molecule that is common to TIPS-tetracene, and the stabilising butterfly wings do not greatly affect the structure of the triplet. We posit that this is key to the surprising persistence of singlet fission.

In TIPS-tetracene, morphology plays a key role in the efficiency of singlet fission, particularly in the separation of the triplet-pair state, which has a broad red-shifted emission. In TTBP, we have observed a similar triplet-pair state emission, along with the characteristic triplet transient absorption spectra, and the magnetic field effect on photoluminescence yield, which is evidence of an equilibrium between singlet fission and triplet-triplet annihilation. The strength of these effects, and therefore the efficiency of singlet fission, can be tuned by film preparation,
especially by the addition of an inert polymer. These findings represent significant progress towards stable and efficient singlet fission materials that can be used commercially to reduce losses in photovoltaics.

4:00 PM EN12.03.04
**Slow Charge Transfer is Characteristic of Triplet States Born of Singlet Fission in Pentacene**
Obadiah Reid¹,², Natalie A. Pace², Nadezhda V. Korovina², Tyler T. Clickeman³, Gerard M. Carroll³, John Anthony⁴, Sanjini U. Nanayakkara², Iain McCulloch⁵, Steven H. Strauss³, Olga V. Boltalina³, Justin C. Johnson² and Garry Rumbles²; ¹University of Colorado Boulder, United States; ²National Renewable Energy Laboratory, United States; ³Colorado State University, United States; ⁴University of Kentucky, United States; ⁵King Abdullah University of Science and Technology, Saudi Arabia

Singlet fission (SF) has the potential to significantly enhance solar cell performance if charges can be efficiently generated from the resulting triplet states. Here, we study charge separation from triplet excitons in polycrystalline pentacene using an electrochemical series of electron-acceptor molecules with varied reduction potentials, and follow the SF and charge transfer dynamics using a combination of transient absorption spectroscopy and time-resolved microwave conductivity. We find that even at the optimal driving force the rate constant for charge transfer from the triplet state is surprisingly small, (~10⁷ s⁻¹) when they are produced by singlet fission, but that triplets transferred into the film by a sensitizer dissociate much more rapidly.

4:15 PM EN12.03.05
**Enabling Efficient Triplet-Fusion Upconversion Using a Tetracene Homodimer**
Christian J. Imperiale¹, Philippe B. Green¹, Ethan Miller², Niels Damrauer² and Mark W. Wilson¹; ¹University of Toronto, Dept. of Chemistry, Canada; ²University of Colorado Boulder, United States

Exciton-mediated photon upconversion (EXUC) can transform low-energy photons into higher-energy fluorescence under low-intensity illumination. A sensitizing species is necessary to generate triplet excitons from absorbed photons and transfer this energy to the triplet state of the acceptor molecules. Here, we demonstrate the use of a structurally rigid, norbornyl-bridged, tetracene homodimer (TIPS-BTc) as a triplet acceptor and emitter for EXUC in solution. Using an organometallic triplet sensitizer (PdPc(0Bu)₈), incident photons of λ=730 nm were upconverted by 0.6 eV to emitted photons of λ=540 nm via triplet fusion (TF). By comparison with Stern-Volmer phosphorescence quenching experiments, we observe that TIPS-BTc can achieve brighter upconversion emission than monomeric controls (rubrene and tri-isopropylsilyl ethynyl tetracene (TIPS-Tc)) for the same number of extracted triplet excitons. We build a rate-equation model to simulate the concentration- and intensity-dependence of the upconverted emission at steady state, and extract rate constants for TF in the monomeric controls comparable to literature. However, for dimeric TIPS-BTc, our kinetic simulation cannot simultaneously reproduce the Stern-Volmer data and the concentration dependence of the threshold for max-efficiency upconversion. This result provides evidence that dimeric annihilators may offer pathways towards triplet fusion that are more efficient than uncorrelated diffusion, and could boost overall upconversion performance when paired with molecular engineering that advances the efficiency of triplet transfer. It also validates the strategy of designing rigid, electronically-decoupled molecular dimers for excitonic upconversion from known monomeric emitters, with the ultimate goal of reducing the collisional dependence of solution-phase exciton-mediated photon upconversion.

4:30 PM EN12.03.06
**Singlet Fission Molecules Among Known Compounds—Finding a Few Needles in a Haystack**
Daniele Padula¹,², Omer H. Omar¹, Tahereh Nematiaram¹ and Alessandro Troisi¹; ¹University of Liverpool, United Kingdom; ²Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

A large set of candidates for singlet fission, one of the most promising processes able to improve the efficiency of solar cells, are identified by screening a database of known molecular materials. The screening was carried out through a procedure exploiting quantum chemical calculations of excited state energies, carefully calibrated against a substantial set of experimental data. We identified ~200 potential singlet fission molecules, the vast majority of which were not known as singlet fission materials. The molecules identified could be grouped into chemical families enabling the design of further singlet fission materials using the hits as lead compounds for further explorations. Many of the discovered materials do not follow the current design rules used to develop singlet fission materials illustrating at the same time the power of the screening approach method and the need of developing new design
principles.

4:45 PM EN12.03.07
Relation between Molecular Packing and Singlet Fission in Thin Films of Brominated Perylenediimides
Ferdinand C. Grozema, Kevin M. Felter and Rajeev K. Dubey; Delft University of Technology, Netherlands

Perylenediimids (PDIs) are well-known dyes that have attractive properties for a variety of applications in optoelectronic devices. These properties include strong absorption in the visible, high charge carrier mobility and excellent electron accepting properties. In addition, they also exhibit close to ideal singlet/triplet energetics for singlet fission and triplet-triplet annihilation upconversion. Interestingly, the electronic properties of solid state materials based on these molecules strongly depend on the way the molecules are organized in the crystalline state. This is true for the optical properties, but also for transport of charges, excited state diffusion and for less common photophysical processes such as singlet exciton fission.

A strong relation has been found between the intermolecular packing of the individual packing in the solid state and the efficiency of singlet fission. This can be effectively tuned by changing the substitution pattern on the conjugated core of the molecule. Until now, most modifications involve introduction of different sidechains on the imid-nitrogen. In this work, we show a new approach by introducing bulky bromine atoms directly in the aromatic core of the PDI, leading to a twisting of the core. This significantly affects the solid state packing but also the optoelectronic properties of the individual molecules.

We show that changes in the molecular packing induced by bromination have a strong effect on the temperature dependent photoluminescence, expressed as an activation energy. These effects are explained in terms of excimer formation for PDIs without bay-area substitution, which competes with singlet fission. Introduction of bromine atoms in the bay-positions strongly disrupts the solid-state packing leading to strongly reduced excitonic interactions and excimer formation. The suppression of this competing process leads to an overall higher yield of singlet fission, despite the expected smaller electronic coupling for singlet fission. This shows that optimizing the electronic coupling is not the only factor that is important in optimizing singlet fission yields, suppression of competing processes is also of prime importance.

SESSION EN12.04: Poster Session I: Properties of Organic Semiconductors I
Session Chairs: Marina Freitag and Harald Hoppe
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EN12.04.01
The Molecular Organization of Non-Fullerene Acceptors for Organic Photovoltaics Pierluigi Mondelli1,2, Priti Tiwana1, Michal Krompiec1,3 and Graham Morse4; 1Merck Chemicals Ltd, United Kingdom; 2Technische Universität Chemnitz, Germany; 3University of Southampton, United Kingdom; 4Natrix Separations Inc., Canada

The topic of Non-Fullerene Acceptors (NFAs) in the field of Organic Photovoltaics (OPV) has become tremendously important to industrial and academic research, as the rapid development of these materials has pushed the device power conversion efficiency over the 15% threshold.1 An efficient chemical design of these molecules has led to a big surge in performance, achieving optimum optical absorptions and reduced voltage losses.2 However, low electron mobilities still represent a major issue for the commercialization of large-scale solution-processed OPV devices.3 Researchers speculate that the highly anisotropic and two-dimensional conjugated structure of these molecules is critical to their organization, which in turn affects their electronic functions (e.g. carrier mobility).2 In our industrial experience, we have also observed unique coating and thermal behaviour of these materials, suggesting the importance of their crystallinity.

Our work aims to provide direct insights into the crystallization of the materials and their charge transport. With this purpose, we compare a large body of newly identified non-fullerene single crystals and previously reported structures, including novel non-fullerene molecules. By meta-analysis, we identify common packing motifs,
elucidate the role of the molecular fragments (sidechains, donor and acceptor groups), perform statistical analysis of close contacts and explore solvated host-guest complexes. Finally, the importance of crystal packing and topological connectivity on the charge transport is explored by linear-scaling Density Functional Theory calculations. Experimental evidences of the influence of the solid-state organization on the charge carrier mobility and performance in OPV devices is the focus of our investigations that are currently underway.

References

EN12.04.02
The Role of the Solvent and the Size of the Nanotube in the Non-Covalent Dispersion of Carbon Nanotubes with Short Organic Oligomers—A DFT Study Jolanta B. Lagowski and Ahmad I. Alrawashdeh; Memorial University of Newfoundland, Canada

Among different dispersants of single-walled carbon nanotubes (SWCNTs), conjugated organic oligomers have the ability to interact strongly with SWCNTs and allow for effective dispersion in several organic solvents. Recently, we have carried out two computational investigations (Phys. Chem. Chem. Phys., 2017, 19, 28071 and J. Phys. Chem. C 2017, 121, 4692) on the intermolecular interactions between conjugated organic oligomers and SWCNTs in order to gain insight into an important process of the non-covalent dispersion of carbon nanotubes with short oligomers. These studies highlighted the fact that two additional factors, namely, the effect of the solvent and the carbon nanotube’s size on these interactions need further investigation. In this work (RSC Adv., 2018, 8, 30520), with the help of model compounds (which are molecular fragments of the short oligomers used in our previous investigations) we analyze the significance of these two factors. We employ three dispersion corrected density functional theory (D-DFT) approximations (B97D, wB97XD, and B3LYP-D3) to assess the effect of the DFT method and two basis sets (6-31G(d) and 6-31++G(d,p)) to assess the importance of using a higher basis set in our computations. The main focus of this work is to assess the effect of solvation and nanotube’s size on the structure, electronic properties, and binding energies of the respective pairs of model compounds and segments of carbon nanotubes. No significant differences are found between the results of (6,5) and (8,7) SWCNTs in either the geometrical parameters of interacting oligomers or the general tendency of wrapping of their long side chains (SCs) around the nanotubes. However, we find that the binding energies/atom between nanotubes and model compounds are larger for nanotubes with smaller diameter. The results of electronic properties also show that all model compounds interact more strongly with the (6,5) SWCNT than with the (8,7) SWCNT. Polar solvents such as chloroform lower binding energies relative to those obtained without a solvent or with non-polar solvents such as hexane. It appears that the presence of a solvent weakens the oligomer/nanotube interactions and, presumably, strengthens the oligomer/solvent and nanotube/solvent interactions to facilitate dispersion of SWCNTs.

EN12.04.03
Ultraviolet Post-Treatment Method for the Mass Production of Highly Crystalline Conductive Polymer Thin Films Jun Hwa Park, Lee Jeong Ik and Yeong Don Park; Incheon University, Korea (the Republic of)

Here, we developed a facile post-treatment method using ultraviolet irradiation that produced crystalline polymer nanofibrils in the solid film state. Ultraviolet irradiation over a few minutes effectively transformed the polymer chain conformational structure and promoted polymer chain extension and association in the film state. Brief ultraviolet irradiation of a thin film fabricated using a high boiling point solvent produced well-ordered molecular structures among the extended P3HT chains, whereas ultraviolet irradiation over longer times led to breaks in the chemical structures of the P3HT, resulting in shortened conjugation lengths. Conformational changes in the polymer main chain and resulting nanofibril morphologies induced by ultraviolet irradiation facilitated charge transport in organic transistors prepared using these films. The relationship between the molecular structural order and the electrical characteristics of the films was used to determine the optimum ultraviolet irradiation time.

EN12.04.04
Degradation Mechanism of Organic Light-Emitting Devices Incorporating Thermally Activated Delayed Fluorescent Dopant Materials Yu Kyung Moon1, Sanju Hwang1, Hojin Jang2, Sinheui Kim1, Jun Yeob Lee2 and
Organic light-emitting devices (OLEDs) are advantageous over conventional flat panel display. The success of OLEDs depends significantly on the performance of emitting molecules. Molecules displaying thermally activated delayed fluorescence (TADF) have emerged as promising dopant materials, because they are capable of harvesting all the electrogenerated excitons without relying on precious late transition metals. However, exploitation of the full potential of electroluminescence from TADF materials is retarded by short operational lifetime of devices. We recently proposed the degradation mechanism involving exciton-mediated electron transfer between a host and a phosphorescent dopant within the emitting layers of OLEDs. The electron transfer results in the formation a radical ion pair (RIP), very vulnerable to degradation. RIP was found to be responsible for irreversible degradation of the emitting layer, and its lifetime was governed by the charge recombination kinetics. We hypothesized an occurrence of the identical electron-transfer processes in OLEDs having a TADF dopant in place of a phosphorescent dopant. To verify our hypothesis, we investigated the degradation behaviors of the pairs of a TADF dopant, phenoxazine-1,3,5-triphenyltriazine (PXZ-TRZ), and a series of commercially available host materials, including 4,4′-bis(9-carbazolyl)-1,1′-biphenyl (CBP), 4,4′-bis(9-carbazolyl)-2,2′-dimethylbiphenyl (CDBP), N,N′-dicarbazolyl-3,5-benzene (mCP), 3,3′-bis(9-carbazolyl)biphenyl (mCBP), 1,3,5-tri(m-pyridin-3-ylphenyl)benzene (TmPyPB), and bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO). Electrochemical measurements predicted positive driving forces (–ΔG_{eT}, 0.69–1.47 eV) for electron transfer from the dopant to host exciton, which suggested the spontaneous formation of RIP between the TADF dopant and hosts. Annihilation of RIP by charge recombination was found to have very positive driving forces (–ΔG_{eT}, 2.62–2.76 eV).

To investigate the electron-transfer processes, we performed steady-state photophysical experiments. The addition of the dopant into a host solution resulted in fluorescence quenching of the host in a concentration-dependent manner. The rate constant for the bimolecular quenching was found to be proportional to –ΔG_{eT}, indicative of the formation of non-emissive RIP. This notion was supported by the observance of strong signals (g = 2.012) in photoinduced electron paramagnetic resonance spectra. The RIP accelerated the degradation of the materials under continuous photolysis, as evidenced by the rates of photodegradation greater than those determined for the individual compound. This result supported RIP being the key intermediate of the intrinsic degradation of TADF emitting layers. Multi-layer electroluminescence devices with a configuration of ITO/DNTPD (60 nm)/BPBPA (20 nm)/PCzAC (10 nm)/host:PXZ-TRZ (30 nm : 10%)/DBF-Trz (5 nm)/ZADN (30 nm)/LiF (1 nm)/Al were fabricated and evaluated. Operation lifetime of the devices was quantitated as the time when the luminance decreased to 90% of the initial value (LT_{90}) under a constant current driving mode. LT_{90} values were 13 h (CBP), 5.9 h (CDBP), 18 h (mCP), 27 h (mCBP), 0.11 h (TmPyPB), and 0.24 h (DPEPO). We found a positive linear correlation between LT_{90} with –ΔG_{eT} for the ‘hole-transporting type’ hosts (i.e., CBP, CDBP, mCP, and mCBP). The significantly short LT_{90}s of the devices having ‘electron-transporting type’ host (i.e., TmPyPB and DPEPO) suggested the presence of a different degradation mechanism, because their –ΔG_{eT} were not very different from –ΔG_{eT} of ‘hole-transporting type’ hosts. The fast charge recombination rate minimized an accumulation of RIP. Collectively, our findings supported that the acceleration of charge recombination within RIP is crucial for device longevity. Our study revealed the importance of electrochemical control between a TADF dopant and a host for realizing long operational lifetimes of OLEDs.

EN12.04.05
**Direct Evidence for Discrete Electronic Traps Induced by Bias Stress in Organic Field-Effect Transistors**
Hamna Haneef1, Qianxiang Ai2, Chad Risko2, John Anthony2 and Oana D. Jurchescu1; 1Wake Forest University, United States; 2University of Kentucky, United States

Organic semiconductors (OSCs) have gained significant attention as active components in various (opto)electronic devices due to low-cost manufacturing, ease of processing, mechanical flexibility, and versatility in chemical synthesis. These attractive properties are a direct consequence of the weak intermolecular interactions of van der Waals type characteristic of these materials. On the other hand, the weak interactions make OSCs susceptible to the formation of localized electronic states in the band gap, which can trap charge carriers at different timescales. Charge carrier trapping is an important phenomenon in electronic devices and its impact on device performance and long-term stability has been extensively studied. However, determining the origin, concentration, and composition of electronic traps in organic semiconductors, as well as their spatial and energetic distribution, is not trivial and remains elusive. In this work, we probe the trap density of states (DOS) using organic field-effect transistor measurements and quantify their energy distribution in response to applying bias stress. DOS analysis provides
direct evidence for the creation of a discrete electronic trap in a solution-processed OSC, namely tri(n-hexyl)silylthynyl benzodithiophene (TnHS BDT) trimer, in response to repetitive electrical measurements performed under ambient conditions. The trap DOS spectrum evaluated over the course of bias stress measurements (total 500 min) shows the dynamics of the trap formation, which starts with an initial broadening of the DOS after 10 min, followed by the appearance of a discrete peak located at ca. 0.3 eV above the valence band edge after 20 mins of bias stressing. The peak is absent in measurements performed under vacuum. The correlation of the trap DOS spectrum with the time evolution of device metrics, including mobility, subthreshold swing, and the threshold voltage, suggests that the generated electronic trap occurs at the interface between the OSC and the dielectric. Density functional theory (DFT) calculations are employed to elucidate the nature of the trap and the mechanism of formation. This work marks as the first of its kind in experimentally detecting electronic traps generated as a result of bias stress and concurrently determining their precise nature by using a combination of trap DOS analysis and DFT calculations.

EN12.04.06
Applications of Organic Field-Effect Transistors in Biomimetic Field Wei Shi; Institute of Chemistry, Chinese Academy of Sciences, China

Organic field-effect transistors (OFETs) possess the accessibility of flexible, large-area, multi-signal detection, and bio-compatibility. For their applications in the biomimetic field, another requirement is the low work-voltage. Usually, the bio-signals are much more difficult to capture compared to the common chemical signals since their magnitudes are very small. Meanwhile, considering that the bio-system is relatively fragile and complicated, the detection method is thus limited. Especially, for the in-situ and non-invasive detection, not only the low work-voltage is required, low/non toxicity and high selectivity are also essential. Here, we mainly focus on the application of OFETs in the field of non-invasive blood glucose detection by introducing the porous film in the OFET device to increase the sensitivity of the OFET device. Usually, the detection of the liquid analyte is realized by the electrochemical transistor since their unique property of integrating the electrochemical gate. The report of using the OFET to detect the liquid analyte is rare. We designed to take advantage of the interface between the organic semiconductor and the dielectric in OFET to achieve the detection of glucose.

EN12.04.07
Structure-Function-Performance Relationships in Conjugated Polymers for Photocatalytic Hydrogen Generation from Water Sam Hillman1,1, Reiner S. Sprick2,2, Drew Pearce1,1, Lucas Flagg1, Michael Sachs1,1, Duncan Woods2,2, Xingyuan Shi1,1, Anne Guilbert1,1, Andrew Cooper2,2, James R. Durrant1,1 and Jenny Nelson1,1; 1Imperial College London, United Kingdom; 2University of Liverpool, United Kingdom; 3University of Washington, United States

Organic semiconductor materials are attracting increasing interest for catalytic hydrogen generation [1]. Despite this, very few studies [2] attempt to deconvolute the factors (structural, optical, and electronic) that affect photocatalytic performance.

Here we investigate a collection of novel linear conjugated polymer photocatalysts which exhibit high rates of hydrogen photo-evolution from water in the presence of a sacrificial electron donor. Unlike most organic photocatalysts, these materials are solution processable, allowing for greater control of structure to explore the structure-activity relationship. These polymers show a positive correlation between the density of hydrophilic groups and the rate of hydrogen evolution. Using transient absorption spectroscopy (TAS) and spectroelectrochemistry, we observe that catalytic activity is correlated with the density of photogenerated electrons in the polymer. Using electronic structure and molecular dynamics calculations, we then investigate the effect of different hydrophilic groups on charge transfer through their role in structuring the liquid environment close to the polymer backbone. We find that the impact of the polar groups on the dielectric properties of the local liquid environment is critical for controlling the driving energy for charge generation.

Charge generation in both polymer particles and thin films is also highly dependent on their physical microstructures. Hydrogen evolution and TAS measurements suggest that catalytic activity exists not only at the polymer-liquid interface but also within the structures, indicating that the materials are partially permeable to the liquid environment. Using photoluminescence spectroscopy, atomic force microscopy and TAS, we show that this activity can be explained by a combination of solvent penetration and exciton diffusion. We demonstrate that this
understanding can be used to control the structure of the photocatalyst and enhance catalytic performance. Together with the control of the solvent environment, this work provides design rules for improved polymer photocatalyst behaviour.


EN12.04.08

**Heating-Induced-Aggregation to Prepare High Performance Non-Fullerene Organic Solar Cells** Tao Wang; Wuhan Univ of Technology, China

The power conversion efficiency of non-fullerene organic solar cells develops dramatically in recent years. Although tremendous efforts have been dedicated to the design and synthesis of new small molecular acceptors, less is known on how the molecular order and aggregation of these small molecular acceptors will affect the device performance. A high structure order is desired to achieve high charge transport property, however, it can also induce excessive phase aggregation and consequently reduce the exciton dissociation efficiency to reduce device performance. We have discovered that heating-induced molecular ordering and aggregation can be an effective approach. The assistance of heating during film casting can suppress the formation of large-scale spherelite from INPIC-4F non-fullerene acceptor, but encourage the formation of p-pstacks to reduce phase separation to results an efficiency over 13%. Heating also convert COi8DFIC from edge-on and flat-on oriented lamellae to face-on H- and J-type p-pstacks, which broadens the light absorption spectrum and reduces the contact between donor and acceptor molecules for efficient exciton dissociation. An high efficiency of 13.8% was achieved in PTB7-Th:COi8DFIC binary solar cells. Heating-induced-aggregation emerges as a new strategy to optimize the morphology of non-fullerene solar cells for high peformacne.

EN12.04.10

**12.5% Flexible Nonfullerene Solar Cells by Passivating the Chemical Interaction between the Active Layer and Polymer Interfacial Layer** Fei Qin and Yinhua Zhou; Huazhong University of Science & Technology, China

Nonfullerene organic solar cells have been attracting significant attention in the past several years. It is still challenging to achieve high-performance flexible nonfullerene organic solar cells. Nonfullerene acceptors are chemically reactive and tend to react with the low-temperature processed low-work function interfacial layers, such as polyethylenimine ethoxylated (PEIE), which leads to the “S” shape in the current-density characteristics of the cells. In this work, we deactivate the chemical interaction between the nonfullerene active layer and the polymer interfacial layer of PEIE by increasing its protonation. The PEIE processed from aqueous solution shows more protonated N⁺ than that processed from isopropanol solution, observed from X-ray photoelectron spectroscopy. Nonfullerene solar cells (active layer: PCE-10:IEICO-4F) with the protonated PEIE interfacial layer show an efficiency of 13.2%, which is higher than the reference cells with a ZnO interlayer (12.6%). More importantly, the protonated PEIE interfacial layer processed from aqueous solution does not require a further thermal annealing treatment (only processing at room temperature). The room-temperature processing and effective work function reduction enable the demonstration of high-performance (12.5%) flexible nonfullerene organic solar cells.

EN12.04.11

**Transferrable Hybrid Graphene Oxide/Silver Nanowire Transparent Electrode Fabricated by Electrophoretic Deposition** Woo Hyun Chae, Thomas Sannicolo and Jeffrey C. Grossman; Massachusetts Institute of Technology, United States

Owing to their high conductivity, transparency, flexibility, and compatibility with solution processes, silver nanowire (AgNW) networks have been widely explored as a promising alternative to indium tin oxide (ITO). However, while AgNW networks have been successfully integrated as transparent electrodes in a range of optoelectronic devices, their susceptibility to corrosion and thermal instability remain limiting factors for widespread adoption. To impart stability, hybrid electrodes that combine AgNW with an encapsulating material such as graphene or semiconducting oxides have been explored, although they have relied on costly processes such
as chemical vapor deposition (CVD) or atomic layer deposition (ALD). Graphene oxide (GO) is an appealing barrier material due to its tunable properties, robustness under a range of conditions, and solution-processability. However, thus far the processing methods to fabricate GO/AgNW hybrid structures have been largely limited to various forms of spray deposition that can only be used on flat substrates with optimized wettability and require expensive equipment for scale-up. Furthermore, many aspects of the chemical and electrical stability of GO/AgNW hybrid electrodes have either not been fully demonstrated or remain poorly understood.

In this study, we propose a scalable and economically viable process involving electrophoretic deposition (EPD) to fabricate a highly stable hybrid transparent electrode with a sandwich-like structure, where the AgNW network is covered by GO films on both sides. The use of EPD allows facile control over the thickness of the GO film, leading to tunable transparency. The newly developed process allows the conductive transparent film to be transferred to an arbitrary surface after deposition and demonstrates excellent sheet resistance (15 Ω/sq) and transmittance (75% at 550 nm) on glass substrates. Unlike bare AgNW networks, the hybrid electrode was found to retain its original conductivity under long-term storage at 80°C. This chemical resilience can be explained by the absence of major silver corrosion products for the AgNW encapsulated by GO as indicated by X-ray photoelectron spectroscopy (XPS). In-situ electrical ramping and resistance measurements up to 20V were conducted in order to assess the electrical stability of our electrodes. The results indicate a novel stabilization mechanism enabled by the presence of GO that prevents abrupt divergence of the resistance to the MΩ range experienced by bare AgNW networks. Finally, the application of our hybrid electrode in a full device is demonstrated by solar cell fabrication and characterization.

EN12.04.12
Structure-Function Relationships in a Novel and Highly Stable Singlet Fission System with an Aromatic Triplet State Peter Budden1, Kealan Fallon1, Andrew Musser2, Hugo Bronstein1,1 and Richard H. Friend1; 1University of Cambridge, United Kingdom; 2The University of Sheffield, United Kingdom

We report clear evidence from transient optical measurements and transient electron spin resonance that a family of derivatives of indolonaphthyridine thiophene (INDT) supports singlet exciton fission, and show excellent ambient stability.

Singlet fission offers the potential for the generation of multiple excitons from one photon in organic semiconductors, which could reduce losses to thermalisation in solar cells by exploiting the relatively low energy of the triplet exciton in certain organic materials. This is a characteristic reserved for only a handful of organic molecules due to the atypical energetic requirement for low energy excited triplet states. The canonical systems on which much singlet fission research is focused - pentacene, tetracene and their derivatives - have such conveniently low triplet energies due to their large diradical nature, greatly compromising their ambient stability. In order to move towards photostable singlet-fission-enhanced solar cells, there is a need for materials that undergo efficient singlet fission at no expense to their stability.

To this end, we have used Baird’s rule of excited state aromaticity to manipulate the singlet-triplet energy gap and create novel singlet fission candidates. We achieved this through the inclusion of a [4n] 3-membered heterocycle, whose electronic resonance promotes aromaticity in the triplet state, stabilizing its energy relative to the singlet excited state. Using this theory, we have designed a family of derivatives of INDT with highly tunable excited state energies which are highly stable and clearly undergo rapid singlet fission at morphological “hot spots”. Not only do we access an original class of singlet fission materials, they also exhibit excellent ambient stability, imparted due to the delocalized nature of the triplet excited state. Spin-coated films retained over 80% activity after several weeks of exposure to oxygen and light, whilst analogous films of TIPS-pentacene showed full degradation after four days, showcasing the excellent stability of this class of singlet fission scaffold. Extension of our theoretical analysis to almost ten thousand candidates reveals an unprecedented degree of tuneability and several thousand potential fission-capable candidates, whilst clearly demonstrating the relationship between triplet aromaticity and singlet-triplet energy gap, confirming this novel strategy for manipulating the exchange energy in organic materials.

Through transient absorption spectroscopy, transient photoluminescence, and transient electron paramagnetic resonance, we can reveal a full picture of the dynamic evolution of excitons in these new materials. Singlet fission, an inherently intermolecular process producing two triplet excitons localized on separate molecules, is highly dependent on morphology. We have found that when tuning the energetics by altering the electron-withdrawing substituent groups on the INDT core, the solid state morphology also changes. We find that with a more H-
aggregate-like morphology, with a blue shift of absorption onset and relative suppression of 0-0 absorption peak, singlet fission yields are enhanced. In recent months, we have made further synthetic progress, which has allowed additional exploration of structure-function relationships down two avenues. Firstly, by editing the length of solubilizing chains, which modifies packing, we can explore different morphologies without affecting the relative energies of the localized singlet and triplet. Secondly, by the synthesis of covalent INDT dimers, bridged with phenyl- and fluorene-linkers, we can vary the coupling and conjugation across an isolated pair of molecules. Both of these pathways offer new insights to how local organization and molecular environment can affect singlet fission, exciton-exciton annihilation, and other critical processes in these films which go on to dictate their performance in optoelectronic devices.

EN12.04.13
Tear Resistant Organic Electronics Song Zhang¹, Yu-Hsuan Cheng², Yu-Cheng Chiu² and Xiaodan Gu¹;
¹University of Southern Mississippi, United States; ²National Taiwan University of Science and Technology, Taiwan

Semiconducting polymers are promising for the application of wearable electronics through blending with rubbery elastomers to achieve the softness and stretchability similar to that of biological skin. However, the inherent tear-resistant and self-healing properties of skin are still unexplored areas for electronic active blends. Here, we present the first tear-resistant semiconducting material using a carefully designed blend system, consisting of conjugated polymers and a high-performance elastomer. This blending system demonstrated excellent mechanical performance with the ultra-low modulus (1 MPa), high stretchability (800% strain), and good electronic property with charge carrier mobility of 0.5 cm²V⁻¹s⁻¹. The charge mobility of the blend system is stable at ambient condition and retains at 70% of charge mobility at 100% strain. More importantly, the semiconducting material is insensitive to precut notches and self-healable at room temperature for two pieces of cut films upon contact within seconds on the water surface. The elastomer has low oxygen and water permeability, allowing better device stability over months of operation, which can be generally applied to a variety of semiconducting polymers to achieve improvements in the mechanical performances for the application of wearable electronic devices.

EN12.04.14
Organic Solar Cells with Nitrogen Containing Organic Charge Carrier Extraction Layers—What is Determining Their Efficacy? Rico Meitzner¹,², Juliette Essomba¹,², Kevin Fulbert¹,², Krisna Kuma¹,², Fernanda A. Kathalia¹,², Nora Engel², Ulrich S. Schubert² and Harald Hoppe¹; ¹Center for Energy and Environmental Chemistry, Germany; ²Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Germany

For the reduction of contact resistances as well as shunting currents in organic solar cells it is important to control the two at the interface towards the respective charge collecting electrodes. Many conductive and non-conductive materials have been investigated so far and several of them offer already good solutions. However, the underlying mechanisms for selective charge extraction are not often well understood. We have systematically varied dipole moments anchored in side-chains of small organic non-conductive molecules as well as non-conductive polymers. We observed a clear correlation between the polarity and various photovoltaic parameters. We present a model on how to achieve proper alignment of dipole moments in that charge extraction materials for improved device function and performance.

EN12.04.15
Ultrafast 2D White-Light Spectroscopy of Wrinkled Carbon Nanotube Films for Use in Stretchable Optoelectronic Devices Jessica Flach; University of Wisconsin-Madison, United States

Optoelectronic devices with semiconducting single-walled carbon nanotubes (s-SWNTs) as the absorbing layer require the photogenerated excitons to diffuse to a heterojunction to drive dissociation into charge carriers. However, current device efficiencies are hindered by a short transverse exciton diffusion length of about 5 nm which in turn limits film thickness and number of photons absorbed. In this work, I have created wrinkled s-SWNT films by depositing a thin layer of nanotubes on a pre-strained stretchable substrate and subsequently releasing so the film wrinkles on itself and effectively increases the optical absorption pathlength. We then use ultrafast 2D white-light (2DWL) spectroscopy to study the underlying photophysics of these wrinkled films. Our 2DWL technique uses a broadband supercontinuum spanning from the visible to NIR to collect information on femtosecond timescales. This
technique allows us to monitor the factors that influence device performance such as exciton lifetime, coupling between nanotubes, and the effects of strain on individual tubes. Furthermore, by depositing a bilayer of s-SWNT with C60 as an electron accepting layer on the elastomeric substrate and allowing it to wrinkle, we create a bulk-like heterojunction architecture with high interfacial area to drive exciton dissociation. These wrinkled s-SWNT/C60 layers are incorporated as the active layer in stretchable phototransistors and their device performance is evaluated.

EN12.04.16
Sequential Solvent Dip-Coating for Increase of Molecular Order in Polythiophene Thin Film Lee Jeong Ik, Jun Hwa Park and Yeong Don Park; Incheon University, Korea (the Republic of)

Recent years have seen significant improvements in the performances of organic electronic devices based on conjugated polymers. Among the methods of forming a polymer thin film, the dip coating technique has an advantage that a uniform large-scale polymer thin film having a low roughness can be manufactured. However the solvent with a high boiling point produced inhomogeneous film coverage with dewetted regions on the dip-coated polymer film. In this study we presented a systematic study of a simple post dip-coating method for controlling the structural and electrical characteristics of dip-coated polythiophene thin films through direct exposure to various solvents. Simply dip-coating of polythiophene thin film into various solvents with different solubility parameter improved the intermolecular order in the films, and the polymer FET device performance. When the polythiophene thin film was dip-coated into various solvents before the film is completely dried, the molecular rearrangement was occurred depending on the solubility of the solvent. The small difference in the solubility parameter between the polythiophene and the solvent in post-treatment process induced the strong rearrangement of the molecular arrays and the production of nanowires. The structural and electrical characteristics of dip-coated polythiophene thin films or thin films dip-coated into various solvents were investigated and compared.

EN12.04.18
Analytical Study of Solution-Processed Tin Oxide—New Insights into the Correlation of Chemical and Electronic Properties Valentina Rohnacher1,2, Sebastian Hell1,2, Florian Ullrich3,2, Marc-Michael Barf4,2, Helge Eggers5,2, Sebastian Beck7,2 and Annemarie Pucci1,2; 1Heidelberg University, Germany; 2InnovationLab, Germany; 3Technische Universität Darmstadt, Germany; 4Technische Universität Braunschweig, Germany; 5Karlsruhe Institute of Technology, Germany

Organic electronic devices consist of stacked organic as well as inorganic materials and the device performance is strongly influenced by the interfaces between the layers. The investigation of charge transport across these interfaces is a major key to the basic understanding of the fundamental mechanisms in organic electronics. Thin films of certain metal oxides are known to be excellent charge-selective interlayers in optoelectronic devices due to their outstanding properties such as high optical transparency, suitable energy level alignment and high electron mobility [1-3].

In this study, solution-processed tin oxide (sSnOx) as promising electron transport layer was analyzed by infrared spectroscopy. This non-destructive method gives insight into the chemical composition of the thin film and can monitor orientation of characteristic vibrations or functional groups. We studied the influence of annealing temperature on bulk and surface properties of thin sSnOx. During subsequent annealing from room temperature up to 400°C, the tin chloride precursor is converted into tin oxide. The infrared spectroscopic investigations show the decrease of tin hydroxide and water in the sSnOx films and the higher crystallinity with increasing annealing temperature. Moreover, the phonon modes of sSnOx in the far-infrared region confirm the conversion from tin oxide into tin dioxide between 350°C and 400°C. Furthermore, we discovered that the solvent of the precursor solution has a crucial influence on the film morphology and the conductivity of sSnOx. Together with the results of photoelectron spectroscopy, atomic force microscopy and conductivity measurements a better understanding of the electronic, chemical and morphological properties can be achieved which is important for the improvement of device performance.

References:
Charge Transport of Phenothiazine:TCNQ Cocrystals
Scott Melis and Edward Van Keuren; Georgetown University, United States

Charge transfer cocrystals have interesting applications in the field of organic electronics due to their unique optical and electronic properties. We have studied cocrystals formed from phenothiazine (PTZ) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as electron donor and acceptor molecules respectively. PTZ:TCNQ cocrystals were found to readily grow using the controlled evaporative self-assembly (CESA) method, in which crystals nucleate at the receding contact line of an evaporating solution. The resulting cocrystals formed an array of long, well-aligned wires that could be easily incorporated into field effect transistors (FETs). Here, we present measurements of carrier mobility in PTZ:TCNQ FETs. In addition, we show that the device performance as a function of temperature agrees with a hopping model of charge transport in the material. Finally, we have investigated the effects of photoexcitation on charge transport in the devices.

Pre-Programmed Organic Semiconductor Assembly with DNA
Jeffrey Gorman1, Florian Auras1, Sarah Orsborne1, Peter Budden1, Afaf El-Sagheer2, Daniel Congrave1, Lisa Sharma3, Raj Pandya1, Akshay Rao1, Hugo Bronstein1, Tom Brown2, Eugen Stultz2 and Richard H. Friend1; 1University of Cambridge, United Kingdom; 2University of Oxford, United Kingdom; 3University of Southampton, United Kingdom

Photosynthetic complexes achieve remarkable spatial control of densely-packed pigments using a protein scaffold to organise multiple organic semiconductors. This promotes strong electronic coupling between adjacent chromophores yielding efficient energy transport and charge separation. In contrast, man-made organic solar cells lack natures precision and are typically limited to a pseudo-random blend mixture.[1] To overcome the limitations of poor assembly we attach acenes, rylene diimides, porphyrins, and push-pull chromophores to DNA. Inspired by how nature uses DNA to encode the structure of peptides, our method allows the unique assembly of monodisperse, hetero-aggregated semiconducting structures; transcribed by Watson-Crick base-pairing. The DNA sequence programs the final aggregate superstructure and give us unparalleled control over an energy landscape encompassing many different molecules. We outline our efforts using on-resin synthetic routes to overcome the incompatibility of large, hydrophobic aromatic molecules used in organic electronics, with hydrophilic DNA.[2, 3] Subsequent DNA hybridisation then forms a scaffolded assembly where a photoexcitation coherently extends over several building blocks.

Using 10-fs time resolution transient absorption spectroscopy we track energy transport and charge separation through a nanoscale heterojunction and energy cascade, where the number of electron donors and acceptors have been predefined by the DNA sequence. Furthermore by instead assembling with acene materials we can control the extent of singlet fission as a function of the number of molecules electronically coupled.

Water/Ethanol-Soluble Naphthalene Diimide-Based Polymer Acceptors for Efficient and Air-Stable All-Polymer Solar Cells
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Water/Ethanol-processed all-polymer solar cells (eco-APSCs) with superior efficiency and stability were developed for the first time by synthesizing a series of aqueous-soluble naphthalene diimide (NDI)-based polymer acceptors P(NDIDEG-T), P(NDITEG-T), and P(NDITEG-T2). The polymer acceptors were designed by using the backbones of NDI-bithiophene and NDI-thiophene in combination with non-ionic hydrophilic oligoethylene glycol (OEG) side chains that facilitate processability in water/ethanol mixtures without causing any electronic trap sites. While all three polymers exhibited semi-crystalline properties and sufficient solubility in the aqueous medium, the P(NDIDEG-T) polymer with shorter OEG side chains was the most crystalline, enabling the fabrication of efficient eco-APSCs with the maximum power conversion efficiency of 2.15%. To date, this is the highest efficiency reported for devices based on water/ethanol-soluble conjugated materials. Furthermore, these eco-APSCs were fabricated under ambient atmosphere by taking advantage of the eco-friendly aqueous process and, importantly, the devices exhibited outstanding air-stability without encapsulation, as evident by maintaining more than 90% of the initial PCE in air after 4 days. These results provide important guidelines for the design of electroactive polymers for sustainable fabrication of organic electronics.

EN12.04.23
Efficient and Air-Stable Aqueous-Processed Organic Solar Cells and Transistors—Importance of Water Content on Processability and Thin-Film Morphologies of Electroactive Materials Seungjin Lee1, Changyeon Lee1, Hae Rang Lee2, Joonyeong Choi1, Youngkwon Kim1, Nguyen Thanh Luan3, Wonho Lee4, Bhoj Gautam5, Kai Zhang6, Fei Huang6, Joon Hak Oh2, Han Young Woo3 and Bumjoon Kim1; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2Seoul National University, Korea (the Republic of); 3Korea University, Korea (the Republic of); 4Kumoh National Institute of Technology, Korea (the Republic of); 5Fayetteville State University, United States; 6South China University of Technology, China

The authors report the development of a desirable aqueous process for eco-friendly fabrication of efficient and stable organic field-effect transistors (eco-OFETs) and polymer solar cells (eco-PSCs). Intriguingly, the addition of water to ethanol was found to remarkably improve the solubility of oligoethylene glycol (OEG) side chain-based electroactive materials (e.g., the highly crystalline conjugated polymer PPDT2FBT-A and the fullerene monoadduct PC61BO12). A water–ethanol cosolvent with a 1:1 molar ratio provided an increased solubility of PPDT2FBT-A from 2.3 to 42.9 mg mL−1 and that of PC61BO12 from 0.3 to 40.5 mg mL−1. Due to the enhanced processability, efficient eco-OFETs with a hole mobility of 2.0 × 10−2 cm2 V−1 s−1 and eco-PSCs with a power conversion efficiency of 2.05% were successfully fabricated. In addition, the eco-PSCs fabricated with water–ethanol processing were highly stable under ambient conditions, showing the great potential of this new process for industrial scale application. To better understand the underlying role of water addition, the influence of water content on the thin-film morphologies and the performance of the eco-OFETs and eco-PSCs were studied. Additionally, it was demonstrated that the application of the aqueous process can be extended to a variety of other OEG-based material systems.

EN12.04.24
Novel Hole Blocking Materials Based on 2,6-Disubstituted Dibenzofuran and Dibenzothiophene Segments for High-Efficiency and Long-Lived Blue Phosphorescent OLEDs Seokhoon Jang and Youngu Lee; DGIST, Korea (the Republic of)

Since phosphorescent organic light-emitting diodes (PhOLEDs) have four times higher quantum efficiency than fluorescent OLEDs in that they can utilize both singlet and triplet excitons, they are focused on the display market and widely used. Many studies have been conducted to enhance the performance of PhOLEDs, but satisfactory efficiency and lifetime have not been achieved for blue emitters. In order to improve the efficiency of the blue PhOLED, a hole blocking layer (HBL) can be introduced between the electron transporting layer (ETL) and emissive layer (EML). In general, the highest occupied molecular orbital (HOMO) energy level of the ETL is not much lower than that of the EML. Holes reaching the EML from an anode can be migrated into the ETL, lowering their efficiencies. Therefore, it is necessary to introduce a HBL with deep HOMO energy level. In addition, if the triplet energy (E_T) of ETL is lower than that of EML, the triplet excitons created in EML can be quenched at the interface between EML and ETL. Therefore, a HBL should have high E_T as well as deep HOMO energy level. In this work, Novel hole blocking materials (HBMs) based on 2,6-disubstituted dibenzo[b,d]furandibenzo[b,d]thiophene segments, 3,3′,3′′,3′′′-(dibenzo[b,d]furanyl-2,6-diylbis(benzene-5,3,1-triyl))tetrapyridine (26DBFPTPy) and 3,3′,3′′,3′′′-(dibenzo[b,d]thiophene-2,6-diylbis(benzene-5,3,1-triyl))tetrapyridine (26DBTPTPy), are rationally designed and synthesized for high-performance blue PhOLEDs for the first time. Computational
simulation is used to investigate the optimal structure, orbital distribution, and physicochemical property of both molecules. Thermal, optical, and electrochemical analysis show that 26DBFPTPy and 26DBTPTPy possess high thermal stability, deep HOMO energy level (-7.08 and -6.91 eV), and $E_T$ (2.75 and 2.70 eV). Blue PhOLEDs with 26DBFPTPy or 26DBTPTPy as a HBL exhibit low turn-on voltage (3.0 V) and operating voltage (4.5 V) at 1000 cd m$^{-2}$. In addition, the blue PhOLEDs with 26DBFPTPy or 26DBTPTPy show superior external quantum efficiency (24.1 and 23.6%) and power efficiency (43.9 and 42.7 lm W$^{-1}$). They also show a very small efficiency roll-off of about 8.5% from 100 to 1000 cd m$^{-2}$. Details of the correlation between the structure of organic molecules and their properties with OLED performance will be presented.

EN12.04.25
Modification of Electron Injection Property in Organic Light-Emitting Diodes Using Amidine-Type Additives
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It is essential to tune the carrier injection barrier between organic semiconductors and electrodes in present-day organic electronics, including organic light-emitting diodes (OLEDs), organic thin-film transistors (OTFTs), organic solar cells (OSCs), and perovskite solar cells (PSCs). Although efficient hole injection can easily be achieved by using stable materials, the most commonly used materials for electron injection are reactive alkali metals, which make the organic devices unstable, especially on flexible substrates. Thus, the development of a novel electron injection layer without the use of such reactive materials is necessary for future flexible electronics. Recently, a stable amidine derivative named 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) has been proposed to be effective for controlling the electronic behavior in organic devices. When a DBU-doped layer was used as an electron transport layer in PSCs and an n-channel layer in OTFTs, the performance of these organic devices was enhanced owing to the increase in the conductivity and the Fermi level shift [1]. We focused on the high electron-donating property of DBU, and we evaluated a similar amidine-type derivative as the additive of the electron injection layer in OLEDs. In the present study, the effect of two amidine-type derivatives on the electron injection efficiency was investigated by adding them to the interlayer of inverted OLEDs (iOLEDs) [2,3]. We fabricated iOLEDs in the following device configuration: ITO cathode/ZnO/interlayer/emitting layer/hole transporting layer/hole injection layer/Al anode. The interlayer, which plays a key role in electron injection, consists of two materials: one is the electron-transporting host and the other is the amidine-type derivative [1]. The host material used in the interlayer was a boron compound, which is suitable for demonstrating operationally stable iOLEDs [3]. DBU and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were used as the amidine-type derivative. We observed from the current density ($J$)–voltage ($V$)–luminance ($L$) characteristics of the fabricated iOLEDs that the electron injection property was improved by adding each amidine-type derivative to the interlayer. In addition, the DBN-added interlayer exhibited a better electron injection property than the DBU-added interlayer when these amidine-type derivatives were added at the same concentration. The driving voltage of the iOLED with the DBN-added interlayer was about 1.0 V less than that of the iOLED without DBN added to the interlayer. Moreover, the optimized iOLED with a DBN-added interlayer exhibited higher operational stability than the iOLED without DBN added to the interlayer, which suggests that the operational stability of DBN is high. To investigate the mechanism of the efficient electron injection resulting from adding DBN, we measured the energy-level alignment at the ITO/ZnO/interlayer (with or w/o DBN) by ultraviolet photoelectron spectroscopy (UPS). The line shape of the spectrum did not change substantially upon the addition of DBN, whereas a shift toward a higher binding energy and a change in the surface work function were detected for the DBN-added interlayer. A relatively large Fermi level shift of about 0.46 eV was observed by adding DBN. Thus, the electron injection barrier can be significantly reduced by adding DBN, and electrons can be effectively injected. In the previous study on DBU in PSCs, a similar Fermi level shift was observed, which was attributed to the electron transfer from DBU to the host. However, electron transfer from DBU to the host was not clearly observed in this study. Thus, we concluded that the origin of the improved electron injection property in iOLEDs is different from that in PSCs.

Phosphorescent OLEDs Tsukasa Owada1, Hisahiro Sasabe1,2,3, Yoshihito Sukegawa1, Taiki Watanabe1, Tomohiro Maruyama1, Yuichiro Watanabe3, Daisuke Yokoyama1,2 and Junji Kido1,2,3; 1Yamagata University, Japan; 2Research Center for Organic Electronics, Yamagata University, Japan; 3Frontier Center for Organic Materials (FROM), Japan

Electron transport materials (ETMs) play a key role in determining OLED performances, such as driving voltage, efficiency and operation lifetime. In this work, we newly designed and developed a series of chrysene-based ETMs, namely BnTPyCs (n=3,4) modified with terpyridine moieties. BnTPyCs showed high $T_m$ of over 390°C. An OLED with a structure of [ITO (130 nm)/triphenylamine containing polymer: 4-isopropyl-4'-methyl diphenyliodonium-tetrakis(pentafluorophenyl)borate (PPBI) (20 nm)/N,N’-di(1-naphthyl)-N,N’-(1,1’-biphenyl)-4,4'-diamine (NPD) (20 nm)/Ir(ppy)312 wt% doped 3,3-di(9H-carbazole-9-yl)biphenyl (mCBP)/2-(3’-(dibenzo[b,d]thiophen-4-yl)-[1,1’-biphenyl]-3-yl)-4,6-diphenyl-1,3,5-triazine (DBT-TRZ) (10 nm)/20 wt% 8-quinolinolato lithium (Liq) doped-ETL (40 nm)/Liq (1 nm)/Al (100 nm)] were fabricated. The device exhibited maximum EQE of 18% with long operation lifetime at 50% the initial luminance (LT50) of over 250 hours at the initial luminance of approximately 10,000 cd cm–1 (current density: 25 mA cm–2), which was approximately 2 times longer than that with B3PyPC[1] and slightly longer than that with anthracene-based ETM (ZADN)[2] (current density: 25 mA cm–2).


EN12.04.27
Optimising Characteristics of Morphology to Improve the Performance of Polymer Solar Cells Fiyanshu Kaka, Ravi K. Singh, Praveen C. Ramamurthy and Abhik N. Choudhury; Indian Institute of Science, India

Organic-Photovoltaics (OPVs) can potentially provide a less energy intensive means of harnessing solar energy. However, optimum OPV performance depends on understanding the Process-Structure-Property (PSP) correlation in organic semiconductors. The working of Bulk-Heterojunction (BHJ) OPVs is such that the morphology plays a key role in device performance1.

It is experimentally observed that there is an optimal blend ratio of p and n-type organic semiconductor as well as annealing time with respect to device characteristics. In this work, we attempt to understand the characteristics of morphology that maximize the device performance by developing a theoretical framework. We first established process-structure correlations by generating a range of morphologies with different blend ratios of P3HT (p-type organic semiconductor) and PCBM (n-type organic semiconductor) for various annealing times. The morphologies were generated using phase-field simulations. In the phase-field model, the free-energy of polymer-fullerene blend was modelled using the Flory-Huggins function. Since the polymer-fullerene blend undergoes Spinodal decomposition, Cahn-Hilliard formulation was used to model the free-energy functional.

Secondly, we developed effective electronic properties of the morphologies which allows us to characterize the performance of each of the obtained morphologies. The structure-property correlation was derived using diffuse interface approach. The application of diffuse interface model to complex morphologies as are typically encountered in BHJ devices is simpler and numerically more robust than the classical sharp interface model used in semiconductor industry. This completes the theoretical PSP linkage which allows the optimization of the process parameters for device applications. We found that the necessary condition for efficient OPV device is bi-continuous network of donor and acceptor phases as that leads to percolating channels for electrons and holes to their respective electrodes. The percolation of the morphology was found out using Hoshen-Kopelman algorithm. Amongst the percolating morphologies, the ones with higher interfacial area lead to higher short circuit current density ($J_{sc}$) and eventually to higher efficiency since open-circuit potential ($V_{oc}$) is a weak function of morphology. Therefore, the key to an efficient solar cell is optimisation of the two important length scales involved in the working mechanism of OPV i.e., exciton dissociation and carrier conduction through the morphology to the respective electrodes. Exciton dissociation is governed by interfacial area. Efficient carrier conduction results from transportation of the electron and hole to their respective electrode via a well-connected network of phases with minimal leakage of current and recombination of charge carriers. Hence, efficient carrier conduction is governed by higher percolation fraction of the morphology. Another important step during device fabrication is annealing the device after production. It is experimentally observed that initially during annealing, $J_{sc}$ increases and then decreases thus resulting in an optimal anneal time. The initial increase in $J_{sc}$ corresponds to existence of better interface between electrode and active layer2. The depreciation in $J_{sc}$ stems from coarsening of morphology resulting in lower exciton...
dissociation. The depreciation in Jsc has been verified numerically by our simulations.


EN12.04.28
Improved Exciton Utilization Resulting from Exergonic Reverse Intersystem Crossing in Blue-Electrofluorescent Organic Molecules Seungyeon Yi and Youngmin You, Ewha Womans University, Korea (the Republic of)

Recent advances in organic electroluminescence benefit from molecular emitters capable of harvesting electrogenerated excitons. The successful emitters include room-temperature phosphorescent complexes of late transition metals and pure organic molecules exhibiting thermally activated delayed fluorescence. These compounds, however, suffer from quenching of triplet excitons due to slow rates during the processes of radiative transition or exciton spin flip. To overcome this limitation we have proposed and investigated an exciton-harvesting strategy which employs exergonic, El-Sayed rule-allowed reverse intersystem crossing (ES-rISC) from the triplet n-π* transition state to the singlet π-π* transition state as the key process of exciton collection.

In order to demonstrate our strategy, we designed and synthesized a series of blue fluorescent organic molecules (SY1-6) based on a 9,10-diphenylanthracene (DPA) scaffold. DPA was chosen because the large exchange energy between the singlet and triplet π-π* transition states would suppress non-emissive loss of triplet exciton through internal conversion. Carbonyl units, including acetyl (SY1), benzoyl (SY2), 4-acetylphenyl (SY3), 4-benzoylphenyl (SY4), 3-acetylphenyl (SY5), and 3-benzoylphenyl (SY6) were introduced into DPA, and provided the triplet n-π* transition state higher than the singlet π-π* transition state in energy. Our structural control aimed at achieving exergonic, rapid conversion of triplet excitons into fluorescent singlet excitons through ES-rISC from the triplet n-π* transition state to the singlet π-π* transition state.

The validity of our strategy was supported by quantum chemical calculations which predicted exothermicity of ES-rISC of the SY compounds. The steady-state photoluminescence spectra revealed that blue fluorescence emissions were attributable to the singlet π-π* transition state of DPA. Photoluminescence quantum yield as high as 0.93 was achieved. The applicability of the exciton harvest by ES-rISC was examined by evaluating the performance of organic light-emitting devices incorporating SY compounds as dopants. Devices containing DPA were also fabricated, and served as a singlet exciton only control. The maximum external quantum efficiency of 4.8% was recorded for the SY3 device. This value was higher than that of the control device even though DPA had a photoluminescence quantum yield greater than SY3. Exciton utilization efficiency of the SY3 device was determined as large as 46%, being a two-fold enhancement from the DPA device (~26%). This enhancement was ascribed to exciton harvest by ES-rISC. Control experiments rebutted any contribution from E- or P-type delayed fluorescence and orientation effects on the improvement and unambiguously confirmed the contribution of ES-rISC.

We hope that our research will provide useful guidance to designing molecules capable of rapid harvesting of excitons for high-efficiency electroluminescence.

EN12.04.29
Vacuum Deposited Small Molecule Bilayer Ternary Organic Photovoltaics Yongxi Li¹, Hafiz Sheriff³, Xiao Liu¹, Kan Ding¹, Chun-Kai Wang², Ken-Tsung Wong² and Stephen R. Forrest¹; ¹University of Michigan–Ann Arbor, United States; ²National Taiwan University, Taiwan

Vacuum thermally-evaporated (VTE) small molecule organic photovoltaics (OPVs) have proven to be efficient and intrinsically stable. However, the high thermalization losses impedes the progress of VTE-grown small molecule OPVs. Ternary blend OPVs can improve light absorption and reduce energy losses beyond that of binary blend OPVs, but the difficulties in optimizing the morphology of three component device active regions, results in ternary systems that have heretofore exhibited performance inferior to analogous binary OPVs. Here, we introduce “a-bi-ternary” OPV comprising two individual binary, bulk heterojunctions fused at a planar junction without component intermixing. In contrast to previous reports where the open circuit voltage (VOC) of a conventional, blended ternary cell lies between that of the individual binaries, the VOC of the bi-ternary OPV is that of either one of the constituting binaries depending on the order in which they are stacked relative to the anode. Additionally, dipole-induced energy-level realignment between two constituting binaries was observed only when using d–a–a’ dipolar donors in the photoactive heterojunction. The optimized bi-ternary single junction OPV shows improved performance.
compared to the two constituent binary OPVs, achieving $PCE = 10.6 \pm 0.3\%$ under AM 1.5G 1 sun (100 mW/cm$^2$) simulated illumination, with $V_{oc} = 0.94 \pm 0.01$ V, a short circuit current density, $J_{sc} = 16.0 \pm 0.5$ mA cm$^{-2}$ and a fill factor, $FF = 0.70 \pm 0.01$. These results open new avenues for achieving highly efficient thermally evaporated, small molecule organic solar cells.

EN12.04.31 Flexible, Printed Non-Fullerene Acceptor Based Near-Infrared Organic Photodiodes Maruf Ahmed$^1$, Anthony Vogliano$^1$, Anju Toor$^1$, Maxime C M Babics$^2$, James Ponder$^2$, Iain McCulloch$^{1,2}$ and Ana Claudia Arias$^3$; $^1$University of California, Berkeley, United States; $^2$Imperial College London, United Kingdom; $^3$KAUST, Saudi Arabia

Organic photodiodes (OPD) are an emerging candidate as photosensors because of their wavelength tunability from Ultraviolet (UV) to Near Infrared (NIR), and processability at low-temperature over large area and variety of substrates [1]. Numerous applications can benefit from OPDs such as biomedical signal detection, imaging, communication, proximity sensing, etc. In particular, broadband OPD’s having response extended to NIR could be useful in optical communications, remote control and environmental monitoring [2].

OPDs can be solution-processed and hence can be fabricated using printing methods e.g. blade coating, which combined with a roll-to-roll process would offer high-throughput production over large areas. Further, the use of flexible substrates would enable applications in wearables as flexible OPDs could increase the comfort of use and quality of the acquired signal.

In this work, blade coated OPD’s have been fabricated with a bulk heterojunction (BHJ) containing a polymer donor material and a novel non-Fullerene acceptor (NFA). The donor material used in this work, PBDTTT-EFT, is proven to result in high efficiency and long lifetime of the resultant devices [3, 4]. The acceptor is an Indacenodithiophene derivative NFA (EHIDTBR) [5] having an absorption spectrum extended beyond red light wavelength. Unlike most conventional OPD’s where BHJ contains Fullerene acceptors because of their efficiency of charge separation [6], an NFA has been used in this work. Because, as opposed to Fullerene acceptors NFA’s can offer good absorption at visible and/or NIR wavelengths. As the donor and acceptor have somewhat complementary absorption spectrum the devices in current work exhibit fairly uniform broadband spectral response extending up to 750 nm. And, use of blade coating method which is compatible with roll-to-roll printing ensures device scalability.

OPD devices fabricated with the photoactive layer comprising PBDTTT-EFT polymer donor material and small molecule (EHIDTBR) NFA shows EQE as high as 55% with the simple conventional device architecture. One of the reasons behind this performance is favorable miscibility of the two components of the BHJ that results in excellent blend morphology [5]. For similar reasons, the dark or reverse leakage current is also small, on the order of 100 nAcm$^{-2}$ and comparable to state of the art devices. Overall, the devices show great promise as flexible printed photodetectors.

References

EN12.04.32
Optimizing Ordered Nanostructures and Crystallization of Regioregular Polythiophene-Based Block Copolymers via Rapid Solvo-Microwave Annealing Junghun Han, Jin-Seong Kim, Jae Man Shin, Hongseok Yun, Youngkwon Kim, Hyeonjung Park and Bumjoon Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Controlling of crystalline structures of conjugated polymers (CPs) within nanostructured block copolymer (BCP) domains is crucial to enhance their electrical properties. However, it has been a challenge due to the intrinsic incompatibility between crystallization and phase-separation process of CP-based BCPs. Herein, we demonstrate solvo-microwave annealing as an effective method for producing highly ordered thin film structures of poly(3-dodecythiophene)-block-poly(lactic acid) (P3DDT-b-PLA) polymers in very short processing time (~ 3 min). The conventional thermal annealing process even with long annealing time (~24h) resulted in incompatibility between ordered nanostructures and crystallization of the conjugated polymer. In contrast, the solvo-microwave annealing with the combination of heat and solvent vapor treatment was employed to grant enhanced chain mobility and solvent interaction with the π-π structure of the conjugated polymer. As a result, this process rapidly generated highly-ordered nanostructures with very few defects within 3 min and, at the same time, the high-crystalline intermolecular ordering of P3DDT blocks was obtained. Furthermore, we demonstrate the successful transfer of highly-ordered P3DDT structures after the removal of PLA domain, which is important for potential nanolithography and electronic applications.

EN12.04.33
Effect of Plasma Treatment in the Sb2S3 and Sbs(SxSe1-x )3 Solar Cells in Order to Improve Their Photovoltaic Characteristics Araceli Hernandez-Granados1, Horacio Martinez-Valencia1, Jose Escorcia-García2 and Hailin Zhao Hu3; 1Instituto de Ciencias Fisicas, Mexico; 2CINVESTAV-Saltillo, Mexico; 3IER, Mexico

In this work was prepared a mesoporous titanium dioxide films (TiO2-mp) with sol-gel method, using different percentages of the polymer polyvinylpyrrolidone (PVP), and they were deposited by the spin-coating technique. It was done several thermal treatments from 120 to 600 °C for 1 and 3 hours. At temperatures of 500 °C. With a x-ray diffraction (XRD), anatase phase with tetragonal structure with crystal size of 19.5-21 nm was identified. The top view morphology of the films showed a porous range size between 15-30 nm. It was estimated for the first time the volumetric porosity of the material by the volume porosity average with the values of the refractive index. The porosity estimated showed a result between 40.3% and 43-6%, the revolutions per minute (rpm) varied from 1000-2500. These films of mp-TiO2 were used as a scaffold and electro transport layers for 3 types of solar cells:

A) sensitized solar cells with quantum dots. For this type of solar cells, it was prepared heterojunctions of antimony sulfide-selenide (Sb2(S,Se1-x)) in solid solution as the absorbing material and cadmium sulfide (CdS) as a sensitized layer deposited by the successive ionic layer adsorption and reaction (SILAR) technique and the (Sb2(S,Se1-x)) with chemical bath deposition. It was shown by increasing the number of CdS layers the photovoltaic performance was improved by the reduction of the Sb2O3 and promoting a better nucleation with the (Sb2(S,Se1-x)) at the chemical bath. The best photovoltaic performance was obtained with a solar cell with 30 cycles of CdS (CdS-30), a voltage of 434 mV, current density of 9.73 mA/cm2 and an efficiency of 1.69%. B) As well were prepared Sb2S3 solar cells and C) Perovskite solar cells (PVK), several PVK solar cells were fabricated varying the hole transport material, for that reason it was used the Poly(3-hexylthiophene-2,5-diyl) (P3HT) and the spiro-MeOTAD and a variation of the percentage of the PVP was used. For the solar cells with P3HT it was used a 20% of PVP and the variation of the rpm at the spin-coating process. With this was possible to correlate the thickness, the volume porosity and the efficiency of the device. It was found for solar cells prepared at 1500 and 2000 rpm, it was obtained a 203 and 168 of thicknesses and efficiencies of 1.24% and 2.14% respectively. The best solar cell with this configuration and 1000 rpm showed a 308 nm of thickness as well 41.6% of porosity. This one showed a current density of 17.15 mA/cm2, generating a 6.29% of efficiency. By changing the HTL for the spiro-MeOTAD, as well increasing the porosity of the material it was possible to obtained a device with a current density of 24.08%, a fill factor of 49.22 and an efficiency of 11.37%.

As an important part of the improvement of the electrical and morphological characteristics it will be done a plasma
Conjugated polymers are promising materials for flexible electronics and energy-relevant applications due to their combination of semiconducting properties, mechanical flexibility and ease of melt and solution processing. Chain length and dimensions in solution can be key factors in influencing the nanoscale and macroscale properties of polymers during processing including crystal architecture, solubility, phase transition temperatures, rheological response, and charge transport efficacy. These, in turn, have been shown to affect performance in various devices, including transistors, photovoltaics and light emitting diodes. Nevertheless, accurate characterization of the conjugated polymers in solution remains a challenge. Conjugated polymers exhibit unique relationships between coil size and contour length due to their semiflexible nature, while also exhibiting low solubilities relative to traditional polymer systems. This means that methods which rely on measurements relative to flexible polymer standards, such as gel permeation chromatography (GPC), can produce inaccurate results for semiflexible polymers. Using absolute measurement techniques such as static light scattering (SLS) and small-angle neutron scattering (SANS), we determine chain length, conformation, and persistence length for a multitude of conjugated polymer systems. Based on these measurements, we have found that the freely-rotating model (FRM) can accurately predict the persistence length for many conjugated polymers. Using this data, we then show that GPC can be made to produce accurate results for conjugated polymers with a range of persistence lengths and molecular weights. We demonstrate this using two additional in-line detectors: a viscometer in order to employ a universal calibration, as well as a differential refractometer to quantify sample loss in the columns. Using these techniques, conjugated polymer size and solution behavior can be accurately and precisely characterized.

BODIPY Based Non-Fullerene Acceptors for All-Polymer Solar Cells—Effect of CF3 Substituent Gourav Tarafdar1, Bryon W. Larson2, Sandeep B. Satyanarayana1 and Praveen C. Ramamurthy1,1; 1Indian Institute of Science, India; 2National Renewable Energy Laboratory, United States

Until recently fullerenes were the commonly used electron acceptor in Organic photovoltaics (OPVs) and had several drawbacks including low absorption in visible wavelengths and phase separation leading to poor performance. Since 2011 major efforts are given on the development of non-fullerene electron acceptors (NFAs) to fabricate fullerene free solar cells. High extinction coefficient is essential for OPV materials to minimize the active layer thickness. We have been therefore investigating the incorporation of BODIPY, a strongly absorbing organic dye, into polymer backbone for design of newer OPV materials. Though BODIPY polymers have been reported for donor applications, to our best knowledge, BODIPY based NFAs are scarce in literature. Herein we present the design of two new BODIPY based D-A polymers (P7 and P8) with fluorene as the donor subunit. The meso substituent on BODIPY, in the acceptor units, is methylphenyl in case of P7 and trifluoromethyl in case of P8. The polymers were characterized using NMR, GPC, UV-vis spectroscopy and Cyclic voltammetry. A lower band gap of 1.6 eV is observed for the trifluoromethylated polymer P8 compared to 1.8 eV in P7. The trifluoromethyl group is seen to improve the electron mobility of the polymer P8 by two orders compared to P7. Further electron acceptor application of these polymers was investigated. Using time resolved microwave conductivity experiments, a number of donor polymers with varying energy offset with P7 and P8 were screened. Photoinduced electron transfer was observed from the donor polymer PTB7-Th into these polymers. Subsequently all polymer solar cells were fabricated with PTB7-Th:P7/P8 using 1:1 blend ratios. The trifluoromethylated polymer P8 performs better than the methylated counterpart P7. The initial set of devices show low efficiency (~ 0.6 %) but high VOC of ~ 0.85 V. Further optimization of device structure is underway to improve the performance.

The Role of PEDOT:PSS on the Stability of Direct and Inverted Organic Solar Cells Christine Dagron-Lartigau1,2, Alberto Gregori1,2, Hussein Awada1,2, Aurelien Tournebize3,4,5, Stephan Schumann6, Roger C. Hiorns2,1, Thomas Chassé3, Heliko Peisert3, Delphine Flahaut1,2, Luc Vellutini7, Ahmed Allal1,2, Antoine Bousquet1,2 and Sylvain Chambon4,5; 1Pau University, France; 2CNRS, France; 3EKUT, Germany; 4IMS, France; 5Bordeaux University, France; 6Heraeus, Germany; 7ISM, France
In an organic solar cell, in addition to electrodes and the active layer, it is necessary to introduce interfacial layers to optimise the transport of charge carriers, and consequently the efficiency. In direct and inverted architectures, a layer of PEDOT-PSS (poly(ethylene dioxythiophene) doped with poly(styrene sulfonate)) is commonly used mainly to help the collection of holes.

In direct devices, the acidic character of PEDOT-PSS tends to promote the degradation of layers in contact, in particular the ITO (Indium Tin Oxide) electrode. The strategy presented here is to avoid this degradation by replacing the layer of PEDOT-PSS by a thin layer of P3HT (poly(3-hexylthiophene) grafted on ITO. We developed an efficient method to graft P3HT on various surfaces, including ITO, confirmed by XPS measurements [1]. This modified electrode was used to prepare direct solar cells and compared to the one with PEDOT-PSS. Devices stored in air without encapsulation with the grafted P3HT as hole transporting layer exhibited the highest stability.

In inverted solar cells, the problem of chemical degradation of ITO is no longer observed as PEDOT-PSS is deposited on the active layer, on the rear side. While the electrical failure mechanisms in such devices have been thoroughly investigated, little is known about their mechanical stability, which is as important and critical to ensure long term reliability [2]. The characteristic thin films stresses of each layer provide the mechanical driving force for delamination of weak interfaces, leading to a loss of device integrity and performance [3]. In this study [4], we developed a technique to probe weak layers or interfaces in thin multilayer devices, establishing a new set-up for the so-called probe tack making it similar to a pull-off test [5]. The technique has been extended varying both active layers, using different p-type low bandgap polymers for the active layer in combination with two different PEDOT:PSS formulations (CleviosHTL Solar and HTL Solar 2). After mechanical tests, the upper and lower surfaces have been characterized by contact angle and XPS to locate the fracture point, which is dependent on the active layer and PEDOT-PSS formulations.

Acknowledgments: Part of the results were funded in the framework of the European Union Seventh Programme (FP7/2011 under grant agreement ESTABLIS n° 290022) and of ANR-13-JS09-0014-01 INSTEP.

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SESSION EN12.05: Physics of Organic Solar Cells I
Session Chair: Donato Spoltore
Tuesday Morning, December 3, 2019
Sheraton, 2nd Floor, Back Bay C

8:30 AM *EN12.05.01
Relationship between Chemical Structure, Microstructure and Interfacial Charge Transfer at Molecular Heterojunctions Jenny Nelson; Imperial College London, United Kingdom

In a molecular photovoltaic device, charge separation and energy conversion result from the evolution of a photogenerated exciton into a charge separated state, in competition with recombination to ground. The efficiency of charge separation is a function of the molecular packing and energy level alignment near the interface, and of disorder in these properties. Understanding the effects of chemical structure, packing, energetics and disorder on the competition between charge separation and recombination helps to identify the factors controlling device photovoltage and ultimately conversion efficiency. Here, we address the factors controlling generation efficiency and photovoltage in molecular donor:acceptor solar cells using a combination of electrical, spectroscopic and structural characterisation techniques along with numerical models. We adapt a recent model [1] of the effect of recombination losses on open-circuit voltage ($V_{oc}$) to incorporate properties of the intermediate charge-transfer state and show how control of these properties, through choice of materials and control of processing, could benefit $V_{oc}$ and device performance [2]. In particular we find that the hybridisation of charge-transfer and local exciton states...
appears to benefit Voc by reducing non-radiative voltage losses [3]. We attempt to develop an improved modeling framework that allows for the evolution of charge states in the molecular environment of the interface. We use our results to consider the importance of chemical structure, phase behaviour and microstructure of the binary system in controlling actual performance and the ultimate limitations placed on solar to electric conversion by the molecular nature of the materials.

References

9:00 AM EN12.05.02
Organic Donor-Acceptor Photovoltaic Devices with Ultrabroad Charge Transfer State External Quantum Efficiency Spectra Saeed-Uz-Zaman Khan1, Giacomo Londi2, Xiao Liu1, Michael Fusella1, Gabriele D'Avino3, Luca Muccioli4,5, David Beljonne2 and Barry P. Rand1; 1Princeton University, United States; 2University of Mons, Belgium; 3CNRS and Grenoble Alpes University, France; 4Universita di Bologna, Italy; 5University of Bordeaux, France

The power conversion efficiency of organic photovoltaic (OPV) devices has recently crossed 15%, thanks to the advent of non-fullerene acceptors, improved material and interface engineering and better understanding of energy loss mechanisms. In recent years, consolidated experimental and theoretical efforts led to empirical design rules, that mandate small frontier orbital energy difference between donor and acceptor molecules to reduce the non-radiative energy loss, one of the major bottlenecks in OPVs. Although charge transfer (CT) states mediated recombination in organic donor-acceptor (D-A) interfaces are considered to be the leading non-radiative loss pathway in highly efficient OPVs, the exact mechanisms of such loss processes are not well understood. Most studies in the literature to date on CT mediated loss processes are performed on D-A blends that feature very small frontier orbital energy offsets with CT spectral features buried under and possibly hybridized with the local molecular energy state spectrum. To conclusively determine the role of frontier orbital energy offset in CT mediated non-radiative energy loss mechanisms, we need to identify D-A systems with spectrally well resolved CT states. On that note, in this work, we demonstrate a class of D-A systems that has ~2 eV broad CT external quantum efficiency (EQE) spectra, originating from the large optical gap of the D-A molecules and very low donor-HOMO acceptor-LUMO gap at the interface (i.e. very large frontier orbital energy offset). Being the exact opposite of the material systems recommended by the efficient OPV design rules, these devices are expected to have severe non-radiative recombination loss and thus are ideal candidate to study loss mechanisms in-depth.

We have identified six D-A systems that exhibit ~2 eV broad CT state spectra, despite their dissimilar molecular structures and HOMO-LUMO energy levels. To investigate the origin of the broad CT spectrum in detail, we have chosen N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB)-1,4,5,8,9,11-hexaaazatriphenylenehexacarbonitrile (HAT-CN) based bulk-heterojunction (BHJ) D-A system, which demonstrates three distinct sub-gap peaks in its EQE spectrum. We have performed comprehensive electrical and optical characterization, along with molecular dynamics and quantum chemical simulations to conclusively prove that the lowest two peaks in the EQE are indeed originating from distinct electronic CT state transitions. We have also found that the lowest energy CT state is non-emissive and acts as a significant non-radiative loss path, possibly due to the large vibrational overlap with the ground state, and as expected from the energy gap law of organic materials. This efficient non-radiative loss pathway in NPB:HAT-CN BHJs results in a photon-energy dependent internal quantum efficiency spectrum and strong voltage bias dependent EQE, unlike most high-performing OPV devices.

9:15 AM EN12.05.03
Insight into the Structural Dynamics of Bulk Heterojunctions Anne Guilbert1, Mohamed Zbiri2, Peter Finn3, Christian Nielsen3 and Jenny Nelson1; 1Imperial College London, United Kingdom; 2Institut Laue-Langevin, France; 3Queen Mary University of London, United Kingdom

Structural dynamics of the active layer of organic photovoltaic (OPV) devices is known to influence their performance and lifetime. By structural dynamics, it is meant dynamics in its larger extent, covering vibrational as well as diffusive and rotational dynamics in such materials.

We study the structural dynamics of blends of various compositions of poly(3-hexylthiophene-2,5-diyl (P3HT) and
Phenyl-C61-butyric acid methyl ester (PCBM) as a function of temperature, using a combination of inelastic neutron scattering (INS), quasi-elastic neutron scattering (QENS), molecular dynamics simulations (MD) and density function theory (DFT). We use the deuteration technique for a contrast variation purpose to access not only the dynamics of the polymer but also the dynamics of PCBM within the blends. We observe, on the picosecond [1] and nanosecond timescales, that the faster polymer dynamics is increasingly frustrated upon blending with higher PCBM concentration, while the slower fullerene dynamics is promoted upon blending with P3HT. We find a good agreement between the simulated and experimental data on this broad timescale.

The MD simulation suggests that in the amorphous mixtures of P3HT and PCBM, P3HT is partially wrapping around PCBM and we speculate that the partial wrapping of P3HT around PCBM is responsible for the relatively high miscibility of PCBM with P3HT. To further probe this specific interaction, we carry out INS experiment on blends of regiorandom-P3HT:PCBM of different compositions. INS allows us to explore molecular vibrations as well as lattice vibrations without selection rule and covers the entire Brillouin zone. By using a combination of MD, molecular and periodic DFT calculations, we reproduce the full INS spectra (10-3500 cm⁻¹) and validate our wrapping hypothesis.

References:

9:30 AM *EN12.05.04
Phase Behavior, Miscibility and Stability of Non-Fullerene Organic Solar Cells
Harald Ade; North Carolina State University, United States

Organic photovoltaics (OPVs) are considered one of the most promising cost-effective options for utilizing solar energy in high energy/weight or semi-transparent applications. Recently, the OSC field has been revolutionized by the development of novel non-fullerene small molecular acceptors with efficiencies now reaching 16% in many systems. The device stability and mechanical durability of non-fullerene OPVs have received less attention and developing devices with both high performance and long-term stability remains challenging, particularly if the material choice is restricted by roll-to-roll and benign solvent processing requirements and desirable ductility requirements. Yet, morphological and mechanical stability is a prerequisite for OPV commercialization. Here we report our current understanding of the phase behavior of OPV mixtures and the relation of phase behavior to performance, processing needs (e.g., kinetic quench), and morphological stability via meta-stability or vitrification. A large range of miscibility (from hyper-miscibility to strong hypo-miscibility) is observed, including complex temperature dependence that can be a complex mixture of upper- and lower critical solution temperature behavior for both the binodal and the liquidus. The measurements presented should help to create molecular structure-function relationships that would allow some predictive guidance on how desired phase behavior and vitrification properties can be targeted by specific chemical design.

10:00 AM BREAK

10:30 AM *EN12.05.05
Non-Fullerene Acceptor-Donor Heterojunctions—Do We Need to Re-Write the Electro-Optical Rulebook?
Paul Meredith; Swansea University, United Kingdom

There is no doubt that the recent emergence of the non-fullerene electron acceptors has rejuvenated the field of organic photovoltaics. The current single junction record is now 15.7% and was achieved with an electron-deficient-core-based fused ring non-fullerene (Y6) in combination with a spectrally matched bespoke donor system [1]. Greater than two decades of reliance on fullerenes as the ‘only n-type in town’ is essentially broken although they still have a significant role to play in organic (and indeed perovskite) optoelectronics.

One critical element of the advances made in fullerene-based organic solar cells is a deep understanding of the device electro-optics – the means by which incident light interacts with the cell junction, creates a free carrier distribution profile, and those free carriers are extracted via various transport pathways. This has led to advanced optimization concepts in junction and interlayer design, manipulation of the external quantum efficiency, minimization of parasitic recombination and voltage loss, and structure-property relationships that guide the development of manufacturable thick junctions [2]. The question is – can we reapply the same electro-optical physics for the non-fullerenes, or must we start again?
In my talk I will address this most important of questions, detail some specific areas requiring thought and describe some of our recent work seeking to begin at least, this new electro-optical journey.


11:00 AM EN12.05.06
**Binding Energy for Disordered Organic Heterojunction Photovoltaic Devices** Nir Tessler and Dan Liraz; Technion-Israel Institute of Technology, Israel

One of the puzzles in the field of organic photovoltaic cells (OPVs) is the experimentally deduced low binding energy despite the fact that simple coulomb based arguments ( ) would predict binding energy of at least $E_b=500\text{meV}$ for intrachain excitons and $150-200\text{meV}$ for charge transfer excitons. Such high binding energies are not in line with devices achieving power conversion efficiency (PCE) of $14\%$ or internal quantum efficiency (IQE) that is almost $100\%$.

There have been several suggestions for the reduced effective binding energy as delocalization, disorder, entropy, as well as a combination of entropy and disorder. By entropic contribution, one means that the more dissociation paths there are, the more likely the exciton is to dissociate, and this can be translated into lower binding energy using the entropy gained in the dissociation process. The process becomes less obvious when disorder is introduced as one has to account for the fact that energetic disorder creates a spatial distribution of the local environments. Namely, each CT experiences a different environment through which it dissociates, and the challenges are in translating the overall processes into effective binding energy. We will describe an improved entropy-disorder model that resolves deficiencies of earlier models that predicted the effective binding energy to become negative at high disorder. To test our model we performed voltage and temperature dependent analysis of charge generation in NFA (PTB7-th:ITIC) based device. We find good agreement between modeling and experiment. Specifically, the activation energy of the dissociation efficiency is about $10\text{meV}$ which translates to an effective binding energy of about $\sim 80\text{meV}$, at room temperature. Using the experimental and theoretical analysis we will discuss the implications for higher efficiency materials.

11:15 AM EN12.05.07
**Non-Equilibrium Site Distribution Governs Charge-Transfer Electroluminescence at Disordered Organic Heterointerfaces** Armantas Melianas$^1$, Nikolaos Felekidis$^2$, Yuttapoom Puttisong$^2$, Stefan C. Meskers$^3$, Olle Inganäs$^2$, Weimin M. Chen$^2$ and Martijn Kemerink$^2$; $^1$Stanford University, United States; $^2$Linköping University, Sweden; $^3$Technische Universität Eindhoven, Netherlands

The interface between electron-donating and electron-accepting materials in organic photovoltaic (OPV) devices is commonly probed by charge-transfer (CT) electroluminescence (EL) measurements to estimate the CT energy, which critically relates to device open-circuit voltage. Despite the lack of a quantitative CT-EL model at disordered organic heterointerfaces and lack of quantitative proof, it is generally assumed that during CT-EL injected charges recombine at close-to-equilibrium energies in their respective density-of-states (DOS).

Combining optical and electrical experiments on a wide range of materials with numerical 3D kinetic Monte Carlo simulations of the entire OPV device we explicitly quantify that CT-EL instead originates from higher energy DOS site distributions far above DOS equilibrium energies. We present an experimentally verified and quantitative model of charge-transfer electroluminescence at donor/acceptor interfaces that reconciles the inconsistencies present in the literature. Our CT-EL model quantitatively and simultaneously accounts for charge transport physics in an energetically disordered DOS and molecular vibration induced broadening, using experimentally measured energetic disorder values and spectroscopically determined phonon-mode energies governing CT luminescence.

The lowest-energy CT states are in fact situated $\sim 180-570\text{meV}$ below the 0-0 CT-EL transition, enabling photogenerated carrier thermalization to these low-lying DOS sites when the OPV device is operated as a solar cell rather than as a light-emitting diode (LED). We reveal how DOS sites relevant to sub-gap photovoltaic action and CT-EL relate to the total DOS. The DOS sites sampled during CT-EL are not necessarily the same as those sampled during charge transport and sub-gap absorption measurements.

The non-equilibrium site distribution governing CT-EL rationalizes the experimentally observed weak current-density dependence of CT-EL and poses new research questions on reciprocity relations relating light emission to
photovoltaic action and regarding minimal attainable photovoltaic energy conversion losses in OPV devices.

11:30 AM EN12.05.08
Hole Transfer in Non-Fullerene (NF) Organic Solar Cells Yanfeng Liu¹, Jianyun Zhang², Jianqiu Wang³, Nannan Yao¹, Yingzhi Jin¹, Xiaozhang Zhu², Yuan Zhang² and Fengling Zhang¹; ¹Linköping University, Sweden; ²Institute of Chemistry, Chinese Academy of Sciences, China; ³Beihang University, China

To efficiently harvest photoinduced current in organic solar cells by extending the coverage of the solar spectrum, many non-fullerene (NF) electron acceptors with complementary absorption spectra are synthesized, which indeed enables the power conversion efficiency of organic solar cells up to 14% in single junction and 17% in tandem devices. There have been intensive studies on electron transfer from electron donors to various fullerene acceptors in fullerene based organic solar cells. However, the mechanism of efficient hole transfer from non-fullerene acceptors (or hole donor, denoted as D_h) to molecular or polymeric electron donors (or hole acceptors, denoted as A_h) is still not fully understood although considerable contribution from non-fullerene D_h materials to photoinduced current in non-fullerene solar cells. There are several reports on high performance non-fullerene organic solar cells with very small or even close to zero LUMO or(and) HOMO offsets between two photoactive components, which challenges the theories on charge generation derived in fullerene based organic solar cells. Currently, to increase the efficiency of organic solar cells, more attention is paid on generating charge with minimized photo-voltage loss by matching energy levels of donors and acceptors. To understand the mechanism of non-fullerene organic solar cells, charge transport and extraction at electrodes also need to be considered.

Here we will present our study on the mechanism of efficient hole transfer from D_h to A_h in non-fullerene organic solar cells. Based on the results, efficient hole transfer from D_h to A_h is not only depends on the offset of HOMOs of D_h and A_h but also charge transport and extraction at electrodes. Therefore, a comprehensive strategy including both charge generation and extraction is desired to further enhancing the PCE of the organic solar cells.

11:45 AM EN12.05.09
Minimum Energetic Driving Force for Charge Generation in Organic Solar Cells Kyohei Nakano¹, Weining Han², Jianming Huang¹, Yujiao Chen¹, Hiroyuki Yoshida² and Keisuke Tajima¹; ¹RIKEN, Japan; ²Chiba University, Japan

Eliminating the excess energetic driving force in organic solar cells leads to a smaller energy loss and higher device performance; hence, it is vital to understand the relation between the interfacial energetics and the photoelectric conversion efficiency. In practice, however, mixing morphology of the donor (D) and the acceptor (A) in bulk heterojunction has a large impact on photovoltaic properties, which prevents us from investigating the minimum energetic driving force at D/A interface for efficient charge generation.

In this study, we systematically fabricate 16 planar heterojunctions of four donor polymers and four acceptors and investigate the relation between state energies at D/A interface and resulting charge generation efficiency. A thin film of donor polymer was transferred onto an acceptor film, forming planar heterojunction, so as to eliminate the effect of morphology. The state energies of singlet excited state, charge transfer state, and charge separated state were experimentally quantified. The charge generation efficiency from donor exciton and acceptor exciton were evaluated using external quantum efficiency combined with transfer-matrix optical modeling with making a simple assumption about exciton diffusion. The charge generation efficiency and its electric field dependence correlated with the energy difference between the singlet excited state and the interfacial charge transfer state. The threshold energy difference is 0.2 to 0.3 eV, below which the efficiency stated dropping and the charge generation became electric-field dependent. In contrast, the charge generation efficiency did not correlate with the energy difference between the charge transfer and the charge separated states, indicating that the binding of the charge pairs in the charge transfer state is not the determining factor for the charge generation.

[Reference]
SESSION EN12.06: Physics of Organic Solar Cells II  
Session Chair: Obadiah Reid  
Tuesday Afternoon, December 3, 2019  
Sheraton, 2nd Floor, Back Bay C

1:30 PM EN12.06.01  
**Fast Screening Donor:Acceptor Blends for Organic Solar Cells**  
Gitti L. Frey¹, Artem Levitsky¹, Giovanni Maria Matrone², Ilaria Bargigia³, Aditi Khirbat¹, Xiaolei Chu⁴, Adam J. Moule⁴, Carlos Silva³ and Natalie Stingelin³; ¹Technion–Israel Institute of Technology, Israel; ²Imperial College London, United Kingdom; ³Georgia Institute of Technology, United States; ⁴University of California Davis, United States

A significant breakthrough in the efficiency of organic solar cells (OSCs) has been achieved due to the synthesis of new materials offering a plethora of donor:acceptor combinations. However, the device performance is interlinked in a complex way not only with the properties of the individual components but also its strong dependence on the blend’s microstructure and phase morphology. Consequently, identifying high-performing donor:acceptor combinations has so far been an intricate process nearly uniquely relying on tedious and time-consuming trial-and-error materials selection methods. To overcome this unsustainable approach we developed a methodology that rapidly elucidates how blend composition and processing conditions affect the final blend morphology and microstructure. We demonstrate that transient absorption spectroscopy (TAS), vapor phase infiltration (VPI) and differential scanning calorimetry (DSC) measurements can be jointly harnessed to fast-screen OSC blends. VPI infuses inorganic materials into an organic matrix by exposure to gaseous precursors that diffuse into the film and in-situ convert to an inorganic product. In BHJ films, the diffusion process proceeds selectively through domains with high free-volume leading to inorganic deposition selectively along the diffusion paths. The diffusion network is easily visualized with electron microscopy. Using this labelling approach to spatially map OSC BHJ is in concept similar to the staining approach used to image low contrast biological. The spatially mapping of the phase morphology of organic solar cells via VPI giving insights into the size, shape, distribution and connectivity of specific domains, resolved through fast and straightforward HRSEM characterization, the information obtained on the general phase behavior as well as the phase purity (or at least degree of order) via DSC, and the indirect correlations on the fine structure of, e.g., the intermixed phases and phase-pure domains, provided by the charge separation dynamics from TAS, can, when combined, be used to identify best working compositions and deliver understanding why specific deposition methodologies do not lead to well-performing devices.

1:45 PM *EN12.06.02*  
**Elucidating Interfacial Structure-Function Relationships in Organic Photovoltaics**  
Aram Amassian; North Carolina State University, United States

The distributed bulk heterojunction in organic solar cells is the result of a delicate nanoscale blend of electron donating (D) and accepting (A) material resulting in different interfacial varietals. These include interfaces between aggregated pure D and A phases, mixed interphases exhibiting significantly different energetics and other interfaces between an aggregated phase and the mixed interphase. Revealing the complex energy landscape that results in real-space can be extremely challenging, yet it locks the secrets of light harvesting of organic solar cells. Considerable debate remains about the nature of interfaces and the importance of sharp D-A interfaces versus the mixed interphase on charge generation and extraction. In this talk, we discuss recent developments in the direct imaging of the real-space energetic landscape of BHJ layers via scanning tunneling microscopy and spectroscopy (STM/STS) measurements. This approach is shown to work on BHJ films directly usable in OPV devices and reveal several heterointerfaces with different energetics that surround aggregated D, A and mixed (M) phase domains. We reveal the coexistence of three types of heterointerfaces within the BHJ and, in total, four types of D-A intermolecular interactions exhibiting different energetics. These scenarios are universally present in classical and modern BHJs exhibiting a wide range of power conversion efficiencies (PCE, ca. 3.5 – 10.8%; P3HT:PCBM, P3HT:O-IDTBR and P3H:PCBM). We provide accurate HOMO/LUMO energy diagrams for D/M, A/M and D/A heterointerfaces in these systems and discuss the most likely pathways for charge generation and recombination.

2:15 PM EN12.06.03  
**Understanding and Reducing Energy Loss at the Organic/Anode Buffer Interface in Organic Photovoltaics**  
Kan Ding¹ and Stephen R. Forrest¹,²; ¹University of Michigan, United States; ²University of Michigan–Ann Arbor, United States

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Final Program 1/13/2020  1114
Understanding various sources of energy loss in organic photovoltaic (OPV) cells is important for achieving high efficiency. In this work we explore energy losses at the interface between a vacuum deposited tetraphenyldibenzoperiflanthene (DBP) donor and C70 as acceptor bulk heterojunction (BHJ) active layer and a MoO3 anode buffer through experimental and computational methods. Material composition at the organic/anode buffer interface is independently controlled to distinguish the energy loss due to the organic/anode buffer interface from that in the BHJ. Interface energy loss is attributed to charge transfer between the organic active layer and anode buffer layer. Monte Carlo simulations are used to quantitatively evaluate the magnitude of the interfacial energy loss and its effect on device performance. A strategy is proposed to reduce this source of loss. Specifically, a thin interlayer is inserted between the organic active layer and anode buffer layer, leading to an increase of up to 6% in power conversion efficiency compared with conventional devices. Finally, basic principles are provided for the design of the interface layer.

2:30 PM EN12.06.04
Emissive and Charge Generating Donor Acceptor Interfaces for Organic Optoelectronics with Low Voltage Losses
Donato Spoltore1, Sascha Ullbrich1, Johannes Benduhn1, Xiangkun Jia1, Vasileios C. Nikolis1 and Koen Vandewal2; 1TU Dresden, Germany; 2Institute for Materials Research (IMO-IMOMEC), Belgium

Intermolecular charge transfer states at the interface between electron donating (D) and accepting (A) materials are critical for the operation of organic solar cells but can be employed also in organic light emitting diodes. Non radiative decay of the charge transfer state is dominant in state of the art D/A organic solar cells and is responsible for large voltage losses as well as electroluminescence external quantum yields in the 0.01–0.0001% range. In contrast, the electroluminescence external quantum yield reaches up to 16% in D/A organic light emitting diodes. In our work we show that proper control of charge transfer state properties allows simultaneously an high photovoltaic and high emission quantum yield within a single system, demonstrating that efficient photogeneration of free carriers and a high electroluminescence quantum yield do not necessarily need to be mutually exclusive in organic semiconductors. This leads to ultralow emission turn on voltages as well as significantly reduced voltage losses upon solar illumination, as low as 0.37eV. These results unify the description of the electro optical properties of charge transfer states in organic optoelectronic devices and encourage the use of organic D/A blends in energy conversion applications involving visible and ultraviolet photons, for example for indoor application and multijunction solar cells.

2:45 PM OPEN DISCUSSION

3:00 PM BREAK

SESSION EN12.07: Charge Transport in Organic and Hybrid Systems
Session Chair: Guillaume Wantz
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Back Bay C

3:30 PM EN12.07.01
General Rule for the Energy of Water-Induced Traps in Organic Semiconductors
Guangzheng Zuo, Mathieu Linares, Tanvi Upreti and Martijn Kemerink; Linkoping University, Sweden

Charge carrier traps are generally highly detrimental for the performance of semiconductor devices. Unlike the situation for inorganic semiconductors, detailed knowledge about the characteristics and causes of traps in organic semiconductors is still very limited and surprisingly few systematic investigations to the energetics of traps in organic semiconductors have been conducted.

Here, we systematically investigate the JV characteristics from hole- and electron-only thin-film devices for a large range of organic semiconductors. Trap energies and densities are extracted directly from the JV curves and, more
accurately, using a method based on the logarithmic slope of the JV curves. For all investigated materials, the hole and electron trap distributions are found to be centered at a more or less constant energy offset of 0.3–0.4 eV above the HOMO and below the LUMO level, respectively. For typical preparation and measurement conditions the total trap density is around $0.5–1 \times 10^{23} \text{ m}^{-3}$ for both electrons and holes. We experimentally identify water absorbed in nano-voids as cause. Using density functional theory (DFT) calculations we show that direct interaction of H$_2$O molecules with the conjugated backbone cannot explain specific conformation locks nor the finding of a generic trap. Instead, we show that electrostatic interaction with an ensemble of H$_2$O molecules that for example are enclosed in a nanoscopic void in the film provides a stabilization of both electron and hole polarons on different model systems of conjugated molecule. The mechanism has a broad relevance as it does not rely on any specific interactions with, or properties of the active material like conjugation length, mobility or transport mechanism, and is shown to affect electron and hole transport in a similar manner. The prerequisite of having nano-voids in the molecular morphology suggests this trapping mechanism to be of lesser relevance for single crystals, but also suggests processing routes to suppress the mechanism; an example of the latter is demonstrated.

The current findings are in marked contrast to earlier works that concluded that the electron trap level is about constant and centered at an energy of $\sim 3.6$ eV below the vacuum level. For p-type materials, trap formation has previously been argued to be due to a specific hydrogen bonding interaction of a single water molecule affecting the torsional potential energy profile of the bond connecting the donor and acceptor subunits of a D-A-type polymer.

References:
molecular mechanism of doping these materials with kinetic Monte-Carlo simulations. The availability of first-principles based models to compute key performance characteristics of organic semiconductors may enable in-silico screening of numerous chemical compounds for the development of highly efficient opto-electronic devices.

4:00 PM EN12.07.03
Effects of Ligand Coordination on the Structure and Electronic Properties of Copper(I) Thiocyanate Pichaya Pattanasattayavong1, Daniel M. Packwood2 and David J. Harding3; 1Vidyasirimedhi Institute of Science and Technology (VISTEC), Thailand; 2Kyoto University, Japan; 3Walailak University, Thailand

In recent years, copper(I) thiocyanate (CuSCN) has been established as a high-potential semiconductor with an impressive range of opto/electronic applications demonstrated, including thin-film transistors (TFTs), organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), extremely thin absorber (ETA) solar cells, and now perovskite solar cells (PSCs). Belonging to the group of coordination polymers, CuSCN has an extended 3D network structure formed by the ambidentate SCN ligand linking the Cu centers together. This gives rise to the electronic structure that leads to its unique properties of optical transparency (wide band gap) and good hole transport (dispersed valence band).

Due to its excellent semiconducting properties and wide-ranging applications, it is of great interest to investigate other derivatives of CuSCN. For coordination polymers, ligand coordination is a common method to modify the structure. Interestingly, CuSCN is routinely processed from dialkyl sulfide-based solutions [Adv. Mater. 2013, 25, 1504; Adv. Energy Mater. 2015, 5, 1401529; Science 2017, 358, 768], and in fact the coordination of these sulfide ligands with Cu center in CuSCN can lead to different 1D structures [Polyhedron 2016, 114, 252]. Moreover, N-containing aromatic ligands have also been reported to react with CuSCN to yield colored compounds with optical absorption/emission variable in the visible range [Inorg. Chem. 2011, 50, 7239]. These examples show the structural versatility and adjustable electronic properties of CuSCN.

In this work, we report a survey of 25 structures of CuSCN-ligand (L) complexes and, for the first time, their electronic structures calculated by density functional theory (DFT). Four groups of ligands were investigated: dialkyl sulfides, aliphatic cyclic amines, aromatic imines, and aromatic diimines. We observed that the dimensionality of the Cu-SCN network decreased with the increasing CuSCN:L ratio. In general, the 3D network of the parent compounds (α- and β-CuSCN) was reduced to 2D sheet or 1D ladder structures when the CuSCN:L ratio was 1:1 and further to 1D zigzag chain or helical chain at 1:2 ratio and 0D monomer at 1:3 ratio. Aromatic diimine ligands resulted in bridged 2D or bridged 1D structures. Importantly, we found the relationship between the Cu-SCN network dimensionality and the width of the top Cu valence band (VB) as well as the energy gap between the Cu and SCN states. With the reducing dimensionality, the Cu VB width also decreases whereas the Cu-SCN energy gap increases. Based on the band structure and the total and partial density of states (DOS) analyses, hole transport prevailed in the 2D structures but became limited in the 1D structures and were completely localized in the 0D structure. Aromatic ligands generated states between the Cu and SCN energy states due to their lower-energy π* states compared to the SCN π* level. As a result, the combination of 2D Cu-SCN network (CuSCN:L ratio less than or equal to 1:1) and aromatic ligands can be employed to tune the electronic properties of CuSCN; we propose that the 2D network should be kept to provide hole transport while using the aromatic ligands to modify the optical absorption/emission properties. In addition, one particular case of the bridging 4,4′-bipyridine (4,4′BPY) ligand was found to exhibit dispersed states both at the valence band and the ligand-dominant conduction band as well as a small fundamental band gap; we speculate that the complex of CuSCN and 4,4′BPY could display ambipolar charge carrier transport properties, expanding further the possible applications of CuSCN-based materials. This work provides a comparative study on the effects of ligand coordination on the structural and electronic properties of CuSCN and could serve as guidelines for further development of semiconductors based on coordination polymers.

4:15 PM EN12.07.04
Ultrafast Nonlinear Photonics in an Organic Superconductor kappa-(ET)2Cu[N(CN)2]Br Shinichiro Iwai; Tohoku University, Japan

Intense light-field application to solids produces enormous/ultrafast non-linear phenomena such as high-harmonic generations and attosecond charge dynamics. They are distinct from conventional photonics. However, main targets have been limited to insulators and semiconductors, although theoretical approaches have been made also for correlated metals and superconductors. Here, in layered organic conductors and a superconductor, anomalous non-linear photonics driven by a nearly single-cycle strong electric field of >10 megavolts /cm are observed as a dynamical localization [1-3], a stimulated emission [4] and a harmonic generation (HG). It should be emphasized...
that they are enhanced by critical fluctuations near a metal-to-insulator transition temperature and a superconducting transition temperature. In particular, observation of the characteristic stimulate emission in an organic superconductor Kappa-(ET)$_2$Cu[N(CN)$_2$]Br on an ultrafast timescale of 10 fs clarifies that the Coulomb repulsion plays an essential role in the superconductor [4]. Moreover, second harmonic generation (SHG) in Kappa-(ET)$_2$Cu[N(CN)$_2$]Br (in which spatial inversion centers exist) shows that the non-perturbative light-driven current can break the inversion symmetry. Temperature dependence, polarization dependence, and carrier-envelope phase (CEP) dependence of the SHG in the organic superconductor will be discussed.


SESSION EN12.08: Organic Photovoltaics, Materials, Processing and Up-Scaling
Session Chairs: Francesca Brunetti and Argiris Laskarakis
Wednesday Morning, December 4, 2019
Sheraton, 2nd Floor, Back Bay C

8:30 AM *EN12.08.01
Organic Photovoltaics—From Lab to Fab Robin Szymanski$^{1,2}$, Uyxing Vongsaysy$^2$, Lionel Hirsch$^{1,3}$, Sylvain Chambon$^{1,3}$ and Guillaume Wantz$^{1,4,3}$; $^1$Univ. Bordeaux, France; $^2$ARMOR, France; $^3$CNRS, France; $^4$Bordeaux INP, France

The communication will display our recent progress Organic Photovoltaics (OPV). Solution-processed organic solar cells are continuously showing increasing performances other the recent years with record power conversion efficiency exceeding 15%. They represent a more and more promising technology with a growing interest from companies and markets. The challenge is surely to maintain the global research efforts in materials development to increase efficiency and stability but also to enable a realistic cost-competitive transfer from lab to fab. Our efforts to increase the stability of OPV cells will be exposed including device engineering and materials developments for thermally stable devices. We have recently shown that impurities such as photo-oxidized fullerene or photo-oxidized polymers (P3HT or PTB7) are responsible for an impressive loss in device performances even in very low amounts. This finding is raising issues for large area manufacturing where organic semiconductors are commonly processed in ambient conditions.

The cost of materials is also a critical when it comes to scale up solar cell production. If the best materials are achieving high PCE, it is crucial that these materials remain as low cost as possible thanks to simplified chemical structures and straightforward synthesis routes and purification steps. If a few simple and efficient polymers are currently emerging, we have been investigating a series of bio-inspired solution-processable compounds derivated from curcuminoids enabling one-pot, one-step synthetized organic semiconductors for OPV.

Finally, large area OPV modules are currently facing two major challenges. (a) The need to be light activated which becomes difficult when the flexible product uses packaging sheets acting as UV filter to promote long lived devices. (b) The fast decay of efficiency within the first hours of usage under illumination; this so-called burn-in effect is still not fully understood and should be overcome. On these two issues, this communication will bring some fundamental understandings and guidelines for more efficient and stable OPV cells.

9:00 AM EN12.08.02
Upscaling of Organic Photovoltaics Using Novel Non-Fullerene Acceptors and Slot-Die Coating Audrey Laventure and Gregory C. Welch; University of Calgary, Canada

Organic photovoltaic stands as one of the most promising clean energy technologies. However, its commercial availability still presents some challenges that have not yet been overcome. To improve the cost effectiveness of the organic solar cell active layer, our group has recently developed a series of N-annulated perylene diimide (PDI) derivatives acting as electron acceptors, one of these is today commercially available. (1) The resulting fullerene-
free photovoltaic devices present a high power conversion efficiency, making them a viable alternative to the more traditional fullerene-containing solar cells. (2) Considering that these molecules can be mass-produced, they are excellent candidates for slot-die coating of large area solar cells. Herein, we present the structure-property relationships of these compounds (3) along with their utility as electron acceptors in bulk heterojunction organic photovoltaics. We also discuss the upscaling results of our efforts towards printing large-scale organic solar cells using slot-die coating. References: (1) Sigma-Aldrich, PDI-DPP-PDI, https://www.sigmaaldrich.com/catalog/product/aldrich/901143); (2) McAfee, S.M., Dayneco, S.V., Josse, P., Blanchard, P., Cabanetos, C., Welch, G.C., Chem. Mater., 2017, 29, 1309; (3) Tintori, F., Laventure, A., Welch, G.C., Soft Matter, 2019, Advance article, 10.1039/C9SM00716D.

9:15 AM *EN12.08.03
Optimization of Large Area Manufacturing of Fully Printed Organic Electronic Devices by Robust In-Line Investigations and Modelling
Argiris Laskarakis1, A. Zachariadis1, C. Kapnopoulos1, Z. Kyroudis, E. Mekeridis2 and S. Logothetidis; 1Aristotle University of Thessaloniki, Greece; 2Organic Electronic Technologies P.C. (OET), Greece

The optoelectronic and charge transport properties of printed semiconductor nano-layers (e.g. polymer donors and acceptors, hybrid perovskites) is mainly controlled by the structural morphology and crystallization dynamics during their fabrication in functional device architectures (as Organic Photovoltaics, Perovskite Photovoltaics, etc). Despite the numerous advances reported on the structure-property relationships on these materials by lab-scale solution-based methods, their reliable manufacturing on flexible substrates by large scale roll-to-roll (R2R) printing processes is accompanied by numerous challenges, such as the formation of structural inhomogeneities, and non-reproducible properties (optical, electrical, structural) and interface quality over large areas. The above limitations provide significant obstacles for R2R printing to meet the requirements for reliable large scale manufacturing of high performance Organic Electronic devices on flexible substrates for commercial applications.

In this work, we present an intelligent in-line optical characterization methodology based on the combination of robust in-line Spectroscopic Ellipsometry (SE) and in-line Raman Spectroscopy (RS) for the investigation of the formation mechanisms and morphology of printed semiconductor nanolayers (e.g. polymer donors as PBDB-T, non-fullerene acceptors as ITIC, and hybrid perovskites based on MAPbI3), on flexible polymer substrates by R2R pilot-to-production lines. In addition, we report on the development of intelligent modelling procedures that can extract from single very fast optical in-line measurements of significant insights from the printed semiconductors properties such as film quality, morphology (surface roughness, voids, pinholes etc), degradation traces and film thickness. By this approach, we demonstrate an optimized fabrication process of fully printed large scale flexible OPV and PPV devices with improved charge transport properties and performance that exceeds 6.5%, and significant device-to-device reproducibility. [1,2] Finally, this methodology will open the way for the reliable scalable nano-manufacturing of high performance flexible electronic devices by large scale processes.

[1] EU Project SmartLine (www.smartline-project.eu)
[2] EU Project CORNET (www.cornet-project.eu)

9:45 AM EN12.08.04
Printable High Efficiency Flexible and Free Design OPV Modules for Indoor Application
Sadok B. Dkhil1, Florent Pourcin1, Donia B. Freqj1, Elena Barulina2, Pavlo Perkhun2, Olivier Margeat2, Christine Videiot-Ackermann2, Jörg Ackermann2, Pascal Pierron1, Jérôme Vernet1 and Brice Crucun1; 1Dracula Technologies, France; 2Aix Marseille University, France

Over the last decade, organic solar cells (OSCs) have become a promising technology for next generation solar cells combining novel properties such as light weight, flexibility, or color design with large-scale manufacturing with low environmental impact. However, the main challenge for OSC will be the transfer from lab-scale processes to large-area industrial solar cell fabrication. High efficiencies in the field of OSCs are mainly achieved for devices fabricated under inert atmosphere using small active areas, typically below 0.2 cm². So far, a small lab scale devices have now reached performances above 17% [1].

In this light, inkjet printed organic solar cells and modules with large area were demonstrated. Inkjet printing allows
direct patterning of four layers, including the top electrode, offering full freedom of design without the use of masks or structuring by hardware. Inkjet printed large area (>1 cm²) organic solar cells with power conversion efficiency exceeding 6.5 % deposited from environmentally friendly solvents in an air atmosphere are demonstrated using the same printer. To prove the great advantage of inkjet printing as a digital technology allowing freedom of forms and designs, large area organic modules with different artistic shapes were demonstrated keeping high performance.

The good module performance at low illumination make our OPV modules good candidates for indoor applications, field in full expansion thanks to the Internet of Things (IoT).

Reported results confirm that inkjet printing has high potential for the processing of OPV, allowing quick changes in design as well as the materials.


10:00 AM BREAK

10:30 AM *EN12.08.05
Fully Spray-Coated Polymer Solar Cells and Modules Realized with Green Solvents—Possibilities and Open Issues Francesca Brunetti; University of Rome-Tor Vergata, Italy

In the field of energy generation, several emerging technologies using new PV materials and innovative device concepts have appeared in the last years: Dye solar cells (DSC), Quantum Dot (QDSC), organic photovoltaics (OPV), and perovskite solar cells (PSC). Among these technologies, PSC are the most promising ones, since they have drastically increased their efficiency up to 24.2 % in just a few years, while DSC have reached 11.9 %, OPV 15.6 % and QDSC 16.6%(according to NREL certified efficiencies chart) [1].

The main characteristic of these technologies is that most of the parts of the devices can be processed from solution, allowing to realize light-weight, flexible, transparent, conformable, roll-to-roll compatible, potential low costs devices.

Among these technologies, OPV has seen in the last few year a fast rise in efficiency thanks to the introduction of new materials such as low band gap polymer donors and non-fullerene acceptors [2,3] allowing to reach the actual record efficiency of 16.5% [4].

Such optimal performance are strongly correlated to the use of spin coating technique to ensure reproducible and homogeneous films and chlorinated solvents that help the suitable nanoscale morphology. This procedure, however, is not industry compatible since spin coating does not allow large scale production and chlorinated solvents are poorly tolerated in workplaces since they are harmful towards environment and human health [5, 6, 7]. In this talk, we will present a possible route toward the realization of large area, high-performing inverted polymer solar cells where all the layers, apart from TCO, have been realized via the spray coating technique with green solvents [8,9].

In particular, we will show via atomic force microscopy (AFM) analysis, how this technique affects the morphology at the interface between photoactive layer (PAL) deposited through a non-chlorinated solvent (ortho-xylene) and hole and electron trasporting layers processed from alcohol based solvents. We will consider the interface between PAL and an electron transporting layer (ETL) fabricated using zinc oxide nanoparticles coated with polyethyleneimine ethoxylated (PEIE). For the interface between PAL and the hole transport layer (HTL)/anode three different combination will be shown: i) a mixture of two commercial poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) formulations (CPP:PH1000), ii) an anhydrous PEDOT:PSS (A-PEDOT) solution developed in our laboratory. The electrical performance in terms of PCE of small area devices (10 mm²) realized using these two typologies are 1.7% in the case of PH1000 and 3.6% anhydrous PEDOT:PSS when the devices were illuminated from ITO side. A study of scaling up of the solar cells will be presented for a fully spray coated organic photovoltaic modules (active area: 12 cm²) realized with structure ITO/ZnO-PEIE/PBT7:PC70BM/V2O5/A-PEDOT. For this module, a power conversion efficiency 0.8% is achieved, while large area modules with metallic anode on top PCE of 3%. Finally, a practical application of our solar module is reported.

References

11:00 AM OPEN DISCUSSION

11:15 AM EN12.08.07
Influence of Thermal Treatment and Humidity on Work Function of PEDOT:PSS Thin Films
Aman Anand, Rico Meitzner, Shahidul Alam, Moritz Beckenkamp, Ulrich S. Schubert and Harald Hoppe; Friedrich Schiller University Jena, Germany

In the field of optoelectronics, Poly (3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) is the most common and successful commercial conductive polyelectrolyte. Its properties such as high transparency in the visible range, high electrical conductivity, excellent chemical and physical stability, high ductility, good film-forming properties, and high work function enable multiple applications in the field of electronics. The work function is one of the main parameters which control the functionality of an electronic device. Properly tuning the work functions within semiconductor devices is very crucial in terms of performance and may be strongly influenced by unmonitored processing conditions. For example, PEDOT:PSS is highly hygroscopic in nature, which may impact on its functionality. In the present work, we have investigated the influence of the thermal post-production treatments and relative humidity during film casting or storage on the work function of PEDOT:PSS films made from various commercial formulations. We find clear trends between the processing conditions and absolute work function as obtained with a carefully calibrated Kelvin Probe setup. As a conclusion, we can suggest suitable processing parameters for a wide range of formulations and targeted electronic properties.

11:30 AM EN12.08.08
Annealing Free Solution-Processable MoOx Hole Transport Layer for Bulk-Heterojunction Polymer Solar Cell
Nhan H. Tran and Shinuk Cho; University of Ulsan, Korea (the Republic of)

Electrode buffer layer plays an important role on the performance of polymer solar cell by facilitating the flow of charges via better energy level alignment at the organic/electrode interface. Transition metal oxide material such as MoOx was found as the good material for anode buffer layer due to high conductivity and high stability. In general, the MoOx layer fabricated by wet chemical method needs a post-thermal treatment around 200 °C in air to archive better quality thin film. However, the usage of high temperature makes the transition metal oxide hard to employ in flexible electronics where flexible substrate can’t stand with the temperature above 100°C. In this work, we developed annealing free modified s-MoOx and have applied on bulk heterojunction (BHJ) polymer solar cell based on a blend of p-type polymer PTB7-Th and fullerene derivative PC71BM. The polymer solar cell with non-annealed c-MoOx hole transport layer prepared by conventional sol-gel method showed poor efficiency of 1.37%. If the c-MoOx layer was annealed at 200°C before active layer deposition, the efficiency was recovered to normal range that typically shown in conventional structure PTB7-Th and PC71BM solar cells. However, the polymer solar cell with our modified-MoOx (m-MoOx) prepared using bis(2,4-pentanedionato)molybdenum(VI)dioxide (MoO2(acac)2) exhibited higher efficiency without high temperature annealing. The solar cell with m-MoOx showed higher efficiency and better stability comparable with that of device with PEDOT:PSS hole transport layer. Note that even PEDOT:PSS also needs annealing process around 120°C normally. Furthermore, annealing free m-MoOx allows successful fabrication of inverted PTB7-Th:PC71BM solar cells with solution processable MoOx.

c-MoOx: MoOx with conventional sol-gel method

11:45 AM EN12.08.09
Additive Solution Deposition of Multi-Layered Semiconducting Polymer Films for Design of Sophisticated Device Architectures
Tucker L. Murrey1, Kunping Guo2, Justin Mulvey1, Owen Lee1, Camila Cendra3, Zaira Bedolla-Valdez1, Alberto Salleo3, Jean-Francois Moulin4, Kunlun Hong5 and Adam J. Moule1; 1University of
Semiconducting polymers (SPs) have received enormous attention due to low-cost scalable solution-processing, and the potential for creating light-weight flexible electronic devices. Most working electronic devices consist of several layers of material, each having a specific optical and/or electronic function. One universal design constraint for complicated device architectures, like organic field effect transistors (OFETs), organic photovoltaics (OPVs) and red-green-blue organic light emitting diode (OLED) displays is that they require multiple components patterned laterally and vertically to operate. Currently, many of these components are comprised of non-flexible inorganic materials. In order to move towards flexible all organic electronic devices, there is a need to develop high precision vertical and lateral patterning methods that are compatible with solution processing techniques. This study demonstrates an additive solution process for depositing multiple layers of semiconducting polymer (SP) films by controlling film solubility with molecular dopants. During multi-layer deposition the bottom layers are exposed to a series of solvent environments that swell the SP films. We use neutron reflectometry (NR) to quantify the film thickness change and solvent content during solvent exposure in a single poly-3-hexylthiophene (P3HT) layer. The film thickness increases by 40-80% with exposure to good solvents. Four layer thin-films composed of alternating protonated and deuterated P3HT layers were additively coated from solution. NR measurements reveal high individual layer purity and that extensive solvent soaking induces no mixing between layers. This facile process enables additive layering of mutually soluble SP films and can be used to design novel electronic device architectures.

SESSION EN12.09: Light Management in Organic and Hybrid Systems
Session Chair: Monica Lira-Cantu
Wednesday Afternoon, December 4, 2019
Sheraton, 2nd Floor, Back Bay C

1:45 PM *EN12.09.01
From Light to Information—Indoor Light Harvesting Devices with Copper Coordination Complexes Marina Freitag; Uppsala University, Sweden

Efficient indoor light harvesters introduce a new design paradigm to Internet of Things (IoT) devices to maximize their ability to process, sense, and communicate data.(1) We here implement an adaptive wireless sensor node powered by dye-sensitized solar cells (DSCs) with an adapted sensitizer combination. Co-sensitizing organic dyes enhances the photovoltage of DSCs based on the CuII(tmby)2 redox couple up to 1080 mV and the power conversion efficiency above 11.5% under simulated sunlight. By adding optical density in the spectral region of 400 – 500 nm, the additional dye efficiently compensates for competitive absorption in the CuII(tmby)2 electrolyte. Cosensitized light harvesting systems maintain a photovoltage of 910 mV when lowering the illumination to 1000 lux of fluorescent light, with the power output over 100 µW cm-2 translating to an unprecedented conversion efficiency of 34.0% for ambient light. Subtle drying of the CuII(tmby)2 electrolyte in ambient environment leads to ‘Zombie’ solid-state DSCs with an amorphous solid hole transport material that maintain power output for high stability.(2–4)

We demonstrate a working example of a self-powered wireless ‘IoT’ device (light harvesting area 8 cm2) to power a microcontroller board with supercapacitor as energy buffer. Indoor light harvesters will lead to a new generation of energy-harvesting IoT.

Abundant Organic Semiconductor Catalysts for a Peroxide Clean Energy Cycle

Maciej Gryszel¹, Eva Miglbauer¹, Magdalena Warczak¹, Renata Rybakiewicz¹,² and Eric D. Glowacki¹,²
¹Linkoping University, Sweden; ²Warsaw University of Technology, Poland

Semiconductor-based catalysts can convert solar energy into chemical fuels such as hydrogen, hydrogen peroxide, or hydrocarbons produced via carbon dioxide reduction. Long overlooked due to stability concerns, some organic semiconductors have recently emerged as promising electrocatalysts and photocatalysts for operation in aqueous environments. We have found that organic semiconductors have, in general, a high selectivity for the two-electron reduction of oxygen to hydrogen peroxide. We find this occurs on numerous organic semiconductors and conducting polymers in a pH range from 1 to 12. As cathodic catalysts, organic semiconductors can demonstrate impressive stability. The possibilities of solar energy conversion into the high-energy molecule $\text{H}_2\text{O}_2$ enabling carbon-neutral energy storage in liquid form, in contrast to gaseous $\text{H}_2$, will be discussed. Finally, I will cover recent results on purely photocatalytic systems, where hydrogen peroxide is produced reductively via one- or two-electron mechanisms, while various substrates are oxidized, including water. Organic semiconductors have potential to become a powerful class of intrinsic catalysts, tunable by molecular design.

Structure-Property Studies of Organic Mixed Ionic/Electronic Conductors (OMIECs) in Aqueous Electrolytes

Jonathan Rivnay; Northwestern University, United States

Organic mixed ionic/electronic conductors have gained considerable interest in bioelectronics, power electronics, circuits and neuromorphic computing. These organic, often polymer based, semiconductors rely on a combination or ionic transport, electronic transport, and high volumetric charge storage capacity. Despite recent progress and a rapidly expanding library of new materials, the understanding of stability and transport/coupling of ionic and electronic carriers remain largely unexplored. We highlight recent synthetic and processing approaches used to tailor electrochemical device properties and stability, as well as new opportunities enabled by such advances. Our understanding of critical processes in electrochemical devices further requires us to study these materials in device-relevant conditions, fully considering the effects of ions and solvent on microstructure and transport. To this end, we report on recent efforts towards structure-property relations in high performance organic mixed conductors using ex-situ, in-situ, and operando scattering and spectroscopic techniques.

Boosting Direct X-Ray Detection Performance in Flexible Organic Thin Films by Small Molecules Tailoring

Ilaria Fratelli¹,², Andrea Ciavatti¹,², Laura Basiricò¹,², Stefano Lai¹, Piero Cosseddu¹, Annalisa Bonfiglio¹, John Anthony² and Beatrice Fraboni¹,²
¹University of Bologna, Department of Physics and Astronomy, Italy; ²National Institute for Nuclear Physics, Italy; ³University of Cagliari, Italy; ⁴University of Kentucky, Center for Applied Energy Research, United States

The development of large area ionizing radiation detection system is a crucial task in several areas of human society such as nuclear waste management, citizens security, radiotherapy or personal protection devices. Despite the excellent detecting performance exhibited by the inorganic materials (e.g. a-Se, CZT...), the increasing quest for flexible, portable, low cost and low power consumption sensors pushed the scientific community to look for alternative materials and technologies able to fulfill these new requirements. Electronic devices based on organic materials have already demonstrated to be a promising alternative to achieve a novel class of direct, flexible,
portable and low-cost ionizing radiation detectors [1][2]. In particular, the excellent direct X-ray detection performance exhibited by solution-processed flexible organic thin film transistors (OTFTs) based on 100 nm thick microcrystalline (e.g. 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene)) active layer has been recently reported [3][4]. This class of detectors exhibits the highest sensitivity to the ionizing radiation among the other polymeric devices thanks to a photoconductive gain mechanism. This effect is based on the role of minority carrier trap states and it leads to an inner amplification of the photocurrent induced by the high-energy ionizing radiation. However, in organic thin film detectors high-energy photon absorption is challenging because of the small active volume and the small cross section of interaction between radiation and low-Z elements of organic materials. In order to enhance the radiation detection performance of this novel class of organic sensors, different strategies exist.

One possibility could be the optimization of the photoconductive gain effect by increasing the density of minority carrier trap states, e.g. varying the morphology of the organic films and the interfaces of the stacked electronic devices. An alternative approach is to increase the radiation capture cross section by tuning the organic material properties through small molecule tailoring, i.e. by means of the addition of high-Z atoms into the basic molecular structure of the material. In detail, by synthesizing new solution-processable organic molecules derived from TIPS-pentacene and 2,8-difluoro-5,11-bis(triethylsilyl ethynyl)anthradithiophene (diF-TES-ADT), with Ge-substitution in place of the Si atoms, we demonstrate boosted X-ray detection performance, reaching higher sensitivity values (up to $9\times10^5 \mu C \text{ Gy}^{-1} \text{ cm}^{-3}$) and better charge transport, with respect to TIPS-pentacene-based detectors [5].

4:15 PM EN12.10.03
Autonomic Self-Healing of Conducting Polymer Films
Yang Li, Xinda Li, Shiming Zhang and Fabio Cicoira;
Ecole Polytechnique de Montreal, Canada

The recently-discovered water-enabled self-healing ability of conducting polymer polyethylenedioxythiophene doped with polystyrene sulfonate (PEDOT:PSS) makes it a candidate for healable electronics. A wetted PEDOT:PSS film can transform into an autonomic healable conductor, but its autonomic healing ability disappears after the water evaporates. In this work, we reveal an eternal autonomic electrically self-healable conductor through the addition of polyethylene glycol (PEG), demonstrating a fast healing response time and high healing efficiency. We also exhibit that the addition of glycerol can further enhance the conductivity while retaining the autonomic healing behavior. We performed systematic experiments to investigate and explain the underlying mechanisms of autonomic self-healing behavior of PEDOT: PSS films. This work provides a simple method to realize an autonomic healable conductor and paves the way for developing PEDOT:PSS based self-healing electronics for flexible and stretchable bioelectronic applications.

References

4:30 PM EN12.10.04
Optical Study of PEDOT:PSS Doped with an Ionic Liquid
Hideo Kishida, Tatsuki Maeda, Yuto Nakamura and Takeshi Koyama;
Nagoya University, Japan

The electric conduction in poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is significantly affected and controlled by the morphology of the polymers [1]. The clarification of the electronic states governing the electric conduction is an important issue; the electronic state of the PEDOT:PSS can be probed by not only infrared spectroscopy but also terahertz spectroscopy [2] and time-resolved photoluminescence measurements [3]. In this study, we control the electronic states of the PEDOT:PSS with an ionic liquid and observe the change of the electronic states by Raman scattering spectroscopy.

PEDOT:PSS films were fabricated on ITO/CaF2 substrates. We put an ionic liquid on the PEDOT:PSS films. Between the electrode under the PEDOT:PSS film and another electrode on the same substrate, we applied voltage and controlled the doped state. The change in the electronic states was monitored with not only infrared absorption bands but also the broad structure in the Raman scattering spectra. The detail of this broad Raman structure will be discussed in comparison with the electronic Raman scattering signals observed in an organic complex $\alpha$-(BEDT-
Reduced graphene oxide (rGO) reduced by functionalized hydrazine from graphene oxide (GO) is a promising alternative material to PEDOT:PSS as hole transport layer (HTL) because rGO based organic solar cells (OSCs) show much better device stability than PEDOT:PSS based OSCs with similar device performance. However, to date, it has not been systematically investigated about effect of sheet size of rGO on the hole transporting properties. In addition, sheet size of rGO can affect the thin film uniformity as well as the electrical properties of the HTL. The thin film uniformity of HTL has a considerable influence on the device performance in inverted OSCs, because HTLs directly contact with the top metals. Therefore, in this study, we evaluate the size effect of rGO sheets on their thin film uniformity and hole transporting properties. In atomic force microscos analysis, the root mean square roughness of rGO films was decreased from 5.7 to 3.2 nm as the size of the sheets decreased meaning that the film uniformity of rGOs was improved. The hole transporting properties of rGOs having different sheets size were investigated by analysis of J-V characteristics in the light and dark, Jph-Veff curves, the plots of Jsc and Voc with respect to the light intensity, etc. The small size rGO based HTL, which have more uniform film than large size rGO based HTL, show the more efficient hole extraction and electron blocking ability due to the improved interface contact with active layer and top metal (Ag), resulting in suppressed carrier recombination at the interfaces. Thus, a higher power conversion efficiency of 9.07%, corresponding to an approximately 20% efficiency improvement compared with that of a large size rGO HTL (7.65%), was achieved by small size rGO HTL.

EN12.11.02
Improvement of Solar Cell Performance by Crystal Phase Transfer for Zinc Phthalocyanine-Based Photovoltaic Cells Tetsuya Taima, Takafumi Horikawa, Md. Shahiduzzaman, Makoto Karakawa and Koshin Takahashi; Kanazawa University, Japan

The p-type organic molecules of zinc phthalocyanine (ZnPc) adapt a standing-up (edge-on) molecular orientation on the indium-tin-oxide (ITO) substrate. On copper iodide (Cul) substrates, ZnPc molecules take on a molecular orientation lying flat on the substrate (flat-on) owing to π−d orbital interactions between the ZnPc molecules and the Cul. Earlier, Taima et al., (Appl. Phys. Lett., 2012, 100, 233302) reported that flat-on molecular orientation of the ZnPc films enhance the light absorption coefficient and charge carriers transport, resulted improved solar cell performance. When edge-on ZnPc films was heated at 200 °C, crystal phase changes from metastable α-ZnPc phase to stable β-ZnPhc phase, resulted the long wavelength shift of the light absorption region and enhance in absorption coefficient. (J Mater Sci: Mater Electron, 2008, 19, 482486) Herein, we report an efficient approach to further increase of the light absorption by changing crystal phase from α-ZnPc phase to β-ZnPc phase through the heating of ZnPc on Cul substrate, followed by enhancing the performance of organic photovoltaic devices. We reveal that that when the ZnPc films was adapted edge-on orientation on the ITO substrate, the long wavelength was shifted owing to the phase transition from α-ZnPc to β-ZnPc. The phase transition of the ZnPc film improved the quantum
efficiency near 650 nm to 750 nm. The improvement of the power conversion efficiency for the resultant solar cell is mainly caused by an increase in short circuit current \((J_{sc})\) from 2.56 to 3.50 mA/cm². These improvements are caused by the \(\alpha\)-phase to \(\beta\)-phase change of ZnPc on the ITO, whose molecular orientation is the edge-on orientation. In contrast, as the ZnPc films was altered flat-on orientation on the CuI substrate, the long wavelength was further shifted in terms of the phase change from \(\alpha\)-ZnPc to \(\beta\)-ZnPc. In addition, molecular stacking of the ZnPc/CuI film yields a higher light absorption coefficient. From these findings, we expect higher carrier transport efficiency and light absorption coefficient could be attributed to the higher \(J_{sc}\), fill factor and open circuit voltage of the resultant solar cells.

EN12.11.03
Decoupling Charge Transfer State Energy and Driving Force in Organic Photovoltaic Devices Featuring Non-Fullerene Acceptors Kaila M. Yallum1, Philipp Krauspe1, Koen Vandewal2 and Natalie Banerji1; 1Universität Bern, Switzerland; 2Hasselt University, Belgium

A steady-state photoconductivity setup capable of taking sensitive external quantum efficiency (sEQE) measurements was constructed. This experimental setup records sEQE spectra used in determining the Charge Transfer (CT) state energy, the \(S_1\) energy of the system, and the DE between the two, the driving force.

These energy-determining steps have thus far been used in two studies. One study in which electron and hole transfer rates were assessed in different Polymer:Non-Fullerene Acceptor (NFA) blends as a result of varying driving force. The driving forces were varied by using different donor polymers (P3HT, PCDT-BT, PBTTT, J61), with the same NFA (m-ITIC), and determined in the EQE setup. Further work with these systems went on to show that charge transfer remained a sub-picosecond process with near zero driving force. This study dispels the commonly-held belief that there is a trade-off between high-lying CT states which allow for high open-circuit voltages and high driving force which allows for faster charge transfer rates.

In a second study, a Polymer:NFA series in which the donor polymer (P3HT) remained constant and the NFA was varied (ITIC, ITIC-4F, or ITIC-DM), was able to decouple the driving force and CT state energy. While the energy of the CT state varied, the driving force remained relatively constant. Further studies will probe the impact of CT state energy levels on organic photovoltaic performance independent of driving force. This study touches on the effects of CT state energy and how this contributes to increasing open-circuit voltages and over-all power conversion efficiencies.

EN12.11.04
PEDOT/BBL Blend—A New Bipolar Conducting Material Sarbani Ghosh and Igor Zozoulenko; Linköping University, Sweden

There is a growing interest in organic electronic devices based on conducting polymers. Most of the conducting polymers show unipolar conductivity based on either p-type (hole transport) or n-type (electron transport). Organic electronic devices e.g., organic light-emitting diodes (OLEDs), organic field effect transistor (OFETs), organic solar cells (OSCs) are functioned by both the p-type and n-type materials. Although there are a lot of polymers which are being used as the p-type materials, due to the stability issue of the n-type polymers, the usual n-type materials are generally limited to the small molecules e.g., fullerene and their derivatives. However, the benzimidazo-benzophenanthroline ladder polymer (BBL) is a stable polymer which has an electron-affinity (~4.0 eV) in the same range of fullerene. Polymer-blend made of both n-type and p-type polymers can act as a bipolar conducting material by showing both the hole transport and electron transport properties.

Here, in this study we consider a polymer blend system consists of poly(3,4-ethylenedioxythiophene) (PEDOT) as a p-type material and BBL as an n-type material where the two polymers are stacked by pi-pi interaction and electrostatic potential. We studied the electronic structures, optical properties, excitation energy transfer of the PEDOT/BBL blend material using ground-state and time-dependent density functional theory.

We found that the addition of positive charges in the system leads ~90% of positive charges to be collected by PEDOT. On the other hand, upon addition of negative charges, ~90% negative charges are collected by BBL. In this way, the material shows an excellent charge collection property. Therefore, this system can efficiently transport the positive and negative charges towards the opposite electrodes in an electronic device e.g., OLED, OSC. The
Electronic structure calculation shows the unoccupied states are localized on the BBL chain and occupied states are localized on the PEDOT chain. Moreover, the ionization potential of PEDOT is close to the electron affinity of the BBL. Thus, BBL as an acceptor material could be a good counterpart of donor PEDOT to replace the polymer/fullerene OSC to all polymer OSC. Oxidation and reduction of the blend material show oxidized PEDOT and reduced BBL, respectively, by forming positive polarons in PEDOT and negative polarons in BBL. The photo-induced electronic energy transfer calculation shows that the material can also be used as a hetero-junction in organic solar cells to dissociate the photo-induced exciton and consecutively, to transfer the free charges to the counter electrodes. The strong electronic coupling between the photo-excited PEDOT and charge-transferred states indicate an enhanced charge separation process. The obtained electronic coupling value of the PEDOT/BBL blend material is higher than the usual average coupling value of the available materials (e.g., polymer/fullerene).

In summary, this study shows BBL has the capability to replace the conventional n-type (acceptor) material, fullerene in order to fabricate all-polymer electronic devices. The PEDOT/BBL blend is a new bipolar conducting polymeric material which can efficiently be used in many energy application e.g., OLEDs, OFETs and OSCs.

**EN12.11.05**
**Epitaxial Growth of Organic Semiconductor Crystals on Charge-Density-Controlled Graphene**

Nguyen Ngan Nguyen, Hyo Chan Lee and Kilwon Cho; Pohang University of Science and Technology, Korea (the Republic of)

Graphene with its sp2 hybridized surface can function as a growth template for novel nano-microstructure, especially for organic semiconductors. We find that the doping tunability and atomic thickness of graphene allow the organic semiconductor ad-molecules on its surface to “feel” and interact with the doping charge carriers. Such interactions vary the molecular surface dynamics and thus the assembly and growth of the organic semiconductor crystals. For high quality organic semiconductor thin films and clean heterostructures of semiconductor-graphene, we unravel a rule-of-thumb that is tuning graphene’s electronic structure so that the interactions between graphene and ad-molecules are loose enough for free motion of these ad-molecules. The thin films grown at such conditions not only provide favorable pathways for both charge-carriers and exciton transports but form nearly ideal Schottky interface with graphene, both important for organic electronics.

**EN12.11.06**
**Can Zero Gravity Give Us a Better Understanding of Morphology Formation in the Active Layer?**

Ishita Jalan1, Jan van Stam1, Leif Ericsson1, Ellen Moons1, Sandra Hultmark2, Christian Muller2 and Benoît Haut3; 1Karlstad University, Sweden; 2Chalmers University of Technology, Sweden; 3Université libre de Bruxelles, Belgium

Solution-processed polymer bulk heterojunction organic photovoltaic (BHJ-OPV) devices have gained serious attention during the last decade. They are one of the leading next generation photovoltaic technologies for low cost power production [1]. The active layer of a polymer solar cell consists of a thin solid film of an electron donor blended with an electron acceptor. The morphology of the active layer is one of the important factors for the solar cell performance. To control the morphology, one needs to understand the morphology formation on a molecular level.

The active layer of these solar cells is often produced by spincoating in the research laboratory, while dip-coating is an alternative that offers better control over the process parameters. Some of the most important parameters in dip-coating are the viscous drag, the gravitational force, and the capillary force. The viscous drag makes the liquid go upward with the substrate upon withdrawal. This force is proportional to the liquid viscosity and the withdrawal speed. Gravity causes the solution to move downwards.

To gain a deeper knowledge on the morphology formation in the active layer, being a consequence of the partial phase separation that occurs during the evaporation of the solvent [2-5]. In order to slow down the phase separation and, hence, get a better picture of the early stages of this process, we have chosen to prepare thin active layer films under microgravity conditions [6]. Under microgravity conditions, Marangoni flow will be the dominant source of convection during solvent drying. Here we try to understand the effects of gravity on the film morphology for system for co-polymer (TQ1) and a fullerene derivative (PC70BM). The ratio between the donor and the acceptor, as well as the processing solvent, were varied. Films prepared at microgravity conditions and at Earth conditions are compared to each other. We have chosen two commonly used solvents, i.e., chlorobenzene (CB) and ortho-dichlorobenzene (oDCB) and their fluorinated counterparts fluorobenzene and ortho-difluorobenzene (FB and oDFB, respectively). The choice of
solvents allows a comparison of the influence of the solvents’ density, viscosity, and surface tension on the morphology. From our experiments, there is evidence for differences in structure between thin films at 1g and those prepared at microgravity conditions.

References

EN12.11.07
Polyfuran-Based Chemical Sensors—Reactivity Analysis via Fukui Indexes and Reactive Molecular Dynamics
Leonardo G. Lascane1, Eliezer F. Oliveira2 and Augusto Batagin-Neto1; 1University of São Paulo State–UNESP, Brazil; 2State University of Campinas, Brazil

Organic polymers are promising materials for the design of active layers of chemical sensors. In this context, polyfuran (PF) derivatives have not been extensively investigated, mainly due to typical drawbacks that have been recently overcome by using appropriate lateral substituents [1]. In the present study we employ electronic structure calculations (based on DFT approach) and molecular dynamics (MD) simulations (based on ReaxFF reactive force field) to evaluate the reactivity of branched PF derivatives and identify promising systems for chemical sensing. Condensed-to-atoms Fukui indexes (CAFI) were employed to identify the most reactive sites on the oligomers structure. The chemical sensing abilities of the most promising systems were evaluated via MD simulations in the presence of distinct gaseous analytes. The results indicate the derivatives PF-CCH and PF-NO2 (i.e. CCH and NO2 as side groups) as the most promising systems for chemical sensor applications, which present higher reactivity on the most accessible sites. An interesting correspondence between DFT and MD results was also identified, suggesting the plausibility of using CAFI parameters for the identification of improved materials for chemical sensors.

Reference:

EN12.11.08
Molecular-Reductant-Induced Control of a Graphene–Organic Interface for Electron Injection
Fengyu Zhang1, Chen Klein2, Elena Longhi2, Stephen Barlow3, Seth R. Marder3, Gabby Sarusi2 and Antoine Kahn1; 1Princeton University, United States; 2Ben-Gurion University of the Negev, Israel; 3Georgia Institute of Technology, United States

The outstanding mechanical properties and transparency of graphene make it promising as transparent conducting electrode for flexible organic light-emitting diodes (OLEDs). However, its work function (WF ∼4.5 eV), like that of ITO, is relatively high and typically unsuitable for use as a cathode in OLEDs. Surface doping of graphene by adsorption of reducing organic and metal-organic molecules has been shown to be able to tune the electronic properties of graphene without forming covalent bonds.[1-2] Such molecular doping method preserves the structure of the graphene lattice and is less perturbing than substitutional doping or alkali metal deposition.[1,3] Here we present a study and application[4] of surface n-doping of graphene with the molecular reductant (pentamethylcyclopentadienyl) (1,3,5-trimethylbenzene) ruthenium dimer ([RuCp*Mes]2).[5] Photoemission spectroscopy, contact-potential measurements, and Hall-effect measurements confirm the dopant-induced changes in the electronic properties of the graphene layer. The graphene WF is reduced from 4.5 eV to a remarkably low value of 2.6 eV upon deposition of 1 nm of the molecular reductant [RuCp*Mes]2 and UV photo-activation, which enhances the electron-donation
The majority carriers of graphene switch from holes to electrons upon doping and the sheet resistance is reduced by 25%, despite the moderate decrease in carrier mobility. Photoemission spectroscopy and carrier-transport measurements are combined to investigate doping-induced changes in the electronic structure of the interface between graphene and phenyldi(pyren-2-yl)phosphine oxide (POPy2), a low electron-affinity (2.2 eV) electron-transport material used in OLEDs. Surface doping with 1–2 nm of [RuCp*Mes]2 reduces the electron injection barrier between graphene and POPy2 by more than 1 eV, enhancing electron injection into POPy2 by several orders of magnitude. Graphene/POPy2/Al diodes with doped graphene cathodes exhibit reasonable stability in both nitrogen and air. This investigation allows a better understanding of the interface between graphene and an organic transport layer. These results represent a significant step toward the use of graphene as a transparent cathode for organic devices in general and for OLEDs in particular.


EN12.11.09
Charge Transfer States and Reorganization Energies of Organic Solar Cells as a Function of Electron Donor Concentration Anna Jungbluth, Pascal Kaienburg, Andreas Lauritzen and Moritz Riede; University of Oxford, United Kingdom

Organic semiconductors have attracted interest over the last decades for their easily tunable optoelectronic properties. Organic solar cells, which utilize organic electron donor and acceptor materials to convert sunlight into electricity, have proven their potential as valuable additions to the field of photovoltaics for their low cost and lightweight. Currently, one of the main limitations of organic solar cells are the relatively large voltage losses of often more than 600 meV between the optical gap and the open-circuit voltage due to radiative and nonradiative recombination. In addition, driving forces required to separate strongly bound excitons are a major contribution to the large overall voltage losses. To fully understand free energy losses in organic solar cells, the influence of donor and acceptor energy levels and microstructure contributions to the charge transfer state need to be understood.

In this work we investigate voltage losses as a function of donor energy levels and donor concentration. We use vacuum deposition techniques to pair the commonly used electron acceptor C60 with Zinc phthalocyanine (ZnPc) or its fluorinated derivatives (F3ZnPc, F5ZnPc, F16ZnPc) in a bulk heterojunction. Fluorination of ZnPc has been shown to simultaneously shift the HOMO and LUMO energy levels away from vacuum, thereby keeping the energy of the first allowed singlet transition approximately constant, but directly affecting the charge transfer state energy of the donor:acceptor system. The concentration of donor molecules is sequentially varied from the “dilute” case of 5% donor molecules in 95% acceptor molecules to a 1:1 ratio of donor:acceptor.

Sensitive external quantum efficiency and sensitive electroluminescence measurements are performed to determine the energy of the charge transfer state and reorganization energy as a function of donor energy levels and donor concentration. The effect of changing charge transfer state energies is correlated with the performance and open-circuit voltage of the devices obtained through current-voltage measurements. Our measurements are further enhanced through X-ray measurements of the microstructure of the active layers to obtain a full picture of the effect of changing energy levels and donor concentration on the device performance.

EN12.11.10
Singlet Fission in Combinatorial Diketopyrrolopyrrole–Rylene Supramolecular Films Andrew Levine¹, Christoph Schierl², Bettina S. Basel², Mehroz Ahmed³, Braden Camargo³, Dirk M. Guldi² and Adam B. Braunschweig³; ¹City University of New York, United States; ²Friedrich-Alexander University, Germany

Two diketopyrrolopyrroles (DPPs) and three rylenes (NDI, dPyr PDI, and dEO PDI) were combined to form six
hierarchical superstructures that assemble as a result of orthogonal H-bonding and π−π stacking. The individual components and the DPP–NDI as well as DPP–PDI pairs were cast into films, and their superstructures were interrogated by electron microscopy and advanced spectroscopy. All six superstructures feature different geometries, causing subtle changes in the solid-state packing of the DPPs. Changes in inter-DPP stacking that are scaffolded by the adjacent rylenes have a subtle impact on both the excited-state dynamics and on activating new pathways such as singlet fission (SF). Our studies demonstrate the unique benefits of combinatorial supramolecular assembly in exploring the impact of structure on advanced light management in the form of SF to afford triplet quantum yields, which are as high as 65% for a correlated pair of triplets and 15% for an uncorrelated pair of triplets.

**EN12.11.12**

**n-Type Conjugated Small Molecule Organic Semiconductor for Device Applications** Seongdae Kang, João Soares and Manisha Gupta; University of Alberta, Canada

Organic semiconductors are amongst the most important materials in the field of organic electronics. They are used for various devices applications like transistors and photovoltaics. The hole-transporting p-type organic semiconductor is most commonly used for these applications, while electron-transporting n-type organic semiconductors lag far behind because they suffer from moisture and air instability, as well as low electron mobility.¹

In this research, we synthesized a small-molecule n-type organic semiconductor, 2,6-Dibromo-N,N’-bis(2-ethoxyethyl)-2-(2-(2-methoxyethoxy)ethoxy)acetate)-1,4,5,8-naphthalenetetraoxycarboxylicdiamide, (gNDI-Br₂). Due to the redox ability of gNDI-Br₂, it is an electroactive material and can be utilized for organic electrochemical transistors (OECTs). OECTs have a channel material which is an electroactive organic semiconductor and its conductivity changes by the influx of ions from the electrolyte. Reduction and oxidation reactions with metal ions in electrolytes such as sodium or potassium ions occurs at the tetracarboxylic oxygen atoms in gNDI-Br₂ molecules. Due to the conjugated structure of this organic semiconductor, it reacts electrochemically and maintains its structure with the change in its conductivity. In addition, gNDI-Br₂ is easily solution processable because it is soluble in common organic solvents, such as chloroform, due to the ethylene glycol side chains attached to the NDI. Furthermore, these ethylene glycol side chains increase the free volume among the semiconducting molecules, providing gaps for the permeation of the metal ions.

The advantage of this gNDI-Br₂ small-molecule organic semiconductor is the improvement of its electrical property due to its ordered structure. It has less distorted structure compared to semiconducting polymers such as p(gNDI-gT2)³ or poly(benzimidazobenzophenanthroline) (BBL)⁴. Due to the coplanar structure of gNDI-Br₂, it allows for a more organized molecular arrangement, unlike polymeric n-type semiconductors. On account of this more orderly orientation, gNDI-Br₂ shows better electron mobility than previously reported n-type organic semiconductors, which enhances device performance. We will present the material, electrical and electrochemical properties of gNDI-Br₂ based on the different techniques like Electrospray (ESI-TOF) mass spectrometry, Nuclear magnetic resonance spectroscopy (NMR), X-ray diffraction (XRD), Atomic force microscopy (AFM), Scanning electron microscopy (SEM), and Electrochemical cyclic voltammetry (ECV).

**Reference**


**EN12.11.14**

**Green-Solvent Processable Semiconducting Polymers Applicable in Dopant-Free Perovskite and Polymer Solar Cells—Molecular Weights and Thermal Stability** Sang Ah Park, Dasol Chung, Seyeong Lim and Taiho Park; Pohang University of Science and Technology, Korea (the Republic of)
In this study, we firstly investigate the effects of the molecular weight (MW) of a green-solvent processable semiconducting polymer (asy-PBTBDT) on photovoltaic performance and thermal stability of the devices. The asy-PBTBDT with high MW (132 kDa) has high μ values (4.91 × 10^{-3} cm² V⁻¹ s⁻¹ without dopants and 5.77 × 10^{-3} cm² V⁻¹ s⁻¹ with dopants) as a result of an increase in π–π stacking with higher MW than low MW asy-PBTBDTs (27 and 8 kDa). The high MW asy-PBTBDT with high μ achieves the highest power conversion efficiencies of 18.2% and 20.0% for the non-doped and doped states in PerSCs, respectively, and 5.7% in eco-friendly processed PSCs. Moreover, as the MW of asy-PBTBDT increases, the glass transition temperature increases, indicating an effective decrease of the thermally-induced morphological degradation in the photovoltaic devices. Likewise, an increase in the chain density along with MW induces the good robustness against humidity and oxygen. This material has important industrial significances because of its environmental processability, reproducibility, stability and efficiency of edible solvents.

Daehwan Lee, Taewan Kim, Yelim Choi and Taiho Park; Pohang University of Science and Technology, Korea (the Republic of)

Morphologies and optoelectronic/mechanical properties of semiconducting polymers are highly affected by polymer backbone configuration. In this study, thiophene units are introduced into the main backbone chain of semiconducting polymer in either a regular (PffBT-T4) or a random (PffBT-RT4) copolymerization to compare the performance of which semiconducting polymers are suitable in developing more efficient and flexible polymer solar cells. The unit composition ratio of the main chain is same, so both polymers show very similar energy levels. However, PffBT-RT4 has lower crystallinity than PffBT-T4 due to its random arrangement. As a result of the microstructure analysis, PffBT-RT4 shows π-π stacking distance shorter than PffBT-T4. Therefore, since short distance benefits in charge transport, PffBT-RT4 shows higher space-charge-limited current mobility, and has a higher power conversion efficiency (PCE; 8.84%) than PffBT-T4 (7.25%). In addition, the PffBT-RT4 shows good performance in green solvent without additives (7.23%). Moreover, PffBT-RT4 maintains stable efficiency even after bending cycle, compared to PffBT-T4. Therefore, this study demonstrates that the random arrangement is a promising donor-acceptor based semiconducting polymer design strategy for efficient, flexible and green solvent processable polymer solar cells.

Effects of Energetically and Spatially Non-Uniform Distribution of Molecular Energy Levels on Open-Circuit Voltage of Organic Solar Cells
Hansol Lee, Segyo Han, Kyu C. Song, Jinhyeok Choi and Kilwon Cho; POSTECH, Korea (the Republic of)

Here, the effects of non-uniform energetic and spatial distributions of molecular electronic states in active layer on the open-circuit voltage (V_{oc}) of organic solar cells are investigated. Model devices are fabricated using active layers that consist of two sublayers. The sublayers have different donor-acceptor blend compositions. The different compositions offer large change in molecular energy levels of the donor and the acceptor materials. Large difference in the V_{oc} is observed depending on the thicknesses and the stacking order of the sublayers. Optical and electrical analyses suggest that the V_{oc} in these devices is not determined by the energy levels of the spatial region where the photocurrent is generated, and that the V_{oc} is not determined by the relative amount of different CT states within the active layer. Instead, we suggested that the energy levels of the regions where the electrons and holes are populated dominantly are important in determining the V_{oc}. This study would provide a new insight in deep understanding of the origin of V_{oc} in organic solar cells, especially for the systems that have spatial variation of energy levels of organic semiconductors within the active layer.

Facile Tuning Method of Crystallinity and Alignment for Organic Semiconductor Layer through Solution Shearing Process
Kibeom Nam¹, Xinlin Li², Se Hyun Kim³ and Dong Yun Lee⁴; Kyungpook National University, Korea (the Republic of); ²Qingdao University, China; ³Yeungnam University, Korea (the Republic of)

In this study, we introduce an evaporative assembly method which can control the growth and align of the
crystalline material to achieve high-quality organic semiconductor patterns via one-step printing process. Organic semiconductor patterns that have a high crystallinity property and its uniform alignment are essential to realizing their application into the high-performance organic field-effect transistors (OFETs). Organic materials have flexible and lightweight properties compared to metallic compounds. Moreover, the recent development of electrical performances emphasized its importance for next-generation electric devices. However, there are obstacles to pattern crystals into large-area, print circuit cost-effectively.

Various patterning methods (e.g., dip coating, slot-die coating, blade coating, inkjet, and electrohydrodynamic jet printing) have been studied, however, there are some problems. In the case of dip coating, it is hard to make highly integrated patterns because the entire substrate is immersed in a semiconductor solution. Lithography needs tons of steps until patterns are made in place and it is hard to control the direction of the crystal. Inkjet and electrohydrodynamic jet printing show slow patterning speed. Flow coating system fulfills requirements i) simplification of patterning steps, ii) accuracy of patterning on the desired position, iii) speed for patterning process and iv) improving crystallinity and alignment of crystal over the large area.

A flow coating technique is a kind of an evaporative self-assembly method. This versatile method utilized the phenomenon of the “coffee ring effect” coupled to the confined convective flow with a controlled stick-slip motion. When the liquid is placed on the solid substrate, the different evaporation rate between the edge and center of the droplet induces migration of solution to the three-phase contact line and deposits solute. Then, intended stick-slip motions determined the distance and width of patterns. Furthermore, flow coating confines the evaporation of the solvent at the solution guiding blade and it gives shear stress on the solution. It induces one-directional coffee ring effect along the blade and the given shear stress determines the direction and morphology of patterns. Different amount of shear stress was given under the various speed of flow coater. It enhances the directional crystallization of the semiconducting layer and electrical properties.

In this study, 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-PEN) was chosen as a crystalline organic semiconductor and deposited by the solution shearing process. The relationships between shearing of the solution and characteristic property of crystal were determined with p-OM, pUV, GIWAX, and NEXAFS. One-directional solution shearing caused a crystal aligned morphology, anisotropic pUV absorption spectrums. The intensity of crystal was differed by coating speed and verified its tendency through X-ray diffraction. Furthermore, flow coating equipment is controlled by the computer system and each condition can be tuned properly. It is possible that adjusting coating condition in demand during the process with any kind of materials. Therefore, this study is essential for cost-effective printing techniques to achieve high-performance OFETs with high-quality organic semiconducting crystals.

EN12.11.18
Beta-Ray Detectors Using Organic Photodiodes with a Thick Organic Semiconductor Layer Isao Takasu, Atsushi Wada, Kohei Nakayama, Yuko Nomura, Fumihiko Aiga, Sara Yoshio, Hyangmi Jung and Rei Hasegawa; Toshiba Corporation, Japan

We report on the development of beta-ray detectors using organic photodiodes (OPD). Beta-ray detectors are used for surface contamination monitoring at nuclear power plants and similar facilities. Various organic radiation detectors for x-ray have been reported but few examples of radiation detectors for charged particles (alpha and beta particles) have been reported. OPDs are advantageous for beta-ray detection in view of their high beta-gamma ray detectability ratios, since organic semiconductors are composed of light elements and therefore expected to show low gamma-ray detection efficiency. We examined indirect- and direct-conversion organic beta-ray detectors and observed Sr-90 and Co-60 beta particles with the respective detectors and a readout circuit. The indirect conversion detectors are composed of an OPD and a scintillator, which converts beta rays into green light. To realize direct-conversion radiation detectors, the organic semiconductor layer must be much thicker than that of conventional organic photodiodes. Therefore, by forming an organic semiconductor layer of 50 μm thickness, we fabricated OPDs with the following structure: ITO electrode/ buffer layer/ P3HT:PCBM/ Al electrode. We also examined photoconductive properties of the OPDs. The OPD with the 50 μm-thick organic semiconductor layer showed high external quantum efficiency of more than 60% at 530 nm wavelength. In addition, molecular doping in the thick organic semiconductor layer brought about a remarkable lowering of the rising voltage of the photocurrent. In the presentation, we will discuss the relationship between the properties of the radiation detection and the photoconductivity of the OPDs.

EN12.11.19
Molecular Doping by Solid-State Diffusion for Enhancing Charge Injection Properties in Organic Field-
Doping has been a key topic in organic electronics since the demonstration of a metallic conductivity in doped pi-conjugated polymers. However, it has been difficult to prevent dopant-induced structural and energetic disorder, while maintaining a high conductivity. We have developed an efficient doping method based on solid-state diffusion of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) in poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) which exhibited a high conductivity of 200 S/cm and one of the highest Hall mobilities for conducting polymers [1]. The observed coherent charge transport in the doped PBTTT could be attributed to a preserved microstructural order upon doping. We have recently employed this doping method to enhance charge injection properties in organic field-effect transistors (FETs) [2]. A selective contact doping of bottom-gated PBTTT FETs by solid-state diffusion of F4-TCNQ achieved a significantly lower contact resistance. In addition, a post-doping treatment on contact-doped PBTTT FETs was shown to be an effective way of improving the device stability. Furthermore, an extra degree of freedom in the choice of gate dielectric material with the bottom-gate structure enabled a low-voltage operation in our contact-doped PBTTT FETs, demonstrating a potential for designing stable and low-power organic electronic devices by utilizing doping of conjugated polymers.

References:


EN12.11.21
Tailoring Functionality of Metal-Organic Frameworks for Optoelectronics by Ab Initio Calculations Mariana Kozłowska, Ritesh Haldar, Marjan Krstić, Zainab Hassan, Shahriar Heidrich, Xiaojing Liu, Lars Heinke, Christof Wöll and Wolfgang Wenzel; Karlsruhe Institute of Technology (KIT), Germany

Properties of organic semiconductors are highly dependent on the chemical composition, the manner of the molecular organization and the electronic properties of the individual components. At the same time, the intermolecular electronic communication among neighboring molecules defines the photoinduced charge generation, separation and transport properties. Here, we design new, highly ordered organic semiconductor materials integrating the diverse organic molecules into surface-anchored metal-organic frameworks (SURMOFs). Even if metal-organic frameworks are known to be poor conducting materials, we show that their semiconducting properties can be significantly tuned due to the control of their nano/microscale material morphology and structure with the understanding of their physicochemical properties both by theory and experiment.

We use quantum mechanical calculations in the density functional theory formalism to investigate the photophysical properties and the mechanism of charge transport in the SURMOF materials made of anthracene, diphenylethynyl-anthracene, naphthalenediimide and porphyrin linkers. We calculate the transfer rates using the semi-classical Marcus theory approach based on the electronic coupling elements and the reorganization energies between the adjacent MOF linkers. Using the in-house developed ab initio method, we explain highly efficient excited-state transport properties of porphyrin SURMOF [1, 2] and predict the photoinduced charge transport in polycyclic aromatic hydrocarbon based MOF as a function of the type of organic linker. We show the reason of the improved conductivity as derived from the spatially ordered structure of a material [3] and confirm the charge transfer anisotropy through the detailed analysis of the transfer rates for electron and hole transport. Finally, we prove that ab initio calculations enable valuable predictions of new promising candidates for semiconducting organic materials made in spatially ordered fashion in the SURMOF. Our data demonstrates the feasibility of MOF-based crystal engineering approaches that can be universally applied to tailor the photophysical properties of organic semiconductor materials.

References:


EN12.11.22
Metal-Organic Frameworks (MOFs) with Improved Photoconductivity and Unprecedented Photoluminescent Quantum Yields

Marjan Krstić1, Mariana Kozłowska1, Xiaojing Liu2, Ritesh Haldar2, Qiang Zhang2,1, Antoine Mazel3, Michael Adams2, Fabrice Odobel3, Ian Howard2, Lars Heinke2, Wolfgang Wenzel1 and Christof Wöll2;
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Metal-organic frameworks are highly ordered structure nanoporous materials with many different properties which can be tailored. In this context, surface-anchored metal-organic frameworks (SURMOFs) are promising subclass of MOFs which offers appealing possibility to tune properties for each specific application. Here, we present recent results of such nanomaterials with focus on photovoltaic activity, photostability and charge transport as well as photoluminescence (PL).

One of the most promising tuning approach is integration of different organic linkers into MOFs with specific properties. Due to their large photoabsorption coefficients for visible light, porphyrin derivatives are widely used in light-harvesting applications, such as photovoltaics and photocatalysis. We use quantum mechanical calculations in order to explain highly efficient excited-state transport properties of porphyrin SURMOF with Pd-coordinated organic linkers [1]. The calculated transfer rates are consistent with experimentally obtained rates, which result in micron-range exciton diffusion length in this MOF. First principle calculations are also applied to understand mechanism of charge transport in Zn-coordinated porphyrin-containing SURMOFs with embedded fullerene molecules [2]. The improved photoconductivity is shown to be derived from the spatially continuous network of donor and acceptor domains in MOF material. Owing to the fact that the porphyrin properties can be tailored by advanced organic chemistry and MOF properties can be tuned for the specific applications, ab initio calculations enable valuable predictions of new promising candidates for light harvesting.

In molecular solids, the intense PL observed for solvated dye molecules is often suppressed by nonradiative decay processes introduced by excitonic coupling to adjacent chromophores. To achieve unprecedented PL quantum yields for MOF crystalline NDI-based materials through predictive crystal engineering and tuning of excitonic coupling we have developed a strategy to avoid this undesirable PL quenching by optimizing the chromophore packing [3]. We integrated the photoactive compounds into metal-organic frameworks (MOFs) and tuned the molecular alignment by introducing adjustable “steric control units” (SCUs). We determined the optimal alignment of core-substituted naphthalenediimides (cNDIs) to yield highly emissive J-aggregates by a computational analysis. Then, we created a large library of handle-equipped MOF chromophoric linkers and computationally screened for the best SCUs. A thorough photophysical characterization confirmed the formation of J-aggregates with bright green emission, with unprecedented photoluminescent quantum yields for crystalline NDI-based MOF materials. This data demonstrates the viability of MOF-based crystal engineering approaches that can be universally applied to tailor the photophysical properties of organic crystalline MOF materials.

References:

EN12.11.23
Influence of Morphology on the Density of Charge-Transfer States in Organic Donor/Acceptor Blends

Thomas Zeche1, Theresa Linderl1, Alexander J. Hofmann1, Thomas Schröther1, Tomoya Sato2, Kohei Shimizu2, Hisao Ishii2 and Wolfgang Bruetting1; 1University of Augsburg, Germany; 2Chiba University, Japan

Organic small molecule solar cells are used as a test bed to investigate the influence of film morphology on the density of charge-transfer (CT) states. CT states are considered as precursors for charge generation and their energy ($E_{CT}$) as the upper limit for the open-circuit voltage ($V_{OC}$) in organic donor/acceptor solar cells. In this study the
morphological influence of using a crystalline donor diindenoperylene (DIP) versus an amorphous donor
tetraphenyldibezoperiflanthene (DBP) with almost identical ionization energy is investigated. As acceptor material
the widely used fullerene $C_{60}$ is used.

By combining electrical measurements with optical spectroscopy and low-energy ultraviolet photoelectron
spectroscopy (LE-UPS) with different excitation energies, a comprehensive picture is obtained that describes how
morphology and the connected density of states (DOS) influence the device performance and the spectroscopic
signature of CT states. Especially for the crystalline donor material DIP strong exponential tail states reaching far
into the gap are observed in the UPS spectra, which can be related to the presence of grain boundaries. A voltage
dependent filling of these states is identified as the origin of a blue shift of the electroluminescence spectra with
increasing applied voltage.

Different approaches to the description of the reduced electroluminescence (EL) and reduced external quantum
efficiency (EQE) spectra, as proposed by Vandewal, Burke and Kahle, are compared. This is done to verify the
necessity of static disorder in the description of CT emission and absorption spectra of organic solar cells. Despite
the fact that both donors yield almost identical $E_{CT}$ (and, thus, the same open-circuit voltage) the Stokes shift
between EL and EQE spectra and, concomitantly, the width of the CT DOS varies by more than a factor of 2. We
discuss this observation in terms of the donor-acceptor reorganization energy ($\sigma$) as well as an additional
contribution of static disorder ($\sigma$). Remarkably, the more crystalline donor DIP shows a significant contribution of the
latter, while for the amorphous DBP this additional term is not required. This highlights the importance of film
morphology in organic solar cells.


EN12.11.24
Rational Designing of Push-Pull Type Small Organic Molecule Having Ambipolar Characteristics and Rich
Linear and Non-Linear Optical Properties Dwaipayan Chakraborty and Priya Johari; Shiv Nadar University,
India

Organic Semiconductor (OS) is an emerging class of energy materials, for its several advantages over its inorganic
counterpart, such as large area, flexibility, low cost, and most importantly their environment-friendly manufacturing
process. Computational designing and study of new semiconducting organic molecules have come up as a great
support in this regard. Push-pull type small organic molecule has recently gained a huge scientific research owing to
their remarkable charge transfer properties, high non-linear optical response, reduced HOMO-LUMO gap and hence
broad range of absorption spectrum, air stability etc. which collectively promotes this class of molecules as potential
candidate for non-linear optical devices, OFETs and organic solar cells. In this effort, we therefore rationally
designed a promising Donor(D)-π-Acceptor(A) (i.e, push-pull) type molecule trans-4-nitro-4'-dimethylamino-α-
aminostilbene (NNDMNH$_2$), by 'backbone engineering' from a standard NLO (Non Linear Optical) dye. We
predicted its crystal structure starting from the experimental crystal structure of another stilbene derivative and
-calculated the charge transport properties, electronic band structure, gas phase linear and non-linear optical
properties. We also did the Hirshfeld surface analysis and plotted the molecular electrostatic potential to get insight
into the structure-property correlation. We found that this new organic semiconductor owns a high charge carrier
mobility of ~ 7.46 cm$^2$/Vs for hole and 2.14 cm$^2$/Vs for electron, together with desirable electronic and linear and
non-linear optical properties revealing NNDMNH$_2$ as a potential candidate for the optoelectronic devices.

EN12.11.25
Vertical, Electrolyte-Gated Organic Transistors—Continuous Operation in the MA/cm2 Regime and Use as
Low-Power Artificial Synapses Jakob Lenz$^1$, Fabio del Giudice$^2$ and Thomas Weitz$^{3,4}$; $^1$Physics of Nanosystems,
Germany; $^2$Walter-Schottky Institute, Germany; $^3$Nanosystems Initiative Munich, Germany; $^4$Center for
NanoScience, Germany

Until now, organic semiconductors have failed to achieve high performance in highly integrated, sub-100 nm
transistors. Consequently, single-crystalline materials such as single-walled carbon nanotubes, MoS$_2$ or inorganic
semiconductors are the materials of choice at the nanoscale. Here we show, using a vertical field-effect transistor
design with a channel length of only 40 nm and a footprint of $2 \times 80 \times 80$ nm$^2$, that high electrical performance with
organic polymers can be realized when using electrolyte gating. Our organic transistors combine high on-state
current densities of above 3 MA cm$^{-2}$, on/off current modulation ratios of up to 108 and large transconductances of
up to 5,000 S m\(^{-1}\) [1]. Given the high on-state currents at such large on/off ratios, our novel structures also show promise for use in artificial neural networks, where they could operate as memristive devices with sub-100 fJ energy usage.


**EN12.11.26**

**Temperature Dependent Studies of IDT-BT Reveal Liquid Crystalline-Like Phase Behavior** Abigail M. Fenton, Ralph Colby and Enrique D. Gomez; The Pennsylvania State University, United States

Some of the highest charge transporting conjugated polymers to date such as Indacenodithiophene-co-benzothiadiazole (IDT-BT) have shown weak to no crystallinity which is puzzling as it deviates from traditional evidence that the higher order of semi-crystalline polymers is needed for high charge mobility. Stiffer conjugated polymers can have liquid crystalline phases, and many of the most common high mobility semi-crystalline conjugated polymers, such as PBTTT, have liquid crystallinity. Using oscillatory shear rheology, X-ray scattering, DSC and polarized optical measurements we have investigated the morphology and phase behavior of IDT-BT as a function of temperature. We have identified the backbone and hexadecyl side chain glass transition temperatures (Tg’s), discovered two phase transitions that are likely disordered liquid crystalline transitions as well as evidence of biphasic behavior. We have also fabricated IDT-BT field effect transistors and annealed them at different temperatures in the disordered phases to track how mobility changes in regard to these phases. We hypothesize that because polymer chains are not restricted to a certain packing structure dictated by crystallization, chains in a liquid crystalline polymer are able to adopt conformations that can maximize interchain charge coupling.

**EN12.11.28**

**Single Solvent Aerosol-Jet Printed Multi-Layers—A New Route for Efficient Blocking Layers in Organic Photodiodes** Mervin Seiberlich\(^{1,2}\), Noah Strobel\(^{1,2}\), Marta Ruscello\(^2\), Ulrich Lemmer\(^{1,3}\) and Gerardo Hernandez-Sosa\(^{1,2}\); \(^{1}\)Karlsruhe Institute of Technology, Germany; \(^{2}\)InnovationLab, Germany; \(^{3}\)InnovationLab GmbH, Germany

The development of high-performing organic photodiodes (OPDs) is presently an intense field of research motivated by its potential applications in the field of imaging, health-care, or environmental monitoring. Yet only a limited number of publications report on fabrication routes that enable fully-printed device architectures facilitating the cost-efficient integration of OPDs in novel sensing applications. One main difficulty lies in the hindrance of device functionality through the successive deposition of the required multi-layer stack. The ink deposition can lead to disruption of film morphology, intermixing of materials and short circuits, reducing the figures of merit such as spectral responsivity, detectivity, or detection speed. To circumvent this problem an orthogonal solvent approach is commonly used. However, as the number of device layers increases, this approach exponentially restricts the palette of materials with suitable optoelectronic properties.

In this work, we present a route to overcome the need of orthogonal solvent systems utilizing Aerosol-jet printing for the fabrication of OPDs. By fine adjustment of the aerosol properties in terms of droplet temperature, solvent concentration and material flow rate, we gain control of the film drying dynamics without negatively affecting the underlying layers. Following this approach, we print a P3HT blocking layer on top of a P3HT:PC\(_{60}\)BM bulk-heterojunction from the same solvent system. The P3HT blocking layer spatially separates the lowest unoccupied molecular orbital (LUMO) of the acceptor from the electrode effectively reducing the flow of electrons from the contact. By following this approach, we demonstrate a reduction of the dark current from 176 mA/cm\(^2\) in a device without the blocking layer down to 0.2 mA/cm\(^2\) at 4 V reverse bias. This leads to a significant increase of the specific detectivity of the device up to 1.2E\(^{11}\) Jones, ~3 orders of magnitude higher than that of the reference device.


Morphological Engineering of Thiazolo[5,4-d]thiazole Based Conjugated Polymers for Optoelectronics
Nimisha Kaippamangalath; Indian Institute of Science Bangalore, India

Conjugated polymers (CP) have gained considerable attention due to their brilliant applications in electronic devices and optoelectronics. We designed and synthesized thiazolo[5,4-d]thiazole (TT) and benzo[1,2-b:4,5-b]dithiophene (BDT) planar fused rings containing donor-acceptor type conjugated polymers (viz., poly[thiazolo[5,4-d]thiazole thiophene-2-yl bis(dodecyloxy)benzo[1, 2-b:4,5-b]dithiophene] (PTDBT), poly[thiazolo[5,4-d]thiazole thiophene-2-yl 2-dodecyl-2H benzo[d][1,2,3]triazole (PTDBDT) and poly[thiazolo[5,4-d]thiazole thiophene-2-yl 9,9-dihexyl-9H-fluorene] (PTOF) with improved optoelectrical features. The molecular engineering of fused hetero-cyclic thiazolo[5,4-d]thiazole based π-conjugated polymers via introduction of substituted donor-acceptor units as backbones could enhanced the optoelectrical features. Conjugated polymers showed bright luminescent properties in yellow-red region of the electromagnetic spectrum having emission maxima in the range of 595-887 nm. PTDBT, PTDBDT and PTOF showed homogeneous morphologies with root-mean-square (RMS) roughness of ca. 0.255 nm, 0.464 nm and 0.303 nm, respectively. Band gaps obtained from cyclic voltammetric analysis are 2.27 eV, 2.04 eV and 2.4 eV, indicating the semiconducting nature of the synthesized systems. The impedance studies of these materials are done for a comprehensive understanding of their capacitive behavior in terms of the components of complex impedance. These all results indicate the application of synthesized systems as active layers in optoelectronics.

Ion Phase Separation upon Electrochemical Doping in Conjugated Polymers
Connor G. Bischak, Lucas Flagg, Kanrong Yan, Chang-Zhi Li and David S. Ginger; 1University of Washington, United States; 2Zhejiang University, China

Conjugated polymers undergo structural changes upon electrochemically-driven ion insertion. The nature of these structural changes influences both the kinetics of doping and electronic mobility of the doped state, impacting the operation of many technologies that rely on the dual ionic/electronic conductivity of conjugated polymers, such as organic bioelectronics, neuromorphic computing, and supercapacitors. Typically, the polymer crystal lattice changes continuously to accommodate ions. We find that the lattice can also expand discontinuously, resulting in phase separation between ion-rich and ion-poor regions of the film. This phenomenon is routinely observed in inorganic materials, yet the flexible nature of conjugated polymers typically prevents phase separation from occurring. Using a combination of ex situ and in situ grazing incidence wide angle X-ray scattering (GIWAXS), as well as observations of ion distributions and migration with photoinduced force microscopy (PiFM), we characterize the phase-separated doped state of poly[2,5-bis(thiophenyl)-1,4-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene] (PB2T-TEG), a conjugated polymer with glycolated side chains. We find that phase separation has important implications for polaron transport within conjugated polymers, as lattice expansion rather than polaron diffusion can restrict transport.

Solution Processed n-Doping of a Low Electron Affinity Polymer for Electron Injection in OLEDs
Hannah L. Smith, Stephen Barlow, Seth R. Marder and Antoine Kahn; 1Princeton University, United States; 2Georgia Institute of Technology, United States

Adding n-dopants to the electron transport layer (ETL) of an organic light emitting diode (OLED) increases its conductivity and improves electron injection into the emissive layer of the device. However, n-doping becomes very challenging when dealing with large gap, low electron affinity (EA ≤ 3 eV) ETLs used in green or blue OLEDs. In this work, we address the problem of solution n-doping of such a material, i.e. the polymer F8BT [poly(9,9-dioctylfluorene-alt-benzothiadiazole)], via incorporation of the air-stable n-type dimeric dopant [RuCp*Mes]₂ [1]. Characterization of the undoped F8BT with ultra-violet and inverse photoelectron spectroscopy (UPS and IPES) places the highest occupied molecular orbital (HOMO) at 3.8 eV and the lowest unoccupied molecular orbital (LUMO) at ~2.8-3.0 eV below vacuum level. As the dopant is incorporated into the F8BT film, the energy levels shift by 0.6 eV, pushing the Fermi level of the material closer to the LUMO. n-Doping with [RuCp*Mes]₂ results from the dimer cleavage mechanism described in previous work, whereby an initial electron transfer to the host is immediately followed by cleavage and release of a stable 18-e⁻ monomer cation and a highly reducing 19-e⁻
monomer [1,2]. In the case of the low EA F8BT, as was shown previously for other low EA hosts [1], photoactivation (here with a 375 nm UV LED) is required to initiate the first electron transfer. The conductivity of the F8BT film is improved by four orders of magnitude. The doped F8BT film is incorporated as an electron transport layer in a TPBi:Ir(ppy)_3-based OLED and found to improve the luminance by over three orders of magnitude, bringing the external quantum efficiency (EQE) to about 14%. The utility of these powerful, air-stable n-dopants, previously demonstrated in the context of vacuum processing of low EA organic electronic materials [2,3], is therefore now also established for solution-based doping of an OLED ETL polymer with an EA as low as 2.8-3.0 eV.


EN12.11.32
Long-Lived Free Charge Carriers at Heterojunctions between Semiconducting Single-Walled Carbon Nanotubes and Perylene Diimide Electron Acceptors
Hyun Suk Kang1, Obadiah Reid1, Thomas J. Sisto2, Samuel Peurifoy2, Boyuan Zhang2, Colin Nuckolls2 and Jeffrey L. Blackburn1; 1National Renewable Energy Laboratory, United States; 2Columbia University, United States

Semiconducting single-walled carbon nanotubes (s-SWCNTs) have been intensively studied as the components of various photovoltaic cells due to several advantages such as spectral tunability, giant aspect ratio, chemical robustness, hydrophobicity, and absence of charge-transfer (CT) states. In the previous study, it was reported that the heterojunctions between s-SWCNTs and perylene diimide (PDI)-based electron acceptors produce long-lived charge separated states whose lifetimes are more than 1.5 µs. Besides the potential of PDI-based electron acceptors to substitute fullerene-based electron acceptors, this study emphasized the significance of the molecular geometries of PDI-based electron acceptors which result in molecular aggregation and the associated charge delocalization in the acceptor phase. However, there is no clear understanding yet for why the charge carriers for these heterojunctions live so long. For instance, it was not determined how much of the charge carriers generated at these heterojunctions are free or trapped. Moreover, the nature of the charge recombination process from these heterojunctions was not yet revealed to be either monomolecular-like or bimolecular-like. In this study, we explored the nature of charge carriers for the heterojunctions between two singly chiral s-SWCNTs and two different PDI-based electron acceptors by combining two effective spectroscopic techniques: transient absorption (TA), probing charge carriers spectrally, and time-resolved microwave conductivity (TRMC), probing free charge carriers only.

Two PDI-based electron acceptors, hPDI2-pyr-hPDI2 and Trip-hPDI2, were synthesized and coated on (6,5) or (7,5) s-SWCNT films to form donor-acceptor heterojunctions. To compare the charge carrier characteristics from these heterojunctions to those from s-SWCNT/fullerene acceptor heterojunction, C60 was also deposited on singly chiral s-SWCNT films. The charge recombination kinetics across the singly chiral s-SWCNT/PDI-based acceptor heterojunctions, deduced from TA and TRMC studies, are well-matched, indicating that most charge carriers from these heterojunctions are free, not trapped. These studies also presented that the charge carrier dynamics from s-SWCNT/PDI-based acceptor heterojunctions remain similar over four orders of magnitude in the absorbed photon fluences of PDI-based acceptors. However, TRMC studies of s-SWCNT/C60 heterojunctions revealed that the fast decay dynamics at early delay time contributes more significantly at high C60 absorbed photon fluences than at low fluences. It is attributed that the fast bimolecular charge recombination processes such as charge collision become more probable at high C60 absorbed photon fluences. The substantially smaller molecular size of C60 than those of PDI acceptors may induce the greater degrees of donor-acceptor intercalation, resulting in the lower probability of the charge carrier extraction out of the donor-acceptor interface at early stage. For each s-SWCNT heterojunction, the charge recombination decay time constants from TRMC studies are independent of absorbed photon fluences of electron acceptors, and this fluence independence indicates that most of free charge carriers from s-SWCNT heterojunctions recombine ‘pseudo’-monomolecularly. The unconventionally high free charge carrier generation and strong suppression of bimolecular charge recombination from these s-SWCNT heterojunctions may be attributed to the high carrier mobility and good charge delocalization in s-SWCNTs.
These photophysical studies provide the fundamental understandings of the charge generation process in s-SWCNT-based heterojunctions and how different electron acceptor materials can influence the nature of charge generation with respect to the heterojunction energetics and molecular orientations. The results can inform rational design strategies for s-SWCNT-based optoelectronic applications.

**EN12.11.33**

**Influence of Partially-Oxidized Silver Back Electrodes on the Electrical Properties and Stability of Organic Semiconductor Diodes** Zhongkai Cheng, Yan Wang and Deirdre O’Carroll; Rutgers, The State University of New Jersey, United States

Silver is an important material for electrodes in high-performance organic optoelectronic devices due to its high reflectivity and low parasitic absorption loss at visible wavelengths. However, the electronic work function of Ag is not ideal for use as either the cathode or anode in many organic optoelectronic devices. Here, we investigate the formation of an ultrathin surface oxide layer on a Ag electrode and its impact on hole injection into an organic conjugated polymer semiconductor. The surface oxide is formed by exposing the Ag electrode to a low-power O2/Ar plasma and it changes the electrical properties of the pure Ag electrode. We study the morphology and the chemical composition of the Ag electrode surfaces after different plasma treatment times through X-ray photoelectron spectroscopy, scanning electron microscopy and dark-field optical microscopy. After plasma exposure the surface oxide is composed of both AgO and Ag2CO3. As plasma exposure time increases from 1 s to 7 s, the fraction of AgO increases while Ag2CO3 decreases gradually. Both the turn-on voltages and barrier heights of poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) hole-only devices decrease with partial oxidation of the Ag electrode surfaces indicating that the work function of the Ag surface is increased by the surface oxide. F8BT hole-only devices with a thin MoO3 layer and a thicker AgOx layer on the electrode are found to be stable compared to thinner surface oxides and untreated Ag electrode surfaces [1].


**EN12.11.34**

**Chemical Reduction of Phosphomolybdic Acids by Metal Dopants for Post-Treatment Free Solution-Processed Hole Injection Layers in Organic Light-Emitting Devices** Yuki Chikayasu, Satoru Ohisa, Kohei Endo, Takayuki Chiba and Junji Kido; Yamagata University, Japan

Abstract: We report novel solution-processable highly efficient hole injection materials, metal-doped phosphomolybdic acids (M-PMAs). PMA includes MoO3 units and works as a hole injection material as reported in the previous papers [1, 2]: however, thermal reduction of PMA at high temperature is indispensable for realizing high hole injection capability, and the thermal treatment is not desired for cost-effective manufacturing. In this work, we reduced PMA chemically by using reactions with various kinds of metals including Mg, Al, Ti, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Sn, Sb, and W metals. Powders of the metals were added to yellow-colored PMA solutions, and the reaction between PMA and the metals proceeded at room temperature to give the chemically reduced blue-colored M-PMA solutions. The M-PMAs were applied to hole injection layers in organic light-emitting devices with a structure of [ITO/M-PMA or thermally reduced PMA (rPMA) (10 nm) / N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (30 nm) / 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl: 8 wt% tris(2-phenylpyridinato)iridium(III) / bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxy)aluminum (10 nm) / tris(8-hydroxyquinolinato)aluminum (40 nm) / 8-quinolinolato lithium (1 nm)/Al (100 nm)]. Here, the rPMA film was formed by baking at 200°C of a PMA film, and has been already known to show high hole injection capability similar to well-known poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) [1]. On the other hand, the M-PMA films developed in this work were formed without any post-baking process. Among the various kinds of metals, the Mn, Co, Cu, Zn, Mo, and Sb-PMA-based devices showed similarly low driving voltages to the rPMA-based device. Moreover, the M-PMAs-based devices showed much longer operation lifetime than the rPMA-based device. Thus, we succeeded in the development of post-treatment free, highly efficient, highly stable hole injection materials.


**EN12.11.35**

**Self-Organization of Small Molecules via Solvent Vapor Annealing for Use in Organic Photovoltaic Cells** Sora
Oh\textsuperscript{1,2}, Chang Eun Song\textsuperscript{1,2} and Sang Kyu Lee\textsuperscript{1,2}; \textsuperscript{1}UST, Korea (the Republic of); \textsuperscript{2}KRICT, Korea (the Republic of)

It is reported the synthesis of two bis-benzodithiophene (BDT\textsubscript{2})-based small molecules, SM1 and SM2, and the effects of solvent vapor annealing (SVA) on their molecular ordering, optical, and photovoltaic properties. Although SM1 and SM2 have similar backbones, they exhibit different photophysical and electrochemical properties, charge carrier mobilities, and morphologies in blend films. SVA profoundly affected the molecular structure and photovoltaic properties. Solvent vapor annealing remarkably enhanced the photovoltaic properties of SM2, increasing the power conversion efficiency (PCE) from 1.47\% to 8.66\% by inducing a favorable molecular orientation, a miscible morphology, and enhanced mobility. The relationship between the morphologies of the active layers comprising SM1 or SM2 with PC\textsubscript{71}BM submitted to SVA and the device performances were elucidated using 3D transmission electron microscope tomography.

SESSION EN12.12: Morphology, Optoelectronic Properties of Active Layers, Device Interlayers
Session Chair: Sabine Ludwigs
Thursday Morning, December 5, 2019
Sheraton, 2nd Floor, Back Bay C

8:30 AM *EN12.12.01
In the Light of Recent Developments in Perovskite Thin Films and Quantum Dots—Morphology, Structure and Composition Ana F. Nogueira; University of Campinas, Brazil

Organic inorganic hybrid perovskites (OIHP) is the most promising material to achieved high power conversion efficiency (PCE) at low cost. The high-quality optoelectronic properties in combination with solution-based preparation methods are responsible for the currently certified PCE record of 24.2\%, which is close to the PCE of single crystal silicon solar cells (26.1\%). The properties of the perovskite film are direct related to film morphology, composition and crystalline structure, thus a clear understanding of how and when the intermediate and the perovskite phases are forming, as well the distribution of these multiple phases in the bulk and grains boundaries are important questions to be addressed in order to improve perovskite film properties and consequently the PCE of the devices. In this presentation, we will summarize our most recent results using \textit{in situ} time-resolved grazing incidence wide angle x-ray scattering (GIWAXS) and synchrotron infrared nanospectroscopy (nano-FTIR). GIWAXS experiments allowed us to understand the influence of the relative humidity, type of solvent and time to drop the antisolvent during the preparation of mixed cation perovskite films. We also identified intermediates formed before and during the spin coating process of mixed cations precursor solutions. Nano-FTIR technique was applied for the first time on OIHP. Our results revealed a spatial heterogeneity of the vibrational signal, which are associated to different chemical composition.

Colloidal perovskite nanocrystals (PQD) and nanoplates are very interesting for LED, however, the most used synthetic method to prepare them relies on a mixture of oleylamine (OLA) and oleic acid (OA) as surfactants. We will discuss an amine-free synthesis that utilizes tetraoctylammonium halides (TOAX) for preparation of OA capped CsPbX\textsubscript{3}PQDs without the need of post-anion exchange methods. As an alternative to cubic nanocrystals, we will present our recent results on the formation of perovskite nanoplates (PNP) using SnX\textsubscript{4} (X = Cl, Br, and I) salts as the halide source. The dynamic equilibrium between OLA, OA and the formation of a complex with Sn(IV) dictate the morphology and size, allowing us to prepare a range of efficient 2D quantum well materials.

9:00 AM *EN12.12.02
Interface Engineering for Stable Halide Perovskite Solar Cells Monica Lira-Cantu; Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and the Barcelona Institute of Science and Technology (BIST), Spain

Highly efficient halide perovskite solar cells (PSCs) can only be cost-competitive if their operational stability is ascertained. Defect control and passivation in the halide perovskite absorber and at the interface with the transport layers, is crucial for stability improvement. Defect act as recombination centres and, under continuous light irradiation can reduce the stability of the solar cell. In this presentation we report our latest results on the engineering of defects at the oxide/perovskite interface and within the halide perovskite structure. We will show the
application of binary and complex oxides as ETL. We will give special attention to the application of ferroelectric oxides, such as PZT, where O\textsubscript{vac} are employed for the creation of defect-dipoles responsible for photo-carrier separation and current transport, evading device degradation. We will also show a new method to passivate defects in the halide perovskite thin film, as a result we are able to fabricate PSC with > 21 % efficiency and 1000 h stability under 1 sun continuous light irradiation. Understanding the mechanism of defect passivation in PSCs materials and interfaces can facilitate the development of highly stable PSCs.

9:30 AM EN12.12.03
Enhanced Environmental Stability of Organic Optoelectronic Devices via a Transparent Superhydrophobic Surface Daekyoung Yoo\textsuperscript{1}, Youngrok Kim\textsuperscript{1}, Keehoon Kang\textsuperscript{1}, Heebeom Ahn\textsuperscript{1}, Woocheol Lee\textsuperscript{1}, Jinsu Pak\textsuperscript{1}, Seungjun Chung\textsuperscript{2} and Takhee Lee\textsuperscript{1}; \textsuperscript{1}Seoul National University, Korea (the Republic of); \textsuperscript{2}Korea Institute of Science and Technology, Korea (the Republic of)

For last decades, organic electronic materials have been widely used for realizing large-area flexible device applications, such as organic field-effect transistors (OFETs), organic light-emitting diodes, and optoelectronic sensors fabricated by low-cost and non-vacuum solution processing. Because of their inherent weakness of environmental instability, many researches have been conducted to improve the reliability of organic devices for further practical applications. Specifically, water-based threats could significantly degrade the electrical performances of organic materials, therefore, one of the key challenges is to integrate effective protection layers against external threats in daily conditions. In this context, introducing superhydrophobic layers has been regarded as an attractive solution because their excellent water-repellency can be helpful to protect organic devices from harmful dusts or water-based threats efficiently. In our previous study, we reported that organo-compatible superhydrophobic protection layers could improve the environmental stability of OFETs [1]. However, the employed TiO\textsubscript{2} nanoparticle-based superhydrophobic layers having a thickness over 10 μm can be a critical hurdle to be utilized in optoelectronic applications due to theiropaque\textsuperscript{ness} [1]. For providing transparency to the nanoparticle-based protection layers, the control of their thickness and surface roughness should allow the enhanced transmittance via reduced light scattering. Specifically, because the high surface roughness is a key parameter for maintaining the superhydrophobicity, the investigation on the optimized conditions for achieving transparent superhydrophobic surfaces is highly desirable as well as organo-compatible low-temperature processing.

In this presentation, we will report a facile method to realize a transparent superhydrophobic layer onto organic phototransistors through an organo-compatible solution process. TiO\textsubscript{2} nanoparticles coated with fluorinated silane molecules are dispersed in a highly fluorinated solvent, so we can introduce a superhydrophobic surface onto organic devices directly. The optimized transmittance over 90 % in the visible wavelength region is attributed to the controlled roughness parameters of our superhydrophobic layer. The transparent superhydrophobic layers exhibit good water repellencies without critical delamination issues even after or during bending and stretching tests. Moreover, flexible organic phototransistors with the transparent superhydrophobic layers show self-cleaning abilities from excellent water repellency, therefore harmful contaminants on the surface can be eliminated by dropping water droplets while preserving their optoelectronic characteristics. This work can provide a key pathway to implement a transparent self-cleaning layer for more reliable organic optoelectronic devices.


9:45 AM EN12.12.04
Anionic Conjugated Polyelectrolytes for Anode Interfacial Engineering in Inverted Organic Solar Cells Silvia Luzzati\textsuperscript{1}, Elisa Lassi\textsuperscript{1}, Benedetta Maria Squeo\textsuperscript{1}, Guido Scaivia\textsuperscript{1}, Marta Penconi\textsuperscript{1}, Simona Mrakic-Sposta\textsuperscript{2}, Maristella Gussoni\textsuperscript{1}, Umberto Giovanella\textsuperscript{1}, Francesco Galeotti\textsuperscript{1} and Maria Cecilia Pasini\textsuperscript{1}; \textsuperscript{1}Istituto per lo Studio delle Macromolecole ISMAC-CNR, Italy; \textsuperscript{2}Istituto di Bioimmagini e Fisiologia Molecolare-CNR, Italy

Interfacial engineering has been identified as a fundamental strategy for maximizing the performances and stability of organic solar cells. To this aim, conjugated polyelectrolytes (CPEs) received increasing attention thanks to their ability of improving the performances of organic solar cells through processing from orthogonal solvents. Most of the CPEs have been utilized as cathode modifiers while their use as anode interfacial layer (AIL) materials was less frequently reported. Recently it was demonstrated that self-doped anionic CPEs are a promising PH-neutral alternative to PEDOT:PSS AIL for organic solar cells\textsuperscript{1}. Actually the library of efficient CPEs anode modifiers has enlarged\textsuperscript{2},\textsuperscript{3}, helping to identify the key CPEs characteristics for effective anode interfacial engineering.
In spite of these advancements, the use of CPEs AILs in organic photovoltaics has been limited to devices prepared with conventional direct architecture, while their application in devices with inverted geometry hasn’t yet been addressed.

In this view we have prepared three conjugated copolymers modifying by chemical design conjugated backbone or alkyl-sulfonate side chain architecture. Their functional behavior as anode modifiers in inverted P3HT:PCBM61 solar cells is herein investigated.

The results indicate that anionic CPEs can be effectively applied for anode interfacial engineering in inverted organic solar cells. Comparable photovoltaic performances to a classical thermally evaporated inorganic MoOx AIL have been achieved. Some insights and guidelines for future development of efficient CEPs anode modifiers for inverted devices are discussed.


10:00 AM BREAK

SEASON EN12.13: Doped Organic Semiconductors, Charge Transport, Material Physics
Session Chair: Elizabeth von Hauff
Thursday Morning, December 5, 2019
Sheraton, 2nd Floor, Back Bay C

10:30 AM *EN12.13.01*

**Interface Energetics and Transport in Organic Semiconductor Blends** Karl Leo; Technische Universität Dresden, Germany

Organic semiconductors with conjugated electron systems are currently intensively investigated for many novel electronic and optoelectronic applications. Their key advantages are flexibility, low cost, and low resource usage since the mostly carbon-based materials are fabricated in nano-meter scale thin film devices. Recently, we have introduced the novel principle of band structure engineering into organic semiconductors [1]: Long range Coulomb interactions allow to continuously tune the energy levels, offering to finely adjust energy levels without synthesis of new molecules. We have now directly proven the electrostatic nature of these phenomena by experiments which show the strong influence of these quadrupole effects at interfaces [2]. This also dramatically changes the interface energetics of organic solar cells, depending on quadrupole moments and molecular orientation. Recently, we have furthermore shown in a detailed study of the conductivity of doped organic semiconductors that the quadrupole interacts play an important role in the activation energy of ground state charge transfer pairs [3]. This opens a new path for the optimum design of host-dopant interactions to achieve the highest possible conductivities.


11:00 AM EN12.13.02

**Charge Transport in Highly Doped Organic Semiconductors Limited by Coulomb Pseudo-Gap** Miina Leiviskä¹, Marten Koopmans¹, Jian Liu¹, Michael C. Heiber² and Lambert Jan Anton Koster¹; ¹University of Groningen, Netherlands; ²Northwestern University, United States

In order to make rational improvements of the charge transport properties of organic semiconductors, a thorough
understanding of this rather complex process is needed. Charge carrier transport in organic semiconductors is usually described as a series of events where a charge carrier hops from one localised state to the next. In this type of description, the disordered nature of such systems leads to a broad distribution of site energies. As a result, the mobility of charge carriers increases as more charge carriers are introduced unless the number of charges is relatively low [1].

While it has been recognised that Coulomb interactions between dopants and charge carriers are important, carrier-carrier interactions in doped organics have received less attention. In a doped organic semiconductor, however, the number of (free and bound) charge carriers equals the number of reacted dopants. As a result, both types of interactions are of importance for a proper description of the transport properties of doped organic semiconductors. However, it has been proposed that carrier-carrier interactions is significantly weaker than the effect of Coulomb interactions between dopants and charge carriers [2].

In this contribution, we use a kinetic Monte-Carlo model to study the transport properties in the presence of dopants and including both carrier-carrier and carrier-dopant interactions. In particular, we can simulate up to the relatively high doping densities that are experimentally relevant even though numerically challenging. We find that the density of states (DOS) of such systems shows a pseudo-gap at the Fermi level due to Coulomb interactions between the charge carriers. Such Coulomb gaps are a manifestation of the carrier-carrier interactions and have been predicted to exist in hopping systems [3], but are usually washed out at anything other than very low temperatures. In contrast, we observe these pseudo-gaps at room temperature, which is a consequence of the low dielectric constant and highly localised charges that are typical of organic semiconductors. We wish to point out that the pseudo-gap is a sole consequence of carrier-carrier Coulomb interactions and is not a result of the dopants. This has profound implications for electrical conductivity as the pseudo-gap limits charge carrier transport at high doping densities. The corresponding (absolute) Seebeck coefficient remains approximately constant in this regime.

Experimentally, we observe that the electrical conductivity of a large number of organic semiconductors shows a maximum: Upon increased doping levels the conductivity decreases and the (absolute) Seebeck coefficient remains approximately constant. This type of behaviour is commonly attributed to changes in the microstructure as a consequence of doping. However, we find that even when using vapour doping, where there are no observable changes in the microstructure, this behaviour persists. The experimental findings match the Monte-Carlo data (drop in conductivity and saturation of the Seebeck coefficient at high doping) very closely, which implies that the Coulomb pseudo-gap is at the root of the limited conductivity at high doping densities.

As a major consequence of our findings, we stress that both dopant-charge carrier as well as carrier-carrier interactions need to be considered when designing new materials for efficient and highly conductive doped organic semiconductors and thermoelectrics.


11:15 AM EN12.13.03
Doping of organic conjugated materials has been proven to be crucial to achieve high conductivities and thus the exploration of their fundamental properties is essential to maximize their potentials for applications in electronic devices. This has motivated the intensive study of the long-range transport properties of doped organic materials that are governed by weak intermolecular interactions, however their intrachain motion has been much less explored. Thus, we have used THz spectroscopy to gain information about the local transport properties of doped organic conjugated polymers in the non-excited state and access the carriers nanoscale mobility. We show that these measurements can serve as a tool to determine the doping efficiency of doped organic materials. Due to the short THz pulse duration, we selectively probe the intrachain motion of the mobile charge carriers in doped organic materials. Moreover, we aim to give an insight on how these properties are affected by the strong interactions...
between the charge carriers formed on the conjugated backbone and the charged dopants necessary to counterbalance the organic material and the impact of the formation of partial charge transfer complexes or structural disruption by external dopant molecules on their local transport properties.

11:30 AM EN12.13.04
n-Doping of Organic Semiconductors—Bulk and Interfaces Frank Ortmann, Sebastian Schellhammer, Christopher Gaul and Sebastian Hutsch; Technische Universität Dresden, Germany

Doping is a key technology in semiconductor physics to tune bulk and interfacial electronic properties. In organic semiconductors, efficient doping may be dominated by different effects, which are presently not well understood and cannot be explained by standard semiconductor models. An improved microscopic picture would therefore be highly desirable.

In our contribution, we will discuss and compare some examples of our current research comprising n-doped bulk systems, organic-organic interfaces and metal-organic ones where we have analyzed the effect of doping in microscopic detail from density functional theory to the statistical description of the resulting Fermi level position. A consistent description is emerging from these different systems. Our discussion finally includes a comparison to various experimental results.

11:45 AM EN12.13.05
Insights into Molecular Doping by Electron Paramagnetic Resonance Alberto Privitera, Ross Warren, Junjie Liu, Arzhang Ardavan and Moritz Riede; University of Oxford, United Kingdom

Molecular p- and n-doping of organic semiconductors has been key for the successful commercialisation of OLEDs and promises to significantly advance the field of organic solar cells and transistors. As recent reports have shown, in-depth comprehension of the doping process is required to guide the design of improved semiconductor materials and molecular dopants [1,2]. In this context, electron paramagnetic resonance (EPR) spectroscopy is a technique ideally suited to study molecular doping as it is sensitive to the nature and dynamics of the paramagnetic species generated upon introduction of dopant molecules into films of organic semiconductors [3].

In this contribution, EPR spectroscopy and electrical measurements are carried out to investigate p-type doping of a layer of ZnPc (host) with the acceptor F6-TCNNQ (dopant) at different dopant concentrations (0 - 5 wt.%) and temperatures (80K – 280K). The samples are fabricated through thermal evaporation under vacuum to achieve a high control over the composition, the thickness and the morphology of the thin films. The EPR analysis performed at different dopant concentrations and at room temperature reveals the presence of two different paramagnetic species distinguished by two different g-tensors. We attribute these two species to the ZnPc positive polaron and the F6-TCNNQ anion. The quantification of the number of paramagnetic species in the film allows us to provide an estimate of the doping efficiency and to clarify the ground-state charge transfer mechanism underlying charge generation in doped films. Furthermore, from the EPR lineshape analysis, we delve into the microscopic transport dynamics of the polarons. The results are in line with conductivity measurements. The analysis performed at different temperatures discloses a further wealth of information on the temperature dependence of the charge transfer process and the thermally-activated transport properties of polarons and elucidates the role of trap states in the framework of the multiple trap-and-release (MTR) model [4]. The results are supported by electrical conductivity measurements performed at different temperatures from 100 to 280K.

With the aim to further validate our investigation, we are currently expanding our work to different energy level offsets between the host and the dopant. Taking advantage of the band structure engineering reported by Schwartze et al. [5], we are using different blended host materials, ranging from ZnPc to fluorinated derivatives FxZnPc (x= 4, 8, 16), co-evaporated with F6-TCNNQ (dopant). The investigation will unravel how the doping process depends on energetic offset and will help us to define novel design rules to control molecular doping.

Emerging Approaches to Measure Orientational Order in Organic Semiconductors  Dean M. DeLongchamp; National Institute of Standards and Technology, United States

Organic semiconductors typically exhibit a rich variety of ordered phases. Orientation occurs during processing, often by passing through lyotropic liquid crystalline phases, and dried films exhibit orientation at many length scales. Liquid crystallinity appears almost ubiquitous in organic semiconductors we have studied, including behaviors similar to nematics, smectics, or sanidics. Uniaxial orientation where the conjugated plane exhibits a preferential “face on” or “edge on” orientation is the most commonly characterized aspect of orientational order, and mature techniques such as near edge X-ray absorption fine structure (NEXAFS) spectroscopy and grazing incidence X-ray diffraction (GIXD) are frequently employed to measure it. Significant challenges remain, even for this seemingly simple aspect of orientational order. For example, these approaches are often found to be insufficient when films exhibit a complex depth profile of orientation, composition, or both.

As the materials diversity of organic semiconductors increases thanks to achievements in synthetic chemistry, and as the complexity of formulation, blending, and coating increases as process design knowledge matures, there is a commensurate need for more advanced approaches to characterizing orientational order. Biaxial orientation is increasingly observed, where “face on” or “edge on” preferences are combined with an in-plane preference imparted by a substrate or processing vector. Domain-relative orientations are also been observed, with correlations in domain-to-domain orientation thought to influence charge transport.

I will describe some emerging approaches to measure orientational order in organic semiconductors. Resonant soft X-ray reflectivity (RSoXR), a method capable of measuring thin film depth profiles using the spectroscopic principles of NEXAFS, will be discussed. I will also summarize progress on in-situ spectroscopic and scattering-based structure measurement techniques that are combined with ex-situ probes including imaging and image analysis to determine how orientation originates during the processing of organic semiconductors. These new measurements will support science-based approaches for orientation control and optimization, helping to maintain the rapid pace of organic semiconductor technology development in an era where increasing complexity renders matrix-style empirical approaches too inefficient to contemplate.

Key Roles of Structural Order and In-Plane Alignment of (Semi)-Conducting Polymers on their Optical and Charge Transport Properties  Laure Biniek; CRNS, University of Strasbourg, France

This presentation focuses on recent advances in growth control and oriented crystallization of (semi)-conducting polymers for organic electronic applications. The performance and lifetime of organic electronic devices are critically dependent on the morphology of the active layers and structural order of the materials. For instance both molecular and crystalline orientations of the polymers determine optical and charge transport properties in thin films since these properties are by essence highly anisotropic.

Particular emphasis will be given to the progress made in high-temperature rubbing of conjugated polymers films. This effective large scale alignment method can orient a large palette of semiconductors with n- or p-type character without the use of alignment substrate. High degrees of crystallinity and in-plane alignment can be obtained which provide well-defined electron diffraction patterns essential for structure refinement. The concurrent roles of polymer molecular weight distribution and rubbing temperature ($T_R$) on the in-plane orientation are rationalized for P3HT and PBTTT. Correlations are drawn between nanomorphology/crystallinity on one side and charge transport and optical properties on the other side. It is shown that the exciton bandwidth in P3HT crystals is determined by the
The length of the average planarized chain segments in the crystals. The high alignment and crystallinity observed for \( T_R > 200 \) °C cannot translate to high hole mobilities parallel to the rubbing because of the adverse effect of amorphous interlamellar zones interrupting charge transport between crystalline lamellae of semi-crystalline P3HT.\(^2\) As opposite, hole mobilities along the polymer chains of rubbed PTB7 films are observed to be 6 times higher than the non-rubbed films.\(^3\) This is due to the smectic-like character of this alternated donor-acceptor copolymer. Interestingly high-Tr rubbing and post annealing process of PTB7 provide well-defined electron diffraction pattern. Combined with DFT calculation, this helps refining the structure and the chain conformation of this benchmark electron donor polymer for OPV application.

In a second part of this presentation, we show that soft doping of aligned P3HT yields highly oriented conducting polymer films with anisotropic charges and thermal conductivities. The thermoelectric properties are enhanced along the rubbing direction. The unique in-plane orientation in such conducting polymer films helps rationalizing the mechanism of redox doping.\(^4\)

References.

2:45 PM EN12.14.03/FF04.10.03
Real-Time Structural Evaluation of Naphthyl End-Capped Oligothiophenes in Organic Thin-Film Transistors During Deposition
Mathias Huss-Hansen\(^1\), Peter Siffalovic\(^2\), Nad’a Mrkyvková\(^2\), Jakub Hagara\(^2\), Martin Hodas\(^1\), Frank Schreiber\(^1\), Eva Majková\(^2\), Jakob Kjelstrup-Hansen\(^1\) and Matti Knaapila\(^1\)\(^1\)
1Technical University of Denmark, Denmark; 2Slovak Academy of Sciences, Slovakia; 3University of Tuebingen, Germany; 4University of Southern Denmark, Denmark

The electrical properties of organic thin film transistors (OTFTs) are strongly influenced by the structural characteristics and thin film morphology. Understanding the growth dynamics that lead to preferential molecular orientation and changes in crystal structure remain an important factor in the design of new high-performance OTFTs as well as in their fundamental studies.

In this contribution, we have investigated the thin film growth behavior of 5,5′-Bis(naphth-2-yl)-2,2′-bithiophene (NaT2) and 5,5′′-bis(naphth-2-yl)-2,2′:5′,2″-terthiophene (NaT3) during the deposition process using real-time grazing incidence X-ray diffraction (GIXRD) *in situ*. The thin films were prepared by vacuum sublimation atop various substrates, including monolayer graphene on 90 nm SiO\(_2\), in a custom-built ultra-high vacuum (UHV) chamber with a 360° cylindrical beryllium window that allows for *in situ* X-ray measurements within realistic deposition time scales. The crystal structure analysis revealed that the preferred orientation of the molecules were dictated by the substrate and that the unit cell underwent significant changes when transitioning from monolayer to multilayer structure. The changes of the unit cell were not readily observed when measuring thin films of corresponding thicknesses *ex situ*, suggesting that the molecules undergo further re-organization/relaxation upon terminating the deposition. From the evolution of the crystal structure, a connection to the film growth mode and kinetics is made. These findings are rationalized based on the surface energies of the studied substrates and supplemented with AFM and helium ion microscopy. Finally, the crystal structure and morphology are correlated with charge transport properties of the final thin films.

3:00 PM BREAK

3:30 PM *EN12.14.04/FF04.10.04
Semiconducting Polymers for High Performance Organic Transistor Applications
Iain McCulloch; King Abdullah University of Science and Technology, Saudi Arabia

The evolution of organic electronics has now reached the commercial phase, with the recent market introduction of the first prototypes based on organic transistors and organic solar cell modules fabricated from solution. Understanding the impact of both the organic semiconductor design and processing conditions, on both molecular conformation and thin film microstructure has been demonstrated to be essential in achieving the required optical
and electrical properties to enable these devices. Polymeric semiconductors offer an attractive combination in terms of appropriate solution rheology for printing processes, mechanical flexibility for rollable processing and applications, but their optical and electrical performance requires further improvement in order to fulfil their potential. Synthesis of conjugated aromatic polymers typically involves carbon coupling polymerisations utilising transition metal catalysts and metal containing monomers. This polymerisation chemistry creates polymers where the aromatic repeat units are linked by single carbon-carbon bonds along the backbone. In order to reduce potential conformational, and subsequently energetic, disorder due to rotation around these single bonds, an aldol condensation reaction was explored, in which a bisisatin monomer reacts with a bisoxindole monomer to create an isoindigo repeat unit that is fully fused along the polymer backbone. This aldol polymerization requires neither metal containing monomers or transition-metal catalysts, opening up new synthetic possibilities for conjugated aromatic polymer design, particularly where both monomers are electron deficient. Polymers with very large electron affinities can be synthesised by this method, resulting in air stable electron transport, demonstrated in solution processed organic thin film transistors. We present an electrical, optical and morphology characterisation of polymer thin films, illustrating structure-property relationships for this new class of polymers.

4:00 PM  *EN12.14.05/FF04.10.05  
Charge Transport in Conjugated Polymers and the Importance of Order—From Atomic to Mesoscale  
Alberto Salleo; Stanford University, United States

Carrier mobility in conjugated polymers continues to increase with recent reports of field-effect mobilities exceeding 10 cm²/V.s. Charge transport is intrinsically dependent on processes occurring across multiple length scales. In order to access order parameters at the molecular scale we use charge modulation spectroscopy combined with theory. Furthermore, we study the mesoscale organization of polymers using a new technique in the transmission electron microscope. These techniques are used on homopolymers and donor-acceptor copolymers. Such multiscale studies of microstructure are instrumental in guiding our understanding of charge transport in conjugated polymers.

4:30 PM  *EN12.14.06/FF04.10.06  
Charge Transfer State Lifetimes in P3HT:F4TCNQ Co-Processed Films  
Bharati Neelamraju, Kristen Watts, Jeanne Pemberton and Erin L. Ratcliff; University of Arizona, United States

Doping is a fundamental strategy to increase the carrier density and conductivity of organic electronic layers for opto-electronic devices. The model system for p-doping is poly(3-hexyl)thiophene (P3HT) with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), whereby increases in conductivity occur through integer charge transfer (ICT) to form mobile carriers in the P3HT. Extensive work in the organic electronics field has revealed the interplay between film microstructure, the opto-electronic properties, and conductivity.

This talk asks the simple question: How stable are ICT states in doped films? An alternate undesired reaction pathway is formation of a partial charge transfer complex (CPX), which results in a localized, trap-like state for the hole on P3HT. Starting first with our recent observation that both ICT and CPX states exist simultaneously in a single film, this talk will focus on thermodynamic and kinetic pathways that lead to conductivity loss in F4TCNQ-doped P3HT films. Both reaction chemistries and microstructural effects will be discussed.

SESSION EN12.15: Poster Session III: Properties of Organic Semiconductors III  
Session Chairs: Marina Freitag and Harald Hoppe  
Thursday Afternoon, December 5, 2019  
8:00 PM - 10:00 PM  
Hynes, Level 1, Hall B

EN12.15.01  
Self-Assembled Conjugated Polymer on Water Surface for Wafer-Scale Ultrasensitive Organic Heterojunction Phototransistors  
Yuanhong Gao and Jia Li; Chinese Academy of Sciences, China
The advent of solution-processed organic semiconductors makes it possible for the realization of heterojunction phototransistor architectures with the feasibility to break through the photodetection limitations in conventional organic photodetectors such as the trade-off in balancing the separation, transport, and recombination of photogenerated charges. The appealing progress was reported in recently with the well-tailored device structure in which the light absorption and carrier transport take place in separately optimized bulk heterojunction (BHJ) photoactive layer and conduction channel, respectively. However, a critical issue hindering the further improvement of this type of device is that the solution-processed upper photoactive layer would degrade the underneath channel layer or induce high-density defect states at their interface, which would significantly lower the carrier mobility and affect the charge transfer process. In this presentation, we will present an ultrafast and scalable approach to fabricate large-area and high-performance organic phototransistors in ambient condition by using solution-floating method (SFM) to prepare both the high-quality channel layer and the BHJ photoactive layer. Based on this approach, the highly smooth and uniform conjugated polymer films with precise control of film thickness at a monolayer level can be prepared, offering the potential to realize low-cost, large-area and mass-manufacturable optoelectronic devices. In addition, the solution-floated organic films can theoretically be transferred to any kind of substrate. With this SFM process, we fabricated the hybrid-layered phototransistors by sequential transferring of channel layer and BHJ photoactive layer on rigid or flexible substrates. And we further demonstrate that carrier mobility was significantly boosted as compared to the spin-coated counterpart, and the high mobility can be well maintained after the covering of the BHJ photoactive layer. Resultantly, high photodetection performance can be expected for the phototransistors due to its excellent light absorption efficiency, highly-efficient charge transfer and high conductivity enabled by the high-quality organic films and interfaces. More importantly, employing SFM to prepare high-quality and well-controlled organic semiconductor film is not only technologically promising for high-performance organic phototransistors, but also opens up new opportunities control charge transfer and electronic transport properties for more efficient optoelectronic devices in general.

**EN12.15.02**

**Novel In Situ Tensile Platform for Thin-Film Characterization** Luke Galuska, Xiaodan Gu and Dakota Ehlenberg; The University of Southern Mississippi, United States

The study of semiconducting polymer deformation mechanics is a challenging area that needs to be thoroughly understood for flexible and stretchable electronics to become a reality. The main challenge lies in handling and measuring these materials, which at the device scale are a mere 100 nm in thickness or less. The Gu research group has specialized in the pseudo free standing tensile test to characterize the thin film mechanical property while supported in a water bath, however there is a question as to what effect, water has on these films. Here, we developed a new free-standing (in air) tensile platform to not only confirm the effect of water on sub-100nm films, but also establish a route for in-situ tensile characterization to probe the morphological change upon deformation. This is accomplished through what our group has termed Supported Shear Release, a gentle transfer method capable of obtaining macroscopic sub-100 nm thin films, which has enabled the tensile characterization of polystyrene and poly(3-hexylthiophene-2,5-diyl) films down to thicknesses of 38 and 80 nm respectively. We have registered negligible differences between the modulus obtained from on water and in air measurements, leading us to conclude that water plays an insignificant role in these hydrophobic films despite other factors such as confinement, which remain evident in the polystyrene system. Our current work is to utilize this newly developed free-standing tensile platform for in-situ UV-vis characterization of mechanochemical polymers. Upon tensile strain, these polymers exhibit a transition marking the appearance of conjugation which is detectable with UV-Vis spectroscopy. Thus, enabling a thorough understanding of the structure property relationships for these systems as well as establishing this novel tensile platform as a multimodal characterization tool for the in-depth understanding of thin film deformation mechanics across multiple length scales.

**EN12.15.03**

**Computational Insight on Solvent Effects on Aggregation in Core-Chlorinated Naphthalene Tetracarboxylic Diimide** Xiangyu Chen1, Geoffrey Purdum2, Nikita Sengar1, Paulette Clancy1 and Lynn Loo2; 1Johns Hopkins University, United States; 2Princeton University, United States; 3Cornell University, United States

Small-molecule organic semiconductors are well studied for applications from cell phones to solar cells due to their electronic properties, flexibility and lower manufacturing cost. Charge transport in these organic materials is normally localized among a π-conjugated core of carbon atoms, making charge transport highly anisotropic, with
higher electron transport in the plane of the π-π bond. Thus, slight differences in π-π stacking can significantly change this transport. As a result, researchers are interested in understanding how to manipulate the processing of organic semiconductor crystals and how to control the formation of specific polymorphs with desirable charge transport properties.

One molecule receiving such attention is the class of core-substituted naphthalene diimide molecules (c-NDI). In this presentation, we studied core-chlorinated naphthalene tetracarboxylic diimide (NTCDI) where the chlorinated core has as an electron-withdrawing effect to lower the LUMO energy level and improve chemical stability by discouraging interactions with oxidants. The Loo group found that using different solvents during the solvent-vapor annealing of NTCDI thin-film transistor resulted in thermodynamically reversible α and β-phases. Here, we have used ab initio density functional theory and molecular dynamics calculations to study how solvent choice (acetone, chloroform, dichloromethane, toluene) affects NTCDI processing. Some force field parameterization was necessary for this study, largely missing dihedrals. For the DFT, we used HF-3c and a continuum solvation model based on charge density.

We found “boat-” and “chair-” like conformations of NTCDI molecules in solvents that cannot be observed experimentally and showed that it has a high-energy barrier that prevents inter-conformer conversion. We calculated the binding energy between two NTCDI molecules immersed in solvent and determined that the tendency of NTCDI aggregation was low in chloroform/dichloromethane, intermediate in acetone and high in toluene. To ensure that entropic as well as enthalpic considerations were made we calculated the free energy of the affinity between two NTCDI molecules in solvent to better understand solvent-NTCDI phenomena. NTCDI molecules preferred to be solvated in chloroform as the free energy decreased when the distance between NTCDI increased. In contrast, in acetone, NTCDI monomers as well as aggregated complexes co-existed, evidenced by two local free energy minima at both short and long distances. Importantly, although our binding energy calculation indicated that NTCDI shows the strongest binding in toluene, it does not necessarily aggregate in toluene. This is because the toluene-NTCDI molecules tend to form a sandwich-like complex in solution and π-π interactions between NTCDI and toluene aromatic carbons played an key role here. We also observed strong differences among the radial distribution function of solvent-NTCDI interactions as a result of solvent choice; e.g., the first maximum in \( g(r) \), around 4 Å, for toluene-NTCDI is significantly higher than in other solvents. All these findings validate experimental results obtained by our collaborators, Dr. Geoffrey Purdum, Dr. Yuen-Lin Loo, and others. But they also offer exquisitely detailed atomic-scale insights, which cannot be observed experimentally and which will help the community understand the small-molecule organic semiconductor processing of thin-film transistor and help researchers achieve more control over preferable crystal structures.

**EN12.15.04**

**Tight Binding Models Accurately Predict Electronic Structures for Copolymer Semiconductors**

Prithvi Tipirneni, Michael J. Janik and Scott T. Milner; The Pennsylvania State University, United States

Conjugated polymers possess a wide range of desirable properties including accessible band gaps, plasticity, tunability, mechanical flexibility and synthetic versatility making them attractive for use as active materials in organic photovoltaics. In particular, push-pull copolymers, which are made of alternating electron-rich and electron-deficient moieties, are increasingly used due to their broad optical absorption, ease of tunability of relevant orbital energy levels (HOMO/LUMO and band gap) and increased charge transfer between the monomer units. However, the existence of a large number of possible copolymers makes the screening for ideal copolymers for OPVs through first-principles strategies computationally intensive. Connecting small molecule (monomer,dimer) or homopolymer properties to copolymer properties helps avoid expensive first-principles calculations on the copolymer itself to determine its electronic properties. Several studies utilizing high throughput computational screening for novel OPV materials have focused on calculating small molecule properties. Revisiting these calculations with a reliable model to predict copolymer band structures eliminates the need for a first-principle calculation. This is useful for day to day predictions and aids the screening for novel materials. Therefore, this work aims to build a recipe to construct copolymer band structures from the monomers involved while avoiding expensive first-principle calculation on the copolymer itself. For this, we use the Tight Binding (TB) approximation to build models, with parameters determined using Density Functional Theory (DFT) calculations on monomers/homopolymers. These models are then used to construct copolymer valence and conduction band structures and validated by comparing them to the DFT calculated electronic structures of the copolymers. In addition, we discuss how such band structures can be qualitatively constructed from monomer HOMOs and LUMOs; available in materials databases, and a simple
estimate of the electronic coupling between monomers of the same kind.

**EN12.15.05**

*Fabrication of PEDOT Organic Electrochemical Transistors by Electropolymerization*  
Michel Bilodeau-Calame, Jo'Elen R. Hagler, Nicolò Rossetti and Fabio Cicoira; École Polytechnique de Montréal, Canada

The conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) is widely used as channel material for organic electrochemical transistors (OECT), due to its mixed ionic-electronic conductivity, chemical stability and biocompatibility. The study presented here aims to explore and optimize the fabrication of OECTs by electropolymerization of the monomer, EDOT, bridging the gap between microfabricated source and drain electrodes. Various types of dopants, namely poly(styrenesulfonate), perchlorate and tetrafluoroborate were used. The channel length and the deposition time were also varied to control the channel dimensions. These parameters were chosen to study their impact on overall film morphology and uniformity, which are known to strongly affect electrical properties, and hence, transistor behaviour. The electropolymerization, which is a relatively simple technique, could therefore be used to fabricate OECTs in bioelectronics.

**EN12.15.06**

*Low-Resistance Ohmic Contacts on Graded InGaN*  
Reem E. Alhelais, Morgan Ware, Pijush Ghosh, Chen Li and Najla Alnami; University of Arkansas–Fayetteville, United States

There is an increasing demand for high-power electronic components and optoelectronic devices with low losses and high efficiency. The III-nitride semiconductor materials have demonstrated great potential for high-power, high-frequency, and high-temperature applications because of their remarkable and wide-ranging electronic and physical properties. For example, In$_x$Ga$_{1-x}$N alloys have optical bandgaps ranging from infrared to ultraviolet, between 0.7 eV and 3.4 eV. A recently explored area of InGaN research is in grading the composition of the alloy to achieve such novel properties as polarization induced p-type doping. However, these graded composition alloys do not yet have well-characterized metal contact materials. Thus, we will present a study of low resistance ohmic contacts characterized by using the transmission line method, on graded layers of InGaN grown on semi-insulating GaN. Carrier concentration and mobility are subsequently characterized in the graded films by temperature-dependent Hall-effect measurements.

**EN12.15.07**

*Morphological Engineering of P3HT Thin Films via Halogen-Bonding for High Performance Electronic Applications*  
Jonathan J. Montes, Harold O. Lee and Sam-Shajing Sun; Norfolk State University, United States

Polymeric conjugated materials are very promising for developing future soft material-based semiconductors, conductors, electronic and optoelectronic devices due to their inherent advantages such as lightweight, flexible shape, low-cost, ease of processability, ease of scalability, etc. There are numerous ways to tune material properties via post-processing treatments such as annealing, solvent additives, or doping. One challenge of solution processed organic thin film electronics is the repeatable and well-defined morphological control of the resulting thin films. In this study, we observed that the addition of para-substituted halogenated benzenes to poly-3-hexy-thiophene (P3HT) solutions can affect the morphological properties of P3HT thin films. These additives have been shown in literature to exhibit halogen bonding interactions with other small molecules. Here we seek to use this interaction to see if this interaction can be used to promote polymer self-assembly on the nanometer-scale. Techniques such as UV/Vis spectroscopy, Raman spectroscopy, X-ray diffraction, and Atomic Force Microscopy were used to probe the evolution of the film morphology as the additives were added to the solutions. This study could reveal new knowledge and insights of approaches that would enhance the solid-state morphology of thin films for high performance electronic applications.

**EN12.15.08**

*Effects of Diiodo-Alkane Additives to P3HT Thin Films for High Performance Electronic Applications*  
Shelita Hall, Harold O. Lee and Sam-Shajing Sun; Norfolk State University, United States

Polymeric conjugated materials are very promising for developing future soft material-based semiconductors, conductors, electronic and optoelectronic devices due to their inherent advantages such as lightweight, flexible...
shape, low-cost, ease of processability, ease of scalability, etc. There are a number of ways to tune material properties via post-processing treatments such as annealing, solvent additives, or doping. One challenge of solution processed organic thin film electronics is the repeatable and well-defined morphological control of the resulting films after deposition. In this study, we observed how the addition of diiodo-alkanes to poly-3-hexy-thiophene (P3HT) solutions effect the formation of resulting thin films. These additives have various boiling points that will affect the drying properties of cast thin films. We also sought to observe if any halogen bonding interaction between iodine and sulfur occurs and if this interaction can be used to promote polymer morphological self-assembly. Techniques such as UV/Vis spectroscopy, Raman spectroscopy, X-ray diffraction, and Atomic Force Microscopy were used to probe the evolution of the film morphology as the additives were added to the solutions. This study may result in a new technique that can be used to enhance the solid-state morphology of thin films for high performance electronic applications.

EN12.15.09  
Nanoscale Analysis of Physical, Mechanical and Electrical Properties of Undoped and Doped Conjugated Polymer Thin Films **Hemanth Meddali**, Krystal House and Deirdre O'Carroll; Rutgers, The State University of New Jersey, United States

Conjugated polymers like polyacetylene, polypyrrole, polythiophene and polyaniline have been studied extensively in terms of their bulk optical and electrical properties due to their potential for various applications in optoelectronic devices. These polymers have various desirable characteristics such as low processing cost and solubility in common solvents, in addition to possessing useful physical properties like light weight and flexibility. The most exciting feature of these polymers is the delocalization of “pi” bonds along the chain axis that makes them intrinsically conductive. The versatility of conjugated polymer materials is increasing due to the introduction of additional electro-active behavior via doping. Doped conjugated polymers have the potential to exhibit electrical conduction that approaches that of metals, which gives rise to altered optical transparency. These optical and electrical properties are of interest for both photonic and organic electronic devices. In recent history, investigations of the nanoscale properties of matter have proven to be fruitful in terms of understanding and exploiting unique characteristics of materials. Studying nanoscale properties of doped conjugated polymers could provide more information on the distribution of dopant sites, which is necessary for improving the charge conduction in these polymers.

In this study, we focus on comparison of nanoscale topological, mechanical and electrical properties of poly(3-hexylthiophene) (P3HT) and doped P3HT thin films. P3HT was spin coated onto an indium-tin oxide (ITO) coated glass substrate followed by electrochemical doping using tetrabutylammonium perchlorate (TBAP). Atomic force microscopy (AFM) was used to perform topography and phase imaging (tapping mode) of both undoped and doped P3HT and their crystallinity was compared to assess the effects of doping. There was a clear loss in crystallinity caused by doping, according to the phase images, and it was found that domains of varying crystallinity were not correlated with film topography. The mechanical properties of the thin films were studied by performing fast force mapping (FFM) using an AFM tip with a lower spring constant and adhesion to the polymer surface. Young’s modulus was calculated from FFM and a relation was established between the modulus and crystallinity for both undoped and doped P3HT at the nanoscale. The crystalline domains in both the polymer thin films exhibited higher Young’s modulus when compared to the amorphous ones. Conductive AFM imaging (CAFM) was employed to perform scans of the local current distribution of the polymer films with the application of a bias voltage. The current values increase by at least 3 orders of magnitude on going from undoped to doped samples. Also, evidence that nanoscale crystalline polymer domains conduct more current than nearby amorphous ones was found by simultaneously acquiring topography FFM and CAFM scans.

EN12.15.10  
Versatile Reductive Interlayers for Efficient Electron Injection of Organic Field-Effect Transistors and Non-Volatile Memory **DongEun Kim** and Kang-Jun Baeg; Pukyong National University, Korea (the Republic of)

Recently, pi-conjugated organic molecules have been attracted a great attention due to their low-temperature processability on flexible substrates and low-cost applications via graphic arts printing techniques. For enabling the high performance electronic and optoelectronic devices, both electron and hole charge carrier injection have to be efficiently controllable. Here, we report an efficient electron injection layer for high-performance n-type organic
field-effect transistors (OFETs) using solution-processed reducing agents. The reductive interlayer plays many different roles depending on an energy level alignment between the reduction potential of a reducing agent and frontier molecular orbitals of organic semiconductors. Basically it induces better electron injection properties so that electron mobility is significantly improved. Moreover, the reducing agent could induce doping effect by direct charge transfer to the semiconductors with the highest unoccupied molecular orbital. Operation modes of ambipolar OFETs could also be changed by completely regulating the hole current, thereby initial ambipolar OFETs converts to n-type only unipolar mode device. Those interlayers increase memory capacity of non-volatile transistor-type memory via changing the operation modes from unipolar to bipolar.

EN12.15.11
Temperature and Solvent Effects on P3HT:PCBM Bulk Heterojunction Morphology—An Atomistic Molecular Dynamics Simulation Approach Marlene N. de Morais, Ranylson M. Savedra and Melissa F. Siqueira; Universidade Federal de Ouro Preto, Brazil

Organic solar cells (OSCs) are an important eco-friendly technology to produce clean and renewable energy, using flexible, low-cost, and lightweight devices. Poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) bulk heterojunctions have stood out among the active layer compositions due to its prominent power conversion efficiency [1]. Experimental data have shown that the chosen conditions for the manufacture processing - as solvent evaporation rate and thermal annealing - can lead to different morphologies. It is well known that the bulk heterojunction microstructure directly influences on the OSC performance. However, due to the amorphous nature of these materials, the physicochemical characterizations are still limited [2]. In this work, we have performed atomistic molecular dynamics simulations aiming to estimate the morphological characteristic of the P3HT:PCBM blend. The evaporation process is reproduced in the simulations, and solvent removal has been carried out in a multistep process until the film formation [3]. At first, we simulated three systems at room temperature: (i) a P3HT film, (ii) a PCBM film, and (iii) a P3HT:PCBM bulk heterojunction. After that, in order to investigate the temperature influence on the arrangements of the backbone chains for the final film morphology, the simulations of these systems were performed under thermal annealing. We evaluated the structural properties of the oligomer backbone chains on both, P3HT film and bulk heterojunction. In addition, we analyzed the distribution of PCBM in the bulk heterojunction, which behavior has a good agreement with experimental results available in the literature.

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References:

EN12.15.12
Charge Carrier Transport in a Polymeric Semiconductor—Poly(3-hexylthiophene-2,5-diyl) (P3HT) Zhaojing Gao1, Arthur Yelon1,2, Clara Santato1 and Manuel Reali1; 1Polytechnique Montréal, Canada; 2Regroupement québécois sur les matériaux de pointe (RQMP), Canada

Organic semiconductors are now widely employed in electronic and optoelectronic devices due to their solution processability and compatibility with flexible substrates. 1 The Meyer Neldel (MN) Rule or isokinetic (IK) law means that a set of comparable samples exhibit kinetic behavior independent of activation energy at an IK or MN temperature.2 It is obeyed by the electron or hole mobility, µ, in many organic semiconductors, including pentacene3, fullerene4, N-Alkyl Perylene Diimides,5 etc. The existence of MNR is still not widely known. Further, despite considerable evidence in its favor, the multi-excitation entropy (MEE) model of its origin is still frequently contested. We fabricated organic field effect transistors (FETs) based on regioregular poly(3-hexylthiophene-2,5-diyl) (RR P3HT) of three different values of molecular weight, MW, and studied the dependence of the mobility upon the gate bias, $V_g$, and temperature, $T$. For all values of MW, we found that in the range 200 to 290 K (low $T$), the $\mu$ of the FET carriers exhibits an exponential dependence upon $1/T$ for different $V_g$, with an MN temperature about 290K. Between this temperature and 350K (high $T$), $\mu$ increases more rapidly than it did below, and is independent of $V_g$. We believe that, in the low $T$ regime, the polaronic carriers hop along the polymer backbone chain. We attribute the high temperature behavior to the alpha relaxation of the polymers, that is to the movement of the backbone chains. We believe that in this regime, the polaronic carriers move with the mobile chains.
Exciton to Charge Conversion in Pristine Non-Fullerene Acceptors—A Computational Study

Anastasia Markina¹, Nicola Gasparini², Derya Baran¹ and Denis Andrienko¹; ¹Max Planck Institute, Germany; ²King Abdullah University of Science and Technology, Saudi Arabia

Organic solar cell efficiencies can be boosted by replacing fullerene acceptors with strongly-absorbing dye molecules, namely, non-fullerene acceptors (NFAs). In fact, even pristine non-fullerene acceptors can serve as efficient exciton charge converters, thereby enhancing the total solar cell efficiency. In this presentation, we explain why excitation dissociation into a charge transfer (CT) state and the splitting of the CT state into charge separated (CS) state are efficient in pristine NFAs.

First, we consider exciton dissociation into particular CT states. Evaluation of dielectric solvation of excited and CT states shows that there is enough driving force for the transition, due to a stronger dielectric stabilization of charges as compared to the localized excited state. We then evaluate electrostatic potential at a disordered interface between NFA domains with different acceptor orientations and show that it provides electrostatic potential bending, sufficient to overcome the Coulomb binding energy of the CT state. Both effects can be traced back to molecular quadrupole moments and their long-range contributions to solid-state ionization energies and electron affinities. The present study demonstrates that the electrostatic configuration of NFA molecules is important for both stages of charge conversion and suggests several design rules for NFAs with efficient charge separation in photovoltaic applications [1,2].

electrical conductivity and UV-Vis-NIR dedoping signatures, independent of the polymer:dopant system and of the dopant concentration. The layer thickness, varying from 15-200 nm, presented a non-negligible impact over the kinetics of the doping degradation. We highlighted the detrimental impact of moisture and/or O2(H2O)n hydrated complexes by evaluating the p-doping stability under different atmospheres (ambient air, anhydrous air and nitrogen). Using X-ray Photoelectron Spectroscopy (XPS) we were able to assign the p-doping instability in ambient air to changes in the oxidation state of the dopant molecules and some degradation signatures. Deeper investigations on the impact of water in the stability of neutral and ionized p-dopant molecules are carried out by Nuclear Magnetic Resonance (NMR) Spectroscopy, Electron Paramagnetic Resonance (EPR) and UV-vis-NIR to better elucidate on the possible degradation mechanism. This work invites to reconsider the requirements for air-stable p-doping of OSCs as a first step towards air-processable thin p-doped layers.


EN12.15.15
Factors Determining Transfer Energetics for Organic Photovoltaics
Shahidul Alam1,2, Ulrich S. Schubert1,2 and Harald Hoppe1,2; 1Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University, Germany; 2Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University, Germany

Recently, non-fullerene acceptors have received increasing attention for use in polymer-based bulk-heterojunction organic solar cells, as they have demonstrated considerably improved photovoltaic performances over classical polymer-fullerene blends. Part of the success of these materials has been attributed to an increased contribution to the overall absorption of the solar cells, thanks to relatively low bandgaps in these materials. In this study a systematic comparison between two acceptor materials, the classical fullerene-derivative PCBM and the non-fullerene-acceptor 2,2′-[[6,6,12,12-Tetrakis(4-hexylphenyl)-6,12-dihydridithieno[2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]dithiophene-2,8-diy]bis[methylidyne(3-oxo-1H-indene-2,1(3H)-diylidene)]bis[propanedinitrile] (ITIC) was performed in combination with a statistically substituted anthracene-containing poly(p-phenylene-ethynylene)-alt-poly(p-phenyleinvinylene)s (PPE–PPV) copolymer (AnE-PVstat), as well as with two other commonly applied materials called Poly[[4,8-bis[5-(2-ethyhexyl)-2-thienyl]benzo[1,2-b:4,5-b′]dithiophene-2,6-diy]-2,5-thiophenediy][5,7-bis(2-ethylhexyl)-4,8-dixo-4H,8H-benzo[1,2-c:4,5-c′]dithiophene-1,3-diy] polymer (PBDB-T) and Poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole) poly][9-(1-octyl)9H-carbazole-2,7-diy]-2,5-thiophenediy-2,1,3-benzothiadiazole-4,7-diy]-2,5-thiophenediy] (PCDTBT).

We find several cases in which the polymer-fullerene blend does function properly in photovoltaic terms; however, when exchanging the fullerene-derivative with ITIC, photovoltaics function seizes down dramatically. While cyclic voltammetry derived energy levels suggest successful charge transfer from the polymer to the ITIC, blend films and photovoltaic studies indicate the opposite. Numbers of spectroscopic methods like ultraviolet-visible spectroscopy (UV-Vis), photoluminescence spectrum (PLS), electroluminescence spectrum (ELS), energy-resolved electrochemical impedance spectrum (ER-EIS), transient absorption spectroscopy (TAS), fourier-transform infrared spectroscopy (FTIR), electron spin resonance spectroscopy (ESR) as well as quantum chemical calculations have been used for finding an explanation.

EN12.15.16
High Electron Affinity Molecular Dopant for Sequential Solution Doping of DPP Copolymer Films
Zaira I. Bedolla-Valdez, Goktug Gonel, Jan Saska, Sean Aronow, Nikolay Shevchenko, Alexander Dudnik, Mark Mascal and Adam J. Moule; University of California Davis, Mexico

Semiconducting polymers (SPs) have received a lot of attention in recent years due their potential for creating low cost solution processable electronic devices. The SP conductivity can be tuned by several orders of magnitude by molecular doping. The molecular dopant 2,3,5,6-tetfluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) has been extensively explored as a p-type dopant for poly-(3-hexylthiophene) (P3HT). With the synthesis of novel high mobility conjugated copolymers with higher ionization potentials, such as diketopyrrolopyrrole (DPP)-based copolymers, there is a need to develop stronger molecular dopants. Recent studies have reported stronger molecular dopants than F4TCNQ, however, most of them present poor solubility that makes them unable to be use for solution...
In this work we present the synthesis and characterization of a new soluble dopant with high electron affinity (-5.5 eV) 2,2',2″-(cyclopropane-1,2,3-triyldene)-tris(cyanoacetate) (TMCN3-CP). Using sequential solution processing we demonstrate that conjugated copolymers such as PDPP-4T, PDPP3T, and PDPP-T-T-T achieve high conductivities when they are p-type doped with TMCN3-CP. To our knowledge, this is the first report of sequential solution doping of these high ionization energy polymers.

EN12.15.17
Polaron Hopping Barriers and Rates in Conjugated Polymers—A Tight Binding Study on Poly(3-hexylthiophene) Joel H. Bombile, Michael J. Janik and Scott T. Milner; The Pennsylvania State University, United States

Semiconductors are the subject of much investigation as next-generation materials for organic electronic devices. The ability of these materials to transport charges is a key factor limiting the performance of these devices. Charge carriers in conjugated polymers are localize by disorder and polaronic effects. As such, charge transport in these materials is often described as non-adiabatic hopping transport, with a rate given by Marcus Theory. An important variable which determines the temperature dependence of Marcus rate is the activation energy barrier for polaron hopping. We use a tight-binding polaron model, in which charge carriers are stabilized by nuclear reorganization and by dielectric polarization to map out the potential energy curve for polaron hopping, and thus determine barriers and rates relevant to intrachain and interchain charge hopping processes in P3HT crystalline lamellae and amorphous melts. We find that the barriers largely depend on polarization effects, and on the electronic coupling between the initial and final location, which penalize hopping events involving longer distances. We also find that transport is limited by interchain hopping in P3HT crystals and amorphous melts. Along the chains, transport is fast and relatively insensitive to dihedral disorder. Our predicted barriers and rates are in excellent agreement with experiment.

EN12.15.18
Eco-Friendly Polyimide Gate Dielectric via Aqueous Solution for High Performance OTFT Yuri Jeong1,2, Hyunjeong Ahn1,2, Yu Jin So4, Hyunjin Park1, Jong Chan Won1,2 and Yun Ho Kim1,2; 1Korea Research Institute of Chemical Technology, Korea (the Republic of); 2University of Science & Technology, Korea (the Republic of)

Solution-processed organic thin-film transistors (OTFTs) have received extensive attention over the past decade due to their noteworthy features: low-material consumption, low-cost manufacturing, and large-area processability. However, hidden behind the virtues is potential damage to environment and human health by using detrimental organic solvents that are not adaptable for future industrial scale. Here, we propose a water-based polyimide (PI) as gate dielectric layer for green chemistry to substitute harmful aprotic solvents that emit toxic vapors during drying process. We find that a water-based precursor shows considerably better compatibility with facile thin film fabrication than a N-methyl-2-pyrrolidone-based precursor. To adopt the water-based precursor facilitates not only escape from a hindrance in humid air through hydrolytic stability buy also use of less thermal energy through faster imidization. As a result, pentacene-based TFTs using water-based PI spin-coated in relative humidity of 43 % exhibit average mobility of 0.132 cm² V⁻¹ s⁻¹, on/off current ratio of over 10⁵, and high yield nearly 100 %. Under the same conditions, on the other hand, OTFTs using NMP-based PI exhibit poorer device performance with lower yield as low as 50 %. The results indicate that the newly designed water-based PI shows a viable path to development of electronic packages using harmless processing with less sensitivity to ambient atmosphere.

EN12.15.19
An Investigation of Acceptor-Unit Steric Bulk on Charge Transport and Photovoltaic Device Performance in Polymer Organic Solar Cells Abigail A. Advincula and John Reynolds; Georgia Tech, United States

In this work, the role of side-chain bulk on the acceptor unit in a Donor-Acceptor (DA) polymer on charge generation and power conversion efficiencies in PCBM blend bulk heterojunction solar cells is investigated through the design and synthesis of novel polymer families and device fabrication. The PCE11 repeat unit is used as a high performing solar polymer whose acceptor unit lacks a sidechain. It was hypothesized that the lack of a substituent on the acceptor unit contributed to better fullerene docking on the acceptor units and facilitated more efficient charge transfer from the DA polymer to the fullerene, enhancing OPV performance (Graham, et. al., J. Am. Chem. Soc. 2014). Previously, we reported a family of PCE11 analog polymers designed with comparatively small methyl...
substituted acceptor units for use as donor phase materials in bulk heterojunction (BHJ) OPV applications. These polymers make use of common acceptor moieties thieno[3,4-c]pyrrole-4,6-dione (TPD), diketopyrrolopyrrole (DPP), and isoindigo (ii) with methyl sidechains to provide sterically unhindered sites for enhanced interactions with a molecular acceptor (MA), either PC71BM or ITIC in this study. The resulting polymers were utilized in BHJ OPV devices where the highest performing DA polymer, P(T4-TPD-M), obtained a maximum PCE of 7.5% with PC71BM and 4.0% with ITIC. These results indicate that minimally sized methyl sidechain derivatives of TPD, DPP, and il can be useful acceptor moieties in DA polymers. As a further effort to probe the effect of acceptor unit bulk on power conversion efficiency, a family of TPD-based polymers with sidechains of increasing bulk, but similar solubility, was synthesized. Devices were fabricated with these polymers under similar conditions to ensure the only variable was the side chain bulk on the acceptor unit. Photophysics studies followed device fabrication to study the nature of charge separation in the respective polymer systems. By using these polymers with precisely controlled side chain bulk, a connection between acceptor side chain bulk steric and charge transport and solar cell performance is probed.

EN12.15.20
Correlation between Morphology and Device Performance of PBDTTT-EFT: PCDTBT: PC71BM Ternary Organic Solar Cells Javed Alam Khan, Ajay Singh Panwar and Dipti Gupta; Indian Institute of Technology, Bombay, India

In recent years, ternary organic solar cells (t-OSCs) have offered the potential of high-power conversion efficiency due to enhanced photon absorption or energy level complimentary materials as the second donor or acceptor based on a single bulk heterojunction architecture. For well promoting the development of t-OSCs, we fabricated ternary blend OSCs with two donors, including one low bandgap PBDTTT-EFT, one wide bandgap polymer PCDTBT, and one inorganic acceptor PC71BM. The incorporation of a wide bandgap PCDTBT polymer as a third component in to the binary blends improve fill factor of 71.62% with high PCE of ~9% and high $J_{sc}$ (16.55 mAcm$^{-2}$) of t-OSCs were observed than those of the binary OSCs with enhanced light absorption, efficient energy transfer and better blend morphology. This increased PCE attributed to not only non-radiative Forster resonance energy transfer (FRET) and enhancement of absorption between two donor polymers but also the formation of a bicontinuous interpenetrating network in ternary blends. The addition of a wide bandgap polymer into binary blends open up a new door for enhancing device performance in a simple, effective and promising way.

EN12.15.21
The Influence of Halogenation on Energetics in Pure and Mixed Phases in Model Organic Semiconductors Composed of Anthradithiophene Derivatives and C60 Ashkan Abtahi1,1, Samuel Mazza1,1, Sean Ryno1,1, Kirkbride Loya1,1, Ruipeng Li2, Sean Parkin1, Chad Risko1,1, John Anthony1,1 and Kenneth R. Graham1,1; 1University of Kentucky, United States; 2Cornell University, United States

Halogenation, particularly fluorination, is commonly used to alter the energetics, stability, and morphology of organic semiconductors. In the case of organic photovoltaics (OPVs), fluorination of electron donor molecules or polymers at appropriate positions can help improve PV performance. In this contribution, we present insights into how halogenation influences the bulk solid-state energetics of model anthradithiophene (ADT) materials, their interfacial energetics with C$_{60}$, and the energetics of various ADT:C$_{60}$ blend compositions using ultraviolet photoelectron spectroscopy, external quantum efficiency measurements of charge-transfer (CT) states, and density functional theory calculations. In agreement with previous work, nonhalogenated ADT molecules show higher energy CT states in blends with C$_{60}$ and lower energy CT states in ADT/C$_{60}$ bilayers. This trend is reversed in the halogenated ADT/C$_{60}$ systems, with the CT state energies of ADT:C$_{60}$ blends lying at lower energies than those in the bilayers. In bulk-heterojunction photovoltaics, the lower energy CT states present in the mixed phase with the halogenated ADT derivatives will likely decrease the probability of charge separation and increase charge recombination. These less favorable energy landscapes observed upon halogenation suggest that the benefits of fluorination observed in many OPV material systems may arise primarily from morphological factors.

EN12.15.23
Fine Tuning of HOMO/LUMO levels of Building Blocks via Thiophene Incorporation into the Indolo[3,2,1-jk]carbazole Scaffold Dorian Bader, Paul Kautny and Johannes Fröhlich; TU Wien, Austria
Triphenylamines are an important class of donor building blocks in the field of organic electronics. Crucial electronic properties such as triplet energy ($E_T$), HOMO/LUMO levels and donor strength can be tuned via modifications of its molecular structure e.g. planarization. Specifically, the donor strength decreases with increased planarization, with the completely planar indolo[3,2,1-\textit{jk}]carbazole (ICz) even exhibiting weak acceptor characteristics. In this contribution an increase in donor strength of the building block, while retaining full planarity, is presented. This is achieved by the incorporation of electron rich thiophene into the scaffold. Furthermore, a fine tuning of the electronic properties depending on the substitution positions is realized. A synthetic approach towards the target molecules employing Ullmann condensation as well as CH activation will be presented. Furthermore, the electrochemical as well as photophysical characterizations of the novel building blocks will be discussed.

EN12.15.24
Characterizing Mechanical Properties of Organic Thin Films for Directed Energy Transport Kanak Datta, Xiaheng Huang and Parag B. Deotare; University of Michigan, United States

We experimentally study organic dye thin films under mechanical strain using engineered microstructures and extract mechanical properties that are essential to the design of next-generation strain based excitonic devices. Such mechanically strained architecture provides a simpler and energy efficient platform to achieve directed energy transport in organic materials. In our measurements, we estimate the elastic modulus of the thin film of red luminescent dye 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM), embedded in Tris-(8-hydroxyquinoline) aluminum (Alq$_3$) matrix to be within 3.6-7.2 GPa. Reported values in literature lie in the range of 1- 100 GPa [1] [2] and so, our results demonstrate a new non-destructive characterization approach based on solid state solvation effect [3] that greatly reduces the range of uncertainty in the measurement of elastic modulus of organic thin films. The effect of strain gradient on energy transport in organic thin films is currently under investigation.

Our device platform consists of buckled silicon di-oxide (SiO$_2$) microbeam patterned using optical lithography and reactive ion etching, followed by deposition of 30 nm Alq$_3$:DCM. 50 nm 2,2′,2″-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) thin film is evaporated to protect the active layer during the subsequent XeF$_2$ gas phase etching used to release the microbeams. Due to internal compressive stress in the oxide, the microbeams are buckled upwards, inducing tensile strain on the organic thin film. The buckling was quantified using optical white light interferometry, to extract the tensile strain on the film.

The Photoluminescence (PL) of the strained organic thin films was characterized using a 450 nm excitation laser in a nitrogen (N$_2$) environment. We observed gradually increasing blueshift in the PL emission towards the center of the microbeam, with the maximum blueshift occurring at the center of the beam. The spectral blueshift is attributed to a change in local molecular concentration that changes the local electric field surrounding the DCM molecules.

We fitted the observed spectral blueshift with respect to the applied tensile strain, using a simple linear equation:

$$E_{\text{Emission}} = B \varepsilon + C; \text{Here, } E_{\text{Emission}} \text{ is the emission energy of DCM from PL measurement, } B \text{ and } C \text{ are fitting parameters, } \varepsilon \text{ is the tensile strain on the thin film.}$$

and estimated the elastic modulus of the organic thin film to be within 3.6-7.2 GPa. By engineering the strain at microscale, we have successfully measured mechanical property on an organic thin film that are vital to the development of wearable and flexible energy conversion devices such as photovoltaics and light emitting diodes.

References:

EN12.15.25
Photo-Excited Carrier Dynamics of Organic Thin-Film Solar Cell Souichiro Sato, Tomoki Miyake, Shota Fujikawa and Mitsuru Inada; Kansai University, Japan

We prepare CuPc/C$_{60}$ organic thin-film solar cell structure and investigate the photo-excited carrier lifetime by using time of flight method to reveal the carrier transport dynamics of the structure.
The structure of the sample was ITO/CuPc(30 nm)/C60(40 nm)/BCP(5 nm)/Al. These layers were deposited on SiO2 substrate by using vacuum evaporation. After the depositions, the sample was taken out into the atmosphere, and then, it was immediately sealed with epoxy resin. Optical absorption spectra for each thin-film layer were measured by ultraviolet to visible light absorption spectrometer (JASCO V-630). Current density-voltage characteristics of the sample were measured using YOKOGAWA GS820 source measure unit with conventional two-terminal method. The spectral sensitivity characteristics were measured using a lock-in amplifier (Stanford Research SR830) and a xenon lamp as the irradiation source. The transient photocurrent properties were investigated irradiating third harmonic (532 nm) of pulsed Nd-YAG laser light (Quantel CFR200, pulse width: 7 ns) and the current decay characteristics were observed on a screen of digital oscilloscope. All measurements were carried out at room temperature and in air.

The obtained carrier lifetime (transit time) was 58 μs. This value is much longer than that of estimated lifetime from the mobility of thin-fillm layers. This means the carrier transport cannot be described by a general carrier drift model. In addition, the carrier lifetime become short (5 μs) under white halogen light illumination. The results suggest that the photo-excited carrier transport is affected by trapping levels in the organic layers.

EN12.15.26
Novel Semiconductors Based on Mixed-Metal Thiocyanate Compounds from Mechanochemical Reactions
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Copper(I) thiocyanate (CuSCN) has become a well-known transparent semiconductor with wide-ranging applications, such as organic photovoltaic cells1, perovskite solar cells2 and organic light-emitting diodes3. CuSCN is a coordination polymer with a 3D extended network; its unique properties of wide band gap and good hole mobility are resulted from its electronic structure which consists of Cu 3d states in the valence band and SCN states in the conduction band. With the objective to develop novel semiconductors based on coordination polymers, we have recently reported on tin(II) thiocyanate [Sn(NCS)2], which was found to exhibit high optical transparency and promising hole transport states of Sn 5s in the valence band4. In this work, we expand the concept of modifying the metal centers of the thiocyanate compounds further by synthesizing mixed-metal thiocyanates via mechanochemical reactions. Starting from CuSCN which has already exhibited excellent semiconducting properties, we experimented with a number of thiocyanate compounds of other metal ions and found that Zn(II), Co(II) and Ni(II) thiocyanates were suitable candidates. After mechanical grinding CuSCN, Zn(SCN)2, Co(SCN)2 and Ni(SCN)2, the powder X-ray diffraction (PXRD) showed that their diffraction peaks appear in the same position but become significantly broadened. This suggested that their lattice structures were sufficiently soft to allow amorphization but at the same time stable enough to retain the same phases. This showed the potential that these compounds could be mixed and reacted using mechanochemical processes. Subsequently, CuSCN and the thiocyanate compounds of Zn(II), Co(II), and Ni(II) were mixed by the solvent-free ball-milling process to realize the homogeneous metal ion combination without an environmental issue from toxic organic solvents. The PXRD results of the final compounds were completely different from the starting thiocyanate materials, suggesting the successful synthesis of new structures of mixed-metal thiocyanates. Analyzing the powder samples with the energy dispersive X-ray spectroscopy (EDX) under a scanning electron microscope (SEM) showed homogeneous distribution of the mixed metal ions. Other characterization results from Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric/differential thermal analyses (TGA/DTA) also confirmed different physical properties of the new compounds compared to the starting materials. In particular, TGA/DTA results showed that some of the compounds display melting behavior at temperatures around 300 °C; this could lead to thiocyanate-based inorganic semiconductors that can be processed into films form melt. Further studies on the electronic properties and applications of these compounds are ongoing. This work shows that the solvent-free mechanochemical processes are promising for the synthesis of new coordination polymers as well as expand the material library of semiconductors based on coordination polymers.

EN12.15.27
New Wide Band Gap Inorganic Semiconductor Tin(II) Thiocyanate [Sn(NCS)2] and Its Application in Organic Photovoltaics Jidapa Chaopaknam1, Chayanit Wechwithayakhlung1, Fumiya Hamada2, Akinori Saeki2 and Pichaya Pattanasattayavong1; 1Vidyasirimedhi Institute of Science and Technology, Thailand; 2Osaka University, Japan
Coordination polymers feature a large library of materials; however, their applications in electronic devices have been mostly unexplored. One recent example that has been demonstrated as a novel semiconductor with extensive device applications is copper(I) thiocyanate (CuSCN).[1-3] We have been developing other coordination polymer semiconductors and recently reported on tin(II) thiocyanate [Sn(NCS)₂] which exhibited a wide band gap and promising hole transport properties due to the dispersed Sn 5s electronic states at the top of the valence band giving rise to a small hole effective mass.[4] Another promising aspect of Sn(NCS)₂ is that it can be solution-processed from common solvents with high polarity, such as alcohol-based solvents. This is in contrast to CuSCN which is normally deposited from alkyl sulfides or aqueous ammonia which are either malodorous or corrosive. Herein, we report the optimization of solution-based thin-film processing of Sn(NCS)₂ and its application as a hole transport interlayer in organic photovoltaics (OPVs). We found that the thin-film formation of Sn(NCS)₂ was not straightforward due to its strong tendency to form clusters and islands resulting in discontinuous and inhomogeneous films. These films led to the absence of conduction pathway in the planar direction and short-circuits in the vertical direction. To resolve this issue, we dried the films at room temperature under inert atmosphere for an extended period of time after the spin-coating step and consistently obtained high-quality Sn(NCS)₂ thin films. These films were highly transparent due to contact with ITO substrates. As such, Sn(NCS)₂ thin films were employed as the hole-transporting/electron-blocking layer in OPVs based on PTB7-Th:PC70BM as the active light-absorbing layer. OPV cells yielded impressive power conversion efficiencies (PCE) up to 7.98% (Jsc= 16.06 mA cm⁻², Voc = 0.80 V, FF = 0.62) with a device area of 0.181 cm². The average PCE from 10 devices was 7.5%. This remarkable result demonstrates the potential of Sn(NCS)₂ in thin-film electronic applications and provides a strong foundation for further development of semiconductors based on coordination polymers.


EN12.15.28
Improving Hole Mobility in CuSCN Films by Anti-Solvent Treatment and Application in Thin-Film Transistors
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Copper(I) thiocyanate (CuSCN) has been demonstrated as a promising coordination polymer semiconductor with extensive opto/electronic applications owing to its p-type characteristic with high hole mobility, excellent optical transparency, and solution processability. CuSCN has been used as a transparent p-type active channel layer in thin-film transistors (TFTs), usually exhibiting filled-effect hole mobility (μFEh) on the order of 0.01 cm² V⁻¹ s⁻¹.[1,2] In order to challenge p-type metal oxide semiconductors, further optimization of the film processing is required to improve the hole transport properties. A few techniques have been reported to enhance μFEh of CuSCN films leading to higher TFT performance; one of the novel examples is the molecular doping of CuSCN with C₆₀F₄₈ to increase the hole concentration and fill the trap states, enhancing μFEh by tenfold.[3] However, the use of such dopant may not be widely applicable. Herein, we report a simple and versatile approach of using anti-solvent treatment that can enhance μFEh in solution-processed layers of CuSCN by fivefold. Acetone (Ace), tetrahydrofuran (THF), methanol (MeOH) and isopropyl alcohol (IPA) were employed as anti-solvents and spin-coated onto CuSCN films which had been prepared from diethylsulfide (DES) solution also by spin-coating. The treated films exhibited similar electronic properties to the neat films, i.e., an optical band gap of 3.9 eV and a valence band maximum at -5.5 eV. Interestingly, the anti-solvent treatment demonstrated a significant effect on CuSCN film morphology with the root-mean-square (RMS) roughness of the films decreased from 4 nm to 1.7, 1.5 and 1.3 nm after treated with MeOH,
Ace and THF, respectively, due to the reduction in CuSCN grain size. This analysis was also corroborated by the results of the extended X-ray absorption fine structure (EXAFS) of S K-edge X-ray absorption spectroscopy, which was employed to study the coordination between Cu and S. THF-treated film showed the highest number of surface Cu-S coordination that resulted from CuSCN grain size reduction. As a result, TFT measurements revealed a significant improvement of $\mu_{FE}$ in THF-treated CuSCN film to 0.05 cm² V⁻¹ s⁻¹ accompanied by a decrease in the turn-on voltage ($V_{on}$) and trap density. In addition, Ace- and MeOH-treated devices could also raise $\mu_{FE}$ to 0.024 cm² V⁻¹ s⁻¹ and 0.012 cm² V⁻¹ s⁻¹, respectively. The trend in the mobility was also further substantiated by microwave conductivity measurements that also showed the mobility of untreated films to increase with anti-solvent treatment in the order: MeOH < Ace < THF. This study shows that the anti-solvent treatment can be used to significantly improve film morphology and hole transport properties in CuSCN thin films. This simple method relies on common chemicals and standard procedures, and thus can be applicable to a wide range of thin-film opto/electronic device processing.

Reference

EN12.15.29
Enhanced Aggregation of Low-Bandgap Polymer in Polymer/Polymer Blend Films
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Blend films of conjugated polymers have been attracting attention as an active layer of organic electronic devices. Nanostructures inside the blend films play essential roles in determining the overall device performance. For instance, the ordered regions of the conjugated polymer could support charge transport while the amorphous counterpart blocks it due to the sizeable energetic barrier. However, it is difficult to expect the nanoscale self-assembly tendency of conjugated polymer chains. Therefore, a systematic study on the structure in the blend films is still limited so far. In this study, we conduct experiments to measure and identify the change in the conformation and aggregation structures of a conjugated polymer, which arises characteristically by blending with another conjugated polymer by the spin-coating method.

Blend films composed of a low-bandgap polymer (PCPDTBT) and a wide-bandgap polymer (P3M4HT) were prepared by spin-coating from the Chlorobenzene solution which dissolves the polymers with different weight ratios. For these blend films, UV-Vis absorption spectroscopy and Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed to characterize structures of the PCPDTBT dispersed in the P3M4HT matrix. Both of the vibrational structure from UV-Vis absorption spectra and the scattering intensity from GIWAXS cleared that fraction of the ordered PCPDTBT aggregates relative to the amorphous PCPDTBT counterpart increases by blending. Furthermore, the GIWAXS analysis reveals that the correlation length of the PCPDTBT chain ordering increased in both its alkyl-stacking and chain backbone directions. These structural ordering of PCPDTBT was enhanced with the decreasing the PCPDTBT weight ratio in the blend film.

Our result concludes that blending of conjugated polymers by spin-coating causes an enhancement of ordering of the polymer chains rather than the corresponding neat film. These changes in the aggregation structure of conjugated polymer chains are beneficial for the improvement of charge transport and the device performances.

EN12.15.30
Achieving Balanced Ionic-Electronic Coupling for Self-Powered Electrochemical Transistors
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Owing to their excellent transconductance property, organic electrochemical transistors (OECT) have been found to be an attractive choice for various kinds of transducers such as biological sensors and neuromorphic devices. Historically, attempts to enhance the ionic-electronic transport focussed on additives that improved the PEDOT packing resulting in better electronic transport. However, the densification of PEDOT domains deleteriously affects the ionic transport. Here, we present a novel approach to engineer these intricately interrelated properties to
simultaneously enhance these figures of merits (μC*) through structural reorganization of the domains with the help of an ionic liquid [1]. Further, owing to their excellent stability, we evidence its application in point of care devices using a self-powered OECT for sensing applications. Our work highlights for the first time, a highly efficient, ambient stable perovskite photovoltaic (PV) powered OECT, whose transconductance (~60.50 μS) is nearly unaffected by the incident light intensity (0.13 – 100 mW/cm²) owing to the excellent balanced electron-hole transport and a nearly non-existent trap assisted recombination processes in the solar cell. Our findings therefore demonstrate the great potential of PV-OECT device for various indoor and outdoor luminance conditions.


EN12.15.31
Tailored Morphology Control of PBDB-T:ITIC Blend for Printable Non-Fullerene Organic Solar Cells
SangHyun Park, Insu Jin and Jaewoong Jung; Kyunghee University, Korea (the Republic of)

The non-fullerene organic solar cells (NFOSCs) has recently have emerged as a promising photovoltaic technology due to their potential in large area printable solar cells with low costs. The typical film casting for the photoactive blend is spin-coating, but it is not suitable to be utilized in actual industries. Thus, the printing technique such as blade-coating has been demonstrated as an efficient method of high-throughput large area coating for NFOSCs. The morphology generation kinetics in the blade-coated blend films are totally different to that of the spin-coating because the amount of residual solvents, the concentration of the photoactive components, and the drying time of the as-cast wet films. In this work, we systematically investigated the influence of the solvent additive (1,8-diiodooctane) and substrate temperature on the blend film morphology, and their correlations with charge transport and photovoltaic properties were analyzed. We also figured out the optimal condition for the blade-coated NFOSCs that surpasses the spin-coated devices.

EN12.15.32
Molecular Factors Governing the Stability of Thermally Activate Delayed Fluorescence Molecules
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Organic molecules producing thermally activated delayed fluorescence (TADF) have emerged as promising dopant materials for electroluminescence. The emergence benefits from the capability of TADF molecules to harvest all the electrogenerated excitons through a thermal equilibrium between singlet and triplet excitons. However, utility of organic light-emitting devices (OLEDs) having TADF dopants is yet to be fully exploited because they suffer from short operation lifetime. The short lifetime of the devices was ascribed to intrinsic degradation of TADF molecules during normal device operation. Various studies have been conducted to identify the chemical mechanism underlying the intrinsic degradation of TADF molecules. Previous studies revealed the occurrence of irreversible bond rupture of TADF compounds upon the formation of exciton or trap of charge carriers. However, the chemical mechanisms underlying the degradation have not been fully elucidated.

To understand the degradation mechanism, we investigated the molecular factors that governed the stability of a series of TADF molecules. Archetype TADF molecules having a 1,3,5-triphenyltriazine (TRZ) acceptor and different cyclic donors, including phenoxazine (PXZ), 10H-phenothiazine (PTZ), 9,10-dihydro-9,9-dimethylacridine (ACR), 10,11-dihydro-5H-dibenzo[b,f]azepine (AZP), and carbazole (Cbz) were synthesized. Our synthetic control aimed at semi-quantitative assessments of the molecular parameters, including an exchange energy, excited-state energy and lifetime, and a bond dissociation energy. Degradation behaviors were monitored during continuous photoillumination (white light, 1.7 × 10⁻⁷ einstein s⁻¹) of an Ar-saturated THF solution of the dopant (500 μM). The photolysis yielded degradation byproducts after the cleavage of the C-N bond connecting the donor and acceptor moieties. We observed that the degradation rate (kₐvg) depended on the identity of the cyclic donor unit.

Multi-layer OLEDs having the donor-TRZ dyad TADF molecules were constructed with a configuration of ITO/DNTPD (60 nm)/BPBPA (20 nm)/PCzAC (10 nm)/mCBP: dopant (30 nm : 10%)/DBF-Trz (5 nm)/ZADN (30 nm)/LiF (1 nm)/Al. Operation lifetime was determined when the luminance reached 90% of the initial value (L₉₀) under a constant current driving mode. A positive linear relationship was found between L₉₀ of the devices and the intrinsic stability (1/kₐvg) of the TADF dopants. This linearity provided firm evidence that intrinsic stability of the
Unexpectedly, we found that the excited-state properties, such as excited-state energy and lifetime, were not the governing factors of both the stability of TADF materials (i.e., $1/k_{dgr}$) and the device longevity (i.e., $LT_{90}$). The two stability parameters increased in proportion with the ratio between the quasi equatorial and the quasi axial forms of the cyclic donors in the TADF molecules. X-ray crystal structure analyses and quantum chemical calculations performed at the CAM-B3LYP level of theory supported this notion. Cleavage of the C-N bond was predicted to be exergonic from the singlet intramolecular charge-transfer ($1\text{ICT}$) transition state of the quasi axial form. On the contrary, the bond cleavage from the $1\text{ICT}$ transition state becomes endergonic in the quasi equatorial form. Our finding established that the equilibrium between the conformers determines intrinsic stability. We believe that our research will provide useful insights into the molecular strategies to achieving prolonged device lifetime.

EN12.15.33
Using Intrinsically Luminescent Charge-Transfer State to Achieve Low Non-Radiative Recombination Loss and Charge Generation in Organic Solar Cells Yun Liu and David S. Ginger; University of Washington, Seattle, United States

An ideal solar cell requires efficient carrier generation as well as minimized carrier recombination loss. Recombination loss in organic photovoltaics (OPVs) mostly originates from non-radiative recombination. Recent studies have demonstrated efficient OPV blends with low non-radiative recombination loss by: 1) reducing the energy difference between the local exciton of inherently bright acceptor materials and donor/acceptor charge-transfer (CT) states to achieve wavefunction mixing and luminescence intensity borrowing; and 2) demonstrating increased photoluminescence yield due to radiative non-geminate carrier recombination.

In the widely accepted carrier dynamics scheme of organic photovoltaics, photogenerated excitons on the acceptor and donor molecules may form charge-transfer states at the donor/acceptor interface, a portion of which then dissociate and generate free carriers. Charge carrier recombination occurs via the CT states. Thus, it naturally follows that increasing the radiative efficiency of the CT states is critical to reduce the overall energy loss in OPVs. We herein propose a new route to reduce non-radiative recombination loss by using intrinsically luminescent system with charge-transfer characteristics—thermally activated delayed fluorescence (TADF) exciplex, as the carrier generation interface in OPVs. We demonstrate a model TADF OPV system with maximum of 10% external quantum efficiency and 40% internal quantum efficiency with ~2% electroluminescence quantum efficiency at 1-Sun injection carrier density. Moreover, photoluminescence efficiency spectrum obtained by scanning through excitation wavelengths and measuring PL quantum yield matches with the photoaction spectrum, indicating that the TADF exciplex is responsible for charge generation, consistent with the OPV carrier generation scheme. We observed fluence-dependent micro-second photoluminescence decay in this system, suggesting radiative non-geminate recombination of photogenerated carriers. Our preliminary results show promise for a proof-of-concept highly emissive and charge-generating OPV device. Furthermore, the large binding energies of excitons and charge-transfer states induce significant energy losses in organic solar cells and poses questions on the equilibrium or the lack thereof between charge carriers and CT states. We aim to understand carrier dynamics in the TADF model OPV blend by directly monitoring charge carrier decay via transient photovoltage experiments and correlating it with photoluminescence emission decay.

EN12.15.34
Non-Photolithographical Patterning Method for Silver Nanowire-Based Transparent Electrode by Controlling Adhesion between Substrate and AgNW Dongwook Ko1, Yoo Han Ma1, Jongbok Kim1 and Junyeong Lee2; 1Kumoh National Institute of Technology, Korea (the Republic of); 2Kyungpook National University, Korea (the Republic of)

AgNW(Silver nanowire)-based transparent electrodes are considered as the most suitable alternative ITO(indium tin oxide) due to excellent electrical, optical and mechanical properties. But, when we apply AgNW-based transparent electrode to optoelectronic devices such as LCD(liquid crystal display), OLED(organic light emitting diode), organic solar cells, a patterning process is essential. Generally, AgNW-based electrodes are patterned by a photolithographical technique and a laser direct technique. Although it is possible to fabricate very fine pattern shapes through photolithographical technique and laser direct patterning method, these methods are required complex processing and environmental hazard. Therefore, researching of a novel patterning method for AgNW-based electrode is indispensable. In this study, we control the surface energy of substrate by UV-Ozone treatment.
system, so we control the adhesion between the substrate and AgNW to form the patterned AgNW-based electrode. And we apply a patterned AgNW-based electrode to organic solar cells.

Hydrophilic treatment such as UV-Ozone, oxygen plasma can increase the surface energy of substrate, thus adhesion between substrate and materials can be increased due to absorption mechanism. So, we control the adhesion between the substrate and AgNWs through UV-Ozone treatment system. When we treat UV-Ozone on substrate, the adhesion between the substrate and AgNWs is strong. So, AgNWs remains on the substrate when the photocurable polymer is peeled off. On the other hand, when we do not treat UV-Ozone on substrate, the adhesion between the substrate and AgNWs is weak. So that, we can fabricate embedded AgNWs-based electrode. For that reason, we fabricate patterned AgNW-based electrode by adhesion patterning method. SEM (scanning electron microscopy) and EDS (energy dispersive spectrometry) mapping are used to confirm patterned line (500, 300, 100, and 50μm). When we apply patterned AgNW-based transparent electrode to organic solar cells, we get the good characteristics of organics solar cells.

As a result, we can control adhesion between the substrate and AgNWs by UV-Ozone treatment system. So, we can fabricate patterned AgNW-based electrode. When AgNW-based electrode is applied to organic solar cells, we confirm that organic solar cells with patterned AgNW-based electrode are exhibited similar or better performance than organic solar cells with ITO transparent electrode.

EN12.15.35
Concurrent Optimisation of Organic Donor-Acceptor Pairs through Machine Learning Daniele Padula1,2 and Alessandro Troisi1; 1University of Liverpool, United Kingdom; 2Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

In this work we deal with an instance of the general problem occurring when optimising multi-component materials: can components be optimised separately or the optimisation should occur simultaneously? We investigate this problem from a computational perspective in the domain of donor-acceptor pairs for organic photovoltaics, since most experimental research reports optimisation of each component separately. We use a collection of organic acceptors and donors we recently analysed [Kuzmich et al., Energy Environ. Sci., 2017, 10, 295, Padula et al., Mater. Horiz., 2019, 6, 343] to train non-linear Machine Learning models of different families to predict the power conversion efficiency of donor-acceptor pairs, considering computed electronic and structural parameters of both components. The trained models are then used to predict photovoltaic performance for donor-acceptor combinations for which experimental data are not available in the data set. We critically assess data structure, and the usefulness of the trained models by predicting some donor-acceptor pairs that recently appeared in the literature, and we propose the best combinations as worth investigating experimentally.

EN12.15.36
Tuning of Thermally Activated Delayed Fluorescence (TADF) Emitter Based on Naphthalimide toward Efficient and Deep Red Organic Light-Emitting Diode (OLED) Seyoung Jung, Chi Hyun Ryoo, Ji Eon Kwon and Soo Young Park; Seoul National University, Korea (the Republic of)

While countless donors and acceptors for TADF emitters have been reported, there is still a thirst for efficient and deep red emitter compared to blue and green emitters because of the potential of brightness and color gamut. One of noticeable acceptor core, 1,8-naphthalimide (NI), has great electron withdrawing property due to its carbonyl group and unique low excited state level, which sounds out about applicability for high-efficiency red TADF emitter. From this, some of orange TADF emitters with outstanding light emitting performance using NI as acceptor core were reported1,2, but there exists possibility for way longer wavelength range of emission to become a deep red TADF emitter.

In this work, deeper and more efficient red TADF emitter using NI as acceptor was realized through two tracks, using phenoxazine as more electron-donating donor moiety and introducing trifluoromethyl group as auxiliary electron-withdrawing group to N-phenyl-naphthalimide. Three newly synthesized materials and PNIDMAC (which is
Functionality of Non-Fullerene Electron Acceptors in Ternary Organic Solar Cells

Ternary organic solar cells, a single active layer comprising three different components, have been demonstrated to be one of the most efficient ways to approach high-performance organic solar cells. But nevertheless, most of the ternary organic solar cells were characterized by the steady-state measurements, which are helpful but inadequate to fully understand the underlying charge carrier behavior at a short time scale. In this work, a comparison of the steady-state and time-dependent measurements was used to investigate the functionality of non-fullerene electron acceptors in ternary organic solar cells. The steady-state measurements indicate that non-fullerene electron acceptors can enlarge the absorption range of photoactive layer, suppress charge carrier recombination, reduce charge carrier transfer resistance and thereby increases photocurrent in ternary organic solar cells. The time-dependent measurements demonstrate that short charge carrier extraction time and high charge carrier mobility are responsible for enhanced photocurrent in ternary organic solar cells. Our studies provide a comprehensive method understanding underlying of enhanced efficiency of ternary organic solar cells.

Synthesis and Characterization of Multi-Substituted Carbazole Derivatives for Optoelectronic Properties—An Approach to Modulate Aggregation-Induced Emission Effect

Extensive research has been done in recent years for the development of fluorescent small organic molecules with aggregation-induced emission (AIE). The application of such solid-state organic luminogens has been widely used in organic light-emitting diodes (OLEDs), biological probes and fluorescent sensors due to their potential enhancement of emission in either solid states or in an aggregated state provided by the aqueous media. In order to produce efficient AIE materials, organic π-conjugate fluorophores play a crucial role with varying the photophysical and electrochemical properties which are strongly dependent on linking position of π-conjugates as well as the design of building blocks. It is believed that there are ample possibilities to modify these characteristic properties to successfully tune their optoelectronic properties. To increase the efficiency of an OLED device, it is desirable to develop a molecule with twisted conformation to generate AIE-active material which not only prevents the π-π stacking but also block the quenching channels. Carbazole being explored as one of the favourite synthon for materials chemists because of its unique characteristics such as rigid molecular structure, amorphous nature, inexpensive of the starting material, good chemical stability assisted by its fully aromatic system, excellent thermal and photochemical stability, good hole transporting ability and high triplet energy (~ 2.9 eV). Apart from these attractive features, due to its electron-rich nitrogen atom carbazole framework can allow large structural diversity to modulate the functional properties of the materials systematically. Therefore, carbazole based functional materials have been exemplified as a promising family for optoelectronic applications such as organic light-emitting diodes (OLEDs), solar cells (OPVs), field-effect transistors (OFETs) and in molecular sensors. It is important to note that multi-functionalization of mono and di-substituted dicyanovinyl carbazole derivatives are rarely reported in the literature. On the basis of above stated discussion, a series of carbazole based derivatives with different functional groups comprising of mono- and disubstituted dicyanovinyl functionalities (MD1, MD2, DD1, DD2) have been designed, synthesized and systematically characterized to effectively modulate the aggregation-induced emission effect by changing the linking position of carbazole and explore the simple structure-function relationship phenomenon. Dyes consist of N-phenylcarbazole (MD1 and DD1) and N-butylcarbazole (MD2 and DD2) as donor substituted at the various position of central carbazole with dicyanovinyl group as acceptor. The substitution effect of different donors on optical, electrochemical and thermal properties on carbazole-dicyanovinyl derivatives is unraveled. The dyes MD2 and DD2 showed red-shifted absorption and higher molar extinction coefficient as...
compared to MD1 and DD1 attributed to extended conjugation tendency of 3-substituted N-butylcarbazole as compared to N-phenyl linked carbazole. The photoluminescence studies revealed the role of auxiliary chromophores loading at C1, C6 and C8 positions of the central carbazole moiety in the excited state. All the compounds showed positive solvatochromism in excited states attributable to intramolecular charge transfer. The higher thermal stability of all the dyes reveals rigidity of carbazole derivatives. Interestingly, all the dyes in particular dyes consist of N-phenylcarbazole substituents (MD1 and DD1) showed aggregation-induced emission properties in THF-H2O mixtures attributable to increased distortion in molecular configuration and restricted π-π stacking among adjacent molecules. OLED device was fabricated based on these dyes as dopant emitter along with a host (CBP) and experiencing the best performance in a doped device of MD2 with 3 wt% having EQE of 4.2% (current efficiency of 13.1 cd A\(^{-1}\)) and maximum brightness \(L_{\text{max}}\) of 6180 cd/m\(^2\).

**EN12.15.40**

**Study on Correlation between Surface Morphology and Work Function of Aluminum Film in Nanoscale**

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This paper reported correlation between surface morphology and work function in nanoscale. Surface nanoscale-morphology of an aluminum film was controlled using colloidal lithography. After the nanopatterning, the averaged work function was decreased from 4.24 eV to 3.94 eV. In addition, high resolution (resolution of 200 nm) Kelvin probe measurement revealed that there was work function difference of 0.31 eV between the top and bottom of the prepared nanospikes. These results indicate to develop stable low work function electrodes.

Low work function materials are essential for electrodes of electronic devices, for example organic light emitting diodes and organic solar cells. Generally, such low work function materials show high reactivity and are unstable, causing surface property changes when they are used in devices. On the other hand, some research reported that work function can be controlled by adjusting the surface roughness with the same material. In general, increment of surface roughness of a metal film causes reduction of the work function based on effect of the dipole barrier, as reported by Saito. However, detailed correlation between surface nanoscale-morphology and work function has not been clarified. Hence, in this study, we studied correlation between surface morphology and work function “in nanoscale” using an aluminum film. The aluminum film was patterned by colloidal lithography, and the work function of the film was evaluated in both millimeter and nanometer-level.

An aluminum film of 100-nm-thick was prepared on a silicon substrate by ion-beam sputtering. In order to analyze correlation between surface morphology and work function, surface of the aluminum film was nanostructured via colloidal lithography. The detailed fabrication process is as follows. Firstly, polystyrene nanoparticles (100 nm in diameter) dispersed as colloidal water solution were regularly aligned on the aluminum film by spin-coating. Then, the nanoparticles were slightly etched by oxygen plasma to separate each nanoparticle. The aluminum surface was etched to form nanospikes using etchant of acids mixture (phosphoric acid, acetic acid, and nitric acid) through the nanoparticles as a mask. Finally, the polystyrene nanoparticles were removed by oxygen plasma. In addition, an aluminum film without nanopatterns was also prepared as a reference. The work functions of the samples were measured by Kelvin probe method. We evaluated not only averaged work function of about 3 mm\(^2\) area, but also nanoscale work function, resolution of 200 nm.

From atomic force microscopy evaluations, we observed that the aluminum film having nanospikes was successfully fabricated with 5.8 nm in arithmetical mean roughness and 49.5 nm in maximum peak to valley height. In the millimeter-level observation, the work function of the aluminum film with the nanospikes was decreased to 3.94 eV compared to that without the nanospikes (4.24 eV). This result indicated that work function of the aluminum film was decreased with increasing the surface roughness, as previously reported. On the other hand, in the nanometer-level observation, the work function changing was obtained along with the surface nanoscale-morphology changes. The maximum difference of the work function between the top and bottom of the nanospike was 0.31 eV. It is a first time to show the relationship between surface morphology and work function in nanoscale to the best of our knowledge. This result implies that electrons are easier to be emitted from top of the nanospikes rather than bottom of them. This is a promising step for developing stable low work function electrodes.

**EN12.15.41**

**Using SnS\(_2\) Underlayer to Reduce the Schottky Barrier between Ag\(_2\)S and FTO**

Yan Lei, Zhi Zheng and
Weiwei He; Xuchang University, China

Ag$_2$S thin film can absorb the sun light from ultraviolet (UV) to near infrared (NIR) region due to its direct narrow band gap ($E_g = 0.9 \text{ eV} \sim 1.1 \text{ eV}$). For such a narrow band gap semiconductor, the related photoelectric conversion efficiency (PCE) can reach to about 30% in an ideal solar cell. It can be a promising semiconductor for next generation solar cell application, even the PCE is still low.

To obtain high PCE, the photoinduced charge carrier recombination at the interface of heterojunction or at the electrode surface must be reduced. Some works have been reported addressing this consideration, such as doping element to tune the Fermi level of Ag$_2$S, using electron transfer layer between the electrode and Ag$_2$S thin film and introducing intermediate layer to form cascade band structure. Despite these efforts, the Ag$_2$S thin film based solar cells are still featuring low PCE. One of the problems is how the electrode/Ag$_2$S interface affecting the photoinduced charge carrier recombination has not been well studied. Therefore, we should furtherly check out the photoinduced charge carrier transportation and recombination in mechanism. To our knowledge, the Schottky barrier will generate at the interface of n-type semiconductor and electrode, once the Fermi levels are different. The band is bending upward at each side of n-type semiconductor and form a “V-type” band structure in electrode/n-type semiconductor/p-type semiconductor structure. The photoinduced charge carrier recombination will happen at the inappropriate interface of electrode and n-type semiconductor. To achieve higher photoelectric performance, such recombination at the electrode surface should be suppressed. Here, FTO surface was modified by SnS$_2$ layer to tune the Fermi level of FTO, which was deposited by thermal evaporation and post thermal annealing treatment. Photoelectrochemical method was carried out to evaluate the variation of charge carrier transfer resistance between the Ag$_2$S/FTO interface. KPFM technique was used to study the Fermi level alignment of Ag$_2$S/FTO interface. Transient surface photovoltage (TSPV) technique has been employed to investigate the photoinduced charge carrier transportation and recombination between the Ag$_2$S/FTO interface. Basing on these results, a more clear charge carrier recombination mechanism at the Ag$_2$S/FTO interface is obtained, which may give more opportunities to furtherly increase power conversion efficiency of new type photoelectric system.

EN12.15.42

Synthesis and Characterization of New Nonfullerene Electron Acceptors for Organic Photovoltaics

Chang Woo Koh$^1$, Jae Hoon Son$^1$, Ziang Wu$^1$, Hwa Sook Ryu$^1$, Hyewon Cho$^2$, Md Al Mamunur Rashid$^1$, Kyungwon Kwak$^1$, Jin Young Kim$^2$ and Han Young Woo$^1$; $^1$Korea University, Korea (the Republic of); $^2$Ulsan National Institute of Science and Technology, Korea (the Republic of)

Recently, non-fullerene acceptors have attracted significant attention for organic photovoltaics (OPVs) due to their frontier energy levels and absorption spectra tunability and good photo/chemical stability rather than fullerene based acceptors. Moreover, with the superior compatibility with several donor polymers exhibiting well-aligned energy levels, complementary absorption and appropriate morphology, outstanding PCEs over 15% have been achieved. However, most of the high performance non-fullerene acceptors are A-D-A type based on linear core structure which contains electron donating core unit and two electron deficient end-capping groups. Although the 2-dimensional (2D) star-shaped molecule has potential to exhibit good efficiency in solar cells, such as improved molar absorption coefficient and face-on oriented columnar packing structures enhancing charge mobility in a vertical direction, little studies have been done. In particular, a number of p-type star-shaped materials which contain electron-rich polycyclic aromatic hydrocarbon structures have been studied, but the advancement of star-shaped n-type materials is still lagging behind.

In this study, triazine-based n-type 2D star-shaped molecules were designed and synthesized. Intramolecular non-covalent cumbic interactions and rigid molecular structure were introduced to induce the structural planarity for enhanced the packing property and the D-A type structures are designed to control the optical/electrical properties with a push-pull effect. The optical/electrochemical properties were monitored by UV-Visible absorption spectroscopy and cyclic voltammetry, and the film morphology and crystallinity were analyzed by grazing-incidence wide-angle scattering and differential scanning calorimetry. It has also been applied as an n-type active layer material for OPVs, and will be presented in detail.

References

SESSION EN12.16: Properties of Organic Semiconductors IV—Interfaces
Session Chair: Benjamin Grevin
Friday Morning, December 6, 2019
Hynes, Level 2, Room 200

9:00 AM *EN12.16.01
Measuring Energetic Disorder and Quantifying Order and Disorder in Organic Semiconductors Thuc-Quyen Nguyen; University of California, Santa Barbara, United States

Characterizing the density of states (DOS) width accurately is critical in understanding the charge-transport properties of organic semiconducting materials as broader DOS distributions lead to an inferior transport. From a morphological standpoint, the relative densities of ordered and disordered regions are known to affect charge transport properties in films; however, a comparison between molecular structures showing quantifiable ordered and disordered regions at an atomic-level and its impact on DOS widths and charge transport properties has yet to be made. In this work, the DOS distribution widths of two model conjugated polymer systems are characterized using three different techniques. A quantitative correlation between energetic disorder from band bending measurements and charge transport is established, providing direct experimental evidence that charge carrier mobility in disordered materials is compromised due to the relaxation of carriers into the tail states of the DOS. Distinction and quantification of ordered and disordered regions of thin films at an atomic-level was achieved using solid-state NMR spectroscopy. An ability to compare solid-state films morphologies of organic semiconducting polymers to energetic disorder, and in turn charge transport, can provide useful guidelines for applications of organic conjugated polymers in pertinent devices.

9:30 AM *EN12.16.02
Elucidating Structure-Function Relationships in Organic Semiconductors with Coupled Electrical and Optical Spectroscopy Elizabeth von Hauff; Vrije University, Netherlands

Organic semiconductors offer many advantages for energy conversion, saving and storage applications. However the underlying processes that govern electrical processes such as charge transport, the separation of photogenerated charge, and carrier recombination, are not well-understood. New experimental and theoretical approaches to correlate molecular structure with electronic processes in organic semiconductors are valuable for gaining insights into smart design for this class of materials. In this talk I will discuss our recent results on coupling electrical and optical spectroscopies to study structure-function relationships in organic semiconductors, such as polaron formation and transport in donor-acceptor polymers for photovoltaics and the influence of molecular morphology on the performance of piezoelectric polymers. By combining optical spectroscopy with device physics and theoretical modeling, we are able to identify relevant aspects of molecular structure and morphology that determine the electronic response of organic semiconducting films.

10:00 AM BREAK
10:30 AM *EN12.17.01
Multimodal Time-Resolved Kelvin Probe Force Microscopy Investigations of Organic Donor–Acceptor Blends
Benjamin Grevin1, Olivier Bardagot2, Lydia Cabau2 and R Demadrille2; 1CNRS, France; 2CEA, France

The development of third generation photovoltaics is massively based on the use of materials displaying a heterogeneous morphology at the meso or nanoscopic scales, or nanostructured by purpose. Whatever the technology, understanding how the nanostructure impacts the electronic transport and photocarrier dynamics is vital for device optimization. This is especially true for organic bulk heterojunctions (BHJs) based solar cells, whose performance continue to be improved over time thanks to the joint efforts of chemists, physicists and material scientists. Despite fierce competition with hybrid perovskites, organic photovoltaics have indeed still a stay in the competition, thanks in particular to the introduction of novel non-fullerene acceptors. As in the case of their fullerene-based elders, optimizing the film morphology and phase composition of novel donor-acceptor blends remains the key to achieve an efficient photocarrier generation, to balance properly the carrier mobilities and to minimize the losses by recombination.

Since their introduction in the 1980s, scanning probe microscopy (SPM) techniques have been continuously improved, and have reach the ability to map not only the surface topography but also a huge range of local functional mechanical, chemical, electronic and optical properties at the nanoscale. Several advanced modes of the atomic force microscope (AFM) are nowadays commercially available from SPM manufacturers, and are (or could be) widely used in routine by the OPV community to characterize the BHJs morphology and phase composition (for instance by quantitative nanomechanical imaging) and their optoelectronic properties (by photo-conducting AFM or surface photovoltage imaging). Some others are still confidential, but will probably experience strong growth in the coming years. In particular, time-resolved electrostatic and potentiometric variants of the AFM [1-6] hold great promise, for they are developed with the aim to map the photo-carrier dynamics and lifetime at the nanoscale.

In this communication, we will present the works undertaken in our group to implement time-resolved imaging modes of the charge dynamics based on the Kelvin Probe Force microscope (tr-KPFM for time-resolved KPFM) combined with non contact AFM under ultrahigh vacuum. Two complementary modes will be introduced: KPFM under frequency-modulated illumination [5] and pump-probe KPFM [6], both operated in spectroscopic data cube mode. These techniques have been applied to model BHJ systems including PTB7-PCBM and NFA-based blends, which phase composition was pre-characterized by quantitative nanomechanical imaging in peak force AFM. It will be shown that in these systems, the surface photovoltage decays probed by tr-KPFM originates from trap-delayed process. Our results stress also the crucial need to combine several KPFM modes to disclose the full temporal range of dynamical process that can coexist in these materials.

11:00 AM EN12.17.02
Pushing the Resolution Limits of Imaging Conjugated Polymers in the Transmission Electron Microscope
Brooke Kuei and Enrique D. Gomez; The Pennsylvania State University, United States

Transmission electron microscopy (TEM) of conjugated polymers has remained a challenge because resolution is limited by the electron dose the sample can handle. We have characterized the effects of beam damage on poly(3-hexylthiophene) (P3HT), poly(3-dodecylthiophene-2,5-diyl) (P3DDT), and poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3’’’-di(2-octyldodecyl)-2,2’’,5’’,2’’’’-quaterthiophene-5,5’’’’-diyl)] (PffBT4T-2OD) via electron diffraction and electron energy-loss spectroscopy (EELS). Critical dose $D_C$ values were calculated.
from the decay of diffraction and low-loss EELS peaks as functions of dose rate, temperature, beam size, and the addition of antioxidants. At room temperature, $D_C$ first increases then decreases with increasing dose rate, whereas at cryogenic conditions this dose rate dependence is less pronounced and the overall $D_C$ increases; these results suggest that the main mechanism for beam damage in conjugated polymers is diffusion of free radicals. Thus, we show with both $D_C$ experiments and high-resolution TEM that the addition of free radical scavengers such as butylated hydroxytoluene (BHT) mitigates beam damage at room temperature. We also observe that $D_C$ increases with decreasing beam size, suggesting that convergent beam techniques are amenable for beam-sensitive materials. Thus, we demonstrate the use of scanning nanodiffraction to map $\pi-\pi$ stacking in several conjugated polymers.

**11:15 AM  *EN12.17.03**

*Digitally-Printed Organic Bulk-Heterojunction Photodetectors—Device Architectures, Polarization and Color Detection* Gerardo Hernandez-Sosa$^{1,2}$; $^1$Karlsruhe Institute of Technology, Germany; $^2$InnovationLab, Germany

Printing technology is set to enable the high-throughput low-cost and customized fabrication of optoelectronic and sensors devices. For this goal to become a reality, this functional printing approach should encompass a material process development which enables high device performance and industrial compatibility, thus enabling a facile transfer of research results into consumer applications.

In this contribution, I will present the fabrication of fully printed organic photodiodes (OPDs) by digital printing techniques (e.g. aerosol and inkjet). The devices show mechanical flexibility, semitransparency and an excellent reproducibility. Moreover, I will demonstrate their integration into fully printed OPD 256-pixel arrays. This was performed through a micro-patterning process based on printed dewetting structures that guide the self-alignment of the functional inks, improving printing resolution, registration accuracy and performance reproducibility. Secondly, I will discuss the use of the ink formulation as way to access and tailor material optoelectronic properties. In this direction, we have focused on the control of the molecular order in organic semiconductors though an inkjet printing process. This enabled us to deposit functional polymers with a high degree of alignment and explore its use in polarization sensitive OPDs. Finally, I will outline our recent efforts in the fabrication of inkjet printed OPDs based on novel non-fullerene acceptors (NFAs). The devices show a photo-response up to 800nm and reach record responsivities of 400mA/W as well as cut-off frequencies surpassing 2MHz. Furthermore, we demonstrate the successful decoupling of the optical and rheological properties by using a visibly transparent polymer donor and color-selective NFAs. This approach offers spectral flexibility without the need for a variation in process parameters. The choice of NFA enabled devices with color selectivity in the ranges of 400-600nm and 500-800nm.

**SYMPOSIUM EN13**

Flexible and Miniaturized Thermoelectric Devices Based on Organic Semiconductors and Hybrid Materials  
December 3 - December 6, 2019

**Symposium Organizers**
Manfred Albrecht, University of Augsburg
Maarit Karppinen, Aalto University
Kornelius Nielsch, IFW Dresden
Mona Zebarjadi, University of Virginia

* Invited Paper

**SESSION EN13.01: Novel Types of Thermoelectric—Materials**  
Session Chair: Kornelius Nielsch
**1:30 PM *EN13.01.01*

**Conducting Polymer Fibers and Yarns for Thermoelectric Textiles** Christian Muller1,2; 1Chalmers University of Technology, Sweden; 2Wallenberg Wood Science Center, Sweden

Recent advances in ubiquitous low-power electronics call for the development of light-weight and flexible energy sources. The textile format is highly attractive for unobtrusive energy harvesting. In my talk, I will present some of our recent work on thermoelectric textiles. I will discuss how n- and p-type yarns can be prepared by coating or dyeing of natural materials such as silk, as well as by melt or wet spinning of conjugated polymers. Some of these fibers and yarns feature a high degree of ambient stability as well as the ability to withstand both machine washing and dry cleaning. Embroidery of base fabrics with such conducting yarns readily permits the fabrication of thermoelectric modules.

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**2:00 PM EN13.01.02**

**Remarkably High Thermoelectric Performance of Flexible and Robust Predominantly Double-Walled Carbon Nanotube Yarn** Yasuhiko Hayashi1,2, Kazuki Omoto1, Shogo Iemoto1, Hirotaka Inoue1, Masaki Hada3,1 and Takeshi Nishikawa1; 1Okayama University, Japan; 2Tokyo Institute of Technology, Japan; 3University of Tsukuba, Japan

Carbon nanotube (CNT) yarns have attracted considerable attention as they are not only flexible, robust and lightweight but also can generate high Seebeck coefficient, $S$ and high electrical conductivity, $\sigma$, they realize remarkably high thermoelectric generators (TEGs). One promising application is a small wearable electronics which can generate electricity from heat gradients between the human body and atmosphere in order to harvest waste heat. One of the critical challenges is the tuning of electrical and thermal transport since they interrelate against the high performance of thermoelectric properties. Although the thermal and electrical properties of CNT yarns are likely to enhance their properties by the post-high temperature annealing process, the phenomena underlying the improvement of properties have not explicated yet. The interface between the components governs the performance of the TEGs made by CNT yarns, but the debates have not expanded to characterization and modification of their complicated interface. Then the thermoelectric properties were characterized for the DWCNT yarns without treatment, with Joule heating, with n-type polyethylenimine (PEI) doped, and with PEI doped after Joule heating. High quality dense and tall vertically aligned CNT forest on Si was grown rapidly by a water vapor free thermal chemical vapor deposition using Fe catalyst, and it consists of more than 80% of double-walled CNTs (DWCNTs). DWCNT yarns were fabricated from CNT forest by a dry spinning process. We doped PEI to realize n-type DWCNT yarn. Electrical Joule heating was done on the DWCNT yarns with and without PEI dope in the vacuum at the temperature of 1800–2000 K for 1 min.

Pristine DWCNT yarn is a p-type semiconductor which exhibits a positive Seebeck coefficient of +25 μV/K. The Joule heating process did not change the polarity of the DWCNT yarn; in contrast, the Seebeck coefficient was enhanced to be +100 μV/K. In case of n-type DWCNT yarn, after Joule heating, PEI was effectively doped in the DWCNT yarn, and the Seebeck coefficient was enhanced to be −100 μV/K (quite high power factor $PE=1000 \mu W/mK^2$). To the best of our knowledge, these positive and negative of 100 μV/K are the highest Seebeck coefficients ever observed in CNT yarn and are close to those of inorganic thermoelectric materials. Raman characterization of the joule-heated CNT yarn, we observed the $G^*$ peak at a wavenumber of 2400 cm$^{-1}$, originated from the double resonance process in graphene or graphite, indicating the presence of graphene or graphite. The computation analysis reviled that the residual amorphous carbon in the interface between CNTs changes into the graphene-like structure. Our results indicate that the improvement of TE properties is due to graphene layers. Our results provide a guiding principle for designing DWCNT yarns and applying them for thermoelectric devices.

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**2:15 PM *EN13.01.03**

**Metal-Organic Frameworks as Thermoelectric Materials—Uncoupling Thermal and Charge Transport and the Role of Defects** Mark D. Allendorf1, Michael E. Foster1, Vitalie Stavila1, Christian Schneider2, Gregor Kieslich2, Roland Fischer2, Monica So3 and Alec Talin1; 1Sandia National Laboratories, United States; 2Technical University of Munich, Germany; 3California State University, Chico, United States
The structural and design versatility of Metal-Organic Frameworks (MOFs) is stimulating considerable activity to develop them for a wide range of applications for which nanoporous materials are extensively used, such as chemical separations and catalysis. However, MOFs also represent a unique opportunity to solve a vexing problem faced in the field of thermoelectrics; namely, the difficulty of uncoupling thermal and electrical transport so that high Seebeck coefficient and power factor can be achieved. In principle, the extremely low density of MOFs, many of which are comprised primarily of empty space, and the poor phonon coupling across the discontinuous covalent vs. coordination bonding in their structures, should inhibit thermal transport. Recent research suggests that electrically conducting MOFs are feasible, although so far the conductivities achieved are very low compared with the best thermoelectric materials. In most cases, electronic coupling in MOFs is weak due to the ionic nature of the bonding, leading to low band dispersion and insulating behavior. Nevertheless, the number and variety of electrically conducting Metal-Organic Frameworks (MOFs) continues to grow and both 2- and 3-dimensional MOFs with conductivities as high as 160 S/cm are known.

This presentation will discuss mechanisms of electronic charge conduction in MOFs and the related class of materials known as Covalent Organic Frameworks (COFs). We will describe theoretical investigations we performed to probe thermoelectronic transport properties and compare these predictions with charge transport and spectroscopic data to gain insight into the intrinsic conductivity mechanisms and their dependence on MOF structure, chemical composition, and morphology. Our studies provide guidance needed to design MOFs suitable for thermoelectric and other design applications. In addition, through a combination of experiments with MOFs infiltrated with guest molecules under highly controlled conditions, ab initio simulations, and band transport theory, we assessed the influence of structural and interface defects on the electronic structure of 2D and 3D MOFs. The results show that interface defects can introduce a transport barrier in 2D MOFs by breaking the π-conjugation, and/or by decreasing the dispersion of the electronic bands near the Fermi level. Both defect types cause a small band gap to form (in the range of 15-200 meV), which is consistent with the experimentally inferred hopping barrier. In 3D MOFs, the guest molecule, which can be considered a defect in much the same way that dopants are in conventional semiconductors can enhance electrical conductivity but also lead to phase transformations that change the majority charge carrier. These results provide strong evidence supporting the ongoing speculation that the charge transport properties of MOFs are strongly influenced by defects, in much the same way as conventional inorganic and organic conducting materials.

2:45 PM EN13.01.04
Signatures of Coherent Phonon Transport in MAPbI3-Based Ruddlesden-Popper Phases Alexander D. Christodoulides1, Lingyun Dai1, Peijun Guo2,3, Richard Schaller2,3 and Jonathan A. Malen1,1; 1Carnegie Mellon University, United States; 2Argonne National Laboratory, United States; 3Northwestern University, United States

We report thermal conductivity measurements of methylammonium lead iodide (MAPbI3) based Ruddlesden-Popper Perovskites which exhibit signatures of coherent phonon transport. The hybrid organic-inorganic halide perovskite, MAPbI3, has exhibited exceptional power conversion efficiency when used in solar cell devices. However, this material is unstable in oxygen and moisture-rich environments, particularly at high temperatures which are practically unavoidable given its ultra-low thermal conductivity. A two-dimensional, layered Ruddlesden-Popper phase similar to MAPbI3, (BA)2(MA)3n-1PbI3n and (BA)2(MA)3n-2PbI3n-1 (where n denotes the number of perovskite layers per two organic layers), has shown improved stability compared to its three-dimensional counterpart due to the inclusion of hydrophobic spacer cations, n-butylamine.

In order to learn about heat dissipation and phonon properties in the Ruddlesden-Popper phase, we measured the thermal conductivity of (BA)2(MA)3n-1PbI3n+1 for n = 1-6 using a non-contact pump-probe technique called frequency-domain thermoreflectance. We find that the thermal conductivity initially decreases at a function of n for n = 1-3 then levels off for n = 4-6. Decreasing thermal conductivity with increased interface spacing is a signature of coherent phonon transport, and opposite to our expectation for diffuse phonon transport. Our results agree with the Simkin-Mahan model which was formulated to describe the wave nature of phonons in superlattices [1].

While Ruddlesden-Popper organic perovskites can be synthesized by solution processes, coherent phonon transport has previously only been observed in superlattices of GaAs and AlAs [2], and SrTiO3/CaTiO3 and SrTiO3/BaTiO3 [3] grown painstakingly by MBE processes. Our work suggests that low n (BA)2(MA)3n-1PbI3n+1 are both more chemically stable and thermally conductive than MAPbI3. These properties may make the Ruddlesden-Popper phases more desirable for photovoltaics, while the demonstration of phonon coherence may open a pathway to...
additional applications in phonon optics and thermoelectricity.

References:


3:00 PM BREAK

SESSION EN13.02: Thermoelectrochemical Energy Harvesters
Session Chair: Mark Allendorf
Tuesday Afternoon, December 3, 2019
Sheraton, 2nd Floor, Constitution B

3:30 PM *EN13.02.01
Controlling Interplay between Graphitic Carbon and Polymers for Enhanced Electronic and Ionic Thermoelectric Effects Choongho Yu; Texas A&M University, United States

Voltage generation in a conductor can be resulted from electron or/and ion transport due to a temperature difference. When a thermoelectric voltage is induced by electron, it is typically much smaller than that of ion transport, particularly for organic thermoelectric materials. Here this study shows how to enlarge the small thermopower of carbon nanotubes (CNTs) using a polymer by controlling electronic transport at the junctions of CNTs with an organic electrochemical transistor configuration where poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) channel was disposed between two separated CNT films. The PEDOT:PSS channel could create energy barriers for abating the contribution of metallic CNT (m-CNT) to thermopower as well as injecting holes to CNT films so that charge imbalance upon imposing temperature gradients can be enlarged. The thermopower was raised up to ~150 mV/K and a remarkably high PF was obtained up to ~1.3×10³ μW/m-K², which is ~460% improvement compared with that of pristine CNT. This study provides not only better understanding of thermoelectric behaviors for organic thermoelectric materials, but also a practical method for suppressing the electronic transport from m-CNT, which would be widely applicable for other organic materials for thermoelectrics and beyond. On the other hand, with the extremely large voltage based on thermally induced ion transport, novel simultaneously harvesting and storing electrical devices using graphene oxides and polystyrene sulfonic acid have been developed without losing the benefit of solid-state non-moving part devices like conventional thermoelectrics. We called the device thermally chargeable supercapacitor (TCSC), and arrays of TCSC have been batch-fabricated, and connected together to raise the output voltage up to 2.1 V, suggesting excellent suitability for roll-to-roll mass manufacturing and practical implementation of thermal energy harvesting. The outcomes suggest that it is feasible to supply power to various distributed electronic systems whenever and wherever a temperature gradient is present.

4:00 PM EN13.02.02
Asymmetric Thermo-Electrochemical Cell for Low-Grade-Heat-to-Electricity Conversion Shien Ping Feng; The University of Hong Kong, Hong Kong

Low-grade thermal energy (<100 °C) is abundantly available in the form of waste heat or in the environment. Current technologies using liquid-based thermo-electrochemical cells (TECs) is both cost-effective and scalable for low-grade heat harvesting, and their temperature coefficient (mV/K) is one order of magnitude higher than that of solid-state thermoelectrics. The research on TECs has mainly focused on the exploit of thermal gradient or thermal cycle, but the potential of these approaches has been limited by the poor energy conversion efficiency or the need of external electricity. We invent a new asymmetric thermoelectrochemical cell (a-TEC) for low-grade-heat-to-
electricity conversion under an isothermal condition without the aid of the thermal gradient across two electrodes or the thermal cycle. The a-TEC consists of graphene oxide (GO)/platinum nanoparticles (PtNPs) cathode and polyaniline (PANI) anode and an aqueous Fe²⁺/Fe³⁺ electrolyte, which can be thermally charged in the open circuit condition. Under isothermal operation, the pouch cell configuration of a-TEC with a short distance between two electrodes can be employed for improving electrolyte conductance and rapid heating. Notably, the thermal voltage is generated based on thermo-pseudocapacitive reaction at the GO-electrolyte interface, demonstrating a very high temperature coefficient of 5.0 mV/K and the a-TEC exhibits the energy conversion efficiency of 5.19% at 70 °C (39.6% of Carnot efficiency). The great applicability of this new thermo-electrochemical system has been demonstrated on supplying power for an electrochromic smart window by immersing a-TECs in a hot water and lightening up an organic light emitting diode by placing a-TECs on a running compressor.

4:15 PM *EN13.02.03
Mixed Ionic Conductive Polymers for a Thermoelectric Capacitor Funkyoung Kim; Yonsei University, Korea (the Republic of)

As conducting polymers are intrinsically semi-metallic, the charge carriers inducing a thermal voltage can be tuned from electronic (hole) to ionic by doping. In particular, controlling the ionic doping level is crucial for maximizing the power factor of thermoelectric materials, as it optimizes the free ion concentration and carrier mobility. Due to the contribution from both electronic and ionic carriers, the thermopower in a mixed ionic electronic conduction (MIEC) system is synergistic and can produce a stable thermal capacity under constant temperature gradient. A robust thermoelectric harvester was explored from an ion doped mixed ionic conductive polymer film to give a high a Seebeck coefficient of over 16 mV K⁻¹ and a thermal voltage of 80 mV for a temperature gradient of 5 K. The thermal charging on the MIEC film device afforded high thermal voltage and current output, reproducibly, to show cumulative thermoelectric nature. Environmentally sustainable thermoelectric harvesting will be demonstrated by introducing a self-humidifying bilayer system.

4:45 PM EN13.02.04
Graphene-Carbon Nanotube Aerogel as ‘Organic’ Thermoelectrochemical Energy Harvesters Sanju Gupta; Western Kentucky University, United States

Three-dimensional scaffolds comprising different ratio of graphene nanosheets and multi-walled carbon nanotubes (GA-MWCNT) macro-assemblies. The resulting hydrothermally synthesized hydrogels are freeze-dried and thermally reduced to yield graphene and graphene-carbon nanotube aerogels with ultralow densities and tunable mesoscopic pore sizes. These ‘all carbon’ aerogels prepared as monolithic solids from suspensions of few-layer graphene oxide nanosheets and small diameter multiwalled carbon nanotubes in which organic wet chemistry is used to cross-link the individual sheets and with carbon nanotubes. In contrast to methods that utilize physical cross-links between graphene oxide nanosheets, this approach with polymeric linkers and organic functionalization provides covalent carbon bonding among the graphene sheets and molecular attachment with carbon nanotubes, respectively, thus facilitating rapid and facile electron transport. As a result they are expected to exhibit improved electrical conductivities, moderate thermal conductivity, highly interconnected multiplexed topology with large internal surface areas thus promoting enhanced surface ion adsorption which makes these mesoporous materials viable candidates for use in harvesting thermo-electrochemical energy and energy storage technologies. Thermoelectric property measurements for both the carbon nanotube aerogels by themselves and for hybrids with graphene nanosheets revealed promising and unprecedented (p-type and n-type) thermopower values especially with electrolyte with an upper bound to 3.2 mV/K. We used complementary analytical techniques including electron microscopy, temperature dependent electrical property, and Raman spectroscopy while evaluating performance to establish microstructure-processing-property-performance correlations. Supported in parts by KSEF-RDE Grant, KY NASA EPSCoR and KY NSF EPSCoR Grants.
8:15 AM *EN13.03.01/EN14.11.01
Simulation of Thermoelectric Properties of Complex Materials and across Interfaces Zhiwei Ding, Qichen Song, Qian Xu, Jiawei Zhou and Gang Chen; Massachusetts Institute of Technology, United States

This talk will discuss our recent work to simulate electron and phonon thermoelectric transport in complex materials and across interfaces based on the density-functional theory and atomic Green’s function. One example of the complex material is Mg$_2$Sb$_3$, which has been recently reported to have high figure of merit. We compare the charge defect scattering due to different dopants using first principle calculation and find weak impact of defect on mobility. Instead, the intrinsic carrier-phonon scattering is the major scattering mechanism. Only specific polar optical phonon modes make dominant contribution to the scattering rates, which we attribute to the atomic structure and electrostatic interactions in Mg$_2$Sb$_3$. For transport across interfaces, an important question to ask is if electron and phonon scatterings conserve lateral momentum, i.e., if they experience specular or diffuse scattering, in the presence of interfacial atomic mixing. We employ atomic Green’s function to simulate electron and phonon transmission across interfaces for SiGe interface with mode-by-mode resolution. We find the angular dependent interfacial transport for electron and phonon are behaving differently, which provides new opportunities for optimizing thermoelectric performance. This work is supported by DARPA MATRIX program (Grant No. HR0011-16-2-0041).

8:45 AM *EN13.03.03/EN14.11.03
Amorphous-Like Thermal Conductivity in Crystalline Solids Saikat Mukhopadhyay and Thomas Reinecke; U.S. Naval Research Laboratory, United States

Thermoelectric materials (TEs) could play an important role in future energy management through environmentally sound cooling and power generation, e.g., converting waste heat into electricity. Efficient TEs inhibit the propagation of heat (low thermal conductivity, $\kappa$) but conduct electricity well (high power factor, PF). Although $\kappa$ in a given material can be reduced via alloying and nanostructuring, identifying materials with intrinsically low $\kappa$ is still needed. It has already been known that soft phonon modes due to weakly bonded atoms and $s^2$ lone-pair electron are common to materials with low-$\kappa$. Here, we predict a series of new materials which are weakly bonded systems with same constituent elements but different stoichiometry either with $s^2$ lone-pair electron or high mass density. Due to giant phonon anharmonicity and low phonon group velocities, they offer extremely low $\kappa$ (0.3-0.6 W/mK) at 300K approaching to those found in the amorphous/disordered regime. In addition to low-$\kappa$, high Seebeck coefficients and electrical conductivities in these materials may provide a new opportunity for designing high-efficiency thermoelectrics at room temperature.

9:00 AM *EN13.03.04/EN14.11.04
New Horizons in Thermoelectric Materials—Inorganic-Organic Hybrids and Machine Learning for Inorganic Crystals Kedar Hippalgaonkar$^{1,2}$; $^1$Nanyang Technological University, Singapore; $^2$Institute of Materials Research and Engineering, Singapore

For the next revolution in thermoelectrics, development of new physics as well as new materials needs to go hand-in-hand. In this talk, I will introduce new perspectives such as correlated electron physics, wave effects in phonons as well as opportunities for new inorganic-organic (hybrid) materials$^1$. Then, I will introduce specifically the case of CuTe:PEDOT thin films and using this as a test case, describe the design principles for creating the next generation of hybrid materials$^2$. In addition, I will describe how data-driven approaches can augment our knowledge: used in conjunction with the right material and transport descriptors, these can prove prescient in predicting new TE materials. I will end with a specific example of how we’ve used a Crystal Graph Convolutional Neural Network (CG-CNN) with training data from Materials Project to learn about TE properties. In addition, we use high-throughput, high-fidelity DFT calculations with the Electron Phonon Averaging (EPA) approximation to calculate carrier relaxation times, we propose that the transport effective mass remains an effective single descriptor that can guide inorganic TE material screening.

9:30 AM EN13.03.05/EN14.11.05
Thermoelectric Transport Descriptors in Data-Driven Thermoelectric Screening Ady Suwardi1, Deng Tianqi2, Daniil Bash1, Hong Kuan Ng1, Jose Recatala Gomez1, D V M. Repaka1, Pawan Kumar1, Anas I. Abutaha1, Michael Sullivan2, Shuo-Wang Yang2 and Kedar Hippalgaonkar1; 1IMRE, Singapore; 2Institute of High Performance Computing, Singapore

With the maturity of sophisticated, high throughput computational tools and the advent of machine learning applications in materials science, identifying the appropriate fundamental level descriptors has never been more relevant and pressing in data-driven materials discovery domain. In this work, we first present the inertial effective mass as an important descriptor in thermoelectric transport. The conclusion was obtained by analyzing data from 1617 compounds of all crystal structures mined from the materialsproject.org. Data was analyzed using polycrystalline averaging Seebeck, effective mass, as well as electrical conductivity. In addition, constant relaxation time approximation was used in all data analysis, which is known not to necessarily reflect experimentally measured compounds.

Subsequently, we present a state-of-the-art approach of using electron-phonon averaging (EPA) to obtain contribution of all possible scattering mechanisms to the relaxation time and challenge the initial assumption of constant relaxation time. More interestingly, we sought to evaluate the veracity of insights and conclusions drawn under constant relaxation time approximation from the EPA point of view and indeed confirm that effective mass is an important descriptor. Further insights gained from analysis of scattering times provide us additional insight towards prediction of new thermoelectric compounds.

9:45 AM EN13.03.06/EN14.11.06
Thickness-Dependent Thermal Conductivity of Titanium Trisulfide Nanoribbon Chao Wu1, Chenhan Liu1, Yongkang Wang1, Juekuan Yang1, Qingyu Yan2 and Yunfei Chen1; 1Southeast University, China; 2School of Materials Science and Engineering, Singapore

The two-dimensional layered materials with interlayer van der Waals (vdWs) bonding such as graphene have attracted tremendous interests in scientific community. Recently, layered materials composed of transition metal trichalcogenides with strong in-plane anisotropy, which show unusual properties based on theory, have been successfully synthesized so that their properties can be explored through experiment. For instance, due to theoretically calculated ZT value (3.1) of monolayer titanium trisulfide along y direction at moderate carrier concentration, layered titanium trisulfide nanoribbons with intralayer covalent bonding and interlayer vdWs bonding burst extensive research, which inspires us to investigate the lattice thermal conductivity of the nanoribbon and the size effects on the thermal conductivity because lowering the thermal conductivity can increase the ZT value significantly. In order to better understand the thermal transport in the titanium trisulfide nanoribbon, the theoretical calculation combined with the experiment are adopted. Through solving the phonon Boltzmann transport equation (implemented in ShengBTE package) with the first-principles second- and third-order force constant (implemented in VASP package), the thermal properties of titanium trisulfide are obtained. The calculation results reveal that the thermal conductivity monotonously decreases with the number of titanium trisulfide layers increasing from one to three and displays a strong in-plane anisotropy as the temperature range from 40 to 500 K. For example, the thermal conductivity along y direction is 2.7 times larger than x direction at room temperature. Compared to layered graphite, due to the weaker interlayer coupling strength, the out-of-plane thermal conductivity (around 1.1 W/m-K) at the room temperature is 5 times lower.

Based on the results of theoretical calculation, we synthesized the titanium trisulfide nanoribbons with different thicknesses and measured the thermal conductivity using a suspended micro-thermometry from 20 to 300 K. The experimental results show that the in-plane thermal conductivity of titanium trisulfide nanoribbons decreases monotonously as the thickness increases, which is same as the theoretical calculation. Interestingly, the thermal conductivity keeps decreasing as the thickness is smaller than 272 nm, which is quite different from multi-layer graphene. In detail, the thermal conductivity decreases rapidly as the thickness is below 60 nm and becomes slowly beyond 150 nm. Due to the computational cost, 4 layers or thicker titanium trisulfide cannot be calculated. The giant large layer thickness dependent in-plane thermal conductivity is surprising and confusing. We speculated that this phenomenon may stem from weak interlayer coupling strength and unique atomic structure, which needs further investigation.
Design and Engineering of Flexible Thermoelectric Devices  
G. Jeffrey Snyder; Northwestern University, United States

Thermoelectric semiconductors directly convert heat into electricity. These solid-state devices have been used reliably in space for over 40 years without maintenance. Temperature gradients and heat flow are omnipresent in natural and human-made settings and offer the opportunity to scavenge energy from the environment recovering waste heat from industry or replacing the need for batteries in remote sensor networks or mobile devices. Particularly attractive is the ability to generate electricity from body heat that could power medical devices or implants, personal wireless networks or other consumer devices. This talk will discuss the design principles for thermoelectric generators using a generalized electrical transport model combined with an effective thermal conductivity approach [1, 2]. Such design principles provide good estimates of the power that could be produced and the size and complexity of the thermoelectric generator that would be required. In addition these design principles can guide the search and optimization new thermoelectric materials. In organic and polymer semiconductors the optimum doping is identified and the peak \( zT \) for a given class of materials can be determined. Also, a complete system design shows the misconception that power factor rather than \( zT \) should be optimized for a TE generator. The power factor misconception also leads to misleading strategies for optimization and discovery of new TE materials. The materials requirements for flexibility, leading to a flexibility figure-of-merit will be discussed.

Hybrid materials consisting of inorganic nanostructures embedded in conducting polymer matrices have emerged as promising systems for room temperature thermoelectric applications. They are attractive due to their intrinsic low thermal conductivities, the ability to engineer interfaces for energy filtering effects and phonon scattering, and their ability to take advantage of high-throughput and solution processable manufacturing. Most polymer and hybrid materials reported in the literature have been p-type, owing to difficulties in n-type doping of conducting polymers in conjunction with the nature of the applied nanocrystals. This has resulted in a strong drive to develop new n-type materials, since both are necessary for module development. Here we explore our recent developments in the synthesis chalcogenide nanowires encapsulated in poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) that are used as templates for the synthesis of Ag2-xE (where E=Te, Se) via topotactic chemical transformation processes. This synthetic method allows us to engineer the composition of our hybrids, whereby we are able to directly influence the thermoelectric properties, including the production of both p-type and n-type materials from the same parent material. We detail the structural and morphological development of our materials with changing stoichiometry during aqueous based synthesis via X-Ray diffraction (XRD), X-Ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) and relate this to their thermoelectric performance. We take the example of one of our n-type Ag2Te/PEDOT:PSS hybrid materials and further manipulate its performance via post-deposition (de)doping schemes, whereby the PEDOT:PSS is reduced by treatment with Tetrakis(dimethylamino)ethylene (TDAE). This process is followed by UV-Vis spectroscopy and electron paramagnetic resonance spectroscopy (EPR) to detail how this (de)doping process affects the charge carrying species. Control of the competing charge carrier concentration allows further improvement in the n-type hybrid device performance.

11:30 AM EN13.04.04/EN14.12.04
Flexible Cellulose Fiber-Based Hierarchical Porous Bismuth Telluride for High-Performance Thermoelectrics and Energy Harvesting Device Kaiping Tai, Qun Jin and Yang Zhao; Institute of Metal Research, China

Porous modification is general approach to endowing the rigid inorganic thermoelectric (TE) materials with considerable flexibility, however, by which the TE performances are severely sacrificed. Thus, there remains a struggling against the trade-off between the TE properties and flexibility. Herein, we develop a novel strategy to combine the Bi2Te3 thick film with the ubiquitous cellulose-fiber (CF) print-paper via unbalanced magnetron sputtering technique (ACS Appl. Mater. Interfaces 10, 1743, 2018). The Bi2Te3/CF TE composites with tailorable shapes and dimensions were successfully obtained by our approach, which have reasonable internal resistance as components of TE devices with in-plane configurations. Owing to the hierarchical nano-micro porous microstructures and the excellent fraction resistance of the Bi2Te3/CFs constructions, the prepared TE composites with Bi2Te3 nominal deposition thickness of tens of micrometers exhibit mechanically reliable flexibility, of which the bending deformation radius could be as small as a few millimeters. Meanwhile, the thermal conductivity was remarkably reduced, due to the phonon-nanopore scattering effects. Enhanced Seebeck coefficients were observed comparing with the dense films and the power factors of ~250 to 400 μW/mK2 were obtained for the composites from room temperature (RT) to 473 K, which can be further improved by optimizing the carrier concentrations. As a result, the TE figure of merit, ZT, is as high as ~0.38 at 473K. Moreover, Fig. 1 depicts the photograph, structure, and working principle diagram of the flexible TE device consisting of 12 pairs of p- and n-type legs integrated on the double sides of CF paper sheet employing a laser beam micro-cutting system, which displays great potential as flexible TE device for thermal energy harvesting. When the light bulb works for about a few minutes, the temperature of the central side rises quickly, the temperature difference between the center and periphery is about 50 K from the infrared image, and the TE device generates an output voltage of 0.144 V. This kind of flexible TE device can realize the collection and recovery of heat energy in daily life to power flexible electronics, such as wearable devices and environmental monitors, which also promotes the development of paper-based and thin-film electronics.

11:45 AM EN13.04.05/EN14.12.05
Creep Behavior of Thermoelectric Materials Muath M. Al-Malki1,2, Qinyi Qiu3, Tiejun Zhu3, G. Jeffrey Snyder1 and David Dunand1; 1Northwestern University, United States; 2King Fahd University of Petroleum and Minerals, Saudi Arabia; 3Zhejiang University, China

Since the 1960’s, NASA has implemented Radioisotope Thermoelectric Generators (RTGs) to supply energy for
many of its satellites and space probes. Similar generators for industrial and automotive waste heat recovery have been proposed and many new thermoelectric generator materials have been investigated. Nonetheless, mechanical integrity for the full operational life of the thermoelectric modules, which can extend to decades, has not been given much consideration in such applications. Among many contributors, clamping forces, vibrational stresses, and thermally-induced mismatch stresses may combine to give stress levels high enough to deform the thermoelectric module by creep, thus diminishing its useful lifetime. To date, few thermoelectric materials have been tested for creep, including Bi$_2$Te$_3$, PbTe, Mg$_{1.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$, and TAGS-85.

In the present talk, we show the case of the compressive creep deformation behavior of two thermoelectric materials; half-Heusler n-type Hf$_{0.3}$Zr$_{0.7}$NiSn$_{0.98}$Sb$_{0.02}$ and n-type skutterudite (Yb-CoSb$_3$) alloys, at 500-705 °C. When subjected to uniaxial compressive stresses at 600°C, the n-type half-Heusler alloy Hf$_{0.3}$Zr$_{0.7}$NiSn$_{0.98}$Sb$_{0.02}$ exhibits Newtonian flow, consistent with diffusional creep of its fine-grain (1-7 μm) microstructure achieved via spark-plasma sintering of powders. In addition to its promising thermoelectric performance at high temperatures, this alloy sustains very high compressive stresses at 600°C (from 21 to 359 MPa, for ~ 23 days) without macroscopic failure. However, the brittle nature of the alloy leads to the formation of numerous cracks at such high stresses, which in turn deteriorate the thermoelectric performance. A more realistic creep stress range (15-46 MPa, for ~ 4 days) preserves the high thermoelectric figure of merit $zT$. Among thermoelectric materials mechanically creep-tested to date, the ZrNiSn-based Half Heusler alloy has the highest creep resistance. On the other side, the n-type skutterudite (Yb-CoSb$_3$) alloy showed acceptable creep resistance under protected environment.

Given their high melting temperature, stiffness, and creep resistance, half-Heusler alloys appear uniquely suited for long-term thermoelectric applications where high stresses and temperatures are present.

SESSION EN13.05/EN14.13: Joint Session: Thermoelectric Devices and Applications
Session Chair: Jayakanth Ravichandran
Wednesday Afternoon, December 4, 2019
Sheraton, 3rd Floor, Commonwealth

1:30 PM *EN13.05.01/EN14.13.01
Advanced Materials and Their Infusion into Efficient Thermoelectric Power Generation Systems Jean-Pierre Fleurial and Sabah Bux; California Institute of Technology, United States

Thermoelectric power sources have consistently demonstrated their extraordinary reliability and longevity for deep space missions as well as terrestrial applications where unattended operation in remote locations is required. The discovery of new, more efficient materials, and the development of practical, robust elements and device technologies are the key to improving existing space power system performance and versatility and expanding the use of thermoelectrics into efficient, cost-effective terrestrial applications using medium to high grade heat sources. We present an overview of NASA-funded collaborative research efforts to identify advanced bulk thermoelectric materials, capable of quadrupling current state-of-practice average ZT values over the available operating temperature range of 1275 K to 475 K, through the exploration of structurally complex compounds allowing for a wide range of chemical tuning and the possibility of forming stable nano- and micro-scale composites. Materials- and device-level experimental performance validation accomplished to date, technical challenges, progress and plans for technology infusion into future thermoelectric power systems are discussed.

2:00 PM EN13.05.02/EN14.13.02
Understanding Thermoelectric Devices at the Micro Scale Nicolas Perez, David A. Lara Ramos, Vida Barati, Javier Garcia, Heiko Reith, Guodong Li, Gabi Schierning and Kornelius Nielsch; IFW Dresden, Germany

Energy harvesting and thermal management are required for applications in the internet-of-things, autarkic sensors, or highly integrated electronic devices. Thermoelectric generators and coolers are promising technologies for localized energy harvesting and thermal management. These devices are currently well optimized for near-room temperature operation at the macroscopic scale. However, the high integration density of today’s most significant applications requires an increasing degree of miniaturization. Using finite element calculations, we gained insight on
the design guidelines for micro thermoelectric devices with realistic material properties, and with concurring size and geometry constraints [1]. Understanding the interplay between thermal and electrical heat fluxes at the micro scale allowed our group to fabricate micro thermoelectric devices for thermal management, efficient enough that can be integrated in electronic packages [2]. Our relevant findings about the design of micro thermoelectric devices will be presented.


2:15 PM EN13.05.03/EN14.13.03
Dual Sensors of Fluid Temperature and Dynamics Based on Engineering Design Using Thermoelectric Effect
Seo Byungseok, Hayoung Hwang, Sunggu Kang, Youngsun Cha and Wonjoon Choi; Korea University, Korea (the Republic of)

The detection of temperature and dynamics of working fluids, including water, is important for experimental and industrial applications, such as detection of precise changes in fluid environment, monitoring of drainage or cooling water at factory facilities, micro / nano flow analysis. However, due to the spatial limitations or complex geometry of fluid channel interfaces, it is important to accurately detect multiple parameters that are optimally integrated into the operating platform. Also, many fluid sensors necessarily disrupt the natural flow within the platform, and even though the installation of the sensing device should not affect the intrinsic properties of the target element in fluid applications. In this work, we develop a flexible, attachable dual-output sensor for fluid temperature and transfer dynamics based on structural design of thermoelectric materials (SDTM). The SDTM flexible substrates using PET was developed to detect real-time changes in temperature and peak voltage reflecting fluid dynamics. Simple sputtering deposition of Bi2Te3 through a patterning mask has allowed the fabrication of dual-power sensors which do not affect the fluid flow shape. When the working fluid contacts the surface, thermoelectric structure pattern induces continuous double thermal wave and time interval without disturbing the natural flow of working fluid. The raw voltage signal induced by thermal gradient wave provides the magnitude of the first peak voltage and the duration between the two peaks, which show the real time temperature and the moving velocity of the working fluid. Furthermore, as a demonstration of an expandable platform using SDTM, a scalable sensor array comprising multiple SDTMs was fabricated as a large-area device for sensing a fluid temperature flow dynamic sensing device. Its performance with respect to sensing the fluctuation of working fluid temperature and kinematics was verified using a 4 × 4 SDTM array. As a result, the new methodology using SDTM can contribute to the development of entirely new technologies for next-generation sensors that require advanced features such as multi-element detection and a variety of integrated flexible and removable features.

2:30 PM BREAK

SESSION EN13.06/EN14.14: Joint Session: Thermoelectric Materials and Applications
Session Chair: Gabi Schiering
Wednesday Afternoon, December 4, 2019
Sheraton, 3rd Floor, Commonwealth

3:30 PM *EN13.06.01/EN14.14.01
Thermoelectric Cooling Using a New p-Type Material Zhifeng Ren; University of Houston, United States

Bi2Te3-based p-type Bi0.5Sb1.5Te3 and n-type Bi2Te2.7Se3 have been the only materials used for thermoelectric cooling for decades. Even though the progress on advancing the thermoelectric figure-of-merit (ZT) has been significant especially the materials with peak ZT at high temperatures, materials with high enough ZT around room temperature are very rare. Up to now, in addition to Bi2Te3-based ones, the only reported is p-type MgAgSb with ZT of ~0.8 at room temperature. There is no report on any n-type material exhibiting ZT similar to that of the n-type Bi2Te2.7Se3. In this talk, I will present a new n-type material that has a ZT of ~0.7 at room temperature, which is comparable to that of n-type Bi2Te2.7Se3. The cooling performance of a unicouple consisting of the new n-type material and the p-type Bi0.5Sb1.5Te3 is also in par with the commercial legs consisting of the p-type Bi0.5Sb1.5Te3 and
4:00 PM EN13.06.02/EN14.14.02
Modeling the Temperature Dependent Seebeck Coefficient of Metastable Amorphous Ge$_2$Sb$_2$Te$_5$ and Impacts of Thermoelectric Effects on the Operation of Phase Change Memory Devices
Jake Scoggin, Noah Del Coro, Md Tashfiq Bin Kashem, Sadid Muneer, Helena Silva and Ali Gokirmak; University of Connecticut, United States

Thermoelectric effects play a significant role in phase change memory (PCM) and Ovonic threshold switch (OTS) devices used as access devices in PCM cells [1]. Typical PCM cells are two-terminal nanometer-scale resistive memory devices which can be reversibly switched between a low-resistance crystalline and a high-resistance amorphous state via nanosecond electrical pulses. Amorphization in PCM devices is achieved by self-heating the phase change material, typically a chalcogenide, close to its melting temperature, followed by a sudden quench. Crystallization is achieved by self-heating the phase change material above its glass-transition temperature. OTS devices typically use amorphous chalcogenides that do not crystallize during normal device operation.

The local current densities in PCM and OTS devices can reach 10$^8$ A/cm$^2$, giving rise to local temperatures in excess of 900 K and thermal gradients as high as 50 K/nm; hence, Peltier effects at material interfaces and Thomson heating within the active area are substantial. Accurate modeling of thermoelectric effects requires knowledge of temperature dependent electrical resistivity and Seebeck coefficients of these materials. These parameters can be measured at low temperatures on as-deposited amorphous films [2]. However, melt-quenched amorphous materials’ parameters tend to differ from as-deposited films, and PCM materials rapidly crystallize at higher temperatures. High-speed metastable electrical resistivity measurements can be performed on nanoscale devices using electrical pulses to uniformly amorphize devices up to approximately 200 nm in diameter [3], but larger devices tend to form current filaments and hence do not amorphize uniformly. On the other hand, measurement of the Seebeck coefficient ($S_e$), which is vital to understanding thermoelectric effects, is very difficult at small scales.

In this work, we model the Seebeck coefficient for metastable amorphous Ge$_2$Sb$_2$Te$_5$ (aGST) based on high-speed experimental results [3] and an energy band diagram proposed by Muneer et al. [4] from 300-850 K [3], [5], and we analyze thermoelectric effects in PCM cells using finite element phase change device simulations [6]–[9]. We calculate the electron and hole Seebeck contributions $S_e$ and $S_h$ in metastable aGST with the band diagram in [4] and find that $S_h$ is similar in both magnitude and slope to $S$ measurements on as-deposited aGST thin films in 300-400 K range [5], [10], consistent with the unipolar conduction assumed when deriving the band gap in [4]. We use $S_h$ as the Seebeck coefficient in metastable aGST and simulate reset and set operations in a PCM double mushroom cell and find that the Seebeck differential between crystalline and amorphous GST results in significant heating/cooling at amorphous-crystalline junctions during both crystallization (set) and melting (reset).


4:15 PM *EN13.06.03/EN14.14.13
Flexible Thermoelectric Materials by Organic Intercalation of Two-Dimensional Layered Compounds
Chunlei Wan1, Kunihito Koumoto2 and Kun Zhang; 1Tsinghua University, China; 2Nagoya Industrial Science Research Institute, Japan

Flexible materials with high thermoelectric performance have attracted growing interest recently. By intercalating organic molecules into the van der Waals gap of varieties of inorganic two dimensional layered compounds, we
developed a large family of thermoelectric materials with excellent mechanical flexibility. The inorganic and organic monolayers are alternatively stacked to form an inorganic/organic superlattice, in which the high electronic transport properties of the inorganic component has been maintained and the thermal conductivity was dramatically suppressed by the organic components, finally resulting in boosted ZT value. We have demonstrated this idea in several two dimensional host materials, including TiS$_2$, Bi$_2$Se$_3$ and TaS$_2$, etc. The abundant choice of the organic molecules also brings new opportunities to optimize the thermoelectric performance, such as the dielectric screening effect and the quantum confinement effect. We finally developed a solution-processed strategy to fabricate large area flexible thermoelectric foil based on this inorganic/organic superlattice, which enables easy integration into energy-harvesting electronic devices.

4:45 PM EN13.06.04/EN14.14.04
Diffusion Behaviors of Bonding Interface of Bi–Te Based Thermoelectric Materials with Ni/Au Barrier Fabricated by Different Deposition Processes Ekubaru Yusufu$^{1}$, Tohru Sugahara$^{1}$, Michio Okajima$^{2}$, Shutaro Nambu$^{2}$ and Katsuaki Suganuma$^{1}$; $^{1}$The Institute of Scientific and Industrial Research, Osaka University, Japan; $^{2}$E-ThermoGentek Co., Ltd., Japan

Recently, our group developed a Bi–Te-based TEG device by using conventional semiconductor packaging technology. In that device, Ni/Au was used as the diffusion barrier, and Sn–Ag-based solder was used as the bonding material. Although Bi–Te-based TE materials can be used up to approximately 300°C, the maximum operating temperature of the device was limited to approximately 150°C owing to the low melting point of the Sn–Ag-based solder (~150°C) that bonds Bi–Te-based TE materials and Cu electrodes. Therefore, in order to apply higher temperature differences to the device, in this study, we attempted to develop a bonding interface resistant to heat up to 250°C. Ni/Au was retained as the diffusion barrier layer, but Ag paste was chosen as the bonding material, instead of the Sn–Ag-based solder, because it has many advantages such as high-temperature stability (melting point ~ 960°C), printability, low electrical resistivity, high thermal conductivity (150 Wm$^{-1}$K$^{-1}$), and a temperature requirement of less than 300°C for sintering-bonding. The Ni/Au diffusion barrier layer was prepared using two different deposition processes, sputtering and electroplating, and the element diffusion behaviors of these two bonding interfaces at 250°C were investigated.

In the bonded sample with sputtered Ni/Au, the Cu electrode diffused violently into the chip and formed a Cu–Te-rich phase. On the other hand, in the bonded sample with electroplated Ni/Au, the diffusion of Cu was blocked, but a NiTe phase formed on the chip side. The above results demonstrate that, with sputtered Ni/Au, grain-boundary diffusion is predominant and Cu electrodes diffused along the grain boundaries, while with electroplated Ni/Au, self-diffusion is predominant because of the instability of the monocristalline–amorphous phase. These results suggest that the highly crystalline Ni layer, which has dense grain boundaries and no pores, is a highly effective diffusion barrier.
to simultaneously increase Seebeck coefficients and electrical conductivities. The combined effect on electronic and structural properties is proven with the help of spectroscopy and x-ray scattering experiments.

8:30 AM EN13.07.02
**Fabrication of PEDOT:PSS/GST Hybrid Composites for High Thermoelectric Performance** Jae-Hong Lim¹, Young Soo Yoon¹, Kyu Hyoung Lee² and Woon-Ik Park³; ¹Gachon University, Korea (the Republic of); ²Yonsei University, Korea (the Republic of); ³Korea Institute of Ceramic Engineering & Technology, Korea (the Republic of)

The thermoelectric performance of organic/inorganic hybrid composites is strongly governed by interfacial interactions where the energetic mismatches provide effective charge carrier scattering for high Seebeck coefficient. In addition, the conformation of polymer chain at the interfaces could engineer electronic structure for a favorable hopping mechanism. Herein, we report on the template-assisted fabrication of PEDOT:PSS/Ge₂Sb₂Te₅ (GST) nanowires hybrid composites for improvement in electrical conductivity and Seebeck coefficient. The GST nanowires array fabricated by a solvent-assisted nanotransfer printing technique was participated as a template to align the PEDOT:PSS. Significantly enhanced thermoelectric performance of PEDOT:PSS/GST nanowires hybrid composites compared to their individual counterparts is because of energy filtering effect at the GST nanowire/PEDOT:PSS interfaces.

The alignment effect of PEDOT:PSS chains on the electrical conductivity was elucidated by measurement in parallel and perpendicular to the GST nanowires. The best power factor of 1560 µWm⁻¹K⁻² was achieved in parallel-direction owing to not only the high Seebeck coefficient but also the conformationally ordered PEDOT:PSS interfacial layer at the GST nanowires template.

8:45 AM *EN13.07.03
**From 2D Roll-to-Roll Printing to 3D Low-Cost Thermoelectric Generators** Ulrich Lemmer; Karlsruhe Institute of Technology (KIT), Germany

Thermoelectric generators (TEGs) transform heat to electricity without any movable parts. These devices will play an important role in energy harvesting for wearables, autonomous sensor nodes, and the Internet-of-Things (IoT). Conjugated polymers as well as printable inorganic nanomaterials offer the unique advantage of being processable on printing machines. They have recently made strong progress in their thermoelectric properties. This opens a pathway for the fabrication of powerful thermoelectric generators with unprecedented low costs for mass applications. We have developed novel printable PEDOT formulations and novel printable inorganic materials for a device layout which allows for a roll-to-roll printing process on ultrathin plastic foils. The TEGs are then subsequently fabricated by an automated folding process which allows to adapt the geometry of the devices such that the desired thermal resistance is matched to the specific thermal boundary condition. Using this approach in combination with designed low power electronics forms the basis for several wireless sensor nodes. The talk will cover our recent developments on printable organic and inorganic nanomaterials.

9:15 AM EN13.07.04
**Enhanced Performance of Thermoelectric P-Type Composite Films Using Naturally Occurring Chitosan Binder and Mechanical Pressure** Deepa Madan, Eunhwa Jang and Priyanshu Banerjee; University of Maryland, United States

Printable thermoelectric generators (TEGs) are attractive to researchers because of their potentially higher power density, scalability and lower cost than rigid conventional TEGs. This additive manufacturing of TEGs requires active thermoelectric (TE) particles to be dispersed in a polymeric binder to synthesize printable slurry inks, and printed films to be subsequently subjected to a long and high temperature curing for grain coalescence and enhancing electrical conductivity. A large quantity of polymeric binder in composite TE films results in a sizable loss of the electrical conductivity and TE performance. Moreover, an energy intensive long and high-temperature curing process is another challenge for printable TEGs.

We report a novel approach eliminating the long and high temperature curing requirements for the printable thermoelectric generators but attain enhanced electrical conductivity. This work presents the feasibility of using a small amount of naturally occurring chitosan as a binder for p-type thermoelectric composite films. Less than 10⁻³ weight ratio of chitosan was sufficient to hold the thermoelectric particles together in the form of composite films. Samples of various weight ratios such as 1:2000, 1:5000, and 1:7000 between binder and TE materials were
prepared and tested. Various particle sizes of the TE materials were also explored to observe their effect on electrical conductivity. These various samples were drop casted and cured at relatively lower temperature (150°C) for shorter time (5 minutes). These cured films were further subjected to uniaxial pressure for densification of the films by reduction of pores, voids and also merge of small particles between big particles to give bulk like structure. Analysis of the obtained samples indicated that a wide range sizes of particles with chitosan binder in composite films under the application of mechanical pressure lead to plate structure which resulted in improved electrical conductivity of the composite films.

The highest power factor achieved for best performing p-type Sb$_2$Te$_3$ composite films is 1236±110 µW/mK$^2$, and the figure of merit (ZT) is 1.236 at room temperature (300K). The highest ZT obtained for p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ film is 0.838 at room temperature.

**9:30 AM EN13.07.05**

Vapor-Printed Polymers for Wearable Thermoelectric Generators Linden K. Allison and Trisha L. Andrew; University of Massachusetts at Amherst, United States

Wearable thermoelectric generators are a promising energy source for powering activity trackers and portable health monitors. However, known iterations of wearable generators have large form factors, contain expensive or toxic materials with low elemental abundance, and quickly reach thermal equilibrium with a human body, meaning that thermoelectric power can only be generated over a short period of wear. Here, we create an all-fabric thermopile by vapor printing persistently p-doped poly(3,4-ethylenedioxythiophene) (PEDOT-Cl) onto commercial cotton and integrate this thermopile into a specially-designed, wearable band that generates thermovoltages >20 mV when worn on the hand. We show that the reactive vapor coating process creates mechanically-rugged fabric thermopiles that yield notably-high thermoelectric power factors at low temperature differentials, as compared to solution-processed counterparts. Further we describe best practices for naturally integrating thermopiles into garments, which allow for significant temperature gradients to be maintained across the thermopile despite continuous wear.

**9:45 AM BREAK**

SESSION EN13.08: Miniaturized TE Devices  
Session Chairs: Ulrich Lemmer and Mona Zebarjadi  
Thursday Morning, December 5, 2019  
Sheraton, 3rd Floor, Gardner AB

**10:15 AM *EN13.08.01**

Reliability of Flexible Thermoelectric Devices under Cyclic Loading Seungwoo Han$^{1,2}$;  
$^1$Korea Institute of Machinery and Materials, Korea (the Republic of);  
$^2$University of Science and Technology, Korea (the Republic of)

As the demand of wearable devices increases, flexible thermoelectric devices are attracting attention as alternative power sources of them. Because wearable devices are worn on the human body, it is possible to create electricity using thermoelectric devices from body heat without the need for other heat sources. In addition, flexible thermoelectric devices have been studied due to their potential for using arbitrary heat source shapes without an additional heat exchanger.

The biggest issue to make a flexible thermoelectric device is that the thermoelectric device has flexibility so that it can maintain its performance even when bent during use. Unlike conventional thermoelectric devices, materials, fabrication processes, and device design have to be changed in order to impart flexibility to thermoelectric devices. Existing rigid ceramic substrates cannot be used. The use of bulk thermoelectric materials limits the flexibility of thermoelectric devices. The joint between the electrodes and the thermoelectric legs in a thermoelectric device reduces its flexibility. If necessary, the structure of the thermoelectric device may need to be changed.

Flexible thermoelectric devices are subjected to cyclic loading during continuous use. The repetitive load generates cracks inside the thermoelectric device, thereby increasing the internal resistance of the device and eventually causing failure of the thermoelectric device. Therefore, in order to develop and commercialize a flexible thermoelectric device, it is essential to establish a method of evaluating the reliability of the thermoelectric devices under cyclic loading.
In this study, the current state of flexible thermoelectric devices research is reviewed in terms of materials, devices and applications. A method for evaluating the reliability of a flexible thermoelectric device is presented.

10:45 AM EN13.08.02
Enhanced Energy Conversion Performance of Compliant Thermoelectric Generators via Intrinsically Stretchable Heat Collectors and Conformal Contacts Hyeon Cho1,2, Byeongmoon Lee2, Kyung Tae Park1, Heesuk Kim1, Seunjun Chung1 and Yongtaek Hong2; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

Emerging energy generators has expanded the potential of electronics in the way that they can operate wireless-interconnected Internet of Things (IoT) devices without the assistance of additional power sources or batteries. Among promising candidates, thermoelectric generators (TEGs) have offered attractive opportunities for realizing self-powered electronics due to their energy conversion ability from waste heat to electricity. For the realization of high-performance TEGs, the maximized temperature difference across the thermoelectric (TE) layers is the most important factor in given temperature boundaries and TE material properties, therefore, efficient heat collection and heat transferring to TE materials is necessary to achieve high energy conversion efficiency. In this context, the demands for compliant TEGs which can collect thermal energy from arbitrary-shaped heat sources minimizing parasitic heat loss have increased, which is not allowed to conventional rigid TEGs. In this regard, there have been many efforts to integrate high-performance cuboid-shape inorganic Bi2Te3 –based TE rods into soft platforms. As a representative approach to realize rod-based compliant TEGs, the infiltration of soft medium and flexible interconnection have been introduced to provide acceptable mechanical tolerance despite brittle and rigid nature of the inorganic alloys. However, unexpected lower TE performances and imperfect conformal contacts have been reported due to parasitic heat loss in hundreds μm-thick polymer substrates and metal contacts, respectively. Therefore, optimized module designs with the minimization of parasitic heat loss and fully soft interconnections have to be developed toward highly efficient compliant TEGs. In this presentation, we will report a new strategy to improve heat collection from arbitrary shaped-heat sources via the soft heat collector embedded in ultra-thin polymer supporting layers. The selectively patterned and aligned thermally conductive soft composites are lined up with Bi2Te3 bulk legs; thus the significantly improved heat transfer ability can be delivered toward in the out-of-plane direction with the minimization of parasitic thermal energy loss, allowing conformal thermal contacts simultaneously. These results indicate that the heat transfer ability of soft heat collectors is much superior to that of the previously used compliant substrates, such as PDMS, pure and engineered Ecoflex, even comparable with that of thermo-pads. In addition, the embedded soft interconnection and infiltrated PDMS offer the opportunity to realize further compliant TEGs. The excellent adhesion property between the Bi2Te3 legs and soft interconnection via the optimized highly conductive epoxy layer also improves the mechanical reliability preventing delamination issues. Finally, we will show, for the first time, facilely customized large-are TEGs with high yields fabricated by fully automatic additive manufacturing.

11:00 AM EN13.08.03
Electrical Properties of Conducting Polymers for Enhancing the Performance of Organic Thermoelectric Devices and Modules Jeonghun Kwak1, Sung Hyun Kim2 and Han Young Woo3; 1Seoul National University, Korea (the Republic of); 2Wonkwang University, Korea (the Republic of); 3Korea University, Korea (the Republic of)

Organic thermoelectric (TE) devices have attract attention as a low thermal energy-harvesting device. Organic materials can be synthesized and processed by tuning the electronic structures and molecular ordering in a solid state. They can be also fabricated with solution-based deposition techniques, such as inkjet printing, spray printing, and spin-coating. These properties are highly related to their electrical properties which are important for practical implementation of organic TE devices and modules. In this presentation, we will present the advances on improving the electrical properties of various p-type polymers, i.e., >70 S/cm for polypyroles and ~4000 S/cm for poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PPS), by tailoring the molecular ordering and by changing the carrier concentration via acid-based doping. The Seebeck coefficients and power factors were also measured and optimized along with the modification. The film properties were systematically investigated to reveal the origin of the enhancement. Also, we will briefly discuss on the performance of TE modules.

11:15 AM EN13.08.04
Design and Manufacturing Textile Shaped Thermoelectric Generators Kun Zhang and Yuanyuan Zheng; Donghua University, China
In this work, we report the design and manufacturing of textile shaped thermoelectric generators (T-TEGs). Carbon nanotube yarns were selected as the base materials to create segmentally-impregnated yarns with p-type materials (PEDOT: PSS) and n-type (PEI), which was assembled into a spacer fabric by an industrial knitting machine. The effect of n-type PEI doping and fabric structure on the thermoelectric performance of T-TEGs will be carefully investigated. Moreover, the potential application of the T-TEG will be demonstrated.

11:30 AM *EN13.08.05
Mobility and Structure Preservation in Conductive Doped Thermoelectric Polymers Howard E. Katz; Johns Hopkins University, United States

The mechanical flexibility, low temperature processing, potential printability, capability of blending to form composites, and use of common elements are attractive features for the use of polymers in thermoelectrics. This presentation focuses on polymers blended with dopants and polymer additives to tune the charge carrier density and Fermi energy-transport energy difference while maintaining charge carrier mobility. Two thiophene polymers, poly(bisdodecylquaterthiophene) and poly(bisdodecyl thioquaterthiophene) (PQT12 and PQTS12, respectively), were used initially. Cyclic voltammetry and current-voltage measurements indicated that the introduction of sulfurs into the side chains induces traps in films containing PQTS12. Doping the polymer with sulfur in side chains (PQTS12) with the strong oxidant nitrosonium tetrafluoroborate (NOBF4), we obtained an especially high conductivity up to 350 S cm\(^{-1}\). Furthermore, the high conductivity is stable in air without extrinsic ion contributions. The thermoelectric power factor compared favorably with prior reports for p-type polymers that were made by the alternative process of immersion of polymer films into dopant solutions, and fit the established models and newly performed simulations for thermoelectric polymers. Additional data obtained from thiophene copolymers containing the ethylenedioxiithiophene and thieno[3,2-b]thiophene subunits supported these conclusions. Blend microstructure, assessed using grazing incidence X-ray scattering, and mobility evaluated in field-effect transistors, was not adversely affected by the blending. This structural preservation is a key aspect of designing additional polymer compositions with high power factor, including n-type polymers. The value of using such polymers as matrices of composites with inorganic thermoelectric particles will be considered.

SESSION EN13.09: CNT/Graphene based Composites for Thermoelectrics
Session Chair: Manfred Albrecht
Thursday Afternoon, December 5, 2019
Sheraton, 3rd Floor, Gardner AB

1:30 PM *EN13.09.01
Flexible Thermoelectric Generators Using Organic Materials by Printing Process Song Yun Cho; Korea Research Institute of Chemical Technology, Korea (the Republic of)

Thermoelectric (TE) energy conversion is an attractive and environmentally friendly way to recover energy from industrial waste heat or natural heat because of its potential for improving the energy efficiency. As TE materials, organic materials have unique advantages, such as cost effectiveness, low intrinsic thermal conductivity, high flexibility, and amenability to large area applications. With increasing attention on flexible or wearable power-conversion devices, intensive research efforts have been devoted to flexible organic TE modules to replace the brittle inorganic ones. First, a highly integrated and flexible TE module with a novel device architecture based on a carbon nanotube (CNT) web is proposed. The pristine CNT web shows superior electrical conductivity of 998.3 S cm\(^{-1}\), owing to the increased longitudinal carrier mobility derived from the highly aligned structure. To realize optimal TE property, the pristine CNT web is alternately doped with p- and n-type carriers using FeCl\(_3\) and benzyl viologen, respectively, via a brush-casting method. Brush-casting is the simple doping process that enables large-scale and continuous fabrication of flexible TE modules by allowing precise doping of the localized area without a shadow mask. Flexible TE modules were then fabricated by repeated brushing and folding of the CNT webs. Owing to the synergic effect of the highly integrated high-performance TE material (highly aligned CNT web) and the facile doping process
(brush-casting), flexible TE modules consisting of 120 \textit{p-n} couples over an area of 8 cm\(^2\) show a maximum power output of 5.3 μW for a temperature difference of 11.7 K.

Second, a rapid solvent evaporation method based on the triple point of a processing solvent to prepare CNT foam with a porous structure for TE power generators is presented. The rapid solvent evaporation process allows the preparation of CNT foam with various sizes and shapes. Furthermore, the density and porosity of the CNT foam are precisely and easily controlled by manipulating the initial CNT/solvent ratio. The obtained highly porous CNT foam with porosity exceeding 90\% exhibits a low thermal conductivity of 0.17 W m\(^{-1}\) K\(^{-1}\) with increased phonon scattering, which is 100 times lower than that of a CNT film with a densely packed network. The aforementioned structural and thermal properties of the CNT foam are advantageous to develop a sufficient temperature gradient between the hot and cold parts to enhance TE output characteristics. To improve the electrical conductivity and Seebeck coefficient further, \textit{p-} and \textit{n-} molecular dopants are easily introduced into the CNT foam, and the optimized condition is investigated based on the TE properties. Finally, optimized \textit{p-} and \textit{n-} doped CNT foams are used to fabricate a vertical and flexible TE power generator with a combination of series and parallel mixed circuits. The maximum output power and output power per weight of the TE generator reach 1.5 μW and 82 μW g\(^{-1}\), respectively, at a temperature difference of 13.9 K.

2:00 PM EN13.09.02
Simultaneous Enhancement of Electrical Conductivity and Seebeck Coefficient in SWNT/PEDOT:PSS Thermoelectric Nanocomposites Siqi Liu\(^1\), Hui Li\(^1\) and Chaobin He\(^{1,2}\); \(^1\)National University of Singapore, Singapore; \(^2\)Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), Singapore

High electrical conductivity and high Seebeck coefficient are the two important prerequisites for achieving high power factor in organic thermoelectric (TE) materials. However, these two properties are quite often in conflict. In this work, we demonstrate that incorporating CNT in a conducting polymer PEDOT:PSS could facilitate the formation of stable and effective conductive channels, which provides an effective approach to optimize the TE parameters with simultaneously enhanced electrical conductivity and Seebeck coefficient against the initial organic TE materials. With further tailoring charge concentration of the SWNT/PEDOT:PSS composite by base treatment, the TE performance could be improved. Nanocomposite of 60 wt\% SWNT and PEDOT:PSS exhibits high TE power factor of \(\sim 526 \text{ μW m}^{-1}\text{ K}^{-2}\) with Seebeck coefficient of 55.6 μV K\(^{-1}\) and electrical conductivity of 1701 S cm\(^{-1}\), which is by far one of the highest power factors among the reported organic TE nanocomposites. The enhancement in both Seebeck coefficient and electrical conductivity could be attributed to the carrier concentration optimization as CNT conductive networks retains the ability for charge transfer, which is revealed by Raman, XPS, UV-Vis and Hall effect measurements. Considering thermal conductivity around 0.4–0.6 W/m K, the highest estimated ZT value of our TE nanocomposite can approach 0.39, demonstrating the feasibility of this strategy to enhance TE performance of organic composite materials.

2:15 PM EN13.09.03
Junction Tunneling-Dominated Thermoelectric Transport in Carbon Nanotube Networks Je-Hyeong Bahk\(^1\), Radhika Prabhakar\(^1\) and Md Sharafat Hossain\(^2\); \(^1\)University of Cincinnati, United States; \(^2\)The University of Melbourne, Australia

As emerging flexible thermoelectric (TE) materials, polymer composites with embedded carbon nanotube (CNT) networks have shown promising properties such as high electrical conductivity through CNT networks, low thermal conductivity by polymer matrix, and high mechanical flexibility provided by both components. However, the thermoelectric transport in CNT networks has not been fully understood to achieve their optimal performance in thermoelectric energy conversion. In this talk, we present a combined experimental and theoretical study on carbon nanotube networks embedded in polydimethylsiloxane (PDMS) elastomers. PDMS offers excellent CNT dispersion within its large thickness (> 1 mm) and volume, along with many other advantages such as low-cost, light-weight, bio-compatibility, and high flexibility, thus making it suited for wearable TE application. Since PDMS is electrically insulating, carrier transport occurs only through the CNT networks, which makes the composites an excellent material system for studying carrier transport in CNT networks with no parasitic transport paths. We synthesize and characterize CNT:PDMS composites over a wide range of CNT content, and analyze the thermoelectric properties using Landauer theory. We find that the simultaneous increase in Seebeck coefficient and electrical conductivity with increasing CNT content up to \(\sim 40\%\) CNTs can be attributed to the tunneling transport at CNT junctions with the junction distance decreasing with increasing CNT content. Beyond \(40\%\) CNTs, both properties are reduced and
saturated due to the reduced PDMS content and increased material non-uniformity, which effectively replaced the PDMS gap with an air gap at the junction, thus imposing a higher potential barrier to reduce the properties. We find that a figure of merit $\zeta T$ greater than 10 at room temperature is possible by doping optimization with appropriate junction parameters in semiconducting single-walled CNT networks. Our results and analysis provide important insights into material optimization for hybrid thermoelectric composites based on CNT networks and many other nanoscale fillers.

2:30 PM EN13.09.04
Non-Oxidized Graphene Flakes for High Power Factor Flexible Thermoelectric Films Travis G. Novak, Jin Kim, Jungmo Kim, Anand P. Tiwari and Seokwoo Jeon; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Research into flexible thermoelectric materials has greatly expanded in recent years as interest in waste heat recovery and wearable electronics has increased. 2D graphene is a potentially high-performance, stable material for thermoelectric applications, but its practicality is somewhat limited by traditional synthesis routes. For graphene produced through oxidative top-down methods, such as Hummer’s Method, numerous defects and oxygenous groups remain in the basal plane of the flakes. These oxygenous groups not only adversely affect electrical conductivity, but also create uncontrollable doping in the graphene flakes because certain oxygenous groups p-dope graphene while others n-dope graphene. This leads to a low overall Seebeck coefficient (typically <20 $\mu$V/K) and reduces the effectiveness of any post-synthesis doping strategies. As an alternative, we introduce a synthesis route of non-oxidized graphene flakes (NOGF) through an intercalation method and demonstrate their superior properties as a thermoelectric material. These non-oxidized graphene flakes (NOGF) show an extremely low defect ratio ($I_d/I_g < 0.1$) and minimal oxidative damage, along with a high aspect ratio. By changing the adsorbed surfactant during graphene synthesis, both n and p type graphene can be synthesized. The n-type NOGF showed electrical conductivity, Seebeck coefficient, and power factor of 3300 S/cm, -45 $\mu$V/K, and 670 $\mu$W/mK², respectively, demonstrating performance that is vastly superior to oxidized graphene flakes in thermoelectric applications. In addition, preliminary results for p-type NOGF revealed values of 650 S/cm, 52 $\mu$V/K, and 180 $\mu$W/mK², which may improve with future optimization. The films were also stable under bending conditions (<3% resistance change after 1000 bending cycles at a bending radius of 3 mm), and a full thermoelectric device based on n-type and p-type NOGF generated stable power output over a wide temperature range (RT to 300 °C). These results demonstrate the potential of NOGF for highly robust, flexible, and high-performance thermoelectric devices.

2:45 PM BREAK

SESSION EN13.10: Organic Semiconductors for Thermoelectrics I
Session Chairs: Manfred Albrecht and Howard Katz
Thursday Afternoon, December 5, 2019
Sheraton, 3rd Floor, Gardner AB

3:15 PM *EN13.10.01
Doping Semiconducting Polymers for Thermoelectrics Michael L. Chabinyc; University of California, Santa Barbara, United States

The thermoelectric properties of materials are strongly dependent on their carrier concentration. The effects of electrical doping of semiconducting polymers are complex due to the interplay between transport properties and microstructure. We will discuss our recent work in understanding the mechanisms of electrical doping of semiconducting polymers and the impact of processing on electrical properties. The thermopower of doped polymers depends on changes in the electronic density of states (DOS) upon doping. We have used electrochemical transistors to control the carrier concentration in semiconducting polymers to study their thermoelectric properties. In-situ X-ray scattering revealed the changes in microstructure of poly(3-hexylthiophene) during gating. In P3HT, and other polymers, a sharp change in the structure of crystalline domains occurs at high carrier concentration. Our results show that chemical doping leads to a broadening of the DOS making it more difficult to predict electronic properties as a function of carrier concentration. Recent models to explain the connection between electrical
conductivity and thermopower in disordered systems will be discussed. A power law form for the electronic density of states of doped semiconducting polymers near the Fermi level provides a reasonable fit to the dependence of transport and thermopower on carrier concentration. The implications of this behavior for improvement of the thermoelectric properties of polymers will be discussed.

3:45 PM EN13.10.02
Charge Transport and Paracrystallinity in Conducting Polymers Anas I. Abutaha1, Pawan Kumar1, Erol Yildirim2, Shi Wen2, Shuo-Wang Yang2, Gang Wu2 and Kedar Hippalgaonkar1; 1Institute of Materials Research and Engineering, Singapore; 2Institute of High Performance Computing, Singapore

Despite their significant impact on electronic applications, charge transport in conducting polymers is still debated due to disorder (paracrystallinity). It has been reported that charge transport in polymers is correlated with paracrystallinity [1]. The shape of the electronic density of states (DOS) determines transport properties in solids. In this work, we establish the missing link to understanding charge transport by connecting paracrystallinity to transport properties of conducting polymers. First, we confirm that the DOS in conducting polymers is represented by a Gaussian distribution by performing tight-binding model calculations supported by density functional theory and Molecular dynamics simulations. We find that the DOS broadening ($w$) increases exponentially with paracrystallinity. Second, by using Gaussian DOS in the Boltzmann Transport Equation, we find that charge transport can be fully described by the energy dependent scattering parameter ($r$) and the ratio of the total number of energy states to broadening, $N_t/w$.

For a wide variety of conducting polymers, we find that $r$ affects all transport properties, while $N_t/w$ affects only electrical conductivity. For example, by fitting literature data of electrical conductivity and thermopower of conducting polymers, we show that PEDOT:Tos ($w$~0.2 eV) is less disordered compared to PEDOT:PSS ($w$~0.8 eV). Furthermore, due to their distinct monomer structure, PEDOT:PSS and PEDOT:Tos, for instance, exhibit $r$=0.5, while P3HT and PBTTT exhibit $r$=1.5. Moreover, we show that charge mobility in conducting polymers is predominantly determined by $r$. For example, our calculated Hall mobility is consistent with the measured values reported for PBTTT and PEDOT:PSS [2], demonstrating different values of $r$. Finally, we provide a design principle for future organic electronics, where $r=1.5$ polymers are exciting as they can exhibit higher mobilities and are also well suited for thermoelectrics.

Noriega et al. (Nature Materials, 12, 1038 (2013))
Kang et al. (Nature Materials, 15, 896 (2016))

4:00 PM *EN13.10.03
Designing Mixed Ion and Electron Conductors Elayne Thomas, Dakota Rawlings, Michael L. Chabinyc and Rachel Segalman; University of California, Santa Barbara, United States

While highly conductive polymers are now commonplace, they generally demonstrate lower thermopower at a given conductivity than inorganic counterparts. Ion conducting materials have previously been demonstrated to have very large Seebeck coefficients, but ions generally have much lower mobility than electronic charge carriers. We have recently shown that doping with protic ionic liquids and other proton conductors can be used to control the thermoelectric power factor. In this talk, I will discuss how electrochemical transistor geometries can be used to understand the scaling of thermopower with carrier concentration and to begin to untangle the intertwined ion/electron effects in mixed conductor thermoelectrics. Further I will discuss how the presence of ionic charges can be used to control the mesoscopic self-assembly of conducting polymers.

4:30 PM EN13.10.04
Significant Enhancement in the Thermoelectric Properties of PEDOT:PSS by Using Ionic Liquids Jianyong Ouyang; National University of Singapore, Singapore

Intrinsically conductive polymers have promising thermoelectric application due to their high mechanical flexibility, high electrical conductivity while low thermal conductivity. But their Seebeck coefficient is usually lower by inorganic thermoelectric materials by 1-2 orders in magnitude. It is important to significantly improve the Seebeck coefficient of thermoelectric polymers. Here, I will present some methods by our lab to significantly enhance the Seebeck coefficient and thus the overall thermoelectric properties of PEDOT:PSS by using ionic liquids. These
methods can enhance the figure of merit (ZT) to ~0.75 at room temperature, comparable to inorganic thermoelectric materials.

4:45 PM EN13.10.05
Effect of Heteroatom and Doping on the Thermoelectric Properties of Poly(3-alkylchalcogenophenes) Shawn A. Gregory¹, Akanksha K. Menon², Shuyang Ye³, Dwight Seferos³, John Reynolds¹ and Shannon Yee¹; ¹Georgia Institute of Technology, United States; ²Lawrence Berkeley National Laboratory, United States; ³University of Toronto, Canada

This talk will discuss the thermoelectric properties of poly(3-alkylchalcogenophene) thin films as a function of heteroatom (sulfur, selenium, tellurium), and how these properties change with ferric chloride dopant concentration. Using UV-Vis-NIR spectroscopy, electrical conductivity, and Seebeck coefficient measurements, we observed that as the heteroatom is substituted from S to Se to Te, the susceptibility to doping increases. The increased doping susceptibility leads to poly(3-alkyltellurophenes) requiring less dopant to achieve an optimal thermoelectric power factor (ca. 10 µW/m-K²) in comparison to the sulfur and selenium derivatives. Poly(3-alkylchalcogenophene) films' electrical conductivities and Seebeck coefficients at each dopant concentration was also measured as a function of temperature and compared with relevant charge transport. We observed that the electrical conductivity increases with increasing temperature, but the Seebeck coefficient is effectively temperature-independent; this is similar to the findings of Crispin, Emin, and coworkers who studied NOPf₆ doped P3HT charge transport using a model similar to the Mott Polaron Model. We therefore analyzed our temperature-dependent charge transport data in the context of the Mott Polaron model and found that as the heteroatom is substituted from S to Se to Te the activation energy required for charge transport decreases. Overall, this talk will cover a systematic study of charge transport in doped poly(chalcogenophenes) and will demonstrate that tuning the heteroatom may lead to optimized thermoelectric performance.
electronics, such as wearable devices and environmental monitors. The inorganic thermoelectric (TE) semiconductors are still the most possible candidates for this technique due to their best efficiencies, although the pristine materials cannot be directly used as their intrinsic brittleness and rigidity. Therefore, great efforts from various interdisciplinary fields have been dedicated to searching solutions to improve the flexibility of conventional inorganic TE materials. Herein, we present a novel approach to fabricate flexible TE hybrids through depositing Bi$_2$Te$_3$-based alloys on the free-standing transparent single-walled carbon nanotube (SWCNT) scaffold (Nature Materials, 18, 62–68, 2019). The nanocomposite reveals well-ordered and porous microstructures, which consists of (000l) textured Bi$_2$Te$_3$ nanograins grown on the SWCNTs with good adhesion and perfect alignment along the Bi$_2$Te$_3$ <-12-10> and SWCNT axes (Fig.1). The freestanding Bi$_2$Te$_3$-SWCNT hybrid exhibits remarkable mechanically reliable flexibility over hundreds bending circles, of which the bending deformation radius could be as high as a few millimeters. Large power factors of ~1600 to 1100 μW/mK$^2$ are obtained for the Bi$_2$Te$_3$-SWCNT hybrids room temperature to 473 K. Owing to the high density of defects, such as Bi$_2$Te$_3$-SWCNT interfaces, stacking faults and nanopores, the in-plane thermal conductivity is as low as 0.53 W/mK. Such high-power factor and low thermal conductivity give rise to a ZT of ~ 0.89 at room temperature. Moreover, flexible n-type Bi$_2$Se$_3$-SWCNT and p-type Sb$_2$Te$_3$-SWCNT TE hybrids with similar crystal structure were also fabricated, indicating that our approach opens a new way to fabricate free-standing flexible TE materials with high performance.

**EN13.11.03**

**Two-Dimensional Conductive Coordinated Polymers for Thermoelectric Power Generator** Yuanhui Sun$^{1,2}$, Dionisius Hardjo Lukito Tjhe$^1$, Ryojun Toyoda$^3$, Ekaterina Selezneva$^1$, Chen Chen$^1$, Ian Jacobs$^1$, Martin Statz$^1$ and Henning Sirringhaus$^1$; $^1$University of Cambridge, United Kingdom; $^2$Xi’an Jiaotong University, China; $^3$The University of Tokyo, Japan

Thermoelectric generators (TEGs) are solid-state devices that can directly convert temperature differences into electrical voltages via Seebeck effect, which neither requires moving parts nor consumes liquid or gas media, implying favorable qualities, such as high reliability and eco-friendliness. Given the ubiquity of heat and the versatility of electricity, thermoelectrics have long been recognized as a highly promising transformative technology to address our global energy needs. At present conventional inorganic TE materials have achieved tremendous advances, which however have drawbacks such as high cost of production, scarcity of materials, toxicity as well as limited scope of application. To overcome these intrinsic issues, organic thermoelectric materials as alternatives has emerged since they are based on abundant elements, together with low cost, light weight, mechanically flexibility and low-temperature solution processing over a large area. Moreover, organic thermoelectric devices (OTEs) can employ low quality heat. All of these imply that OTE materials have wide application prospects, especially in the development of personal, portable, wearable and flexible heating devices and near-room temperature energy generation. However, for the lacking of high performance OTE materials and proper device architecture design, the efficiency of thermoelectrics is still lower than other energy conversion technologies. It remains full challenges before fully realizing their potential. In 2016, research on poly(Ni-ethylenetetrathiolate) brought our attention to conjugated coordination polymers, which provided the best thermoelectric performance among n-type OTE materials, with an optimum power factor over 453 μW/mK$^2$, benefit from the well-ordered arrangement and stronger π-π interaction of molecular. In metal-organic conjugated coordination polymers, high electrical conductivity can be achieved, whether 1D or 2D coordination polymers (CPs). It is an essential advantage for developing efficient OTE materials. By the targeted design with proper metal and ligand and precisely controlling the oxidation or reduction, the Fermi level, band gap and density of state etc. can be modified, which will significantly affect the thermoelectric performance of polymers. Therefore, it is reasonable to believe the research on TE properties of 2D coordination polymers will be greatly accelerated while providing high-efficient materials for OTEs design. We aim to explore a feasible strategy for developing high-performance 2D coordination nanosheets polymers, reveal the internal transport mechanisms and obtain a better-performing OTE device based on the 2D materials we obtained. It will open up new possibilities for the development of organic thermoelectrics.

**EN13.11.04**

**Understanding Hybrid Organic Polymer Nanowires Interfaces for Optimized Thermoelectric Performance** Xinyi Chen; Donghua University, China

Energy filtering phenomenon has been evidenced in hybrid organic-inorganic composites. It has been reported that appropriate barrier on the organic-inorganic surface is beneficial for the enhancement of thermoelectric performance. However, in the hybrid organic-organic system, the existence of energy filtering phenomenon has not
been strongly confirmed in organic system, nor it is clear that if it shares same rules as the inorganic thermoelectric system. In this work, we develop a novel organic thermoelectric composite composed of poly(3,4-ethylenedioxythiophene) nanowires (PEDOT) and polypyrrole nanowires (PPy) at different contents for the optimization of ZT and power factor. The optimized thermoelectric performance is achieved at 0.5 wt.% PPy. By varying the treatment time of PPy with ferric chloride (FeCl₃), the degree of oxidation of polypyrrole is tuned, which further influences the value of energetic barrier. The relationship between thermoelectric performance and the barrier has been verified. To the best of our knowledge, we are the first to quantitatively investigate the effect of energy filtering on thermoelectric performance of organic composite. By comparing experimental data with the series-parallel model, it is found that energy filtering is possibly an important factor the enhancement of Seebeck coefficient and power factors due to that energy filtering can selectively scatter low-energy carriers.

**EN13.11.05**

**Improvement of Thermoelectric Output of PEDOT:PSS by Controlling Electrostatic Interaction**
Duckhyun Ju, Daegun Kim, Sanghyo Kim, Jiwoo Min and Kilwon Cho; Pohang University of Science and Technology, Korea (the Republic of)

To improve thermoelectric output, we positively deviated the thermoelectric trade-off rule of electrical conductivity and the Seebeck coefficient by modifying the electrostatic interaction between conductive polymers and dopant molecules, i.e., poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS), by addition of alkylsulfonate anions. We analyzed the conformational change of PEDOT:PSS by the added anions from a solution level to a film morphological level, and verified that the intervention of added anions brought about molecular ordering in PEDOT domain by pulling down existing tight-bounded state between PEDOT and PSS. Furthermore, different lengths of alkyl chains of added anions controlled the oxidation levels of PEDOT backbone by changing the chain-chain interaction between PEDOT and PSS to different extents. As a result, we found that these changes could augment both electrical conductivity and the Seebeck coefficient of PEDOT:PSS simultaneously, which produces a remarkable power factor of 715.2 uW/mK².

**EN13.11.06**

**Polyaniline/SnS Nanocomposites for Flexible Thermoelectric Materials**
Lenin Ramanujam, Ajit Singh and Chandan Bera; Institute of Nanoscience and Technology, India

The addition of nanomaterials into the polymer matrix has been shown increased thermoelectric properties due to the internal organization of the polymer molecules at the nanomaterial template. The preparation methods, the concentration of the nano-inclusions, nature of the nanotemplates (oxidised or reduced) defects, and impurities in the nanotemplates affect the organization of the molecules at the surface of the nanotemplates and eventually influences the thermoelectric properties. The internal organization of the molecules at the interface plays a major role in the enhancement in electrical conductivity and Seebeck coefficient eventually affects the power factor of the thermoelectric material. The effect of the interface at the polymer and nanomaterial on the power factor or the conversion efficiency of the thermoelectric material is still not well understood. The conducting polymer polyaniline (PANI) has many attractive features such as inexpensive, environmental stability, easy synthesis protocol, easy processability, and tunable electrical conductivity etc. over the other conducting polymers. The SnS is more earth-abundant material and easy to synthesize, moreover, it has lower thermal conductivity, high Seebeck coefficient and it has good thermoelectric properties. We mainly focused on the synthesis of polymer nanocomposite by mixing the SnS nanoparticles into the polyaniline matrix and studied their thermoelectric properties.

**References**

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**EN13.11.07**

**A Study on a Flexible Thermoelectric Generator for Wearable Energy Harvesting System**
Jeong Hun Kim, Jong-Pil Im, Solyee Im, Jiyong Woo and Seung Eon Moon; Electronics and Telecommunications Research Institute, Korea (the Republic of)
In this paper, we proposed the fabricated process of a flexible thermoelectric generator (TEG) module that can use body heat and evaluated its electrical performances. The metal/ceramic materials have been widely used for substrate of TEG but there is a difficulty of conformal contact because of their rigidity, therefore, flexibility of the module is required in order to maximize the use of curved heat sources such as the human body. For this reason, we suggest a manufacturing method of flexible thermoelectric devices based on inorganic thermoelectric material. As a thermoelectric element for fabrication of TEG, we used BiTe-based material which is most widely used for TEG system. It has much better performance than other organic materials such as carbon nanotube and PEDOT:PSS used for flexible TEG.

In previous researches, metal electrodes were formed by a deposition process followed by the printing of thermoelectric material. And a flexible device was fabricated by laser-lifting method with filling of flexible polymer. In this research, we have proposed a novel fabrication process that using the flexible silver electrodes. The silver electrodes were printed on the sacrificial layer which can be removed by an etching process to obtain a flexible thermoelectric device. Through this method, flexible TEG can be easily fabricated without complex laser process or organic materials or by using sacrificial layers such as PVA and PVP that can be etched by water.

We also have studied the performance changes of the TEG by various polymer materials that have different thermal conductivity. As a supporting layer which have flexibility, the filler material is needed after the etching of the sacrificial layer. Also, because external pollution can make degradation of TE in the actual usage, passivation is required. But high thermal conductivity of polymer filler reduces temperature difference between hot and cold side that concludes the output power of the TEG. We compared the electrical performance of the TEG modules by different filler material, and it was confirmed that the porous polyurethane foam can be good candidate of wearable TEG system.

Though metal fin is most widely used structure for the heat sink, but it is not suitable for wearable system because of the rigidity and bulky structure. To overcome those limitation, inspired by nature, we introduce an artificial perspiration membrane that automatically regulates the evaporation by programming a deformation of thermo-responsive hydrogels. The thermo-responsive hydrogel is patterned with pinwheel-like shape and supported by backbone through copolymerizing at the interface to control the evaporation area depending on the temperature. To prevent the unintended evaporation through the hydrogel, the stretchable rubber is selectively coated, which layer leaves the water path for swelling of the hydrogel. Our heat sink can absorb the water and its latent heat can decrease the temperature of the cold side during drying process. Compared to metal fin heatsink, it was confirmed that the power of TEG module increased more than 2.5 times.

EN13.11.08
Manufacturing Multifunctional Textile Based Thermoelectric Generators Yuanyuan Zheng and Kun Zhang; Donghua University, China

Wearable flexible organic thermoelectric materials harvesting low-grade heat especially human body’s heat have drawn a lot of attention because of their lightweight, flexible, nontoxic and easy-processing et al. In this work, we report organic-based T-TEGs by assembling segmentally-impregnated carbon nanotube yarn with PEDOT: PSS (p-type) and PEI (n-type) into a spacer fabric. The T-TEG shows multi-functionality with superior electrical power output, ultrahigh sensitivity to tactile touch and excellent wearing performance. Finally, this kind of CNT yarn based thermoelectric fabric can be continuously and automatically produced in bulk using traditional knitting machine. In addition, we successfully demonstrate an all-in-one T-TEG based self-charging power package for wearable electronics, which has never been succeeded in previous studies. This package can power a series of essential electronics in extreme environment when the battery cannot work even damaged (T< -20 degrees Celsius). All these results make the T-TEG outperforming all reported flexible organic-based TEGs. The developed strategy can inspire the manufacturing of cost-effective smart T-TEGs using well-established textile industrial processes.

EN13.11.09
Induced Energy-Filtering Effect in Organic Composites for Enhanced Thermoelectric Efficiency Daegun Kim, Seong Hyeon Kim, MinKyu Kim and Kilwon Cho; Pohang University of Science and Technology, Korea (the Republic of)

Thermoelectric (TE) composites have turned out to be a promising way to enhance the $ZT$ value of organic TE materials. However, a comprehensive study on TE charge transport in composite material has been scarce. Here we demonstrate that designed physical and energy structures in TE composite materials cause all three critical TE parameters to contribute to the improvement of the $ZT$ value. Adding the carbon quantum dot (CQD) to poly(3,4-
ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) provided additional charge transport pathways, which also acted as an energy-selective mobility enhancer. These contributed to increase both the electrical conductivity and the Seebeck coefficient, simultaneously. Addition of the CQD also reduced the thermal conductivity by increasing the interfaces in the film. With an optimized interfacial potential gap between CQD and PEDOT:PSS, the composite film showed significant increases in the power factor and the $ZT$ value.

EN13.11.10
Development of Thermoelectric Simulation of Carbon Nanotube Thin Films Kotaro Fujisaki and Takahiro Yamamoto; Tokyo University of Science, Japan

Nanocarbon materials are expected to be potential candidates for nontoxic and flexible thermoelectric materials with high power, which are suitable for wearable power generation technology [2][3]. Carbon Nanotube (CNT) thin films being the network consisting of randomly distributed numerous CNTs is one of nanocarbon materials. CNT films require high electrical conductance and Seebeck coefficient to enhance the performance of the films. In order to increase the conductance and Seebeck coefficient of CNT films, we have to understand the relation between the CNT network structure and its electrical and thermal transport properties.

To understand the relation between the CNT network structure and its thermoelectric performance, we theoretically investigate the effect of several parameters such as nanotube length and nanotube density on thermoelectric performance using the thermal circuit theory, electrical circuit theory, and the percolation theory. First, we generated a two-dimensional random network by changing the nanotube density and the nanotube length and calculated the temperature distribution by solving thermal circuit equations for the CNT networks. Then, we calculated the voltage of CNT own and contact between CNTs generated by temperature difference using the temperature distribution. Finally, we calculated the Seebeck coefficient and electrical conductivity by solving electrical circuit equations for the CNT networks. The obtained results in this study are summarized as follows.

1. The electrical conductance of the film increases with the nanotube length.
2. The Seebeck coefficient of the film is almost dependent on the contact between CNTs in any nanotube length from 0.5µm to 1.5µm.

References

EN13.11.11
Enhanced Output Characteristics of All-Printed Organic Thermoelectrics by Reducing Internal Resistance Seongkwon Hwang1,2, Inho Jeong1,3, Hoichang Yang4, Jeonghun Kwak5 and Seungjun Chung1; 1Korea Institute of Science and Technology, Korea (the Republic of); 2University of Seoul, Korea (the Republic of); 3Korea University, Korea (the Republic of); 4Inha University, Korea (the Republic of); 5Seoul National University, Korea (the Republic of)

Thermoelectric generators that can directly convert wasted heat into electricity have gained much attention as a sustainable energy generator. Specially, for the last decade, organic-based thermoelectric materials have attracted interests due to their inherent flexibility that offer great opportunities to realize geometrically versatile energy harvesting systems with high degree of design freedom. However, there are still challenges on the low output power of organic thermoelectrics compared to that of rigid inorganic based counterparts. The practical strategy for enhancing the output power is to increase the number of organic thermoelectric legs; therefore, emerging solution processing, especially additive printing technologies, have been widely used due to its large-area processability in ambient. In addition, the efficient reduction of internal resistance can pave a key pathway for further improved output power of large-area organic thermoelectric applications.

In this presentation, we will present all-printed organic thermoelectric modules using the combination of spray printing and inkjet printing. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and nanoparticle-type Ag inks were used for the thermoelectric and highly conductive metallic layers formation, respectively. Especially, spray printing enabled us to make few-µm thick organic films onto large area flexible substrates, resulting in the higher output power compared to that of counterparts fabricated by using conventional
Spin coating. To reduce the internal resistance of organic thermoelectrics, functionalized interlayers are introduced between the PEDOT:PSS legs and Ag electrodes using inkjet-printing that significantly reduce the contact resistance by modulating the dominant carrier injection mechanism. With these efforts, the interface-engineered organic thermoelectrics exhibit the two times higher output power comparing to the pristine counterparts. These results will provide a practical solution to realize high-performance printed organic thermoelectric modules.

**EN13.11.12**

**Effect of Conformation in Main-Chain with Pyrene-Based Conjugated Polymers for Selective Dispersion of Single-Walled Carbon Nanotube on Thermoelectronics**

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Single-walled carbon nanotube (SWNT) has been regarded as one of the nanomaterials for future electronic devices because of their outstanding mechanical and electrical properties. For these reasons, researches for implementation of their electronic applications such as field-effect transistors and thermoelectric devices have been substantially promoted. Therefore, various techniques to isolate the electronically-pure SWNTs have been developed for the utilization in electronic devices. In particular, conjugated polymer wrapping of SWNT has specially aroused great attraction as a method for isolation of SWNTs due to their advantages of high selectivity toward semiconducting (sc-) SWNT and simple polymer sorting process. Various wrapping polymers such as polyfluorene and polythiophene derivatives have been studied for the selective dispersion of sc-SWNT, but the selection rule between the main chain of polymer and specific sc-SWNT still remain question. In this research, we introduce the pyrene moiety to control the conformation over the main-chain on polymer. New pyrene-based conjugated polymers were carefully designed and synthesized via suzuki polymerization. Their dispersion selectivity and diameter of sc-SWNTs enriched by pyrene-based conjugated polymers were characterized by various measurements such as UV-vis absorption spectra, Raman spectroscopy and Photoluminescence analysis.

**EN13.11.13**

**Thermoelectric Application of CNT Composite Threads Patterned with Different Kinds of CNTs**

Ryota Arakaki and Takahide Oya; Graduate School of Engineering Science, Yokohama National University, Japan

Nowadays, as one of environmental problems, it is focused that much consumed energy is wasted as heat. Therefore, to realize a "low-carbon society," the way to utilize the wasted heat is required. As one of candidates for the solution of this problem, the thermoelectric power generating technologies are focused. Carbon nanotubes (CNTs) are expected to be new thermoelectric materials because they have high electrical conductivity and thermoelectromotive force, but there are the following issues in using them as thermoelectric materials. First, low thermal conductivity is required for efficient thermoelectric generation, but CNTs have high thermal conductivity. Second, CNTs are generally produced as powders and are difficult to handle. To solve these problems, we have proposed using carbon-nanotube-composite threads (CNTCTs). CNTCTs are composite materials produced by coating cotton thread fibers with CNTs. It is expected that CNT can be easily handled by combining it with thread, and cotton thread with low thermal conductivity also prevents heat diffusion. In previous study, we examined methods to fix CNTs on cotton thread surface efficiently, and succeeded in producing CNTCTs that can be used as thermoelectric materials. In this study, we examined a method of coating two types of CNT on thread with a pattern suitable for thermoelectric power generation in order to fabricate thermoelectric elements using CNTCTs. CNTCTs are produced by traditional dyeing methods. In concrete, we prepare CNT dispersion by mixing CNT (Sigma-Aldrich, (6,5)-chirality) and sodium dodecyl sulfate as dispersant in pure water and ultrasonication for them, firstly. After that, the cotton thread is dipped in the CNT dispersion, taken out, dried, and washed with pure water. By performing the above operation, CNTCTs in which the same kind of CNT uniformly covers the thread surface are obtained. However, if CNTCTs in which two types of CNTs having different Seebeck coefficients cover the thread surface at equal intervals can be obtained, the thermoelectric generation element can be easily manufactured. This is because when the thread is sewed on a cloth, it becomes a structure like a π-type thermoelectric generator. So, in addition to the operation described above, we carry out the process called "fusenori" in this study. Fusenori is a Japanese traditional dyeing method to partially prevent the dye from being fixed to the thread. In concrete, we prepare a rubber paste by dissolving latex in tetrachloroethylene, and apply the rubber paste at intervals of 1 cm to cotton thread before the above-mentioned dyeing operation. Because tetrachloroethylene is volatile, the latex covers the thread surface when it is dried. The latex is hydrophobic and keeps covering the thread surface without melting out of the CNT dispersion. Therefore, it can be expected to prevent CNT from being fixed on the surface of the cotton thread in the
part coated with rubber paste. After the dyeing operation is performed on the thread, the latex is removed from the thread surface by washing with tetrachloroethylene heated to 80°C. The resistance value and Raman spectrum of the produced CNTCTs were measured, and it was confirmed that the CNTs were hardly fixed at the place where the rubber paste was applied. After removing the latex, we apply a rubber paste to the portion where the CNTs are fixed, and perform the above-mentioned dyeing operation using CNT (Nanocyl, multi-walled) whose Seebeck coefficient is different from that used previously. The CNTCTs obtained by the above operation were sewed on a cloth, and it was confirmed that an electromotive force was generated when only one side of the cloth was heated. From the above results, it was confirmed that CNTCTs whose surface is covered two different types of CNTs at intervals of 1 cm by fusenori, and a thermoelectric element could be produced simply by sewing it.

EN13.11.14
Fluorinated Polyimide Gate Dielectrics for Transparent Organic Field-Effect Transistor and Logic Gate Circuit with Electrical Stability Hong Gi Min1, Seongchan Kim2, Benzheng Lyu3, Hyungseok Kang4 and Jeong Ho Cho5; 1Yonsei University, Korea (the Republic of); 2Sungkyunkwan University, Korea (the Republic of)

Fluorinated polyimides gate dielectric based on 6FDA-BisAAF-PI and 6FDA-TFDB-PI were synthesized to use as a gate dielectric to fabricate high performance organic field-effect transistors (OFETs). The fluorine substituted into polyimide chain was improved the efficiency of solution-process to make uniform film. These fluorinated polyimide make it possible to fabricate transparent devices. Especially, OFETs based on 6FDA-TFDB-PI which has low surface energy have high-performance because defect density formed by grain boundary is lowest. The OFETs based on 6FDA-TFDB-PI gate dielectric have high carrier mobility (1.83 cm²V⁻¹s⁻¹ for the p-type pentacene FETs and 0.56 cm²V⁻¹s⁻¹ for the n-type PTCDI-C8 FETs) and a high on/off ratio exceeding 10⁶. And, we check that the devices have excellent electrical stability from measured bias stress experiment. The 6FDA-TFDB-PI film was used to fabricate complementary inverters that have high gain value. Lastly, the logic gate circuit (NAND, NOR) were successfully fabricated using 6FDA-TFDB-PI gate dielectric.

EN13.11.15
Effect of Dopant Clustering on Thermoelectric Properties of Polymer Films Michael Lu-Díaz, Connor Boyle, Meenakshi Upadhyaya, Zlatan Aksamija and Dhandapani Venkataraman; University of Massachusetts Amherst, United States

Heavily-doped conjugated polymers are among the most promising organic materials for thermoelectric applications due to their outstanding charge transport properties and low thermal conductivity. These properties are well-known to be dependent on the structural arrangement of the polymer, disregarding the state and position of the dopants. In this study, we utilize Kelvin Probe Force Microscopy to track iodine dopants across P3HT and PDPP4T films and show that their distribution within the polymer film alters the distribution of the density of states. As a consequence, it impacts the shape of the Seebeck coefficient—electrical conductivity curve and thus its thermoelectric properties. Our study shows that it is necessary to control the distribution of dopants within the films for optimal properties in thermoelectric and other organic electronic applications.

EN13.11.16
Thin-Film Heater with Thermally Evaporated WO₃ₓ/Ag/WO₃ₓ Multilayer Electrode and Optimization by Controlling Deposition Rate Sang-Hwi Lim, Jin H. Park and Han-Ki Kim; Sungkyunkwan University, Korea (the Republic of)

We investigated method to improve properties of thermally evaporated WO₃ₓ/Ag/WO₃ₓ (WAW) multilayer using the deposition rate of WO₃ₓ layer and Ag layer as parameters, in order to fabricate flexible and transparent thin film heaters (TFHs). In this work, we demonstrate increase of grain size and reduce interface roughness and enhance electrical and optical properties of WAW multilayer by simply control of deposition rate. And we analyzed properties of WAW multilayer in aspects of electrical, optical, morphological, and mechanical properties. Especially, unlike conventional research which were just focused on and thickness control of each layer to optimize oxide/metal/oxide multilayer, our work presents you how deposition rates affect to properties of WAW multilayer and suggest another way to optimize OMO multilayer. For evaluation, we measured electrical properties and optical properties of WAW multilayers by hall measurement and UV-Vis measurement to optimized performance of WAW multilayer. When WAW multilayer deposited at optimized deposition rate of 2.5 Å/s, 10 Å/s, 2.5 Å/s, showed low sheet resistance of 3.78 ohm/square and high transmittance of 92.16 % at 550 nm wavelength. Morphological
properties of surfaces, interfaces are investigated by FE-SEM, XRD, and mechanical stability and flexibility were investigated bending test, rolling test, twisting test. In mechanical deformation test, after 10000 times of inner and outer bending tests, there were no sheet resistance change in WAW multilayer compare to WAW multilayer before the test. Furthermore, we fabricated the WAW based TFHs to investigate heating profile of WAW multilayer based TFHs. Compare to typical ITO based TFHs, WAW based TFHs show low DC voltage to achieve 120 °C due to its low sheet resistance. Moreover, WAW based TFHs show higher convective heat transfer coefficient than ITO based TFHs. Therefore, WAW based TFHs are promising as flexible and transparent highly efficient convection TFHs.

EN13.11.17
Sticky Thermoelectric Materials for Flexible Thermoelectric Module Norifusa Satoh1, Masaji Otsuka1, Yasuaki Sakurai2, Takeshi Asami2, Yoshitsugu Goto2, Takashi Kawamori1, Takeshi Masaki2, Go Yatabe1, Jin Kawakita1 and Takao Mori1; 1National Institute for Materials Science, Japan; 2Denka Company Limited, Japan; 3Hitachi Chemical Company, Ltd., Japan

To examine our hypothesis of sticky thermoelectric (TE) materials to ease the fabrication processes of flexible TE modules at reasonable cost, we investigated hybrids of inorganic TE powders and low-volatilizable solvents as a series of sticky TE materials. Through our previous study, we have specified that common electric conductive adhesives (ECAs) do not have enough electric conductivity and mechanical strength to hold the structure of flexible TE modules when rolled. As a possible research direction, we have hypothesized sticky TE materials, which can adhere to electrodes pressure-sensitively without ECAs and transform the shape to cancel the mechanical stress when bent. In this study, we prepared p-type and n-type sticky TE materials from antimony and bismuth and examined electric contacts and measured thermoelectric voltages. This presentation discusses the outcomes in details.

EN13.11.18
Flexible Organic Thermoelectric Device Based on PEDOT:PSS and Oxygen Plasma Treated Polyimide Substrate Juheon Lee, Kiho Nam, Seohyun Kim, Haksoo Han and Hyanghee Choi; Yonsei University, Korea (the Republic of)

Flexible organic thermoelectric devices based on poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and Polyimide (PI) were fabricated and investigated in this work. PI was selected as a substrate because of its excellent mechanical property to secure from repeated bending cycles of flexible device. However, due to hydrophobicity of PI, there was limited research on utilizing PEDOT: PSS and PI for flexible devices. A facile method, oxygen plasma treatment was adopted on PI’s surface. The effect of the surface treatment with oxygen plasma on the synthesized PI substrate was significant. The polar component of surface free energy of PI was increased from 2.8 mJ/m2 to 31.8mJ/m2. Therefore, PEDOT: PSS could be stably coated on the PI substrate. The power factor of PEDOT:PSS on the PI substrate was increased from 25.86μW mK-2 to 43.78μW mK-2. Also, as a result of 10k times of bending test, the electrical performance consistency and the mechanical stability of the fabricated devices were confirmed. This verified fabricated flexible organic thermoelectric devices based on PEDOT: PSS and PI are suitable for the various applications

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EN13.11.19
Improved Thermoelectric Properties of Flavin-Extracted Semiconducting Single-Walled Carbon Nanotubes Angana Borah and Tsuyohiko Fujigaya; Kyushu University, Japan

Single-walled carbon nanotubes (SWNTs) have remarkable electrical conductivity, ($\sigma$), Seebeck coefficient ($S$), light weight, mechanical toughness and flexibility which makes them ideal candidates for thermoelectric (TE) applications. Among SWNTs, semiconducting SWNTs (s-SWNTs) have been found to have larger $S$ than metallic SWNTs (m-SWNTs) both theoretically and experimentally. However, SWNTs are synthesized as a mixture of s-SWNTs and m-SWNTs, which limits the maximum possible $S$ for SWNTs. Therefore, it is of utmost importance to extract s-SWNTs having high purity as a TE material. Among the various extraction methods, Flavin derivative (dmc12) extraction method reported by Kato et. al. is profitable due to its many advantages, namely, high yield of s-SWNTs, easy operation of the extraction method, low damage to the s-SWNTs and easy removal and recycling of
In this study, we investigated the effect of doping s-SWNTs extracted by dmc12 having different bundle size of s-SWNTs. Purified SWNTs (eDips, Meijo Nano Carbon) were used to extract s-SWNTs and the extracted s-SWNTs were collected by vacuum filtration. The addition of CH2Cl2 to remove dmc12 before and after the filtration provided bundled and isolated s-SWNT sheets, respectively. The bundled sheet represented thicker bundles of s-SWNTs in the sheet while the isolated sheet comprised of thinner bundles. The sheets were doped at various concentrations with triethyloxonium hexachloroantimonate (OA) and 2-(2-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1H-benz[d]imidazole (o-MeO-DMBI) as p- and n-dopant, respectively. The highest obtained $S$ for p- and n-doped s-SWNT sheets were 83.3 $\mu VK^{-1}$ and -89.5 $\mu VK^{-1}$, respectively. Both values are higher than the values attained previously for doped-unsorted SWNT sheets (p-doped: 54 $\mu VK^{-1}$, n-doped: -49 $\mu VK^{-1}$). Moreover, it was found that the isolated s-SWNT sheet showed larger $S$ value than the bundled sheet in the n-doped region. We consider doping is more effective for isolated than bundled sheets as the power factor of 126.3 $\mu W m^{-1} K^{-2}$ was achieved for isolated sheets.

References-

EN13.11.20
Strategic Design of Conjugated Polymer for High Doping Efficiency and Correlation of Resulting Conductive Pathway with Thermoelectric Effect Sang Eun Yoon1, Jaehong Park2, Bong-Gi Kim2 and Jong H. Kim1; 1Ajou University, Korea (the Republic of); 2Konkuk University, Korea (the Republic of)

The low dielectric constant of organic materials and inhomogeneous distribution of molecular dopants in a conductive matrix impose difficulties in populating free charge carriers in organic materials, leading to practical challenges in developing highly conductive organic materials. We designed a novel conjugated polymer (PIDF-BT) having long side chains and a strong electron-donating moiety in a way that the PIDF-BT strongly interact with molecular dopant, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethan (F4-TCNQ), and the doping efficiency was further enhanced through the management of the diffusion degree of F4-TCNQ into CP matrix. With these strategies, dramatic enhancement of electrical conductivity over 200 S/cm, was achieved from PIDF-BT, which is much larger than that obtained from the conventional blending approach (5 S/cm). Furthermore, the doping level was scalable with the exposure duration in the F4-TCNQ solution as well as the solution’s concentration. The diffusion degree of F4-TCNQ was systematically correlated with physical properties (glass transition temperature and crystallinity) of PIDF-BT through the characterization of electrical conductivity according to the thermal annealing temperature of the pre-deposited PIDF-BT films. Finally, characteristic connections between charge carrier density, mobility and thermoelectric effects were extracted with doping level-controlled PIDF-BT films prepared under different thermal annealing conditions.

EN13.11.21
Modification of Producing Way for "Thermoelectric Power Generating Paper" Using Carbon-Nanotube-Composite Paper to Improve Its Performance Ayumu Miyama and Takahide Oya; Yokohama National University, Japan

We propose a unique thermoelectric power generation material based on a carbon-nanotube(CNT) composite paper that a composite material of the CNT and a paper, i.e., “thermoelectric power generating paper.” Recently, thermoelectric power generation is attracted attention because it can effectively use heat that is often discarded. However, there is a problem that many of the currently used thermoelectric materials are rare metals. For this, we focus on CNTs because CNTs have been confirmed to have high electrical conductivity and thermal conductivity. Moreover, showing a high Seebeck coefficient has been found in recent studies. However, the CNT is difficult to handle because it exists in powder form. Also, having high thermal conductivity is a disadvantage for the thermoelectric generation. Therefore, we are developing a thermoelectric power generating device as the CNT composite paper by combining the CNT with the paper that is easy to handle and has the thermal insulation. In this study, we are aiming to improve the performance of thermoelectric power generating paper. In the previous
work, we studied the suitable amount ratio of the CNTs and pulps to make the CNT composite paper. Because if there was little pulp or more CNTs, it was unable to maintain the temperature difference between both ends. For obtaining low thermal conductivity, we found the ratio. However, the following problems remained. They are that the resistance value of the CNT composite paper was high and enough current could not be obtained.

In this report, we conducted following things to improve the performance of our thermoelectric power generating paper. First, we tried to modify the making method of the CNT composite paper. We here use the “kamisuki” that is Japanese washi paper making method. In “kamisuki,” we prepare a pulp dispersion and a CNT dispersion. Then, we mix the two dispersions and remove moisture by using a fine net. Finally, we dry it and finalize making. Previously, we used “silicone case method” not “kamisuki.” In “silicone case method,” we use the silicone case to evaporate the moisture. Therefore, the CNT composite paper contains many dispersants. Because dispersants are insulator, the resistance value of the CNT composite paper become high, i.e., the dispersant remains on the paper. In contrast, in “kamisuki,” the dispersant is expected to flow with water. So, we change the production method of CNT composite paper “Silicone case method” to “kamisuki.” As a result, we succeeded in lowering the resistance value by about 13%.

Second, the semiconducting CNT usually behaves p-type property in the atmosphere. For efficient thermoelectric generation, not only p-type but n-type semiconducting CNTs are required and they must be connected alternately. So, we applied a doping way to our CNT composite paper for obtaining n-type property. As results, we found temperature dependence of the doping, i.e., there was suitable temperature condition for the doping. Moreover, we also found sustainability of the n-doped CNT composite paper.

We believe our CNT composite paper will be used as flexible thermoelectric power generating elements in near future.

EN13.11.22

**The Effect of Single Selenophene Substitution on the Thermoelectric and Charge Transport of Highly Doped Polythiophene Polymers**

Chen Chen¹, Ian Jacobs¹, Martin Statz¹, Lu Zhang¹, Yuanhui Sun¹, James Ponder², Cameron Jellett³, Iain McCulloch³ and Henning Sirringhaus¹; ¹University of Cambridge, United Kingdom; ²Imperial College London, United Kingdom

Heavy heteroatom substitution of the backbone is an effective strategy to improve charge delocalization and increase ionised potential of organic polymers. This facilitates the doped states of those materials more conductive without sacrificing the seebeck coefficient a lot at the fixed doping level. Here, we report the effect of the single selenophene replacement on the thermoelectric transport mechanism of polythiophene polymers at different doping levels. By feat of a novel doping method, we achieve the maximum conductivity of ~700S/cm for doped selenophene polymer, which is 3 times higher than its counterpart thiophene polymer with the metallic-like seebeck coefficients of ~25 uV/K for both. Interestingly, temperature dependence of conductivity for the highly doped selenophene shows upturn behaviour (metal-semiconductor) while the seebeck coefficients show linear dependence versus temperature. This indicates we approach a regime where the conductivity is decoupled with the seebeck coefficient. By introducing heavy atom into polymer backbones, it is potentially possible to improve the thermoelectric performance via conductivity boost.

EN13.11.23

**Enhanced Thermoelectric Performance of FeCl₃ Doped Cyclopentadithiophene-Benzothiadiazole Based Copolymer Films**

Juhyung Park¹, Yeran Lee², Han Young Woo² and Jeonghun Kwak¹; ¹Seoul National University, Korea (the Republic of); ²Korea University, Korea (the Republic of)

For a decade, π–conjugated semiconducting polymers have attracted great attention for thermoelectric materials because of their easy tunability, solution processability, and mechanical flexibility. Molecular doping is widely used to improve the thermoelectric properties of the polymer films, because it can easily control the electrical conductivity ($\sigma$) by changing the carrier concentration ($n$). Among various molecular doping methods, solution mixing is typically performed due to its simplicity. However, it is not easy to heavily dope the polymer film due to solubility limit. In addition, the presence of a significant amount of dopant molecules in the doped polymer films can distort the film morphology, limiting the thermoelectric properties. Therefore, it is important to select appropriate doping methods to enhance the thermoelectric properties. Previously, we reported the organic thermoelectric device using p-type conjugated polymer poly[(4,4’-bis(hexyldecylsulfanylmethylene)cyclopenta[2,1-b:3,4-b’]dithiophene)-alt (benzo[c][1,2,5]thiadiazole)] (PCPDTSBT), showing the electrical conductivity of 7.47 S cm⁻¹ using BCF as a dopant. In this study, we changed
the dopant to FeCl₃, and introduced a overcoating method to dope the PCPDTSBT film, demonstrating high electrical conductivity up to 300 S cm⁻¹, which is ~40 times higher than that of the BCF-doped film. The resulting power factors of FeCl₃-doped PCPDTSBT film was 29.75 μW mK⁻², which is ~4 times higher than that of the BCF-doped film. The reason of rapid increase in \( \sigma \) is systemically investigated using various analysis methods like UV absorption, Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) and impedance spectroscopy. Kang-Snyder model is also used to investigate the charge transport in the PCPDTSBT film.

**EN13.11.24**

**Impact of Polar Side Chain Engineering of CDT-Based P-Type Polymers on Thermoelectric Devices**

Ayushi Tripathi¹, Juhyung Park², Nguyen Thanh Luan¹, Miso Kim¹, Yeran Lee¹, Jeonghun Kwak² and Han Young Woo¹; ¹Korea University, Korea (the Republic of); ²Seoul National University, Korea (the Republic of)

Driven by the prospects of organic thermoelectric(OTE) devices, which have the potential for energy generation, have gathered considerable attention worldwide. We compared various properties of poly[(4,4’-(bis(hexyldecylsulfanyl)methylene)cyclopenta[2,1-b:3,4-b’]dithiophene)-alt (benzo[c][1,2,5]thiadiazole)] (PCPDTSBT) and its analogue with oligoethylene glycol (OEG) side chains in place of alkyl ones (PCPDTSBT-A), before and after doping. Incorporation of polar OEG side chains improves intermolecular ordering and exhibits ‘self-doping’ with enhancement in doping efficiency, thereafter resulting in higher electrical conductivity and power factor of PCPDTSBT-A surpassing those of PCPDTSBT. OEG chains improve the miscibility of dopant solution and polymer film during sequential doping which was performed by casting dopant solution (by varying the concentration of F4TCNQ in acetonitrile) onto the film. This study emphasizes the importance of the polar side chain engineering to modulate doping efficiency, inter-chain packing, crystalline morphology and miscibility whose outcome is revamped electrical and thermoelectrical properties.

**EN13.11.25**

**Thermoelectric Performance Improvement of Polymer Nanocomposites by Selective Thermal Degradation**

Daniel L. Stevens¹, Aaron Parra¹ and Jaime C. Grunlan¹,²,¹; ¹Texas A&M University, United States; ²Texas AM University, United States

Our current energy production results in a tremendous amount of waste heat. In an effort to more efficiently utilize dissipated heat, multilayer thin films, comprised of poly(diallyldimethylammonium chloride) (PDDA), graphene, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and double-walled carbon nanotubes (DWNT), were prepared using layer-by-layer assembly followed by heating in an inert atmosphere to degrade film constituents to varying degrees. PEDOT:PSS was used to stabilize graphene and DWNT. A 20 QL thin film, that is 21 nm thick, heated to 425 °C for 60 minutes exhibits a simultaneous increase in electrical conductivity and Seebeck coefficient as compared to an unheated film. This behavior is not commonly observed in bulk thermoelectric materials. The power factor of this film is 153 uW m⁻¹ K⁻², which is an order of magnitude larger than the unheated control. This marked improvement in thermoelectric performance is the result of degrading the insulating PDDA:PSS complex from the film, while maintaining the highly ordered conductive network formed during layer-by-layer deposition. This strategy of thermally degrading non-conductive material required for film fabrication can be used to prepare numerous high performing thermoelectric materials.

**EN13.11.26**

**Mechanically Robust Conducting Polymer-Polyurethane Blends for Plastic Thermoelectrics**

Desalegn Alemu Mengistie¹,², David Kiefer¹ and Christian Muller¹; ¹Chalmers University of Technology, Sweden; ²California Polytechnic State University, United States

PEDOT:PSS is considered as the most promising p-type material for organic thermoelectrics due to its high electrical conductivity, high power factor, stability and solution processability from an aqueous dispersion. However, the neat PEDOT:PSS lacks flexibility and stretchability. Here, we demonstrate mechanically robust thick free-standing films of PEDOT:PSS blended with waterborne polyurethane (PU). As the blend is prepared from water dispersions, it is solution processable and convenient for large area coating and printing. We explored the mechanical properties, nanostructure and thermoelectrical performance of the blend with different PU loading. Films with ≤50% PU are mechanically robust with high electrical conductivity while those with >50% PU are stretchable but show low conductivity. At 50% PU loading, the blend film maintained a power factor of ~10 μW m⁻¹ K⁻² with excellent flexibility and even twistability. The blend film with 75% PU loading withstands 1000 stretching cycles at
10% strain with no loss in power factor.

SESSION EN13.12: Organic Semiconductors for Thermoelectrics II
Session Chair: Maarit Karppinen
Friday Morning, December 6, 2019
Hynes, Level 2, Room 205

8:30 AM EN13.12.01
Synthesis and Thermoelectric Characterization of Hollow Spherical \( \text{Ca}_3\text{Co}_4\text{O}_9 \) Particles
H. Merve Ertugrul and Ahmet Macit Ozenbas; Orta Dogu Teknik University, Turkey

The aim of this study is increasing power factor and decreasing thermal conductivity simultaneously through the production of hollow spherical \( \text{Ca}_3\text{Co}_4\text{O}_9 \) and air composite materials. This structure comprises of hollow spherical \( \text{Ca}_3\text{Co}_4\text{O}_9 \) particles and porosities dispersed in the matrix. This means that air having very low thermal conductivity is trapped in the structure, so thermal conductivity of the materials can be decreased. Also, high amount of porosity provides increase in Seebeck coefficient. \( \text{Ca}_3\text{Co}_4\text{O}_9 \) is environment friendly, nontoxic, humidity resistant at high temperatures, oxidation resistant, abundant, chemically and thermally stable in air and light. Also, \( \text{Ca}_3\text{Co}_4\text{O}_9 \) is favored due to its natural layered structure composing of conduction and insulation layers alternately which provide electronic transport and phonon scattering layers separately. Therefore, natural superlattice structure of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) brings about high thermopower and low electrical resistivity at the same time.

Ultrasonic spray pyrolysis (USP) method is used to obtain hollow spherical particles. Many parameters have an effect on forming hollow spherical structure such as frequency of ultrasonic generator, the concentration of initial solution, the temperature of reactor and the flow rate of the carrier gas which influence the morphology, dispersity, structure and the phase composition of the end product. High evaporation rate and high mass transfer are required for getting hollow spherical structure. Three different solutions were prepared using deionized water, dimethylformamide and methanol. These solvents were chosen according to their capability of producing an aerosol. Being nontoxic and eco-friendly, deionized water was determined as the solvent in USP technique.

The production of high porosity structure was achieved by using pressure-less sintering method. Furthermore, the surfaces of hollow spherical particles comprising of nanoscale constituents are about 2D, so this leads to quantum confinement effect and energy filtering which increase the power factor and phonon scattering at interfaces resulting in a decrease in lattice thermal conductivity. The temperature dependence of Seebeck coefficient and electrical resistivity were measured using a lab-made system in the temperature interval from 300 K to 900 K. Seebeck coefficients of the samples having 2.3 mm, 1.5 mm and 500 nm diameter at 900 K are 204.8 mV/K, 216.9 mV/K and 228.4 mV/K, respectively. Electrical resistivities of the samples having 2.3 mm, 1.5 mm and 500 nm diameter at 900 K were measured as 18.6 mW.cm, 12.4 mW.cm and 8.1 mW.cm, respectively. Power factors of the samples having 2.3 mm, 1.5 mm and 500 nm diameter at 900 K are 0.23 mW/mK², 0.38 mW/mK² and 0.64 mW/mK², respectively. It was shown that, by reducing the particle size to submicron range, Seebeck coefficient and power factor values were successfully increased together with a decrease in electrical resistivity using our air composite approach employed in this work.

8:45 AM EN13.12.02
Improved Thermoelectric Performance by Incorporating Pores/Defects in PEDOT/Tosulate Films
Balwinder Kaur, Ezaz Hasan Khan, Lian Li, Jayant Kumar and Dionysios Christodoulou; University of Massachusetts Lowell, United States

Poly 3,4-ethylenedioxythiophene (PEDOT) is a conducting polymer that has thermoelectric properties that has been studied extensively. The majority of the studies, however, were focused on the thermoelectric properties of PEDOT:PSS. PEDOT:tosulate could exhibit up to two times higher thermoelectric efficiency than PEDOT:PSS but a limited number of studies have been devoted to the optimization of the performance of PEDOT:tosulate films. After a systematic study of the parameters that could affect the efficiency of the films of PEDOT:tosylate (e.g., oxidative status, introduction of defects in the film, secondary dopants, improving thermal conductivity) we have concluded that the incorporation of defects/pores in the PEDOT:tosulate films increase the thermoelectric efficiency of the films significantly (from a ZT value of 0.39 to 1.07). A proof-of-concept, flexible thermoelectric device that
contain strips of porous PEDOT/tosulate films as p-type elements and strips of bismuth films as n-type elements was prepared and its performance in realistic conditions was evaluated.

9:00 AM EN13.12.03
Improved Thermoelectric Performance of Polymer Nanocomposites by Salt Doping Daniel L. Stevens1, Geethal Amila Gamage2, Zhifeng Ren2 and Jaime C. Grunlan1,1,1; 1Texas A&M University, United States; 2University of Houston, United States

Thermoelectric materials that have a large Seebeck coefficient and electrical conductivity are required to effectively convert waste heat into electricity, but their interdependence makes simultaneous improvement a significant challenge. To address this problem, multilayers of poly(diallyldimethylammonium chloride) (PDDA) and double-walled carbon nanotubes (DWNT), stabilized by KBr-doped poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were deposited using layer-by-layer assembly (LbL). Doping PEDOT:PSS with KBr before LbL assembly results in a simultaneous increase in the Seebeck coefficient and electrical conductivity. A maximum power factor of 534534 μW m⁻¹ K⁻² was achieved after doping with 3 mmol KBr, which is a six-fold improvement compared to the undoped control. This improvement in thermoelectric properties is attributed to charge screening effects between PEDOT and PSS from the added KBr, which leads to a denser deposition of DWNT. This facile salt-doping strategy can be used to prepare high performance PEDOT:PSS-based thermoelectric materials for lightweight, low temperature applications.

9:15 AM EN13.12.04
Pro-Quinoid Based Conjugated Polymers for High Performance Solution-Processed Thermoelectrics Teck Lip Dexter Tam and Jian Wei Xu; IMRE, Singapore

Here we will show the use of pro-quinoid moieties like benzobistriazole and benzobisthiadiazole in conjugated polymers as an effective strategy towards high performance solution process thermoelectrics. The pro-quinoid character of these moieties allow efficient doping and the formation of highly delocalized polarons even by sequential solution-phase doping. This led to high electrical conductivities, and enhancement in Seebeck coefficient due to carrier-induced softening could be observed. As a result, power factor approaching 70 μW m⁻¹ K⁻² was achieved. These results are among the highest for conjugated polymer thermoelectric using solution-phase doping.

9:30 AM EN13.12.05
Effect of Doping Distribution on Charge Transport Dynamics in Polymer Thermoelectrics Meenakshi Upadhyaya, Connor Boyle, Michael Lu-Díaz, Dhandapani Venkataraman and Zlatan Aksamija; University of Massachusetts Amherst, United States

Organic semiconductors (OSC) hold tremendous potential to address the demand for cheap and sustainable thermoelectric (TE) materials. OSCs offer a major advantage with their inherently low thermal conductivity, but have to be heavily doped to improve the electrical conductivity which has the undesirable effect of significantly reducing their Seebeck coefficient. Hence efficient design of organic TEs requires deep understanding of the role of doping and charge transport dynamics on the Seebeck vs. electrical conductivity trends. In this work, we investigate the TE properties of disordered OSCs, and establish the effect of disorder and correlation in energy and position on the Seebeck coefficient, electrical conductivity, and the Lorenz number. We find that the electronic and morphological properties of the polymer alone cannot account for the experimentally observed Seebeck and conductivity trends. Importantly, it is the doping and the clustering of dopants within the polymer films that dictates the slope of the Seebeck vs. conductivity plots. Our charge transport model is based on electron hopping between localized sites with a modified Gaussian disorder model to account for the impact of doping and clustering of dopants on the energies. We iteratively solve the non-linear Pauli’s master equation to compute the time-averaged occupational probabilities of the sites from which relevant transport quantities are calculated. We measure the Seebeck coefficient and electrical conductivity across a broad range of dopings by a de-doping technique where the sample is measured continuously while gradually de-doping over time. We then fit experimentally determined data of iodine-doped P3HT and PDPP4T to our hopping simulations, which revealed that the shape of the DOS is responsible for the observed Seebeck and conductivity trends. The physical distribution of dopant molecules within the sample affects the carrier DOS (fortified by Kelvin probe force microscopy), with dopant clustering dramatically increasing the energetic disorder resulting in a heavy-tailed distribution [3], whereas homogenous doping maintains
a Gaussian DOS. This ‘change in shape’ of the DOS results in a qualitative change of the Seebeck vs. conductivity curve. A Gaussian distribution leads to a sharp drop off in Seebeck at high conductivity values, whereas, a heavy-tailed distribution leads to a gradual decrease in Seebeck with increasing conductivity and a flatter curve. This can be correlated to the value of the Kang-Snyder transport parameter ‘s’ [4]. Seebeck vs. conductivity curve from a Gaussian DOS is best fit by a lower value of s (mostly<1), whereas, one from a heavy-tailed DOS distribution can only be partially fit with higher s values, indicating the limitations of a band model in predicting transport in highly disordered systems. Our results highlight the importance of tuning the energetic disorder using spatial distribution of dopants to obtain the highest power factor for TE applications. We conclude that it is not just how much the semiconductor is doped; thermoelectric performance is affected by how the semiconductor has been doped across all carrier concentrations.


9:45 AM BREAK

10:15 AM EN13.12.06
Increasing the Thermoelectric Power Factors in Pi-Conjugated Polymer Blends through Combining Experiment with Theory Ashkan Abtahi1,1, Stephen Johnson2, So Min Park1,1, Xuyi Luo3, Zhiming Liang1, Jianguo Mei1 and Kenneth R. Graham1; 1University of Kentucky, United States; 2Transylvania University, United States; 3Purdue University, United States

Conjugated polymers can be used in mechanically flexible and low cost thermoelectric (TE) devices, but their thermoelectric performance must be improved to make them commercially viable. The performance of thermoelectric materials depends on the electrical conductivity, Seebeck coefficient and thermal conductivity. However, higher electrical conductivity is typically accompanied by a decrease in the Seebeck coefficient. Blending two or more π-conjugated polymers together provides a means of manipulating charge transport properties and potentially improving the performance of organic thermoelectrics by minimizing this tradeoff between electrical conductivity and the Seebeck coefficient. By modifying the model introduced by Bässler and Arkhipov, we model how the electronic properties of the individual polymers influence the Seebeck coefficient, electrical conductivity, and power factor in the polymer blends. These calculations show that gains in the power factor should be attainable when the homogenous blend of two polymers have a small (e.g., 0.1-0.2 eV) offset in their density of states (DOS) distributions and the polymer with the higher energy DOS has a wider DOS distribution and a larger localization length, where the larger localization length translates to higher charge-carrier mobility. Experimentally, power factors in an appropriate polymer blend are demonstrated to exceed the power factors of the individual polymers by nearly two-fold. With the combined theoretical and experimental approach presented, this work provides insight into designing higher performing organic thermoelectric materials based on π-conjugated polymer blends.

10:30 AM EN13.12.07
A New Approach for High Performing N-Type Polymer Thermoelectrics—Heavily P-Doped Polymers Kenneth R. Graham1, Zhiming Liang1, Hyun Ho Choi2, Ashkan Abtahi1, Alex M. Boehm1, Xuyi Luo3, Jianguo Mei1 and Vitaly Podzorov2; 1University of Kentucky, United States; 2Rutgers, The State University of New Jersey, United States; 3Purdue University, United States

Conductive polymers are promising thermoelectric materials, particularly for use in devices where mechanical flexibility or low-cost are primary considerations. Currently, the record power factors of P-type polymer thermoelectric materials are approximately 20 times greater than that of record N-type polymers. We have recently discovered that heavy P-doping of donor-acceptor based conjugated polymers can change the sign of the Seebeck coefficient from positive to negative, which for some polymers can lead to near record N-type power factors. Moderate P-doping of a DPP-containing polymer leads to a P-type power factor of 24.5 µW m⁻¹ K⁻¹, while further increases in doping concentration lead to an N-type power factor of 9.2 µW m⁻¹ K⁻², where 9.2 µW m⁻¹ K⁻² is a near the record power factor for an N-type donor-acceptor (D-A) conjugated polymer. Additional investigation into the origin of the sign change through a combination of ultraviolet and inverse photoelectron spectroscopy measurements
shows that the density of unoccupied and occupied states converges upon heavy doping; thereby giving rise to either positive or negative Seebeck coefficients based on the relative charge-carrier mobilities and density of states near the Fermi energy for electrons and holes. AC Hall effect measurements of heavily doped polymers confirm that the dominant band-like carriers are indeed electrons. This work provides fundamental insight into the thermoelectric behavior of heavily doped conjugated polymers and shows a promising route to developing P- and N-type polymer thermoelectrics based on the same polymer-dopant combination.

10:45 AM EN13.12.08
Control of Chemical Doping and Functionality of Conjugated Polymers via Anion Exchange Yu Yamashita1,2, Junto Tsurumi2, Masahiro Ohno1, Ryo Fujimoto1, Shohei Kumagai1, Tadanori Kurosawa1, Toshihiro Okamoto1,3, Jun Takeya1,2 and Shun Watanabe1,3; 1The University of Tokyo, Japan; 2NIMS, Japan; 3JST PRESTO, Japan

Chemical doping in a conjugated polymer always involves redox reaction between a host polymer and guest dopant. Even though physics and chemistry in material science have been evolving rapidly, an efficiency of chemical doping is limited primarily by the redox potential of employed materials, which has been well described by Marcus theory. In contrast, we have successfully overcome this limitation by introducing anion exchange [1]. A thin film of poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT) is doped by exposing it to solution of tetracyano-2,3,5,6-tetrafluorooquinodimethane (F4TCNQ). When a salt containing bis(trifluoromethane)sulfonamide (TFSI) anion is introduced to this system, the additional TFSI anion is instantaneously exchanged with the F4TCNQ radical anion that forms the intermediate ion-pair [PBTTT+ F4TCNQ●-]. Spontaneous anion exchange (from F4TCNQ●- to TFSI-) is confirmed comprehensively by UV-Vis-NIR, FTIR and ESR spectroscopies, where a lower limit of exchange efficiency is determined to be 98 %. Surprisingly, Hall measurements suggest that the efficient anion exchange increases the doping level up to almost one hole per monomer unit, which is three times higher than that of conventional F4TCNQ doping [2]. Promotion of chemical doping is also demonstrated with a weak acceptor tetracyanoquinodimethane (TCNQ). Even though the LUMO level of TCNQ (−4.5 eV) does not exceed the HOMO band edge of PBTTT (−4.8 eV), UV-Vis-NIR confirms a reasonably high doping level achieved by introducing anion exchange.

To examine the observed increase in doping level, one needs to consider equilibrium of doping reaction, where the forward reaction is charge transfer, and the reverse reaction is back-charge transfer. In a standard binary system, charge transfer takes place between neutral PBTTT and F4TCNQ, while back-charge transfer makes ionized [PBTTT+ F4TCNQ●-] back to the neutral state. In a steady state of equilibrium, these charge transfer and back-charge transfer occur at the same rate, where the doping level would not increase any more. Introduction of efficient anion exchange to this system converts [PBTTT+ F4TCNQ●-] to [PBTTT+ TFSI-], which results in suppression of back-charge transfer. Note that [PBTTT+ TFSI-] does not contribute to back-charge transfer because TFSI- is a stable closed-shell anion. Thus, efficient anion exchange biases the charge transfer equilibrium by suppressing back-charge transfer, so that the doping level increases.

Anion exchange doping provides a platform to explore material science in conjugated materials. In terms of charge transport property, the high doping level of PBTTT thin film results in Hall mobility of 2.0 cm² V⁻¹ s⁻¹ at room temperature and weak temperature dependence of it, which manifest that this system is close to onset metallicity. Another perspective would be creation of functional host-guest structures. One example here is that thermal stability is improved remarkably when a closed shell anion is introduced into polymeric semiconductors as a dopant. We believe that this study will be a benchmark for storage, transport and conversion of functional molecules within a solid-state of conjugated materials, which are the essential phenomena in broad fields of material science, e.g. catalytic activity, molecular recognition, and energy conversion.

Thermoelectric Performance of Carbon Nanotube Film and Its Composites Jiang Li and Mei Zhang; Florida State Univ, United States

Carbon nanotubes (CNTs) are expected as a high-performance thermoelectric material because of their one-dimensional nanostructure and their excellent electrical and mechanical properties. However, the thermoelectric performance is not as good as expected when they are assembled into a macroscale film. The main reason is the poor interconnections among CNTs in the film especially when the length of the CNTs is in micrometer scale. In this work, we used the special multiwalled CNTs, which have length in 1-2 mm and diameter less than 10 nm, and we employ polyacrylonitrile (PAN) as precursor to create crosslinks among CNTs after carbonization. The CNT films have improved conductivity and they are elastic and robust. For enhancing the thermoelectric performance, we further infiltrated PAN into the CNT network and investigated the effects of the PAN contents and its different status after stabilization and carbonization through thermal treatments. The results show that a maximum power factor of 13 µW/mK² was obtained from the CNT/PAN composite when the PAN content was 48% and thermally treated at 300 degree in air for 2 hours. A model was built to explain the phenomena.

11:15 AM EN13.13.02
High-Quality Textured Thermoelectric SnSe Thin Films for Quick Response Photothermoelectric Detection Yujia Zhong and Hongwei Zhu; Tsinghua University, China

Tin selenide (SnSe), a thermoelectric (TE) materials, has attracted much attention, since the record figure of merit (ZT=2.6) is discovered in SnSe single crystals (SC). Nevertheless, the practical application of SC is limited due to the high cost and extreme growth condition. With the development of flexible intergrated electronics, using flexible TE polycrystalline films to substitute rigid SC becomes a main trend. SnSe thin films, a flexible TE polycrystalline films, demonstrate potential high TE performance and low cost, which enable the thin films to be widely used in diverse applications. However, the lack of approach to synthesize scalable high-quality SnSe thin films constitute a main obstacle for their applications. Here, we report scalable high-quality SnSe polycrystalline thin films with strong (400) texture directly synthesized via chemical vapor deposition (CVD). Our SnSe thin films exhibit a ZT of 0.15 and power factor (PF) of 0.322 mWm⁻¹K⁻² at 550 K, demonstrating that TE performance of this SnSe thin films at low temperature region is at the SC level. Moreover, the SnSe thin films-based photothermoelectric (PTE) detectors illustrate a higher responsivity and speed than SnSe SC-based PTE detectors, which is resulted from small heating volume, small conductive heat flux and large dissipation content in the thin films. The high performance of PTE detectors demonstrates the superiority of TE thin films in a practical application. Based on the position sensitive PTE effect, in-plane laser positioning and tracking are further conducted when using the PTE detectors with two pairs of electrodes. We pave the way for fabrication and practical application of TE thin films.

11:30 AM EN13.13.03
High Thermoelectric Performance in n-Doped Silicon-Based Chalcogenide Si₂Te₃ Rinkle Juneja, Tribhuwan Pandey and Abhishek K. Singh; Indian Institute of Science, India

Silicon-based thermoelectric materials would be of great significance due to the huge dependence of electronic industry on silicon. Bulk silicon is not a good thermoelectric material due to its very high thermal conductivity, thereby limiting its thermoelectric efficiency. Nanostructuring and alloying are alternative solutions to reduce thermal conductivity, but the techniques involved are complex and costly. Recently, a silicon-based chalcogenide Si₂Te₃ has been experimentally synthesized. Si₂Te₃ exhibits layered structure, in which Te atoms form hexagonal sub-lattice and Si atoms can occupy any of the octahedral voids. Due to uncertainty in Si positions, previously unknown ground state structure of Si₂Te₃ was obtained using the Wyckoff positions of space group P-31c. The minimum energy configuration exhibits combination of desirable electronic and transport properties. In particular, n-doped Si₂Te₃ has an unprecedented figure of merit of 1.86 at 1000 K, which is comparable to some of the best state-of-the-art thermoelectric materials. Hence, n-doped Si₂Te₃ can be a long-sought silicon-based thermoelectric material which could be integrated to the existing electronic devices.

SYMPOSIUM EN14
SESSION EN14.01: Physics of Thermoelectric Materials
Session Chair: G. Jeffrey Snyder
Monday Morning, December 2, 2019
Sheraton, 3rd Floor, Gardner AB

8:00 AM *EN14.01.01
Goniopolar Thermoelectrics Joseph P. Heremans, Bin He, Yaxian Wang, Michael R. Scudder, Joshua E. Goldberger and Wolfgang Windl; The Ohio State University, United States

Goniopolar materials are metals and degenerate semiconductors with a thermopower that is n-type in one crystallographic direction, but p-type in another. This effect is due to a particular geometry of their Fermi surface [1], which must be concave and cannot be 1-simply connected in the Brillouin zone. Very interestingly, in some cases, the sign of the Hall effect is exactly the reverse of the sign of the Seebeck effect, which can again be explained by the topology of the Fermi surface. The same properties can arise in (pxn) materials [2], composites made from alternate p and n-type layers. They also arise in solids in which the Fermi surface consists of electron pockets and hole pockets. When single crystals of such materials are cut at a particular angle with respect to the axes that have positive and negative thermopower, a transverse thermopower arises, in the geometry a Nernst thermopower would appear, but in zero magnetic field. This can be used to design transverse thermoelectric power generators and transverse Ettingshausen-like coolers. In this talk, several members of this new genus of materials will be described, beyond the original materials (NaSn2As2) on which the effect was discovered [1].


8:30 AM EN14.01.02
Geometrically Defined Thermoelectricity in 2D Materials Achim Harzheim1, Charalambos Evangelis2, Jean Spicée2, Ed McCann2, Yuewen Sheng1, Jamie Warner1, Andrew Briggs1, Vladimir Falko3, Jan Mol1, Pascal Gehring4, and Oleg V. Kolosov5; 1University of Oxford, United Kingdom; 2Lancaster University, United Kingdom; 3University of Manchester, United Kingdom; 4Delft University of Technology, Netherlands

Classical view of thermoelectricity (TE) requires a junction of two differing conductors – two dissimilar metals, p and n doped semiconductors, etc. in order to create the electric potential when the junction is heated (Seebeck effect), or to cool/heat the junction depending on the direction of current flow (Peltier effect). With the efficiency of TE devices defined by both the electronic and heat transport properties of materials, contradictory requirements have to be satisfied, with nanostructuring offering additional “degrees of freedom” allowing to find optimal solutions.

Here we studied atomically flat 2D materials that include zero-gap semiconductor graphene (GR) and semiconducting transition metal dichalcogenides known for their extraordinary electronic and thermal properties. With relativistic carrier dynamics and exceptionally large mean-free path (MFP) of carriers in GR, combined with its highly anisotropic and environment dependent thermal conductance, one can expect unusual thermoelectric properties in such nanostructures. In order to study TE phenomena in these, we applied scanning thermal microscopy (SThM) that uses a sharp tip in point contact (few nm across) with the probed surface. SThM can
measure the local temperature of the heated sample or create a controlled local sample temperature rise, while measuring the resulting heat flow. We used e-beam lithography patterned GR devices of different geometry with attached electrodes that allow to either inject the current into the device, while mapping and measuring the local heat rise (Joule heating and Peltier effect) or to actively heat the SThM probe while providing nanoscale maps of the resulting “thermovoltage” (Seebeck effect). The latter method (we call it scanning thermal gate microscopy, or SThGM) developed for the first time in these experiments turned out to be very efficient in studying TE materials. We used high vacuum environment to eliminate spurious heat dissipation channels boosting accuracy and sensitivity down to mK range, and allowing measurements of samples down to cryogenic temperatures.

Using this methodology, we investigated TE phenomena in GR devices with varying geometry – starting with the simple bow-tie shape with the constriction of about 100 nm wide and 100 nm long connected to the triangular shaped areas expanding to the Au electrodes. While mapping and measuring Peltier cooling at the Au electrode – Gr interface (fully expected in the classical TE phenomena), we completely unexpectedly found that a much stronger Peltier cooling was observed around the constriction area. This phenomenon was confirmed by measuring the Seebeck thermovoltage map. This constriction had no dissimilar materials and we confirmed that no local doping was present by manipulating the back gate of the device to shifting the Dirac point, suggesting novel phenomenon of “geometrically” defined TE.

We then conducted a series of experiments on different geometries (multiple “necks, long constrictions, holes in the uniform ribbon) and varying current densities, comparing these with the MFP and heat flow models, for matching thermovoltage and cooling-heating measurements. These allowed to confirm that the new effect can be explained solely by the geometrical effect of the constriction on the MFP of the carriers in the GR layer. We also analyse experimental measurements of the effect for varying GR layer number, doping as well as nonlinear TE phenomena of “electron wind” effect observed at higher current densities when carrier drift velocity in 2D material becomes comparable with the carriers Fermi velocity.

In summary, we report the novel TE phenomena in 2D materials where geometry of the device alone can produce significant Peltier and Seebeck TE effects, offering new solutions for the efficient and compact TE devices. Additionally, a novel scanning thermal gate microscopy is presented allowing to very effectively study of TE phenomena in a broad range of nanostructures.

8:45 AM EN14.01.03
Enhanced Thermopower of Three-Dimensional Topological Insulators Yu S. Matsushita, Kakeru Ichimura, Khuong K. Hyunh and Katsumi Tanigaki; Tohoku University, Japan

Recent research on thermoelectrics (TE) focuses not only on phonon engineering but also on electronic engineering. Generally, metallic materials have low TE performance as can be explained by Mott relation, where the thermoelectric power (S) of metallic materials is related to the Fermi energy $E_F$ and carrier density $n$ depending on the dimension of the system. Consequently, a large number of carrier density $n$ in metallic materials gives a quite small value of $S$ in contrast to its large electrical conductivity $\sigma$, resulting in a very small value of power factor. Such a general conclusion, however, can be expected to be broken by introducing nonconventional electronic states such as the special surface states in topological materials. Dirac fermions existing on topological materials can be one of the candidates for non-trivial electronic systems, which attract much attention as the unique research platform in this decade. Three-dimensional topological insulators (3D-TIs) show intriguing gapless helical massless Dirac fermions on a two-dimensional (2D) surface of insulating bulk materials. The electronic band of Dirac fermions is characterized by a linear energy dispersion, which gives an extremely high carrier mobility that could enhance conductivity $\sigma$ without decreasing thermoelectric power to be compared with many conventional metals. This is because the thermopower in a 2D Dirac system is related to the carrier concentration $n$ with the special relation and can be different from the relation in the conventional metals, indicating a larger $S$ with the same value of $n$. Such a unique $n$ dependence of $S$ has been observed for graphene first in the past. In the case of 3D-TIs, however, the contribution from bulk carriers prevents such observations and discussions on the TE properties of topological surface Dirac states (TSDs) had been very limited and still ambiguous. In order to have clear understanding for thermoelectrics (TE) of 3D-TIs, it is essential to observe simultaneously the pure surface TE properties and the accurate band structure. Here, we demonstrate clear observations of both thermopower and quantum spin Hall effect (QSHE) using high quality single crystal flakes of 3D-TIs. According to the high bulk insulation of our 3D-TIs, we succeeded to observe clear QSHE of the TSDS at high temperatures and in the thickness of mm. Our high quality
3D-TIs enable one to determine accurate thermoelectric parameters. The details of band picture of surface states can be evaluated from both Shubnikov-de-Hass (SdH) oscillations and the QSHE. By employing the fine and accurate experimental data, we will discuss how the high efficient TE properties of 3D-TIs can be available.

9:00 AM EN14.01.04
High Thermoelectric Figure of Merit via Tunable Valley Convergence Coupled Low Thermal Conductivity in $A^\text{II}B^\text{IV}C^\text{V}$ Chalcopyrites Madhubanti Mukherjee, George Yumnam, Rinkle Juneja and Abhishek K. Singh; Indian Institute of Science, India

Development of efficient thermoelectric materials requires a designing approach that leads to excellent electronic and phononic transport properties. Tetragonal chalcopyrites materials have recently attracted significant attention in optoelectronic and photovoltaic applications. Using first principles density functional theory and semiclassical Boltzmann transport theory, we report unprecedented enhancement in electronic transport properties of chalcopyrites $A^\text{II}B^\text{IV}C^\text{V}_2$ (group II = Be, Mg, Zn, and Cd; group IV = Si, Ge, and Sn; and group V = P and As) via isoelectronic substitution. Multiple valleys in conduction bands, present in these compounds, are tuned to converge by substitution of group IV dopant. Additionally, this substitution improves the convergence of valence bands, which is found to have a direct correlation with the tetragonal distortion of these chalcopyrites. Furthermore, several chalcopyrite compounds with heavy elements such as Zn, Cd, and As possess low phonon group velocities and large Gruneisen parameters that lead to low lattice thermal conductivity. Combination of optimized electronic transport properties and low thermal conductivity results in maximum ZT of 1.67 in CdGeAs$_2$ at moderate n-type doping. The approach developed here to enhance the thermoelectric efficiency can be generalized to other class of materials.

9:15 AM EN14.01.05
Using Energy Filtering to Change the Thermoelectric Design Paradigm Seyed Aria Hosseini$^1$, Jackson R. Harter$^2$, Devin Coleman$^1$, Todd S. Palmer$^2$, Lorenzo Mangolini$^1$ and P. Alex Greaney$^1$; $^1$University of California, Riverside, United States; $^2$University of Oregon, United States

Complex Materials and Novel Theoretical Methods Researchers have recently developed processes for synthesizing monolithic Si with improved thermoelectric figure-of-merit, ZT. These materials obtain higher ZT through a finely controlled array of secondary phase inclusions. In this work we elucidate the role these particles play in two processes to increase ZT: (1) scattering of phonons to reduce thermal conductivity, and (2) energy selective scattering of electrons to increase the seebeck coefficient. For (1) Boltzmann transport simulations are used to predict the collective effect of the scattering mechanisms on thermal conductivity of different silicon samples and compared with equilibrium molecular dynamics counterpart. For (2) Fermi’s golden rule is used to compute electron scattering interactions with nanoparticles. There scattering rates are combined with electron-phonon and electron-impurity scattering rates using Mathessen’s method. The results are used to predict the electrical properties of the Si with different volume fraction of nanoparticles. We further present a semiclassical model of thermoelectric transport properties in the presence of energy selective electron scattering — electron energy filtering. The model is validated against a set of Si based thermoelectrics containing silicon carbide dispersoids. The model is extrapolated to explore how energy filtering can be used to enhance the thermoelectric figure of merit, ZT, in a wide range of materials. Counterintuitively, this model predicts that the highest ZTs can be achieved in the tails of the Fermi-dirac distribution of thermoelectrics doped to have high carrier concentration. Boltzmann transport simulations are used to predict the collective effect of the scattering mechanisms on thermal conductivity of different silicon samples. Together, these models present a new strategy for optimization of thermoelectrics that breaks materials engineers free from the traditional paradigm of engineering the fermi energy at the band edge.

9:30 AM EN14.01.06
Revealing the Intrinsic Electronic Structure of ZrNiSn Half-Heusler Thermoelectric Materials Chenguang Fu and Claudia Felser; Max Planck Institute for Chemical Physics of Solids, Germany

Half-Heusler compounds have recently been developed as the most promising high-temperature thermoelectric materials due to their excellent power factor. However, experimental investigations of their intrinsic electronic structures, underpinning the high power factor, are still rare. Herein, high-resolution angle-resolved photoemission spectroscopy, electrical and optical measurements, and first-principles calculations were performed to explore the intrinsic electronic structure of ZrNiSn, the archetypical n-type half-Heusler thermoelectric material. For the first time, the real bandgap of ZrNiSn was revealed as 0.5–0.6 eV using various methods, which are significantly larger.
than the values reported in previous literature. Additionally, a large anisotropic conduction band was directly identified to contribute to the high power factor. This successful observation of intrinsic electronic structure relies on the synthesized high-quality single crystals, which have much fewer Ni interstitial defects and negligible in-gap states. This work demonstrates the significance of processing-structure-property relationships in materials research and provides new insights to improve the thermoelectric performance of half-Heusler compounds.

9:45 AM EN14.01.07
**Thickness Dependent Magneto-Thermoelectric Effects in Co2MnGa Thin Films** Gyuhyeon Park1,2, Helena Reichlova3,4, Richard Schlitz3,4, Michaela Lammel1,4, Anastasios Markou5, Dominik Kriegner6, Claudia Felser4, Kornelius Nielsch1,2, Sebastian T. Goennenwein3,4, Andy Thomas1,4 and Nicolas Perez1; 1Leibniz-Institute for Solid State and Materials Research (IFW), Germany; 2Technische Universität Dresden, Germany; 3Institute für Festkörper- und Materialsphysic and Würzburg-Dresden Cluster of Excellence ct.qmat, Technische Universität Dresden, Germany; 4Center for Transport and Devices of Emergent Materials, Technische Universität Dresden, Germany; 5Max Planck Institute for Chemical Physics of Solids, Germany; 6Institute of Physics ASCR, v.v.i., Czechia

The anomalous Nernst effect (ANE), which is magneto-thermo-electronic transport, manifests itself experimentally as an anomalous transverse voltage perpendicular to both the heat current and magnetization.

We report a robust ANE in Co2MnGa thin films in the thickness series between 10 and 50 nm at 300 K. We further employ this thickness series to study the Mott relation and show that the anomalous Hall coefficient, which is thermoelectric counterpart of ANE, and the NANE measured in identical structures under equal conditions exhibit a similar dependency. Moreover, in selected samples, we measure all four transport coefficients – longitudinal and transversal resistivity, Seebeck and NANE – and we show that the values of measured and calculated Nernst coefficients and conductivity are comparable when assuming the validity of the Mott relation.

10:00 AM BREAK

**SESSION EN14.02:** Oxide and Chalcogenide Thermoelectrics
Session Chair: Jayakanth Ravichandran
Monday Morning, December 2, 2019
Sheraton, 3rd Floor, Gardner AB

10:30 AM *EN14.02.01
**Making Quantum Transport Visible in Thermoelectric Bi2Te3, Sb2Te3 and Bi2Se3 Nanoparticles** Gabi Schiering1, Sepideh Izadi1, Patrick Kawulok1, Lauritz Schnatmann1, Heiko Reith1, Manuel Loor2,1, Sarah Salloum2, Kornelius Nielsch1, Nicolas Perez Rodriguez and Stephan Schulz2; 1Leibniz-Institut IFW Dresden e.V., Germany; 2University of Duisburg-Essen, Germany

Bi2Te3, Sb2Te3, and Bi2Se3, are well established thermoelectric materials. To improve the thermoelectric performance of these materials, nanoparticles from a wet-chemical synthesis using metal-organic precursors and ionic liquids were synthesized as starting materials. By hot pressing these nanoparticles under inert conditions, record figure of merit ($zT$) values were demonstrated, for example of $zT=1.5$ at 470 K for Sb2Te3 nanoparticles from this synthesis. But these materials are also three-dimensional (3D) topological insulators (TI) exhibiting a bulk bandgap and highly conductive, robust, gapless surface states. Using the same nanoparticles, but slightly different compaction parameters, highly porous bulk materials were obtained. The high porosity and high interface density creates a situation in which surface transport from the topological states becomes visible in the transport properties at low temperatures. The high surface-to-volume ratio is hereby beneficial, because usually the transport properties of Bi2Te3, Sb2Te3, and Bi2Se3 are dominated by the bulk carriers. Using this nanoparticle-based materials’ design, the highly porous macroscopic sample features a carrier density of the surface states in a comparable order of magnitude as the bulk carrier density. Further, the sintered nanoparticles impose energetic barriers for the transport of bulk carriers at the interfaces (hopping transport), while the connected surfaces of the nanoparticles provide a 3D percolation path for surface carriers. This also helps to emphasis the topological transport properties. Within this
article, both the synthesis and nanoparticle processing as well as the transport properties of these combined thermoelectric and 3D TI samples will be discussed.

11:00 AM EN14.02.02
Thermoelectric Properties of SnSe—Improving Semiclassical Models Andrea Cepellotti and Boris Kozinsky; Harvard University, United States

Tin chalcogenides and specifically SnSe have recently gathered significant attention thanks to reports of record-high thermoelectric efficiency while devoid of toxic elements that might hinder commercial usage. The origin of the large thermoelectric figure of merit of SnSe, i.e. the ZT factor, is still subject of investigations, due to a number of interesting properties combined in this material. The large lattice anharmonicity is responsible for the low values of lattice thermal conductivity, whereas the presence of multiple valleys in the electronic band structure close to the chemical potential enhances the electrical transport characteristics. So far, theoretical modeling has mostly focused on describing the transport properties of SnSe using a semiclassical approach based on the Boltzmann transport equation. However, such model may not be sufficient to accurately describe the properties of this material. In this work, we study corrections to the Boltzmann transport equation, that can be derived more generally from many-body perturbation theory and parametrized using first-principles calculations. In particular, these corrections become more important for crystals with complex band structures (e.g. multi-valleys) and large temperatures, which routinely occur in thermoelectric materials, where electrons and holes are not a well-defined material excitations, and a description based on the density-matrix becomes necessary. We test these corrections in SnSe and show how they improve estimates of thermoelectric properties (by up to a factor 2), leading to an overall better agreement with experiments and providing a general path towards improved simulations of thermoelectric materials.

11:15 AM EN14.02.03
Thermoelectric Properties of Hexagonal Perovskite Chalcogenides with Low Thermal Conductivity Shanyuan Niu1, Sam Miller2, Joanna M. Guerrero1, Boyang Zhao1, Brent C. Melot1, G. Jeffrey Snyder2 and Jayakanth Ravichandran1; 1University of Southern California, United States; 2Northwestern University, United States

The ternary perovskite oxides with good stability and high power factor, epitomized by SrTiO3, have been studied for high temperature thermoelectrics. Their relatively large lattice thermal conductivity remains an obstacle towards achieving high thermoelectric figure of merit, ZT. Binary chalcogenides such as PbTe benefit significantly from reduction of lattice thermal conductivity due to heavy elements and give rise to several materials with record ZT values about 2. Ternary chalcogenides with perovskite and relates structures could potentially marry the attractive features of both materials systems. We have recently explored these semiconductors for optoelectronic applications.1,2 We chose the model system of BaTiS3 with a low bandgap and a hexagonal perovskite structure to study the thermoelectric properties. Low thermal conductivity around 0.6 W/mK, Seebeck coefficient of around 170 mV/K and electrical conductivity of about 1 W/cm were obtained at room temperature. Differential scanning calorimetry and thermogravimetric analysis indicate stability up to 1000K in air. The thermoelectric figure of merit was extracted as a function of temperature and a ZT value up to 0.03 was obtained at 700K. We attempted doping BaTiS3 with Nb and La, but no significant improvement on electrical conductivity was observed. More in-depth doping studies are needed to achieve higher ZT in these materials.

References:

11:30 AM EN14.02.04
Simultaneous Increase in Seebeck Coefficient and Electrical Conductivity of BiCuSeO/Ca3Co4O9 Composites Emre Burak Yurdakul1,2, Murat Gunes3 and Ahmet Macit Ozenbas1; 1Orta Dogu Teknik University, Turkey; 2Aselsan, Turkey; 3Erzincan University, Turkey

In this work, we report a simultaneous increase in Seebeck coefficient and electrical conductivity, that results in increasing power factor, of Ca3Co4O9 (C-349) ceramic by forming a composite system together with another promising oxyselenide; BiCuSeO (BCSO). Composite engineering is a promising method to develop the existing properties of thermoelectric materials. The aim of this work is therefore to explore the unique thermoelectric properties of promising C-349 and BCSO oxides, then to investigate the new properties of their composites.
Pristine C-349 and BCSO were synthesized using sol-gel and solid-state reaction methods, respectively and mixed by several ball-milling steps followed by cold compaction. Bulk composites as pellets have been prepared and thermoelectric properties have been investigated. The electrical properties of samples were investigated by Hall effect measurements at room temperature. Lakeshore 7700A system was used with van der Pauw geometry between 0.15 and 1.5 T. Non-destructive measurements of the Seebeck coefficient and the electrical conductivity were carried out under vacuum in a temperature interval between 300 and 900 K using a lab-made system. As the BCSO content increased, the electrical conductivity and Seebeck coefficient were simultaneously enhanced. The highest power factor was obtained as 0.17 mW/mK² in the composite system that contains 5 wt % BCSO. This value represents nearly 41% improvement in the power factor of pristine C-349 at 900 K. The addition of BCSO phase causes a slight decrease in carrier concentration and at the same time creates more porous structure. Both consequences have a positive impact on Seebeck coefficient. The reason for enhancement in electrical conductivity is related with a high increase in electron mobility without significant decrease in carrier concentration. These results prove that composite engineering technology will provide a promising advantage in developing thermoelectric materials with higher efficiencies. However, most works carried out about composite engineering intend to reduce the thermal conductivity. Therefore, this work shows the potential of power factor enhancement of composite materials in order to produce highly efficient thermoelectric materials.

11:45 AM EN14.02.05
Oxide Thermoelectric Materials—Porous Influence Leilane R. Macario¹,², Edson R. Leite¹,³ and Holger Kleinke²; ¹National Center for Research in Energy and Materials, Brazil; ²University of Waterloo, Canada; ³Federal University of Sao Carlos, Brazil

As the concern about depletion of non-renewable resources is growing, waste heat harvesting has become one of the effective approaches for solving the energy shortage issue. Thermoelectric materials are promising candidates for solid-state energy generators for converting the huge amount of industry and automobile generated waste heat into electricity. The material’s performance is characterized by the figure of merit \( zT = S^2\sigma T/\kappa \), where \( S \) is the Seebeck coefficient, \( \sigma \) the electrical conductivity, \( T \) the absolute temperature, and \( \kappa \) the thermal conductivity of the material. Oxide thermoelectric materials have the advantages of low cost, environment-friendly manufacturing and chemical stability at high temperatures. However, oxides have been historically regarded as out of the question for good thermoelectric materials, because they are mostly poor conductors due to their high ionic nature and good heat conductors due to the light oxygen. Thus, alternatives such as presence of dopants, densification mechanisms, introduction of a second phase, and nanostructuring are considered to enhance the thermoelectric properties in oxides. The possibility of controlling the pores for optimization of materials properties motivates studies relating to the presence of dopants and densification mechanisms. Bi-layered pellets contain a layer of tin oxide doped with antimony, Sb-SnO₂, and a sintering additive, manganese oxide, MnO₂ allowed the production of materials with lower thermal conductivity and possible enhanced electrical conductivity. Thereby, these materials have the potential to improve the energy conversion and contribute to the expansion of new thermoelectric oxides materials.

1:30 PM *EN14.03.01
Thermal Conductivities and Phonon Mean Free Paths of Silicon Germanium Nanowires of Different Lengths Gabriella Coloyan¹, Brandon P. Smith¹, Kevin D. Parrish², Feng Wen¹, Evan Fleming¹, Karalee Jarvis¹, Alan J. McGaughey², Emanuel Tutuc¹ and Li Shi¹,¹; ¹University of Texas at Austin, United States; ²Carnegie Mellon University, United States

Silicon germanium (SiGe) is a high-temperature thermoelectric material. Due to alloy scattering of short-wavelength phonons in SiGe, long-wavelength phonons make an important contribution to the lattice thermal conductivity of SiGe. The effects of nanostructures on suppressing the lattice thermal conductivity have been extensively studied for different materials including SiGe. However, the phonon mean free paths and lattice thermal conductivities of SiGe
bulk crystals and nanowires have remained one of the outstanding questions in the study of phonon transport and nanostructured thermoelectric materials due to inconsistent results obtained in previous experiments. Here we report multi-probe measurements of the intrinsic thermal conductivities of different segments of the same SiGe nanowires. Our measurement results reveal a weak length dependence of the thermal conductivity of the SiGe nanowires, and are in agreement with a Monte Carlo simulation of phonon transport in SiGe nanowires with diffuse surface.

2:00 PM EN14.03.02
Phonon Scattering Mechanism in Thermoelectric Material Revisited via Resonant X-Ray Dynamical Diffraction Adriana Valerio1, Marli d. Cantarino1, Fernando A. Garcia1, Claudio M. Remedios2, Guilherme Calligaris3, Stefan Kycia4 and Sergio L. Morelhao1,4; 1University of Sao Paulo, Brazil; 2Universidade Federal do Pará, Brazil; 3Brazilian Synchrotron Light Laboratory, Brazil; 4University of Guelph, Canada

Thermoelectric properties of the materials originate from thermal conduction by free charge carriers instead of by collective lattice vibrations (phonons). Understanding the scattering mechanism, or dissipation, of phonons allows the engineering of materials with higher coefficient of Seebeck [1], i.e. higher difference of electric potential created for a given thermal gradient. In skutterudite type of thermoelectric materials, dissipation of phonons are attributed to localized, low frequency and anharmonic vibrations of heavy ions of the lanthanide family introduced into the large voids of the crystalline structure. Since most of these materials can be synthesized in the form of high quality single crystals, we have the possibility of revisiting the phonon scattering mechanism through x-ray phase measurements via dynamic diffraction effects [2]. Structure factor phases are susceptible to the differences between the vibration amplitudes of the atoms (root mean square atomic displacements), or in other words, phase values are invariants with temperature only when all occupied sites of the unit cell have the same Debye-Waller factor.

Structure factor calculation in model structures revealed suitable Bragg reflections and x-ray energies to resolve the difference in atomic vibrations as a functions of temperature. It also revealed a giant resonant phase shift for the whole family of filled skutterudites RFep12 (R=Ce, La, Nd, Pr, Sm). By exploiting this resonant phase shift with synchrotron x-rays at different temperatures in CeFe4P12, we were able to demonstrated that rattling of Ce alone inside the icosahedral cage is not enough to explain phonon scattering and that the whole cage of 12 P is taking part of scattering mechanism.


2:15 PM EN14.03.03
Anharmonic Phonons and Electron-Phonon Coupling in Thermoelectrics SnSe and SnS Shan Yang1, Tyson Lanigan-Atkins1, Dipanshu Bansal1,2, Jennifer Niedziela3, Andrew May1, Tao Hong3, Georg Ehlers5, Songxue Chi3, Douglas Abernathy1 and Olivier Delaire1,1; 1Duke University, United States; 2Indian Institute of Technology Bombay, India; 3Oak Ridge National Laboratory, United States

Understanding electron-phonon and phonon-phonon interactions is critical for the design of new thermoelectric materials, in which the energy conversion efficiency is determined by the concurrent optimization of electrical and thermal conductivities. SnSe is a high-efficiency thermoelectric material, whose ultralow thermal conductivity originates predominantly from phonon anharmonicity [1,2], while SnS is of interest for both thermoelectric and photovoltaic applications. Previous inelastic neutron scattering (INS) measurements and first-principles simulations of SnSe identified the dramatic softening of TO (transverse optical) mode in the ambient Pnma phase, anisotropic dispersion of acoustic modes and velocities [2,3,4]. SnSe and SnS have similar crystal structures and electronic band structures below and above a second-order structural phase transition to a Cmcm phase at T=800K. Our INS measurements of SnS and SnSe extended previous studies to higher temperatures and directly revealed the condensation of a zone boundary TA (transverse acoustic) mode in Cmcm phase, which yields the Brillouin zone folding and re-emerges as the zone-center TO mode in Pnma. By including anharmonic
renormalization effects into the temperature-dependent force-constants, our first-principles calculations successfully reproduce the experimental phonon dispersions and the soft-mode condensation across the Cmcm-Pnma transition. The significant suppression of thermal conductivity near the phase transition temperature could be captured by including renormalized anisotropic group velocities into thermal conductivity calculations. Further, our ab initio molecular dynamics simulations could be used to understand electron-phonon coupling behaviors accounting for the response of SnSe and SnS under photo-excitation.


**2:30 PM EN14.03.04**
*Estimations of Thermal Conductivity and Thermoelectric Performance through Phase Transitions* Matthias T. Agne, Peter W. Voorhees and G. Jeffrey Snyder; Northwestern University, United States

The accurate characterization of thermal conductivity \( \kappa \), particularly at high temperature, is of paramount importance to many materials, thermoelectrics in particular. The ease and access of thermal diffusivity \( D \) measurements allows for the calculation of \( \kappa \) when the volumetric heat capacity, \( \rho c_p \), of the material is known. However, in the relation \( \kappa = \rho c_p D \), there is some confusion as to what value of \( c_p \) should be used in materials undergoing phase transformations. Herein, it is demonstrated that the Dulong-Petit estimate of \( c_p \) at high temperature is not appropriate for materials having phase transformations with kinetic timescales relevant to thermal transport. In these materials, there is an additional capacity to store heat in the material through the enthalpy of transformation \( \Delta H \). It is shown in a model Zn4Sb3 system that the decrease in \( D \) through the phase transition at 250 K is fully accounted for by the increase in \( c_p \). Importantly, \( \kappa \) changes smoothly through the phase transition. Consequently, reports of \( \kappa \) diverging through phase transitions have likely overlooked the effects of excess heat capacity on thermal properties measurements and overestimated the thermoelectric efficiency, \( zT \).

**2:45 PM EN14.03.05**
*Correction of Lattice Thermal Conductivity in Compounds with Electrically Resistive Grain Boundaries* Max Wood, Jimmy Kuo and G. Jeffrey Snyder; Northwestern University, United States

Nano structuring thermoelectric materials has long been a technique to scatter phonons and lower a material’s lattice thermal conductivity\(^1\). The lattice thermal conductivity of a material has historically been estimated by subtracting the electrical portion of thermal conductivity (calculated using the Weidman-Franz law) from the total thermal conductivity of a material (\( k_L = k - \sigma T \)). This method treats heat conducted by phonons and heat conducted by electrons as two separate and independent transport channels. While nano-structuring is known to scatter phonons, in some materials shrinking the grain size can have a detrimental effect on the electronic properties through additional grain boundary scattering\(^2\). Herein we discuss how this grain-boundary scattering can lead to underestimating the electronic thermal conductivity, which necessitates a correction term to our estimation of lattice thermal conductivity. We demonstrate this correction using experimental data on \( \text{Mg}_3\text{Sb}_2 \) and show examples in the literature of \( \text{CoSb}_3 \), \( \text{Bi}_2\text{Te}_3 \), and other materials that might have benefitted from using this type of correction.

(1) Minnich A. et al., Energy Environ. Sci., 2009, 2, 466
(2) Kuo J. et al., Energy Environ. Sci., 2018, 11, 429

**3:00 PM BREAK**

SESSION EN14.04: Theory of Phonon Transport in Thermoelectric Materials
Session Chair: Alexandra Zevalkink
3:30 PM *EN14.04.01

Point Defects as Phonon Superscatterers Georg Madsen; Technische Universität Wien, Austria

Dopants play an important role in engineering the electronic properties of semiconductor materials. At the same time they can strongly influence the phonon scattering processes and thereby the thermal conductivity. We have recently shown how Boron point defects in 3C-SiC act as “superscatterers” and exhibit resonant phonon scattering which is one to two orders of magnitude higher than other defects.[1] The increased scattering leads to a thermal conductivity that is suppressed by one to two orders of magnitude.

In order to understand the physics behind and the factors causing resonance scattering, we explain the results with the help of a simple 1D mono-atomic linear chain.[2] We show that small lattice distortions emanating from two or more close energy minima in potential energy surface lead to very large perturbations of the interatomic force constants. Such a behavior is characterized by a peak in the trace of imaginary part of the T matrix (which is closely related to the scattering rates) and a reflection coefficient approaching unity.

The strong influence of the potential energy surface surrounding the defect atom on the thermal conductivity opens a new path to tailor thermal conductivities where required values range from very low in thermoelectric materials to very high in power electronics applications. Using doping of GaAs as an example[3], we show how the provided insights can be used to identify potential superscatters.


4:00 PM EN14.04.02

Finite Element Modelling of Optically Pumped Thermoreflectance David A. Lara Ramos¹,2,3, Kerry Maize⁴,4, Nicolas Perez¹, Gabi Schierning¹, Kornelius Nielsch¹,2 and Ali Shakouri⁴,4; ¹Leibniz Institute for Solid State and Materials Research, Germany; ²TU Dresden, Germany; ³Consejo Nacional de Ciencia y Tecnología (CONACyT), Mexico; ⁴Purdue University, United States

Thermoreflectance microscopy is a noninvasive optical technique that is capable of mapping 2D temperature fields of surfaces with high spatial and time resolution. State of the art thermoreflectance microscopy set-ups use electrical current to thermally excite the device or sample under study and so generate temperature differences. This technique is particularly useful for investigating hot spots in integrated circuitry leading to failure or premature fatigue of microelectronic components [1]. It is also a powerful tool for investigating thermal properties of materials [1, 2] and thermal characterization of micro thermoelectric devices [3]. All-optical pump probe thermoreflectance microscopy, which thermally excites the sample by a pump laser spot focused on the sample’s surface, has recently been proposed as a promising tool for investigating anisotropic thermal properties of thin film hetero structures [4]. The later research efforts motivates the technique’s further development, since thermoelectric materials often present anisotropic thermal transport properties whose experimental characterization is challenging, especially in thin films. In this work an all-optical pump probe thermoreflectance microscopy is used to study a series of thin film multilayers of TiN/AlScN deposited on MgO substrates [5] which present tunable anisotropy. The temperature distribution on the surface of the sample was then analyzed by the probe laser and correlated to finite element modelling (FEM) simulations. FEM allowed us to systematically analyze, using realistic parameters, the impact of various experimental factors that affect the result of measurements. We gained understanding about the required experimental conditions in order to extract cross plane and in plane thermal conductivity of the thin films. Using FEM, a measure of the sensitivity required by the experimental device was obtained.

References:


4:15 PM EN14.04.03
Thermoelectric Materials with Large Anharmonic Phonons Katsumi Tanigaki1 and Jiazhen Wu2; 1Tohoku University, Japan; 2Tokyo Institute of Technology, Japan

Anomalous and nearly dispersionless phonons have recently been observed in many materials with a void (an inner space with large freedom of motion) inside a host cage containing a filler as the guest atom inside (usually called rattler), such as intermetallics, brownmillerite, skutterudite, pyrochlore and clathrate. The cage atoms are connected by covalent bonds, providing a robustly solid wall and a sufficient space for accommodating a guest atom. Since the guest atom in a cage is only weakly interacted with the surrounding atoms forming a cage, it can vibrate freely under a weakly-bound condition and shows an anomalous motion with low-energy excitation (ALE) and a large atomic displacement parameter (ADP). The rattling phonons of the ALE modes are scientifically important for: (1) large coupling with conduction electrons, giving rise to a significant modification of electron effective mass; (2) interactions with propagating phonons, leading to an enhancement of scattering probability of phonons and consequent low thermal conductivity which is useful for thermoelectric applications. ALE rattling phonons observed in cage materials have been both experimentally and theoretically investigated. The rattling phonon branches were shown to be optical-branch-like at around 5 meV, which was lower than the energies of the top of acoustic phonon branches, giving rise to ALE peaks in the phonon density of states (PDOS). The ALE vibration modes have also been detected and intensively discussed by Raman spectroscopy, optical conductivity, heat capacity (HC), and temperature dependent ADP obtained from crystallographic refinement of x-ray/neutron diffraction data. However, the origin of the low energy modes was still not perfectly clear. In the present paper, we address that van der Waals-type repulsive interactions between a guest atom and the atoms residing a host cage can be the origin of the ALE modes. The ALEs of three typical cage compounds of clathrates, skutterudites and pyrochlores have intensively been investigated. An exponential-form relationship between the force constant Fc and the free space derived based on the Morse-type van der Waals potential, gives very reasonable interpretations on ALEs. The Fc’s evaluated from the characteristic energies of the guest atoms are shown to vary exponentially as a function of the free space of guest atoms, being in good agreement with the unified relationship. By comparing the fitting parameters among clathrates, skutterudites, and pyrochlores, the features that specify each family of cage material are discussed. The anisotropic 3D van der Waals-type interactions significantly modify the physical properties of cage materials via phonon-phonon and electron-phonon interactions and play a very important role in thermoelectrics. The strategy of how to improve the figure of merits of these thermoelectric materials will be presented.

4:30 PM EN14.04.04
Effects of Structural Correlation on Phonon Transport in Random Composites and Bayesian Optimization Taishan Zhu, Giuseppe Romano and Jeffrey C. Grossman; Massachusetts Institute of Technology, United States

Structural defects have become a primary driver for materials design in thermoelectrics and (opto-)electronics, but the understanding of correlated disorder and their effects on material properties is still incomplete. In this work, we theoretically study the effects of correlated disorder on lattice conduction, taking graphene-hexagonal boron nitride...
composites as our model system. While the kinetic theory suggests that the effective conductivity is independent of structural correlation, our non-equilibrium Green’s function analysis and Green-Kubo formalism implemented within molecular dynamics simulations both show a strong dependence on the correlation functional, which we propose as a new designing degree of freedom viewing all defects collectively. Among all functionals considered, we show that a hyperuniform distribution of defects leads to the highest conductivity, while the Cauchy and Dagum correlation functions give conductivities as low as amorphous limit. Our spectral analysis shows the preservation of long-wavelength modes in the former, while the latter approach the amorphous limit where phonon concepts are no longer invalid. Aiming at thermoelectric applications, we apply Bayesian learning techniques to minimize the thermal conductivity at a given defect density, which could be extended to thermoelectric optimization with constraints in electrical properties.

4:45 PM EN14.04.05
First Principles Investigation of Anomalous Pressure Dependent Thermal Conductivity of Chalcopyrites Loay A. Abdelhafiz; RWTH Aachen, Germany

The effect of compression on the thermal conductivity of CuGaS₂, CuInS₂, CuInTe₂, and AgInTe₂ chalcopyrites (space group I-42d) was studied at 300 K using phonon calculations. The lattice thermal conductivity (κₚ) was evaluated by solving the Boltzmann transport equation with harmonic and third-order force constants. Striking differences are obtained between the κₚ behavior of CuGaS₂, CuInS₂, CuInTe₂, and AgInTe₂ under compression. The κₚ value of CuGaS₂ always increases with pressure up to 9.5 GPa. A drastically different functional dependence is obtained as soon as heavier In is considered instead of Ga (BIII in AIBIIICVI₂). Under pressure up to 6 GPa, κₚ of CuInTe₂ decreases from 7.6 to 4.1 W m⁻¹ K⁻¹, which is anomalous. This is consistent with the experimental data [1,2], implying that important physics is captured within the methodology employed herein and structural modulations are not indispensable to drive the anomaly. By exchanging Te with lighter S (CVI in AIBIIICVI₂) and hence forming CuInS₂, κₚ increases up to 2 GPa, which is again a common behavior and equivalent to that of CuGaS₂. Upon a further pressure increase, κₚ begins to decrease and reaches a slightly lower value at 8 GPa than that at 0 GPa. To account for the effect of the transition metal constituent (Al in AIBIIICVI₂), Cu in CuInTe₂ is exchanged with heavier Ag. AgInTe₂ exhibits a significantly lower κₚ value and a steeper decrease in κₚ under pressure, reaching 0.2 W m⁻¹ K⁻¹ at 2.6 GPa.

Using the Slack model, Gui et al. [3] have showed that the Thermoelectric Figure of Merit for CuInCVI₂ (CVI = S, Se, and Te) uniformly increases at elevated temperatures up to 850 K. However, the effect of pressure on κ has not thoroughly been studied. Using the quasi-harmonic Debye model, Sharma et al. have evaluated electronic, thermal, and mechanical properties of AgInCVI₂ (CVI = S, Se, and Te) under pressure and reported a noticeable reduction in the Grüneisen parameter and volumetric thermal expansion coefficient as well as bulk modulus [4]. Since the Grüneisen parameter and volumetric thermal expansion coefficient can be related to κ, it appears that pressure effects on κ are considerable. This is consistent with an experimental study reporting a decrease in κ by 30% for CuInTe₂ under pressure up to 2.3 GPa [1]. Generally, κ should increase under compression [5]. This implies that the behavior of CuInTe₂ is anomalous. Two possible mechanisms have been proposed based on experiments: (i) anharmonic behavior of lattice vibrations [1] and (ii) structural modifications under high pressure (e.g. stacking faults) [2]. The underlying physics of the κ reduction under compression of CuInTe₂ and possibly other AIBIIICVI₂ compounds is not fully understood.

This can be understood based on the phonon dispersion curves. Softening of the acoustic phonon modes occurs for these anomalous chalcopyrites. This leads to the negative Grüneisen parameter and negative volumetric thermal expansion coefficient. The decrease in phonon frequency upon compression is suggested to be due to the phonon oscillations in the form of a rotational motion rather than compressive waves. The physical origin of the anomalous thermal conductivity is thus identified in this work and AgInTe₂ with a very low thermal conductivity of 0.2 W m⁻¹ K⁻¹ at 2.6 GPa is proposed to be a promising thermoelectric compound.

Reference:
EN14.05.01
High and Low Thermal Conductivity Phase Boundary in SrTiO$_3$–SrNbO$_3$ Solid-Solution System Yuqiao Zhang$^1$, Hai Jun Cho$^1$, Kenyu Sugo$^1$, Masashi Mikami$^2$, Sungmin Woo$^3$, Myung-Chul Jung$^4$, Woosuck Shin$^2$, Woo Seok Choi$^2$, Myung Joon Han$^4$ and Hiromichi Ohta$^1$; $^1$Hokkaido University, Japan; $^2$National Institute of Advanced Industrial Science and Technology, Japan; $^3$Sungkyunkwan University, Korea (the Republic of); $^4$Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Electron-doped strontium titanate (SrTiO$_3$) is one of the candidate materials of thermoelectrics. In order to increase the carrier electron in SrTiO$_3$, usually, a part of Ti ions are substituted by Nb ions or a part of Sr ions are substituted by La ions. Although many researches on the electrical conductivity and thermopower of Nb or La-doped SrTiO$_3$ and Nb or La-doped SrTiO$_3$-based superlattices have been done thus far$^{[1,2]}$, there are only a few researches on the thermal conductivity because of the low solubility limit of dopant ions in SrTiO$_3$ bulk. Recently, we successfully fabricated SrTi$_{1-x}$Nb$_x$O$_3$ ($0 \leq x \leq 1$, STNO)$^{[1]}$ and Sr$_{1-x}$La$_x$TiO$_3$ ($0 \leq x \leq 1$, SLTO) full-range solid-solutions by PLD and found the anomalous behaviour of the electron transport properties. Since thermal conductivity is strongly correlated with the electron transport properties, we studied the thermal conductivity of the solid-solutions. Here we report high and low thermal conductivity phase boundary in SrTiO$_3$–SrNbO$_3$ solid-solution system. The $x$-dependent thermal conductivities ($\kappa$) of STNO and SLTO were measured by time-domain thermoreflectance (TDTR) method at room temperature. Steep increase in $\kappa$ was observed around $x \sim 0.5$ for STNO, suggesting the existence of a phase transition. However, in SLTO case, all the samples show a $\kappa$ at lower levels compared with SrTiO$_3$ single crystals, where no special behavior was observed. We attributed this special behavior to the polaron effect which only exists in STNO at $x \leq 0.5$ and SLTO and suppresses the $\kappa$. Furthermore, unlike the traditional alloy systems, SrNbO$_3$ with larger average atomic mass shows much higher $\kappa$ than SrTiO$_3$. According to the phonon dispersion calculations, the phonon transport of SrTiO$_3$ shows much more intense scattering between optical and acoustic branches than SrNbO$_3$, which is likely to suppress phonon mean free path for SrTiO$_3$. The Grüneisen parameters of SrTiO$_3$ were much higher than those of SrNbO$_3$, which also will reduce the phonon transport properties. Our findings revealed important role of polaron in heat transport for system with strong electron-phonon couplings, which will be a fundamental contribution to the current knowledge in heat transportation and may be utilized to develop new thermoelectric materials.

References

EN14.05.02
Enhanced Thermoelectric Efficiency in $n$-Type Ga-Doped PbTe via Asymmetrical Phase Boundary Mapping Ping-Yuan Deng$^1$, Yi-hui Du$^2$ and Hsin-Jay Wu$^3$; $^1$National Chiao Tung University, Taiwan; $^2$National Tsing Hua University, Taiwan

Lead-tellurides are important mid-temperature thermoelectric (TE) materials. Nevertheless, the moderate $zT$ of $n$-type PbTe limits the development of mid-temperature TE generator. Gallium (Ga) has been a successful $n$-type dopant for PbTe through contributing extrinsic carriers and optimizing the carrier concentration. In this study, the isothermal section of ternary Ga-Pb-Te is determined by various post-annealed alloys. In particular, the single-phase PbTe region could only tolerate a very small amount of Ga, and that single-phase region shows an asymmetrical homogeneity in the ternary Ga-Pb-Te. The combination between TE properties and phase diagram provided a better understanding in the dopant capability, which makes it serves as a crucial guideline for searching the high-efficient alloys where the compositional regions are seldom being explored before. With an as-determined isothermal section in hand as a map, the selective Ga-doped PbTe alloys are grown through the Bridgman method. In the temperature range of 550 K-673 K, an average $z$Tave value $\sim1.21$ (peak $zT$ $\sim1.5$) could be achieved in the Ga-PbTe alloy with the existence of nano-scale strain field.
Thermoelectric (TE) materials convert energy from waste heat into electricity and have been used, e.g., to charge batteries and for refrigeration. Thermoelectric properties are characterized by a figure of merit ($ZT$), $ZT = S^2 \sigma T/k$. $S$ is the Seebeck coefficient, $k$ the thermal conductivity, $\sigma$ the electrical conductivity, and $T$ temperature. This investigation reports respective properties of lead ruthenate Pb$_2$Ru$_2$O$_{6.5}$ and some derivatives. Lead ruthenate has a defect pyrochlore crystal structure. Molar fractions of Ru have been substituted by Pb, using the formula of Pb$_{2+y}$Ru$_{2-y}$O$_{6.5}$ with $y$ increasing from 0 to 0.9. All samples were prepared by solid-state synthesis and characterized by XRF, X-ray diffraction, SEM/EDX, for composition, structure and phase content. Thermal conductivity, electrical conductivity, the Seebeck coefficient and the $ZT$ values will be reported as a function of temperature (room temperature to 300°C) and stoichiometry.

Bulk Nanostructured Calcium Cobalt Oxide Ceramics—A Step towards Significant Enhancement in Thermoelectric Power Factor

Here, the calcium carbonate (CaCO$_3$) and cobalt oxide (Co$_3$O$_4$) in stoichiometric ratio of 3:4:9 for Ca, Co, and O are mixed using high energy ball milling (HEBM), processed for optimized time duration of 48 h followed by drying on hot plate, and calcined at 1123 K for 6 h to achieve Ca$_3$Co$_4$O$_9$ (CCO) powders. The resulting as-synthesized CCO powder was further ball-milled for 2, 6, 12, and 24 h and the FESEM images indicates of nanostructure formation after HEBM for 24 h. The hot-pressed pellets (HPPs) of bulk and nano-powders of CCO are prepared by placing the respective powders in a graphite die, heating the die to 1173 K inside a vacuum chamber, and applying a continuous pressure of 200 MPa for 15-20 mins. These processing parameters (pressure and temperature) are optimized to obtain pure, fully dense (99.2 ± 0.5%), and thermally stable pellets. The microscopic, crystallographic, thermal, and spectroscopic analysis suggest samples processed with longer HEBM time require less time for calcination during synthesis of highly pure crystalline phases of CCO.

The X-ray diffraction (XRD) patterns of all the CCO powders shows the signature (002) plane at ~16.5° along with other peaks and is in well-correlation with JCPDS #00-023-0110 assigned for CCO, consisting of alternate stacking sub-systems of rock-salt-type [Ca$_2$CoO$_3$] layers sandwiched between two hexagonal [CoO$_2$] layers along c-axis. However, XRD signals from both the pellets, B-HPP and N-HPP show peaks for (00$l$) crystallographic planes of CCO. The disappearance of other diffraction (hk$l$) planes corresponding to CCO crystal structure could be attributed to recrystallization and formation of textured growth due to simultaneous application of high temperature and pressure. The degree of orientation of crystallographic planes in the HPPs is evaluated by calculating the Lotgering factor (LF) for the perfectly oriented HPP samples (B-HPP and N-HPP) and their respective randomly oriented CCO powders. The estimated value of LF=1 supports the appearance of ideally aligned (00$l$) crystallographic planes of CCO and indicates achievement of texturing in B-HPP and N-HPP and further confirmed through FESEM.

The significant improvement of ~11 times in PF at 770 K for bulk nanostructured CCO (64.2 $10^{-3}$ Wm$^{-1}$K$^{-2}$) ceramics compared to the HPPs of as-synthesized CCO microstructures (5.8 $10^{-3}$ Wm$^{-1}$K$^{-2}$) is attributed to the enhancement in $S$ triggered due to oxygen vacancies and structural deformations developed during HP process along with introduction of enlarged interface area at grain boundaries. This concept of structural modulation could be adopted for understanding the TE properties in other nanostructured materials as well. The currently prepared bulk nanostructured CCO could be further utilised commercially for mass scale production.
Quantification of Uncertainty in the Lattice Thermal Conductivity of Thermoelectric Materials from a First-Principles Prediction Method

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Phonon transports in thermoelectric materials are affected by various different factors. One of these factors is the electron-phonon coupling phenomenon, which serves as a scattering source not only to charge carriers but also to heat-conducting phonons, especially in highly-doped thermoelectric materials.

We propose a relatively simple numerical method for estimating lattice thermal conductivity, including the effect of the electron-phonon coupling phenomenon, and present statistical approaches for quantifying the uncertainty in the predicted values. The method employs a formulation similar to that of the EPA (electron-phonon averaged) method. The electron-phonon coupling matrix elements, which are explicitly dependent on the momentum of charge carriers and that of scattering phonons, are approximated as a function of two energies only. At the same time, the energy levels of the involved electron bands are averaged over the Brillouin zone. These simplifications enable us to estimate the effect of the electron-phonon coupling phenomenon in phonon transports. We also demonstrate that the quantification of uncertainty in the predicted values can also be carried out by using statistical techniques like Gaussian process regression (GPR) and empirical bootstrapping, within our proposed method.

EN14.05.07

Effect of Heavy Doping of Aliovalent Cations on Structure and Thermoelectric Properties of NiO-Based Epitaxial Thin Films

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Thermoelectric oxide semiconductor thin films contribute to development of conversion devices due to their thermal and chemical stability in a wide temperature range, and property modification derived by to quantum effect[1]. Nickel oxide (NiO) thin films with rocksalt-type crystal structure has also been researched as an p-type semiconductor for thermoelectric sensors, though layered cobalt oxides have acquired interests for the thermoelectric conversion[2,3]. The p-type conductivity of NiO thin films has been modified by doping heterovalent cations such as Li+ (~10 atm%), and by epitaxial synthesis which improves the carrier mobility owing to structural consistency[4]. Reduction of the epitaxy temperature contributes to development of multilayered thermoelectric devices by surface and interfacial flatness, and homogeneous crystallites boundary as phonon scattering sites. Furthermore, low-temperature epitaxial growth allows extraordinarily high doping ratio because of the suppressed re-evaporation and phase segregation, which results in generation of charge carriers associated with local strain. In this study, epitaxial NiO thin films heavily doped with monovalent or trivalent ions, e.g. M=Li and Fe, were grown as Ni1-xMxO (0≤x≤0.7) solid-solution oxide semiconductor at room-temperature, and the effect of dopant ratio on local structure and thermoelectric properties were investigated.

The thin films were grown on atomically stepped α-Al2O3 (0001) substrates by laser molecular beam epitaxy (Laser-MBE) technique equipped with KrF excimer laser (κ=248 nm, d=20 ns, E~1.5 J/cm2) and NiO–Li2O or NiO–Fe2O3 targets. The growth took place in ultra-high vacuum to 10−3 Pa of O2 at room-temperature. As a result, the epitaxial growth of both Ni1-xLi,xO (111) and Ni1-xFe,xO (111) thin films with ultra-flat surface well reflecting morphology of the substrates was obtained. The remained rocksalt-type crystal structure of NiO and expansion of d$_{111}$-spacing along the increased doping ratio up to x=0.5 suggested substitution of Ni2+ with the dopants. The epitaxial thin films demonstrated semiconducting behavior at low-temperature (15—293 K), that electric resistivity decreased along the raised doping ratio (0≤x≤0.6) for either dopants of Li and Fe. The electric conductivity of Ni1-xLi,xO and Ni1-xFe,xO epitaxial thin films at room-temperature were ~3.3×102 Sm−1and ~5.3×101 Sm−1, which properties improved to ~5.0×103 Sm−1 and ~2.9×103 Sm−1 at 493 K, respectively. The Ni1-xLi,xO film demonstrated thermoelectric power factor of ~16 μWm−1K−2 at relatively low-temperature of 593 K, and the Ni1-xFe,xO film revealed negative thermopower which indicated n-type conduction above 493 K. Further detailed structural analyses, and effect of dopant species and ratio on the thermoelectric properties would also be presented.


EN14.05.08

High Temperature Structural and Thermoelectric Study of Argyrodite Ag$_8$GeSe$_6$ Xingchen Shen1,2, Jian He2
Argyrodites with a general chemical formula of \( A_8BX_6 \) (\( A = \text{Cu, Ag}; B = \text{Si, Ge, Sn}; \) and \( X = \text{S, Se, and Te} \)) are known for the intimate interplay among mobile ions, electrons, and phonons, which yields rich material physics and materials chemistry phenomena. In particular, the coexistence of fast ionic conduction and promising thermoelectric performance in \( \text{Ag}_8\text{GeTe}_6, \text{Ag}_8\text{SnSe}_6, \text{Ag}_8\text{SiTe}_6, \text{Ag}_8\text{SiSe}_6, \text{Cu}_8\text{GeSe}_6 \) at high temperatures ushered us to their chemical neighbor \( \text{Ag}_8\text{GeSe}_6 \), whose high temperature crystal structure and thermoelectric properties are not yet reported. In this work, we have employed a growth-from-the-melt technique followed by hot pressing to prepare polycrystalline \( \text{Ag}_8\text{GeSe}_6 \) samples, on which the crystal structure, micro-morphology, compositional analysis, UV-vis absorption, specific heat, speed of sound, and thermoelectric properties were characterized as a function of the Se-deficiency ratio and temperature. We found \((i)\) the crystal structure of \( \text{Ag}_8\text{GeSe}_6 \) evolved from orthorhombic at room temperature to face center cubic above 410 K, with a region of phase separations in between; \((ii)\) like other Argyrodite 816 phases, \( \text{Ag}_8\text{GeSe}_6 \) exhibited ultralow thermal conductivities over a wide temperature range as the phonon mean free path was down to the order of inter-atomic spacing; and \((iii)\) Varying Se deficiency effectively optimized the carrier concentration and power factor, a figure of merit \( zT \) value \( \approx 0.55 \) was achieved at 923 K in \( \text{Ag}_8\text{GeSe}_{5.88} \). These results not only fill a knowledge gap of \( \text{Ag}_8\text{GeSe}_6 \) but also contribute to a comprehensive understanding of 816 phase Argyrodites at large.

EN14.05.09
Dual Role of the Copper Layer to Integrate Electric and Thermal Transport in BiCuSeO
Bin Wei, Yingcai Zhu, Yongheng Li and Jiawang Hong; Beijing Institute of Technology, China

Reducing the lattice thermal conductivity without simultaneously decreasing the charge transport is a challenge to design high-performance thermoelectric materials. The rattling motion of fillers in cage structures has been verified to effectively reduce the lattice thermal conductivity recently. Here, we propose a rattling motion in layered structures to reduce the lattice thermal conductivity without suppressing the charge transport in a leading thermoelectric material---\( \text{BiCuSeO} \) (BCSO). Using a combination of inelastic x-ray scattering (IXS), inelastic neutron scattering (INS) measurements and first-principles calculations, we identify a Cu-dominated rattling mode, reflected as a low lying flat optic band in BCSO. The present results provide new evidence to clarify the origin of the intrinsic ultralow thermal conductivity of BCSO and pave a path for designing high-performance thermoelectric materials.

EN14.05.10
Dynamic Ag\(^+\)-Intercalation with AgSnSe\(_2\) Nanoprecipitates in Cl-Doped Polycrystalline SnSe\(_2\) toward Ultra-High Thermoelectric Performance
Lei Miao and Chengyan Liu; Guilin University of Electronic Technology, China

Recently, thermoelectric lead-free selenides have attracted great attention due to their earth-abundant, low-cost and environment-friendly characteristics. Here we report a new strategy to simultaneously enhance the electronic transport properties and reduce the thermal conductivity of polycrystalline SnSe\(_2\). By combining weak van der Waals bonding with the mobile behavior of Ag\(^+\) ions, the carrier concentration is optimized over a wide temperature range, which can be attributed to the dynamic Ag\(^+\)-intercalation into the van der Waals gap from the Ag\(^+\) ion reservoir AgSnSe\(_2\). On account of additional electrical bridges between interlayers contributed by the intercalated Ag\(^+\) ions and weak anisotropy, an exciting high power factor of up to 7.46 mW cm\(^{-1}\)K\(^{-2}\) at 789 K is achieved along the pressing direction. In addition, the thermal conductivity is simultaneously reduced to 0.57 W m\(^{-1}\)K\(^{-1}\) at 789 K, owing to numerous line defects, phase interfaces, twin boundaries, dislocation and intercalated atomic layers generated after Ag introduction, as well as the anharmonic vibration of Ag\(^+\) ions. As a result, a record peak \( ZT \) of 1.03 at 789 K is realized along the pressing direction, which is 1.6 times larger than the highest reported value (0.63) of polycrystalline SnSe\(_2\) and even comparable to that of p-type polycrystalline SnSe. This study opens a new way to achieve ultra-high thermoelectric performance, especially in layered materials.

EN14.05.11
The Thermoelectric Properties of Scandium Sesquitelluride
Dean Cheikh\(^1\), Kathleen Lee\(^1\), Wanyue Peng\(^2\), Alexandra Zevalkink\(^2\), Jean-Pierre Fleurial\(^1\) and Sabah Bux\(^1\); \(^1\)Jet Propulsion Laboratory, United States; \(^2\)Michigan State University, United States
Thermoelectric generators (TEG) are solid state heat engines which convert thermal energy to electrical energy. The efficiency of thermoelectric materials is related to Carnot efficiency and a material’s ability to convert heat into electricity. Thermoelectric efficiency is defined by the dimensionless thermoelectric figure-of-merit, $zT$, where $zT = (S^2/\rho\kappa)T$ where low electrical resistivity ($\rho$), high Seebeck coefficient ($S$) and low total thermal conductivity ($\kappa$) are essential for a good thermoelectric materials. Rare earth (RE) tellurides have been studied extensively for use as high-temperature thermoelectric materials, with lanthanum and praseodymium tellurides ($La_{3-x}Te_4$ and $Pr_{3-x}Te_4$) having $zT^*$s = 1.1 and 1.7 at 1273 K, respectively, with optimized carrier concentrations. The high-performance of these compounds warrants further investigation of additional RE tellurides.

While not part of the lanthanide series, scandium is classified as a RE element due to its chemical similarity to other elements of the lanthanide series. However, previous studies of scandium sesquitelluride ($Sc_{2}Te_{3}$) were limited to structural analysis, with the electronic and thermal properties remaining a mystery. In this study, we used a mechanochemical approach to synthesize $Sc_{2}Te_{3}$ and formed compacted pellets using spark plasma sintering (SPS). The thermoelectric properties were then measured from room-temperature to 1100 K. It was found to have a high power factor ($S^2/\rho$) at low temperature and a low $\kappa$, leading to a $zT = 0.3$ from 500 – 750 K. Additionally, temperature-dependent resonant ultrasound spectroscopy was utilized to measure the temperature dependent elastic constants and thermal expansion of $Sc_{2}Te_{3}$.

**EN14.05.12**

**High Efficient Thermoelectric pn-Junction Device Based on Bismuth Telluride and Molybdenum Disulfide Films**

Gilbert Kogo, Sangram K. Pradhan, Bo Xiao, Messaoud Bahoura and Makhes K. Behera; Norfolk State University, United States

Layered structure Bi$_2$Te$_3$ and MoS$_2$ thin films were successfully deposited on different substrates using radio-frequency magnetron sputtering technique. Structural, morphological and thermoelectric transport properties of Bi$_2$Te$_3$ and MoS$_2$ thin films have been investigated systematically to fabricate high-efficient thermal energy harvesting TE device. Magnitude of Seebeck coefficient of Bi$_2$Te$_3$ decreases with increase in film thickness. Bi$_2$Te$_3$ grown at 350 °C for 10 minutes which is approximately 120 nm display a maximum value of -126 $\mu$VK$^{-1}$ at 435 K. The performance shows strong temperature dependence when the films were deposited at 300 °C, 350 and 400 °C. Power factor increase from 0.91X10$^{-3}$W/mK$^2$ at 300 K to about 1.4x10$^{-3}$W/mK$^2$ at 350 K. MoS$_2$ films shows positive Seebeck coefficient values. The open-circuit voltage of the pn-junction TEG device increases with increase in $\Delta T$ to about 0.13 V at $\Delta T= 120$ °C. We demonstrated high efficient pn-junction thermoelectric generator device for waste heat recovery applications.

**EN14.05.13**

**Study of Conventional Sintered Cu$_{2-x}$Se Thermoelectric Material via Copper-Vacancy Engineering**

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As the featured material of the superionic thermoelectric (TE) material family, copper-chalcogenide Cu$_{2-x}$Se is attracting growing research interest for its excellent TE performance derived from the satisfactory power factor and the ultra-low thermal conductivity induced by the superionic effect. Various efforts have been made and proved to be effective to further enhance the TE performance for Cu$_{2-x}$Se. However, this material is still far from the application stage, which is mainly due to concerns regarding control of the properties and the costly complex fabrication technology. Here we report a scalable pathway to achieve high-performance and tunable Cu$_{2-x}$Se, utilizing conventional sintering technology and copper (Cu)-vacancy engineering with an effective mass model. The figure of merit $zT$ is a competitive value of 1.0 at 800 K for the optimized binary Cu$_{2-x}$Se, based on the precise modeling prediction and Cu-vacancy engineering. The changes in TE properties of Cu$_{2-x}$Se under heating-cooling cycle tests are also revealed. Our work offers the referable method along with the decent parent material for further enhancement of TE performance, paving a possible route for the application and industrialization of Cu$_{2-x}$Se TE materials.

**EN14.05.14**

**Soluble Sb$_2$Te$_3$ Molecular Precursor for Solution Processing of High-Performance Thermoelectric Thin Film**

Seungki Jo$^1$, Sun Hwa Park$^2$, Seung Hwae Heo$^1$ and Jae Sung Son$^1$; $^1$Ulsan National Institute of Science and
The recent interest in portable and wearable electronics lead flexible thin film thermoelectrics to be regarded as promising candidates for the power supply of self-powered systems. Herein, we report a cost-effective solution process to fabricate flexible Sb\textsubscript{2}Te\textsubscript{3} thermoelectric thin films using molecular Sb\textsubscript{2}Te\textsubscript{3} precursors, synthesized by the reduction of Sb\textsubscript{2}Te\textsubscript{3} powder in ethylenediamine and ethanedithiol with superhydride. This synthetic route decreases the size of the Sb\textsubscript{2}Te\textsubscript{3} precursor to the molecular level, thereby dramatically improving the uniformity and continuity of the thin film. Furthermore, thermally stable FePt nanoparticles are homogeneously embedded in the Sb\textsubscript{2}Te\textsubscript{3} thin film by using the mixed ink solution. The fabricated Sb\textsubscript{2}Te\textsubscript{3} thin films on flexible polyimide substrates exhibit a power factor of of \( \sim 8.5 \, \mu \text{W cm}^{-1} \, \text{K}^2 \) at 423 K. Moreover, such thermoelectric performances of thin films are well preserved during 1000 bending cycles. The current study offers considerable potential for a cost-effective manufacturing for high-performance flexible thin film devices.

**EN14.05.15**

Temperature-Dependent Thermoelectric Properties of Directly Deposited Chalcogenide Films

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Thermoelectric (TE) materials can directly convert heat into electricity. The leading commercialized thermoelectric materials are mainly tellurium (Te) based, despite Te being extremely scarce in the Earth crust as well as highly toxic. Among them, bismuth telluride (Bi\textsubscript{2}Te\textsubscript{3}) based materials show the best efficiencies for near room temperature applications.

First, we measure electrochemically deposited Bi\textsubscript{2}Te\textsubscript{3} films and show that a parallel circuit measurement technique is accurate to measure their temperature dependent Seebeck and electrical conductivity. This is in-line with expected properties for grain sizes and doping levels typical in electrochemical deposition. Next, in order to explore cheaper and less toxic alternative chalcogenide materials, we then perform direct nanoscale patterning of Bi\textsubscript{2}Se\textsubscript{3} using a spin-coatable and electron beam sensitive bismuth selenide resist, tris(N,N-diisobutyl-N’-(benzoylselenoureato))bismuth(III), without the lift-off or etching step. Subsequently, we perform temperature dependent TE characterization. The room temperature electrical resistivity of the film is measured by four probe I-V and is equal to 3400 \( \Omega \) cm. This large value of resistivity is attributed to the pristine nature of the Bi\textsubscript{2}Se\textsubscript{3} as well as to its low thickness (10 nm, as determined by Atomic Force Microscopy). Optimization of the film’s geometry as well as chlorine (Cl) and hafnium (Hf) doping of the Bi\textsubscript{2}Se\textsubscript{3} are ongoing in order to obtain films with enhanced TE performance.

**EN14.05.16**

Rapid Stoichiometry Control in Cu\textsubscript{2}Se Thin Films for Room Temperature Power Factor Improvement

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Cu\textsubscript{2}Se thin films provide a promising route to relatively safe, sustainable and solution processable flexible thermoelectric (TE) modules in contrast to more expensive and toxic materials currently on the market such as Bi\textsubscript{2}Te\textsubscript{3}. Cu\textsubscript{2}Se is known in the thermoelectric community for its high performance at high temperature and has recently attracted attention from its large theoretically predicted figure of merit at room temperature. If the performance can be optimized at room temperature, flexible Cu\textsubscript{2}Se thin films will be the material of choice to utilize in TE modules for powering miniature electronics and sensors, which has been an increasingly popular and rapidly expanding market. Unfortunately, one of the main limitations encountered so far in Cu\textsubscript{2}Se thin films is that the carrier concentrations are not optimized for TE operation after solution processing. In this work, we conduct a comprehensive study of the structural, optical and TE properties of Cu\textsubscript{2}Se thin films and demonstrate that non-optimized carrier concentrations in these films lead to observations of poor performance at room temperature. Through a simple soaking procedure in a Cu\textsuperscript{2+} ion solution for only a few minutes, we demonstrate a 200-300\% increase in power factor. This soaking process pushes the carrier concentration of the Cu\textsubscript{2}Se thin film towards its optimal value for TE operation and marks the highest TE performance for any solution processable Cu\textsubscript{2}Se thin film at room temperature thus far.

**EN14.05.17**
Development of High Quality Na0.5CoO2 Thick Film for a Planar-Shape Thermoelectric Device Akihiro Tsuruta1, Miki Tanaka1, Masashi Mikami1, Yoshiaki Kinemuchi1, Woosuck Shin1, Yoshitake Masuda1 and Ichiro Terasaki2; 1AIST, Japan; 2Nagoya University, Japan

In our project, we are developing a planar-shape mW-class thermoelectric device with thick film thermoelectric materials for the advanced utilization of thermal energy by the recovery of abundant low-temperature and small-scale waste heat. We chose oxides as the thermoelectric material in favor of the high stability and low toxicity, and in particular Na0.5CoO2 as the p-type thermoelectric material. The Na0.5CoO2 thick film was formed by screen printing technique on an alumina substrate, but the simple printing and sintering process caused serious cracking and peeling from the substrate. We have developed the process to obtain a crack-free Na0.5CoO2 thick film with good adhesion to the substrate and its thermoelectric properties have been investigated.

The low chemical reactivity of Na0.5CoO2 and alumina made direct adhesion of the thick film to the substrate difficult. Therefore, we adopted the CuO interlayer to achieve good adhesion. Furthermore, we have found that the slight Co-Cu substitution in Na0.5CoO2 further improves the adhesion of the thick film to the interlayer. On the other hand, NaCl, which have been used as a flux for synthesizing of Na0.5CoO2 crystal, was mixed in Na0.5CoO2 in order to avoid the crack formation during sintering. Since the liquid phase NaCl promoted the sintering of the Na0.5CoO2 thick film, the film was densified and the cracks was removed. Through these developments, the thermoelectric power factor of the Na0.5CoO2 thick film reached 0.30 mW/K²m equivalent to the sintered body (0.31 mW/K²m). We will discuss the mixing effect of NaCl on morphology and properties of Na0.5CoO2 thick film at the presentation.

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EN14.05.18
Engineered Porosity and Thermoelectric Properties in Porous SnSeS Nanosheet Hyun Ju, Hyunwoo Oh, Kwanwoo Kim, Jaehyun Wie, Youjin Kim and Jooheon Kim; Chung-Ang University, Korea (the Republic of)

IV-VI group Tin (Sn) chalcogenide-based nanomaterials (SnSe, SnS, and SnTe) have intensive interest in various research fields because of the unique characteristics distinct from the bulk counterparts. The introduction of a number of pores into the nanomaterials can manipulate their electrical and thermal transport characteristics of a material, which is considered as a promising strategy to improve the transport properties. Herein, we report on that the successful fabrication and optimization of porous SnSeS-based nanosheets and their thermoelectric enhancement. Two-dimensional SnSe0.8S0.2 (SnSeS) nanocrystals are chemically exfoliated from the layered bulk structure through a Li-intercalation and an exfoliation process. A large number of pores are successfully introduced into the SnSeS nanosheets through a solution-phase chemical transformation procedure, and the porosity of the materials can be optimized with different reaction time, resulting in the effective reduction of the thermal conductivity and the enhanced thermoelectric performance. The incorporation of nano and porous structure can boost the research advances regarding nano and porous materials and high-performance thermoelectrics.

EN14.05.19
Improving the Transport Properties of Bi2Te3-xSe_x Alloys by Enhancing the Preferred Orientation via Melt-Spinning Method Omer Meroz and Yaniv Gelbstein; Ben Gurion University of the Negev, Israel

Thermoelectric devices fit power generation applications by converting excess heat, either directly from solar energy or as a byproduct of fuel burn, into electricity. A thermoelectric device is made of both n-type and p-type semiconductors. Bismuth–telluride-based alloys are of great importance not only as the best thermoelectric materials with the maximal ZT values close to unity near room temperature, but also due to the potential for further performance improvement.

The performance of thermoelectric devices is assessed by the dimensionless figure of merit ZT of the material, defined as $ZT = \alpha^2\sigma T/k$, where $\alpha$, $\sigma$, $k$ and $T$ are the Seebeck coefficient, the electrical and thermal conductivities, and the absolute temperature, respectively. The thermal conductivity is a combination of thermal conductivity via electrons, $\kappa_e$, and via phonons, $\kappa_l$. The main difficulty in improvement of the efficiency of a thermoelectric device is due to the complex relation between $\sigma$, $\alpha$ and $k$.

In this study Bi2Te2.4Se0.6 alloys were prepared and examined. The synthesis process included melting ingots via rocking furnace, melt spinning with two different wheel RPMs and hot pressing under optimal conditions. The
samples were characterized in the direction parallel and perpendicular to the pressing direction. The anisotropic properties of the material were maintained throughout the process and a high ZT of 1.06 was achieved at ~65°C.

**EN14.05.20**
**Microstructural Engineering of Sn-Te Eutectic/Near-Eutectic Thermoelectric Alloys** Sireesha P and Shanmukha Kiran Aramanda; Indian Institute of Science Bangalore, India

Conversion of dissipated heat into electricity is the basic principle of thermoelectricity. It has a wide variety of applications in the areas such as automobile engineering, refrigerating coolants, satellite etc. In search of such materials, thermoelectrics has given wide scope to complex materials like Tellurides, Clathrates, Zintl compounds, Half Heusler alloys, Si-Ge, Skutterudite etc. The defining factor for thermoelectric materials is ZT, thermoelectric figure of merit. This attributes to the power factor (P=σS², σ-electrical conductivity S-Seebeck coefficient) enhancement and thermal conductivity reduction. Bandgap tuning, carrier concentration are a few ways to improve power factor whereas, in parallel, grain size reduction, point defects, dislocations are key ways to thermal conductivity reduction. These can be achieved experimentally through microstructural engineering and processing. The issues existing with available thermoelectric materials are associated with the stability of performance for a long range of temperatures. Fine tuning of the microstructure is the key factor in overcoming thermal stability issues.

Currently, we are exploring a program of microstructure-transport properties correlation of newly processed thermoelectric alloys by fine-tuning the eutectic microstructure. In this current work, we have synthesized a set of thermoelectric alloys which are eutectic and near-eutectic compositions in Sn-Te system. The microstructure of these alloys shows microstructure consisting of SnTe and Te phases. We varied the morphology, orientation, fraction, spacing of the eutectic phases (SnTe and Te) using different processing conditions. Variations of transport properties with respect to different processing conditions have also been studied. Third component additions with various at% to Eutectic microstructure has been studied. To these alloys, the effect of **Directional solidification** has been studied and has improved TE properties significantly.

The elemental distribution mapping and the compositional analysis using electron probe microanalysis (WDS), demonstrates that the matrix is rich in tellurium and the continuous phase has the composition of Sn50Te50 (at%). Transport properties of the current alloy are attractive in terms of standard thermoelectric material. Further elemental additions have enhanced properties. They were directionally solidified at various speeds and TE properties were studied with microstructural modification. The detailed microstructure-transport properties correlation will be presented.

**Acknowledgement:** The authors would like to acknowledge the facility of the AFMM.

**References:**

**EN14.05.21**
**Defect Formation Mechanism in Thermoelectric SnSe Structure Employing Atomic-Resolution Transmission Electron Microscope** YongKyu Lee¹², Sung-Pyo Cho¹² and In Chung¹²; ¹Institute for Basic Science, Korea (the Republic of); ²Seoul National University, Korea (the Republic of); ³National Center for Inter-University Research Facilities, Seoul National University, Korea (the Republic of)

Exceptionally high thermoelectric figure of merit $ZT$ of $-2.6$ at $923$ K for p-type and $-2.8$ at $773$ K for n-type were reported in the single crystalline form of SnSe along the crystallographic b-axis and a-axis respectively. Due to its undesirable mechanical properties and strict demands of crystal growth conditions, its polycrystalline counterparts have been extensively investigated as an alternative. However, polycrystalline SnSe has poor thermoelectric performances with higher total thermal conductivity than single crystals.

Defects such as point defects, nanoprecipitates and dislocations can significantly affect charge and phonon transport behavior. Accordingly, defect engineering has been a proven tool to control charge-carrier and thermal transport properties of thermoelectric materials. However, its formation mechanism at the atomic level has not been fully understood. In this presentation, we synthesized new SnSe materials involving a high degree of vacancy to induce
dense dislocations in the SnSe matrix. We traced the formation of atomic defects and edge dislocations with respect to annealing temperature at near the phase transition temperature employing spherical aberration corrected transmission electron microscope.

As a result of induced defect structure in SnSe, the resulting polycrystalline samples exhibit remarkably high power factor with a maximum of 6.3 μW cm⁻¹K⁻² at 800 K and substantially suppressed thermal conductivity. They synergistically contribute to remarkably high thermoelectric figure of merit over 2.0 at 800 K.

EN14.05.22
Dual-Beam Pulsed Laser Deposition of Diamond-like Carbon Added Bi-Sb-Te Based Nanocomposite Films with Enhanced Thermoelectric Performance Cheng-Chao Liu, Chih-Chuan Su, Po-Hung Chen and Chun-Hua Chen; National Chiao Tung University, Taiwan

The introduction of heterogeneous dopants could not only selectively improve intrinsically-poor specific properties of the base materials but potentially break the physically coupled thermoelectric properties due to the created various functional interfaces for further enhancing the overall thermoelectric figure of merit (ZT) [1]. In this work, a series of novel heterogeneous nanocomposite films comprising amorphous carbon materials (a-C) and BiₓSb₂ₓTe₃ (BST) were successfully deposited on SiO₂/Si substrates using a dual-beam pulsed-laser deposition system. BST and pyrolytic carbon targets were individually ablated for fabricating the a-C/BST films with different a-C contents (0~20 wt%). The highest Seebeck coefficient of the a-C/BST film (4 wt% a-C) was found to approach 650 μVK⁻¹ which is over three times higher than that for intrinsic BST. According to Pisarenko plot, the significantly enhanced Seebeck coefficient originated from the a-C/BST hetero-interfaces induced energy filtering effect. Besides, the significantly suppressed thermal transport as evidenced by micro-Raman and thermal diffusivity characterizations reasonably came from the grain refining of BST and the intrinsically low thermal conductivity of a-C. To further adjust the preferential orientation and interfacial structure, the laser energy ratio for providing the highest Seebeck coefficient was maintained for film preparation with a higher deposition temperature of 450 °C and 500 °C. It was found that preferential orientation gradually shifted from (015) to (00l) with temperature increasing. Besides, the TEM images attested high-density and strongly oriented twin bands almost across the whole BST flake-like structure, clearly indicate the potential for scattering multi-wavelength phonons and further decreasing the thermal conductivity, without substantially interfering the carrier transportation. An enhanced Seebeck coefficient of 620 μVK⁻¹ and the corresponding power factor of ~40 μWcm⁻¹K⁻² obtained from the a-C/BST film prepared at 450 °C (4 wt% a-C) are comparable to or higher than previously reported values of BST or Bi-Sb-Te-based nanocomposites.


EN14.05.23
A Descriptive Model of Thermoelectric Transport in a Resonant System of PbSe Doped with Tl Zhenyu Pan and Heng Wang; Illinois Institute of Technology, United States

Thermoelectric properties are governed by classic Boltzmann transport equations. This often sets limits for how much each material can be optimized for thermoelectric application. The resonant effect from dopants in certain systems presents one of a few successful strategies to work outside this classic limit. Using PbSe co-doped with Tl and Na as a platform, we have presented a method to describe the influence of resonant levels on thermoelectric properties at room temperature and above. We showed (and modeled) the impact of resonant levels on the Seebeck coefficient and mobility at different temperatures, which, especially for mobility, has not been shown before. In general, resonant dopants are not always beneficial for thermoelectric properties overall. This is because the enhanced Seebeck coefficient comes at the price of mobility reduction. Three parameters, namely the resonant level position E_res, the width of resonant levels G, and the percentage of participating resonant levels H, determine the observed transport properties. Among them E_res is crucial in deciding whether the resonant levels are beneficial (in terms of peak zT). Resonant levels could increase zT if E_res is inside the band but very close to the band edge. Our model also confirmed that it is possible to achieve moderate improvement of performance with resonant levels in systems similar to PbSe. This work could help the rational use of resonant levels to their full potential for thermoelectric materials.

EN14.05.24
Lead-Free Hybrid Perovskite Thin Film for Thermoelectric Applications Luyao Zheng, Yifan Li, Jiahua Zhu
In this work, we have investigated the thermoelectric properties of formamidinium tin iodide (FASnI3), lead-free hybrid perovskite, in terms of electrical conductivity, Seebeck coefficient and thermal conductivity. By doping with small amount of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ), both electrical conductivity and Seebeck coefficient of solution-processed FASnI3 thin film are substantially improved, resulting in enhancement on overall thermoelectric performance. The optimal FASnI thin film with 0.05 mg/mL of F4-TCNQ doping exhibits higher electron/hole mobilities and lower trap densities with finely modified thin film morphology by F4-TCNQ. An ultralow thermal conductivity (~0.45 W m⁻¹ K⁻¹) is found in FASnI3 thin film by estimation based on quantitative scanning thermal microscopy (SThM). The thermoelectric figure of merit, value, of optimal FASnI3 thin film is enhanced to be 0.085 at room temperature, which is almost 10 times of pristine FASnI3. Our findings open a door for realizing room-temperature-operated thermoelectric applications by low-cost processing of less-toxic hybrid perovskite materials.

EN14.05.25
Thermoelectric Properties of All-Inorganic Perovskite Semiconductor CsSnBr₃

Yingyue Zhang, Jiangchao Qian and Qixi Mi; ShanghaiTech University, China

Thermoelectric materials have consistently been the focus of research efforts for energy conversion and harvesting. In recent years, organic-inorganic hybrid perovskite materials started to draw attention for thermoelectric applications, thanks to their low thermal conductivity and high Seebeck coefficient. Compared with the organic-inorganic hybrid perovskite materials, especially lead-based perovskites, the all-inorganic perovskite CsSnBr₃ is advantageous for its low toxicity, relative thermal stability, and higher electrical conductivity. In this work, we grew cubic CsSnBr₃ single crystals about 8 mm in size from ethylene glycol solutions, and measured its electrical conductivity to be ~64 S/m and p-type carrier concentration to be 10¹⁷–10¹⁸ cm⁻³ at room temperature. Its Seebeck coefficient increases steadily from ~400 μV/K at 325 K to ~700 μV/K at 575 K, while its thermal conductivity drops from 0.50 to 0.25 W/mK in the same temperature range. In summary, the highest figure-of-merit ZT that we recorded for single-crystal CsSnBr₃ is ~0.067 at 572 K, with a power factor (PF) of ~34 μW/(mK²). The electrical conductivity as well as ZT value can be further enhanced by heavy doping or replacing Br by I in CsSnBr₃.

SESSION EN14.06: Zintl Thermoelectrics

Session Chair: Eric Toberer
Tuesday Morning, December 3, 2019
Sheraton, 3rd Floor, Gardner AB

8:00 AM *EN14.06.01
Structural Complexity and High Thermoelectric Performance of the Zintl Phase: Yb₂₁Mn₂Sb₁₈

Allan He¹, Sabah Bux², Davide Donadio¹ and Susan M. Kauzlarich¹; ¹University of California, Davis, United States; ²Jet Propulsion Laboratory, United States

The family of ternary Zintl phases with the 21-4-18 composition has several different structure types and has been explored for their electronic and magnetic properties. Yb₂₁Mn₂Sb₁₈ adds a new composition to this class of Zintl phases, crystallizing in the alpha-Ca₂₁Mn₄Sb₁₈ structure type (monoclinic, space group C2/c). The expected low thermal conductivity, due to the large primitive unit cell, and potentially high Seebeck, because of the significant number of states at the Fermi level, make this phase of interest for its thermoelectric properties. The complex crystal structure has been studied through synchrotron powder x-ray diffraction, single crystal x-ray diffraction and pair distribution function analysis using time-of-flight neutron diffraction that reveal positional disorder on several sites. The electrical and thermal transport properties show that the high efficiency of Yb₂₁Mn₂Sb₁₈ results from its large Seebeck coefficient (~290 μV/K at 650K) and extremely low thermal conductivity (~0.5 W/(mK) at room temperature). The optimum hole carrier concentration was tuned according to a single parabolic band model through Na doping which has improved ZT over all temperature ranges compared to the parent compound yielding a maximum ZT ≈ 0.8 at 800K, fairly high performance in the mid-to-high temperature regime. Electronic structure
Intermetallic compound of Mg$_2$Si and its solid solutions are promising thermoelectric materials since they exhibit high thermoelectric performance and consist of eco-friendly elements. In these materials, two types of Mg-related point defects (Mg vacancies and interstitial Mg atoms), as well as dopant elements, have significant influence on the carrier concentration \( n \) and resulting thermoelectric properties \[1\]. For example, Mg vacancies compensate the carrier from the dopant in heavily Sb-doped Mg$_2$Si (Mg$_{2-x}$Si$_x$Sb$_y$) \[2\], where a decrease in the Mg content of 0.01 corresponds to a decrease in \( n \) of ca. \( 3 \times 10^{20} \text{ cm}^{-3} \). While the carrier concentration is very sensitive to the Mg content, its precise control has not been achieved because of the high vapor pressure of Mg.

Here, we have developed a new approach, Mg-pressure-controlled annealing \[3,4\], to achieve the precise control of the Mg content for ternary and quaternary Mg$_2$Si-based materials (Mg$_{2-x}$Si$_x$Sb$_y$ and Mg$_{2-x}$Si$_x$Sb$_y$)$_{1-x}$Sn$_x$). Annealing under low and high Mg partial pressures (0.1 and 10 Pa) leads to low and high carrier concentrations (e.g. \( 1.4 \times 10^{20} \text{ and } 6.3 \times 10^{20} \text{ cm}^{-3} \) for Mg$_{2-x}$Si$_{0.90}$Sb$_{0.10}$, respectively). The change in \( n \) is reversible and attributed to an equilibrium reaction, where the Mg vacancies in the sample are partly filled by Mg atoms in the gas phase. In addition, annealing under an intermediate Mg partial pressure (2 Pa) results in an intermediate value of \( n \) (e.g. \( 4.1 \times 10^{20} \text{ cm}^{-3} \) for Mg$_{2-x}$Si$_{0.90}$Sb$_{0.10}$), suggesting that the Mg content in Mg$_2$Si-based materials can be tailored via the Mg-pressure-controlled annealing.

The variable range of \( n \) (\( \Delta n \)) due to the Mg non-stoichiometry in Mg$_{2-x}$Si$_x$Sb$_y$ depends on the Sb content and the maximum \( \Delta n \) of \( 4.9 \times 10^{20} \text{ cm}^{-3} \) is obtained at \( x = 0.10 \). The same \( x \)-dependence of \( \Delta n \) is also observed for the quaternary compound Mg$_{2-x}$Si$_x$Sb$_y$(Si$_{0.5}$Sn$_{0.5}$)$_{1-x}$Sb$_y$, where \( \Delta n \) at \( x = 0.10 \) is \( 3.5 \times 10^{20} \text{ cm}^{-3} \). In the case of Mg$_{2-x}$Si$_x$Sb$_y$(Si$_{0.5}$Sn$_{0.5}$)$_{1-x}$Sb$_y$, the high value of \( n \) due to Mg-rich composition suppresses the bipolar diffusion, which decreases the Seebeck coefficient and increases the thermal conductivity, at high temperatures. Owing to the suppression of the bipolar diffusion, Mg$_{2-x}$Si$_x$Sb$_y$(Si$_{0.5}$Sn$_{0.5}$)$_{1-x}$Sb$_y$ shows \( zT \) value of 0.9 at 773 K at Mg-rich composition whereas \( zT \) value of 0.6 is obtained at Mg-poor composition.

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8:45 AM EN14.06.03
Evidence for Pronounced Influence of Guest Atoms on Anharmonicity in Intermetallic Clathrates Matt Beekman$^1$, James Kaduk$^{2,3}$, Winnie Wong-Ng$^4$, Antti Karttunen$^5$ and George S. Nolas$^6$; $^1$California Polytechnic State University, United States; $^2$Illinois Institute of Technology, United States; $^3$North Central College, United States; $^4$National Institute of Standards and Technology, United States; $^5$Aalto University, Finland; $^6$University of South Florida, United States

The detailed understanding of the mechanism(s) responsible for the very low and sometimes even glass-like lattice thermal conductivity in thermoelectric clathrates continues to develop. Of particular interest is the role of the guest atoms and the unique features of the structure of these materials. Despite a wide variety of novel mechanisms proposed over the past two decades to explain the unusual low temperature thermal transport, more recent theoretical and experimental analyses have suggested that phonon-phonon scattering, e.g. 3-phonon Umklapp-like processes, plays an important role in producing the low lattice thermal conductivity in select clathrate compositions, especially at elevated temperatures. We have shown this is supported by the application of a simple model due to Slack, which shows the lattice thermal conductivity values above the Debye temperature can be predicted relatively well assuming only 3-phonon scattering processes involving acoustic phonons, for a large number of clathrate compositions. Furthermore, our studies of thermal expansion using temperature dependent powder and single crystal X-ray diffraction from 20 K to 500 K on Na$_3$Si$_{136}$ clathrates with variable guest content (0 < \( x < 24 \)) reveal the mode averaged Grüneisen parameter increases dramatically by more than a factor of 2 as the guest content increases from...
0 to 100% filling, indicating the guest atoms have a pronounced effect on the anharmonicity of the interatomic interactions. Taken together, all of these results confirm the important role the guest atoms play in significantly influencing the lattice dynamics in these materials, and that anharmonic phonon-phonon scattering may play a leading role in the thermal transport and thermoelectric performance in the clathrates in the temperature range of interest for thermoelectric applications.

9:00 AM EN14.06.05
Development of High Performance Complex Zintl Phases for Thermoelectric Space Power Generation Applications Sabah Bux¹, Giacomo Cerretti¹, Trinh Vo¹, David Uhl¹, Paul Von Allmen¹, Susan M. Kauzlarich² and Jean-Pierre Fleurial¹; ¹Jet Propulsion Laboratory, United States; ²University of California, Davis, United States

Since the 1960s, the state-of-the-art power systems for space applications has typically been based up on either SiGe alloys or PbTe. Although reliable and robust, the thermal to electric conversion efficiency of these systems remains fairly low at only 6.5% with an average thermoelectric figure of merit of about 0.55. A factor of 2 improvements in the thermoelectric conversion efficiency is needed to support future space missions. In recent years, complex Zintl phases such as n-type La₃₄Te₄ and p-type Yb₁₄MnSb₁₁ have emerged as new high efficiency, high temperature thermoelectric materials with peak ZTs of 1.2 at 1275K. The high performance of these materials is attributed to their combination of favorable characteristics such as: semi-metallic behavior due to small band gaps, low glass-like lattice thermal conductivity values due to structural complexity and reasonably large Seebeck values near their peak operating temperatures. However, significant enhancements in material systems such as the Yb₁₄MnSb₁₁ have remained stagnant since its initial discovery in 2010. We will present an overview of recent research efforts at JPL and UC Davis collaborators on thermoelectric properties of new 14-1-11 formulations phases as well their suitability for advanced TE devices.

9:15 AM EN14.06.06
Compositing in Yb₁₄MnSb₁₁ as an Effective Strategy to Improve Thermoelectric Transport Giacomo Cerretti, Sabah Bux and Jean-Pierre Fleurial; NASA Jet Propulsion Laboratory, United States

Composite materials are conceptualized with the intent of obtaining a final material with improved characteristics. In thermoelectrics this has been achieved for organic-inorganic composites where conducting materials embedded in polymeric matrixes improved the thermoelectric properties. A completely different situation is the combination of two inorganic compounds. Although according to several studies a thermoelectric composite cannot have better properties than its constituents, a study from Bergman and Fel (1999) proved that the enhancement of the figure of merit of a composite material is possible under specific conditions. The purpose of this work is to show the effect of Co inclusions on the electronic and thermal property of Yb₁₄MnSb₁₁. Yb₁₄MnSb₁₁, with a zT of about 1.2 at 1200 K, is already the most performing p-type material for high temperature thermoelectric applications. Our intent is to further increase its thermoelectric performance by decoupling the electronic transport properties (σ, S). Even though cobalt is characterized by a metallic electrical conductivity, it shows a relatively high Seebeck coefficient (S ≈ -25 μV/K at 1100 K). Therefore, cobalt inclusions are expected to provide a boost to the electrical conductivity, while affecting only marginally S. At the same time, if the inclusion size can be kept in the nm-μm range, inclusions can act as active phonon scattering centers and hence reduce the lattice thermal conductivity. To verify the validity of our assumptions, we synthesized four samples with different inclusion density (0, 2, 5, 10 vol%). The samples have been chemically, electrically, and thermally characterized and the obtained results will be shown and compared with the baseline of the Jet Propulsion Laboratory for the Yb₁₄MnSb₁₁ ATEC (Advanced ThermoElectric Converter). In the end, the sample with 5vol% cobalt inclusions is the one that showed the best thermoelectric properties achieving a peak zT of 1.6 at 1250K.

9:30 AM EN14.06.07
Enhanced Thermoelectric Performance of Yb Filled CoSb₃ Due to Type-I Clathrates Addition Keshav P. Dabral, Kalpna Rajput and Satish Vitta; Indian Institute of Technology Bombay, India

Filled skutterudites such as Yb-Co₄Sb₁₂ have a high potential for medium temperature thermoelectric energy conversion due to their high power factor. Their high thermal conductivity, however, limits large scale practical application. In order to enhance both power factor and figure-of-merit of Yb filled Co₄Sb₁₂, type-I clathrates and modified type-I clathrates Ba₉Al₁₆Si₃₀ and (DyBa)₉Al₁₆Si₃₀ which also exhibits open cage structure have been added.
The skutterudite and clathrates were synthesized separately by vacuum alloying, and the mixed materials were obtained by hot pressing the requisite amount of powders at 873 K for 10 min and 60 MPa. All the materials, Yb$_{0.3}$Co$_4$Sb$_{12}$, (Ba$_{9}$Al$_{16}$Si$_{30}$)$_x$(Yb$_{0.3}$Co$_4$Sb$_{12}$)$_{100-x}$ and (Ba$_{7.5}$Dy$_{0.5}$Al$_{16}$Si$_{30}$)$_y$(Yb$_{0.4}$Co$_4$Sb$_{12}$)$_{100-y}$ with $x = 2.4$ and $y = 1.2$ wt.% respectively, exhibit a single phase X-ray diffraction pattern corresponding to the skutterudite phase. The X-ray diffraction peaks corresponding to the clathrates are extremely weak due to the small amount present in these materials. All the materials exhibit a negative Seebeck coefficient indicating electrons to be the major charge carriers. The materials with 1 wt.% Dy-modified clathrates addition has the highest Seebeck coefficient at all temperatures and has a peak value of 210 $\mu$V K$^{-1}$ at ~725 K, 15 % higher than Yb$_{0.3}$Co$_4$Sb$_{12}$. The electrical conductivity of this material is lowest compared to other materials, 1150 S cm$^{-1}$ at room temperature, which decreases to ~ 700 S cm$^{-1}$ at 750 K. The high value of Seebeck coefficient coupled with good electrical conductivity results in good power factor of 3.2 mW K$^{-2}$, 25 % increase compared to single filled skutterudite at 650 K. The power factor for $T > 650$ K decreases due to the onset of bipolar conduction. The thermal conductivity of this composite, however, does not decrease significantly compared to Yb$_{0.3}$Co$_4$Sb$_{12}$ indicating that the interfaces between Yb$_{0.3}$Co$_4$Sb$_{12}$ and Ba$_{7.5}$Dy$_{0.5}$Al$_{16}$Si$_{30}$ are band matched for charge transport as well as phonon transport. The figure-of-merit of $y = 1$ wt.% material reaches a value of ~ 0.85 compared to 0.7 for Yb$_{0.3}$Co$_4$Sb$_{12}$ at ~ 750 K, an increase of 20 %.

9:45 AM EN14.06.08
First-Principles Simulation of Mg$_3$Bi$_2$ Thermoelectric Properties Qian Xu$^1$, Weishu Liu$^2$ and Gang Chen$^1$; $^1$Massachusetts Institute of Technology, United States; $^2$Southern University of Science and Technology, China

Mg$_3$Sb$_2$-Mg$_3$Bi$_2$ alloy is recently found to have high performance n-type thermoelectric (TE) properties for low-grade waste heat recovery near room temperature. It rivals current best thermoelectric materials (e.g. Bi$_2$Te$_3$-Bi$_2$Se$_3$ alloy) for thermoelectric performance in the temperature range of 0°C to 250°C and features a higher fracture toughness and lower cost. While previous first-principles studies on Mg$_3$Sb$_2$ and Mg$_3$Bi$_2$ have revealed their complex electronic band structures, the effect of alloying, particularly on the electron transport properties has not been thoroughly understood. In this study, we perform first-principles calculations on Mg$_3$Bi$_2$ to investigate the major scattering mechanisms for both electrons and phonons in this system. Our results can provide guidelines for the design of better materials for low-temperature thermoelectrics.

10:00 AM BREAK

SESSION EN14.07: High Throughput and Machine Learning Approaches to Thermoelectrics
Session Chair: Anubhav Jain
Tuesday Morning, December 3, 2019
Sheraton, 3rd Floor, Gardner AB

10:30 AM *EN14.07.01
On the Dopability of Semiconductors and the Governing Materials Properties Vladan Stevanovic; Colorado School of Mines, United States

To be practical, semiconductors need to be doped; in thermoelectric applications to nearly degenerate levels. However, many materials are not dopable at all, especially those with wide band gaps, while many other exhibit strong preference toward either p- or n-type conductivity, but not both. These doping bottlenecks and doping tendencies are well known but our present understanding of these phenomena is fairly qualitative and phenomenological. In this talk I will describe our recent work dedicated to advancing our understanding of the intrinsic materials properties that govern dopability of semiconductors. This we do by developing an analytic (model) description of the defect formation in semiconductors which allows formulation of rigorous design principles. Our approach, which builds upon the semiconductor defect theory applied to a suitably devised (tight-binding) model system, reveals analytic relationships between intrinsic materials properties and semiconductor dopability, and elucidates the role of previously suggested heuristic descriptors such as the absolute band edge positions and/or the branch point energy. We validate our model against the present state-of-the-art defect calculations as well as experimental data on a number of classic binary semiconductors. Finally, I will discuss the
model extension to more complex chemistries and its utility in large-scale material searches.

11:00 AM EN14.07.02
First-Principles Study of Thermal Conductivity and Thermoelectricity in Magnetic Half-Heusler Alloys
Fumiyuki Ishii, Akihiro Hori, Susumu Minami and Mineo Saito; Kanazawa University, Japan

The thermoelectric effect that is drawing attention from the viewpoint of energy saving is typically the Seebeck effect in which an electromotive force is generated in the same direction as the thermal gradient. In magnetic materials, there is also an anomalous Nernst effect that generates an electromotive force in the direction perpendicular to the thermal gradient due to spontaneous magnetization, and has recently been attracting attention for the improvement of energy conversion efficiency[1]. In each effect, it is important to examine the contribution of thermal conductivity in evaluating the thermoelectric figure of merit ZT that represents the performance of the material. Since the thermal conductivity can be described for each electron and lattice, in this research, we theoretically computed both electronic and lattice thermal conductivity, and then evaluated ZT.

Theoretical analysis of lattice thermal conductivity is conducted by Boltzmann transport theory with relaxation time approximation. In order to do this, it is necessary to determine the inharmonic atomic force constant exactly, and an accurate analysis is carried out by first-principles calculations based on density functional theory. As computational codes, OpenMX[2] is used as a density functional calculation, and ALAMODE[3] is used as a lattice thermal conductivity calculation.

The half-Heusler compounds are ternary compounds, have composition formula of XYZ, and are expected as thermoelectric materials that exhibit high power factor in a medium temperature range of about 600 to 1000 K. In this study, we analyzed thermoelectricity and thermal conductivity of ferromagnetic half-metallic half-Heusler MnCoSb[4]. We evaluated the ZT for the Seebeck and anomalous Nernst effect. We will discuss carrier and temperature dependence of ZT.


11:15 AM *EN14.07.03
Predicting Thermoelectric Transport from First-Principles Electron-Phonon Dynamics Boris Kozinsky1 and Geory Samsonidze2; 1Harvard University, United States; 2Bosch, United States

We develop and investigate fast automated first-principles methods for computing electronic and thermal transport properties of complex semiconductors and low-dimensional quantum materials, without empirically fitted parameters. Using these electron-phonon averaged (EPA) methods we performed screening and discovered new thermoelectric alloy compositions with leading performance and stability. The computational approaches achieve good predictive accuracy and transferability while greatly reducing complexity and computation cost compared to the existing methods. The first-principles calculations of the electron-phonon coupling demonstrate that the energy dependence of the electron relaxation time varies significantly with chemical composition and carrier concentration, suggesting that it is necessary to go beyond the commonly used approximations to screen and optimize materials' composition, carrier concentration, and microstructure. The new methods are verified using high accuracy computations and validated with experimental data before applying it to screen and discover promising compositions in the space of half-Heusler alloys. We discuss the universality of the Wiedemann-Franz law and deviations from it in semiconductors, computing the Lorenz number from first principles.

11:45 AM EN14.07.04
High-Throughput Prediction of Anisotropic Transport Properties and Thermoelectric Performance Prashun Gorai, Robert W. McKinney, Eric S. Toberer and Vladan Stevanovic; Colorado School of Mines, United States

Anisotropic electronic and thermal transport properties can be harnessed to enhance the thermoelectric (TE) performance of materials. There is also a growing interest in exploring the functionality of single crystals, especially of materials with layered motifs, for thermoelectrics. Layered materials often exhibit anisotropic transport properties. Therefore, it is crucial to account for the anisotropy in transport properties in computational searches for TE materials. Traditional computational approaches are expensive and not amenable to high-throughput searches. In
this work, we build upon our intuition from prior semi-empirical models to create a new anisotropic model of carrier mobility by utilizing the elastic stiffness and the conductivity effective mass tensors. Similarly, we extend our prior semi-empirical lattice thermal conductivity model to account for anisotropy by calculating the speed of sound tensor. By combining the models for anisotropic mobility and lattice thermal conductivity, we predict the anisotropic TE performance quantified by the thermoelectric quality factor. We apply these models to predict the TE performance of a large number of layered materials (>2000) and identify candidates with predicted high performance.

SESSION EN14.08: Heusler Thermoelectrics
Session Chair: Sabah Bux
Tuesday Afternoon, December 3, 2019
Sheraton, 3rd Floor, Gardner AB

1:30 PM *EN14.08.01
Magnetic Topological Materials Claudia Felser, Kaustuv Manna and Chenguang Fu; Max Planck Institute, Germany

Topology, a mathematical concept, recently became a hot and truly transdisciplinary topic in condensed matter physics, solid state chemistry and materials science. In magnetic materials the Berry curvature and the classical anomalous Hall and the anomalous Nernst effect helps to identify potentially interesting candidates. As a consequence, the magnetic Heusler compounds have already been identified as Weyl semimetals: for example, Co2YZ, Mn3Sn and Co3Sn2S2. The Anomalous Hall angle also helps to identify materials in which a QAHE should be possible in thin films.

2:00 PM EN14.08.02
Anomalous Reduction of Lattice Thermal Conductivity in Half-Heusler ZrCoSb Ran He1, Zhenhui Liu1,2, Nicolas Perez1, Ulrike Wolff1, Andrei Sotnikov1, Kornelius Nielsch1,2 and Gabi Schiering1; 1Leibniz-Institut für Festkörper- und Werkstoffforschung, Germany; 2Technical University Dresden, Germany

The reduction of lattice thermal conductivity (κ_L) can be realized by introducing large mass contrast through atomic substitution within pristine compounds. Such process are usually termed as “point-defect scattering” and has been proved effective in the improvement of thermoelectric figure-of-merit (zT). Recently we synthesized two sets of half-Heusler compounds: ZrCoSb1-xSnx and Zr1-yTiyCoSb, and compared their lattice thermal conductivity with respect to the substitution level. Contrary to the general conception that larger mass difference are more effective in phonon scattering, we find a much lower κ_L in compounds with Sn substitution at the Sb site than the ones with Ti substitution at the Zr site. The origin of phonon scattering in the Sn-containing compounds will be discussed in great detail based on transport property measurement and microstructure characterization. Our work propose a novel strategy for increasing phonon scattering without large mass contrast so that a high carrier mobility can be preserved.

2:15 PM EN14.08.03
Ultrahigh Intrinsic Thermoelectric Performance, Phase Stability and Defect Energetics of Full-Heusler Compounds Junsoo Park1, Yi Xia2, Anubhav Jain1 and Vidvuds Ozolins3; 1Lawrence Berkeley National Laboratory, United States; 2Northwestern University, United States; 3Yale University, United States

This study shows that ultrahigh bulk thermoelectric performance across all temperatures is physically possible and within reach, and also that pocket multiplicity can hurt at high temperatures when the pockets have disparate scattering rates. Using state-of-the-art ab initio approaches to explicitly treat electron-phonon and phonon-phonon scattering for accurate electronic and phonon transport, we predict that full-Heusler Sr2BiAu and Sr2SbAu are theoretically capable of delivering ultrahigh n-type thermoelectric performance at cryogenic-to-high temperatures: zT=0.3-5.1 at 100-800 K. The feature critical to such high performance is a set of dispersive conduction band pockets, at the L-point in addition to those along Γ-X, for a total of ten. Relative to Ba2BiAu, the additional L-pockets significantly increase the power factor at low temperatures, generating as high as 10 mW m⁻¹ K⁻² at 200 K.
However at high temperatures, because the less dispersive L-states experience much heavier scattering, their existence damages the overall electron lifetime, mobility, and hence the power factor. The dominant intrinsic defect at play in these compounds is Bi/Sb$_{au}$ antisites, which limit their n-dopabilite. Nevertheless, Sr$_2$SbAu potentially has both a large enough stability region and high enough Sb$_{au}$ formation energies to retain some chance at experimental realization as a high-performance thermoelectric.

2:30 PM EN14.08.04
TaIrGe—A p-Type Half-Heusler with Ultra Low Lattice Thermal Conductivity and the Possibility of High ZT
Kieran B. Spooner, Benjamin A. Williamson, Alex M. Ganose, John Buckeridge and David O. Scanlon; University College London, United Kingdom

Thermoelectrics are unique materials which can transform heat into electricity and vice versa. They have applications ranging from renewable energy generation to heating and cooling units. Thus far, however, thermoelectric efficiency remains low, in part because of the contradictory requirements of high electrical conductivity and high Seebeck coefficient coupled with low thermal conductivity. Most TE materials possess small band gaps. A transparent TE that can operate near room temperature was discovered in 2014 [1], and the first inorganic one in 2017. [2,3] The discovery of a high performance transparent, room temperature TE would open up new fields of research in a range of novel applications such as smart windows (or screens) with energy harvesting, cooling and thermal sensing functionalities. Using density functional theory (DFT) with hybrid functionals we have screened the novel p-type transparent half-Heusler TaIrGe [4] for its thermoelectric ability. We will demonstrate that TaIrGe possesses an ultra-low lattice thermal conductivity and has the potential to yield the highest ZT ever for a transparent TE.


2:45 PM EN14.08.05
Thermoelectric Properties of Half-Heusler TaFeSb
Natalya Fedorova, Andrea Cepellotti and Boris Kozinsky; Harvard University, United States

Half-Heusler alloys are among the most promising candidates for applications in thermoelectric power generators, since they are thermally and mechanically robust, do not contain toxic elements and exhibit some of the largest ZT values among bulk systems. In particular, exceptionally high ZT values (1.52 at 973 K) have been recently reported from the experimental measurements of transport properties of TaFeSb-based compounds, following up on theoretical predictions. However, the microscopic origin of such high ZT values in these systems is still not fully understood. In this work we use ab initio calculations to investigate the transport properties of TaFeSb in terms of semiclassical Boltzmann transport equation, beyond the constant relaxation time approximation. We take into account the effects due to electron-phonon interaction by calculating corresponding scattering rates using Wannier-Fourier interpolation of electron-phonon matrix elements as well as the recently developed electron-phonon averaged approximation. We discuss the likely mechanisms of high ZT in TaFeSb-based systems and possible ways to further improvement of these materials.

3:00 PM BREAK

Session Chair: Kedar Hippalgaonkar
Tuesday Afternoon, December 3, 2019
Sheraton, 3rd Floor, Gardner AB

3:30 PM *EN14.09.01
Accelerating the Discovery of Thermoelectric Materials through High-Throughput Synthesis and
Characterization Eric S. Toberer; Colorado School of Mines, United States

Over the last decade, significant effort has been devoted to creating computational predictive frameworks for predicting the thermoelectric performance of materials. Such efforts shine light into reciprocal space, where we often have less chemical intuition, and thus enable the accelerated down-selection of candidate materials. Computational predictions, interrogated by experiment, has revealed new classes of thermoelectric materials, thereby validating this approach as a key tool in the search for thermoelectric materials. However, we now face a new problem: We have more predicted candidates than experimental bandwidth to test these candidates. Further, the expansion of thermoelectric training sets for machine learning remains quite slow. As such, our current efforts are focused on developing the infrastructure to accelerate synthesis and characterization of thermoelectric materials by x50 without significant sacrifices in material or data quality. These efforts are inspired by developments over the last three decades in combinatorial thin film growth, but are focused instead on bulk materials. Efforts to develop high throughput weighing, milling, consolidation, and transport measurements will be discussed in the context of pnictide and chalcogenide thermoelectric materials.

4:00 PM EN14.09.02
Carrier and Thermal Transport in Hierarchically Engineered Superlattice Structures and Their Comparison to Single-Period Superlattices Rama Venkatasubramanian1, Jonathan Pierce1, Meiyong Himmtann1, Geza Dezsi1, John Gaskins2 and Patrick E. Hopkins2; 1Johns Hopkins Applied Physics Lab, United States; 2University of Virginia, United States

In the past, we have developed thin-film P-type Bi2Te3/Sb2Te3 single period superlattice structures [1] with ZT ~2.4 at 300K and N-type Bi2Te3/Bi2Te3-xSex structures, with more modest ZT ~0.7-0.8. These thin-film superlattices have been utilized to demonstrate extraordinarily large (>1000 W/cm2K) heat-pumping in microelectronic devices [2]. There is a need to advance the ZT of N-type materials, in particular, as well as optimize both the P- and N-type materials for the temperature range of 300K to 100K to enable solid state cryogenic cooling devices. In this presentation, we will describe the concept of hierarchically engineered superlattices in thin-film thermoelectrics to improve the ZT of both P-type and N-type materials, to values approaching ~3 and ~2, respectively. We will present the electrical conductivity, Seebeck coefficient and thermal conductivity data in these materials in the 300K-100K range. Additionally, we will delineate the advantages of hierarchically engineered superlattices, as compared to conventional single-period superlattices, for designing efficient cooling down to cryogenic temperatures. The electrical transport of these hierarchically engineered superlattices has been studied by Hall-effect from 300K-77K. Parabolic band is assumed with energy dispersion relation of \( E = \frac{0.5}{h} \left( \frac{h}{2p} \right)^2 k^2 / m^* \) and carrier velocity \( \sim \left( \frac{h}{2p} \right) k / m^* \), with a relaxation time \( \tau (E,T) = \tau_0 (E/kT)^{-1/2} \). This model of transport data suggests that the scattering is dominated by optical phonons \( (T^{-1/2}) \) and less of acoustic phonons \( (T^{-3/2}) \); the hierarchical structuring seems to result in more optical phonon and less acoustic phonon carrier scattering than superlattices, consistent with lower \( K_{\text{attenu}} \) seen with hierarchically engineered nanostructures. The thermal conductivity measurements carried out by time domain thermo reflectance, between 300K and 100K, also indicates the benefit for scattering of a range of heat-conducting phonon wavelengths in such hierarchically engineered superlattices. The ZT advancements obtained with these hierarchically engineered superlattices will be presented along with cooling device advancements.


4:15 PM EN14.09.03
Development of a Full In-Plane zT-Characterization Platform for Electrodeposited Materials Vida Barati1, Javier García2, Kevin Geishendorf3, Lauritz Schnatmann1, Michaela Lammel1, Alexander Kunzmann1, Nicholas Perez Rodriguez1, Guodong Li3, Gabi Schierning1, Jens Freudenberger1, Kornelius Nielsch1 and Heiko Reith1; 1Leibniz Institute for Solid State and Material Research, Germany; 2University of Oviedo, Spain; 3Institute of Physics, China

Thermoelectric (TE) energy harvesting or Peltier cooling devices will be prospectively used in a broad range of applications from industry to consumer products. Successful optimization of the TE figure of merit, \( i.e., zT \), is a key enabler for the introduction of these devices to application. While \( zT \) of bulk materials is accessible by a variety of well-established measurement set-ups that are commercially available, exact determination of \( zT \) for thin and thick films remains a great challenge. This is especially true for thick films grown by the electroplating technique, which is favored for the fabrication of many micro TE devices. In this method the TE material is deposited onto an
electrically conductive seed layer. Such layer causes an in-plane short-circuit that makes the determination of transport coefficients almost impossible. Here, we develop a platform for full in-plane zT characterization of TE materials produced by electroplating technique, eliminating the impact of the electrically conducting seed layer. Such characterization is enabled by using a suspended TE material within a transport device which is prepared by photolithography and etching processes. This full in-plane zT characterization provides an inevitable milestone for a materials optimization under realistic conditions in a micro TE device. In addition, a comparative study is performed between an electrochemical deposited Co75Ni25 film and a bulk ingot with identical composition. The validation of the thermal conductivity measurement is done by Comsol simulation and analytic approach using heat transfer equation with specific boundary conditions dedicated to experimental setup.

4:30 PM EN14.09.04
Tackling Seebeck Coefficient Measurement Challenges with AC Technique Zhenyu Pan1, Fan Yang2, Jeffrey Urban3 and Heng Wang1; 1Illinois Institute of Technology, United States; 2Stevens Institute of Technology, United States; 3Lawrence Berkeley National Laboratory, United States

Seebeck coefficient (S) is the ratio of open circuit voltage generated per unit degree of temperature difference across a semiconductor. It is of essential importance to thermoelectric materials. In a broader context, S is a fundamental transport parameter. It can be used to extract various information including carrier type, position of Fermi level, effective mass, scattering mechanism, even the complex shape of electronic bands. Seebeck coefficient measurements on typical semiconductors are routinely done in labs with fairly simple requirement on methodology and hardware. However, at extreme cases, reliable measurement of a small voltage of 100 nV to 1 mV can be very challenging. We present here an AC measurement technique which has several advantages over DC methods. The first is the ability to measure high impedance samples: We demonstrate the successful measurement of S on a halide perovskite CH3NH3PbI3 film, with resistance over 100Gohms, can be determined whereas DC signal is totally obscured by random voltage fluctuations. The second, when a sample is inhomogeneous like often seen in lightly doped semiconductors, the AC method with a little modification can measure both the average S between the two points and the difference. In contrast, DC measurement under the same condition will only yield non-linear voltage behavior. Lastly, the great accuracy of phase sensitive detection allows the use of very small temperature gradients, for instance, DT = 0.1°C, revealing true S at a given temperature, which is useful when studying material behavior close to a phase transition.

4:45 PM EN14.09.05
Effects of Structural Phase Transition on Thermoelectric Performance in Lithium-Intercalated Molybdenum Disulfide (LixMoS2) Hong Kuan Ng1,2, Anas I. Abutaha1, Damien Voiry1, Ivan Verzhbitskiy2, Yongqing Cai4, Gang Zhang4, Yi Liu2, Jing Wu2, Manish Chhowalla1, Goki Eda2 and Kedar Hippalgaonkar1; 1Institute of Materials Research and Engineering, Singapore; 2National University of Singapore, Singapore; 3University of Montpelier, France; 4Institute of High Performance Computing, Singapore; 4University of Cambridge, United Kingdom

Layered transition metal dichalcogenides (TMDCs) intercalated with alkali metals exhibit mixed metallic and semiconducting phases with variable fractions. Thermoelectric properties of such mixed-phase structure are of great interest because of the potential energy filtering effect, which can enhance Seebeck coefficient and thermoelectric performance due to the alteration of energy-dependent scattering. The thermoelectric properties of mixed-phase LixMoS2 are studied as a function of its phase composition tuned by in-situ thermally driven deintercalation. We find that the sign of Seebeck coefficient changes from positive to negative during initial reduction of the 1T/1T’ phase fraction, indicating crossover from p- to n-type carrier conduction. These anomalous changes in Seebeck coefficient, which cannot be simply explained by the effect of deintercalation-induced reduction in carrier density, can be attributed to the hybrid electronic property of the mixed-phase LixMoS2. Our work shows that careful phase engineering is a promising route toward achieving thermoelectric performance in TMDCs.
EN14.10.01
Thermoelectric Properties of Two-Dimensional Materials Beyond the Confinement Effect
Nguyen Tuan Hung, Ahmad R.T. Nugraha and Riichiro Saito; Tohoku University, Japan

Thermoelectric research has been significantly activated during the past two decades by the quantum confinement effect, a characteristic of low-dimensional (1D & 2D) materials, thanks to the pioneering work by Hicks and Dresselhaus [1]. The confinement effect leads to an enhancement of the density of states at the Fermi energy, which enhances thermoelectric power factor (PF) of low-dimensional materials. In particular, for 2D material, the PF is enhanced only when the thickness of the material is smaller than the thermal de Broglie wavelength [2]. 2D semiconductors naturally satisfy this condition so that they are a good candidate for thermoelectricity. However, the thermoelectric performance of 2D semiconductors still needs to be improved for industrial applications because of large thermal conductivity. In this work, we propose two possible strategies to improve the thermoelectric performance of the 2D materials beyond the confinement effect. Firstly, we show that the thermoelectric performance of the 2D semiconductors can be improved by the band convergence, in which some distinct valleys become degenerate in energy [3]. This technique is possible to realize, for example, by applying mechanical strain in monolayer InSe [3,4]. Further, we show that the nonparabolic Kane bands and large anharmonicity of phonons could lead to better thermoelectric performance of the 2D tetracyamides [5].


EN14.10.02
Development of A Method for Quick and Rough Estimation of Electron-Defect Interactions in Thermoelectric Materials Based on Gaussian Process Regression
Minkyung Han¹, Semi Bang² and Daehyun Wee¹; ¹Ewha Womans University, Korea (the Republic of); ²Samsung Electro-Mechanics, Korea (the Republic of)

It is well known that the thermoelectric properties of materials are critically affected by the scattering due to impurities. Empirical or semi-empirical formulations like the effective-mass theory are typically being used for studying impurity scattering, and a fully ab initio study of the phenomenon remains a rather difficult task even today. Only a few detailed ab initio studies have been reported for relatively simple materials. Application of these ab initio methodologies to realistic, complex thermoelectric materials is still far from realistic. In this presentation, a method for quick and rough estimation of electron-defect interactions in thermoelectric materials is proposed. The method is based on Gaussian process regression (GPR), which is a statistical procedure used widely in machine learning communities. By using the GPR procedure, relatively coarse observations of electron-defect interaction coefficients in the Brillouin zone can be effectively interpolated in an appropriate energy window, whose results can be further utilized to estimate the scattering rate due to impurities. A numerical example to demonstrate the feasibility of our proposed method is also provided.

EN14.10.03
Intrinsic and Extrinsic Point-Defects in Thermoelectrics NbFeSb—Experimental and Calculational Studies
Yefan Tian¹, Joseph H. Ross¹, Lan Huang¹, Tahir Cagin¹, Hantian Zhu², Wuyang Ren² and Zhifeng Ren²; ¹Texas A&M University, United States; ²University of Houston, United States

The half-Heusler NbFeSb-based semiconductors have been of considerable interest due to their excellent thermoelectric performance, especially an enhanced power factor [1]. For enhanced performance, various substitutional elements can be incorporated, with Ti substitution, in particular, providing outstanding performance as a p-type material. However, intrinsic and extrinsic defects play an important role in adjusting the carrier concentrations and mobilities. To better understand the inherent defects in these materials and then improve the thermoelectricity, we used experimental and computational methods to study NbFeSb-based semiconductors.

To investigate the defects in NbFeSb-based semiconductors, we have performed XRD, ⁹⁵Nb NMR, and magnetic
measurements on pure NbFeSb and a series of Ti-substituted (Nb, Ti)FeSb samples with different substitution levels. Magnetic measurements combined with an observed Schottky anomaly and changes in the NMR line width indicate the presence of a 0.2% concentrated native magnetic defect in stoichiometric NbFeSb sample [2]. For Ti-substituted samples, the breaking of the 18-electron rule leads to heavily p-type materials. A small but consistently increasing paramagnetic defect density is observed with the increase of titanium substitution concentrations revealing the existence of additional Ti-induced paramagnetic defects. Also, with Ti substitution, the $^{95}$Nb NMR spectra show progressive increases in Knight shift providing a measure of band-edge carrier densities, and we have also mapped changes in the NMR line shapes to local carrier density distributions connected to different local configurations.

To further identify the origin of the defects in NbFeSb, DFT calculations have been utilized. In this work, we applied the pyCDT package [3] on p-type half-Heusler thermoelectric NbFeSb, combined with DFT calculations. The Fe(Nb) antisite is identified as an important n-type defect, and this defect was also identified to match the magnetic signature seen in undoped samples in NMR and magnetic measurements. In addition, we identified the Fe interstitial and Nb vacancy as other important native defects, and we discuss their relation to the observed NMR shift behavior. The iron interstitial is identified as an n-type native defect with relatively low formation energy, even though Ti-substituted NbFeSb forms as nearly a line compound, with very little interstitial formation. This stands in contrast to the end member of the series, TiFe$_{1+x}$Sb, in which a significant number of interstitials form spontaneously to balance the 18-electron rule. In addition, we discuss different local configurations in Ti-substituted alloys and their effect on the transport behavior.


**EN14.10.05**

**Prospects for Thermoelectric and Current Rectification Devices Using Electron Waveguides** Sathwik Bharadwaj and L. R. Ram-Mohan; Worcester Polytechnic Institute, United States

There have been several attempts in literature to provide a variational formalism for solving quantum transport problems. However, the asymptotic boundary conditions used in such methods do not take the evanescent modes into account, which is crucial for applications in meso- and nano-scale devices. We develop a novel method based on sources and absorbers to study quantum transport in confined geometries in the presence of defects [1]. This method overcomes the limitations of the currently prevalent approaches to provide a complete non-asymptotic variational description for quantum transport in meso- and nano-scale systems. We apply this method to study electron transport in disordered waveguides, and examine the impact of evanescent modes in enhancing the Seebeck coefficient and power factor beyond the earlier proposed limits. We also discuss a new way of fabricating current rectifiers using tapered electron waveguides [2].

References:

**EN14.10.07**

**Enhancement of Thermoelectric Performance via Defect Engineering** Hanhwi Jang$^{1}$, Yeon Sik Jung$^{1}$ and Min-Wook Oh$^{2}$; $^{1}$Korea Advanced Institute of Science and Technology, Korea (the Republic of); $^{2}$Hanbat National University, Korea (the Republic of)

To deal with an unprecedented energy crisis nowadays, humongous attention is concentrated on the developing high-performance thermoelectric material to effectively recover a lot of waste heat. However, intrinsic trade-off relationship between thermoelectric properties make it harder to improve the performance. Especially, improving Seebeck coefficient while preserving electrical conductivity is challenging as both of them are electron-related phenomena. Therefore, simultaneous enhancement of the both properties is required for efficient thermoelectric material.

References:

**EN14.10.08**

**Enhancement of Thermoelectric Performance via Defect Engineering** Hanhwi Jang$^{1}$, Yeon Sik Jung$^{1}$ and Min-Wook Oh$^{2}$; $^{1}$Korea Advanced Institute of Science and Technology, Korea (the Republic of); $^{2}$Hanbat National University, Korea (the Republic of)

To deal with an unprecedented energy crisis nowadays, humongous attention is concentrated on the developing high-performance thermoelectric material to effectively recover a lot of waste heat. However, intrinsic trade-off relationship between thermoelectric properties make it harder to improve the performance. Especially, improving Seebeck coefficient while preserving electrical conductivity is challenging as both of them are electron-related phenomena. Therefore, simultaneous enhancement of the both properties is required for efficient thermoelectric material.

References:
Here, we present the peculiar behavior of both electrical conductivity and Seebeck coefficient, which show a constant value along wide range of temperature, in Na- and Ag-doped PbTe. This temperature-robust electronic transport properties yield a broad plateau in power factor, while thermal conductivity keeps decrease as temperature increases. As a result, sharp increase of thermoelectric figure of merit ($\zeta F$) is achieved. This unconventional thermoelectric property is mainly attributed to the re-dissolution of the Na segregated at the grain boundary. Segregated Na can be incorporated into the lattice at the high temperature, increasing hole concentration significantly. As the optimum hole concentration in p-type PbTe shows monotonic increase as temperature increases, inducing segregation at low temperature and re-dissolution at high temperature can be an effective strategy to keep up with it.

It is further founded that Ag promotes the solubility drop of the incorporated Na, leading to the temperature-robust transport property even at the lower Na doping concentration. Formation of Ag$_x$ defect induces a huge lattice strain on the already shrunk Na-doped PbTe, thus phase separation between Na and PbTe lattice occurs. Microstructure analysis using SEM and TEM reveals that the segregated Na indeed exists at the grain boundary, and the defective structures such as dislocation and precipitation are uniformly distributed through the lattice.

**EN14.10.08**

**Lattice Thermal Conductivity of α-, β- and γ-graphyne—Molecular Dynamics and Boltzmann Transport Study**  
Minkyu Park, Mehmet E. Kilic, Seungchul Kim and Kwang-Ryeol Lee; Korea Institute of Science and Technology, Korea (the Republic of)

Graphyne is one of the two-dimensional carbon allotrope and consisting of $sp$ and $sp^2$ hydridized carbon atoms. Herewith we investigate the lattice thermal conductivities of α-, β- and γ-graphyne by perform large-scale non-equilibrium molecular dynamics simulations and solve linearized phonon Boltzmann transport equation. Up to the length of 1.5 μm along the heat transport direction is investigated, at which the converging behavior is found. The previous molecular dynamics simulations have been only limited up to few hundred nanometer scale in length, which may result in a large discrepancy with the experiments. Based on the results, the intrinsic macroscopic lattice thermal conductivities of α-, β- and γ-graphyne is evaluated to be 24.7, 23.8 and 42.0 W/m-K at room temperature. The previous theoretical studies with about few hundred length of graphyne are suggested here to have still ballistic thermal transport components and can give a smaller value than the macroscopic thermal conductivity of graphyne. We also calculate lattice thermal conductivity, mode-dependent phonon relaxation times, group velocities and dispersions based on density functional perturbation theory and linearized phonon Boltzmann transport equation. The calculated results are consistent with molecular dynamics calculation results, and we found that number of acetylene linkages in graphyne play significant roles on lattice thermal conductivities.

**EN14.10.09**

**Expansion of Ba and Ca Solubility Limit into SrSi$_2$ Thin Film and Their Thermoelectric Properties**  
Kodai Aoyama$^1$, Takao Shimizu$^1$, Hideto Kuramochi$^2$, Masami Mesuda$^2$, Ryoo Akiike$^2$, Ide Keisuke$^1$, Takayoshi Katase$^1$, Toshio Kamiya$^1$, Yoshisato Kimura$^1$ and Hiroshi Funakubo$^1$; $^1$Tokyo Institute of Technology, Japan; $^2$TOSOH Corporation, Japan

Silicide-based materials, such as Mg$_2$Si and MnSi$_{1.73}$, attract attention as promising candidate for thermoelectric materials because they have advantages such as high compatibility with Si process and good thermoelectric properties. SrSi$_2$ (α phase) is also a promising candidate as a thermoelectric material because it consists of abundant nontoxic elements and a good thermoelectric power factor ($S^2\rho^{-1}$) over 1 mWm$^{-1}$K$^{-2}$ near the room temperature. It is reported that the thermoelectric performance is improved by substituting Ca or Ba for Sr. In this study; we prepared (Ca$_{x}$Sr$_{1-x}$)Si$_2$ and (Ba$_{x}$Sr$_{1-x}$)Si$_2$ thin films on insulating substrates and measured their thermoelectric properties. Films are deposited at nonequilibrium condition that possible to increase the solubility limit of Ba and Ca into α phase. This larger solubility of Ba and Ca expects to improve the thermoelectric properties of α phase. (Ca$_{x}$Sr$_{1-x}$)Si$_2$ and (Ba$_{x}$Sr$_{1-x}$)Si$_2$ thin films were deposited on (001) Al$_2$O$_3$ substrates at various deposition temperatures by using co-sputtering method. Constituent phases strongly depended on the deposition temperature and film composition. At 700 ℃, the single phase of α phase was observed up to 26% of Ba/(Ba+Sr) ratio, while main phase of BaSi$_2$ structure phase (stable phase of BaSi$_2$) was observed over 30%. When the deposition temperature decreased to 650 ℃, the Ba/(Ba+Sr) ratio of main phase of α phase expanded to 30% and BaSi$_2$ structure phase was observed over 35%. Note that this solubility limit was larger than that of reported value of the powder. Linear relationship between the lattice parameter and the Ba/(Ba+Sr) ratio in the film was observed for the films deposited at both temperatures. This result
shows that the Ba soluble for Sr site of α-phase and its solubility limit increased as the deposited temperature decreased. When the deposition temperature further decreased to 600 °C, the metastable phase with CaSi2 structure became a main constituent phase up to 30% of Ba/(Ba+Sr) ratio and α phase was hardly observed. In case of (Ca,Sr1-x)Si2 films, the CaSi2 structure phase was the main phase except for the film with 6% of Ca/(Ca+Sr) ratio for the film deposited at 700 °C that consist of α phase. This shows that the solubility limit of Ba in α phase is larger than Ca. However, α phase was hardly observed at 600 °C. Power factor of α-phase was beyond 700 mW m⁻¹ K⁻² at room temperature and was not strongly dependent on the film composition. This value is larger than (111) one-axis-oriented Mg₂Si films prepared by the same deposition process, maximum 130 mW m⁻¹ K⁻² at 300 °C. The present result shows that α-phase of MₓSr₁₋ₓSi₂ (M = Ca, Ba) is one of the promising candidates as thin film thermoelectric materials.

EN14.10.10
Optimization of Degreasing-Sintering Process for Mg₂Si/PLA Mixture and Influences of Additive Amount of Al on Sintered Density and Thermoelectric Performance of Mg₂Si Fabricated by the Optimized Process
Takashi Itoh and Takumi Nakano; Nagoya University, Japan

Fused deposition modeling (FDM) type of 3D printing is widely used for manufacturing complex shaped polymer products. Recently, the metal/polymer composite products can be made by 3D printer using metal/polymer composite filament. Now, we are planning to develop a new manufacturing process of the thermoelectric (TE) elements or modules by combining the FDM type of 3D printing and the degreasing-sintering process. In this work, we focused on the degreasing-sintering process of the mixture of Mg₂Si and polyactic acid (PLA) powders. Mg₂Si compound powder was synthesized by a liquid-solid phase reaction (LSPR) method. Mixture powder of Mg₂Si, Al and PLA was pressed and heated in a pulse discharge sintering (PDS) chamber under a vacuum in various degreasing conditions. Following the degreasing, the sintering of Mg₂Si was carried out in the same PDS chamber at various starting sintering temperatures. Sintered density, Seebeck coefficient and electrical resistivity of the consolidated Mg₂Si were measured and power factor as TE performance was estimated from the TE properties. The optimum conditions of degreasing-sintering process maximizing the sintered density and the TE performance of Al-doped Mg₂Si were investigated. Furthermore, influences of additive amount of Al on the sintered density and the TE performance of Mg₂Si fabricated by the optimized degreasing-sintering process were investigated.

EN14.10.11
Quasiperiodic Branches in the Thermoelectricity of Nanowires
Vicenta Sanchez, Fernando Sanchez, Carlos Amador-Bedolla and Chumin Wang; Universidad Nacional Autonoma de Mexico, Mexico

Huge energy demand and pollution constitute two major problems of modern society. A large amount of normally wasted heat is present in many places around us, from human and animal bodies, natural thermal springs, combustion engines, up to numerous friction sources. The solid-state thermoelectric devices allow a direct conversion of heat into electricity without harmful contamination and those based on nanowires have demonstrated to be a promising route to reach a high thermoelectric efficiency [1,2]. Furthermore, branches attached to a nanowire may significantly modify the transport of excitations along it due to the wave interference [3]. In this work, we study the thermoelectric properties of thin nanowires with quasiperiodically placed branches by means of a real-space renormalization plus convolution method developed for the Kubo-Greenwood formula, in which tight-binding and Born models are respectively used for the calculation of electrical and lattice thermal conductivities [4]. The results show a substantial growth of the thermoelectric figure of merit (ZT) induced by the long-range quasiperiodic disorder, because it diminishes the thermal conduction of long wavelength acoustic phonons being such phonons usually not altered by local defects neither impurities [5]. A remarkable reduction of the thermal conduction can be further achieved by using low sound velocity materials [6].

This work has been partially supported by UNAM-IN115519, UNAM-IN106317 and CONACyT-252943. Computations were performed at Miztli of DGTIC, UNAM.

EN14.10.12
Characterization of Magnesium Silicide Stannide Powder for Use in Selective Laser Melting
Rachel Gray and Saniya LeBlanc; The George Washington University, United States

The aim of this study was to establish the feasibility of using magnesium silicide stannide ($\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$) powder in the selective laser melting process to produce thermoelectric generators (TEGs). $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ powder is a thermoelectric material optimal for high temperature applications and shows potential for use in TEGs. Currently TEGs are being manufactured using bulk material processing with multiple integration and assembly steps. Leading to decreased product efficiency, high manufacturing costs, and offering little flexibility in device geometry. Selective laser melting (SLM) an additive manufacturing technique, on the other hand, could provide a unique solution to these manufacturing challenges. However, current additive manufacturing techniques exist only for limited materials- namely polymers, ceramics, and metals- which do not include semiconductors (like thermoelectric materials). As well as require specific starting powder characteristics: desired particle size distribution, and high levels of circularity and convexity. Powder parameters such as convexity, circularity, and particle size distribution not only effect the flowability through the selective laser melting process but also the density of the final thermoelectric device. With a higher density, thermoelectric generators are more efficient and resilient to internal fractures.

Powder morphology and particle size distribution were analyzed through optical microscopy and the image analysis software FIJI. The ability to spread was assessed across 100 μm and 500 μm thick grooves using two rolling techniques, as well as a blade. Flowability was examined through the measurements of, angle of repose, angle of spatula, and compressibility. Each of these measurements follows the United States Pharmacopeia flowability standards. The results of these measurements show the potential for $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ to be integrated into SLM and paves the way for future studies looking to use $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ in thermoelectric devices.

EN14.10.13
Investigation of Three-Dimensional Thermoelectric Nanomaterials
David Osenberg$^{1,2}$, Laetitia Philippe$^{1,2}$, Stefano Mischler$^2$ and Johann Michler$^1$; $^1$Swiss Federal Laboratories for Materials Science and Technology, Switzerland; $^2$École Polytechnique Fédérale de Lausanne, Switzerland

Thermoelectric energy conversion is of great interest since most processes produce waste heat. Thus much effort has been devoted to enhancing the comparatively low conversion efficiency. Sufficient evidence has been provided that nanostructuring can enhance the thermoelectric conversion efficiency through size effects on the thermoelectric transport. These include phonon boundary scattering at grain boundaries, surfaces or interfaces within heterostructures, quantum confinement effects and modification of the phonon dispersion. While some of these effects have been investigated in simple low-dimensional systems, three-dimensional nanostructured materials are not as well understood, even though they are more relevant with regard to applications. Moreover most of the demonstrated enhancements of the figure of merit are due to a decrease of the lattice thermal conductivity, exploiting quantum confinement has been difficult, mostly due to strict requirements with regard to feature sizes.

In this work we apply electrochemical methods together with colloidal crystal lithography to tackle these problems, since this allows the fabrication of nanostructured and yet well-defined periodic materials. This facilitates relating the thermoelectric to structural properties and thus more accurate quantification of size effects. Additionally electroplating allows the growth of heterostructures by making use of the potential dependence of the composition in binary systems, in our case Bi-Te, which is expected to lead to enhanced phonon scattering due to the large acoustic mismatch and improved electrical properties (thermopower and mobility). The structural and thermoelectric characterization of the obtained materials is carried out both in- and cross-plane and numeric and analytic modelling is used to determine the material properties and quantify size effects.

EN14.10.14
Complex Mixed Anion Oxypnictides as Novel Thermoelectrics
Maud Einhorn, David O. Scanlon and Benjamin A. Williamson; University College London, United Kingdom
Thermoelectric materials, capable of directly and reversibly converting thermal energy into electricity, present a promising direction for renewable energy conversion.[1] The effectiveness of a thermoelectric material is measured using the dimensionless figure of merit $ZT$, with the world record set at 2.6 for single-crystal SnSe along the through-plane direction.[2] Realising reasonable conversion efficiencies generally requires high electrical conductivity and low thermal conductivity, with the maximum $ZT$ of a material often limited by the strong correlation between these properties.

Despite efforts to find promising thermoelectrics containing earth abundant and non-toxic elements, bismuth telluride (Bi$_2$Te$_3$) and lead chalcogenides remain the champion materials, with the performance of oxide thermoelectrics generally lagging behind the efficiencies achieved by chalcogenide-based materials.[3] Oxides generally present properties valuable for thermoelectric applications, including low cost, thermal and chemical stability and environmental benignity, but broadly thermoelectric performance has been hindered by the inherent high lattice thermal conductivities.[4] However significant progress has been made through novel materials with complex crystal structures which possess lower lattice thermal conductivities than usually seen in oxides.

In this study, we calculate the electronic band structures and corresponding $ZT$s of a range of novel mixed-anion quaternary oxypnictides using hybrid density functional theory, including spin-orbit effects. We have identified that LaZnOP and YZnOP possess promising properties for thermoelectric applications, including low intrinsic lattice thermal conductivities predicted from third order lattice dynamics calculations, and low charge carrier effective masses. In addition, we have examined the intrinsic defect chemistry of LaZnOP, to predict optimal carrier concentrations and an insight into ideal growth conditions for maximized performance. We conclude that these materials possess $ZT$’s greater than many existing oxide thermoelectric materials, and have the potential to perform as high-performance thermoelectric components.


**EN14.10.15**
**Analytical and Numerical Characterization of a Hybrid Thermophotovoltaic Coupled with a Thermoelectric Generator (HTPV-TEG) and a Microchannels-Based Cooling System** Pablo Araya, Jose Lincoleo, Tomas Salinger, Mario A. Di Capua and Amador M. Guzman; Universidad Catolica de Chile, Chile

A thermophotovoltaic (TPV) mounted on a thermoelectric generating (TEG) conceptual device is modeled analytically and numerically with the final goal developing a Hybrid Thermophotovoltaic (HTPV-TEG) system that offers improvements on efficiencies obtained with standard Thermophotovoltaic devices. The HTPV-TEG shall use inexpensive and simple components such as commercial photovoltaic cells and absorber/emitters, thermoelectric modules, and a microchannel-based cooling device. Special attention is given to the selection of specific absorber/emitter components, placed between a radiative heat source and a receiving Photovoltaic Cell (PVC). The goal is to predict the temperatures that will be reached by the absorbing/emitting element, the lower PVC and the TEG stacked under a controlled heat concentrating device. The objective is to determine heat input and resulting surface temperatures that will be reached under steady state conditions. Conduction, convection and radiative heat transfer will be present in the device. The resulting power generated by the PVC and TEG will be used to determine the overall device efficiency. Heat transfer simulations of conduction, natural convection and radiation of the device are performed using Computational Fluid Dynamics software in order to predict temperatures that will be reached by the test device as a function of input power, before its actual construction. Simulations allow for the selection of appropriate components and results are compared to studies by other authors. Preliminary results show that at 410 K a maximum theoretical improvement in efficiency of 7% can be obtained. These results are compared to studies conducted by others. HTPV-TEG improved efficiency therefore exceeds the performance of common solar photovoltaic cells, and TPV devices, and may be used for applications in the housing, agriculture and mining sectors, that do not necessarily require solar radiation.
Persistent, Single-Polarity Energy Harvesting from Ambient Thermal Fluctuations Using a Thermal Resonance Device with Thermal Diodes

Ge Zhang, Anton Cottrill, Michael Strano and Volodymyr Koman; Massachusetts Institute of Technology, United States

There is a pressing need for durable energy harvesting techniques that are not limited by intermittency, and capable of persistent and continuous operation over extended periods of time in a variety of environments. Our laboratory has identified ambient thermal fluctuations of various frequencies as potentially abundant, ubiquitous sources of such energy. We have developed a type of novel devices called thermal resonator for transient thermal energy harvesting, tested them in various environments and are working on integrating them with energy storage systems.\(^1\) \(^2\) In this work, we present a mathematical theory for the operation and design of a thermal resonator interfaced with optimized thermal diodes that we show is capable of much higher productivity than previous possible. This work is a significant advance over resonators that we have previously introduced using high thermal effusivity materials for a dual polarity electrical output from input temperature fluctuations. Herein, we outline the optimal design of a thermal resonance device incorporating optimal thermal diodes on its external boundaries with the environment, and we show that such a configuration is able to produce single polarity electrical generation drastically exceeding the performance of previous thermal resonators by a factor of 5. We also characterize additional thermal fluctuations in the environment, expanding the scope of resonator application. Lastly, we analyze the capability of thermal diodes available in the literature to realize such an enhancement in thermal resonance performance, and we conclude that current thermal diodes in existence could produce approximately a factor of 2 improvement in thermal resonator performance. This work points out the significant role of thermal diodes in ambient energy harvesting, and outlines important directions for next generation thermal diodes, independent of advances in thermoelectric or pyroelectric materials.

Reference:

Development and Application of an Interatomic Potential to Model Thermal Conductance at GaAs-Ge Interface

Spencer Wyant and Asegun Henry; Massachusetts Institute of Technology, United States

Understanding the thermal conductance of solid-solid interfaces is important for applications like the thermal management of nanoelectronic devices and the engineering of novel thermoelectric materials. An ideal method to investigate interfacial thermal conductance with minimal assumptions is to explicitly model the atomistic interactions and their subsequent dynamics in a molecular dynamics simulation. However, prior attempts to perform such simulations often describe atomistic interactions using simple but unrealistic classical potentials that are not explicitly fit to capture thermal properties at an interface. An ideal interatomic potential used for this application would be able to replicate the interatomic force constants (IFCs) obtained from first-principles density functional theory calculations, remain stable at high temperatures, and would be quick to evaluate so as to enable large simulations over long time scales. Systems with heterointerfaces are especially challenging, as there are three distinct sets of IFCs: two for the different bulk regions surrounding the interface and one for the interface itself. We explore this challenge by developing an interatomic potential for a GaAs-Ge interface, a model III-V/IV heterointerface with minimal lattice mismatch. Our potential directly incorporates a Taylor expansion of the energy landscape of the different regions of our system. Comparisons are made with recent machine-learning inspired potentials, especially with respect to training data size and evaluation speed. Using this potential, the interface conductance modal analysis (ICMA) method is then applied to study the modal contributions to thermal conductance at the Ge-GaAs interface.

Improvement of Low-Temperature zT in MgSb\(_2\)-MgBi\(_2\) Solid Solution via Mg-Vapor Annealing

Max Wood, Jimmy Kuo, Kazuki Imasato and G. Jeffrey Snyder; Northwestern University, United States
The thermoelectric community strives to find new materials with better performance by looking for higher peak $zT$s. However, in real devices it is often more important to have a high average $zT$ over a broad range of temperatures in order to maximize the devices Carnot efficiency. Mg$_3$Sb$_2$-Mg$_3$Bi$_2$ alloys have recently garnered renewed attention due to their high performance at mid-range temperatures ($zT \approx 1.5$ at 700K). While having a relatively high performance at 700K, these materials suffer from grain boundary resistance at lower temperatures leading to an overall lousy performance at room temperature$^1$. Synthesis and optimization process to mitigate these grain boundary effects have been limited due to the loss of Mg, which hinders a sample's n-type dopability$^2$. Herein we demonstrate that a Mg vapor anneal can preserve a sample's n-type dopability, while allowing us to grow the grains within our material. We show that with different processing steps we can change the room temp performance of Mg$_3$Sb$_{1.49}$Bi$_{0.5}$Te$_{0.01}$ from $zT = 0.2$ to $zT = 0.8$.

(2) Ohno S. et al., Joule, 2018, 2, 141–154

**EN14.10.19**

Wearable Thermoelectric Generator Harvesting Body Heat and Solar Energy Simultaneously for High Performance

Kyoung Jin Choi, Myeong Hoon Jeong and Sung Bum Kang; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Recently, wearable and sustainable self-powering technologies have become increasingly important due to the development of wearable electronics such as sensors, health monitoring, and smart gears. Renewable energy sources include solar light, mechanical motion, thermal energy, and can be developed in the form of solar cells, piezoelectric and thermoelectric generators (TEGs), respectively. Among these, the wearable TEGs (WTEGs) operating based on the temperature gradient between the body and ambient temperature have generated significant amount of interest because the body heat can be used at any time and stable with time unlike other renewable energy sources. WTEGs are fabricated either by printing TE inks directly onto flexible substrates, or by embedding rigid TE legs, made small enough not to compromise the flexibility, in flexible matrixes. Chen et al. synthesized printable thick-film TE ink by mixing Bi$_2$Te$_3$ and Sb$_2$Te$_3$ powders with epoxy resin and fabricated TE legs using a dispenser printing on a polyimide (PI) substrate. On the other hand, Wang et al. reported a vertical-type WTEG using BiTe-based rigid TE pellets embedded in polydimethylsiloxane (PDMS) between the top and bottom PI thin films. The WTEG, composed of 52 pairs of p-n legs, generated an open-circuit voltage ($V_{OC}$) of 37.2 mV and output power ($V_{OUT}$) density of 16.7 $\mu$W cm$^{-2}$ at a $\Delta T$ of 50 °C. Suarez et al. enhanced the flexibility of a WTEG by replacing stiff electrodes with eutectic gallium-indium (EGaIn) liquid metal interconnects and filling the empty space between TE legs with PDMS in a commercial BiTe-based TE modules. These WTEGs exhibited relatively high TE material performances, because they were fabricated based on proven inorganic materials such as Bi$_2$Te$_3$ and Sb$_2$Te$_3$. However, a limit in temperature difference is observed when the body heat is used as a heat source. When the ambient temperature, at which the TEGs are driven, is in the range of 15 to 25 °C, the $\Delta T$ values of the body-heat-based WTEGs are only 1.5 – 4.1 °C. Previously, we first demonstrated a wearable solar TEG (WSTEG) with a solar absorber in WTEG and reported a high $\Delta T$ of 33.4 °C. The TE legs were fabricated by dispenser-printing a BiTe-based ink, prepared by dissolving mechanically alloyed BiTe powders and Sb$_2$Te$_3$ sintering additive in glycerol. However, despite the high temperature difference, high power density was not obtained due to low thermoelectric properties of Printed TE leg compared to the rigid TE legs. Herein, we proposed a dual-mode wearable thermoelectric that can obtain both body heat and solar energy by placing a solar absorber on the bottom surface of a bulk TEG. The WTEG can improve the temperature difference compared to conventional TEGs using only the body heat. In addition, a PDMS was filled between the rigid TE legs obtaining both flexibility and high value of power density.

**EN14.10.21**

Fabrication of Highly-Efficient Nanoscale Multilayered Thin-Film Based Integrated Thermoelectric Devices

Joevonte Kimbrough, Aalandria Henderson, Abigayle Glenn, Sam Chance, Samuel Banks, Broanna Rodgers, Zhigang Xiao and Lauren Williams; Alabama A&M University, United States

In this research, we report the growth of nanoscale multilayered thermoelectric thin films and fabrication of integrated thermoelectric devices for high-efficiency energy conversion and solid-state cooling. Nanoscale multilayered thin films such as Sb/Sb$_2$Te$_3$ and Te/Bi$_2$Te$_3$ thin films were grown using the e-beam evaporation with DC bias on the substrate. The multilayered films were prepared to have 150 to 300 layers, where each layer was
about 5 nm thick. The effects of DC substrate bias on the growth of films such as the crystalline structures in the films were studied. Integrated thermoelectric devices with a high density of thermoelectric elements were fabricated with the nanoscale multilayered thin films using the clean room-based microfabrication techniques such as UV lithography. X-ray diffraction and reflection and high-resolution tunneling electron micrograph (HR-TEM) were used to analyzed the e-beam-grown nanoscale multilayered thin films. SEM was used to image and analyze the fabricated devices. The thermoelectric characteristics of the fabricated devices such as the open-circuit voltage and output power were measured and analyzed. The effects of cooling and annealing on the nanoscale multilayered thin films and the integrated thermoelectric devices were studied. Highly-efficient thermoelectric thin-film materials and integrated devices will be demonstrated and reported.

EN14.10.22
Tuning Phonon Scattering by Interlayer Coupling Ben Xu; Tsinghua University, China

Interlayer interaction can introduce profound effects on thermal conductivity, which is strongly dependent on the properties of the coupling itself. Here we develop a model showing the ratio between the high-order and harmonic terms plays the dominate role in the phonon scattering behavior and demonstrated this relationship by carrying out comparison between the layered materials MoS2 and PtS2, using first principles calculation and solving phonon Boltzmann transportation equations. Moreover, series of materials with BiCuSeO structure are also analyzed, where geometry factor was constructed to indicate the delicate variance of the interlayer distance of these structure. These understanding can be used as guidelines for designing materials of particular phonon properties, for example low thermal conductivity.

EN14.10.23
A Time-Dependent Modeling and Characterization of a Concentrated Photovoltaic-Thermoelectric Hybrid System Cooled by a Microchannel Heat Sink Mario A. Di Capua; Pontificia Universidad Catolica de Chile, Chile

Photovoltaic electrical energy has experimented a significant increase in the last decade motivated mostly for the reduction of the PVC costs, the emergence of new PVC technology and increase amount of new large projects, particularly in areas with large levels of irradiance. However, despite the above factors, the worldwide electricity generated by photovoltaic technologies continue being low compared to other renewable technologies such as the ones based on water, biomass, and wind and with traditional fossil-based technologies. One of the main reasons that can explain this low participation is the low conversion efficiency of traditional PV technologies, which ranges from 10% to 25%. This low participation has pushed to developer and researchers to create novel and more efficient photovoltaic technologies that combine multi-junction solar cells with high solar concentration to achieve a conversion efficiency equivalent to 40%. By using a concentrated photovoltaic (CPV) system, it is possible to reduce the use of expensive and not easy disposable semiconductor materials. However, since only a fraction of the concentrated direct normal irradiance (DNI) is converted into electricity, a cooling system is completely necessary to avoid solar cell overheating, which reduces the solar cell efficiency and accelerates the solar cell degradation. Additionally, we consider integrating a thermoelectric generator (TEG) to produce extra electrical energy by mean of Seebeck and Peltier effect that can convert part of the solar cell heat into electricity. Several researchers have proposed and evaluated the use of microchannel heat sinks as a cooling system solution for CPVs, due to its high thermal performance at low Reynolds numbers and small heat transfer area, low weight, and its possible incorporation to the solar cell system structure ((Leonardo Micheli et al. 2013, M Di Capua H et al. 2018, Radwan et al. 2019).

The present work seeks to evaluate a CPV-TEG hybrid system cooled by a microchannel heat sink (MCHS) under variable DNI, ambient temperature, and wind velocity by developing an analytical model that is numerically simulated and solved. A time-dependent thermodynamic model has been developed to analyze the behavior of the CPV-TEG-MCHS system considering both, clear and cloudy day. The principal objective of our current work is to evaluate the thermal inertia of the hybrid system under variable surrounding conditions, as well as the coolant flow rate that allows achieving the maximum conversion efficiency and safe solar cell temperature. The system evaluated is composed of a concentration photovoltaic system that uses a Fresnel lens to concentrate the solar radiation over a multi-junction (GaInP/GeAs/Ge) solar cell with a concentration factor equivalent to 1000x. In the bottom solar cell face, a TEG is integrated ann an MCHS with several microchannels of Wc and Hc, the width and height, respectively, in a parallel flow configuration is incorporated in the cold side of the TEG. The considered PV cell areas in the analyzes are 3x3 mm2 and 10x10 mm2. The MCHS material is copper and the coolant is deionized
demineralized single phase water.

**Keywords:** CPV, cooling, microchannel

**References:**


**EN14.10.25**

**Thermal Characterization and Modeling of Silicon Nanowires with Nickel Silicide Nanoinclusions** Laia Ferrer-Argemi and Jaeho Lee; University of California, Irvine, United States

Efficient silicon-based thermoelectric materials compatible with the existing electronic and photovoltaic technologies would provide excellent energy harvesting opportunities. Although the high bulk thermal conductivity of silicon has been successfully reduced during the past decade through nanostructures such as nanowires, nanograins, and nanomeshes, the fundamental mechanisms that reduce the thermal conductivity through nanometer-sized inclusions of other materials still require further investigation. Here, we report the thermal conductivity of silicon nanowires with epitaxial nickel silicide nanoinclusions (Si-NiSi$_2$ NWs) and develop a model to explain the observed thermal conductivity trend. We synthesize silicon nanowires using metal-assisted chemical etching and deposit nickel nanoparticles on their surface with electroless deposition. Annealing the nanowires allows the nickel to diffuse into the silicon, resulting in silicon nanowires embedded with metallic nickel silicide nanoinclusions grown in the diffusion plane [1 1 1], which results in diamond or rectangular-shaped inclusions. We measure the thermal conductivity of single nanowires using suspended micro-membranes in a cryo-chamber from 40 to 300 K in high vacuum. We report the thermal conductivity of two Si-NiSi$_2$ NWs with 30% inclusion density and diameters of 120 and 170 nm, respectively, which increases with temperature and saturates at 150 K with ~15 Wm$^{-1}$K$^{-1}$ with little difference between both wires. The consistent thermal conductivity among Si-NiSi$_2$ NWs wires with the same inclusion density differs from the reports on the thermal conductivity of silicon nanowires synthesized using metal-assisted chemical etching depending on their surface roughness, which can have large variability even within the same batch. This indicates that the nanoinclusions consistently decrease the phonon mean free path and dominate thermal transport. To better understand the underlying mechanisms that maximize the thermal conductivity reduction through diamond and rectangular nanoinclusions, we integrate Monte Carlo ray-tracing simulations with the kinetic theory and Landauer formalism, including the Diffuse Mismatch Model to calculate the thermal boundary resistance and the two-temperature model to estimate the electron-phonon coupling. We demonstrate that by incorporating nanoinclusions into a film with high interfacial density, the matrix phonon mean free path and the film’s thermal conductivity can be minimized without compromising the electrical properties. Additionally, metal/silicon junctions produce chemically stable Schottky barriers at the nanoinclusion interface that can filter low energy electrons and increase the Seebeck coefficient without damaging the electrical conductivity. The results of this work expand the understanding of transport phenomena in complex nanoengineered materials and open promising optimization paths for silicon-based thermoelectric materials.
This talk will discuss our recent work to simulate electron and phonon thermoelectric transport in complex materials and across interfaces based on the density-functional theory and atomic Green’s function. One example of the complex material is Mg2Sb3, which has been recently reported to have high figure of merit. We compare the charge defect scattering due to different dopants using first principle calculation and find weak impact of defect on mobility. Instead, the intrinsic carrier-phonon scattering is the major scattering mechanism. Only specific polar optical phonon modes make dominant contribution to the scattering rates, which we attribute to the atomic structure and electrostatic interactions in Mg2Sb3. For transport across interfaces, an important question to ask is if electron and phonon scatterings conserve lateral momentum, i.e., if they experience specular or diffuse scattering, in the presence of interfacial atomic mixing. We employ atomic Green’s function to simulate electron and phonon transmission across interfaces for SiGe interface with mode-by-mode resolution. We find the angular dependent interfacial transport for electron and phonon are behaving differently, which provides new opportunities for optimizing thermoelectric performance. This work is supported by DARPA MATRIX program (Grant No. HR0011-16-2-0041).

8:45 AM EN14.11.02/EN13.03.02
Amorphous-Like Thermal Conductivity in Crystalline Solids Saikat Mukhopadhyay and Thomas Reinecke; U.S. Naval Research Laboratory, United States

Thermoelectric materials (TEs) could play an important role in future energy management through environmentally sound cooling and power generation, e.g., converting waste heat into electricity. Efficient TEs inhibit the propagation of heat (low thermal conductivity, $\kappa$) but conduct electricity well (high power factor, PF). Although $\kappa$ in a given material can be reduced via alloying and nanostructuring, identifying materials with intrinsically low $\kappa$ is still needed. It has already been known that soft phonon modes due to weakly bonded atoms and $s^2$ lone-pair electron are common to materials with low-$\kappa$. Here, we predict a series of new materials which are weakly bonded systems with same constituent elements but different stoichiometry either with $s^2$ lone-pair electron or high mass density. Due to giant phonon anharmonicity and low phonon group velocities, they offer extremely low $\kappa$ (0.3-0.6 W/mK) at 300K approaching to those found in the amorphous/disordered regime. In addition to low-$\kappa$, high Seebeck coefficients and electrical conductivities in these materials may provide a new opportunity for designing high-efficiency thermoelectrics at room temperature.

9:00 AM *EN14.11.03/EN13.03.03
New Horizons in Thermoelectric Materials—Inorganic-Organic Hybrids and Machine Learning for Inorganic Crystals Kedar Hippalgaonkar1,2; 1Nanyang Technological University, Singapore; 2Institute of Materials Research and Engineering, Singapore

For the next revolution in thermoelectrics, development of new physics as well as new materials needs to go hand-in-hand. In this talk, I will introduce new perspectives such as correlated electron physics, wave effects in phonons as well as opportunities for new inorganic-organic (hybrid) materials1. Then, I will introduce specifically the case of CuTe:PEDOT thin films and using this as a test case, describe the design principles for creating the next generation of hybrid materials2. In addition, I will describe how data-driven approaches can augment our knowledge: used in conjunction with the right material and transport descriptors, these can prove prescient in predicting new TE materials. I will end with a specific example of how we’ve used a Crystal Graph Convolutional Neural Network (CG-CNN) with training data from Materials Project to learn about TE properties. In addition, we use high-throughput, high-fidelity DFT calculations with the Electron Phonon Averaging (EPA) approximation to calculate carrier relaxation times, we propose that the transport effective mass remains an effective single descriptor that can guide inorganic TE material screening.

Thermoelectric Transport Descriptors in Data-Driven Thermoelectric Screening Ady Suwardi1, Deng Tianqi2, Daniil Bash1, Hong Kuan Ng1, Jose Recatala Gomez1, D V M. Repaka1, Pawan Kumar1, Anas I. Abutaha1, Michael Sullivan2, Shuo-Wang Yang2 and Kedar Hippalgaonkar1; 1IMRE, Singapore; 2Institute of High Performance Computing, Singapore

With the maturity of sophisticated, high throughput computational tools and the advent of machine learning applications in materials science, identifying the appropriate fundamental level descriptors has never been more relevant and pressing in data-driven materials discovery domain. In this work, we first present the inertial effective mass as an important descriptor in thermoelectric transport. The conclusion was obtained by analyzing data from 1617 compounds of all crystal structures mined from the materialsproject.org. Data was analyzed using polycrystalline averaging Seebeck, effective mass, as well as electrical conductivity. In addition, constant relaxation time approximation was used in all data analysis, which is known not to necessarily reflect experimentally measured compounds.

Subsequently, we present a state-of-the-art approach of using electron-phonon averaging (EPA) to obtain contribution of all possible scattering mechanisms to the relaxation time and challenge the initial assumption of constant relaxation time. More interestingly, we sought to evaluate the veracity of insights and conclusions drawn under constant relaxation time approximation from the EPA point of view and indeed confirm that effective mass is an important descriptor. Further insights gained from analysis of scattering times provide us additional insight towards prediction of new thermoelectric compounds.

9:45 AM
EN14.11.05/EN13.03.05
Thickness-Dependent Thermal Conductivity of Titanium Trisulfide Nanoribbon Chao Wu1, Chenhan Liu1, Yongkang Wang1, Juekuan Yang1, Qingyu Yan2 and Yunfei Chen1; 1Southeast University, China; 2School of Materials Science and Engineering, Singapore

The two-dimensional layered materials with interlayer van der Waals (vdWs) bonding such as graphene have attracted tremendous interests in scientific community. Recently, layered materials composed of transition metal trichalcogenides with strong in-plane anisotropy, which show unusual properties based on theory, have been successfully synthesized so that their properties can be explored through experiment. For instance, due to theoretically calculated ZT value (3.1) of monolayer titanium trisulfide along $y$ direction at moderate carrier concentration, layered titanium trisulfide nanoribbons with intralayer covalent bonding and interlayer vdWs bonding burst extensive research, which inspires us to investigate the lattice thermal conductivity of the nanoribbon and the size effects on the thermal conductivity because lowering the thermal conductivity can increase the ZT value significantly. In order to better understand the thermal transport in the titanium trisulfide nanoribbon, the theoretical calculation combined with the experiment are adopted. Through solving the phonon Boltzmann transport equation (implemented in ShengBTE package) with the first-principles second- and third-order force constant (implemented in VASP package), the thermal properties of titanium trisulfide are obtained. The calculation results reveal that the thermal conductivity monotonously decreases with the number of titanium trisulfide layers increasing from one to three and displays a strong in-plane anisotropy as the temperature range from 40 to 500 K. For example, the thermal conductivity along $y$ direction is 2.7 times larger than $x$ direction at room temperature. Compared to layered graphite, due to the weaker interlayer coupling strength, the out-of-plane thermal conductivity (around 1.1 W/m-K) at the room temperature is 5 times lower.

Based on the results of theoretical calculation, we synthesized the titanium trisulfide nanoribbons with different thicknesses and measured the thermal conductivity using a suspended micro-thermometry from 20 to 300 K. The experimental results show that the in-plane thermal conductivity of titanium trisulfide nanoribbons decreases monotonously as the thickness increases, which is same as the theoretical calculation. Interestingly, the thermal conductivity keeps decreasing as the thickness is smaller than 272 nm, which is quite different from multi-layer graphene. In detail, the thermal conductivity decreases rapidly as the thickness is below 60 nm and becomes slowly beyond 150 nm. Due to the computational cost, 4 layers or thicker titanium trisulfide cannot be calculated. The giant layer thickness dependent in-plane thermal conductivity is surprising and confusing. We speculated that this phenomenon may stem from weak interlayer coupling strength and unique atomic structure, which needs further investigation.

10:00 AM BREAK
SESSION EN14.12/EN13.04: Joint Session: Organic and Hybrid Thermoelectrics
Session Chair: Kornelius Nielsch
Wednesday Morning, December 4, 2019
Sheraton, 2nd Floor, Back Bay D

10:30 AM *EN14.12.01/EN13.04.01
Design and Engineering of Flexible Thermoelectric Devices G. Jeffrey Snyder; Northwestern University, United States

Thermoelectric semiconductors directly convert heat into electricity. These solid-state devices have been used reliably in space for over 40 years without maintenance. Temperature gradients and heat flow are omnipresent in natural and human-made settings and offer the opportunity to scavenge energy from the environment recovering waste heat from industry or replacing the need for batteries in remote sensor networks or mobile devices. Particularly attractive is the ability to generate electricity from body heat that could power medical devices or implants, personal wireless networks or other consumer devices. This talk will discuss the design principles for thermoelectric generators using a generalized electrical transport model combined with an effective thermal conductivity approach [1, 2]. Such design principles provide good estimates of the power that could be produced and the size and complexity of the thermoelectric generator that would be required. In addition these design principles can guide the search and optimization new thermoelectric materials. In organic and polymer semiconductors the optimum doping is identified and the peak $zT$ for a given class of materials can be determined. Also, a complete system design shows the misconception that power factor rather than $zT$ should be optimized for a TE generator. The power factor misconception also leads to misleading strategies for optimization and discovery of new TE materials. The materials requirements for flexibility, leading to a flexibility figure-of-merit will be discussed.


11:00 AM EN14.12.02/EN13.04.02
Thermoelectric Transport at Organic-Silicon Interface Mona Zebbarjadi, Naiming Liu, Md Golam Rosul and Tianhui Zhu; University of Virginia, United States

Nanopatterned holey silicon materials follow the concept of “phonon glass and electron crystal” and possess potential for thermoelectric device applications as it is also compatible with the well-developed Si-based industry. We fabricate a boron-implanted holey Si thin-film device, and study the thermoelectric transport properties. A novel method to measure in-plane thermal conductivity of thin film materials using thermal reflectance imaging is successfully conducted. Subsequently, we fabricate a hybrid F4TCNQ-silicon, which utilizes a non-destructive doping mechanism by charge transfer at the heterointerface. We conduct transport measurements and validate that organic F4TCNQ molecules effectively p-type dope the Si surface, resulting in power factor enhancement. Outcomes of this study serve as proof of concept in designing 3D hybrid structures with closely packed interfaces towards an efficient thermoelectric device, using organic-inorganic transfer doping mechanism.

11:15 AM EN14.12.03/EN13.04.03
Tuning the Thermoelectric Performance of Hybrid Polymer/Nanoparticle Composites Katherine A. Mazzio1, Danny Kojda1, Jens Niederhausen1, Britta Ryll1, Anyssa L. Derj2, Johannes Frisch1, Klaus Habicht1 and Simone Raoux1,3; 1Helmholtz-Zentrum Berlin, Germany; 2Université Paris Sciences et Lettres (PSL), France; 3Humboldt-Universität zu Berlin, Germany

Hybrid materials consisting of inorganic nanostructures embedded in conducting polymer matrices have emerged as promising systems for room temperature thermoelectric applications. They are attractive due to their intrinsic low thermal conductivities, the ability to engineer interfaces for energy filtering effects and phonon scattering, and their ability to take advantage of high-throughput and solution processable manufacturing. Most polymer and hybrid...
materials reported in the literature have been p-type, owing to difficulties in n-type doping of conducting polymers in conjunction with the nature of the applied nanocrystals. This has resulted in a strong drive to develop new n-type materials, since both are necessary for module development. Here we explore our recent developments in the synthesis chalcogenide nanowires encapsulated in poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) that are used as templates for the synthesis of Ag$_{2-x}$E (where E=Te, Se) via topotactic chemical transformation processes. This synthetic method allows us to engineer the composition of our hybrids, whereby we are able to directly influence the thermoelectric properties, including the production of both p-type and n-type materials from the same parent material. We detail the structural and morphological development of our materials with changing stoichiometry during aqueous based synthesis via X-Ray diffraction (XRD), X-Ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) and relate this to their thermoelectric performance. We take the example of one of our n-type Ag$_{2}$Te/PEDOT:PSS hybrid materials and further manipulate its performance via post-deposition (de)doping schemes, whereby the PEDOT:PSS is reduced by treatment with Tetrakis(dimethylamino)ethylene (TDAE). This process is followed by UV-Vis spectroscopy and electron paramagnetic resonance spectroscopy (EPR) to detail how this (de)doping process effects the charge carrying species. Control of the competing charge carrier concentration allows further improvement in the n-type hybrid device performance.

11:30 AM EN14.12.04/EN13.04.04
Flexible Cellulose Fiber-Based Hierarchical Porous Bismuth Telluride for High-Performance Thermoelectrics and Energy Harvesting Device Kaiping Tai, Qun Jin and Yang Zhao; Institute of Metal Research, China

Porous modification is general approach to endowing the rigid inorganic thermoelectric (TE) materials with considerable flexibility, however, by which the TE performances are severely sacrificed. Thus, there remains a struggling against the trade-off between the TE properties and flexibility. Herein, we develop a novel strategy to combine the Bi$_2$Te$_3$ thick film with the ubiquitous cellulose-fiber (CF) print-paper via unbalanced magnetron sputtering technique (ACS Appl. Mater. Interfaces 10, 1743, 2018). The Bi$_2$Te$_3$/CF TE composites with tailorable shapes and dimensions were successfully obtained by our approach, which have reasonable internal resistance as components of TE devices with in-plane configurations. Owing to the hierarchical nano-micro porous microstructures and the excellent fraction resistance of the Bi$_2$Te$_3$/CFs constructions, the prepared TE composites with Bi$_2$Te$_3$ nominal deposition thickness of tens of micrometers exhibit mechanically reliable flexibility, of which the bending deformation radius could be as small as a few millimeters. Meanwhile, the thermal conductivity was remarkably reduced, due to the phonon-nanopore scattering effects. Enhanced Seebeck coefficients were observed comparing with the dense films and the power factors of ~250 to 400 μW/mK$^2$ were obtained for the composites from room temperature (RT) to 473 K, which can be further improved by optimizing the carrier concentrations. As a result, the TE figure of merit, ZT, is as high as ~0.38 at 473K.

Moreover, Fig. 1 depicts the photograph, structure, and working principle diagram of the flexible TE device consisting of 12 pairs of p- and n-type legs integrated on the double sides of CF paper sheet employing a laser beam micro-cutting system, which displays great potential as flexible TE device for thermal energy harvesting. When the light bulb works for about a few minutes, the temperature of the central side rises quickly, the temperature difference between the center and periphery is about 50 K from the infrared image, and the TE device generates an output voltage of 0.144 V. This kind of flexible TE device can realize the collection and recovery of heat energy in daily life to power flexible electronics, such as wearable devices and environmental monitors, which also promotes the development of paper-based and thin-film electronics.

11:45 AM EN14.12.05/EN13.04.05
Creep Behavior of Thermoelectric Materials Muath M. Al-Malki$^{1,2}$, Qinyi Qiu$^3$, Tiejun Zhu$^3$, G. Jeffrey Snyder$^1$ and David Dunand$^1$; $^1$Northwestern University, United States; $^2$King Fahd University of Petroleum and Minerals, Saudi Arabia; $^3$Zhejiang University, China

Since the 1960’s, NASA has implemented Radioisotope Thermoelectric Generators (RTGs) to supply energy for many of its satellites and space probes. Similar generators for industrial and automotive waste heat recovery have been proposed and many new thermoelectric generator materials have been investigated. Nonetheless, mechanical integrity for the full operational life of the thermoelectric modules, which can extend to decades, has not been given much consideration in such applications. Among many contributors, clamping forces, vibrational stresses, and thermally-induced mismatch stresses may combine to give stress levels high enough to deform the thermoelectric
module by creep, thus diminishing its useful lifetime. To date, few thermoelectric materials have been tested for
creep, including Bi$_2$Te$_3$, PbTe, Mg$_{0.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$, and TAGS-85.

In the present talk, we show the case of the compressive creep deformation behavior of two thermoelectric
materials; half-Heusler n-type Hf$_{0.3}$Zr$_{0.7}$NiSn$_{0.98}$Sb$_{0.02}$ and n-type skutterudite (Yb-CoSb$_3$) alloys, at 500-705 °C.
When subjected to uniaxial compressive stresses at 600°C, the n-type half-Heusler alloy Hf$_{0.3}$Zr$_{0.7}$NiSn$_{0.98}$Sb$_{0.02}$
exhibits Newtonian flow, consistent with diffusional creep of its fine-grain (1-7 μm) microstructure achieved via
spark-plasma sintering of powders. In addition to its promising thermoelectric performance at high temperatures,
this alloy sustains very high compressive stresses at 600°C (from 21 to 359 MPa, for ~ 23 days) without
macroscopic failure. However, the brittle nature of the alloy leads to the formation of numerous cracks at such high
stresses, which in turn deteriorate the thermoelectric performance. A more realistic creep stress range (15-46 MPa,
for ~ 4 days) preserves the high thermoelectric figure of merit $zT$. Among thermoelectric materials mechanically
creep-tested to date, the ZrNiSn-based Half Heusler alloy has the highest creep resistance. On the other side, the n-
type skutterudite (Yb-CoSb$_3$) alloy showed acceptable creep resistance under protected environment.

Given their high melting temperature, stiffness, and creep resistance, half-Heusler alloys appear uniquely suited for
long-term thermoelectric applications where high stresses and temperatures are present.

SESSION EN14.13/EN13.05: Joint Session: Thermoelectric Devices and Applications
Session Chair: Jayakanth Ravichandran
Wednesday Afternoon, December 4, 2019
Sheraton, 3rd Floor, Commonwealth

1:30 PM *EN14.13.01/EN13.05.01
Advanced Materials and Their Infusion into Efficient Thermoelectric Power Generation Systems Jean-Pierre
Fleurial and Sabah Bux; California Institute of Technology, United States

Thermoelectric power sources have consistently demonstrated their extraordinary reliability and longevity for deep
space missions as well as terrestrial applications where unattended operation in remote locations is required. The
discovery of new, more efficient materials, and the development of practical, robust elements and device
technologies are the key to improving existing space power system performance and versatility and expanding the
use of thermoelectrics into efficient, cost-effective terrestrial applications using medium to high grade heat sources.
We present an overview of NASA-funded collaborative research efforts to identify advanced bulk thermoelectric
materials, capable of quadrupling current state-of-practice average $ZT$ values over the available operating
temperature range of 1275 K to 475 K, through the exploration of structurally complex compounds allowing for a
wide range of chemical tuning and the possibility of forming stable nano- and micro-scale composites. Materials-
and device-level experimental performance validation accomplished to date, technical challenges, progress and
plans for technology infusion into future thermoelectric power systems are discussed.

2:00 PM EN14.13.02/EN13.05.02
Understanding Thermoelectric Devices at the Micro Scale Nicolas Perez, David A. Lara Ramos, Vida Barati,
Javier Garcia, Heiko Reith, Guodong Li, Gabi Schierning and Kornelius Nielsch; IFW Dresden, Germany

Energy harvesting and thermal management are required for applications in the internet-of-things, autarkic sensors,
or highly integrated electronic devices. Thermoelectric generators and coolers are promising technologies for
localized energy harvesting and thermal management. These devices are currently well optimized for near-room
temperature operation at the macroscopic scale. However, the high integration density of today’s most significant
applications requires an increasing degree of miniaturization. Using finite element calculations, we gained insight on
the design guidelines for micro thermoelectric devices with realistic material properties, and with concurring size
and geometry constraints [1]. Understanding the interplay between thermal and electrical heat fluxes at the micro
scale allowed our group to fabricate micro thermoelectric devices for thermal management, efficient enough that can
be integrated in electronic packages [2]. Our relevant findings about the design of micro thermoelectric devices will
be presented.
The detection of temperature and dynamics of working fluids, including water, is important for experimental and industrial applications, such as detection of precise changes in fluid environment, monitoring of drainage or cooling water at factory facilities, micro/nano flow analysis. However, due to the spatial limitations or complex geometry of fluid channel interfaces, it is important to accurately detect multiple parameters that are optimally integrated into the operating platform. Also, many fluid sensors necessarily disrupt the natural flow within the platform, and even though the installation of the sensing device should not affect the intrinsic properties of the target element in fluid applications. In this work, we develop a flexible, attachable dual-output sensor for fluid temperature and transfer dynamics based on structural design of thermoelectric materials (SDTM). The SDTM flexible substrates using PET was developed to detect real-time changes in temperature and peak voltage reflecting fluid dynamics. Simple sputtering deposition of Bi2Te3 through a patterning mask has allowed the fabrication of dual-power sensors which do not affect the fluid flow shape. When the working fluid contacts the surface, thermoelectric structure pattern induces continuous double thermal wave and time interval without disturbing the natural flow of working fluid. The raw voltage signal induced by thermal gradient wave provides the magnitude of the first peak voltage and the duration between the two peaks, which show the real time temperature and the moving velocity of the working fluid. Furthermore, as a demonstration of an expandable platform using SDTM, a scalable sensor array comprising multiple SDTMs was fabricated as a large-area device for sensing a fluid temperature flow dynamic sensing device. Its performance with respect to sensing the fluctuation of working fluid temperature and kinematics was verified using a 4 × 4 SDTM array. As a result, the new methodology using SDTM can contribute to the development of entirely new technologies for next-generation sensors that require advanced features such as multi-element detection and a variety of integrated flexible and removable features.

2:30 PM BREAK

SESSION EN14.14/EN13.06: Joint Session: Thermoelectric Materials and Applications
Session Chair: Gabi Schierning
Wednesday Afternoon, December 4, 2019
Sheraton, 3rd Floor, Commonwealth

3:30 PM *EN14.14.01/EN13.06.01
Thermoelectric Cooling Using a New p-Type Material Zhifeng Ren; University of Houston, United States

Bi2Te3-based p-type Bi0.5Sb1.5Te3 and n-type Bi2Te2.7Se3 have been the only materials used for thermoelectric cooling for decades. Even though the progress on advancing the thermoelectric figure-of-merit (ZT) has been significant especially the materials with peak ZT at high temperatures, materials with high enough ZT around room temperature are very rare. Up to now, in addition to Bi2Te3-based ones, the only reported is p-type MgAgSb with ZT of ~0.8 at room temperature. There is no report on any n-type material exhibiting ZT similar to that of the n-type Bi2Te2.7Se3. In this talk, I will present a new n-type material that has a ZT of ~0.7 at room temperature, which is comparable to that of n-type Bi2Te2.7Se3. The cooling performance of a unicouple consisting of the new n-type material and the p-type Bi0.5Sb1.5Te3 is also in par with the commercial legs consisting of the p-type Bi0.5Sb1.5Te3 and n-type Bi2Te2.7Se3.

4:00 PM EN14.14.02/EN13.06.02
Modeling the Temperature Dependent Seebeck Coefficient of Metastable Amorphous Ge2Sb2Te5 and Impacts of Thermoelectric Effects on the Operation of Phase Change Memory Devices Jake Scoggin, Noah Del Coro,
Thermoelectric effects play a significant role in phase change memory (PCM) and Ovonic threshold switch (OTS) devices used as access devices in PCM cells [1]. Typical PCM cells are two-terminal nanometer-scale resistive memory devices which can be reversibly switched between a low-resistance crystalline and a high-resistance amorphous state via nanosecond electrical pulses. Amorphization in PCM devices is achieved by self-heating the phase change material, typically a chalcogenide, close to its melting temperature, followed by a sudden quench. Crystallization is achieved by self-heating the phase change material above its glass-transition temperature. OTS devices typically use amorphous chalcogenides that do not crystallize during normal device operation. The local current densities in PCM and OTS devices can reach $10^8$ A / cm$^2$, giving rise to local temperatures in excess of 900 K and thermal gradients as high as 50 K / nm; hence, Peltier effects at material interfaces and Thomson heating within the active area are substantial. Accurate modeling of thermoelectric effects requires knowledge of temperature dependent electrical resistivity and Seebeck coefficients of these materials. These parameters can be measured at low temperatures on as-deposited amorphous films [2]. However, melt-quenched amorphous materials’ parameters tend to differ from as-deposited films, and PCM materials rapidly crystallize at higher temperatures. High-speed metastable electrical resistivity measurements can be performed on nanoscale devices using electrical pulses to uniformly amorphize devices up to approximately 200 nm in diameter [3], but larger devices tend to form current filaments and hence do not amorphize uniformly. On the other hand, measurement of the Seebeck coefficient ($S$), which is vital to understanding thermoelectric effects, is very difficult at small scales.

In this work, we model the Seebeck coefficient for metastable amorphous Ge$_2$Sb$_2$Te$_5$ (aGST) based on high-speed experimental results [3] and an energy band diagram proposed by Muneer et al. [4] from 300-850 K [3], [5], and we analyze thermoelectric effects in PCM cells using finite element phase change device simulations [6]–[9]. We calculate the electron and hole Seebeck contributions $S_e$ and $S_h$ in metastable aGST with the band diagram in [4] and find that $S_h$ is similar in both magnitude and slope to $S$ measurements on as-deposited aGST thin films in 300-400 K range [5], [10], consistent with the unipolar conduction assumed when deriving the band gap in [4]. We use $S_h$ as the Seebeck coefficient in metastable aGST and simulate reset and set operations in a PCM double mushroom cell and find that the Seebeck differential between crystalline and amorphous GST results in significant heating/cooling at amorphous-crystalline junctions during both crystallization (set) and melting (reset).


4:15 PM *EN14.14.03/EN13.06.03*

Flexible Thermoelectric Materials by Organic Intercalation of Two-Dimensional Layered Compounds

Chunlei Wan¹, Kunihioto Koumoto² and Kun Zhang³; ¹Tsinghua University, China; ²Nagoya Industrial Science Research Institute, Japan

Flexible materials with high thermoelectric performance have attracted growing interest recently. By intercalating organic molecules into the van der Waals gap of inorganic two dimensional layered compounds, we developed a large family of thermoelectric materials with excellent mechanical flexibility. The inorganic and organic monolayers are alternatively stacked to form an inorganic/organic superlattice, in which the high electronic transport properties of the inorganic component has been maintained and the thermal conductivity was dramatically suppressed by the organic components, finally resulting in boosted ZT value. We have demonstrated this idea in several two dimensional host materials, including TiS$_2$, Bi$_2$Se$_3$ and TaS$_2$, etc. The abundant choice of the organic
molecules also brings new opportunities to optimize the thermoelectric performance, such as the dielectric screening effect and the quantum confinement effect. We finally developed a solution-processed strategy to fabricate large area flexible thermoelectric foil based on this inorganic/organic superlattice, which enables easy integration into energy-harvesting electronic devices.

4:45 PM  EN14.14.04/EN13.06.04
Diffusion Behaviors of Bonding Interface of Bi–Te Based Thermoelectric Materials with Ni/Au Barrier Fabricated by Different Deposition Processes  Ekubaru Yusufu1, Tohru Sugahara1, Michio Okajima2, Shutaro Nambu2 and Katsuaki Suganuma1; 1The Institute of Scientific and Industrial Research, Osaka University, Japan; 2E-ThermoGentek Co., Ltd., Japan

Recently, our group developed a Bi–Te-based TEG device by using conventional semiconductor packaging technology. In that device, Ni/Au was used as the diffusion barrier, and Sn–Ag-based solder was used as the bonding material. Although Bi–Te-based TE materials can be used up to approximately 300°C, the maximum operating temperature of the device was limited to approximately 150°C owing to the low melting point of the Sn–Ag-based solder (~150°C) that bonds Bi–Te-based TE materials and Cu electrodes. Therefore, in order to apply higher temperature differences to the device, in this study, we attempted to develop a bonding interface resistant to heat up to 250°C. Ni/Au was retained as the diffusion barrier layer, but Ag paste was chosen as the bonding material, instead of the Sn–Ag-based solder, because it has many advantages such as high-temperature stability (melting point ~ 960°C), printability, low electrical resistivity, high thermal conductivity (150 Wm⁻¹K⁻¹), and a temperature requirement of less than 300°C for sintering-bonding. The Ni/Au diffusion barrier layer was prepared using two different deposition processes, sputtering and electroplating, and the element diffusion behaviors of these two bonding interfaces at 250°C were investigated.

In the bonded sample with sputtered Ni/Au, the Cu electrode diffused violently into the chip and formed a Cu–Te-rich phase. On the other hand, in the bonded sample with electroplated Ni/Au, the diffusion of Cu was blocked, but a NiTe phase formed on the chip side. The above results demonstrate that, with sputtered Ni/Au, grain-boundary diffusion is predominant and Cu electrodes diffused along the grain boundaries, while with electroplated Ni/Au, self-diffusion is predominant because of the instability of the monocrystalline–amorphous phase. These results suggest that the highly crystalline Ni layer, which has dense grain boundaries and no pores, is a highly effective diffusion barrier.

**SYMPOSIUM EN15**

Nanomaterials for Sensing and Control of Energy Systems—Processing, Characterization and Theory
December 2 - December 4, 2019

Symposium Organizers
Pu-Xian Gao, University of Connecticut
Paul Ohodnicki, National Energy Technology Laboratory
Lyubov Titova, Worcester Polytechnic Institute
Zhaoliang Zhang, University of Jinan

* Invited Paper

SESSION EN15.01: Chemical Sensors for Advanced Energy Systems
Session Chairs: Pu-Xian Gao and Paul Ohodnicki
Monday Morning, December 2, 2019
Sheraton, 3rd Floor, Commonwealth
Perovskite metal oxides have been studied thoroughly in the literature as electrode materials for solid oxide fuel cells, which necessitate stability at high-temperature and in chemically harsh environments. The stability of the perovskite crystal structure under high concentrations of dopants allows for a great deal of versatility in material design, due to the unique electrical, magnetic, and optical properties exhibited by materials within this family. The incorporation of metallic nanoparticles into metal oxide thin films has also been previously demonstrated as a method for introducing a strong, surface-sensitive optical absorption, which can be tracked for harsh environment sensing on the optical fiber platform.

In this work, the gas and temperature sensing properties will be presented for several perovskite oxide thin films (i.e., LST, LSM, LSF, LSC) incorporated with gold nanoparticles, measured under both oxidizing and reducing conditions at high temperature (up to 800 C). On their own, the optical absorption spectrum of these perovskite oxide films is governed by oxygen-defect sensitive interband transitions, in some cases extending into the visible and NIR, and the free-carrier absorption characteristic of other conducting metal oxides. Using modeling and in-situ optical transmission measurements at high temperature, the interaction between the nanoparticle localized surface-plasmon resonance (LSPR) and the unique properties of the individual host films will be examined. The sensing response is further studied using principal component analysis (PCA) to demonstrate improved sensing discrimination of several parameters of interest (i.e., temperature and gas concentration). The combined versatility of the perovskite oxide class of materials and LSPR-based sensing will be discussed as a tool for developing optical sensors able to provide “electronic nose”-like discrimination, suitable for harsh environment.

Differentiating Multiple Gas Analytes Using a Single Nano-Array Sensor

Commonly adopted resistive-type chemical sensors are based on metal oxide semiconductors, which usually display significant cross-sensitivities for different gaseous analytes, resulting in a low selectivity.1 By collecting sensing signals from a number of different individual sensors, so called a sensor array, the selectivity could be remarkably enhanced.2 However, complex and costly fabrication protocol is usually associated with integration of such an sensor array, limiting their applications , especially upon operation under extreme environments. Specifically, the complexity is due to the increased number of dissimilar sensor devices in need of complex electrical wiring, contacts, as well as electrodes, which may dramatically increase the risk of potential system malfunction. Besides, the bulky size and shortened service life resulted from complex circuitry may increase the cost of deployment, operation, and maintenance. In this study, a new pattern-recognition strategy has been developed based on correlation of resistance-metric mode and impedance-metric mode for differentiation of multiple gas analytes using a single ZnO nanorod array (nano-array) gas sensor. Uniform ZnO nano-arrays were grown on silicon substrate using a microwave-assisted hydrothermal synthesis method. The characteristic signature for the target analyte is successfully extracted by incorporating the resistive response and frequency-dependent dielectric response via global Electrochemical Impedance Spectroscopy (EIS). Targeting differentiation of three different oxidative gases, i.e., NOx, SO2 and O2, a database was established using the sensitivities characterized from three sensing data sets from resistance-metric mode, real part and imaginary part of the impedance-metric mode. These three oxidative gas analytes have been successfully differentiated through a principal component analysis (PCA) practice. Linear and non-linear decision boundaries have been computationally built for pattern recognition and analytes quantification utilizing machine neural network training. A facile user interface (UI) for recognition of unknown gas analyte has been developed using the MATLAB codes, with the error of analyte concentration achieved as low as 2%. The identification of test analytes beyond the available training data sets could be accomplished using a deep learning training-set; the error of corresponding concentration prediction is around 4.5%. In addition to the single analyte analysis, the on-board interrogation could be achieved towards gas mixture (i.e. NO and NO2) through correlation between the electrical and electrochemical responses. According to the in-situ DRIFTS spectra, no mutual interaction occurs between the NO and NO2 in the co-adsorption scenario. As such, a pair of equations could be derived between gas mixture responses and components’ concentration on the basis of charge carrier concentration. Facilitated by a graphical method, the detailed concentration of component gas could be quantified using the measured responses of NOx mixture in the bimodular sensing on such a single nano-array sensor platform.
Reference


9:15 AM EN15.01.03
Oxygen Diffusion in Functional Ultrathin Materials Generated by Atomic Layer Deposition for Gas Sensing Applications (FunALD) Hartmut Finger¹, Dorothee Dietz², Anna M. Knauß², Jupe Andreas², Holger Kappert³ and Tim Huelser¹; ¹Institute of Energy and Environmental Technology e.V., Germany; ²Fraunhofer Institute for Microelectronic Circuits and Systems IMS, Germany

Air quality sensors and sensors in measuring systems detect toxic and explosive gases and warn against the escape of hazardous pollutants. Today's sensors have a comparatively low sensitivity and a large cross-sensitivity for many applications with high power consumption and high costs. Actually, established nano-techniques use nanoparticles or nanowires that are processed at high temperatures separately from the substrate. Subsequently, these particles are suspended in liquids and applied to electrodes - the electrodes are arranged on the CMOS surfaces. However, the established nano-techniques provide only disordered structures. In addition, there are problems in the reproducibility of production.

"FunALD" is now taking a significant step further: the nano-electrodes are not produced by applying nanoparticles, but based on the ALD method (Atomic Layer Deposition). Ultrathin single and multiple layers with a layer thickness of less than 50 nm are deposited monolayer after monolayer. With the ALD method, layers with exact thicknesses and tunable electrical properties can be deposited. Ultrasensitive self-supporting nanowires, made of metal oxide and produced in a sacrificial layer process, are used as the sensing component.

As a first step we investigated the oxygen diffusion within tin oxide as sensing material. The sensor was heated up from room temperature to 313 K to evaporate surface water from the sensor surface. Resistance measurements reveal an increase of conductivity by a factor of about 10 during this process. After that process, the temperature was cycled between 313 K and 353 K and the resistance was measured. Within this temperature range an increase of conductivity with increasing temperature is observed as it is expected for a semi conducting material. An activation energy of 58 meV has been calculated from an Arrhenius representation and linear regression of the data for the charge carrier transport process. The oxygen diffusion capability of the sensing material was tested under N₂ atmosphere at 428 K. For this purpose the sensitivity $S = R_{N₂}/R_0$ was measured for 50 minutes, where $R_{N₂}$ represents the resistance in dry N₂ and $R_0$ the initial value. In dry N₂, the resistance decreased reversibly by 1–2 orders of magnitude and this decrease can be attributed to increased electronic conduction associated with loss of O₂ on reducing oxygen partial pressure $pO₂$ in the surrounding atmosphere. $S$ remains constant after 40 minutes, which can be attributed to a saturation of oxygen loss within the tin oxide. An immediate change of resistance was observed by introducing 400 ppm O₂ into the measurement chamber, which reveals an extremely fast increase of resistance by about 15 % with 5 s. Finally, ALD processed tin oxide shows a remarkable high, reversible loss of oxygen, in N₂ and air at temperatures of 428 K and the changes can be attributed to sample surfaces effects, at least on short timescales.

9:30 AM EN15.01.04
Polymers Coated Palladium Sensors for H₂ Detection—Insights from First-Principles Calculations Lucy Cusinato and Anders Hellman; Chalmers University of Technology, Sweden

Hydrogen-powered vehicles are part of a more global answer in order to develop a sustainable society. However, like with other energy sources, safety issues are crucial, and because of the high flammability of hydrogen gas, efficient hydrogen sensors are needed. Hydrogen sensors meeting performance targets for use in hydrogen-powered vehicles are scarce, and a lot of effort has been invested in material design to improve the sensitivity and response time of such sensors. Palladium-based materials have been known for long for their capacity to easily form hydride phases, making them good candidates for hydrogen sensing applications. Those rely on two fundamental features of metallic palladium: the ability to dissolve hydrogen to form stable hydride and the possibility to easily release the stored hydrogen. More than a bare protective layer, polymer coating of palladium nanoparticles has been shown to enhance sensing
behavior. Using DFT, we shed light on how this phenomenon can be explained. We propose a large scope model for this system, going from the modelling of H₂ diffusion in a polymer matrix to the study of subsurface hydrogen diffusion in palladium hydride via the comprehension of the processes occurring at the polymer-metal interface. In order to do this, the effect of several polymer coating on H₂ adsorption/desorption as well as subsurface diffusion is considered. Rationalization on how and why the polymers affect the metal NP is proposed. The diffusion of H₂ molecules in polymer environment is studied as to take into account a realistic medium for those nanoparticles. Finally, the challenging task of properly describing the metal NP-polymer interface is addressed in order to be able to give an as complete and as accurate as possible view of the whole phenomenon.

9:45 AM EN15.01.05

Nanoparticle Chemisorption Printing of Silver Nanocolloid—Underlying Mechanism and Sensing Application Tatsuo Hasegawa; Univ of Tokyo, Japan

Silver nanocolloid (or nanoink), a dense suspension of ligand-encapsulated silver nanoparticles, is an important material for printing-based device production technologies. Here we present and discuss a groundbreaking printing technique that takes advantage of the unique nature of specific silver nanoinks that show self-sintering characteristics [1]. The technique, which we call as surface photo-reactive nanometal printing (SuPR-NaP), is based on chemisorption effect of silver nanoparticles on activated patterned perfluoro-polymer surfaces. The technique is extremely simple, only composed of two-step processes: fabrication of a patterned activated surface by masked vacuum ultraviolet (VUV) irradiation of the perfluoro-polymer (Cytop) layer surface, and then blade coating to expose the silver nanoinks on the surface for a short period of time at ambient conditions. Eventually, it allows easy, high-speed, and large-area manufacturing of ultrafine metal wiring with a minimum line width of 800 nm that is conductive without any post-heating treatment, and strongly adheres on substrate surfaces. These features are in striking contrast to the conventional printing technique which usually suffer from the limitations of the physisorption phenomena of the fluidic ink. The technique is applicable to the production of flexible and transparent touch screen sensor sheet composed of printed ultrafine metal mesh.

We found that the technique is possible only with a class of silver nanoinks, obtained by thermal decomposition of oxalate-bridging silver alkyl-amine complexes [2]. The peculiar nature of these nanoinks is that the high dispersion stability is preserved for several months at room temperature, whereas the silver nanoparticles are readily self-fused with each other, if the metal nanoinks are dried out, eventually exhibiting metallic conductivity at room temperature. Based on the confocal dynamic light scattering study, we recently demonstrated that these silver nanoinks are composed of a unique balance of ligand formulation and dispersant composition, and that the unique balance enables the rapid silver nanoparticle chemisorption [3,4]


10:00 AM BREAK

10:30 AM *EN15.01.06

Harsh Environment Compatible Multivariable Chemical Sensors Michael Carpenter¹, Nora M. Houlihan¹ and Radislav A. Potyrailo²; ¹SUNY Polytechnic Institute, United States; ²GE Global Research, United States

Monitoring the levels of combustion gases such as H₂, CO and NO, within high temperature (>300°C) environments requires multivariable sensing materials with demonstrated stability and resilience. Au nanoparticles (AuNPs) have shown potential in plasmonic gas sensing applications due to their catalytic activity, redox stability, and plasmonics sensitivity to changes in its surrounding environment. Encapsulation of the AuNPs in a variety of 2D metal oxide thin films enables both the sensitive and selective detection of target gases within a multivariable sensing array or a single sensing element system design. Au nanorods (AuNRs) embedded in metal oxides allows for the plasmonically active wavelength region to range from the visible to the NIR through variation of the AuNR aspect ratio. Furthermore, AuNRs can be designed to have both the transverse and longitudinal dipole modes as well as multipole plasmon modes for extended multivariable sensing applications within a single array element. Recent multivariable sensor platforms which utilizes Morpho butterfly wing dimensionality for bio-inspired inorganic 3D structures will also be detailed. Functionality and performance parameters of metal-metal oxide thin film coatings on 3D structures will be compared with 2D thin films within the framework of general sensor design as well as their
application for the oxygen free detection of steam reforming gases.

**11:00 AM EN15.01.07**  
**Selective Sensing of Formaldehyde in Indoor Air**  
A. T. Güntner, S. Abegg and Sotiris E. Pratsinis; ETH Zürich, Switzerland

A major challenge in environmental sensing is the detection of trace-level pollutants (e.g. carcinogenic formaldehyde\(^1\)) in complex gas mixtures. Devices based on chemo-resistive gas sensors would offer sufficient sensitivity and low detection limit down to ppb, _but lack selectivity_. Here, we present a highly sensitive, selective and compact sensor array for real-time quantification of formaldehyde at realistic conditions\(^2\). This array consists of four nanostructured and highly porous Pt-, Si-, Pd- and Ti-doped SnO\(_2\) sensing films directly deposited onto silicon wafer-based microsubstrates by flame spray pyrolysis (FSP). The constituent sensors offer stable responses and detection of formaldehyde down to 5 ppb (signal-to-noise ratio > 30) at breath-realistic 90% relative humidity. Each dopant induces different analyte selectivity enabling selective detection of formaldehyde in 2- and 4-analyte mixtures by multivariate linear regression. In simulated breath (FA with higher acetone, NH\(_3\) and ethanol concentrations), formaldehyde is detected with an average error ≤ 9 ppb using the present array.

In a next step, this can be improved further when combining the sensors with highly selective _zeolite membranes_ pre-separating gas mixtures\(^3\). Zeolites - broadly applied in catalysis and gas separation - effectively separate molecules based on kinetic diameter, sorption and diffusion characteristics\(^4\). Therefore, zeolite membranes are suitable filters for gas sensors removing undesired species from indoor air. As proof-of-concept, a zeolite MFI/Al\(_2\)O\(_3\) membrane is placed upstream a highly sensitive but weakly selective Pd-doped SnO\(_2\) sensor. Their combination exhibits exceptiona selectivity (>100) for formaldehyde down to 30 ppb at 90% relative humidity, outperforming state-of-the-art detectors by more than an order of magnitude. This novel concept is readily extendable to other tracers, as manifold combinations of _widely tunable_ microporous membranes and gas sensor types can be realized in the modular sensing device. This could enable a new class of highly sensitive and selective environmental monitors.

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vehicle operation. Unfortunately, ammonia is one of the byproducts of reduction of NOx during the process, which is often referred to in the industry as "ammonia slip". Released ammonia participates in the oxidation of SO2 into SO3, which reacts with atmospheric water vapor to form sulfuric acid fumes, and also forms ammonium sulfate which can clog flue lines and filters. In this work, we report on the development of a one-time electronic ammonia fuse. Formic and citric acids were reacted with ammonium vanadate precursor to synthesize vanadium oxides. Powder X-ray diffraction (PXRD) confirmed the formation of the orthorhombic and monoclinic crystal structure of V2O5 and VO2 respectively. Energy dispersive x-ray analysis (EDX) confirms the purity of the samples. Using transmission electron microscopy (TEM), we inferred that the average diameter of vanadium oxides particles was in the range of 90-120 nm and some small size particles ~70-90nm are also observed. Chemical composition of the synthesized vanadium oxides was confirmed using Raman spectroscopy. V2O5 shows Raman shift at 993 cm−1, 698 cm−1, 478 cm−1 and 404 cm−1 which can be attributed to the V=O bonding, stretching modes of triple-bonded oxygen, stretching mode of V−O−V, and bending vibrations of the V−O bonds respectively. VO2 show a weak hump at 224 cm−1 which can be attributed to motions of V, highlighting the phase transition of monoclinic phase to rutile phase. Commercial silicon dioxide wafers (University Wafers) were cleaned (RCA) and a bottom metal stack was deposited using DC sputtering (Cr) and RF sputtering (Au). Using the synthesized VxOy (x=1,2, and y= 2, 5) species, a film of the oxide was deposited using spin-coating. Top contact (Ag) was deposited using thermal evaporation to complete a metal insulator metal structure. Current-voltage (IV) characterization of devices (Keithley 4200-SCS) showed an on/off ratio of 102 and less than 101 respectively for V2O5 and VO2. On exposing these devices to ammonia solution (boiling point 24°C) by introducing 5-10 µl of ammonia (30%) solution at 60-70°C, the IV characteristic of the device started exhibiting a distorted waveform, without any retention, possibly due to the effect of the corrosive ammonia. We are at present establishing the minimal exposure level of ammonia to achieve the destruction of the device. In deployment, the exhaust from the catalytic converter would be monitored by this sensor to provide feedback to the automotive control to reduce ammonia emissions from the vehicle.

11:45 AM EN15.01.10
Facile Conversion of Zn5(CO3)2(OH)6 to ZnO Induced by Ca(OH)2 to Form CaO-ZnO—Role of Active Nanointerfaces in Selective CO2 Gas Detection
Shravanti S. Joshi1,2,3; 1G.S. Mandal's Marathwada Institute of Technology, India; 2CSIR Indian Institute of Chemical Technology, India; 3RMIT University, Australia

Environmental pollution as a result of rapid urbanization and industrialization and its indirect effect on global warming, climate change, and ocean acidification has been of increasing scientific concern worldwide over the past few decades. Carbon dioxide (CO2) is one of the many such toxic pollutants that contribute to environmental pollution, thus stimulating extensive research and concerted efforts for its detection, monitoring, capture, and storage. However, the development of metal oxide semiconductor (MOS) based heterostructures with controlled structural motifs such as a large number of active nanointerfaces for low temperature (sub 200°C) CO2 sensing applications continues to be an alluring task. Herein, we report on the highly selective CO2 sensing performance of CaO-ZnO heterostructures achieved using an elegant strategy of calcium hydroxide (Ca(OH)2) mediated transformation of zinc hydroxide carbonate (Zn5(CO3)2(OH)6) to zinc oxide (ZnO) at 50°C. FE-SEM analysis of zinc hydroxide carbonate powder revealed hierarchical microspheres (referred here as ZMS) with diameters of 3–8 μm, primarily composed of numerous thin sheets (thickness ~10 nm) interleaved to form floral architectures. Feasibility of the synthetic route was probed by comparing CO2 sensing characteristics of CaO-ZnO heterostructures achieved at 50° C for 12 h with the ones obtained by heat treatment at 600°C for 2 h and referred to as Ca-ZMS and CaO-ZnO, respectively.

Case 1: Synthesis of Ca-ZMS hierarchical heterostructures
Briefly, ca. 67 mg of as-synthesized ZMS was added to 40 ml of water in a beaker and sonicated for 60 min. To this solution, 33 mg of Ca(OH)2 was added to the prepared solution containing 100 mg/40 mL Ca-Zn-C-O-H complex mixture. The calculated amount of Ca(OH)2 varied based on weight percentages. The complex mixture solution was then continuously stirred for 12 h followed by drying overnight at 50°C using a hotplate and will be referred to as “R-Ca-ZMS” (where R = Ca(OH)2 concentration in wt.%).

Case 2: Synthesis of Ca-ZnO hierarchical heterostructures
Ca-Zn-C-O-H complex mixture (100 mg/40 mL) was sonicated for 30 mins followed by centrifuging and drying overnight at 70°C in an ambient air atmosphere using a furnace. Subsequently, the dried Ca-Zn-C-O-H mixture was weighed (20 mg) and calcined at 600°C for 2 h in a muffle furnace under air atmosphere and post-calcination will be referred to as “R-CaO-ZnO” (where R = Ca(OH)2 concentration in wt.% added before the calcination). Calcination
at high temperature was deemed necessary to completely convert Zn$_5$(CO$_3$)$_2$(OH)$_6$ to ZnO and Ca(OH)$_2$ to CaO with an increased adhesion among the singularities.

Pure ZnO, Zn$_5$(CO$_3$)$_2$(OH)$_6$, Ca(OH)$_2$ and CaO microsensors exhibited low sensitivity (≤20%) towards 500 ppm of CO$_2$, whereas the CaO-ZnO heterostructures from both the cases exhibited significant sensitivity (from 26 to 91%) towards CO$_2$ concentration in the 100-10000 ppm range, respectively, when operated at 150°C. In this study, 25Ca-ZMS heterostructures exhibited promising sensitivity of 77% and a superior selectivity of 98%, while 25CaO-ZnO heterostructures revealed lower sensitivity of 59% and selectivity of 87% upon exposure to CO$_2$ gas (500 ppm). The gas sensing mechanism in dry and humid conditions underlying the high selectivity in presence of 6 analyte gases that commonly coexist with CO$_2$ (such as methane, ethanol, hexane, H$_2$, CO, NO$_2$, SO$_2$ etc) and faster kinetics (response and recovery times of 230 s and 280 s to 100 ppm) compared to control samples as well as to the ones reported in the literature is detailed. Improved performance is attributed to the low-temperature synthesis route which results in a gas-accessible hierarchical morphology. Additionally, the high CO$_2$ adsorption capacity of CaO combined with the compatibility of CaO-ZnO in forming highly active $n$-$n$ nanointerfaces is a promising step towards developing a precise and cost-effective CO$_2$ gas microsensor.

SESSION EN15.02: Environmental Energy Detection and Utilization
Session Chairs: Pu-Xian Gao and Feng-Yuan Zhang
Monday Afternoon, December 2, 2019
Sheraton, 3rd Floor, Commonwealth

1:30 PM *EN15.02.01
Terahertz Spectroscopy and Microscopy for Non-Destructive Optoelectronic Characterisation of Advanced Functional Nanomaterials Jessica L. Boland; University of Manchester, United Kingdom

The terahertz frequency range (0.1-10THz) provides the perfect probe for investigating electronic processes within these nanomaterials. The energy range of terahertz radiation extends over the energies of several typical quasiparticles, such as free electrons and holes, plasmons, magnons and polarons, and can stimulate collective excitations, such as optical phonons. Terahertz spectroscopy therefore forms a powerful, non-contact, non-destructive technique for measuring electrical conductivity in advanced functional nanomaterials.

In this talk, I will demonstrate how terahertz spectroscopy can reveal the ultrafast carrier dynamics of an ensemble of semiconductor nanowires on ultrafast (<1ps) timescales, allowing characterisation of photoconductivity lifetimes, mobility and doping levels1,2. This technique will directly be applied to InAsSb nanowires to demonstrate the effects of alloying on optoelectronic properties and elucidate the scattering mechanisms governing their carrier transport. I will show that these nanowires have a record-holding electron mobility due to a reduction in defect density and impurity scattering, making them promising candidates for MIR photodetectors and thermoelectric devices3. Following this, I will also introduce near-field THz microscopy, which allows direct imaging of key optoelectronic properties on nanometre length scales with surface sensitivity, as well as direct electrical probing within a device architecture4,5. I will present recent results on topological insulator thin films, highlighting the capability of this technique. Finally, I will show how these techniques can be used to develop novel THz devices based on semiconductor nanowires: single-nanowire THz detectors6,7 and THz modulators8. These devices are promising candidates for active components in THz imaging devices, shrinking down current THz technologies down by 3 orders of magnitude accelerating the development of nanoscale/microscale THz sensing systems.

4. Mooshammer, F. et al. Nanoscale Near-Field Tomography of Surface States on (Bi0.5Sb0.5)2Te 3. Nano Lett. acs.nanolett.8b03008 (2018). doi:10.1021/acs.nanolett.8b03008

2:00 PM  EN15.02.02
Radio Frequency Organic Field-Effect Transistors on Plastic Substrates Bianca Passarella1,2 and Mario Caironi2; 1Politecnico di Milano, Italy; 2Istituto Italiano di Tecnologia, Italy

–The organic electronic field is nowadays collecting increasing interest by both the scientific and industrial world. Compared to the inorganic counterparts, Organic Thin Film Transistors (OTFT), show some important advantages such as flexibility and stretchability but, most importantly, the compatibility with low-cost high-throughput printing-based manufacturing: all these advantages are mainly due to the use of Organic Semiconductors (OSCs). 

OSCs’ properties like, for example, solution processability and easy molecular structure’s tailoring, open a wide range of applications that could not be covered by traditional electronic devices, such as into the medical field with biocompatible sensors, into the consumable electronic field with flexible and infrangible screens, into the wearable electronics field, or into the smart tags and distributed sensors fields. 

On the other side, the stability of these materials and the overall performances of the Organic Field Effect Transistors (OFETs), mainly in terms of operational speed, should be improved. The figure of merit widely adapted to evaluate the operational speed of a single transistor is called Transition Frequency (\(f_t\)) and is defined as the frequency at which the current gain of a transistor, in short circuit condition, is equal to 1. At the state of the art, the highest \(f_t\) measured on planar OFET made by techniques compatible to large-printing is 20 MHz\(^1\), while on a vertical transistor is 40MHz\(^2\). In this contest, the aim of this work is to overcome this limit, bringing the transistors to operational frequencies in the order of hundreds of MHz or of the GHz, keeping the flexibility requirements.

In this landscape, to maintain flexibility and guarantee good performances together, bottom-contacts top-gate OFETs have been fabricated, mainly on flexible and very thin substrates of Polyethylene Naphthalate (PEN) (around 100μm thin and a rms roughness around 50nm) by means of several different techniques: lithography and laser sintering has been used to make bottom contacts, bar coating and/or spin coating have been used to deposit the organic semiconductor and the dielectric layers, thermal evaporation or inkjet printing have been used to deposit the gate electrode. Once the lithography process and the laser sintering have been optimized on plastic substrate, different kind of organic semiconductors and dielectric materials have been used. For example, among the n–type semiconductor, the poly \{N,N’– bis (2–octyldodecyl) – 1,4,5,8 – naphthalene dicarboximide – 2.6 – diyl]–alt–5,5’– (2,2’–bithiophene)} ((P(NDI2OD–T2)) has been optimized and tested on short channel devices, obtaining a directly measured transition frequency of 11MHz. Among the p–type semiconductor materials, optimizations have been carried out on the diketopyrrolopyrrolethieno [3,2–b] thiophene copolymer (DPP–T–TT), obtaining a directly measured transition frequency of 22MHz. This represents an important result because it is the best frequency achieved until now on flexible substrate (with respect to the 14MHz obtained by Perinot et al.\(^3\)).

[1] “Direct-written polymer field-effect transistors operating at 20 MHz”; A. Perinot et al.; Scientific Reports; 2016; DOI: 10.1038/srep3894;

2:15 PM  EN15.02.03
Germanium Nanowire Based Bolometer for Mid-IR Sensing Maximilian G. Bartmann, Masiar Sistani, Juergen Smoliner and Alois Lugstein; Technische Universität Wien, Austria

With the ever-growing number of applications demanding photodetectors in the Mid-IR, ranging from astronomy, pollution monitoring and fire sensing to healthcare, security and automotive, thermal photodetectors especially bolometers gained significant research interest over the last years. Per definition, a bolometer consists of an absorptive element, which is connected to a thermal reservoir through a thermal link and a thermometer. Any radiation, which is incident on the absorptive element, will raise its temperature above that of the reservoir.
proportional to the radiation intensity. Quasi 1D germanium (Ge) nanowires (NWs), embedded between two electrical contacts are perfect building blocks for bolometers according to the above definitions. They have an extremely small thermal mass, and in addition, the same highly temperature dependent electrical resistance as bulk Ge-bolometers, which are already used since decades. Here we present a Mid-IR sensing device based on an individual aluminum (Al) contacted Ge NW on a 40 nm thick Si₃N₄ membrane. By using a thermally induced exchange reaction between the polycrystalline Al contact pads and a single crystalline Ge NW, the length and thus the thermal mass of the NW can be tuned. The resulting self-aligned single crystalline Al leads provide a highly effective heat link to the surrounding macroscopic Al metallization, which acts as the thermal reservoir. The final quasi 1D monolithic NW heterostructure thus resembles an ultrascaled Ge NW segment contacted to crystalline Al leads with atomically sharp interfaces. An electrically contacted multi-layer graphene (MLG) flake placed on the opposite side, acts as the absorber and as an electrostatic gate controlling the Fermi level and thus the intrinsic resistivity of the Ge NW. The heat generated in the absorbing MLG flake is transferred via the ultrathin Si₃N₄ membrane to the NW thus controlling the temperature dependent electrical transport in the diffusive as well as quasiballistic/ballistic for ultrascaled devices with Ge NW length down to 20 nm. In a detailed analysis we investigated the temperature dependence and transient response as well as the the influence of surface traps defining the overall functionality of the bolometer device.

2:30 PM EN15.02.04
A Humidity-Resistance, Super-Durable Triboelectric Nanogenerator from a Fluorinated Polymer Sponge for Efficiently Harvesting Biomechanical Energy Zehua Peng; City University of Hong Kong, Hong Kong

Wearable electronics are becoming increasingly significant owing to their widespread and far-reaching applications in the forthcoming Internet of Things (IoTs) era, including but not limited to health monitoring, motion tracking, and interactive entertainment. The rapid development and potential market of wearable technologies make it urgent to strategically re-aligning currently predominant power supplies, i.e. batteries, considering the limitations in terms of regular recharging and replacing, size and weight, as well as environmental pollution. In this regard, alternative energy supplying technology with the merits of sustainable, maintenance-free, and eco-friendly is highly desired. Triboelectric nanogenerators (TENGs) are proven to be efficient, simple, and environmentally friendly to generate power by daily human motion. Nevertheless, it remains a challenge to improve its unsatisfactory performance under the humid condition that obstructs the practical wearable applications, e.g. being integrated into clothes or shoes, since sweating is inevitable for the body to release excessive heat routinely.

In this work, we report a fluorinated polymer sponge-based TENG (FPS-TENG), which is capable of addressing the moisture-sensing issue benefiting from intrinsic hydrophobicity of the sponge structure and chemical introduction of hydrophobic terminated functional groups, achieving a relatively stable output performance over a wide range of ambient humidity. Concurrently, the FPS-TENG is super durable even under heavy abrasion (simulated via wearing away 1mm-thickness surface layer), indicating the capability in long-term operation under harsh conditions. Specifically, the FPS-TENG is primarily assembled with electropositive copper electrodes and a critical electronegative component, i.e. polydimethylsiloxane (PDMS) based functionalized polymer sponge (FPS), which is suitable for wearable applications for its excellent shock absorption and comfortability due to the elastic property. Under a relative humidity of 40%, the open-circuit (OC) voltage, volume current density, and transfer volume charge density can reach 181 V, 0.55 A/m³, and 17.5 mC/m³ by the FPS-TENG treated at 95°C for 60min during the fluorinated process, respectively, corresponding to a volume power density of 60 W/m³, providing up to 364 % increase compared with those of pristine PDMS sponge-based TENGs (PPS-TENGs) and pristine PDMS film-based TENGs (PPF-TENGs). With the remarkable humidity resistance of FPS-TENGs, 60% electrical output is reserved from 20% RH to 85% RH, comparing to only 10% for PPF-TENGs, demonstrating the feasibility of FPS-TENGs to be applied in potential wearable applications. Last but not least, quasi-bulk-phase functionalization brings about dramatic improvement in working stability and durability than surface functionalization, by which the improvement would vanish once the functionalized surface is worn away. Herein, the enhanced performance of FPSs from functionalization is certified to degrade by only 10% after wearing away 1mm-thickness surface layer. Additionally, the FPS-TENG charges a 50μF capacitor from zero to 5 V within 10min and successfully lights up a LED panel through tapping by hands.

2:45 PM EN15.02.05
Reduced Transition Temperature in Low Powered Potential Smart Window Coatings Based on Al:ZnO and VO₂ Multi-Layered Structure Grown Using Pulsed Laser Deposition Makhes K. Behera, Sangram K. Pradhan
and Messaoud Bahoura; Norfolk State University, United States

In the modern world of an impending energy crisis, energy saving low powered devices will become a commodity of necessity to help prevent the total depletion of the present natural resources. One of the major chunks of energy being used in today’s world is the HVAC systems installed all around, accounting for ~ 10% of the total energy generated in the United States. Low powered smart window devices are a viable alternative to help saving this major part of the energy generated. In this regard, researchers all around the globe have been working on being able to tune the Metal-to-Insulator Transition (MIT) properties in VO₂ thin films, which, because of the MIT property is a potential candidate for smart window coating applications. In this work, we report successful fabrication of VO₂ thin films despite their highly metastable nature using pulsed laser deposition by systematic optimization of the deposition and annealing oxygen partial pressures. The as-grown films were able to demonstrate a transition temperature of ~ 64 °C, approximately 4-6 °C lower than the reported transition temperature for bulk VO₂. Moreover, in this work we were able to successfully fabricate a potential smart window device structure using aluminum doped zinc oxide (Al:ZnO) thin films as a resistive heating layer which has an added advantage of being transparent. Using a conventional VO₂/Al:ZnO structure resulted in certain degradation to the properties of the films, such as decrease in the magnitude of the MIT as well as a total loss of the Joule heating in the Al:ZnO films. The fabricated device using a modified structure was able to display the MIT transition successfully, all while maintaining the Joule heating effect in the Al:ZnO thin films and the magnitude and sharpness of the MIT in the VO₂ thin films along with reducing the transition temperature of the films to ~ 60 °C, approximately 10 °C lower than bulk VO₂. The results shown in this work demonstrate the structural, electrical and optical properties of all the fabricated films as well as the multi-layered films proving the effectiveness of the films to serve as a potential standalone smart window device. In addition, the results will open up doors to incorporate different structures to the multi-layered film in order to improve the performance of the device.

Acknowledgement:
This work has been supported by NSF-CREST Grant number HRD 1036494 and NSF-CREST Grant number HRD 1547771

3:00 PM BREAK

3:30 PM *EN15.02.06
Piezoelectret for Wearable Healthcare Sensor Jun Zhou; Huazhong University of Science & Technology, China

Wearable electronics for detecting physiological and biomechanical signals of human body are key sensors for healthcare. The vision of non-invasive, automated personalized healthcare is a new and fast-growing multidisciplinary research area. To make the sensors work independently and sustainably, self-powered sensors that can extract energy from human body motions is particularly desirable. In this talk, i’ll present our research progress on the fabrication of piezoelectret for wearable healthcare sensor. For an integrated sensor device based on a piezoelectret film, continuous reliable heartbeat and respiration information is successfully detected and transmitted to a mobile phone. The study promisingly has great influence for professional motion detecting, touch screens, artificial intelligence, mobile healthcare, and wearable electronics.


4:00 PM EN15.02.07
OPEN SLOT
Multidirectional, Small-Scale Human Motion Detection by Directionally-Aligning Carbon Nanotube-PDMS Conductive Films with Enhanced Sensitivity as Wearable Strain Sensors

Mehmet Tas, Mark Baker and Vlad Stolojan; University of Surrey, United Kingdom

Recent interest in the fields of human motion monitoring, electronic skin and human-machine interface technology demand strain sensors with high stretchability/compressibility ($\varepsilon > 50\%$), high sensitivity (or gauge factor ($GF > 100$)) and long-lasting electromechanical compliance. However, current metal and semiconductor-based strain sensors have very low ($\varepsilon < 5\%$) stretchability and low sensitivity ($GF < 2$) indicating that a new generation of strain sensors are required where the stretchability is not sacrificed for high-sensitivity. We propose a simple one-step, low cost fabrication of mechanically compliant, physically robust metallic carbon nanotube (CNT, grown via photo thermal vapour deposition method)- polydimethylsiloxane (PDMS) strain sensors. The process allows the alignment of CNTs within the PDMS elastomer permitting directional sensing. Aligning CNTs horizontally (HA-CNTs) on the substrate before embedding in the PDMS reduces the number of CNT junctions as well as introduces scale-like features on the CNT film perpendicular to the tensile strain direction, resulting in improved sensitivity compared to vertically aligned CNT (VA-CNT)-PDMS strain sensors under tension. The CNT alignment combined with the scale-like features with CNTs bridging-over modulate the electron conduction pathway affecting the electrical sensitivity. Resulting GF are 316.1 for HA-CNT-PDMS and 140.9 for VA-CNT-PDMS sensors under 50 % tensile strains. We further show that these sensors behave differently under compressive strains. VA-CNT-PDMS show more sensitivity to small-scale deformation than HA-CNT-PDMS due to the CNT orientation and the continuous morphology of the film demonstrating that the sensing ability can be improved by aligning the CNTs in certain directions. Furthermore, mechanical robustness and electromechanical durability are tested for over 6000 cycles up to 50 % tensile and compressive strains with good frequency response with negligible hysteresis. Finally, both sensors can detect human motion induced mechanical deformations multidirectionally, both at large and small-scale such as swallowing, frowning, wrist and finger bending with ability to distinguish the motions with reaction and recovery times as low as 130 ms and 240 ms, respectively. These sensors could help people with severe disabilities and limited movement to translate small muscle movements into electrical signals that can be developed into gestures/new alphabet to help communication.

Solution Based Infrared Sensing Using Deep Silicon Carbide Gratings

Thomas G. Folland1, Guanyu Lu1, Autumn Bruncz1, Joshua R. Nolen1, Marko Tadjer2 and Josh Caldwell1; 1Vanderbilt University, United States; 2U.S. Naval Research Laboratory, United States

Infrared spectroscopy is a versatile tool for the identification of trace levels of various volatile chemicals which act as common pollutants. However, for applications in environmental monitoring, trace quantities of a target analyte need to be detected to make a practically useful sensor, which can be difficult using simple transmission geometries. One of the routes to enhancing the sensitivity of infrared spectroscopy is to exploit the surface enhancement of the electric field at the surface of certain materials. This is called surface enhanced infrared absorption (SEIRA) spectroscopy, and typically exploits surface polaritons which form at the surface of certain materials. Surface polaritons form when light couples to coherently oscillating charges in a material, most commonly electrons (surface plasmon polaritons, SPPs) or phonons (surface phonon polaritons, SPhPs). This type of wave can be excited in nanostructured optical antennas, which support a series of resonant modes at a sense of defined frequency. To realize SEIRA using surface polaritons the analyte is typically coated onto the antenna which supports the SPP or SPhP mode. As a consequence, one of the challenges in realizing practical SEIRA is achieving an excellent coating over the optical antennas in order to get a predictable and reproducible response. One appealing route to achieving repeatable SEIRA results is to perform measurements directly within a liquid environment. This gives a consistent overlap between the analyte and the polaritonic material, and provides compatibility with microfluidic applications. Here we fabricate deep gratings (up to 24 $\mu$m depth) of 4H-SiC, in order to perform SEIRA within liquid environments. Our gratings support SPhP modes in the spectral region between ~792 and 972 cm$^{-1}$, coincident with the frequencies of spectral signatures of fluorocarbon pollutants. Resonant modes exhibit strong absorption of incident infrared light (>80%) and high Q factors (>90). This is due to the formation of waveguide type modes in-between the grating teeth, with strong electric field enhancement. This provides an ideal platform for SEIRA, as the high Q factor provides excellent chemical selectivity for individual chemical bonds. After characterizing our sample in air, we then characterize our gratings when submerged in a range
of solvents, including water, isopropyl alcohol, acetone and toluene. We find that resonant modes are still supported in these different environments, despite infrared absorption from the medium itself. We then assess the possibility of performing SEIRA on a target molecule with an absorption band in this frequency range. Our results suggest that deep gratings offer a versatile platform for SEIRA, which could be tuned using a range of different materials to target specific molecules.

4:45 PM EN15.02.10
Multi-Axis Joystick Position Tracking Using Crack-Based Strain Sensor and Machine Learning Seongjin Yang1, Seong Kyung Hong1, Seong Jin Cho2 and Geunbae Lim1; 1POSTECH, Korea (the Republic of); 2Chungnam National University, Korea (the Republic of)

Recently research on sense of touch has been carried out in a great deal of research, and research is being conducted to detect hand movement and body movement as well as accurate implementation of strength and touch. In order to realize this, modern science not only measures and utilizes motion of one axis or independent two axes, but also detecting the motion of three or more axes to measure human motion more accurately. Therefore, it is necessary to measure the movement as well as the feedback of the device.

Strain sensors, especially flexible sensors, can be attached to the surface of a moving object or any type of object to measure the deformation of the object, so that various types of elastic strain sensors can be developed in a variety of materials and structures. As part of this research trend, we have recently developed a sensor that is very flexible but sensitive, cost-effective, has a wide measurement range and is highly applicable. With this method, our noble strain sensors can measure up to 150% strain and have fast response, good linearity, repeatability, etc.

In general, however, polymers used in strain sensors have defects due to material limitations such as mullins effect. When the strain is restored after stretching in one direction, the mechanical response of the strain-stress curve varies with the maximum load, which is a fundamental limitation of the polymer-based sensor. In order to solve this problem, the resistance information received from the high-precision strain sensor can be used to learn the position of the current polymer according to the previous resistance change using machine learning. In this way, even if the mechanical characteristics and the resistance information change depending on the maximum load, it is possible to compensate for the more accurate position tracking.

In the case of the strain sensor developed in this way, when the device is attached to a specially manufactured device, the accurate movement of the device can be predicted according to the deformation of the device. In addition, learning algorithms can be used to learn and feedback on the exact position of the polymer. This approach allows precise motion measurement by attaching a stretchable strain sensor to a multi-axis deformable joystick. This is expected to play a useful role in medical surgical robots and virtual reality, which require precise movement.
material which has better stability and proper conductivity in reducing atmosphere and evaluated the hydrogen sensing performance in material and optical points of view. Based on the obtained sensitivity results, distributed sensor tests have been performed to check the feasibility in the final applications such as solid oxide fuel cells.

**EN15.03.02**

**Electrical Sensing of Methane Oxidation with Ultrathin Films of Transition Metal Oxide Nanosheets** Yoshiaki Ishihara¹, Ryo Nouchi¹,² and Wataru Sugimoto³,³; ¹Osaka Prefecture University, Japan; ²Japan Science and Technology Agency, Japan; ³Shinshu University, Japan

A change in an electrical resistance is a facile platform for monitoring chemical reactions. However, a reaction-induced change in resistance is usually masked by a high bulk conductivity of the sensing layer. Therefore, an ultrathin sensing layer is desired to enhance the surface sensitivity. In this study, an atomically thin film of transition metal oxide nanosheets was employed as the sensing layer to monitor surface chemical reactions. Oxides of transition metals such as iridium and ruthenium are known to possess a hydrocarbon oxidation activity. A change in an electrical resistance was clearly observed upon methane exposure, which is ascribable to an electron transfer process associated with the oxidation of methane molecules adsorbed on the nanosheets.

**EN15.03.03**

**Theoretical Study of the Geometrical and Optoelectronic properties of VO₂ and Mg-VO₂** Arpita Varadwaj and Takashi Miyake; National Institute of Advanced Industrial Science and Technology (AIST), Japan

This study examined the geometrical, charge density topologies, electronic band structures, optical and dynamical properties VO₂ and its Mg-substituted species in the rutile and monoclinic phases using density functional theory implemented in VASP.[¹] It was found that the strongly constrained and appropriately normed meta-GGA functional SCAN[²] could correctly predict the insulating and metallic behaviors of these materials, in appreciable agreement with the photoemission data.[³] In particular, it was found that the singly-substituted Mg atom in VO₂ promotes significant widening of the band gap in both the phases, which is not only consistent with experiment but also explains the enhanced optics of the Mg-VO₂. Substitution of Mg in VO₂ did not contribute directly to either the conduction band or the valence band extrema, which were primarily due to the orbital contributions from the constituent V and O atoms. Although the GGA functionals, such as PBE and PBEsol, provided erroneous density of states and electronic band structures for the low-temperature phase of these materials, these were efficient in revealing the dielectric properties of both VO₂ and Mg-VO₂ in the near infrared to the visible region. From phonon band structure analyses, it was found that VO₂ in both phases is dynamically stable, but this is not so for Mg-doped VO₂.

References:


Acknowledgment:

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**EN15.03.04**
Gate-Voltage Control of the Persistent Photoconductivity Effect (PPC) in SnO₂ Nanobelts

Emilson R. Viana¹,², Geraldo M. Ribeiro³, Alfredo G. de Oliveira² and Juan C. Gonzalez²; ¹Universidade Tecnológica Federal do Paraná, Brazil; ²Universidade Federal de Minas Gerais, Brazil

The persistent photoconductivity (PPC) effect was studied in individual tin oxide (SnO₂) nanobelts as a function of temperature and gate-voltage, in air, helium, and vacuum atmospheres, and low temperature. Photoluminescence measurements were carried out to study the optical transitions and to determine the acceptor/donors levels and their best representation inside the band gap. Under ultraviolet (UV) illumination and at temperatures in the range of 200–400 K, we observed a fast and strong enhancement of the photoconductivity, and the maximum value of the photocurrent induced increases as the temperature or the oxygen concentration decreases. By turning off the UV illumination, the induced photocurrent decays with lifetimes up to several hours. The photoconductivity and the PPC results were explained by adsorption and desorption of molecular oxygen at the surface of the SnO₂ nanobelts. On the basis of the temperature dependence of the PPC decay, an activation energy of 230 meV was found, which corresponds to the energy necessary for thermal ionization of free holes from acceptor levels to the valence band, in agreement with the photoluminescence results presented. The molecular-oxygen recombination with holes is the origin of the PPC effect in metal oxide semiconductors, so that the PPC effect is not related to the oxygen vacancies, as commonly presented in the literature [1]. Was also observed that the gate-voltage V_G can control the maximum value of the photocurrent induced up to 10⁴.


EN15.03.05
Metal-to-Insulator Transition Induced by UV Illumination in a Single SnO₂ Nanobelt

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An individual tin oxide (SnO₂) nanobelt was connected in a back-gate field-effect transistor (FET) configuration and the conductivity of the nanobelt was measured at different temperatures from 400 K to 4 K, in darkness and under UV illumination. In darkness, the SnO₂ nanobelts showed semiconductor behavior for the whole temperature range measured. However, when subjected to UV illumination the photoinduced carriers were high enough to lead to a metal-to-insulator transition (MIT), near room temperature, at T_MIT = 240 K. By measuring the current I_ds versus gate-voltage V_G curves, and considering the electrostatic properties of a non-ideal conductor, for the SnO₂ nanobelt on top of a gate-oxide substrate, we estimated the capacitance per unit length, the mobility and the density of carriers. In darkness, the density was estimated to be 5–10 × 10¹⁸ cm⁻³, in agreement with our previously reported result (Phys. Status Solid. RRL 6, 262-264 (2012)). However, under UV illumination the density of carriers was estimated to be 0.2–3.8 × 10¹⁹ cm⁻³ near T_MIT, which exceeded the critical Mott density estimated to be 2.8 × 10¹⁹ cm⁻³ above 240 K. These results showed that the electrical properties of the SnO₂ nanobelts can be drastically modified and easily tuned from semiconducting to metallic states as a function of temperature and light.

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EN15.03.06
Controlled Growth of Layered Double Hydroxide and its Optoelectronic Applications

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People living in modern society in the 21st century live in a place where fire does not go out 24 hours a day. These lights are sometimes helpful to people, but sometimes there are lights that cause discomfort to humans, such as light pollution. Thus, as important as the generation of light is the detection of light. The range of applications of photodetectors is very diverse. Photodetectors are also used for image sensors, missile defense, daily UV detection, environmental pollution monitoring, and optical communication. Light sensing materials have various band gaps and various structures. Among them, we used a Layered Double Hydroxides (LDHs) material that is easy to synthesize and environmentally friendly. The general formula of a LDH is [M(II)₁₋ₓM(III)ₓ(OH)₂]⁺[(Aⁿ⁻ₓ/n°yH₂O)⁻], where M(II) and M(III) are divalent and trivalent metal cations, respectively, and Aⁿ⁻ is an exchangeable n-valent anion, such as CO₃²⁻, Cl⁻, NO₃⁻, and CH₃COO⁻. In this study, we fabricated the photodetector using a material that grows in a scroll structure. The ZnAl-LDH nanosheet scrolls exhibit highly resistive semiconducting properties with
a band gap of 3.2 eV and work function of 3.64 eV. The photodetector grown in a scroll structure has shown a performance suitable for fabricating flexible and reliable devices.

EN15.03.07
Anisotropic Dielectric Properties of Cs-Doped Tungsten Oxide Nanoparticles Studied by Electron Energy-Loss Spectroscopy
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Selective and wide near-infrared (NIR) absorption property realized by Cs-doped hexagonal tungsten bronze (Cs-HTB) in the form of nanoparticulate dispersion has been applied to various industrial use such as solar control windows, optical filters for imaging units, agricultural heat-shading sheet, photothermal conversion materials, and others. However, the understanding of the NIR absorption mechanism of Cs-HTB nanoparticles has been still controversial among preceding studies. In our recent report, optical absorption spectra of Cs-HTB nanoparticles were analyzed with a conclusion that the crucial factors determining the optical absorption property are the anisotropic dielectric property derived from the hexagonal crystal structure and the alteration in dielectric property of nanoparticles. In this study, high energy-resolution electron energy-loss spectroscopy (EELS) electron microscope was applied to measure the anisotropic dielectric properties of coarse and nano-sized Cs-HTB particles, and also examine the possibility of alteration in dielectric property.

A mixture of cesium carbonate and tungstic acid was calcinated under reductive atmosphere to synthesize coarse Cs-HTB powders of mm size. The powder was mixed with propylene glycol monomethylether and a dispersing agent, followed by bead-milling to be pulverized into nanoscale size.

For the coarse particles, EELS spectra with momentum transfer vectors ($q$) along with a- and c-axes of hexagonal structure, which reflect each component of dielectric tensor, have been measured. Those EELS spectra showed plasmon peaks at 1.2 eV and 1.8 eV respectively, whose energies are close to reported values obtained by an optical measurement on bulk Cs-HTB. By using anisotropic dielectric functions derived from those spectra of coarse particles, an optical extinction coefficient was calculated based on Mie’s scattering theory. However, the calculated extinction coefficient did not reproduce the optical absorption curve of nanoparticles well even though the size and shape effects were included, which suggested the alteration in the dielectric property of nanoparticles.

For the nanoparticle measurement, different EELS spectra were obtained depending on probe positions just outside a nanoparticle facing different surface orientations. Such a dependence on probe positions should reflect each dominant component of dielectric tensor. EELS spectra obtained along a- or c-axes showed plasmon peaks at different energies of around 0.8 and 1.2 eV, respectively. Those anisotropic plasmon peak energies were smaller than those energies determined of μm-sized Cs-HTB particles, which provides evidence of the alteration in dielectric properties from bulk sample to pulverized nanoparticles. It was also confirmed that energy positions of the plasmon peaks varied within the ranges of 0.6-1.1 eV for a-axis and 0.9-1.5 eV for c-axis among nanoparticles. These various plasmon energies should be due to the different degree of dielectric alterations and/or the shape effect of individual nanoparticles.

EN15.03.08
Morpho-Butterfly Inspired Gas Sensors for High Temperature Applications
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It is well known that Morpho butterflies get their intense shimmering colors from the ordered, nanostructured arrays on their wings. Using these butterflies as inspiration, we are developing optical sensors with three-dimensional (3D) nanostructures using a conventional cost-effective fabrication process of photolithography and chemical etching. These 3D nanostructures are built with vertical ridges that support several horizontal lamella. These nanostructures are coated with materials designed to be sensitive to specific gases such as hydrogen or carbon monoxide. The concentrations of these gases can be measured through changes in the intensity of the reflected light at different wavelengths upon interactions of the 3D nanostructures with analyte gases.

Development of these new sensing paradigms are needed since mature analytical techniques, including vibrational spectroscopy, are currently used because of the need of accurate quantitation of these gases. The use of these techniques is unavoidable because existing sensors have several prominent limitations such as poor dynamic range, poor stability, slow response time, and inability to accurately detect one or several gases of interest in the presence of numerous interferences and contaminants. Therefore, in the present study Au nanoparticles embedded within cerium oxide thin films have been deposited on 3D nanostructures and are evaluated for the sensitive, stable and selective detection of hydrogen and carbon monoxide, at elevated temperatures.
The future of these sensors is to simultaneously detect multiple gases, such as for solid oxide fuel cell applications where numerous gases are present (such as hydrogen, carbon monoxide, carbon dioxide, methane, and water). These sensors will be used to complement existing analytical instruments in situations when multi-point or distributed measurements are needed and as such sensors with demonstrated stability, selectivity and sensitivity will ensure a series of parallel measurements for enhanced system control.

EN15.03.09

A Self-Powered Smart Rotation Movement Sensing System with a Triboelectric Nanogenerator Roller-Bearing Daehwan Choi, Taehoon Sung and Jang-Yeon Kwon; Yonsei University, Korea (the Republic of)

Triboelectric nanogenerators (TENGs) technology have been one of several candidates for energy harvesting. TENGs can convert external mechanical energy into electrical energy without other electrical power source. The invented TENG technology has rapidly developed with various approaches such as energy harvesting, mechanical/chemical sensors, self-powered systems, etc. Measuring the rotating motion in mechanical motions is one of common and essential technology in industrial and manufacturing systems. We believe that our triboelectric sensors provide high potential in terms of applicability. It shows that it can be used in many ways from a point of industry, not simply from a device. Through this, we have enhanced capability of self-powered triboelectric mechanical sensors.

In this work, we have roller-bearing structure applied to triboelectric sensors. Herein a simply fabricated, cost-effective, triboelectric sensor with a roller-bearing structure which is composed of rollers and electrode is presented. By integrating the structure of bearing and TENG technology, our triboelectric bearings would be applied to a variety of mechanical areas, particularly those involving mechanical movement. Based on the triboelectric effect, this smart bearing generates the output electrical signals in response to rotation movement or displacement of an object mounted with the bearing. Notably, our self-powered bearing exhibits high output performance, compared to other TENG based on the structure of bearing, of 45 V (open-circuit voltage) and 6 μA (short-circuit current) at a rotation rate of 400 r/min. Using the output signals of the smart bearing, the angular velocity and position as well as damage in the components can be continuously monitored. Furthermore, the smart bearing shows the sensing capabilities of various angle movements. We showed that our smart bearing mounted to the steering wheel can be utilized as an energy harvester, a rotation direction detector, and a driving style sensing system at the same time. This work greatly expands the applicability of triboelectric nanogenerators as self-powered sensing systems.

EN15.03.10

Effect of Loading rGO on Room Temperature NO2 Sensing Performance of CuO Nanochains Jyoti Jyoti and Ghanshyam D. Varma; IIT Roorkee, India

The synergistic effects among different nanomaterial induces new physical and chemical properties of the composite materials which can be applied for advanced applications. In the present work, CuO nanochain structure was fabricated via wet chemical method. Composite films of CuO/ graphene oxide (GO) with different ratio of CuO and GO were synthesised by drop casting method on glass substrate, where GO in the CuO/GO films was reduced by the thermal reduction treatment. The structures and morphologies of the CuO nanostructure and composite films were investigated by X-ray diffraction (XRD), field-emission electron scanning microscopy (FESEM), transmission electron microscopy (TEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). XRD patterns revealed the presence of reduced graphene oxide (rGO) sheets in the CuO nanochains by showing a broad peak of rGO along with the peaks indexed to monoclinic CuO. FESEM and TEM images of CuO nanostructure exhibited nanoparticles arranged to form chain like structure. High resolution transmission electron microscope (HRTEM) image CuO nanochains displayed the lattice fringes of spacing 0.232 nm that correspond to (111) crystalline plane of the monoclinic CuO. Selected area electron diffraction (SAED) pattern showed several concentric diffraction rings masked by spots, thus, indicating the polycrystalline nature of the nanochains. FESEM image of the composite films showed well dispersed CuO nanochains affixed onto the rGO sheets. Furthermore, XPS spectroscopy confirmed Cu to be present in Cu2+ state. The study on the gas sensing properties of CuO at room temperature (RT~25 °C) was carried out by loading different amount of rGO in the CuO nanochain sample. A maximum sensor response value of 29.1% for 20 ppm NO2 was obtained for the optimized material ratio of CuO and rGO (4:1) which was almost four times of the sensor with ratio of CuO and rGO (1:3). Furthermore, the optimal CuO/rGO film sensor exhibited fast response rate and excellent reversibility within the detection range of 5–100 ppm NO2. Moreover, the sensor showed good repeatability when tested over five repeated cycles of 20 ppm NO2 at RT. The
presence of local p-n heterojunctions between rGO sheets and nanochain structure of CuO was attributed to the enhanced sensor response. The present study suggest that GO addition would be an effective approach for developing RT NO2 sensors based on CuO.

**EN15.03.11**

**Composition and Optical Properties of Ordered Arrays of Ag Nanorods in a Polymer Matrix**

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Optics of metal-dielectric composites reveals variety of new effects: surface plasmon excitation, related resonant enhancement of the electromagnetic field through multiple optical antennas, poles and nearly zero values of the dielectric coefficient (epsilon near zero, ENZ), etc. Of great interest are so called hyperbolic metamaterials, which got this name from the hyperbolic dispersion low that is realized due to the uniaxial anisotropy of a nanostructured metal-dielectric composite medium. We suggest and implement one of the ways for the composition of the hyperbolic medium based on Ag and ferromagnetic metals incorporated in the pores of the nuclear filters. The main goal was the search of the proper design of the structure for the realization of the hyperbolic dispersion.

Metal-polymer composites (arrays of nanowires (NWs) embedded in a polymer matrix) were obtained and investigated. Two types of samples were grown: pure silver NWs and silver NWs with a short layer of iron on top. NWs were obtained by galvanic deposition into the pores of etched-track matrix (track membranes with pore diameter - 30-100 nm, pore length - 12 μm, pore density 1.5*10⁹, JINR, Dubna). The filling of the pores was carried out by the two-bath technique. Two solutions were used: silver iodide (AgCl - 20 g/l; KI – 300 g/l) and ferrous sulphate (FeSO₄ * 7H₂O – 120 g/l; H₃BO₃ - 45 g/l; SDS and C₆H₈O₆). The deposition potentials were 400 mV for silver and 1200 mV for iron; the dependence of the current on time was recorded. SEM investigation of obtained NWs confirmed the calculated length: for silver part it was 500 - 3500 nm, while for iron part (cap on the silver NW) it was 100 nm.

We performed the modelling of the optical spectra of the composed samples using the analytical expressions for the Maxwell Garnett anisotropic effective medium. It was found that for all types of structures should reveal strong absorption close to 400 nm wavelength due to the local plasmon excitations, and a deep valley in the red-IR wavelength at oblique incidence associated with ENZ spectral point. In particular, for the arrays of Ag NWs (L=3 mcm, diameter-70 nm) the ENZ point corresponds to the wavelength of 1450 nm. The theoretical predictions are consistent with the experiment obtained via the transmission spectroscopy measurements, which proves high homogeneity of the structures, which can be used as hyperbolic media with properties tunable by varying the design of the NWs. We also composed similar structures consist in part of ferromagnetic metals (Ag/Fe NWs) which reveal specific magnetooptical (MO) spectral features, while their resonant behavior is controlled mostly by the geometry of Ag nanowires. The data obtained for Ag/Fe NWs are also presented and discussed. Such materials are rather perspective as MO media with tunable resonance behavior.

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**EN15.03.12**

**Reaction Acceleration of Nanoporous High Purity Pd Film Formation by Dealloying of Al-Pd-N Film in pH-Controlled EDTA Solution**

Tomoya Nishi, Takuji Ube, Takashi Ishiguro and Syuya Hasegawa; Tokyo University of Science, Japan

Palladium (Pd) is expected material as one of hydrogen gas detection and/or hydrogen storage material. Furthermore, by forming the nanoporous (NP) structure, the specific surface area is increased, and improvement in sensitivity can be expected. In our previous study, we succeeded in the preparation of NP-Pd films by dealloying of Al-Pd alloy films using chelating solution of citric acid [1]. However, there were problems, that is slow reaction rate and residual Al (about 13 at%) in the film after dealloying. In this study, using ethylene-diamine-tetraacetic-acid (EDTA) as dealloying agent instead of citric acid speeds up the dealloying reaction. Furthermore, in order to increase the purity of Pd after dealloying the nitrogen-containing Al-Pd alloy (Al-Pd-N) film was used as the mother alloy film.
These 70-nm-thick Al_{0.82-Pd}_{0.18} or Al_{0.82-Pd}_{0.18-N} mother alloy films were prepared by the rf-sputtering method in the ambient gas of pure Ar or in the mixture gas of Ar and N\textsubscript{2}. The pH value was controlled to optimize the chelating ability of EDTA to Al ions in solution. EDTA dissociates four ionic states, i.e., EDTA\textsuperscript{-}, EDTA\textsuperscript{2-}, EDTA\textsuperscript{3-}, and EDTA\textsuperscript{4-} by increasing pH value from 4 to 10 by adding sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}).

The dealloying process was performed at 368K and at the same time, in-situ observation of light transmittance change was performed to evaluate the dealloying rate. The membrane structure of dealloyed film was also evaluated by using SEM and STEM.

When the pH value of the EDTA solution was increased from 4 to 10, the ionization of EDTA proceeded, and the dealloying reaction saturation time (T\textsubscript{s}) of the Al_{0.82-Pd}_{0.18} mother alloy film was reduced to 1/33 from about 4000s to 120s. Furthermore, the T\textsubscript{s} was reduced to 40s by dealloying the nitrogen-containing Al-Pd-N film in EDTA solution at pH=10 instead of the Al-Pd alloy film without containing nitrogen. As a result, the T\textsubscript{s} was reduced to 1/100, and the composition of the NP-Pd film was purified to 99.5 at%Pd.


EN15.03.13
Preparation Nanopatterned Graphene (NPG) Structure for Gas Sensing Duyoung Choi, Myeonghoon Kim and Siwhan Lee; Korea Institute of Industrial Technology, Korea (the Republic of)

First, Thin anodized aluminum oxide nano-mask was prepared by facile self-assembly technique without using polymer buffer layer, which was utilized as direct-contact template for oxygen plasma etch to produce near periodic, small-neck-width NPG. This work also demonstrates that our direct-contact, self-assembled mask lithography is a pathway for low-cost, high throughput, large scale nanomanufacturing of graphene nano devices. The average neck width on graphene after controlled etching time is 25.0 ± 4.3 nm. It is expected that a neck width reducing process, such as utilizing a controlled oxygen plasma etch, could be utilized, which can lead to a substantially reduced neck width.

By using the fabrication of large-scale NPG network, its applications for gas sensing are reported. NPG network shows significantly enhanced sensitivity to ammonia gas compared to pristine graphene. The detection sensitivity of the nanoscale NPG network is even further improved by decorating NPG network with palladium (Pd) nanoparticles, which shows a relative resistance response of 65 % to 50 ppm of ammonia in nitrogen at room temperature as well as good reversibility in air.

EN15.03.14
Effect of Yb Doping on Piezoelectric Properties and Crystal Structure of AlN Piezo Thin Film Masato Uehara\textsuperscript{1}, Yuki Amano\textsuperscript{2}, Sri Ayu Anggraini\textsuperscript{1}, Kenji Hirata\textsuperscript{1}, Hiroshi Yamada\textsuperscript{1} and Morito Akiyama\textsuperscript{1,2}; \textsuperscript{1}National Institute of Advanced Industrial Science and Technology, Japan; \textsuperscript{2}Kyushu University, Japan

Piezoelectric functional material is an vital for microelectromechanical systems (MEMS) such as physical sensor, energy harvester, ultrasonic transducer for fingerprint and resonator for radio frequency. Aluminum nitride (AlN) is a piezoelectric material. Because this material has good properties such as sensor sensitivity, thermal stability and elastic modulus, we can use in harsh environments such as industrial plants and geothermal power generators as well as cars and smartphones. Additionally, it was revealed that a doping scandium (Sc) significantly increases the piezo response of AlN. This finding made the doped AlN a candidate for advanced MEMS device applications but Sc is an expensive element for the industry. In this study, we investigated the effect of Yb doping into AlN piezo thin film as an alternative for Sc. The Yb doped AlN YbxAl\textsubscript{1-x}N films were prepared on the silicon substrates by a radio frequency co-sputtering. The concentration of Yb, x was controlled by the cathode power. The prepared films had a column texture less than 100 nm in diameter. The piezoelectric coefficient increased by Yb doping. The coefficient reached to about twice that of AlN at x= 0.33. Because the rate of increase at concentrations below 0.1 was comparable to that of Sc doping, Yb can replace Sc in this concentration region. However, Yb could not be doped as much as Sc. Although Sc can be doped at 0.4 or more and the film shows giant piezo response, Yb did not exhibit piezoelectric response at 0.37 or more. The decrease of piezo response would be caused by a phase transition. In case of Sc doping, it is known that the crystal structure changes from wurtzite (polar phase) to rock salt (non-polar phase). In this study, the lattice constant changed continuously until the Yb concentration of X = 0.37. However, the change in lattice constants was discontinuous above x= 0.4 according to the conventional XRD analysis. This result would indicate the phase transition. We analyzed the crystal structure of prepared films in detail by a wide area X-
To cope with surging demand for highly sensitive, responsive, long term stability and selective Volatile Organic Compounds (VOCs) and Humidity Sensor’s in IoT applications, requires the development and exploration of innovative materials which can be considered as stepping stone in next generation sensing applications.\textsuperscript{1} Gas sensors with high sensitivity and selectivity at room temperature have been expected for practical applications. But the limitations of conventional metal oxide based sensing materials and their unstable outputs caused by ambient environment or harsh conditions, significantly restrict their practical applications.\textsuperscript{2}

Here in this study, we are exploring a heptazine based microporous polymer sensor for ammonia detection at room temperature and ambient conditions. The chemiresistive sensor performance was investigated for ammonia over a wide concentration range (1-200 ppm) and in the presence of relative humidity range (23-85 %RH). The presence of active sites (C=N and NH groups) and porous network of heptazine gas sensor enables enhanced response (16.6 @ 70 %RH & 47 @ 84 %RH) towards 50 ppm of ammonia with response and recovery times of 65 and 9s, respectively. The electron withdrawing nature of heptazine enables better selectivity towards ammonia over other VOC analytes.

Therefore, we believe that the developed sensing material presents an excellent opportunity for the development of high performance, portable, easy-to-use device for disease diagnosis via breath analysis and environment monitoring in ambient conditions.

References:
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Thin films of Pb(ZrxTi1-x)O3 have been most widely used for piezoelectric sensors and gyro applications due to their large piezoelectricity. These films have been also investigated for the vibration energy harvesters. In particular, the giant electromechanical response is obtained at the Zr/(Zr+Ti) ratio near the so-called morphotropic phase boundary, MPB. Most of studies have been only focused on the relationship between the crystal structure of the as-deposited films and the piezoelectric response. However, studies on the relationship between the crystal structure during the poling process and the piezoelectric response are very limited. Because the piezoelectric response is considered to accompany the crystal structural change under applying an electric field. Thus, it is crucial to investigate the change of crystal structure via the poling process and under applying an electric field after the poling.

In the present study, we investigated the change of crystal structure by the poling process and under applying an electric filed using a micro-beam XRD study. The measurements were performed for \{100\}-one-axis -oriented Pb(Zr,Ti\textsubscript{1-a})O\textsubscript{3} films with 1.5 µm in thickness and near MPB composition. The crystal structures and their change by these treatments strongly depended on the Zr/(Zr+Ti) ratio of the films. Films with Zr/(Zr+Ti)=0.65 changed from (100)-oriented rhombohedral phase to (001)-oriented tetragonal one by the poling process. Furthermore, Zr-rich films with Zr/(Zr+Ti) = 0.67 changed from (100)-oriented rhombohedral phase to (001)-oriented tetragonal one only under an electric field. The present results suggest the change from (100)-oriented rhombohedral to (001)-oriented tetragonal phases by not only the poling process but also under applying an electric field. This study provided fundamental insights on the crystal structure change with an electric field for Pb(Zr,Ti)O\textsubscript{3} films with composition near phase boundary.
Vanadium dioxide has been intensively explored as a viable material for numerous applications such as smart windows coatings and miniaturised optoelectronic devices and a great progress has been achieved on laboratory-scale. To realise its commercialisation, industrially-viable synthetic techniques are highly required for large-area thin films that meet commercial demands. DC reactive sputtering is such a robust technique which offers high quality large-area thin films on large-scale with controllable stoichiometry and composition for various applications in optoelectronic and energy harvesting devices. Herein, we report synthesis, characterization and IR photoresponse properties of 150.8 nm thick VO$_2$(M1) thin films synthesized by DC reactive sputtering. Phase purity was confirmed by XRD and Raman spectroscopic studies. Morphological and microstructural analysis by atomic force microscope (AFM), field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) revealed the polycrystalline nature of the nanosized films with rms roughness value of 8.69 nm. Electrical characterization showed a first order transition of the films with a resistance change of more than two orders of magnitude and a TCR of -1.24 % K$^{-1}$ at 30 °C. The fabricated IR photodetector based on VO$_2$(M1) thin films exhibited high photoresponse properties with excellent stability and reproducibility in the ambient conditions with a sensitivity of 1775 %, responsivity of 40.09 mA/W, quantum efficiency of 4.67 % and detectivity of 7.07 X 10$^{11}$ Jones upon illumination with a 1064 nm laser having a power density of 250 mW/cm$^2$ at 5 V bias voltage.

Ag-Pt Core-Shell Nanowires with Enhanced Environmental Stability

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Silver nanowire (Ag NW) networks hold great potential to replace commercial transparent conducting oxides due to their superior properties in conjunction with their competitive cost, availability and flexibility. However, there are still challenges to overcome for the wide scale utilization of Ag NWs in devices due to oxidation/sulfidation of nanowires depending on the operating conditions, which leads to loss in performance. Here we develop a solution based strategy to deposit a thin platinum (Pt) shell layer to improve environmental stability of the Ag NWs. Ag NWs were synthesized by polyol method [1] and coated with a thin conformal Pt layer. In a typical coating process, ascorbic acid was used as the reducing agent, polyvinylpyrrolidone (PVP) was used for the directional growth, surface of Ag NWs acted as nucleation sites for Pt ions and deionized water was used as the solvent. Fabricated core-shell nanowires were then deposited onto glass substrates in the form of networks via spray coating. Environmental stability of the core-shell nanowire networks was monitored under different relative humidity conditions (43, 75 and 85%) and compared to that of bare Ag NWs. In order to further evaluate their stability and simulate organic electronics fabrication conditions, both electrodes were kept at 75 °C for 120 hours and 150 °C for 24 hours. Finally, hydrogen peroxide stability of core-shell nanowire networks was tested and compared to that of bare Ag NW networks. All in all, this highly effective and simple strategy to improve the stability of Ag NWs will certainly open new avenues for their large scale utilization in various optoelectronic devices. The applicability of the fabricated highly stable networks has been demonstrated both in resistive and capacitive touch screens and capacitive sensors are fabricated.


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Systematic Study on Helium Induced Nanostructure Formation of 5th Period Transition Metals for Gas Sensor Application

Kazuki Yuzawa, Kenya Uehata, Issei Hirai, Kenzo Ibano, Heun Tae Lee and Yoshio Ueda; Osaka University, Japan

Helium(He) plasma exposure to various metals with low irradiation energy and high ion fluence greatly changes the surface structure of the metals. Among them, the unique structure induced on tungsten (W) is called tungsten nanostructure or fuzz because it has a fluff-like shape [1]. Since this fluff-like fibrous structure (fuzz) has a nano-order sized and complicated structure, its surface area is greatly increased compared with flat surfaces. Therefore, application of fuzz to various gas sensors is very attractive. In particular, with regard to an ethanol gas sensor, an experiment was conducted for a molybdenum (Mo) layer deposited on a quartz surface, which was irradiated with...
He plasma to form fuzz [2]. By using this Mo fuzz, significant improvement in sensitivity of ethanol was confirmed and the possibility of application to various gas sensor was shown. Presently development of hydrogen gas sensor with W fuzz is in progress for future hydrogen based energy society.

For the gas sensor applications of the fuzz structure, it is necessary to produce nanostructures with larger surface area and durability. For this purpose, understanding of formation mechanisms controlling the thickness and length of the fuzz structure must be known. However, although a lot of experimental and simulation researches have been performed, there still remain many uncertainties in formation mechanisms and the detailed control methods of fuzz. So far, in order to elucidate the formation mechanism, various 6th period transition metals were irradiated with He plasma under various conditions [3]. In this work, fuzz structures were observed for several 6th period transition metals except tantalum (Ta) in the region where the normalized temperature $T/T_m$ is 0.3 or above ($T$: specimen temperature, $T_m$: melting temperature).

Based on the above mentioned research, He plasma irradiation to the 5th period metals have been also performed to systematically investigate the surface morphology changes and to acquire basic data for controlling fuzz structure. He plasma irradiation experiments have been conducted for zirconium (Zr), niobium (Nb), molybdenum (Mo), palladium (Pd), silver (Ag), and we found that thin fibers are formed in the region where the normalized temperature $T/T_m$ is 0.3 or above for all of these except for Nb. Similar tendency was observed for the same group elements such as tantalum (Ta) and Nb (5th group), and tungsten (W) and molybdenum (Mo) (6th group) [4]. A thick rod-like structure was formed for Nb and Ta, while fibrous structure (fuzz) was formed for W and Mo. In the presentation, experimental results on alloys with two metals which have different responses to He irradiation (e.g. Mo and Nd) are also shown, and the formation mechanism of fuzz will be discussed in detail.

**EN15.03.20**

**Microfabrication of Graphite by Oxygen Plasma Etching**  Jianwei Fu¹, Genki Hirobe², Yasushi Ishiguro² and Kazuyuki Takai¹,²; ¹Graduate School of Science and Engineering, Hosei University, Japan; ²Department of Chemical Science and Technology, Hosei University, Japan

Graphite has excellent properties, such as high strength, high thermal conductivity, and chemical stability. A variety of applications such as high performance batteries and heat dissipation materials for highly integrated electronic devices are expected for graphene as the next-generation materials. Recently, focusing on the high thermal conductivity of graphite in particular, investigations for the mechanism of phonon-scattering at crystalline domain interfaces have attracted attention. In this study, we tried to microfabricate nano-sized graphite by oxygen plasma etching process for highly oriented pyrolytic graphite (HOPG) in order to clarify the size-dependent thermal conductance of graphitic materials.

By an ICP plasma etching system (RIE-101iPH, Samco), a HOPG plate (10×10×3mm) was etched by using a copper / nickel-made metal mesh, a SiO₂ (285 nm) / Si plate and micro-patterned Au / Cr islands (1 µm circle) as masks, in the conditions of ICP power of 100 W, Bias power of 50 W, and process pressure of 0.05 Pa. AFM measurement was performed by using SPA400-DFM, Seiko Instruments Inc. with the Si cantilever. SEM images were acquired by using SU-8020, HITACHI High-Technologies in the condition of acceleration voltage of 15.0 kV. Both of copper and nickel mesh are deformed during etching process above 60 min. The longer etching time, the more significant deformation of the mask. On the other hand, SiO₂ (285 nm) / Si masks exhibit sufficient etching-proof nature. The etching rate gradually decreases as the etching time increases. It is known that a deposition layer is formed at etched step by the reattachment effect during plasma etching of graphite, where etching in the sample region just below the deposition layer is prevented [1]. This is why the etching rate becomes dropped in the initial etching process below 5 hours. By using micropatterned islands mask, well-aligned and uniform micro-fabricated graphite pattern is successfully obtained, where the horizontal size of the island was found to be slightly larger than that of the mask pattern.

References


**EN15.03.21**

**Elliptical Capacitive Pressure Sensor for High Pressure and Harsh Environment Deployment for Underwater Pressure Monitoring**  Rishabh B. Mishra and Aftab M. Hussain; International Institute of Information Technology (IITT) Hyderabad, India

Pressure is one of the most important process variables for wide area applications. Various principles used to design
pressure sensors include strain, piezoresistivity, piezoelectricity, capacitance and so on. Among these, capacitive pressure sensors have several advantages such as high measurement sensitivity, low temperature sensitivity, low power consumption and high stability. However, non-linearity of change in capacitance with respect to applied pressure is a major consideration in capacitive pressure sensors, thus necessitating the need for detailed modelling and analysis. An interesting characteristic of capacitive pressure sensors is insensitivity to harsh environments such as extreme temperature, strong chemicals and radiation. Further, for harsh environment applications, selection of materials with suitable properties is also very important. In literature, materials such as silicon nitride, silicon carbide, stainless steel, sapphire and diamond have been studied for applications in capacitive pressure sensors for harsh environment applications. In this work, we have designed and modelled capacitive pressure sensor membranes using composite membranes of silicon carbide and silicon nitride to reduce the dielectric constant while maintaining structural stability and manufacturability.

The basic capacitive pressure microsensor consists of two parallel plates, one is a movable diaphragm under applied pressure, and the other one is fixed. In this work, mathematical modelling of elliptical capacitive pressure sensors has been carried out. In order to perform mathematical modelling, the fourth order partial differential plate equation of clamped elliptical diaphragm was solved, following which the capacitance change was calculated using the area integral of the capacitance of the diaphragm. While developing the mathematical model, the small deflection Kirchhoff’s plate theory and pull-in phenomena were considered. To follow the small deflection theory, the deflection in diaphragm should be less than 1/10th of diaphragm thickness and the maximum deflection was limited to 1/3rd of the separation gap between plates to avoid pull-in phenomena. While performing the mathematical modelling of elliptical pressure sensor, the effect of electric field was ignored. We also performed finite element analysis (FEA) to validate the mathematical model. Various performance parameters of capacitive pressure sensors such as diaphragm deflection, capacitance variation, mechanical sensitivity, electrical sensitivity, non-linearity of sensor have been studied as a function of diaphragm physical dimensions, flexural rigidity, applied pressure and separation gap.

To compare various sensor designs, we designed the elliptical diaphragm using the same total area with different eccentricities. The designs were also compared with a circular shape diaphragm of the same area. The sensors were designed for measurement of pressure underwater in marine environments. After study of elliptical sensors of the same overlapping area between plates, it was found that the deflection decreases as the semi-major axis increases, which results in decrease in change in capacitance, which, in turn, reduces the mechanical and electrical sensitivity. However, the responses become more linear as eccentricity is increased. It was observed that circular diaphragm pressure sensor shows more deflection, capacitance change, mechanical and electrical sensitivity, however the repose is more nonlinear than the elliptical-shaped diaphragm. Hence, there is a trade-off between linearity and sensitivity. Thus, the ideal eccentricity for elliptical (circular) pressure sensors can be calculated based on the particular requirements of the application.

EN15.03.22

Effects of Hydrogen Molecule Adsorption and Defects on the Electronic Properties of Graphene

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Graphene is a two-dimensional material with a thickness of single atomic layer where carbon atoms are arranged into a honeycomb lattice. Molecular adsorption effects are significant in graphene because all of carbon atoms belong the surface, where the electronic properties are modulated by the interactions at the interface between graphene and other materials. Hydrogen molecule adsorption is one of the most important examples in terms of applications for the transistor devices accompanied with band gap opening technology and hydrogen storage materials. Meanwhile, introducing defects is one of the interesting strategies to give additional adsorption sites to graphene in view of enhancing the interactions between hydrogen molecule and graphene. In this study, we investigated carrier doping and scattering caused by hydrogen molecule adsorption and defects introduction into graphene by electric conductivity measurement and Raman spectroscopy.

A 4-terminal field effect transistor using single-layer graphene obtained by exfoliation of graphite (g-FET) was fabricated on SiO2/Si substrate. Time dependence of the electrical conductivity for the g-FET was measured after annealing in a vacuum chamber under hydrogen atmosphere (1 atm) at room temperature. For Raman spectroscopy, epitaxial graphene grown on SiC was used, where atomic vacancies were introduced by sputtering with Ar ion beam after pre-annealing, followed by exposed to ambient atmosphere and hydrogen molecule and atomic hydrogen,
respectively. The charge neutral point where the minimum conductivity appears in a g-FET exhibits no significant shift from 30 min after the hydrogen molecule adsorption up to 24 hr. This means little carrier doping occurs into graphene when hydrogen molecule adsorbed at 1 atm at room temperature. However, for a theoretical calculation, where hydrogenated atomic vacancies in graphene have a low energy barrier and little adsorption heat for additional hydrogen molecule [1]. Thus, we verified hydrogen molecule adsorption to defect-introduced graphene by Raman spectroscopy. The ratio of D-band to G-band in Raman spectroscopy is smaller for graphene with defects adsorbed by hydrogen molecule and atomic hydrogen than that exposed to ambient atmosphere containing oxygen. This might be explained by that holes are injected into graphene through oxygen-terminated defects and electrons are injected into graphene through hydrogen-terminated defects. The scattering probability of carriers at the defect site depends on the Fermi energy. Thus, D-band intensity which is related to carrier scattering processes in graphene is different between 

References

Effect of MS₂ Layer on the Heating Effect of Al Doped ZnO Multilayer Transparent Heaters
Brandon A. Obasogie¹, Mamadou T. Mbaye¹, Jasmine Beckford¹, Laura Sweet², Sangram K. Pradhan¹ and Messaoud Bahoura¹;
¹Norfolk State University, United States; ²ODU, United States

In the last years, much effort has been dedicated to the development of high-performance transparent heaters (TFTFs) due to their versatile use in consumer electronics, automobiles, and smart windows. We successfully fabricated and studied the electrical, optical and thermal properties of Al:ZnO (AZO) / MS₂ multilayer thin film heaters by keeping the AZO layer fixed and varying the MoS₂ layer thickness. The multilayers (3 – 5 layers) of AZO and MS₂ films were grown at 200-400°C temperature range on glass, kapton, and silicon substrates using radio-frequency magnetron sputtering. The transparent heaters show a stable and reproducible heating effect with low consuming power (<10 V) as well as maintaining a high optical transparency higher than 75%. The temperature dependent resistivity behavior of the films was investigated using linear four probe measurement technique. The AZO films exhibit good electrical conductivity. These heaters offer an alternative to conventional and expensive ITO electrodes at a much lower cost. The potential applications are automobile window defrosters, foldable and wearable electronics, pain/injury therapy, smart windows, and low-cost power electronics.

This work has been supported by NSF-CREST Grant number HRD 1036494 and NSF-CREST Grant number HRD 1547771

Transition Metal (V, Nb and W) Doped TiO₂ Nanostructures for Chemiresistive Ozone Sensors
Ariadne C. Catto, Emerson dos Santos, Luis F. da Silva and Waldir J. Avansi; DF-UFSCar, Brazil

Chemiresistors based on metal oxide semiconducting (MOS) nanostructures have drawn researchers’ attention because of their several advantages related to gas sensor performance, such as stability, sensitivity, and reversibility [1]. Despite having wide-ranging applications, the gas-sensing performance of TiO₂ nanostructures, still needs to be better evaluated and TiO₂ in anatase phase has demonstrated interesting sensing properties related to gases such as CO, NO₂ or acetone [2-3]. Thereby, a facile and environmentally friendly synthesis approach for the production of MxTi₁−xO₂ (M=V, Nb and W) nanostructures was demonstrated via hydrothermal decomposition of their respective peroxy-complexes. The effect of metal ions addition on the structural, morphological and electronic properties of the as-prepared samples were investigated by X-ray diffraction (XRD), Raman Spectroscopy, UV-visible diffuse reflectance spectra (DRS), X-ray photoelectron spectroscopy (XPS), and electron microscopy techniques. XRD analysis confirm that all MxTi₁−xO₂ (M=V, Nb and W) samples presented only the TiO₂ anatase phase, despite the different amounts or metallic ions. Despite the different amount or metallic ions, scanning electron microscopy (SEM) shows that the increasing of metallic ions contents leads to a morphological evolution, from anisotropic to isotropic nanostructures, reducing their size (at around 5nm) as the surface area. From the studied samples, W doped
TiO₂ nanostructures presented interesting ozone (O₃) gas-sensing performance evidenced by their working temperature (below 200°C), sensor response, repeatability, as well as a good range of detection.


EN15.03.25
Electrical, Optical and Thermal Transport Properties of Oxygen Deficient Amorphous WOₓ (2.5 < x < 3) Films
Gowoon Kim¹, Hai Jun Cho¹, Yu-Miin Sheu² and Hiromichi Ohta¹; ¹Hokkaido University, Japan; ²National Chiao Tung University, Taiwan

Tungsten oxide (WOₓ) is attracting attention as an active material for many useful applications such as material for electrochromic device, electrode of Li-ion batteries, gas sensors and so on. Especially, amorphous tungsten oxide a-WOₓ films are essential material for advanced thin film devices, for example, the recently developed electrochromic transistor (ECT) because a-WOₓ films show clear electrochromism as well as flexibility, and it can be fabricated at room temperature (RT). One can expect that practical smart windows, which can store the information both electronically and visually utilizing the electrochromism of a-WOₓ. In order to improve the a-WOₓ-based ECT performance, fundamental physical properties of a-WOₓ are strongly required. Although the relationships between the electrical, optical and thermal properties and the chemical composition of crystalline WOₓ have been investigated, there is no systematic report in the case of a-WOₓ. Here we report the relationship between the valence state of W ion and the properties of oxygen deficient a-WOₓ thin films continuously against x.¹[1] We fabricated a-WOₓ films with various x ranging from 2.511 to 2.982 by the pulsed laser deposition technique and measured the electrical, optical, and thermal properties systematically. Although the +6 dominant films were electrical insulators with optical transparency in the visible region, we found that both optical transmissivity and electrical resistivity decreased drastically with increasing the +5 concentrations, which also enhances the thermal conductivity due to the fact that heat can be carried by additional conduction electrons. As the +4 states became dominant in the film, the resistivity slightly increased whereas the low transmission was maintained in the visible range. We believe that the results would provide useful information to improve recently developed a-WOₓ-based ECTs, which utilized reversible electrochromism of the active material to change the valence state of its transition metal ions, enabling the control of both the electrical conductance and visible transmission.


EN15.03.26
Resonant Inelastic X-ray Scattering Studies of Temperature-Varied Metal Insulator Transition in Vanadium Dioxide Nanoparticles
Emma Anquillare¹,², Dana Goodacre¹, Vedran Jovic³, Connor Gallagher¹, Xuefei Feng², Yi-Sheng Liu³, Feipeng Yang², Yang Har², Jinghua Guo², Linda Doerrer¹ and Kevin Smith¹; ¹Boston University, United States; ²Lawrence Berkeley National Laboratory, United States; ³University of Auckland, New Zealand

Monodisperse Vanadium Dioxide nanoparticles were synthesized using a hydrothermal method and characterized using Transmission Electron Microscopy and Synchrotron X-ray Diffraction. The particles were then studied using Soft X-ray Absorption (XAS) and Resonant Inelastic X-ray Scattering (RIXS) at both above and below the metal insulator transition, in order to reveal the extent of particle size and lattice effects on nano-scale sample bandstructure. For the first time to our knowledge, the XAS peak indicating the prominent presence of vanadium dimers in the low-temperature monoclinic phase has been identified as a stand-alone peak in VO₂ nanoparticles. Implications for extent of dimerization and the metal insulator transition will be discussed.

EN15.03.27
Substrate Dependent Active Channel Characteristics in Low-Temperature Polycrystalline Silicon Thin-Film Transistors
Dong Hyun Kim, Soohyun Kim, Jung Chun Kim and Jae Woo Lee; Korea University, Korea (the Republic of)

Nowadays, thin film transistor (TFT) are utilized in various display application like TV, mobile phone, car, etc. Backplane contains an array of TFTs which operate for switching the individual pixels on and off. It determines performance when it comes to resolution and power consumption. Active channels of TFTs include amorphous
silicon (a-Si), low-temperature polycrystalline silicon (LTPS) and indium gallium zinc oxide (IGZO). Especially, LTPS channel has an advantage of compatibility on a-Si fabrication processes.

In this study, we focus on electrical properties of LTPS TFT as a function of temperature in the range of 300 – 375 K. The characterization of LTPS TFTs fabricated on glass and plastic substrates is measured by using the semiconductor parameter analyzer (Keithley 4200) in vacuum chamber with thermal chuck. Electrical performances (Threshold voltage $V_{TH}$, Subthreshold swing $SS$, Effective mobility $\mu_{eff}$) of LTPS TFTs on glass and substrates are different. Although active channels have similar dimension, $V_{TH}$ $SS$ related to switching operation on plastic substrate ($1.44$ V/decade) is larger than glass substrate’s one ($0.60$ V/decade) at 300 K. $SS$ is explained by equation $SS=2.3nkT/q$, ($n = 1+(C_{dep}+C_{iT})/C_{ox}$). $C_{dep}$ is inverse proportional to temperature, also $C_{i}$ exponentially decreases according to increasing temperature. Compared to LTPS, single crystalline Si can be the ideal $60$ mV/decade at 300K because the effective $C_{dep}$ and $C_{i}$ are negligible. But, LTPS channel has many grains and grain boundaries which related to channel depletion capacitance and then glass and plastic substrates which have different interface quality are the cause of interface trap capacitance. It can affect $\mu_{eff}$ difference between glass ($75$ cm$^2$/Vs) and plastic ($59$ cm$^2$/Vs) substrates.

Ascending temperature in the range of 300 – 375 K, the characterization of LTPS TFTs on glass and plastic substrates get worse that $SS$ is proportional to temperature. Compared to extracted $SS$ and equation which applies the thermal dependency of depletion and interface capacitance, $C_{dep}$ of plastic substrate among grains is near 2 times larger ($0.33$ µF/cm$^2$) than one of glass substrate ($0.16$ µF/cm$^2$). It might describe that small grain size and large number of grain boundaries for plastic substrate affect depletion capacitance and lower effective mobility.

Meanwhile, glass substrate which has lower interface traps between gate oxide, active LTPS layer, and substrate than plastic substrate operates deeper and faster. Consequently, active LTPS channel layers on glass and plastic substrate have different physical factors like grain size, grain boundaries, and trap densities among another layers (gate oxide, substrate). It has been shown that these factors affect switching operation and driving performances of TFTs, respectively.

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**EN15.03.28**

**Synthesis Pd-Au(Alloy)@ZnO Core-Shell Nanoparticles and Their Enhanced H$_2$ Gas Sensing Performance**

Yeon-Tae Yu, Ha-Nui Choi and Dong-Seok Kim; Chonbuk National University, Korea (the Republic of)

Among various Metal Oxide Semiconductor (MOS) gas sensor materials, ZnO is an n-type semiconductor, which has a band gap of 3.37eV, is recognized as a noticeable sensing material due to its chemical stability, its high electron mobility, and the variation of donor density. Typically, optimal working temperature of ZnO based gas sensors is above 300°C. However, ZnO has a problem in that it has no selectivity for target gases. Recently, as the hydrogen age comes, there is a growing interest in hydrogen gas sensors having selectivity to hydrogen gas.

In recent years, noble metal nanoparticles (NPs) have been used to improve the sensing properties of gas sensor. Among the various noble metal catalysts, palladium has excellent ability to adsorb hydrogen, so that it can increase the selectivity of the gas sensor to hydrogen gas when used as a catalyst. However, since palladium can be easily oxidized at a high temperature, when it is used as a catalyst of a gas sensor at a high operating temperature, it is oxidized so as to lose its function as a metallic catalyst. Therefore, palladium alloy needs to be considered as a catalyst. On the other hand, one of the new strategies for using noble metal NPs in MOS gas sensors is to design core-shell NPs. In the core-shell structure, the shell helps maintain the catalytic properties of the metal core.

In this study, Pd-Au alloy nanoparticles with different composition were synthesized to prevent oxidation of palladium. Subsequently, Pd-Au(alloy)@ZnO core-shell NPs were prepared using Au colloid, Zn(NO$_3$)$_2$ and ascorbic acid. To investigate the oxidation behavior of the Pd-Au alloy core, Pd-Au(alloy)@ZnO core shell nanoparticles were annealed at the range of 200 to 500°C. The synthesis of Pd-Au alloy nanoparticles was confirmed by using HRTEM, and the oxidation behavior of Pd-Au alloy core with different composition was observed through X-ray diffraction analysis. In addition, the gas sensing tests were performed at operating temperature of 200–500°C for various gases (H$_2$, CO, CH$_4$, C$_2$H$_6$O), and the composition effect of Pd-Au alloy on H$_2$ gas sensing response was investigated.

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**EN15.03.29**

**Battery Intercalation Strategy for Material Synthesis, Energy Application and Mechanism Study** Zhiyuan Zeng; City University of Hong Kong, Hong Kong

In this talk, I will focus on Material Synthesis, Energy Application and Mechanism Study using Battery Intercalation Strategy. For material synthesis, I will discuss how to design battery intercalation “environments” to obtain a serials
of high quality single layer transition metal dichalcogenides (TMD) nanosheets (MoS$_2$, WS$_2$, TaS$_2$, TiS$_2$ and ZrS$_2$)-
the Li insertion can be monitored and finely controlled in the battery testing system, so that the galvanostatic
discharge is stopped at a proper Li content to avoid decomposition of the intercalated compounds; Moreover, the
battery intercalation strategy can be optimized and the controllable lithiation process can be extended to BN, NbSe$_2$,
WSe$_2$, Sb$_2$Se$_3$, Bi$_2$Te$_3$ and so on. The prepared noble metal-2D TMD composites are promising candidate for sensing
and hydrogen evolution reaction. For mechanism study, I am interested in failure mechanism study of
Lithium/Sodium Ion Batteries at nanometer scale utilizing imaging and spectroscopy protocols. With the self-
designed electrochemical liquid cell TEM, we can directly capture the dynamic electrochemical lithiation and
delithiation of electrode in a commercial LiPF$_6$/EC/DEC electrolyte, such as lithium metal dendritic growth,
electrolyte decomposition, and solid-electrolyte interface (SEI) formation. This technique opened a venue by which
looking inside the dynamic electrochemical reactions in real-time. Which render us to improve the electrode design
for reducing short circuit failure and improving the performance of lithium/sodium ion batteries.

SESSION EN15.04: Environmental Sensors and Related Devices
Session Chairs: Paul Ohodnicki and Zhaoliang Zhang
Tuesday Morning, December 3, 2019
Sheraton, 3rd Floor, Commonwealth

8:00 AM EN15.04.01
Reticulate Dual Nanowire Aerogels for Multiple Applications Zhipeng Wang and Anyuan Cao; Peking
University, China

Nanowire aerogels (NWAs) possess an unusual conglomeration of many useful properties: lightweight, large surface
area, high electrical conductivity and low thermal conductivity. They have been used in many applications such as
electronics, energy generation/storage, thermal management, sensing, catalysis, etc. However, most synthesized
NWAs are composed of single component that may produce unsatisfactory aggregated performance in mechanical
strength, conductivity and electrochemistry. Therefore, it is hard to apply them in a multifunctional application.
To address this issue, we synthesized the reticulate dual-nanowire aerogels (rDNWAs) composed of FeS$_2$ nanowires
and carbon nanotubes (CNTs) via a simple solvothermal method. In the typical synthesis process, highly porous
CNT sponge was used as the matrix to allow the in-situ growth of nanowires and thus the two components densely
intertwined with each other to form the reticulate structure. This structure is versatile and TiO$_2$ based rDNWA was
also successfully fabricated by a similar process. The FeS$_2$ based rDNWA shows high porosity (> 98%), good
conductivity (0.65 S cm$^{-1}$), and excellent mechanical properties (maximum Young’s modulus: 1.32 MPa). Due to its
high compressibility, it can be used as the strain sensor. The sensor exhibits good sensitivity and enhanced stability
compared to the CNT matrix. Besides, it can be directly compacted to produce a high-performance free-standing
electrode for lithium ion batteries (LIBs) that exhibits high mass and areal specific capacities (10 mAh cm$^{-2}$
with the mass loading of 14.4 mg cm$^{-2}$). Further, the obtained TiO$_2$ based rDNWA shows not only similar properties and
applications but also some uniqueness. When applied as the electrode for the LIBs, it can be utilized to fabricate the
compressible LIB devices by controlling the voltage window to 1-3 V. The outstanding overall performance and
multiple applications of our hybrid aerogel are derived from the synergistic effect of intertwined two components
and the reticulate structure can be extended to fabricate more NWAs with novel multi-functional capabilities.

8:15 AM EN15.04.02
Transparent and Wearable Single-Electrode Triboelectric Nanogenerators for Self-Powered Touch and
Strain Sensors Using Electrospun AgNW/P(VDF-TrFE) Composite Nanofibers Seung-Rok Kim and Jin-Woo
Park; Yonsei University, Korea (the Republic of)

Healthcare monitoring devices assess the health status of a person by detecting the physiological signals such as
heartbeat, respiration rate, and temperature measured directly or in relation to the deformation and vibration of the
human body. Due to the needs for maintenance-free operation of wearable and wireless sensing units, the demand
for self-powered sensors is continuously growing. Using various kinds of nanogenerators that convert thermal,
mechanical or chemical energy into electricity, self-powered sensors can continuously measure physiological signals
of the body. Among these power-generators, triboelectric nanogenerators (TENGs) have attracted interest for
wearable sensing applications because they can scavenge energy from mechanical body motion with high energy conversion efficiency. There are four fundamental operation modes of TENG; vertical contact-separation, in-plane sliding, single-electrode, and free-standing operation mode. Compared with other paired-electrode modes, the single-electrode mode has a much simpler structure that does not need an auxiliary electrode on the surface. Hence, only the single-electrode mode TENG (SETENG) fulfills the energy harvesting conditions necessary for human-machine interfaces, such as touch panels, where human skin acts as the opposite triboelectric surface to the component surface of the TENG. In this work, we fabricated the SETENG using the electrospun silver nanowires (AgNWs)/P(VDF-TrFE) composite nanofibers (NFs). The inclusion of a small fraction of AgNWs in the NFs promoted the β-phase formation of P(VDF-TrFE), a higher surface charge density, and the output performances. The SETENG generated an output power density of up to 217 W/m² with repetitive contact and separation. To the best of our knowledge, this power density is one to two orders larger than that of other single-electrode-type TENGs (3.4 ~ 27 W/m²) reported by others. Conducting high-resolution X-ray diffraction (HR-XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and Kelvin probe force microscopy (KPFM) analyses, we could confirm that AgNWs create the β-phase and induce a much lower surface potential. Using highly efficient SETENG, we demonstrated a self-powered, transparent and wearable touch panel for a human-machine interface by arraying SETENG units as a touch sensing component. The SETENG array was connected to Arduino microcontroller for real-time communication using low-pass RC filters with 10 Mohm resistors and 10 nF capacitors for noise filtering. We could successfully type any text on the computer using the SETENG array. Additionally, we designed a self-powered strain sensor connecting SETENG with the strain sensor as a power source. Touching and detaching the SETENG, saturated open-circuit voltage signal by transferred charges was transformed by resistive transducer (the strain sensor). It showed the linearity with 16 gauge factor (GF) at 35% strain. It also had no hysteresis behavior up to 10% strain of and showed stable ε sensing performance during the repeated stretching test at ε of 10% for 10,000 cycles. Using self-powered strain sensor, we could successfully measure the strain on the finger without any power supply.

8:30 AM *EN15.04.03
Advances in Low Dimensional Metal Oxide Chemiresistive Sensors for Environmental Monitoring Oomman K. Varghese; University of Houston, United States

Recent developments in the areas of energy, environment and public health have made the role of chemical sensors more relevant than ever before. While efforts to increase process efficiency without environmental impact and new technologies emerging in the areas of energy conversion and storage demand development of reliable chemical sensors for process monitoring and safety, concerns over increasing pollutants in the environment and rapidly increasing mortality rates related to a wide range of diseases including cancer prompt their use in environment and health monitoring. Nevertheless, the concentrations of gases/vapors of interest are, in many of these cases, in the range of parts per million to trillion (ppm to ppt) levels and the environment is complex. Metal oxide semiconductor based chemical sensors are attractive for such applications because of their ability to detect a wide range of chemical species. These devices are generally low cost and fast responding and have the ability to operate in harsh environments. Inadequate sensitivity and selectivity are often problems with these sensors. Advent of new low dimensional metal oxides facilitated the development of sensors with unique functionalities. These materials offer high surface area and nanoscale features for improved receptor and transducer functions. As a result, highly selective sensors with ppm to ppt range detection ability can be developed using these materials. For example, we recently developed a zinc oxide nanomaterial based sensor that could detect parts per billion levels of certain volatile organic compounds (VOC) in air with reasonable selectivity. Such VOC sensors find applications in various areas including pollution monitoring and early diagnosis of diseases. This presentation will give an overview of the current status of the nanostructured oxides based chemiresistive sensor technology for environmental monitoring. The focus of discussion will be on trends in volatile organics detection technology.

9:00 AM EN15.04.04
Effect of Twinning on Nanowire Electromigration Lifetime Mohammad Waliullah and Rodrigo Bernal; The University of Texas at Dallas, United States

Electromigration is a critical failure mode in the semiconductor industry, and in the emerging fields of flexible and wearable electronics. This failure can be attributed to the diffusion of metallic atoms due to momentum transfer of electrons flowing through a metallic interconnect when voltage is applied. The diffusion eventually leads to formation of voids and hence a time-dependent increase of electrical resistance of the interconnect. Since it is a
diffusion process, the microstructure of the interconnect is one of the controlling factors of electromigration. Twin boundaries, in contrast to grain boundaries, can have the potential to reduce diffusion of atoms and consequentially improve electromigration performance. In flexible electronics, it is common to have twinned interconnects. Unfortunately, very few studies have been conducted about the diffusion performance of these interconnects. Even those studies consider a few twin boundaries in grain boundary diffusion. No literature is available about the collective effect of twin boundaries throughout the interconnect. Moreover, some of the studies said that twinning slows down the diffusion and hence void growth [1], [2] and some said that twinning does not necessarily hinder void growth [3]. Given these conflicting reports, there is clearly a need for a systematic study of the electromigration reliability of twinned interconnects.

In this work, we investigated electromigration failure of penta-twinned silver nanowires, with a nominal diameter of 100 nm and length ranging from 3 μm to 15 μm, to yield reliability estimates for nanowire-based flexible electronics. Samples were prepared by random deposition of nanowires on a substrate containing gold electrodes fabricated by photolithography. The nanowires were connected with the electrodes by e-beam lithography. The electrodes were then connected to a printed circuit board (PCB) through a wirebonding package. Under a fixed current density and temperature, the resistance was measured using 4-point measurement method so that it can be measured continuously without the influence of contact resistances. The currents were applied in an automated fashion to test a large number of nanowires. The failure criterion was set as 10% increase in resistance which is also widely used in the electronics industry. The median time to failure of nanowires was determined using Black’s equation. The experimental data not only provides a significant guideline about reliability of flexible electronics in terms of electromigration failure but also valuable information about diffusion parameters through twin boundaries. Comparison between the data obtained in this experiment and the published data for interconnects currently used in the electronics industry, depending on the variation in diameter and length, revealed promising prospect for twinned interconnects in the next generation electronic devices.

References

9:15 AM EN15.04.05
Nanoparticle-Based Chemiresistor Array for Classification of Tea Aromas Tuo Gao, Yongchen Wang, Chengwu Zhang, Jing Zhao, Ranjan Srivastava and Brian Willis; University of Connecticut, United States

As one of the world’s favorite beverages, teas have been consumed by many generations. Due to their high health benefits, it is important to understand the quality of teas. The objective is therefore finding an economic way to identify aromas of tea that can eventually help with the purpose of tea quality control. Conventionally, similar to wine products, a tea-tasting expert will tell how good a tea is. However, it is very expensive and subjective as there is no measurable parameter. For that reason, a more reliable and easy-to-operate alternative approach is desirable. Based on earlier success using organo-functionalized nanoparticles to differentiate volatile organic compounds, we continue to investigate the performance of gold nanoparticle chemiresitive sensor arrays using more complex analytes - tea samples.

In this work, we demonstrated a nanoparticle-based electronic nose system that separates 35 flavors of teas, ranging from black teas, green teas, and herbal teas. Four types of gold nanoparticles (AuNPs) with chemically diverse ligands were chosen as sensing elements. The functionalization includes DMAP (4-dimethylaminopyridine), ODA (octadecylamine), 3-MPA (3-mercaptopropionic acid), and 4-ATP (4-aminothiophenol). To assemble the electrodes, nanoparticle solutions were drop-cast on the active sensing region that consists of castellated microstructures with 2-μm gap. The sensor chip was designed with separated active sensing regions so that each AuNP can have 12 working sensors maximum. This allowed diversity as well as redundancy for sensing experiment. Fresh tea powders were added to a glass syringe and the dosing was completed by a syringe pump with controlled delivery speed. Dry nitrogen gas was used for purging. Sensing responses, expressed as ΔR/R0, were measured simultaneously for all sensors using a switch matrix/multimeter system. Raw data processing and statistical analysis were performed using
MATLAB to evaluate the performance of the chemiresistive electronic nose array.

Depending on flavors, sensing elements, and baseline resistance difference, $\Delta R/R_0$ of 1-20% were achieved. The resulting variation enables statistical analysis, such as principal component analysis (PCA), linear discriminant analysis (LDA), support vector machine (SVM), and random forest (RF). With five-fold cross validation, we have achieved 99% accuracy with LDA for all 35 flavors of teas. We also found that multi-particle assembly works better than using single type of particles. For example, by choosing two working sensors from each particle, we obtained $91.4 \pm 3.3\%$ accuracy for 13 black and green teas, and $88.6 \pm 3.7\%$ for 22 herbal teas. On the other hand, if we chose 8 sensors from each of the four particles, the classification accuracy dropped. This is a significant improvement (>10%) from single particle assembly. The results showed accurate classification of 35 flavors of teas and provided a promising approach to monitor the quality and grade of tea products. Moreover, by increasing the chemical variation in ligands, it is possible to select the ligand combination that gives the best overall performance.

9:30 AM EN15.04.06
Graphene Nanoresonators for Molecular Detection in Solvated and Complex Environments Maicol A. Ochoa$^{1,2}$ and Michael Zwolak$^2$; $^1$University of Maryland, United States; $^2$National Institute of Standards and Technology, United States

New nanoscale devices and protocols for molecular detection in aqueous environments at room temperature are desirable for their potential application in biomolecular analysis and in vivo cell studies. Due to their electromechanical properties, graphene and other 2D materials provide a platform for electromechanical sensing in noisy and complex environments. We have investigated this idea by analyzing representative tight-binding models and extended Huckel models for suspended graphene nanoribbons. In particular, we have derived analytic expressions for the current, the electromechanical susceptibility, and signal-to-noise ratio. These expressions reveal the relative importance of thermal fluctuations, strain, and geometric properties in the signal and electromechanical response. We find that as a result of the environmental fluctuations, electromechanical structures have an electron transmission function that follows a generalized Voigt profile, in close analogy to the inhomogeneous lineshapes found in spectroscopic and diffraction studies. These results allow us to formulate optimal sensing protocols in terms of detector parameters, and give the underlying mechanics and fundamental operational principles for the design of graphene-based nanoelectromechanical detectors.

9:45 AM EN15.04.07
A New Route of Developing Stable Super-Nernstian Performance pH Sensing IrO$_2$ Films with Nanoparticles Yi-Chieh Hsieh$^1$, Tzu-Ying Chan$^1$, Kuang-Chih Tso$^1$, Bo-Han Huang$^1$, Pu-Wei Wu$^1$, Pochun Chen$^2$ and Tsung-Eong Hsieh$^1$; $^1$National Chiao Tung University, Taiwan; $^2$National Taipei University of Technology, Taiwan

The pH sensing applications have been widely used in various fields, and its redox reaction is the determining mechanism of sensitivity. However, regular pH sensing materials are limited to a pH sensing slope under -59 mV/pH due to the Nernst equation. In contrast, the IrO$_2$ is known to reveal a super-Nernstian response, a characteristic slope as high as -88.7 mV/pH. In our recent work, we have developed a facile method to synthesize robust IrO$_2$ thin films via a bipolar pulsing processing combining electrophoresis and electro-flocculation of IrO$_2$ nanoparticles in a colloidal suspension. The synthesized IrO$_2$ thin film exhibits a pH sensing slope of -73.6 mV/pH, with impressive surface uniformity and strong adhesion to the substrate.

10:00 AM BREAK

10:30 AM *EN15.04.08
ZnFe$_2$O$_4$/TiO$_2$/Au@Pt Nanoarray Modified Paper-Based Biochip for Ultrasensitive Immunosensor Lina Zhang, Li Li, Yan Zhang, Hongmei Yang and Jinghua Yu; University of Jinan, China

A novel photoelectrochemical (PEC) immunosensor based on the ZnFe$_2$O$_4$/TiO$_2$/Au@Pt nanoarray functionalized paper working electrode (ZnFe$_2$O$_4$/TiO$_2$/Au@Pt-PWE) was developed and used for ultrasensitive detection of carcinoembryonic antigen (CEA). To achieve a boosted PEC response under visible light excitation, the ZnFe$_2$O$_4$ nanocrystals served as photosensitizer were grown in-situ on the surface of the paper fibers with modification of highly ordered TiO$_2$ nanotube arrays and Au@Pt alloy nanoparticles, which was further used as the 3D electron collector to boost the separation of the photogenerated electron-hole pair of the TiO$_2$ arrays. The probable PEC
promoting mechanism was investigated by Mott-Schottky tests, phosphorescence decay measurements as well as X-ray photoelectron spectroscopy analyses. The obtained ZnFe$_2$O$_4$/TiO$_2$/Au@Pt-PWE was explored as the immunosensor substrate for fixing biomolecules. By virtue of sandwich-like immunoreaction, ultra-sensitive quantification of CEA was obtained. Under the optimized experimental conditions, the developed sensor exhibited a fast response, a broad linear range, and low detection limit. This work may provide a universal method for preparing multifunctional paper-based electrode and offer an innovative platform for the highly sensitive antigen-analysis.

11:00 AM EN15.04.09
Bioinspired Nanosensors for Energy and Environmental Detection Wen Shang, Qingchen Shen, Zhen Luo, Jiaqing He, Lingye Zhou and Tao Deng; Shanghai Jiao Tong Univ, China

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With billions of years of nature evolution, biological systems have developed many elegant sensing structures with superior sensing performance. Inspired by such biological sensing systems, different man-made sensors have been designed and fabricated to match or surpass the performance of those biological counterparts. In this presentation I will discuss our effort in design, fabrication, and characterization of bioinspired nanostructured sensors for energy and environmental detection. In particular I will discuss the nanosensors for thermal energy detection. The detection of thermal energy is critical in many industrial applications, including the thermal energy distribution within both steam turbine and gas turbine, the thermal energy signal within the component of aerospace vehicles, and the thermal energy distribution within a solar-thermal energy conversion system (1). With the critical roles played by the thermal detection technologies in a growing range of applications, the need of portable and high performance thermal sensing systems drives up the technology development (2, 3). We explored an alternative thermal detection mechanism that is based on the desorption of vapor molecules from the butterfly-inspired nanosensor under the stimulation of incoming thermal radiation, and demonstrated the use of such stimulated desorption for both broadband and wavelength selective thermal radiation detection. This new detection mechanism enables more than an order of magnitude of improvement in both the response of relative reflectance and also the signal-to-noise ratio at the maximum heat-sink-free response speed. The stimulated desorption also provides the opportunity to achieve the wavelength selective thermal radiation detection due to the wavelength selective thermal absorption of the molecules. Based on the similar approach, a self-powered thermal radiation nanosensor that can convert thermal radiation into electric signals was also demonstrated. Besides the thermal energy detection, these bioinspired nanosensors can also be used for the detection of other environmental targets, including both vapor detection and noise detection (4, 5). Such detection approach thus offers a platform for a range of high performance sensing systems, including energy, environmental, chemical vapor, and biological sensing systems.


11:15 AM EN15.04.10
Light-Controlled Deformations of High-Aspect-Ratio Liquid Crystalline Elastomers Microstructures Michael M. Lerch1,1, Shucong Li1, Yuxing Yao1, James T. Waters2, Anna C. Balazs2 and Joanna Aizenberg1,1; 1Harvard University, United States; 2University of Pittsburgh, United States
Liquid crystalline elastomers (LCEs)\cite{1} are crosslinked polymeric systems with the ability to undergo temperature-dependent anisotropic shape changes. These changes are governed by the orientation of liquid crystal mesogens connected to the polymer backbone. The dynamic behavior of LCEs makes them interesting for actuators in soft robots and sensors.

Drawing inspiration from nature\cite{2,3} we can build materials with microstructures\cite{4,5} that can perform tasks for applications such as wetting, microfluidics, information processing and cargo transport, capture and release. When composed of LCEs, these arrays of microstructures can variously tilt, twist, stretch or contract upon heating depending on a director alignment encoded magnetically during fabrication.\cite{6} Upon incorporation of a molecular photoswitch (e.g., an azobenzene), they can be rendered light-responsive\cite{7} which further extends their range of deformations. Here, we use light-responsive microstructured LCE surfaces with unprecedented deformation behavior. In arrays of pillars of different geometry, reversible twisting of these pillars can be triggered with directionality governed by the angle of UV irradiation with respect to the director alignment. Achiral surfaces can thus be dynamically converted into surfaces with controlled chirality. Moreover, depending on the light intensity, deformation modes beyond twisting are accessible. This bioinspired LCE platform offers new modes of deformation, coupled motion, and energy conversion that may be interesting in contexts such as soft robotics and microfluidic devices.

**Keywords**: Actuators; Bio-Inspiration; Multi-Functionality; Light-Control; Autonomous Materials

**References**

**11:30 AM EN15.04.11**

**Fire Detection from Light Scattering** Georgios A. Kelesidis¹, Reza M. Kholghy¹, Joel Zuercher², Julian Robertz², Martin Allemann², Aleksandar Duric² and Sotiris E. Pratsinis¹; ¹ETH Zürich, Switzerland; ²Siemens AG, Switzerland

Early and reliable fire detection is essential to prevent thousands of human deaths and injuries every year in the US alone [1]. Modern fire (smoke) sensors detect the light scattered from carbonaceous particles (soot) emitted during open fires. Such particles have fractal-like structure formed by agglomeration and surface growth [2]. Yet, their optical properties are calculated typically by Rayleigh or Mie theories for spheres impeding their selective sensing among other airborne particles [3]. So, fire detectors are not selective enough for such particles producing false alarms costing up to 1 billion £/y in United Kingdom alone [4].

Here, carbonaceous agglomerate structure and light scattering are measured from premixed ethylene flames [5] and simulated by coupling Discrete Element Modeling (DEM) for surface growth and agglomeration with the Discrete Dipole Approximation (DDA) [6]. Using the Mie theory for spheres overestimates the measured particle mass up to 10 times. This results in 60 % larger differential light scattering cross-sections than those measured in premixed ethylene flames. In contrast, the DEM-derived particle structure and light scattering is in excellent agreement with those measured here in premixed flames. Thus, the DEM-DDA can be used to optimize the selective sensing of fire detectors.

**References:**
Ultrasensitivity of Self-Powered Wireless Triboelectric Vibration Sensor for Operating in Underwater Environment Based on Surface Functionalization of Rice Husks

Sz-Nian Lai1,2,3, Chih-Kai Chang1, Cheng-Shiun Yang1, Chun-Wei Su2, Chyi-Ming Leu2, Ying-Hao Chu1, Pao-Wen Sha3 and Jyh Ming Wu1; 1National Tsing Hua University, Taiwan; 2Industrial Technology Research Institute, Taiwan; 3National Chiao Tung University, Taiwan

We demonstrate the self-powered wireless triboelectric vibration sensor as made from the naturally nanoporous SiO2 particles for allowing the detection of the vibrations and movement in the underwater environment. The nanoporous SiO2 particles are directly converted from rice husks (referred to as RH_SiO2), which exhibit strongly interacting surface hydroxyl groups. Through the enzymatic treatments, the surface potential of the RH_SiO2 can be modulated to obtain either an extremely low or strongly high electronegativity. Specifically, by adding fluorinated groups using fluoroalkylsilane (FOTS) treatment to obtain RH_SiO2-F, the charge density of the RH_SiO2-F triboelectric nanogenerator (TENG) can be enhanced ~ 56.67-fold as compared to the untreated RH_SiO2-TENG. The power density of the RH_SiO2-F TENG is increased from 0.077 mWm⁻² to 261 mWm⁻². The RH_SiO2-F particles are encapsulated in a quartz cube to fabricate a self-powered wireless sensor that can be stabilized for operating in water at various temperatures. The theoretical calculation further demonstrates that the triboelectric potential is dramatically established between the surface functionalized RH_SiO2-F particles and the quartz’s surface. With porous nature of rice husks covered with nano-Si is of a high functionality for designing a new-type TENG which has a great potential to apply in the environmental monitoring.

SESSION EN15.05: Novel Sensor Materials and Related Electronics

1:30 PM *EN15.05.01
Scalably-Nanomanufactured 2D Tellurene for Ubiquitous Electronics and Sensors  Wenzhuo Wu; Purdue University, United States

The reliable production of atomically-thin crystals with tailored properties is essential for exploring new science and implementing novel technologies in the 2-D limit. However, ongoing efforts are limited by the vague potential in scaling-up, restrictions on growth substrates and conditions, small sizes, and instability of synthesized materials. In this talk, I will discuss our recent progress in the discovery and production of tellurene (2-D form of elemental tellurium) with an intriguing chiral-chain structure. The solution-synthesized tellurene crystals exhibit process-tunable thickness from a monolayer to tens of nanometers, lateral sizes ~ 100 nm, and can be transferred to designer substrates. I will further discuss our findings in 2-D tellurene’s material properties, as well as our efforts in the prototypical device explorations with the acquired fundamental understandings of tellurene’s properties. Our results show that the air-stable tellurene, as an emerging 2-D material, exhibits a plethora of intriguing physical properties appealing for applications in electronics, optoelectronics, energy, sensors, and quantum devices.

2:00 PM EN15.05.02
Beyond p-n Junctions—Flexoelectric Photo-Detection and Energy Harvesting in Bismuth Telluride Thin Films  Bruno Lorenzi1,2, Yoichiro Tsurimaki2, Akihiro Kobayashi3, Masayuki Takashiri3, Gang Chen2 and Svetlana Boriskina2; 1University of Milano-Bicocca, Italy; 2Massachusetts Institute of Technology, United States; 3Tokai University, Japan

Bulk photovoltaic (PV) effect has recently attracted an increasing interest for its potential in simplifying the structure of optical sensors and photovoltaic cells, and as a possible solution to overcome the Shockley – Queisser limit in the solar cell energy conversion efficiency. Until recently, the bulk PV effect has only been observed and
exploited in non-centrosymmetric materials, strongly limiting the range of possible applications.

A possible way to overcome this limitation comes from the so-called flexo-PV effect, in which a gradient strain is used to induce an internal polarization within the material, enabling the collection of photo-generated carriers also in centrosymmetric materials. In this context flexo-PV has already been demonstrated in many large and intermediate bandgap materials, including titanium dioxide, strontium titanate, and silicon under visible and ultraviolet light illumination.

Low bandgap materials, such as Bismuth Telluride (Bi$_2$Te$_3$) are sensitive to infrared (IR) light, opening opportunities for the implementation of the bulk PV effect to develop new types of IR sensors. However, a comprehensive theoretical and experimental analysis of the strain-induced flexo-PV effect in this kind of materials is still missing. Furthermore, the flexo-PV effect has been mainly demonstrated at the nanoscale, leaving doubts on its applicability in wider contexts and for macroscopic device footprints.

In this communication we present the experimental demonstration of flexo-PV effect in Bi$_2$Te$_3$ thin films, under different illuminations and conditions. Depositing Bi$_2$Te$_3$ thin films on flexible substrates, by magnetron sputtering, and developing ohmic contact and anti-reflective coating by e-beam evaporation, we were able to create a strain gradients in the material, and analyze its electrical response. We will show and discuss how the power output in our samples can be varied as a function of the applied strain, sample temperature, and illumination level at different wavelengths. Our results help to shed light on the relation between applied strain, material polarization, and the photon detector performance, and reveal new possible applications of the flexo-PV effect in low-gap materials under different illumination scenarios. The new flexo-electric photo-detectors can operate under real-life conditions, i.e., without cryogenic cooling and in the self-powered regime, and provide an opportunity to integrate energy-harvesting and conversion as well as environmental sensing capabilities on a single cheap, lightweight, and flexible platform.

2:15 PM EN15.05.03

**Novel Solvent Exchange Process of a Highly Conductive PEDOT:PSS by Ultrafiltration for Conformal Nano-coating on Micropyramids towards a Highly Sensitive and Stable Pressure Sensor**

Jung Joon Lee$^{1}$, Srinivas Gandla$^{1}$, Byeongjae Lim$^{2}$, Sun-ju Kang$^{1}$, Sunyoung Kim$^{2}$, Sunjong Lee$^{2}$ and Sunkook Kim$^{1}$; $^{1}$Sungkyunkwan University, Korea (the Republic of); $^{2}$Korea Institute of Industrial Technology, Korea (the Republic of)

Water, a solvent for a poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) solution, was solvent-exchanged with various solvents by an ultrafiltration method, while PEDOT:PSS continuously remained in a wet state for stable redispersion without aggregation. Among the tested solvents, we demonstrated for the first time that PEDOT:PSS was successfully and stably dispersed in ethanol (EtOH) and ethylene glycol (EG) by the facile ultrafiltration method. Compared to water, the EtOH based PEDOT:PSS exhibited enhanced wettability over Polydimethylsiloxane (PDMS) substrates without any additional surface treatments, as measured by the contact angle measurements. The solvent exchange process (SEP) did not alter the conductivity of PEDOT:PSS from its pristine form, but increased the pH from 2.4 to 4.5 by removing the excess PSS. An exceptionally uniform with conformal nano-coating of EtOH-based PEDOT:PSS solution on PDMS pyramids resulted in a pressure sensor exhibiting very high sensitivity in the low-pressure regime (~21 kPa$^{-1}$, < 100 Pa), a fast response time (90 ms) with a maximum load of 1 kPa, and high mechanical stability over 10000 cycles. In addition, the pressure sensor functioned as a human pulse rate sensor that produced a precise pulse waveform with peaks clearly indicating incident, systolic, and diastolic pressure. Additionally, it exhibited excellent selective accuracy with little interference in a 4 x 4-pixel pressure mapping panel. We believe that the solvent-exchange process developed in this study provide the pressure sensor could deliver new opportunities in wearable electronic applications.

2:30 PM EN15.05.04

**Oligomers with Mechanical Bistability as a Promising Material for Nanosensing Elements**

Anastasia Markina$^{1,2}$ and Vladik Avetisov$^{1,2}$; $^{1}$N. N. Semenov Institute of Chemical Physics of the Russian Academy of Sciences, Russian Federation; $^{2}$Molecular Machine Corporation Ltd, Israel

Nanosystems capable of reversible transitions between two states in response to applied stimuli are attracting more and more attention given the pursuit of miniaturization of trigger-type and switch-type elements. These elements are key units of many functional nanodevices (e.g., molecular and macromolecular switches, single molecular sensors, molecular actuators, electric- and optoelectric devices, as well as logic gates). The desire to create nanometer-scale switching devices has motivated an active search for bi-state macromolecular systems allowing for sharp
conformational transitions in response to stimuli. Short oligomers possessing such mechanic-like characteristics are a promising platform for the design of nanodevices and molecular machines.

Using full-atomistic simulations, we demonstrate that oligomers of thermosensitive polymers, themselves only a few nanometers in size, possess conformational bistability, and react to power loads as non-linear mechanical systems. We establish the bifurcation effect, the hysteresis effect, spontaneous vibrations, as well as the stochastic resonances of these oligomers [1]. This study shows how such switching-like behavior of oligomers of thermosensitive polymers can be used in molecular nanosensing, in particular for single molecule detection.


2:45 PM EN15.05.05
Reversible Light-Induced Insulator-to-Metal Transition in Yttrium Oxy-Hydride Epitaxial Thin Films

Yuya Komatsu1, Ryota Shimizu1,2, Kazunori Nishio1, Masahiro Miyachi1, Markus Wilde1, Katsuyuki Fukutani1 and Taro Hitosugi1; 1Tokyo Institute of Technology, Japan; 2Japan Science and Technology Agency, Japan; 3The University of Tokyo, Japan

Yttrium oxy-hydride (YO\textsubscript{1-x}H\textsubscript{x}, cubic, \(a = 5.35\) Å) is a promising material for optoelectronics applications such as smart windows and optical sensors, because optical transparency and electrical resistance can be reversibly switched by sunlight irradiation [1]. It is reported that the resistance of YO\textsubscript{1-x}H\textsubscript{x} is reduced by one order of magnitude on irradiation of sunlight [1]; however, the resistance change is smaller than that of the commercially available CdS (three orders of magnitude). A possible reason of the small response in the resistance is their polycrystalline nature of YO\textsubscript{1-x}H\textsubscript{x} films deposited on glass substrates [1, 2].

In this study, we fabricated epitaxial YO\textsubscript{1-x}H\textsubscript{x} thin films, and investigated the influence of crystallinity on the photochromic response. We observed a sunlight-induced resistance decrease by three orders of magnitude, comparable to that of CdS, and finally achieved reversible light-induced insulator-to-metal transition using UV-laser irradiation.

Epitaxial thin films of YO\textsubscript{1-x}H\textsubscript{x} were deposited on single-crystalline yttria-stabilized zirconia (YSZ) (111) substrates using reactive magnetron sputtering (thickness: \(~150\) nm). We monitored the four-probe resistance of the YO\textsubscript{1-x}H\textsubscript{x} epitaxial thin films during the light irradiation using a solar simulator (intensity: 1 mW/mm\textsuperscript{2}) and a UV laser (wavelength: 375 nm, intensity: 15 mW/mm\textsuperscript{2}).

Irradiation of sunlight for 30 min. reduced the resistance in YO\textsubscript{1-x}H\textsubscript{x} epitaxial thin film by three orders of magnitude (2\times10\textsuperscript{8} W to 2\times10\textsuperscript{5} W). Furthermore, we found that the irradiation of UV-laser (more intense light) for 90 min. induced insulator-to-metal transition in YO\textsubscript{1-x}H\textsubscript{x} epitaxial thin films. The original four-probe resistance of as-grown YO\textsubscript{1-x}H\textsubscript{x} epitaxial thin film was \(~5\times10\textsuperscript{7} W\) (high resistance state). After the UV laser irradiation, the resistance sharply dropped accompanying color change, and finally reached 2\times10\textsuperscript{1} W (low resistance state). In this low resistance state, surprisingly, the temperature dependence was metallic in the range of 4 – 300 K. We next annealed the UV irradiated sample at 125°C for 2 h in 4%-H\textsubscript{2}/Ar gas atmosphere of 0.05 MPa. As a result, the optical transparency and the high resistance state recovered. We again irradiated UV-laser onto the YO\textsubscript{1-x}H\textsubscript{x} sample and confirmed the metallic behavior. These results demonstrate the reversible light-induced insulator-to-metal transition in YO\textsubscript{1-x}H\textsubscript{x} epitaxial thin films.

References:

3:00 PM BREAK

3:30 PM *EN15.05.06
Free-Standing 2D Oxide Nanomaterials and Hybrids with Exotic Physical Properties

Xudong Wang; University of Wisconsin--Madison, United States

Two-dimensional (2D) nanomaterials, particularly when their thickness is just one or a few atomic layers, exhibit
physical properties dissimilar to those of their bulk counterparts and other forms of nanostructures. Nonetheless, 2D nanostructures so far have been largely limited to naturally layered materials, i.e. the van der Waals solids. A much larger and diverse portfolio of 2D materials including non-layered compounds are desirable to meet the specific requirements of individual components in various devices. We demonstrate that surfactant monolayers could serve as a soft template supporting the nucleation and growth of 2D nanomaterials in large area beyond the limitation of van der Waals solids. Through this approach, 1 to 2 nm thick, single-crystalline free-standing ZnO nanosheets with sizes up to tens of microns were synthesized at the water-air interface. This technique was denoted as Ionic Layer Epitaxy (ILE) – the first solution-based technique for growing large-area ultrathin nanosheets without the support of crystalline substrates. Mimicking the biomineralization processing by using mix charge surfactants led a successful synthesis of single-crystalline nanosheets from a broad range of functional oxide materials, including CoO, MnO₂, Bi₂O₃, etc. New physical properties emerged from the ultrathin geometry. For example, stable p-type conductivity was observed from the ZnO nanosheets as a result of electron depletion. High concentration of cation or oxygen vacancies could be controlled by the surfactant modulation, leading to superior magnetic property and memristive behavior. Substantially enhanced electrochemical catalytic performance was also discovered from multiple ultrathin oxide systems. In general, ILE vastly broadens the range of 2D nanomaterials from layered van der Waals solids to oxide ceramics, opening up opportunities for discoveries of exciting transport, magnetic, photonic, and catalytic properties.

4:00 PM EN15.05.07
van der Waals Epitaxy of Ferroelectric LiNbO₃ Thin Film Ru Jia and Jian Shi; Rensselaer Polytechnic Institute, United States

The superior ferroelectric and nonlinear property of LiNbO₃ makes it a popular and promising candidate for electro-optics, energy converter and memory devices. However, integration of LiNbO₃ on technologically important substrates has been a challenge. In this work, by pulsed laser deposition, we synthesize epitaxial LiNbO₃ thin films on muscovite mica through van der Waals epitaxy. We apply X-ray diffraction to characterize the impurity phase and optimize the growth condition. We reveal the in-plane epitaxy relation by pole figure/X-ray diffraction phi scan. We obtain freestanding LiNbO₃ thin films by mechanical exfoliation. Raman spectroscopy is used to confirm LiNbO₃ phase after transfer from muscovite mica. Ferroelectric and pyroelectric devices out of freestanding LiNbO₃ reveal giant polarization in film of a few tens of nanometers in thickness. Our work shows that van der Waals epitaxy may enable the feasibility of integrating high-quality LiNbO₃ onto semiconductor substrates such as Si, opening a window in pursing novel heterogenous devices and circuits.

4:15 PM EN15.05.08
Study of Charge Transfer in IGZO Phototransistor with Various Type of Quantum Dots Byoung-Hwa Kwon, Sooji Nam, Chul Woong Joo, Jae-Eun Pi, Sung Haeng Cho, Seong-Deok Ahn and Seung-Youl Kang; Electronics and Telecommunications Research Institute, Korea (the Republic of)

Amorphous oxide semiconductor based thin film transistors (TFTs) using quantum dots (QDs) have great potential for photosensors because they show high sensitivity to light and excellent electrical properties (field effect mobility and on/off ratio) [1]. In most studies, characteristic evaluation of QD-based oxide phototransistors is the effect of interest. However, the interface and the charge transfer between the oxides and the QDs are rarely reported. In this presentation, indium–gallium–zinc oxide (IGZO) TFTs with QDs are fabricated and characterized. We uses QDs with core and core/shell structures and with various surface ligands. In order to explore the change of electrical energy levels and chemical bonding between the IGZO and the QD according to different surface treatments, ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) measurement are carried out. Lastly, we perform time resolved photoluminescence (TRPL) measurement on the IGZO with various type of QDs to clarify the carrier transfer mechanism.

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References
The excellent intrinsic properties of aligned nanofibers, such as carbon nanotubes (CNTs), and their ability to be easily formed into multifunctional 3D architectures motivates their use as shape-engineerable materials for a variety of commercial applications, such as batteries, chemical sensors for environmental monitoring, and energy harvesting devices. While controlling nanofiber adhesion to the growth substrate is essential for bulk-scale manufacturing, application-specific performance, and integration with advanced device platforms, limited experimental approaches and models to date have neglected to address the scaling of CNT array-substrate adhesion ($F_a$) with processing conditions, and a mechanistic understanding of this phenomenon is still unknown. In this work, we synthesize vertically aligned CNT arrays by chemical vapor deposition and combine experimental and modeling techniques to study a simple, post-growth annealing step we call 'cementation' and its effect on $F_a$ as a function of temperature ($T_c$) up to $1000^\circ$C. This process, which increases $F_a$ by two orders of magnitude ($\sim 0.5$–$50$ N/cm², as measured via uniform CNT array delamination from a flat growth substrate) enables the capillary densification of CNT arrays spanning three orders of magnitude in height (μm-mm scale) to create dense, patterned architectures whose geometries can be accurately predicted by elasto-capillary theory. Here, the non-monotonic scaling of $F_a$ with $T_c$ is quantified and modeled analytically based on contact mechanics theory and the atomic- and meso-scale evolution of CNT-catalyst-substrate interfaces. Extensive morphological, structural, and chemical characterization of the CNT arrays and CNT-substrate interfaces is performed via scanning and transmission electron microscopy, Raman spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. These results show that higher $T_c$ reduces the CNT-catalyst number density, graphitizes and stiffens the CNT roots to increase $F_a$, and alters the mechanical deformation mode during CNT-substrate separation, consistent with the model results. Using this approach, this work provides new insights into the interfacial interactions responsible for variable nanofiber-substrate adhesion and enables the creation of shape-tunable architectures for advanced sensors, energy devices, and emerging nanoscale technologies.
build a model between two forms of precursor alloys, ligament sizes and the resultant products. Finally, the electrochemical reactions within the NPC structures could be predicted and well-controlled.

**EN15.06.02**

**Analysis and Detection Based on Solid Nanopore/Channel**

Fan Xia; China University of Geosciences, China

Various types of transmembrane pores and ion channels in the range of 1-100 nm are found in each biological cell, playing crucial roles in various significant physiological activities such as maintaining cell osmotic balance and stabilizing cell volume. Inspired by this natural phenomenon, different biomimetic nanodevices (nanopore/channel) with different characteristics have emerged as an attractive and powerful platform and have been used for a wide range of applications. Generally, the principle of analysis applications based on solid nanopore/channel can be described as follows: molecules access or attach on the inner surface of a nanopore/channel, change the effective diameter of the nanopore/channel, or affect the charge transfer as well as the wettability of the inner surface of the nanopore/channel, leading to ionic current changes that can be detected.

**EN15.06.03**

**Non-Enzymatic Sensing of Glucose Based on Au Nanoparticles and TiO2 Modified Polyaniline**

Wan-Ting Chiu1, Tso-Fu Mark Chang2, Masato Sone2, Agnès Tixier-Mita1 and Hiroshi Toshiyoshi1; 1The University of Tokyo, Japan; 2Tokyo Institute of Technology, Japan

In this study, Au NPs and TiO2 integrated into PANI are synthesized by facile and time-saving electrochemistry techniques of low waste emission. The stability of Au NPs-TiO2/PANI, which superior than most of reported results, reached up to 70 days. The sensitivity and detection limit are 355.8 μA mM⁻¹ cm⁻² and 0.15 μM (S/N=3), respectively. It is also confirmed that Au NPs-TiO2/PANI performs high selectivity by the interference test. The current response of the developed Au NPs-TiO2/PANI electrodes were tested 5 times, and the relative standard deviation was obtained to be 1.30%, indicating a high reliability of the electrode preparation method. The evaluated results suggest the applicability of Au NPs-(0.05)TiO2/PANI electrode for glucose sensors. More than 285 million people worldwide are suffering from diabetes mellitus, which is a major public health problem today [1]. Therefore, accurate, fast, and reliable sensors for detecting glucose are attracting a great attention to prevent further development of diabetes mellitus. Electrochemical sensors are considered to be the most promising measure due to its good sensitivity, rapid response, outstanding selectivity, high reliability, portability, and user friendliness. Electrochemical glucose sensors are further divided into enzymatic and non-enzymatic types. Enzymatic sensors are considered to be less stable than non-enzymatic ones since its accuracy tend to fluctuate easily with temperature, humidity, pH, and toxic chemicals.

In the non-enzymatic glucose sensors, metals such as Pt, Pd, Au, Ag, Cu, Ni, CuO, NiO, and their derivatives are found to be intrinsically electroactive to the electrooxidation of glucose. Since the faradic current arising from the glucose oxidation can be enhanced by increasing the surface area, the aforementioned metals and metal oxides in nano scale have been considered as a promising candidate. In particular, Au is at the top of the list due to its high electrocatalytic activity and negative oxidation potential for the oxidation of glucose [2]. Oxides such as ZnO, CeO2, and TiO2 were utilized for achieving well distribution of nano-structure Au, since they have an effect to immobilize the Au nanoparticles (NPs) and impede the aggregation of Au NPs due to the anchoring effect. In this work, TiO2 was chosen to control the Au NPs due to its low cost, biocompatibility, and ease of modification. TiO2 also showed a great affinity to H2O and OH⁻, which is a critical factor for the oxidation of glucose in the aqueous solution. Electrooxidation of glucose, which is catalyzed by Au NPs, is benefited from the OH⁻ on the adjacent TiO2, and hence the current of electrooxidation of glucose is enhanced. Polyaniline (PANI), which is a common electrically conductive polymer, was utilized as a supporting material in this study, for its low cost, good stability, and good electrical conductivity [3]. Nano-materials (i.e. metal NPs and/or oxides) integrated with PANI enhanced the electrochemical properties, such as augmented amount of nano-materials loading on electrode, accelerated electron transfer, and homogeneous distribution of nano-materials. These improvements accordingly result in improved electrocatalytic activity to the oxidation of glucose.

It has been known that the fabrication process for the non-enzymatic glucose sensor is tedious and time-consuming. In this study, however, a facile and time-saving procedure to fabricate Au NPs-TiO2 decorated PANI was conducted. Furthermore, by virtue of the facile and time-saving procedure, little waste-solution emission was realized.

Reference


Infrared thermal imaging is a key technology used in night vision, surveillance, medical diagnosis, firefighting, as well as in the chemical, metallurgical and petroleum industry, where the monitoring of thermal processes is fundamental for correct and safe operation. A microbolometer measures the temperature changes through the change in the resistance of a thermosensor material as a result of the absorption of infrared radiation. The operation of the uncooled microbolometers is carried out at room temperature, which is convenient and advantageous for systems of smaller size, weight, power, and cost (SWPaC). Microbolometers are generally made of vanadium oxide (VOx) or amorphous silicon (a-Si:H), both types must meet the requirements of low resistivity to perform a coupling with the reading circuit and a large temperature coefficient of resistance (TCR). In addition, the material must have low electrical noise and, in order to reduce manufacturing costs, be compatible with standard integrated circuit (IC) fabrication processes. As a result of the current trend, it is evident that amorphous silicon is receiving a lot of attention in its application and improvement as the active sensing layer due to its compatibility with IC processes. However, it still has a high level of noise and electrical resistivity. By modifying the deposition parameters during the growth of a-Si:H, it can be turned into a nanostructured material. Hydrogenated polymorphous silicon-germanium (pm-Si$_x$Ge$_{1-x}$:H) is a material composed mainly of an amorphous matrix with embedded nanocrystals (approximately 2-5 nm) produced in the plasma cloud and incorporated during growth. These nanocrystals improve transport properties and resistance to radiation-induced degradation, which translates into better performance and long-term stability. Here we present the characterization of a pm-Si$_x$Ge$_{1-x}$:H alloy deposited by plasma enhanced chemical vapor deposition (PECVD) at 200 °C and the application of this in microbolometers. The material properties as surface roughness, TCR and resistivity have been investigated. Device performance having an area of 50x50 µm$^2$ was evaluated through responsivity and noise measurements.

Hierarchical nanoscale structure plays a vital role in achieving excellent property, which can successfully be used in preparing tailor-made materials for sensing applications. These hierarchical nanostructures can successfully be prepared with the help of structure directing agents (SDAs). This work reports the preparation of polyaniline (PANI) nanorods in the presence of anionic (sodium dodecyl sulfate, SDS) and nonionic surfactant (Pluronic F127) as the SDAs. We prepare a series of ternary composites with varying ratio of PANI and F127 for a given amount of SDS. The SDS and F127 play a pivotal role as SDAs in delivering a hierarchical nanostructure of PANI. Detailed characterization reveals that the in-situ polymerization of PANI confirms the formation of the well-disperse composite. The amphiphilic character of F127 facilitates the formation of a core-shell micellar structure, which in turn facilitates the polymerization of PANI in the core region. We have observed a composition based structure formation of the ternary composites. At the increasing amount of F127, the composite exhibits higher crystallinity (viz. less porosity) ensured via XRD and microscopy images. Among them the synthesized composite at the 1:1 ratio of PANI and F127 exhibits less porosity (viz., high crystallinity) explored by BET surface area measurements. The XRD analysis does not show a sharp peak, which signifies that the material acquires a polycrystalline structure, as revealed by HRTEM analysis. The polycrystalline nature of the nanorods facilitates the highest thermal stability, contributes significantly towards the enhanced electrochemical activity and thus, can successfully be used in sensing applications. The 1:1 material shows remarkably highest glucose sensitivity (~485.787 µA/cm² mM) compare to ternary composites under amperometric measurements. The sensor shows an excellent electrochemical performance within a range of 5 to 50 mM with a lower detection limit of ~3.202 µM.

Detection of Digitized Phase on Electromagnetic Wave by Nanomechanical Resonator and Influence of Temperature Keita Funayama$^{1,2}$, Hiroya Tanaka$^1$, Jun Hirotani$^2$, Keiichi Shimaoka$^1$, Yutaka Ohno$^{2,3}$ and Yukihiro Tadokoro$^1$; $^1$Toyota Central R&D Labs., Inc., Japan; $^2$Nagoya University, Japan
Nanomechanical resonator offers the possibility of an ultrasensitive detection of various physical quantities, with emerging applications including signal processing, biological detection and fundamental tests of quantum mechanics. By exploiting a vibration of nanoscale cantilever, electromagnetic wave has been reported to be detected even with a nanoscale detector. However, the detector cannot correct the whole energy of the wave due to its ultra-small size, which results in the failure of the detection. Here, to improve the detection performance, we introduce digital signal processing for nanomechanical systems.

We first suggested the nanomechanical phase detector, which consists of single carbon nanotube (CNT) cantilever\(^1\). Here, the digitized phase of the electromagnetic wave is to be detected. In the proposed detector, the tip of the CNT vibrates according to the phase. The amplitude of the vibration can be observed via field emission current; the oscillation of CNT varies the current, and the original phase information can be estimated by observing the current. Analytical investigation reveals an interesting point that the information is contained in two frequency components of the current. By introducing a simple signal processing that combines these components with optimum weights, our analysis shows that the detection performance is significantly enhanced.

One of the critical issues in the detector is the dependence on temperature. In traditional semiconductor physics, the current inherently depends on temperature, which affects on the detection performance. To analyze the influence of the temperature variation, a mathematical model of the mean and variance of the current was first derived based on experimental results\(^2\). The obtained mathematical expression shows that both the mean and variance exponentially increase with increasing temperature. Based on this result, the detection performance was also analyzed; as the increase of the temperature, the variance is significantly increased, and then the detection is likely to be failed. This analysis indicates that to secure the reliable detection, temperature should be kept low like room temperature.

Above results provide a novel framework of detecting the electromagnetic wave in nanomechanical systems. The operational condition regarding temperature was also derived. Notable point is that the digitized phase of the electromagnetic wave can be detected in the nanoscale detector. This indicates that digitally modulated signals, which are often used in digital communications, can be detected even with nanomechanical systems. This opens up a new paradigm to transfer digital data, which contributes to the forthcoming age with IoT and AI-based systems.


EN15.06.07

**Highly Sensitive and Transparent Polymer Thermistors Composed of Silver Fractal Dendrites and Polyacrylate**

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Temperature is an important parameter that regulates chemical reactions of the environment and has been developed until recently for monitoring in various fields. Particularly, developing polymer positive temperature coefficient (PTC) thermistors is attracting much attention because they have several advantages including high sensitivity, flexibility, conformability, biocompatibility, and biodegradability. However, most polymer PTC thermistors including containing a high concentration of opaque filler materials still have issues such as low sensitivity, low optical transparency, and poor operational durability due to low electrical conductivity and inefficient hopping transport. Here, a highly sensitive, flexible, and transparent polymer thermistor based on silver fractal dendrites (AgFDs) and a polyacrylate (PA) matrix has been successfully demonstrated. AgFDs–PA composite films are prepared using a simple melt-mixing process for the AgFDs and molten PA. It exhibits a superior PTC effect (about \(10^6\text{~}10^7\) Ω) around body temperature because of the high electrical conductivity of the AgFDs and the quantum tunneling effect resulting from their unique structures. A flexible and transparent thermistor based on the AgFDs–PA composite shows excellent sensitivity, detection resolution, and fast sensing response through dramatic resistance changes in the human body temperature range. Moreover, it exhibits excellent optical transparency, mechanical flexibility, and operational durability. In addition, electrical impedance spectroscopy (EIS) analysis proved that the quantum tunneling effect amplified by the AgFD branch has a significant effect on the changes in resistance. Based on these characteristics, the thermistor was successfully demonstrated for real-time temperature monitoring of human body.

EN15.06.08

**Atomistic Molecular Dynamics Simulations of Nanomaterial Adhesion on Calcite Surface Defects in Deionized Water and Reservoir Fluids**

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Calcium carbonate (CaCO₃) is a widely important mineral that is found extensively in biological and geological systems. The interaction of water, ions, organic molecules, macromolecules, and nanomaterials with calcite surfaces controls a broad range of natural and industrial processes such as ion exchange, contaminant migration, enhanced oil recovery, biomineralization, and flocculation. Previously, an atomic force microscopy (AFM) study and molecular dynamics (MD) simulations demonstrated that carboxylate alkanethiols functionalized AFM tips (as surrogates for nanomaterials) showed mitigated adhesion to calcite surfaces in fluids with specific ions. The MD study also showed that calcite crystallography affected adhesion as a result of surface calcium ion exposure. Here, we extended the MD simulations to explore the effects of calcite surface defects. Specifically, we focused on four line and point defects on the calcite (104) surfaces: (1) acute step, (2) obtuse step, (3) Ca⁺² vacancy, and (4) CO₃²⁻ vacancy. In addition, we considered three fluids: (1) deionized water (DI), (2) seawater (SW; 0.7 M NaCl), and (3) brine (B; 1.28 M NaCl + 0.34 M CaCl₂), which the latter two are relevant in subsurface hydrocarbon reservoir applications. The simulation results showed that the calcite surface defects have the strongest effects on adhesion in DI compared to in SW and B, where in DI the adhesion were changed by -30% on obtuse step, -10% on Ca⁺² vacancy, and +25% on CO₃²⁻ vacancy. On the other hand, in SW and B the adhesion changed within ±10% in most cases. Interestingly, we observed an inversion of the adhesiveness of vacancies compared to no-defect surfaces in different fluids, where the Ca⁺² vacancies were less adhesive in DI but more adhesive in SW and B, and the CO₃²⁻ vacancies were more adhesive in DI but less adhesive in SW and B, due to counter ion accumulations on the vacancies. We believe the atomic-level understanding obtained in this work can be helpful for developing novel nanomaterials for subsurface applications and may further the understanding of wettability alteration mechanisms in ionic fluids.

EN15.06.11
Structural and Optical Properties of In-Doped ZnO Thin Films Prepared for Flexible and Transparent UV Photodetector Euije Jo, Dongwan Kim and Jae-Young Leem; Inje University, Korea (the Republic of)

Zinc oxide (ZnO) has attracted a great deal of interest because it has direct wide band gap of 3.37 eV at room temperature (RT) and large exciton binding energy of 60 meV, and these properties make ZnO a suitable material to fabricate a variety of optoelectronic devices, such as light-emitting diodes, laser diodes, optical communication, and solar cells. In addition, ZnO represents several other interesting advantages like high optical transparency in the visible region and high carrier mobility, so it can be applied as flexible and transparent UV photodetectors. But, ZnO has high electrical resistivity owing to its low carrier concentration induced by native donor defects, interstitial zinc, and oxygen vacancies which degrade the optical and electrical properties of ZnO thin films-based UV photodetector. Thus, many researchers have doped with group three elements such as aluminum, gallium, and indium acted as donor dopants for ZnO to reduce the electrical resistivity of ZnO thin films [1]. Particularly, the indium-doped ZnO (IZO) represents higher optical transmittance, better conductivity, and excellent surface roughness than the other dopants doped ZnO. IZO thin films can be synthesized by various techniques such as physical or chemical vapor deposition, pulsed laser deposition, atomic layer deposition, and sol-gel spin coating method. Among these methods, sol-gel spin coating method has some advantages including uniformity of thickness, controllability of composition, simplicity, and low cost [2]. However, since the sol-gel spin coated IZO thin films must be annealed at high temperature to crystallize the amorphous phase of IZO, the IZO thin films-based flexible and transparent UV photodetectors which utilize the polymeric substrate couldn’t have been fabricated by sol-gel spin coating method. Therefore, it is necessary to develop a new annealing method which prevents damage to polymeric substrate that are affected by high temperature during annealing process. In this study, we annealed the sol-gel spin-coated IZO thin films by using a novel method, synchronized heat and cool annealing (SHCA) method, which anneals thin films on top with IR heaters and simultaneously removes the high light energy transferred to polymeric substrate using cold plate. To investigate the effect of indium on the structural and optical properties of IZO thin films annealed by SHCA method, we measured the IZO thin films by using X-ray diffraction (XRD), and photoluminescence (PL). As a result of the measurement, in the XRD, IZO thin films showed the three diffraction peaks corresponding to ZnO (100), (002), and (101) plane, and the diffraction peak of ZnO (002) plane was red-shifted. For PL, the intensity of the near-band-edge and deep-level emissions for IZO thin films significantly increased, which indicates that carrier concentration and the number of defects in the ZnO lattice increased, respectively.

EN15.06.12
Gas Detection System Using Color Films by Chitin Based Colorimetric Thin-Film Effect Dong Jin Han and
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By detecting gases, we can take early measures in keeping the safety and freshness of our life. So far, various types of highly sensitive and selective gas sensors have been reported using carbon nanotubes or nanowires as sensing materials. However, these previous reports have limits in their practical application due to the need of electrical power and high manufacturing cost. Here, we introduce a biomimetic colorimetric film that can be utilized for the detection of ethylene glycol. The film is fabricated by Chitin on a silicon surface by a thermal evaporation from a Chitin powder. The film enable to thin-film effect into stable color patterns. By controlling the evaporation times 1 to 3, the film thickness could be controlled from 50 to 180 nm, resulting in films with different colors in the visible range.

When the Ethylene glycol reacted with the amine groups on the Chitin-film by etherification, the films underwent both chemical and structural changes, resulting in color changes in sub-ppm concentrations.

We demonstrated that sensing data analysis interlocked with a phone camera and discriminant analysis algorithms can further discriminate gas concentration in air. We expect that our results will be utilized in providing a low-cost and low-power systems for the monitoring of gas.

EN15.06.13
Structural, Electrical, Optical and Thermal Properties of Gallium Doped Zinc Oxide (GZO) Thin Film for Transparent Heater Applications
Jasmine Beckford, Makhesh K. Behera, Kelsea Yarbrough, Sangram K. Pradhan and Messaoud Bahoura; Norfolk State University, United States

There is an increased interest in thin film transparent heaters (TFTH) for applications in optoelectronics, military, de-icing of airplane wings, defogging of windshields, and a plethora of domestic usages such as smart windows, defrosters in automobiles and many other applications. In this work we present the growth and characterization of one of the potential TFTHs, Gallium doped zinc oxide (GZO). GZO thin films were deposited by pulsed laser deposition (PLD) on transparent substrates such as glass and flexible polymer. Ga doped (5 atomic weight percentage) ZnO target was made in the laboratory using Ga2O3 and ZnO powder. GZO films with thickness 110 and 125 nm were deposited on glass and flexible polymer at substrate temperatures of 400°C and 120°C, respectively. Atomic force microscopy images reveal that the films are very smooth with excellent surface roughness (~1.18 nm). The temperature dependent resistivity measured was done using linear four probe measurement and the samples showed a very low sheet resistance value of about 2.6×10-4 Ω cm and also exhibited high optical transparency value of (>90%) from transmission data. GZO transparent heater also showed a stable and reproducible Joule heating effect and the temperature can reach easily 100°C by the application of low input (~8V) voltage. This research finding may be beneficial for the potential use of GZO as a transparent oxide material for possible applications in the emerging area of low-cost power electronics, and flexible and wearable optoelectronics devices.

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EN15.06.14
Spectral Photosensitivity and Lifetime of Mg2Si Photodiodes for SWIR Sensor Application
Fumiya Takahashi, Yuutarou Fuse, Takeru Miyauchi and Haruhiko Udonou; Ibaraki University, Japan

Photodetectors in the short wavelength infrared region (SWIR: 0.9 to 2.5 μm) have attracted attention for use in environmental monitoring, night vision, automotive autonomous driving and also biological research. Recently, we thermally diffused Ag to an n-type Mg2Si substrate to fabricate a Mg2Si pn junction photodiode (PD), and succeeded in obtaining photosensitivity below a cutoff wavelength of about 2.1 μm. The lifetime of minority carrier is important to enhance the photosensitivity of PDs, but so far the lifetime of Mg2Si has not been investigated. In this paper, we measured the lifetime of Mg2Si pn junction PDs fabricated by the thermal diffusion method in the temperature range from 300 K to 77 K by the open circuit voltage method (OCVD) method. The observed voltage decay waveform which is a result of the time required for the minority carrier decay became longer with decreasing the temperature and reached maximum at about 160K. The minority carrier lifetimes determined from the OCVD measurements were 0.5 μs at 300 K, 5.3 μs at 160 K, and 3.8 μs at 77 K, respectively. Furthermore, the relationship between the measured minority carrier lifetime and the photosensitivity of the fabricated device was investigated.

EN15.06.15
Near Infrared Reflective Coatings for LiDAR Sensor with Optically Controlled Multilayers Youngseok Kim, Jin Hwan Kim, Hyunsang Park and Sangwon Seo; Korea Electronics Technology Institute, Korea (the Republic of); Kangnam Jevisco Co., LTD., Korea (the Republic of)

LiDAR sensors, a primary sensor used on AVs, utilize emitted light pulses, typically at 905nm, to remotely detect the location of objects. Incident light from the LiDAR sensor is both specularly reflected by the clearcoat and absorbed/reflected by pigments in the basecoat. Paint colors that reflect a greater amount of light at 905 nm are more easily detected by LiDAR. Thus, technologies to enhance paint reflectivity at 905 nm, while not affecting the appearance of the paint, are desirable. However, most black and dark tone cars are painted with paints based on carbon black pigment that exhibits very low reflectivity not only for the visible but the infrared light. Alternately, autonomous vehicles need to raise the laser power to detect the black vehicles, which is highly energy consuming. As the automotive market changes, the development of new black paint with high infrared reflectivity has become necessary.

Here, we design a dark-tone multilayer with low reflectivity at the visible wavelengths and high reflectivity at 905nm at the same time. Various oxide materials including Fe₂O₃, CuO, TiO₂, SiO₂, and Al₂O₃ are investigated, and the reflectivity is calculated as a function of the multilayer’s composition, the number of layers, and the layer thicknesses. We find an optimized multilayer and deposit the constituents by using sputtering on a glass substrate alternately. Finally, the measured reflectivity shows a good agreement with the simulation. We expect it can be materialized as a pearl pigment that is a plate type particle with tens of aspect ratio by depositing the oxide materials on pulverized substrate materials or by pulverizing the substrate with deposited materials.

Hybrid Cellulose Nanocrystal Nanocomposite-Based Biosensor for Detection of Uric Acid and Lactate Joseph Laws, Pedro Cortes, Eric Macdonald and Byung-Wook Park; Youngstown State University, United States

The advanced nanomaterials and fabrication methods for various biomarkers, including pH, glucose, uric acid, and lactate, are important to monitor the wound healing process. Numerous sensing techniques have been developed for effective wound monitoring. Cellulose nanocrystals (CNCs) have been attractive bio/nanomaterials, due to the high specific surface area and specific strength, hydrophilicity, biodegradability and surface functionalization. In this study, we have successfully developed hybrid CNC nanocomposite biosensors for detection of uric acid and lactate. The CNC and polypyrrole (Ppy) nanostructures were fabricated on the electrode by electropolymerization. Subsequently, the urease or lactate oxidase was immobilized on the CNC-Ppy modified electrode. The structural investigation was performed to examine the growing mechanism of the CNC-Ppy nanocomposite on the electrode surface using physical and chemical characterization methods, such as SEM, FTIR, EIS, and CV. The stability, reproducibility, repeatability, selectivity and linearity of the biosensor were investigated. The proposed biosensor exhibits high sensitivity and was fully selective. The developed hybrid nanocomposite biosensor is cost effective and the fabrication method is relatively simple, providing an excellent sensing platform for efficient electrochemical biosensing of uric acid and lactate.

A Scalable Solution-Processed Inorganic Passive Radiative Cooler for Tropical Regions Chongjia Lin, Yang Li and Baoling Huang; Hong Kong University of Science and Technology, Hong Kong

Air conditioning consumes a significant amount of electricity in summer, especially in humid tropical regions. Passive radiative cooling can radiate heat to the outer space through the infrared atmospheric window (8-13 um) without any energy consumption, providing an attractive approach for cooling buildings. Most of the state-of-the-art daytime radiative coolers show high solar reflection but high emission in the whole mid-infrared (mid-IR) regime (5-25 um) without good spectral selectivity beyond the atmospheric window, and their cooling performances under humid climates are limited. Besides, most of them adopt organic components that face aging issues when exposed to sunlight. In this study, we developed a solution-processed inorganic passive radiative cooler with high mid-IR emissivity, good mid-IR selectivity and high solar reflectivity. It illustrates a high solar reflectivity up to 98% and a high infrared emissivity of 90% within the 8-13um atmospheric window. Compared with the state-of-the-art passive coolers, it can achieve high cooling power in both mid-altitude (>85W/m²) and humid area (>25W/m²) and better cooling temperature (-7.6°C) in tropical areas, due to its good mid-IR selectivity. Its high cooling performance and excellent scalability render it promising for space cooling in humid tropical regions.
Domain Spacing versus Chain End Density Effect on Energy Storage Capacity of Lamellar Block Copolymer Film Capacitors

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Designing next generation light-weight pulsed power sources hinges on understanding the factors influencing the performance of high energy density storage materials. We have demonstrated the use of Cold Zone Annealing with Soft Shear (CZA-SS) as a processing strategy to fabricate highly stratified lamellar block copolymer (L-BCP) films which results in ~50% enhancement in breakdown voltage ($E_{BD}$) or ~225% increase in stored energy density ($U$), compared to unordered as-cast films. Increasing L-BCP layer thickness, $d$ by increasing $M_w$ increases $E_{BD}$ but kinetics of ordering is challenging at high L-BCP $M_w$. Modestly high molecular weight films of amorphous L-BCP of PS-$b$-PMMA with layered morphology exhibited $U$ of 4.8 J/cm$^3$, comparable to the industry standard of semi-crystalline BOPP films of ~5 J/cm$^3$. Efforts continue to demonstrate the full potential of the method. Notably, $E_{BD}$ was found to increase linearly with $M_n$ of neat L-BCP and will be reported. Blending L-BCP with homopolymers or cyclics is an alternate approach to increase layer thickness. While blending increases L-BCP layer thickness, chain ends of linear homopolymers act as defect sites for promoting breakdown in the L-BCP polymer films, that may be avoided by addition of cyclic polymers. Neutron Reflectivity and X-ray scattering (GISAXS) measurements confirm stratified lamellar structure in blend systems for correlations to $E_{BD}$. Neutron reflectivity measurements show that the ‘wet brush regime’ swelling of L-BCP with cyclics and homopolymer are comparable while ‘dry brush regime’ swelling differ significantly. The breakdown strength of L-BCP swollen with cyclics will be reported. These findings can be vital in the selection of L-BCP for designing next generation high energy density, solid-state polymer capacitors for flexible electronics.

Nanoporous Silver for SERS Fabricated by Nucleation and Growth Control During Evaporation

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Evaporation techniques for making dense metal films typically utilize a high vacuum process. Through the conversion of the idea of high-pressure evaporation, it was possible to create highly porous structure of silver by increasing background working pressure to a few Torr. In this evaporation process, opposite to the typical thermal evaporation, evaporated silver atoms encounter repeated collision with the surrounding Ar gas molecules and this causes homogeneous nucleation and growth of silver. The nucleation and growth are controlled by adjusting the working pressure, temperature, evaporation rate, etc., resulting in different morphology and porosity. The higher the pressure, the higher the porosity and the darker the structure becomes absorbing light more. As evidenced by SEM and TEM, the porous structure consists of aggregates of crystalline nanoparticles of silver ranging tens of nanometer to hundreds of nanometers. Especially, a lot of nano-sized gaps are found between the particles. These nanogaps can act as a hot-spots for surface-enhanced Raman spectroscopy (SERS). Using rhodamine-6G, we show these nanoporous structures of silver outperform commercial test substrates of SERS. This new approach of metal deposition can contribute to other areas that need high surface-to-volume ratio such as catalysts and gas sensors.

Cellulose Based Triboelectric Nanogenerator for Electronic Paper and Environmental Sensors

Inkyum Kim and Daewon Kim; Kyung Hee University, Korea (the Republic of)

With the development of internet of things (IoT), energy harvesting technologies are evolved to increase the operation time of small electronics without consuming more fossil fuels in recent years. In addition, natural materials have recently been attracting much attention due to their eco-friendly and abundant properties. Above all, cellulose, which plays a role of the primary cell wall of green plants, is the most abundant organic compound on earth. In this work, we investigate a cellulose nanofiber-based triboelectric nanogenerator (CN-TENG), which was developed to convert vertical moving energy into an electrical energy. The top and bottom parts of the CN-TENG consist of silver nanowires (AgNWs) and cellulose nanofiber (CNF), respectively. The electrical output of this CN-TENG was measured by contacting and separating with only two sheets of fabricated devices. The CN-TENG with a
higher pressure and increased number of passes in the homogenizer during fabrication from the suspension represents highest open-circuit voltage of 21 V and short-circuit current of 25 µA, respectively. AgNWs layer with the concentration of 0.1 wt% showed saturated electrical outputs. Scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) were utilized to analyze the components and surface morphology in order to investigate the correlation between the surface morphology and the electrical output. Additionally, a 693 mW/m² power density was observed at an external resistance of 10 MΩ. Moreover, this fabricated film shows the characteristics of foldable, writable, erasable This fabricated CN-TENG can be developed as a paper-based electrical energy generator for various applications such as e-paper.

EN15.06.21
The Depth Analysis to Enhance the Efficiency of Triboelectric Nanogenerator as a Wind Speed Sensor and Energy Harvester Hyoeunhee Roh and Daewon Kim; Kyung Hee University, Korea (the Republic of)

A triboelectric nanogenerator (TENG) can convert mechanical energies into electrical power with excellent conversion efficiency. TENGs can generate electrical energy based on contact-electrification and electrostatic induction. Among the various operating modes, a rotating-disk-based TENG harvesting wind energy is being studied extensively because it can produce high current. Deep analysis of the flow of the fluid is essential to improve the conversion efficiency of the TENG.

In this paper, the propeller TENG (P-TENG) was designed to demonstrate the relationship between TENG and fluid mechanics as a wind energy harvester and wind speed sensor. The P-TENG is mainly composed of three parts: a rotator (propeller) and a stator (electrode), and a main body. The P-TENG has the cylindrical structure—having a diameter of 8.8 cm and height of 3 cm—and an inlet and outlet on the side and top, respectively. The rotator (propeller) and main body were 3D-printed of acrylonitrile butadiene styrene (ABS). The ABS has outstanding resistance to chemicals, heat, and impact. When the wind energy is injected into the main body, it collided with the perpendicular plane of the propeller and cause the rotational motion.

The five factors (the pressure of the injected gas, the distance between the stator and rotator, the number of propeller wings, and the height and angle of the inlet) were changed to verifying the electrical characteristics of the disk-based TENG and to examine the gas flow within the P-TENG. The highly injected pressure of the fluid causes the higher rotating speed, as a result, it contributes to increasing the current. In this regard, the P-TENG can act as a wind speed sensor without an external power source. Also, the comprehensive analysis conducted based on these electrical output results. The COMSOL simulation was carried out to calculate the value of pressure to the propeller and the flow of fluid. The laminar flow was applied as physics condition and solved with the Navier–Stokes equations. The injected fluid was analyzed by dividing it into four flows in the vertical and horizontal directions and each flow influences the rotational motion in a way to improve or reduce.

Based on the comprehensive analysis, the optimized P-TENG consists of the 16-sector propeller, a low inlet height, a 60° inlet angle, and PTFE film with a nanostructured surface. Finally, the P-TENG can power 205 LEDs as well as a commercial stopwatch in real time, without any other power source. The P-TENG enabled Bluetooth transmission and reception and drove the sensing, processing, and data transmission of a commercial temperature and humidity sensor, so it can be used as a power source for a self-powered wireless sensor system. The investigation of P-TENG provides not only the possibility that using as a self-powered wind speed sensor and maximized energy conversion efficiency by optimizing the structure of the device based on depth analysis of the flow of fluid.

EN15.06.22
Anti-Kasha Effect of Graphite-ZnO Nanocomposite without Dropping Fluorescence Intensity in Water—A Cyanide Sensor Somrita Mondal; Calcutta University, India

Of late, carbon-based nanomaterials have been prevalent research topic owing to their potential application and especially excitation-dependent diverse fluorescence emissions. The later property can be tremendously useful in sensing, imaging, and photovoltaics. However, applications using this unique fluorescence property of carbon-based nanomaterials have not been explored so far, which may be due to a significant drop in fluorescence intensity in longer wavelength region after photoexcitation of the nanomaterials. In this paper, we report a simple aqueous synthesis of ZnO-graphite nanocomposite, which displayed unusual excitation dependent fluorescence emission violating the Kasha’s rule, without significant shrink in the fluorescence intensity at longer wavelength region. Moreover, the fluorescence intensity of the nanocomposite monotonically increased with the addition of cyanide ion of millimolar concentration. The fluorescence enhancement followed Langmuir binding isotherm, which enables quantitative detection of cyanide. The phenomenon of unique excitation-dependent emission along with
fluorescence enhancement in the presence of cyanide ion opens up a new avenue for the design of a multichannel array-based sensor to detect toxic and environmentally hazardous analytes.

EN15.06.23
A Study of Lifetime and Binding Energies of Excitons in Mn-Doped PbS Nanoparticles Grown in Solution
Gen Long1, El Mustapha Lotfi2, Elmustapha Feddi3 and Mostafa Sadoqi1; 1St. John's University, United States; 2Université Mohammed V de Rabat Maroc, Morocco; 3Mohammed V University, Morocco

Lead Sulfide (PbS) is a unique material system that is interesting for photovoltaic, thermoelectric, and sensing applications. In this work, we report a systematic study of syntheses of Manganese (Mn) doped lead sulfide (PbS) nanoparticles via varying growth temperature (50°C to 120°C), growth time (10min to 24hrs), with various precursors’ ratios (Mn : Pb). The synthesized nanoparticles (2~5nm) were characterized by UV-VIS absorption, XRD, EDS, TEM, XRD, etc. The lifetimes of emissions of doped nanoparticles measured by ultrafast spectroscopy were found to be affected by Mn concentration, ranging from 5ns to 100ns. The DOS of nanoparticles simulated by DFT method were also found to be dependent upon the doping concentration. The band gaps were found out to be not affected by the doping concentrations. Through tuning of doping concentration, the material properties of Mn-PbS nanoparticles can be modified based on specific applications.

EN15.06.25
Optical Properties of Mechano-Luminescence-Optoelectronic Composites for Vibration-Based Structural Health Monitoring
Alfred Mongare, Donghyeon Ryu, Willow Lindsey-Paek, John Huckabee and Nikolai Kalugin; New Mexico Tech, United States

Vibration-based structural health monitoring (SHM) systems allow to evaluate the state of the structure and the presence of damage. [1] For the detection of damage by sensing strains under vibrations without external electrical energy supply, multifunctional mechano-luminescence-optoelectronic (MLO) composites were suggested. [2] MLO composites use two transformative materials – vibration-sensitive light-emitting mechano-luminescent (ML) material, and photosensitive electrical-response generating material. [3] As a result, MLO composites generate direct current (DC) by harvesting mechanical energy from ambient vibrations in tested structures via the coupled two-step energy conversion mechanism (i.e., mechanical-radiant and radiant-electrical energy conversions). [4] The two functional constituents – ML copper-doped zinc sulfide (ZnS:Cu)-based elastomeric composites and mechano-optoelectronic (MO) poly(3-hexylthiophene) (P3HT)-based films – of the MLO composites are designed to selectively sense different modes of vibrations. [5] The MO P3HT-based thin films generate DC by utilizing light emitted from ML ZnS:Cu-based composites. Being combined together, our materials and devices represent a new class of self-powered and multi-modal sensor technology that can potentially enhance self-sustainability of, for example, unmanned aerial vehicles, or other remotely controlled mechanisms.

In our study, two functional constituents – ZnS:Cu-and P3HT-based composites – will be prepared and characterized. Optical spectra of ZnS:Cu and PDMS; ZnS:Cu-PDMS composites will be obtained using Raman, FTIR, and photoluminescence spectroscopies. Depending on the Cu doping concentration, the PL spectra of ZnS:Cu-PDMS have a maximum of emission in green (low doping concentration) or blue (higher Cu concentration). Composites with ZnS, which is co-doped with Cu and Mn, show orange luminescence. In addition, all tested samples demonstrate broad-range room temperature luminescent signals in the range of 0.86-0.84 eV, which seems to be attributed to optical transitions via AN, AS and PS centers of Cu2+ in ZnS. This indicates possibilities of the coexistence of different structural forms and different particle sizes of ZnS in the ML ZnS:Cu-PDMS composites. ML spectrum from different repetition loading frequencies and strains will be obtained. Luminescence from ZnS:Cu-PDMS was found to be sensitive to the strain and strain rate. The photodetection spectra of MO P3HT-based composites show a sensitivity peak around 590-600 nm (2-2.1 eV); the experiments with different light modulation frequencies reveal the dynamical limitations of this type of photodetector. Overall, simultaneous optical characterization of ML and MO constituents of MLO composites opens up possibilities for “fine tuning” of both ML and MO constituents for the achievement of maximal mutual compatibility and optimal performance of the entire multifunctional MLO composites.

We would like to thank NASA’s Space Grant College and Fellowship Program and NASA EPSCoR CAN (grant #: 80NSSC17M0050) for supporting this study.

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CNTs can have the ability to act as compliant small-scale springs or as shock resistance micro-contactors. This work investigates the performance of vertically-aligned CNTs (VA-CNTs) as compliant, micro-contactors in electromechanical testing applications for testing at wafer-level chip-scale-packaging (WLCSP) and wafer-level-packaging (WLP). Fabricated on ohmic substrates, 500-μm-tall CNT-metal composite contact structures are electromechanically characterized. The probe design and architecture are scalable, allowing for the assembly of thousands of probes in short manufacturing times, with easy pitch control. We discuss the effects of the metallization morphology and thickness on the compliance and electro-mechanical response of the metal-CNT composite contacts. Pd-metallized CNT contactors show up to 25 μm of compliance, with contact resistance as low as 460mΩ (3.6 kΩ/mm) and network resistivity of 1.8 x10^{-5} U cm, after 25000 touchdowns, with 50 μm of over-travel; they form reproducible and repeatable contacts, with less than 5% contact resistance degradation. Failure mechanisms are studied in-situ and after cyclic testing and show that, for top-cap-and-side metallized contacts, the CNT-metal shell provides stiffness to the probe structure in the elastic region, whilst reducing the contact resistance. The stable low resistance achieved, the high repeatability and endurance of the manufactured probes make CNT micro-contactors a viable candidate for WLP and WLCSP testing. Furthermore we show the addressability of individual probes for an array with 200 μm pitch by utilising ink-jet printing after on-chip CNT-metal hybrid probe fabrication allowing to address 144 individual probes. The stable low resistance achieved, the high repeatability and endurance of the manufactured probes make CNT micro-contacts a viable candidate for WLP and WLCSP testing.

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EN15.06.28
Designing and Structural, Optoelectronic Characterization of Nanocrystalline TiO2-Based Hybrids for Solar Devices Sagar D. Delekar, Ananta Dhodamani and Krantiveer More; Shivaji University, India

Herein, the different chemical strategies have been adopted for tuning the properties of nanocrystalline TiO2 so as to form the ternary hybrids and thereafter these hybrids have been tested for efficient solar-to-electrical conversions through photovoltaic measurements. Initially, nanocrystalline TiO2 have been anchored with the different systems such as dyad system, dye-quantum dot system, composites with carbon nanostructures sensitized through dye. Along with optical coverage for better absorption, the interconnectivity between the various components and their charge-transport properties of modified TiO2 for solar energy conversions have been studied in detail. In the dyad system, a supramolecular ruthenium (II) phthalocyanine (RuPc) with peryleneimide (PI) has been anchored on the surfaces of TiO2 and thereafter these TiO2-dyad sensitized solar cells have assembled in a bottom-up fashion. Upon photo-irradiation at air-mass (AM) 1.5, the dyad-based solar devices convert solar light to electricity of 2.1%; which is higher than that of individual dyes. In next strategies, the synthesized CdS quantum dots (QDs) have connected electrostatically to the surfaces of TiO2 nanoparticles (NPs) and thereafter, this binary hybrid heterojunction is further self-assembled physically with N719 dye to form ternary TiO2 NPs-CdS QDs-N719 photoelectrodes. These co-sensitization devices reported the solar energy conversion efficiency (η) up to 2.35 %. In addition, anatase TiO2 NPs is anchored on the surface of functionalized carbon nanostructures (MWCNTs or RGO); which is further sensitized with Ru(II) dyes for solar devices having efficiency reached to 6.21%. In another modification, Cr(III) as well as Mo(VI) ions are inserted into TiO2 host lattice and then their composites with CNs are further sensitized with dyes for boosting the solar energy conversions and reached up to 7.69 % of efficiency.

EN15.06.29
Surface Modification of Gold Nanorods to Enhance the Detection of Hg2+ John Crockett1, Luan Tianqi1,2 and Eli Doebler1; 1Western Washington University, United States; 2University of Georgia, United States

The abundance of mercury (II) in trace amounts throughout the ecosystem, combined with its ability to accrue in human tissue has motivated the need for highly sensitive and selective detection methods. Gold Nanorods (AuNR) have demonstrated a unique facility for the detection of mercury due to their plasmonic properties and the propensity for mercury and gold to form an amalgamation. Prevalent methods for the synthesis of AuNR’s utilize high concentrations of cetyl trimethylammonium bromide (CTAB) which forms a dense micelle bi-layer on the exterior of the AuNR’s. The sensitivity of AuNR’s to mercury has been shown to be extremely diminished with increasing concentration of CTAB, however reduction of CTAB concentration led to aggregation of the AuNR’s. CTAB was exchanged for polyethylene glycol thiol (PEG) as a capping agent on the AuNR’s resulting in much better stability and a significant increase in both sensitivity and selectivity for detection of mercury (II) over CTAB coated AuNR’s. The increased stability of PEG coated AuNR’s also allows for manipulation of the region of highest sensitivity to mercury (II) by changing the concentration of AuNR’s. It was also discovered that the sensitivity of PEG coated AuNR’s to mercury (II) could be as much as tripled with incubation of the PEG coated AuNR’s. This increased sensitivity has been attributed to the preferential removal of PEG from the tips of AuNR’s by the formation of a complex between PEG and mercury (II) which has a higher stability than the complex between gold and PEG.

EN15.06.31
Identifying Chemical Structure Responsible for the Reactivity of GO Regarding Oxidative Amine Coupling Reaction Kazuyuki Takai, Ryutaro Suzuki, Takuya Isaka, Kentaro Tajima and Tomoki Yamashina; Hosei University, Japan

Graphene oxide (GO) having oxygen-containing groups is expected as metal-free and environment-compatible catalyst. The research on GO catalyst progressed [1 - 3], although the detail mechanism for GO catalytic activity is not clear yet. Investigating Graphene Oxide (GO) properties before / after the catalytic reaction is a promising strategy for clarification of the mechanism for GO catalytic activity. Additionally, it is known that removing oxidative debris on GO by base-treatment is important factor to get the higher yield for the following catalytic reaction [1]. In this study, the principle for reactivity of GO is investigated by conducting the oxidative amine coupling reaction of benzylamine (1) to N-benzylimidobenzylamine (2) using baGO and thermally reduced one (rbaGO) as catalysts. baGO-Pristine was obtained by washing GO, synthesized by Hummers method, with NaOH. rbaGO was prepared by reducing baGO at 450C under Ar gas flow. After the reaction, the reaction media filtered for
removing the catalyst was characterized by GC-MS. After the 1st cycle reaction, the recovered catalyst was used as that for the 2nd cycle (baGO-1st cycle, rbaGO-1st cycle). The chemical structure of each catalyst after the reaction was evaluated by XPS (Al Ka), where it was washed with ethanol after the reaction. The atomic ratio O/C of catalyst much decreases after the reduction or 1st cycle reaction and rbaGO shows poor yield, suggesting roles of baGO / rbaGO not as catalyst but as oxidant. However, baGO-1st cycle exhibits the highest yield in spite of C1s spectrum and O/C similar to that of rbaGO and rbaGO-1st cycle, which also indicates no more reduction for rbaGO in the 1st cycle reaction. Taking these results and appearance of nitrogen content after the 1st cycle reaction into consideration, a different mechanism in the 2nd cycle reaction is suggested, where nitrogen incorporated into rbaGO / baGO in the 1st cycle reaction plays an important role for the reactivity. To clarify the most responsible functional groups in rbaGO / baGO for the higher catalytic reactivity in the 2nd cycle reaction, we have derived the amount of nitrogen-containing functional group per 100 mg in each GO sample for the 2nd cycle reaction. By plotting the amount of nitrogen-containing functional group and the GC-yield of the product, the correlation coefficient r is calculated for each functional groups. In particular, the GC-yield tends to increase as Graphitic N (correlation coefficient r = 0.94) and Oxidized N (correlation coefficient r = 0.87) increase. The important roles of those functional groups in the oxidation amine coupling reaction could be explained by the enhancement in the oxygen adsorption ability, which is important to produce O2*- species from ambient oxygen molecules for proceeding the oxidative coupling reaction.

References

EN15.06.32
Novel Highly Accurate and Sensitive Graphene-based Nanocomposite Electrochemical Sensor of Cilostazol Pharmaceutical Agent Mahmoud A. Saleh1, Manar M. Taha1, Nasaah Ahmed1, Mona Mohamed2 and Nageh K. Allam1; 1American University in Cairo, Egypt; 2National Organization for Drug Control and Research, Egypt

Cilostazol is a quinolone antiplatelet agent that contributes to vasodilatation. It can be used to relief the symptoms of intermittent claudication (decreased blood supply in the lower limps) that is attributed to ischemia. Also, it relieves the cramping pain that occurs during heavy exercises. Its main mode of action is the inhibition of both primary and secondary agglomeration of platelets, which is an important issue in drug monitoring. Herein, we report on the modification of carbon paste electrodes (CPE) with transition metal oxides (TMO), which showed a superior accuracy and sensitivity towards cilostazole than unmodified CPE. Characterization of the composite was done by scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform Infrared (FTIR), Cyclic voltammetry (CV), and square wave voltammetry (SWV). Moreover, the addition of reduced graphene oxide as a composite material has increased the current and sensitivity of the CPE to cilostazole. The ratio of the graphene to TMO in the composite was optimized to achieve the maximum response. The electrochemical sensor showed high linearity, sensitivity, and very low limit of detection in both Britton Robinson Buffer (BRB) and spiked plasma and urine samples.

SESSION EN15.07: Processing and Characterization of Catalytic and Sensing Materials
Session Chairs: Pu-Xian Gao and Lyubov Titova
Wednesday Morning, December 4, 2019
Sheraton, 3rd Floor, Commonwealth

9:00 AM EN15.07.01
Crystal Facet Selective Photo-Induced Etching of GaN Nanostructures in Water Max Kraut, Florian Pantle, Julia Winnerl, Martin Hetzl, Felix Eckmann, Ian D. Sharp and Martin Stutzmann; Technische Universität München, Germany
GaN nanowire (NW)-based devices have gained increasing interest for applications in solar driven photocatalysis and sensing due to the intrinsically high surface-to-volume ratio, the excellent achievable crystal quality and possible electro-magnetic field enhancement within periodic array [1]. Many materials that are catalytically active and sensitive to environmental changes, suffer from insufficient stability under operational conditions. By investigating the accelerated corrosion of hexagonal, dodecagonal and round GaN NWs in deionized water under high intensity illumination, we find that the crystallographic c-plane facet is stable, while a- and m-plane are etched with rates up to 11 nm/min, depending on the applied light intensity and wavelength. We identify photo-excited holes that are driven to the NW surface by the upward band-bending present in not intentionally doped GaN as the driving force of this process. Consequently, structural defects decrease the etching rate by serving as recombination centers for photo-induced carriers, which is shown by low-temperature photoluminescence and scanning electron microscopy investigations. The gained fundamental insights allow the development of viable strategies for the stabilization of the nanostructures under light-driven reaction conditions and harsh environments, which include facet engineering, change of doping type and shell growth.

In the present work, we investigate routes towards a direct photo-electrochemical water-splitting and conversion of CO₂ into useful chemicals via the integration of a light absorber and boron-doped diamond electrodes as cathode and anode material. In such a system, silicon photoelectrode is responsible for the light absorption, charge carrier generation and separation (p-n junction), while BDD electrodes protect the Si surface from its inherent corrosion in an aqueous media.

Nanocrystalline BDD electrodes have been fabricated via microwave plasma-enhanced chemical vapour deposition process [3]. We show that nanocrystalline BDD layer (thickness of 150 - 300nm) deposited onto Si photoelectrode allows for photogenerated hole charge carrier transfer from the underlying Si towards the electrolyte solution to participate in water oxidation reaction. Addition of the water oxidation catalyts onto the BDD surface reduces the overpotential for the water oxidation. Nanocrystalline BDD electrodes of various thicknesses and electrical conductivity values have been investigated for the CO₂ reduction in water-based electrolytes to establish a relationship between the BDD layer structure/composition and the products observed from CO₂ conversion. This work has been supported by the Grant Agency of the Czech Republic (GACR) contract 19-09784Y.


10:00 AM BREAK

10:30 AM EN15.07.04
Efficient 3D Printed Pseudocapacitive Electrodes with Ultrahigh MnO₂ Loading Bin Yao¹, Swetha Chandrasekaran², Marcus A. Worsley² and Yat Li¹; ¹University of California, Santa Cruz, United States; ²Lawrence Livermore National Laboratory, United States

Achieving excellent electrochemical performance of electrodes at high mass loading holds significant importance to energy storage. Pseudocapacitive materials such as manganese oxide (MnO₂) deposited on current collectors have achieved outstanding gravimetric capacitances, sometimes even close to their theoretical values. Yet, this is only achievable with very small mass loading of active material typically less than 1 mg cm⁻². Increasing mass loading often leads to drastic decay of capacitive performance due to sluggish ion diffusion in bulk material. In this talk, I will demonstrate a 3D printed macroporous graphene aerogel electrode with MnO₂ loading of 182.2 mg cm⁻², which achieves a record-high areal capacitance of 44.13 F cm⁻². The engineered porous structure allows efficient ion diffusion and therefore enables the ultrahigh mass loading of pseudocapacitive materials without sacrificing their gravimetric and volumetric capacitive performance. Most importantly, this 3D printed graphene aerogel/MnO₂ electrode can simultaneously achieve excellent capacitance normalized to the area, gravimetry, and volume, which is not possible for traditional electrodes. This work successfully validates the feasibility of printing practical pseudocapacitive electrodes, which might innovate the conventional layer-by-layer stacking fabrication process of commercial supercapacitors.

10:45 AM EN15.07.05
MnO₂/Multi-Walled CNT Electrodes for Supercapacitors Manufactured by Material Extrusion 3D Printing Yuqi Gao and Junjun Ding; New York State College of Ceramics at Alfred University, United States

The development of electrodes with high specific capacitance remains the main challenge for energy storage nowadays [1]. As an emerging technique, material extrusion 3D printing [2] provides an alternative pathway for designing and fabricating electrodes of supercapacitors by controlling the 3D macrostructures and nanocomposites.

In this work, MnO₂-nanoparticles and multi-walled CNT are mixed with polyvinylpyrrolidone (PVP) and deionized water as designed inks for desired rheological properties, which allow material extrusion from the nozzle. The inks are then used to print the nanocomposite electrodes layer by layer, followed by thermal treatment in the argon atmosphere. The ink composition is studied for the printability. PVP and deionized water tune the viscosity of the ink so that the ink can be printed fluently and completely, while multi-walled CNTs, served as conductive networks and interconnects in the nanocomposites for the high efficiency of electron delivery [3].

The 3D printed electrodes effectively integrate MnO₂ and multi-walled CNT, which achieves more abundant interactions caused by the higher loading of MnO₂ without the traditional binder of polyvinylidene fluoride (PVDF)
In addition, the stacking and alignment of MnO\textsubscript{2} and multi-walled CNT via material extrusion 3D printing provides the flexible tunable thickness \cite{5} of electrodes by controlling the printing layers (design and test one, two, four, eight layers with a 0.4 mm in diameter nozzle, respectively). This approach provides a promising way of manufacturing the needed electrodes in multiple aspects of size, shape, and dimension.

**Keywords:** MnO\textsubscript{2}/multi-walled CNT electrodes, supercapacitors, material extrusion 3D printing.

**Reference**


**11:00 AM EN15.07.06**

Assessment of MgZr\textsubscript{4}P\textsubscript{6}O\textsubscript{24} Composite Electrolyte for Fabricating Solid-State Mg-Sensor and Sensing Mg in Liquid Al

Mohammed Adamu and Girish M Kale; School of Chemical and Process Engineering, University of Leeds, United Kingdom

The potential solid-state electrolyte, MgZr\textsubscript{4}P\textsubscript{6}O\textsubscript{24} was synthesised by a modified sol-gel method. The structural, electrical and thermodynamic properties of this solid-state electrolyte were determined. DSC-TGA analysis indicated that pure dried xerogel powder when calcined at 800°C and 900°C, converts to single phase MgZr\textsubscript{4}P\textsubscript{6}O\textsubscript{24} nanopowder with good crystallinity. Pellets of 13-mm diameter and 3.8-mm thickness made by uniaxial compression were sintered at 1300°C for 24h. XRD and HR-TEM indicated that the crystalline phase is monoclinic having crystallite sizes of approximately 32nm and 40nm, after calcining at both temperatures, respectively, showing positive temperature effect on crystallite size. The sintered pellets were stable in the temperature range from 1000 to 1300°C, with minor extraneous peaks indicating traces of a coexistent second phase, Zr\textsubscript{2}(PO\textsubscript{4})\textsubscript{2}O at higher temperatures. Using electrochemical impedance spectroscopy, the electrical conductivity of MgZr\textsubscript{4}P\textsubscript{6}O\textsubscript{24} was determined as 7.23 x 10\textsuperscript{-3} Scm\textsuperscript{-1} at 725°C \cite{1}. MgZr\textsubscript{4}P\textsubscript{6}O\textsubscript{24} pellet was successfully employed for the design and fabrication of solid-state Mg-sensors for sensing Mg concentration in liquid Al at 700±5°C, with a biphasic powder mixture of MgCr\textsubscript{2}O\textsubscript{4}+Cr\textsubscript{2}O\textsubscript{3} as the ceramic reference electrode in air. A linear dependence of emf on logarithm of Mg concentration was obtained. Thermodynamic measurements using electrochemical method was deployed. The measured voltage of the sensor emf against the theoretical emf was achieved and compared, and an average transport number for Mg\textsuperscript{2+}-cation in the MgZr\textsubscript{4}P\textsubscript{6}O\textsubscript{24} solid-state electrolyte is approximately 0.85(±0.03) at 700±5°C, which is in agreement with an earlier study \cite{2}. The thermodynamic activity of Mg in liquid Al shows a negative deviation from the Raoult’s law. MgZr\textsubscript{4}P\textsubscript{6}O\textsubscript{24} solid-state electrolyte has useful applications in a stable, highly-sensitive, high-temperature electrochemical Mg-sensors during scrap metal recycling, refining and virgin metals alloying.

**References**

\cite{1} M. Adamu and G.M. Kale, Novel Sol-Gel Synthesis of MgZr\textsubscript{4}P\textsubscript{6}O\textsubscript{24} Composite Solid Electrolyte and Newer Insight into the Mg\textsuperscript{2+}-Ion Conducting Properties Using Impedance Spectroscopy. *J. Phys. Chem. C*. 2016;120:17909-17915.

Electronic and diffusion properties of hydrogen in ZnO have been extensively studied, since efficient defect engineering is essential to fabricate electronic, ferroelectric, and optical devices [1-2]. We introduced the protons in ZnO from chemical doping and/or proton implantation. To investigate the properties, we employed $^1$H nuclear magnetic resonance (NMR) relaxometry, which is a powerful technique of atomic-scale access to probe ion hopping motion in solids. Herein, we unambiguously identify the proton species which were occupied at the surface or in the bulk of ZnO, from their distinct NMR relaxometry and resonance shifts. NMR relaxometry gives the activation barriers of interstitial H in the bulk to be 0.46 eV by means of the rotating-frame spin-lattice relaxation measurements. Besides, it turns out that correlated jump diffusion of the surface hydroxyl group of multiple lines at ~1 ppm indicates the presence of structural disorder at the ZnO surface [1]. Hence, $^1$H NMR relaxometry may shed light on identifying proton species and investigating proton dynamics in hydrogen-incorporated systems.


(This work has been supported through KOMAC operation fund of KAERI by Ministry of Science ICT and Future Planning of Korean Government.)

1:30 PM EN15.08.02
Study of Nano-Materials for Hydrogen Leak Detection Sensors Nicolas Javahiraly; University of Strasbourg, France
We present in this work the study of nano materials for hydrogen leak detection sensors. On example of a configuration that can be used is based on a original transducer layers deposited on the core of a multimode fiber optic. The reference transducer layer is a multilayer stack based on a silver, a silica and a palladium layer. The spectral modulation of the light transmitted by the fiber allows to detect hydrogen. The sensor is only sensitive to the Transverse Magnetic polarized light and the Transverse Electric polarized light can be used as a reference signal.

The multilayer thickness defines the sensor performances in terms of sensitivity, SNR and time response. The silica thickness tunes the resonant wavelength, the silver (or gold) supports the plasmon and the palladium detects the hydrogen gas in the environment.

This study synthesizes the sensors performances as a function of different parameters such as the sensitive materials, different thicknesses, numerical apertures…

2:00 PM EN15.08.03

**Nanocarbon Icing Sensor and Dew Point Hygrometer** Vladimir Samuilov; Stony Brook University, The State University of New York, United States

This research is devoted to the development of a totally novel platform of carbon nanomaterial icing sensors and dew point hygrometers and to the fundamental understanding of the adsorption of water molecules, the mechanisms of nucleation of liquid water and crystallization into solid ice at the molecular level and nano-scale.

Our sensor is a film of carbon nanomaterial. Water molecules adsorption and phase transition of the first order of water into ice can be precisely detected by measuring of this carbon nanotube or graphene oxide film resistance. Further applications of the icing sensor will help to detect and to prevent the ice building up on specific surfaces like airfoils in aerospace vehicles, and will helps to the development of the methods to mitigate or inhibit icing phenomena.

The sensitivity range of the nanocarbon dew hygrometer ($T_D$) (frost ($T_F$)) is extremely wide from as low as -90°C to higher than +30°C. The applications can include the standard ones, like dew point hygrometers and cryopreservation of cells and tissues, food processing, or ice-templating the morphology of materials, etc.

2:15 PM EN15.08.04

**Thermal Transport in Additively Manufactured Glassy Carbon Nanowires and Nanolattices** Shiva Farzinazar and Jaeho Lee; University of California Irvine, United States

Advanced additive manufacturing has enabled an unprecedented material design space that spans over a wide range of structures and properties. While the additively manufactured nanomaterials have demonstrated fascinating mechanical properties, their thermal properties, and potential capabilities of controlling heat transfer have received little attention. The controlled thermal properties of additively manufactured nanomaterials could lead to efficient sensing and control of various energy systems, and the understanding will contribute to the emerging field of thermal metamaterials. Here we use a combination of two-photon polymerization direct laser writing (TPP-DLW) and pyrolysis to create glassy carbon nanowires and nanolattices. The pyrolysis process induces a high-strain shrinkage up to 80% and allows the formation of glass carbon nanowires with an aspect ratio as large as 640, in which the nanowire length is in an average of 48 µm, and the diameter is in an average of 75 nm. The large aspect ratio allows characterization of the heat capacity as well as the thermal conductivity. We use an electrical resistance thermometry technique known as the 3ω method to simultaneously characterize the electrical conductivity, thermal conductivity, and heat capacity of the glassy carbon nanowires over a wide range of temperature. The electrical conductivity of the glassy carbon nanowires increases from 22740 S/m at room temperature to 27757 S/m at 748 K, and their thermal conductivity increases from 2.4 Wm⁻¹K⁻¹ at room temperature to 7.0 Wm⁻¹K⁻¹ at 748 K. The increase in electrical and thermal conductivities is attributed to an increasing rate in graphitization ratio as a function of temperature. We measured the volumetric heat capacity of 2.1×10⁶ J/m³K for glassy carbon nanowires as compared to the amorphous carbon which has a specific heat capacity of 1.8×10⁶ J/m³K. The glassy carbon nanowires also provide excellent thermal stability, high Young’s modulus (20-30 GPa), and low density (1.3-1.5 gcm⁻³), which would be useful for sensing and control systems in extreme environments. Furthermore, we use the same manufacturing and characterization methods to create glassy carbon nanolattices and control the porosity up to 99%. Our investigations show that thermal properties of nanolattices can range from that of bulk materials to nanowires and offer unique capabilities of decoupling mechanical and thermal properties. The outcomes of this work advance our understanding of size, shape, and temperature dependences of thermal transport in additively
manufactured nanomaterials, and these findings will guide future designs of sensing and control of various energy systems.

2:30 PM BREAK

3:30 PM EN15.08.05
Unique Plasmonic Coupling at Nanojunction and Ultrafast Detection Nasrin Hooshmand and Mostafa El-Sayed; Georgia Institute of Technology, United States

Merging optics and nanotechnology has led to a remarkable fundamental insight into the interaction between light and matter at the nanoscale. The unique capacity of plasmonic nanostructures to concentrate electromagnetic fields, scatter electromagnetic radiation, makes them important in many scientific areas, including imaging, near field scanning optical microscopy, and chemical and biological sensing. Taking advantage of plasmonic nanoparticles especially those made of gold and silver is necessary to develop techniques to design responsive material with high sensitivity, selectivity, and high spectral resolution. Manipulation of the tight confinement of light across the gap of assembly of plasmonic nanoparticles could enable possibilities to achieve this idea. Plasmonic optical modes are very sensitive to the surrounding media, because of their electromagnetic field distribution around the particles. With considering a plasmonic nanoparticle as a thousand dipole points, when they are exposed to electromagnetic radiation, for nearby particles, dipole-dipole interaction has the most contribution in their plasmonic coupling. However, achieving even more tightly hot spots (confined fields) at the gap size of 2 nm or less requires to consider other multipole modes in the coupling phenomenon. This study develops new models of plasmonic equation that takes account the contribution of multipolar modes in the plasmonic coupling of pairs of silver nanoparticles at nanojunction separation. As the inter-dimer axis decreases, an increase in the plasmon dipolar and multipolar interaction takes place. It reveals that the plasmonic coupling depends on the density of the dipoles on the nanoparticle; as the dipole density increases, the average multipole density increases, resulting in higher dipole-multipole interactions. This research aims to design more sensitive optical sensors, which have many applications including single-molecule spectroscopy, biomedical and ultrafast optoelectronic applications.

3:45 PM EN15.08.06
Aligned, Suspended PVDF-TRFE Nanofibre Webs Fabricated by Dynamic Near-Field Electrospinning (dNFES) Patrick Stipp1,2, Wenyu Wang1 and Yan Yan Shery Huang1; 1University of Cambridge, United Kingdom; 2ETH Zürich, Switzerland

Most acoustic sensors are based on rigid Micro-Electro-Mechanical Systems and are optimised for high-frequency applications (>10k Hz). These systems often distort the airflow during measurement and require an additional output power source. Herein, we demonstrate a high performance, self-powered acoustic sensor platform. A dynamic Near-Field Electrospinning (dNFES) method is developed to fabricate suspended and interconnected sub-micro scale fibre webs. Permissive to flow, these interconnected and suspended sub-micro scale fibre webs can precisely imitate tiny variations triggered by the surrounding airflow motion. Electroactive Poly(vinylidene fluoride-co-trifluoroethylene) P(VDF-TRFE) copolymers are used as material to create the self-powered sensing ability of the fibre webs. Our dNFESFP process enables us to fabricate novel fibre webs to produce an acoustic sensing device in a one-step process. Due to the suspension and flexibility of the fibre webs, the acoustic sensing device shows particularly high sensitivity at most audible acoustic waves (between 200-5000 Hz). Furthermore, the dNFESFP process is an easy-to-use and stable technique that demonstrates a high reproducibility. Lastly, the process allows the tuning of fibre webs to optimise the sensitivity of the acoustic sensing device to the frequency range of interest.
MEMS-Type Gas Sensor of Pd-Loaded SnO2 for Ultra-High-Sensitive Detection in ppt Level
Kengo Shimano, Koichi Suematsu and Ken Watanabe; Kyushu University, Japan

Ultra-High-Sensitive gas detection in ppt level have been proposed by using pulse-heating of MEMS attached with Pd-loaded SnO2. My group reported three important factors, receptor, transducer functions and utility factor, for gas sensor material designs and their integration in 2003 and 2006, respectively. In 2014, the gas sensor using Pd-loaded SnO2 clusters based on the idea of the above integration could successfully detect toluene in ppb level. To enhance the sensor response more, we investigated the combination of utility factor and pulse-heating of MEMS. The MEMS-type gas sensors are repeatedly heated and allowed to cool by the application of voltage to the microheater; the target gas can penetrate into the interior of the sensing layer (Pd-loaded SnO2 clusters) during its unheated state. In 2018, we reported that such sensor responded to toluene in 0.1 ppb. In addition, the sensor response was found to increase by considering the oxygen adsorption state in the preheating and waiting-time before pulse-heating for measurement. The response of MEMS-type gas sensors showed a linearity to toluene concentration. It is found that the sensor response depends on the waiting-time between pre-heating and measure-heating. For example, in relationship of sensor response to gas concentration, the short waiting-time gave a steep slope, but the long waiting-time gave a gentle slope with lower detection limit. In the presentation, I will show the details as such Ultra-High Sensitive gas sensor.

Flexible Metal Oxide Nanowire Chemoresistors
Miriam Alvarado, Ernesto Gonzalez, Silvia DeLaFlor, Alfonso Romero, José Luis Ramirez and Eduard Llobet; Universitat Rovira i Virgili, Spain

New developments in consumer electronics, especially in the rapidly evolving field of wearable electronics require the use of different types of sensor devices. However, the use of gas sensors within this paradigm remains incipient, yet shows potential for developing wide spectrum of applications with enormous associated markets. Gas sensitive nanomaterials such as single crystalline (pure or metal loaded) metal oxide nanowires (NWs) will find commercial application provided they are produced employing scalable techniques that enable the mass production of high quality materials at affordable costs. Solution processing methods and additive fabrication techniques are seen as interesting enabling technologies for coupling nanomaterials to their application substrates. Here we show how metal oxide NWs can be integrated in flexible polymeric substrates for achieving chemoresistors employing either direct growth or transfer techniques. In addition, we discuss the results of careful studies on the reliability of the resulting flexible sensors having undergone stringent, automated bending tests.

Results:
The transducers for chemoresistive sensors were produced via the inkjet printing of silver or gold electrodes and heating elements on a Kapton substrate. The electrode area was then coated with mats of pure or Pd-loaded tungsten oxide NWs. Two approaches were used for integrating the nanomaterials on the transducers: 1) The direct growth of
the nanomaterial via a single step aerosol assisted chemical vapor deposition (AACVD) process, which was run at 380°C, for ten minutes. 2) The ex-situ growth of metal oxide nanowires via AACVD, ink preparation and screen-printing onto the flexible transducer. For the bending tests, an AGS-X 10 kN, Shimadzu universal testing machine was used. A compression force was exerted and the sample buckled achieving a maximum deflection. The loading speed of the crosshead displacement was high to reproduce the real situation of a sudden bending (i.e. buckling). Moreover, the curvature radii achieved (<4 mm) represent very harsh conditions, well beyond what can be expected to happen to a wearable during its normal operational life. When directly grown onto flexible substrates, NW coatings showed better adhesion than their screen-printed counterparts. However, the direct growth of Pd-loaded NWs onto silver electrodes suffered from delamination failures because Pd reacts with Ag during the AACVD process. This was solved by inkjet printing Au, instead of Ag tracks. For tungsten oxide NW sensors, the permanent increase in electrical resistance of the active layer after bending was small (about 3%). The sensitivity to hydrogen remained unchanged. The differences observed before and after the bending process, resulted mainly from cracks that developed both in the gas sensitive layer and tracks. Such cracks generate permanent changes in the electrical resistance of the active layer, and therefore, modify the baseline and sensor response. Also, during the bending tests, NWs may change orientation and their NW to NW distance, which possibly modifies the binding energy and charge transfer between the gas sensing layer and the target gas molecules, producing slight variations (positive or negative) in sensor response. However, our results show that it is possible to produce reliable, flexible chemoresistors employing scalable, additive fabrication. After 50 cycles under tensile strain, the response of the sensors remains almost unchanged, which means that the sensing properties of the material are preserved despite the bending. This demonstrates that WO3 chemoresistive sensors on flexible substrates can withstand different harsh mechanical conditions and afterwards still be usable. In particular, inkjet-printed gold electrodes demonstrated to withstand the AACVD growth process and the bending tests, which allowed us to obtain truly flexible sensors that remained functional after over 200 cycles of harsh bending.

9:15 AM EN16.01.03
Fabrication of Oxide Nano-Structured Sensor Device for Low-Molecule Gas Sensor Tohru Sugahara¹, Leila Alipour¹, Yukiko Hirose¹, Jun-ichi Nakamura², Hironobu Ono², Nobuyuki Harada² and Katsuaki Suganuma¹; ¹Osaka Univ, Japan; ²Nippon Shokubai Co. Ltd., Japan

Sensing with tenuous volatile organic compounds (VOC) gas which contain in human exhalation is important issue for next generation healthcare. In recent years, gas sensors are much attention research topics to use synthesis nano-materials and fabricate conventional device product process. In the previous study, MoO3 nanorod arrays growth on the silica substrate with fixed diameters of 10 nm but controllable length of 20 - 600 nm has been successfully synthesized by a simple solution metal organic decomposition (MOD) method. Here, we are demonstrating fabrication of some oxide nanostructure gas sensor device for VOC gas with a very simple printed coating process. The sensor devices are evaluated gas sensing properties such as sensitivity, responsivity through morphology of the oxide nanorod arrays with each EtOH, MeOH, IPA and ACE volatile gas in this study. The gas sensors show good response performance with quick response and recovery time, as well as various selectivity of each VOC gas at 573 K. The relationship between adsorption/desorption abilities and morphology of the nanorod arrays will be discussed in detail on the symposium.

9:30 AM EN16.01.04
Optimally Designing Self-Powered Hydrogen Gas Sensor Platform—Toward Outstanding Response, Durability and Humidity-Independence Hyeonghun Kim and Gun Young Jung; Gwangju Institute of Science and Technology, Korea (the Republic of)

Following a research trend for mobile sensors being miniaturized and consuming negligible power, a chemo-resistor consisting of semiconductor and metal catalyst has become a promising platform as a gas sensor. However, a requirement of the continuous power supply into the device limits the miniaturization of the entire sensing system owing to the demand of energy storage system bulkier than the main body of the sensor. Moreover, gradual deterioration of the sensor arisen from aggregation or surface contamination of the metal catalyst, and humidity-interference on the sensing performance remain as major barriers. Herein, we fabricated a self-powered H2 sensor based on Pd-decorated n-indium gallium zinc oxide (Pd-IGZO)/p-silicon (Si) photodiode operated under white light. To induce significant photocurrent change before and after an H2 exposure, a novel diode architecture consisting of finger-type electrodes interposed between the Pd-IGZO film and Si substrate were contrived. The device surface
was covered by zeolitic imidazolate framework-8 (ZIF-8) in which micropores not only enabled amplifying the photocurrent change by accumulating gas (H\textsubscript{2} or O\textsubscript{2}) molecules at the vicinity of the Pd surface but also prevent instability issues of the Pd nanoparticles mentioned above. The sensor exhibited remarkable sensing response of 1.57×10\textsuperscript{4} % at 1 % H\textsubscript{2} under white light at an irradiance of 5 mW cm\textsuperscript{-2} without external bias, a limit of detection of 35 ppm, and outstanding durability indicated as negligible change after 3 months. Besides, a self-powered humidity sensor with identical architecture to the H\textsubscript{2} sensor except the Pd was separately fabricated and exploited to correct the humidity-interference of the H\textsubscript{2} sensor, resulting in marking an accurate H\textsubscript{2} concentration even at ever-changing humidity. In conclusion, the dual sensing platform paves the way for resolving the main drawbacks of the traditional chemo-resistor.

9:45 AM
**EN16.01.05**
Highly Selective and Sensitive Distinct Flower-Like ZnO Microstructure Based Gas Sensor with Optimized CTAB Concentration for Detection of NO\textsubscript{x} at Room Temperature

Srijita Nundy\textsuperscript{1} and Tae-yil Eom\textsuperscript{2};
\textsuperscript{1}Sungkyunkwan University, Korea (the Republic of); \textsuperscript{2}Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of)

Nitrogen oxides (NO\textsubscript{x}) is considered as toxic molecule giving harmful influences not only on the human body but also on the environment [1]. A highly selective and sensitive NO\textsubscript{x} gas sensor operating at room temperature (25 °C) based on flower-like ZnO (FZO) microstructures were successfully fabricated by a CTAB-assisted hydrothermal process at 90 °C. We report the hydrothermal synthesis of ZnO microstructures with a gradual increase of CTAB concentration forming nanorods (0M), nanorods assembled structure (0.001M) to flower-like (0.005M) and studied morphology dependent gas sensing behavior to NO\textsubscript{x} gas at low temperature (25 °C). The characterizations of the as-prepared samples were done in detail by using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, photoluminescence (PL) spectroscopy and Brunauer-Emmett-Teller (BET). The gas sensing performance of sensors fabricated with as-prepared ZnO structures to various concentrations of NO\textsubscript{x}, ammonia, toluene, carbon monoxide, acetone, and ethanol, at various operation temperatures (25 to 150°C) was noted. A clear trend showing the effects of the morphology on the sensing behavior with temperature was demonstrated. The flower-like ZnO exhibited stability (up to 140 days) and excellent sensitivity with a high gas response of 29 which drops sharply with the increase of temperature and is highly selective towards 0.74 ppm of NO\textsubscript{x} at 25 °C without additional use of UV irradiation or doping materials such as Pt or Pd. The ZnO sample with 0.001M of CTAB shows a similar trend but with much lower sensitivities at low temperatures. For the sample without CTAB, the temperature behavior switches to a volcano-type one, in which the sensitivity is low at a low temperature and increases gradually with the temperature increasing. Thus, we proposed a possible reason for the evolution of overall characteristics by suggesting changing reactions between ZnO and reacting gases in various operating temperatures.

10:00 AM BREAK

10:30 AM
**EN16.01.06**
Selective Humidity Sensing at Ambient Temperature Using Individual Gallium Oxide Nanowires

Albert Romano-Rodriguez\textsuperscript{1,2}, Guillem Domenech-Gil\textsuperscript{1,2}, Irmina Peiró\textsuperscript{1}, Jan Romano-deGea\textsuperscript{3,4}, Elena López-Aymerich\textsuperscript{1,2}, Paolo Pellegrino\textsuperscript{1,2}, Christophe Serre\textsuperscript{1,2}, Mauricio Moreno\textsuperscript{1,2}, Sven Barth\textsuperscript{1}, Isabel Gràcia\textsuperscript{4} and Carles Cané\textsuperscript{4};
\textsuperscript{1}Universitat de Barcelona, Spain; \textsuperscript{2}Institute of Nanoscience and Nanotechnology (IN2UB), Spain; \textsuperscript{3}Physikalisches Institut, Goethe University, Germany; \textsuperscript{4}Institut de Microelectrònica de Barcelona-Centre Nacional de Microelectrónica, CSIC, Spain

Gallium oxide (β-Ga\textsubscript{2}O\textsubscript{3}) is a wide band gap semiconductor material used in the high power, high temperature and gas sensing fields. It is widely reported that Ga\textsubscript{2}O\textsubscript{3} in form of thin films is sensitive towards oxygen and reducing gases at temperatures above 600 °C. To decrease the working temperature and, consequently the power consumption, different modifications for its use as gas sensor have been introduced. The innovations proposed to overcome the material limitations concern surface functionalization, material doping or the increase of the surface-to-volume ratio using the nanowire (NW) morphology. In this work, single β-Ga\textsubscript{2}O\textsubscript{3} NWs grown via vapor-liquid-solid (VLS) mechanism are studied as gas sensors.

β-Ga\textsubscript{2}O\textsubscript{3} nanowires are fabricated via a metal-assisted VLS mechanism using carbothermal reduction and the synthetized NWs, after a structurally and optically characterization, are individually contacted using Focused Electron Beam Induced Deposition techniques for their use as gas sensors. The fabricated devices are tested towards
different concentrations of relevant gases in air quality monitoring, from ambient temperature and up to 200 °C, resulting in fast and reproducible responses towards water vapor at room temperature (25 °C), giving rise to a very low power consumption, in the range of nW.

Different features of the response towards moisture were studied, revealing similarities with carbon-based materials. Furthermore, the summarized response of the sensor, resembles an isotherm type V, typically from charcoal. As-grown β-Ga2O3 NWs were studied using Electron Energy Loss Spectroscopy, confirming the presence of a carbon layer at the surface of the nanowires forming a core-shell structure. The carbon layer, result of the growth process, is crucial to understand the sensing behaviour of the fabricated devices and should be considered in other gas sensing studies.

10:45 AM EN16.01.07
Synthesis and Enhanced Gas Sensing Performance of Conducting Polymer Functionalized In2O3 Flower-Like Nanostructures Hung-Chieh Lin, Wang W. Chien and Chun-Hua Chen; Department of Materials Science and Engineering, National Chiao Tung University, Taiwan

Human breath contains numerous volatile organic compounds (VOCs). Several studies have demonstrated a strong correlation between exhaled breath components and specific diseases. For instance, the acetone concentration in exhaled breath of diabetes is much higher than that of healthy people (~0.39 to 1.09 ppm). So accurate detection of specific VOCs in exhaled breath can thus provide essential information for the diagnosis of particular diseases. To develop highly sensitive gas sensors for detecting low concentrations of specific VOCs, a series of three-dimensionally assembled hierarchical oxides nanostructures with a high surface-to-volume ratio and porosity will be specially designed and synthesized as the base sensing materials. For further improving the selectivity while detecting specific VOCs, the synthesized three-dimensionally assembled hierarchical oxides nanostructures will be subsequently decorated with polymers with desired mass fractions and chemical procedures to form a novel organic-inorganic heterogeneous nanocomposite. The sensing performance, as well as the sensitivity of the fabricated organic-inorganic nanocomposite sensors, will be systematically characterized by a variety of VOCs for investigating the potential of diagnosis of diseases with the exhaled breath.

Up to date, we have successfully synthesized a series of porous three-dimensional metal oxides nanostructures having a high specific surface area by optimizing a variety of synthesis parameters. The underlying physical and chemical properties, as well as the critical parameters of spin and drop coating, are still under investigation for the subsequent decoration procedures. Also, we have designated and are modifying a unique gas sensing system which could safely, rapidly, and precisely create an atmosphere with single or multiple targeting gases for sensing characterizations. It was found that the prepared three-dimensionally assembled hierarchical oxides nanostructures, organic-inorganic heterogeneous nanocomposites exhibit similar tendency in selectivity for these target gases, and the addition of organic polymers improved the sensitivity of the three-dimensionally assembled hierarchical oxides nanostructures as our expectation.

11:00 AM EN16.01.08
Synthesis and Ozone Sensing Properties of Highly Stable Zinc Peroxide Thin Films Valmor R. Mastelaro, Maria I. Bernardi and Bruno S. de Lima; University of São Paulo, Brazil

Zinc peroxide (ZnO₂) is a semiconductor material with a wide band gap in the vicinity of 4.5 eV. Due to its oxidative capacity, this compound has been explored in various applications from medicine to photocatalysis. Its main application, however, is to be used as a precursor of zinc oxide (ZnO), a promising material for the semiconductor industry. Although several authors have reported the synthesis of ZnO₂ nanoparticles, little effort has been given to the deposition and growth of ZnO₂ thin films. Furthermore, several authors report that ZnO₂ nanoparticles decompose in ZnO and O₂ in temperatures higher than 230°C. Within this context, we present XRD, XPS, and SEM characterization of ZnO₂ thin films deposited by RF-magnetron sputtering with a reactive atmosphere of oxygen. Our results suggest that ZnO₂ thin films do not exhibit long-range order and are stable at temperatures as high as 500°C. The gas sensing properties of this material were also investigated by monitoring the electrical resistance of these films during exposure to ozone. Preliminary results show that when operating at 300°C the response (R₀₃/Rₐir) is higher than 500 for 40 ppb of O₃ with response time in the vicinity of 50 s.

11:15 AM EN16.01.09
In Situ X-Ray Spectroscopy to Identify the Tunable Surface Space Charge Layer as Origin for Oxygen
Sensing with Doped SrTiO$_3$ David N. Mueller$^1$, Michael Andrae$^1$, Misha Vorokhta$^2$, Filip Dvorak$^2$, Vladimir Matolin$^2$, Hendrik Bluhm$^3$, Regina Dittmann$^1$, Claus M. Schneider$^1$, Rainer Waser$^{1,4}$ and Felix Gunkel$^1$; 
$^1$Forschungszentrum Juelich, Germany; $^2$Charles University, Czechia; $^3$Lawrence Berkeley National Laboratory, United States; $^4$RWTH Aachen University, Germany

Many oxides of the perovskite structure not only exhibit fascinating properties originating from the bulk defect chemistry, but also show intricate behaviour at the solid/gas or solid/liquid interface leading to applications such as resistive gas sensing.$^1$

One particular example is donor doped SrTiO$_3$ (STO), which shows gas sensing behaviour similar to Taguchi type materials,$^2$ albeit at higher temperatures. This is usually explained by the formation of a space charge layer, however the underlying mechanisms and defect chemistry are yet to be fully understood: The space charge layer may either be formed by charged adsorbate molecules on the surface, or by defect chemical rearrangements at the surface in the form of Sr vacancies as observed in the bulk defect chemical model.$^3,4$

As the space charge region extends only a few nanometres form the surface into the bulk, this state is virtually impossible to quench in order to access it with conventional ultra-high vacuum spectroscopic techniques. With the advent of near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), this shortcoming is alleviated, allowing us to access the surface electronic and ionic structure of any material under conditions close to technologically relevant ones, often times requiring high temperatures and gas pressures far from UHV.

Lab- and Synchrotron-based NAP-XPS conducted on n-SrTiO$_3$ thin films under applied thermodynamic bias ($T$, $p_{O_2}$) reveals the presence of a variable surface potential and a corresponding negative surface charge.$^5$ $p_{O_2}$-dependent surface potential profiles were mapped by spectroscopic depth profiling, revealing an electron depletion layer present at the surface of n-SrTiO$_3$ thin films in both nominally reducing (ultra-high vacuum) and oxidizing conditions. Sr Core level XPS indicated Sr vacancy formation in the perovskite by SrO precipitation as the governing process, resulting in a resistance change at the surface. Depth resolved spectra furthermore revealed that a reversible conversion of the charge-neutral strontium oxide surface termination into strontium oxide clusters upon oxidation takes places, rendering the mechanism of resistive gas sensing in STO more complex as nanoscopic morphology changes also need to be considered.$^7$

References:

11:30 AM EN16.01.10
Effect of Nanostructuring of Cu$_2$O Films on Detection Properties of Chemical Gas Sensors Jan Lancok$^1$, Misha Vorokhta$^2$, Martin Vondracek$^1$, Jiri Bulir$^1$, Michal Novotny$^1$, Premysl Fitol$^1$, Jan Vlcek$^3$, Jakub Cizek$^2$ and Martin Vrnata$^3$; $^1$Institute of Physics CAS, Czechia; $^2$Faculty of Mathematics and Physics, Charles University, Czechia; $^3$University of Chemistry and Technology Prague, Czechia

Copper oxide Cu$_2$O is an important and well known p-type transition metal oxide semiconductor material which has the advantages of direct band gap 2.1 eV at 300 K, a high absorption coefficient in the visible spectral range. This material has already been employed in the fabrication of electronic devices, thanks to its low cost, non-toxicity and fairly good carrier mobility. For example Cu$_2$O has been used in thin photovoltaic devices, resistive switching, transistors, gas sensors or catalyzers.

In our work the either epitaxial Cu$_2$O (110), Cu$_2$O(100) or nanocrystalline Cu2O films has been fabricated by Pulsed Laser Deposition on MgO(100), MgO(110) and fused silica substrates, respectively. The oxygen pressure in the chamber was varied between 10$^{-5}$ Pa and 1 Pa, while the substrate temperature was held between 200 and 750 °C.
The crystalline quality and out-of-plane orientation of the films were characterised by means of X-ray diffractometers. The epitaxial single crystalline films were fabricated on MgO substrate at substrate temperature above 500 °C, contrary on amorphous substrates (fused silica, alumina) the films were polycrystalline. The surface morphology was characterised by Atomic Force Microscopy. The role of the deposition conditions on crystalline structures and following to structural properties were examined in detail by XPS, SEM and TEM. The attention was focused also on determination of defect especially cooper and oxygen vacancies by means of Electron Paramagnetic Resonance and Positron Annihilation Spectroscopy. Because we focused on utilization of the Cu2O films as gas sensors, the powerful technique near ambient pressure photoelectron spectroscopy (NAP-XPS) was carried out to investigation of surfaces composition in the presence of gasses and vapours such as ethanol, hydrogen, NO2 and acetaldehyde. The idea was to observe the reaction of species on the surface of Cu2O while exposed to atmosphere as a function of temperature as well as in-situ- resistivity measurements. The following chemical responses of the films on the gasses mentioned above were measured at the same condition as NA-XPS.

11:45 AM EN16.01.11
Toxic Methanol Detection by Handheld Filter–Sensor Device Jan van den Broek, S. Abegg, Sotiris E. Pratsinis and A. T. Güntner; ETH Zürich, Switzerland

Methanol is poisonous when ingested or inhaled, resulting in devastating consequences including organ failure, blindness and death.1 This is a potential hazard as methanol is commonly used as solvent and feedstock in laboratories and chemical plant, but increasingly also as alternative fuel.2 Also, alcoholic beverages adulterated with methanol are a threat, commonly leading to poisoning outbreaks in developing countries with hundreds of victims. While chemical sensors, such as nanostructured metal-oxides, are portable, inexpensive and can detect alcohols down to ppb concentrations,3 they cannot differentiate methanol from ethanol and other interferants.4 To improve selectivity between ethanol and methanol, sensor can be combined with filters.5 Here, we present a detector capable to selectively detect methanol in the presence of high ethanol background. It consists of a filter placed upstream of a highly sensitive, but non-specific Pd-doped SnO2 microsensor. The filter is a small packed bed (150 mg) of an adsorbent that separates analytes based on their chemical interaction. After passing the filter, analytes are detected by the sensor consisting of a highly porous network of Pd-doped SnO2 nanoparticles fabricated by flame spray pyrolysis (FSP).6 The resulting methanol detector can selectively detect methanol without interference of simultaneous ethanol and other interferants. In specific, methanol is detected within 2 min in a large concentration range from 1–1,000 ppm at ambient 50% RH. The detection of methanol is thereby independent of the interfering ethanol concentration up to 95% relative saturation (~60,000 ppm). As a proof-of-concept, the detector was tested on methanol-spiked breath samples and rum where it could reliably detect and quantify toxic methanol concentrations. It shows thus great promise for detection of toxic methanol concentrations in ambient air or in the headspace of beverages, as well as for fast screening of methanol poisoning from breath.


SESSION EN16.02: Metal Oxides for Gas Sensors II
Session Chairs: J. Daniel Prades and Kengo Shimanoe
Monday Afternoon, December 2, 2019
Sheraton, 3rd Floor, Berkeley AB

1:30 PM *EN16.02.01
Advanced Materials—Challenges and Opportunities for Gas Sensing Performances Sandrine Bernardini; Aix Marseille Univ, Université de Toulon, CNRS, France
Advanced materials have a huge potential of providing sensing data on air quality environment and individual health. The need for low-cost sensor used continuously to monitor air quality around people has sharply growing up with human activities and world industrialization. Nowadays, environment and health concerns drive the sensor market. Chromatography, optical, and spectroscopy approaches are accurate methods to obtain sensing data however they are generally expensive and non embedded equipment. Metal OXide (MOX) materials offer an alternative way to develop miniaturized resistive gas sensors with repeatable, reliable and reproducible sensing results. Since the fifties, it is well-known that the material conductivity changes with the adsorption or the desorption of a gas on a metal oxide surface. It has been proved first with Zinc Oxide (ZnO) thin layer in 1962 [1]. Then, tin oxide (SnO2) and ZnO have been demonstrated to be good gas-sensing materials for several gases such as O3, NO2, NH3, CO, and ethanol.

This talk will present the work being carried out in Microsensors and Instrumentation group in the Institute of Materials Microelectronic Nanoscience of Provence (IM2NP) at Aix-Marseille University (France). The design and the conception of the transducer is one of an important aspect. In 2013, a new design patterned in our group allows us to integrate heaters and reach low powered operation as low as 25mW [2]. Furthermore, the measurement metrology needs to be taken account. Recently, studies on the chamber design based on microfluidic simulations lead to improve our measurement reliability [3]. Concerning the sensing layer, MOX material synthesis is one of the key challenge to control the morphologies and the sensing performances. Hydrothermal and microwave hydrothermal synthesizes have been used to prepare metal oxide nanoparticles and will be presented. The deposition method plays also a major part in the sensing layer properties. Technics from solid target like Radio Frequency sputtering and from solution like spin coating or ultrasonic spray will be discuss. Repeatability, fast response and recovery times have been demonstrated. Thanks to a high surface/volume ratio, the nanostructuration for MOX like SnO2 and ZnO improves the sensing properties at temperatures around 200 or 300°C depending on the target gases. Due to the optical properties of these materials, our studies demonstrate that these temperatures are reduced to room temperature by considering sensing activity under continuous light activation [4]. However, selectivity is still challenging with MOX materials. The combination of several sensors based on different nanomaterials is one possible way to overcome this lack of selectivity. By changing the heterojunction composition and the light wavelength, the gas sensing properties have been enhanced and a selectivity have been reached. Access to toxic gaseous detection by such resistive micro-sensors and multi-sensors is promising for applications in individual environmental monitoring devices.

References

Direct Integration of Multifunctional Nanowire and Nanofiber Networks on Sensor Platforms for Selective Gas Detection David Graf1, Aida Jamil1, Albert Queraltó2, Thomas Fischer1, Isabel Gessner1 and Sanjay Mathur1;
1University of Cologne, Germany; 2Institut de Ciencia de Materials de Barcelona, Spain

The high surface-to-volume ratio as well as the typically high crystallinity and directional charge carrier transport of metal oxide NWs are beneficial for the use in chemo-resistive gas sensors. Semiconducting n-type SnO2 nanowire networks have been site-selective deposited on gas sensor platforms by chemical vapor deposition approach based on a catalyst-mediated vapor-liquid-solid (VLS) growth mechanism. Compared to classical screen-printed SnO2 sensors showed the direct integrated nanowire network superior sensing performance in terms of sensitivity and response time. The selective detection of target gas molecules in complex gaseous composition or high humidity is quite challenging. We improved the lack of selectivity toward gaseous species through surface decoration with metal oxides (VO2) and noble metals (Rh) nanoparticles by a second CVD step. For this approach, we developed tailored volatile molecular precursors based on bidentate heteroarylalkenolate and enaminonate ligands. An enhanced gas detection capability under high humidity was achieved by deploying hydrophilic zeolite microcrystals embedded in nanofiber meshes on top of the sensing material. Moreover, we fabricate ternary metal oxide (BiFeO3, LaFeO3 and Sn2Nd2O7) nanofibers meshes by electrospinning, which exhibit excellent selective and sensitive sensing characteristics. High-resolution transmission electron microscopy in conjugation with 3D tomographic analysis confirmed an interwoven network of hollow and porous (surface) LaFeO3 nanofibers. Owing to their high surface area and p-type behavior, the nanofiber meshes showed...
high chemoselectivity toward reducing toxic gases (SO2, H2S) that could be reproducibly detected at very low concentrations (< 1 ppm) well below the threshold values for occupational safety and health. In contrast, pyrochlore Sn2Nd2O7 nanofibers showed a highly selective detection towards Hydrogen (H2). The interdependence between structure, porosity and surface chemistry were evaluated in detail to achieve a high-detection performance.

2:15 PM EN16.02.03
Sputtered Metal Oxide Semiconductor n-p Heterojunctions for Volatile Organic Compound Sensing Andrea Fasoli1, Giulio Tilde2, Lisa Thornquist1, Krystelle Lionti1, Linda Sundberg1 and Luisa Bozano1; 1IBM Almaden Research Center, United States; 2Politecnico di Torino, Italy; 3San Jose State University, United States

Metal Oxide Semiconductors (MOS) have been the subject of decades of investigation directed towards integrating them in multi-sensorial electronic-nose systems1. Despite tremendous research efforts, a key limitation persisting to date is the lack of diversity in response to analytes, especially among the materials that reached the stage of commercialization. By and large represented by n-type MOS, predominantly doped SnO2, the materials comprising this limited set show high output correlation upon exposure to many gaseous species. Interestingly, it has been shown2,3 that the formation of a heterojunction between n- and p-type MOS can be leveraged to enhance and tune sensing performance. Thanks to the differentiation in surface interactions and charge transport mechanism, such materials combination gives access to a different range of gas selectivities and can mitigate the deleterious effect of humidity on sensitivity, as well as improve the sensor recovery time. It remains to be seen, however, whether highly-reproducible and cost-effective manufacturing processes can be developed to realize the untapped potential of this new class of sensing materials.

Here, we report on the fabrication and characterization of SnO2/NiO n-p heterojunctions thin films and analyze their response to Volatile Organic Compounds (VOCs) at sub-ppm concentrations. Films of varying thickness (20 – 200 nm) are deposited by conventional magnetron sputtering and subject to different annealing protocols. We show that in optimal processing conditions, the response of the films to VOCs can be greatly increased and its dependence on temperature, typically described in the context of a Diffusion-Reaction model, altered. In addition, we show that p-type NiO layers of given thickness can trigger a reversal in the response pattern of ultra-thin n-type SnO2 underlayers. The chemophysical and transport mechanisms leading to the emergence of such behavior are discussed.

Our results pave the way for the practical realization of n-p heterojunction MOS sensors of orthogonal response to VOCs compared to their n-type counterpart, thus expanding the range of functionalities of electronic noses.


2:30 PM EN16.02.04
Evaluation of Surface Responsivity of a Tin Dioxide Thin Film for the Highly Sensitive Gas Sensing Reo Kometani1, Ryotaro Ueki2, Penekwong Khennat1, Kenta Yoshihara1, Shinji Kunori2, Katsuya Ikeda2, Kazuyuki Sashida2, Kenichi Yoshida2, Ichiro Yamada2, Yoshio Mita1 and Shin’ichi Warisawa1; 1The University of Tokyo, Japan; 2Shindengen Electric Manufacturing Co., Ltd., Japan

Tin dioxide (SnO2) enables us to detect various low concentration gases for the application of environment monitoring and healthcare. Therefore, a great number of research and development has been carried out. However, relationships between surface responsivity and the other properties such as device structure and fine structure have not been completely clarified. We conducted basic researches on surface responsivity in order to understand SnO2 thin film more deeply, as well as in order to achieve the higher sensitivity. In this study, SnO2 thin film-based gas sensing devices were fabricated on SiO2/Si substrate. Length and width of SnO2 film for gas sensing were 500 μm and 100 μm, respectively. Pt catalyst was placed on SnO2 film to enhance the gas sensitivity. It was confirmed by Raman spectroscopy that the structure of the sputtered thin film was SnO2 although it contained SnO and SnO2-δ slightly. As a basic property, sensitivities for acetone gas (concentration: approx. 200 ppm - 800 ppm) and ethanol gas (concentration: approx. 10 ppm - 40 ppm) were increased with a decrease in thickness of SnO2 film. Thickness of SnO2 thin film on device were 120 nm, 200 nm and 340 nm. This indicates that the proportion occupied by the
gas sensitive region increases with decrease of thickness. Then, we carried out researches on the gas sensitive region. Considering the mechanism of gas sensing, the presence or absence of oxygen in an atmosphere around the device is important to discuss the gas response on the surface. Therefore, the relationships between the electrical property, thickness, operating temperature and atmosphere were evaluated systematically using the device with thickness of 100 nm and 700 nm under the atmosphere of pure air and N2. As a distinctive result, we found that the both devices had almost the same resistance under the N2 atmosphere, even though the thickness was different. Resistance at the operating temperature of 300 deg. C was approximately 40 kΩ. It seems that this was caused by the removal of the influence of oxygen that SnO2 surface was responding to. This is an interesting property for elucidating the depth of the sensitive region because it may imply that the sensitive region can be made to appear under N2 atmosphere. There is also a possibility that surface fine structure is different from the inner structure and this difference may be a key for the higher sensitivity. Although the fine structure and surface condition need to be clarified, fabrication of the higher sensitive devices can be expected if the sensitive region can be structured effectively. The relationships between surface responsivity, material fine structure, and device structure will be reported in detail.

2:45 PM EN16.02.05
Chemical Sensing with Amorphous Oxide Quantum Materials Yifei Sun and Shriram Ramanathan; Purdue University, United States

Chemical sensing is an active area of research with wide implications in environmental monitoring including air quality in urban areas, inside air-conditioned buildings, near natural gas pipelines and confined underground areas. Advancing the limits of detection as well as designing new mechanisms for sensor response to external stimuli is therefore of interest. In this presentation, we will report on a class of rare-earth nickelate systems as gas sensors, with specific results on hydrogen and ozone monitoring. Typical oxide semiconductor sensors such as In2O3 operate based on surface or near-surface redox processes that change their electrical resistance depending on the nature of chemical species encountered. In quantum materials such as nickelates, one can exploit instead strong electron correlations from electrode-mediated electron transfer from the chemical gas to induce change in electrical resistance or optical transmittance. The change in resistance is non-linear with electron filling due to Coulomb repulsion within the oxide lattice opening the possibility for trace gas detection. We will compare and contrast single crystal perovskite nickelates such as NdNiO3 films grown on LaAlO3 substrate versus their amorphous counterparts (deposited at room temperature on glass and polymers) with respect to both dynamics of resistance modification under dilute hydrogen or ozone exposure and the self-limited sensor response. Our initial results show > 800% change in electrical resistance in the amorphous mixed Ni oxides to hydrogen in forming gas near room temperature, while the crystalline counterparts show few orders of magnitude change in conductivity. Both materials show reversible modulation of resistance once the sensor is exposed to air and can be cycled multiple times. Finally, we will contrast the nickelates with better-studied wide gap oxide semiconductor sensors to discuss future materials challenges in this field.

3:00 PM BREAK

3:30 PM EN16.02.06
Fabrication of Pt/WO3-Coated Polydimethylsiloxane Membrane for Transparent/Flexible Hydrogen Gas Monitoring Ryo Ishihara1,2, Yuki Yamaguchi1, Kanta Tanabe1, Yoshihiro Makino1 and Keishi Nishio1; 1Tokyo University of Science, Japan; 2Juntendo University, Japan

Hydrogen gas has attracted significant attention as a promising next-generation clean energy source[1]. For sustainable hydrogen energy generation systems, safe, repeatable, and cost-effective hydrogen gas-leakage monitoring is urgently needed. In this study, transparent and flexible hydrogen gas sensor membranes that satisfy the above requirements were prepared utilizing two techniques; ultraviolet light-induced graft polymerization (UV grafting) of hydroxyethyl acrylamide (HEAAm) and platinum-catalyst-loaded tungsten trioxide (Pt/WO3) deposition using a novel sol-gel method.

Pt/WO3 thin film coated materials render promising hydrogen gas sensing[2]. Pt/WO3 particles show clear colorimetric changes from yellow to blue in response to hydrogen gas without the need for heating[3]. This color change is reversible and repeatable, enabling the detection of colorless hydrogen gas with the naked eye. In addition,
due to the complex shape of pipes and joints for hydrogen gas transportation, flexible and easy-to-attach sensors are desirable. The general coating methods of Pt/WO₃ thin film on substrates require heat treatments above 350°C for WO₃ crystallization on the solid substrates; however, such heat treatments prevent soft organic materials from being used as substrates. Still, the use of soft organic materials is preferable owing to their superior flexibility, cost effectiveness, and lightweight.

To achieve Pt/WO₃ thin film coating on soft organic materials, a novel Pt/WO₃-thin film coating protocol was developed. The present protocol using only a sol–gel method involves acid and mild heat treatments; thus, soft organic materials with acid- and mild heat-resistant-hydrophilic surfaces can be employed as substrates. In this process, the acid acts as the catalyst to enhance the sol–gel reaction. Polydimethylsiloxane (PDMS) membranes were used as the substrate for Pt/WO₃-thin film coating, because PDMS exhibits high gas permeability, high optical transparency, and cost effective in addition to the typical properties of soft organic materials. These properties are ideal for hydrogen gas-leakage monitoring. However, because the surface of bare PDMS is hydrophobic, the sol–gel method could not be applied directly. Thus, to obtain an acid- and mild heat-resistant hydrophilic surface, UV grafting of HEAAm was performed. We selected UV grafting and HEAAm because, unlike other modification techniques the technique can easily provide stable hydrophilic surfaces.

The UV light irradiation time, the reaction temperature, and monomer concentration for UV grafting of HEAAm were optimized. Stability of the obtained hydrophilic surface was confirmed by water contact angle. The presence of a Pt/WO₃ film on the HEAAm-modified PDMS surface was confirmed by X-ray diffraction analysis. The stability of the prepared WO₃ H₂O structure was demonstrated because the membrane retained 80% color response even after the heat treatment at 250°C for 30 min. The thickness of the thin film was ca. 100 nm, as determined from the cross-sectional scanning electron microscopy image. The fabricated Pt/WO₃ thin film-coated PDMS membranes were transparent, flexible, easy-to-attach and exhibited a clear and selective colorimetric change soon after exposure to 1.0 vol% hydrogen gas, which is below the concentration range for the rapid combustion of hydrogen-containing air (4–75 vol%). The membrane color returned to transparent immediately after switching back to air flow. The prepared Pt/WO₃-thin film-coated PDMS membrane is likely to play an important role in the future hydrogen economy.

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3:45 PM EN16.02.07
BTEX Gas Sensor Based on Hematite Nanocrystals—Preparation and Characterization Luis F. da Silva¹, Tomas Fiorido², Sandrine Bernardini², Ariadne C. Catto¹, João V. de Palm¹, Waldir Avansi¹, Khalifa Aguir² and Marc Bendahan²; ¹Universidade Federal de São Carlos, Brazil; ²Université Aix-Marseille, France

The development in industrial and agricultural activities, mainly in emerging economies, has resulted in an increase of toxic gases dumped into the atmosphere, such as CO, NOₓ, NH₃, O₃, and VOC’s (volatile organic compounds). Among the VOC’s, BTEX (benzene, toluene, ethylbenzene, xylene) is the most harmful gas; being used as organic solvents in the production of paints, dyes, etc. It becomes prejudicial to human health may cause some sickness, such as respiratory irritative symptoms, headaches, rashes, and fatigue. Gas sensors based on metal semiconducting oxides (MOX) have drawn the attention due to their potential for detection of various gases. Among the MOX, hematite (α-Fe₂O₃) has been investigated as resistive gas sensors, mainly, for detection of acetone, and ethanol. Based on these motivations, we present herein an investigation on the gas-sensing properties of α-Fe₂O₃ nanocrystals towards BTEX gas. The nanocrystals were synthesized by the hydrolysis of iron (II) chloride and then crystallized via hydrothermal treatment. The structural, surface and morphological properties were characterized by X-ray diffraction (XRD), X-ray absorption near-edge structure and, X-ray photoelectron spectroscopies, and high-resolution transmission electron (HR-TEM) analyses. The XRD and Fe K-edge XANES measurements indicated that pristine hematite phase was obtained, where iron ions are in octahedral coordination. In addition, XPS spectroscopy indicated the presence of Fe³⁺ ions on the sample surface. HR-TEM analyses showed that hematite crystals exhibit a rhombus-like shape with an average size of approximately 80 nm. Gas-sensing measurements
revealed that α-Fe₂O₃ nanocrystals are sensitive towards lower BTEX levels, i.e., from 3 till 400 ppb (parts-per-billion) when kept at 280°C. Additionally, the experiments showed that hematite nanocrystals presented total reversibility, good repeatability and stability, and high selectivity (towards ethanol and acetone). These findings demonstrate the potential of hematite nanocrystals as sensing material to manufacture BTEX gas sensor devices for practical applications.

4:00 PM EN16.02.08
Influence of the O₂/Ar Flow Ratio on the Gas Sensing Properties of Reactive Sputtered ZnO Thin Films
Adrian Camacho-Berrios¹, Zulmari Silva-Pedraza² and Wilfredo Otaño-Rivera²; ¹Univ of Puerto Rico-Rio Pedras, United States; ²University of Puerto Rico-Cayey, United States

Metal oxides such as zinc oxide (ZnO) are potential candidates for gas sensors for environmental monitoring. Oxygen-deficient ZnO, in particular, has attracted much attention due to the possibility to adapt their electrical response to sensing oxidative and reducing gases. The introduction of oxygen vacancies (V₀) modifies the surface by creating active sites where the molecular or atomic gas can interact with environmental gases of concern. They can be used to modify the band structure changing the electrical properties of ZnO. In the preparation of oxygen-deficient ZnO nanomaterials, it is essential to understand how the growth parameters promote the formation of V₀. Thus, this work focuses on studying the influence of plasma processing parameters on the formation of V₀ and testing oxygen-deficient ZnO thin films as gas sensors for environmental monitoring. The thin films were deposited on interdigitated transducers at room temperature by reactive magnetron sputtering at different O₂/Ar flow ratios. The influence of the flow ratio on the composition and sensing response of the thin films was examined by X-ray Photoelectron Spectroscopy and by measuring the change in electrical current in argon and hydrogen atmosphere. The results show that films prepared at low percent of oxygen in the sputtering gas exhibit the best response, at working temperatures of 200 °C and 1 % of hydrogen in Ar, with an increase in electrical current from 0.17 μA to 48.3 μA. The results will be discussed in terms of the oxygen partial pressure key role in the formation of oxygen vacancies during plasma deposition, which in turn produce excellent sensing responses.

4:15 PM EN16.02.09
Mesoporous Silica Metal Oxide Nanocomposites—An Extremely Sensitive RH Sensor
Ekta Poonia¹, Jasbir Sangwan² and Krishan Kumar¹; ¹Deenbandhu Chhotu Ram University of Science and Technology, Murthal, Haryana, India; ²Tau Devi Lal Govt. Girls College Murthal Sonipat Haryana, India

Scientific investigation for the development of extremely sensitive nanohybrid sensors and precise detection of internal climatic conditions has always remained a challenging task. It deals with template synthesis of 3D-cubic mesoporous silica with in-situ loading of metal oxides to obtain a nanocomposite material with huge number of surface active sites. The humidity sensing behavior of synthesized nanostructures divulge the high sensitivity, fast response/recovery (4.5/3.3s), negligible hysteresis and high stability to relative humidity (%RH) in the 11–98%RH range. The structural insights have been reported by analyzing the results obtained for HRTEM, FESEM, LAXRD, HAXRD, BET and FTIR absorption analysis. X-ray diffraction confirmed 3D-cubic structure of silica with Iad symmetry and existence of anatase metal oxide species and a decrease in surface area on loading of metal oxide nanoparticles is exposed via BET surface area analyzer. The present work highlights an efficient scheme in designing of high performance %RH sensors and suggested their promising applicability in futuristic humidity/gas sensing applications.

4:30 PM EN16.02.10
1D Anodic TiO₂ Nanotube Layers with Secondary Materials for Gas Sensing
Siow Woon Ng¹, Jan Prasek¹,¹, Raul Zazpe²,¹, Jan Príkryl², Hanna Sopha²,¹, Jaromír Hubalek¹,¹ and Jan M. Macák¹,²; ¹Brno University of Technology, Czechia; ²University of Pardubice, Czechia

Gas sensors are extensively used in various fields, such as medical, automotive, automation, agriculture, biogas, and mining industries for safety and environmental monitoring. This includes also the detection of toxic compounds to prevent hazardous emission and explosion along with an air quality monitoring. The increasing development of various technologies and processes signify the increase of monitoring demands for the human’s health impact.[¹,²]

1D nanostructured sensing materials have shown potential in the miniaturization of the physical size of a sensor. The high surface-to-volume ratios provide large absorption sites, fast diffusion of gas molecules. In addition, the 1D
Self-organized anodic TiO$_2$ nanotube layers have garnered considerable scientific and technological attention over the past 15 years, particularly for photo-catalysis, solar cells, hydrogen generation and biomedical uses.$^5$ The synthesis of 1D TiO$_2$ nanotube structure is carried out by conventional electrochemical anodization of a Ti sheet. This technique has matured into a well-controlled synthesis process with the flexibility to tailor the tube dimensions such as diameter and layer thickness.$^6$ On the other hand, Atomic Layer Deposition (ALD) enables a conformal and homogeneous deposition of a thin layer of various chemical compositions, with precise control of the coating thickness, according to the deposition cycles. Therefore, very thin films matching the thickness of the Debye length of a material can be deposited by ALD. The Debye length on the scale of nanometers is the key factor of the sensitivity of a semiconductor gas sensor.$^7$ The ALD was shown to conformally coat the high-aspect-ratio TiO$_2$ nanotube layers with ultrathin coatings of secondary materials$^8$ such as Al$_2$O$_3$,$^9,10$ ZnO$^{11}$ and TiO$_2$.$^{12,13}$

This presentation will focus on the coating of the nanotube layers by various secondary materials using ALD. Experimental details and some very recent sensing results based on ZnO$^{14}$ and SnO$_2$ modified TiO$_2$ nanotubes will be presented and discussed.

Reference
Using the regime of constant voltage homogeneous alloys (Fe-Ni, Fe-Co and Fe-Ni) were obtained. Pulse deposition was used for synthesis of heterogeneous layered NWs (Ni/Cu and Co/Cu) using “one-bath” technique. “Double-bath” method was used for synthesis of another layered NWs- Fe/Ni and Fe/Co. Specific features of galvanic process for processes mentioned above were investigated. Topography and crystal structure were estimated by SEM, TEM and X-ray methods. Magnetic properties were also investigated by magnetometry and MFM methods. For ALLOY NWs it was found: non-linear dependence of grooving process on time, dependence of NWs composition on deposition voltage. It was also found that ratio of elements (Fe to Co or Fe to Ni) was changed along the wires length. Effect of anomalous co-deposition of Fe was detected- it was much higher for FeNi alloys (than for FeCo NWs). The difference of NWs elemental composition from the same in electrolyte also was higher for FeNi NWs.

For LAYERED NWs deposition parameters (voltages in pulse-regime for deposition in “single-bath” regime) were determined. Element mapping (in TEM experiments) determined the concentration of elements: for example, in Ni/Cu NWs there were layers of pure Cu and Ni-based alloy (83%Ni and 17%Cu). Using of the “constant time” leads to formation of layers with variable length (due to the diffusion limitations for ions in the narrow pores). In order to obtain the NWs with regular layer length the regime of “constant charge” should be used. TEM with diffraction analysis demonstrated the polycrystalline structure of NWs. Symmetry of Ni (Fm3m), Cu (Fm3m) and oxides (Cu2O and CuO) were determined. It was shown that decrease of time of each pulse effectively leads to decreasing of layer length down to 20 nm. For shorter time the mixed structure or the “stick-shell” structures could be obtained.

Magnetic properties data for both types of NWs are given and discussed. The effect of application of external magnetic field on grooving process (acceleration of electrodeposition) and obtained NWs (texture, formation of cavities) also presented.

It is expected that layered NWs could be used as effective gas sensors.

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EN16.03.02
Facilitated Gold Standard Microbiological Safety Assessment Supported by Paper Device Rapidly Profiling Bacterial Enzymatic Phenotypes Hyeok Jung Kim1, Chanho Kwon2, Hyeon Ah Lee1 and Hyeran Noh1, 1Seoul National University of Science and Technology, Korea (the Republic of); 2Research Institute, Biomax Co., Ltd., Korea (the Republic of)

Cultural methods based on bacterial growth rates have played a key role in all spheres related to biosafety—including food industry and medical areas—as long regarded as the ‘gold standard’. Despite profitable advantages such as low cost, manifestations of biochemical traits in a specimen, and less susceptibility to food matrix effects, still are limitations associated with the requirements of facilities and expertise workforces, and specific laborious procedures such as plating and colony counting. Paper substrates have been remarked as a platform material with high efficacy, an array of applications and other beneficial features like non-powered fluid delivery, facile sensor fabrication, and biocompatibility when used as a sensing platform. Under the supportive conditions with these traits, numerous applications have been released into the microbiological field with majorly incorporating with biosensing molecules such as antibody and aptamer. Chromogenic agar substrates have been recently involved in paper-based microbiological assessments; the paper-based diagnostics with this detecting motif compensates the drawbacks of the conventional gold standard microbiological assessment, as it diminishes time spends, the number of steps and total cost for analysis.

Herewith, we present a device aiding a rapid report of specific enzymatic phenotypes in microbiological analytes. The device was devised with stratifying paper layers that each contains chemical reagents for cell lysis, oxidation, and coloration. Optimal colors charging each detection zone on the array were respectively determined with either single uses of chromogenic substrates or blended mixtures for a selective coloration. Time length for an enzymatic assay and an enrichment step were optimized for shorted total analysis bringing about enhanced its feasibility. Provided respected sensitivities of each assay, specimens at low bacterial concentrations below 10 cfu/mL were readily sensed expending time around four hours. The robust sensing capability, when situated with food matrices, was validated by real-food spiking tests. Sophisticated sensor designs and analysis of RGB channel pattern enabled an evolution toward to a multiplex reporting for predominant hazardous pathogens in a simultaneous manner.
The multiplex biosafety assessment was miniaturized based on visually reporting respective enzymatic phenotypes of bacterial analytes. Its potentials in practical uses are appreciated when considering the high applicability to the current standardized methodology for water- and foodborne pathogen testing. Furthermore, the diagnostic device can benefit particularly in dealing with an outbreak setting by the outstanding features, low-cost, ready-to-use, and feasible traits, to name but a few.

**EN16.03.03**

**Preparation of Nanostructures and Their Application as UV-Light Assisted Gas Sensors**

Ariadne C. Catto¹, Luís F. da Silva¹, Sandrine Bernardini², Khalifa Aguir² and Waldir Avansi¹; ¹Universidade Federal de São Carlos, Brazil; ²Aix Marseille Univ, Université de Toulon, CNRS, IM2NP, France

The investigation of metal oxide semiconductors (MOX) is a fundamental point in the area of physics, chemistry, and material science, in particular nanostructured compounds. Despite the potential application of MOX, the electronic effect adverse during the charge separation process reduces the efficiency of the isolate semiconductors. Thus, great efforts have been made to further improve the MOX properties, for example, the coupling of junctions between semiconductors has been a promising option to hinder the charge recombination and thus enhancing their performance. In this way, heterostructures such as NiO/ZnO, Co₃O₄/ZnO, ZnO/CuO and ZnO/SnO₂ obtained by different methodologies, have exhibited potential properties to be applied as sensing layer. The photoactivation process has been an efficient way for the operation of sensors devices at room temperature. Based on these motivations, we present herein an investigation on the UV-assisted gas-sensing properties of the ZnO, Fe₂O₃, and SnO₂ as well as their respective heterostructures applied as ozone and nitrogen dioxide sensors operating at room temperature. The samples were prepared via microwave-assisted method. The structural, surface, and morphological properties were characterized by X-ray diffraction (XRD), X-ray absorption near-edge structure and, X-ray photoelectron spectroscopies, and high-resolution transmission electron (HR-TEM) analyses. The XRD patterns indicated the presence of ZnO, α-Fe₂O₃ and SnO₂ crystalline phases, without the evidence of solid solution formation. HR-TEM analysis reinforced the incorporation of α-Fe₂O₃ and SnO₂ nanostructure onto ZnO nanorods. The gas sensing properties were investigated for several concentrations of ozone (O₃), carbon monoxide (CO), and nitrogen dioxide (NO₂) gases. The experiments showed that nanocomposites presented total reversibility, good repeatability and selectivity toward oxidant gases. Furthermore, we also observed an enhancement of the gas-sensing properties of the heterostructures when they were kept under UV-illumination, suggesting a reduction in the charge carriers recombination. These findings demonstrate the potential of as sensing material to manufacture gas sensor devices operating at room temperature.

**EN16.03.04**

**Geometric Structure Modification in Nanoweb Impacting Liquid Resistance/Repellency**

Jihye Lim¹,², JR Kim² and Juhea Kim²; ¹Delaware State University, United States; ²Korea Institute of Industrial Technology, Korea (the Republic of)

A liquid resistant/repellent surface is beneficial to improving human health and safety when people are exposed to harsh or harmful environment. The surface can protect people from a direct contact with toxic liquids or enhance the hydrophobic filters’ functionality, purifying air or water. The lotus leaf in nature repels water and is characterized by superhydrophobic and self-cleaning effects. And, the features are attributed to its hierarchical structure and wax coating on the surface. Particularly, roughness on the lotus leaf’s surface contributes to creating the liquid-vapor interface, reducing the liquid contact area to a solid surface, and this plays an important role in maximizing the liquid resistance/repellency. The surface roughness is varied in size and geometric structure and those affect its performance.

In this study, creating nano-scale roughness is considered in nanoweb by incorporating nano particles into an electrospinning process. To identify the most efficient geometric structure, a geometric model is developed by extending the Cassie-Baxter model and the newly developed model is justified through evaluating liquid resistance/repellency in nanoweb with nano-scale roughness. It is expected that the works including modeling, modifying and evaluating the nano-scale surface will contribute to developing a liquid resistant/repellent material, highly performing for sensing and controlling fine/ultrafine particle (PM 2.5) pollutants, which can cause lungs and heart diseases and threaten human life.

**EN16.03.05**
Fabrication of Nanofiber Air Filter with Self-Cleaning through Superhydrophobic Bead Coating

Hyonguk Kim1, Seong Kyung Hong2, Chan Park1, Cheol Jeong Park1, Byeongjun Lee1, Jungmin Kim1, Yeon-Do Jeong1, Geunbae Lim2 and Seong Jin Cho1; 1Chungnam National University, Korea (the Republic of); 2Pohang University of Science and Technology, Korea (the Republic of)

Recently, in air quality management has gained great attraction as PM2.5 has been shown to have a close association to causing health problems123. The Global Burden of Disease Study reported that exposure to outdoor PM2.5 was responsible for around 3.2 million premature deaths in 2010 worldwide4. Such outdoor air pollution can enter the indoor environment through ventilation and infiltration processes.

Various nanofiber filters have been developed for the removal of PM2.55,6,7. These filters exhibit high fine dust removal efficiency and relatively low air resistance. However, these filters have a problem in that their filtration performance degrades in long-term operation. To grant the previous fine dust filters with recyclability, self-cleaning effect via superhydrophobic surface can be considered, though few studies have been conducted on the application of superhydrophobicity to air filters.

In this study, polyacrylonitrile (PAN) nanofibrous membrane was fabricated on aluminum mesh and Polydimethylsiloxane/Polyvinylidene fluoride (PDMS/PVDF) microbeads were coated to make a superhydrophobic air filter. The filter exhibited high PM2.5 removal efficiency and superhydrophobicity. The filter was washed with water after a long-term filtering operation as the running water removed fine dust on the filter. The filter with the contaminants removed was tested and it was confirmed that PM2.5 removal performance was restored.

Reference

EN16.03.06
Mechanical Cleaning for Barristor-Based Gas Sensor to Achieve Sensitivity of 10^4 % for 1 ppm of NO2

Do-Hyun Park1, Young Jin Cho1, Jun-Ho Lee1, In-Chul Choi1, Stephen Hodge2 and Hyun-Jong Chung1; 1Konkuk University, Korea (the Republic of); 2University of Cambridge, United Kingdom

Impurities of graphene during fabrication process increase doping level and decrease electron mobility. To fabricate gas sensor with high sensitivity, cleaning process is essential. In this poster, we present a mechanical cleaning for barristor-based gas sensors with high quality graphene. We adopted mechanical cleaning method based on contact mode of atomic force microscopy (AFM) to remove residues. During the cleaning processes, 2D/G intensity ratio by Raman spectroscopy increased and Dirac voltage of graphene decreased. Finally, the sensibility was improved significantly.

Also, we demonstrated a barristor-based gas sensor. Barristor junctions, graphene and tungsten disulfide (WS2) junctions, were cleaned using contact-mode AFM. Then the cleaned sensor exhibits sensitivity of 10^4 % at 1 ppm of nitrogen dioxide (NO2). The sensitivity could be projected to sub ppb concentration of NO2.
We studied a facile and practical 1D PC for real-time monitoring humidity sensor with remarkable color change, sensitivity and reversibility. High refractive index polymer and four different quaternization degree of low refractive index polymers were synthesized. Multilayers polymeric 1D photonic crystal(PC) films were fabricated by alternating low/high refractive index polymer by a simple spin-coating. 1D films were prepared 5 films of similar thickness and four samples of varying thickness, and the color change and photonic stop band are observed relative humidity from 10% to 90%. Depending on the degree of quaternization of the low refractive polymer, the color change and response time which are sensitive to the relative humidity are changed. A film having a relatively low hydrophilicity can be applied as an anti-counterfeiting film, and a film having a high hydrophilicity and remarkable sensitivity, rapid response time, various color change can be applied as a humidity sensor.

**EN16.03.08**

**Polyacetylene-Like Modified Graphene Oxide Aerogel and Its Enhanced Electrical Properties for Electro-Catalytic Devices**

Enrico Greco, Jing Shang, Jiali Zhu and Tong Zhu; Peking University, China

A graphene-based or carbon-based aerogel is a three-dimensional (3D) solid material in which the carbon atoms are arranged in a sheet-like nanostructure. In this study, we report the synthesis of low-density polymer-modified aerogel monoliths by 3D macro-assemblies of graphene oxide sheets that exhibit significant internal surface areas (982 m²/g) and high electrical conductivity (~0.1 to 1 × 10² S/cm). Different types of materials were prepared to obtain a single monolithic solid starting from a suspension of single-layer graphene oxide (GO) sheets, and a polymer, made from the precursors 4-carboxybenzaldehyde and polyvinyl alcohol. These materials were used to cross-link the individual sheets by covalent bonds with polyacetylene (resulting from the transformation of polyvinyl alcohol). The obtained wet-gels were supercritically dried and then, in some cases, thermally reduced to yield graphene aerogel composites. The average densities were approaching 15-20 mg/cm³. This approach allowed for the modulation of the distance between the sheets, pore dimension, surface area, and related properties. This specific GO/Polymer ratio has suitable malleability making it a viable candidate for use in conductivity 3D printing; it also has other properties suitable for energy storage, catalysis, sensing and biosensing applications, bioelectronics, and superconductors. An electro-catalytic prototype device for environmental monitoring and remediation is under development for the municipality of Beijing in China.

**EN16.03.09**

**Ultrasensitive and Highly Stable Humidity Sensor Using Cesium Lead Halide Perovskite/Ceramic Nanocomposite Films by Aerosol Deposition Method**

Sunghoon Kim¹², Sang-Wook Kim¹ and Jong-Min Oh³;

¹Ajou University, Korea (the Republic of); ²LG Innotek, Korea (the Republic of); ³Kwangwoon University, Korea (the Republic of)

Humidity sensing devices have attracted significant attention for their numerous potential applications, such as structural health monitoring, precise control for living systems, hospital apparatus, and agricultural fields, etc. Recently, various transduction mechanisms and sensing materials for a humidity sensor have been widely studied to provide high sensitivity, fast response/recovery time, excellent linearity, and low hysteresis by reading out electrical or optical signals (e.g., capacitance, resistance, photoluminescence, and gate effect in semiconductor devices). Recently, metal halide perovskites (MHP) have received great attention in optoelectronic application fields including solar cells, down-converting materials, light-emitting diodes, and photodetectors, due to their superior optical properties. Particularly, CH₃NH₃PbI₃₋ₓClₓ and CH₃NH₃PbBr₃ have been shown by converting the moisture exposure with increasing relative humidity using photoluminescence intensity or resistance, resulting in an ultrasensitive performance. Nevertheless, major problems of halide perovskites were shown up by the dissolution or chemical reaction with water molecules in humid environments. It is inevitably weaker in their reproducibility and stability as a long-term humidity sensor. For overcoming stability and response/recovery issues by water-MHP reaction, the latest research suggested Cs₂BiAgBr₆ with outstanding stability in the ambient environment. From this research, an excellent stability below 70 RH% and superfast response/recovery time (1.78 sec/0.45 sec) was obtained, whereas the sensing performance still exhibited high attenuation above 80 RH%. Therefore, the sole use of
the MHP is recognized as a disposable sensor and is not preferable in a humidity sensing material. In order to prevail all previous shortcomings, our pilot study demonstrated a novel capacitive-type humidity sensor combining aerosol deposition (AD) process and MHP-based ceramic composite materials employed on fully room-temperature to achieve high sensing performance as well as good stability.

Herein, by keeping the room temperature during the process, we fabricated the composite films with CsPb2Br5 nanocrystals embedded in ceramic matrices for novel sensing characteristics with ultra-sensitivity, fast response/recovery time, and long-term stability. The humidity sensor exhibited the high sensitivity of 17773.5 pF/RH%, linearity of 0.9954, and hysteresis of 2.98%.

**EN16.03.10**

**Influence of Boron Contamination in Mg$_2$Si Substrate on the Device Performance of Mg$_2$Si SWIR Sensor**

Yuutarou Fuse, Ryouhei Masubuchi, Fumiya Takahashi and Haruhiko Udono; Ibaraki University, Japan

The detectors in the short wavelength infrared (SWIR: 1 - 2.5 um) light are applied to imaging and sensing such as astronomical observation, remote detection of minerals and chemical process monitoring [1]. Commercially available SWIR light detectors are used toxic substances as their constituent elements like mercury-cadmium telluride-MCT and indium-gallium-arsenide (InGaAs). The Mg$_2$Si is inexpensive and nontoxic semiconducting material consisting of abundant elements. The Mg$_2$Si has attracting attentions as a novel, mass-consumable SWIR photodetector with low environmental impact and low cost because its band gap of about 0.6 eV at room temperature corresponds to the cut-off wavelength at 2.1 um[2-4]. However, Mg$_2$Si substrates has not been sufficiently advanced and is not commercially available, so far. One of the significant problems to overcome the developing of high quality Mg$_2$Si substrate is a sticking of Mg$_2$Si crystal to common crucibles used in melt growth. The high purity Mg$_2$Si single crystals which were grown in the PG-coated graphite crucible by the vertical Bridgman (VB) method contained the small angle tilted grains [3] due to the sticking of the crystal to the crucible. In this report, we grew the Mg$_2$Si crystals in a pBN or BN crucibles and investigate the influence of contaminated boron on the device performance of Mg2Si pn-junction photodiode. The crystals grown in the pBN crucible was unstuck to the crucible and had a nearly convex crystal tail. The contamination of B was found to be about 30 ppm in the grown crystals by the GDMS analysis. In addition, increase of electron concentration was also found in the crystals grown using pBN. The value of (6.8-7.0) 10$^{16}$ [cm$^{-3}$] in the pBN-crystal is more than one order of magnitude than that of PG-crystals (3×10$^{15}$ [cm$^{-3}$]). We also investigated the I-V characteristics and photosensitivity of the Mg2Si pn-junction photodiodes. Those results will be discussed in the presentation.


**EN16.03.11**

**Effect of Band Alignment on the Photosensitivity of Mg$_2$Si-SWIR Detector**

Daisuke Niioka$^1$, Fumiya Takahashi$^1$, Misa Yoshida$^2$, Daiju Tsuya$^2$ and Haruhiko Udono$^1$; $^1$Ibaraki University, Japan; $^2$NIMS, Japan

A high sensitive and high responsive short wave infrared detector (SWIR-detector) is expected to be use in a variety of industrial and scientific applications such as environmental monitoring, remote sensing of resource, growing observation in agriculture and night vision systems in social safety. We have been developing the Mg$_2$Si photodiode (PD) [1-4] as an alternative low-cost SWIR-photodetector suited for mass-consumption compared with the commercially available MCT and InGaAs photodetectors in the SWIR region. In this paper, we investigated the spectral photosensitivity of ring-electrode type Mg$_2$Si pn-junction PDs of which the band alignment between the p-Mg$_2$Si and metal ohmic contact was varied using Au/Ti or Au/Ni electrode. The spectral photosensitivity of the PDs was measured using a conventional lock-in technique with a monochromatic incident light which passed through a 10 cm- monochromator from a silicon carbide light source. The temperature of the PDs was varied between 77K and 300K in the cryostat (Oxford, Optistat DN2). The photosensitivity of the PD with the Au/Ti/p-Mg$_2$Si electrode was increased approximately 400 % compared with that of the PD with the Au/Ti/p-Mg$_2$Si electrode due to the favorable band alignment of Au/Ni/p-Mg$_2$Si electrode, where the band off-set could not form between the p-Mg$_2$Si and Ni. The photosensitivity was raised below about 2.1 um in both Au/Ni and Au/Ti electrode type Mg$_2$Si PDs and increased with decreasing the wavelength. The maximum photosensitivity under zero bias condition in the Au/Ni electrode type PD was about 0.17 A/W at about 1.42 um. The maximum photosensitivity was increased with decreasing the temperature and reached to 0.67 A/W at 1.3 um at 100K. Decrease of cut-off wavelength due to the
band gap widening was also observed with decreasing the measurement temperature. The value of cut-off wavelength was about 1.85 um at 100K.


EN16.03.12
Fabrication of Thermoelectric Based Hydrogen Sensor Using Tellurium Nanowire with Graphene Supported Pt Catalysts for H₂ Sensing Gwang-Myeong Go, Yoseb Song, Han Kim, Hong-Baek Cho and Yong-Ho Cho; Hanyang University, Korea (the Republic of)

For decades, hydrogen has been considered the most renewable and sustainable energy source which can be alternative of fossil fuel, owing to its environmentally friendly and perfect combustion without carbon included emissions.[1, 2] Despite these advantages, it is required to ensure safety regarding the use of hydrogen gas due to its colorless, odorless properties and especially its explosive behavior in wide range of concentration (from 4% to 75%) in ambient air.[3] Therefore, most of research efforts have been focused on the development of hydrogen gas sensor with high sensitivity and fast response time to prevent unexpected risks.

Among various hydrogen gas sensor devices, thermoelectric based hydrogen sensors, which are composed of a thermoelectric layer that generates voltage due to temperature difference from exothermic reaction of hydrogen oxidation by catalyst layer, have shown a great potential as a next generation of hydrogen gas sensor, owing to low power consumption, fast response time and room temperature operability.[4, 5]

In this research, we have developed an ultra-fast thermoelectric hydrogen gas sensor composed of tellurium nanowires-based thermoelectric layer and graphene-supported Pt catalysts layer. The tellurium nanowires which is a p-type semiconductor were synthesized by solvothermal method without any additives. The thermoelectric layer was fabricated by tape casting method using tellurium nanowire paste and exhibited excellent Seebeck coefficient of 428 µV/K. Graphene supported Pt catalysts were synthesized by anchoring effect and confirmed the impact of the amount of Pt precursor. The device showed great sensing performance due to the high Seebeck coefficient of tellurium at room temperature and excellent exothermic performance of graphene-supported Pt catalysts. The device can detect with a wide range from 50 ppm to 3% of H₂ concentrations and which showed relatively fast response and recovery time at room temperature. In addition, interference of relative humidity was greatly minimized by using the graphene-supported Pt catalysts.

References

EN16.03.13
WS2: Synthesized on Porous SiO₂ Nanorods Template for Highly Sensitive NO: Sensor at Room Temperature Jun Min Suh, Ki Chang Kwon, Tae Hyung Lee, Kootak Hong, Seokhoon Choi and Ho Won Jang; Seoul National University, Korea (the Republic of)

There have been increasing demands on high-performance sensors with the development of technologies in data acquisition and processing. Especially, those for gas detection can give various helpful information about human health and life. For example, exhaled breath of human has many biomarkers for potential diseases, and indoor air monitoring can alert any harmful gaseous species before exposure to human. In order to collect gaseous information from various sources in real-time, the gas sensors should be small-sized for portability and exhibit low power consumption to be embedded on mobile devices. To date, various types of gas sensors have been developed.
including electrochemical sensors, optical sensors, mass-sensitive sensors, or chemoresistive sensors. Among them, chemoresistive gas sensors are the most suitable candidates for future commercialization into mobile devices due to their simple structure and relatively cheap fabrication processes. Previously reported chemoresistive gas sensors have widely adopted metal oxide semiconductors (MOS) like SnO₂ or WO₃, and they are actually commercialized. However, MOS gas sensors need a relatively high operating temperature over 300°C for reliable operation and this leads to inevitable high power consumption. Although some manufacturers have been optimizing off-state current and on-state current for reduced power consumption, still lower power consumption is desired for mobile application. Therefore, two-dimensional (2D) materials have been proposed as an alternative to MOS for their high surface-to-volume ratio beneficial for operation at room temperature. Among various 2D materials, transition metal dichalcogenides (TMDs) have attracted a great amount of attention due to superior mechanical properties and remarkable electronic properties. Herein, we synthesized tungsten disulfide (WS₂) on a porous SiO₂ nanorods template for highly sensitive NO₂ sensors operating at room temperature. The SiO₂ nanorods with 500 nm thickness were prepared by the glancing angle deposition method using an e-beam evaporator. The precursor solution for WS₂ was spin-coated on SiO₂ nanorods and sulfurization was conducted using a chemical vapor deposition system. Uniformly coated WS₂ on SiO₂ nanorods exhibited the gas response of 152% to 5 ppm NO₂ at room temperature with a theoretical detection limit of 13.7 ppb. This promising gas sensing properties with excellent recovery at room temperature can offer a new perspective towards the real application of TMDs-based gas sensors.

**EN16.03.14**  
**Synthesis of Bismuth Nanoflowers and Their Application for Electrochemical Sensing of Heavy Metal Ions**  
Edward Fratto, Mary Joens, Jirui Wang and Zhiyong Gu; University of Massachusetts Lowell, United States

Heavy metal ion contamination is a significant, invisible threat to public health largely presupposed as eliminated by governmental supervision. Government agencies actively survey and maintain established regulatory limits on heavy metal contamination, but only prioritized to localized hotspots in high-risk communities. The characterization techniques of heavy metal ions are typically expensive and time consuming, requiring specialized training and extended sample shipping times, with a purview restricted to public infrastructure. As residential plumbing systems corrode and contaminants leach into private water systems, independent means of oversight are becoming increasingly vital in effectively identifying and mitigating toxic exposure. In this work, a bismuth nanoflower structure has been developed as a potential nontoxic sensor material for detection of heavy metal ions. The high surface area nanostructure was synthesized via aqueous chemical reduction of bismuth chloride salt in a micellar environment of sodium dodecyl sulfate, designed for high sensitivity by consideration of the crystallization mechanism in optimization of associated parameters. The nanoflower structure was deposited onto a glassy carbon electrode and coated with a protective Nafton layer, prior to cyclic voltammetry analysis of analyte ion reactivity, achieving a lower detection limit for lead and zinc, respectively. These results indicate the viability of bismuth-based nanoflower structures for portable, accessible detection of heavy metal ions, with enhanced sensitivity.

**EN16.03.15**  
**Structural and Property Modification of Wide-Bandgap β-Ga₂O₃ and ZnO Thin Films via Laser-Assisted Room-Temperature Epitaxy for Gas Sensor Applications**  
Hiroyuki Morita¹, Tomoaki Oga¹, Takumi Matsushima¹, Nobuo Tsuchimine², Satoru Kaneko³, Akifumi Matsuda⁴ and Mamoru Yoshimoto⁴; ¹Tokyo Institute of Technology, Japan; ²TOSHIMA Manufacturing, Japan; ³Kanagawa Institute of Industrial Science and Technology, Japan

Thin-film gas sensors utilizing oxide and nitride semiconductors have attracted interests according to the materials high thermal and chemical stability as well as to their sensitivity improved by nanostructures and surface effects. Gallium oxide (Ga₂O₃) and zinc oxide (ZnO) are anticipated wide-bandgap semiconductors for gas sensing applications, which have been researched detection of reactive gases (e.g. H₂, O₂, CO, CH₄) utilizing the oxides with their conductivity modified by doping technique [1–3]. On the other hand, epitaxial thin films with high crystal orientation would contribute to gas sensing characteristics in β-Ga₂O₃ and ZnO by modifying surface chemistry and carrier mobility of crystal materials to obtain sufficient on/off ratio in the devices. The β-Ga₂O₃ and ZnO epitaxial thin films generally have been grown at high-temperature above 400°C, though reduction of epitaxy temperature advances development of refined devices according to improved surface flatness, interfacial sharpness, and compositional reproducibility [4]. The increased specific surface due to nanoparticulation would also enhance the gas detection properties. In this study, room-temperature syntheses of heteroepitaxial β-Ga₂O₃ and ZnO thin films using excimer laser processing, and the effect of structural and morphological modification of the films on physical
properties were investigated. The ZnO and precursor amorphous Ga2O3 thin films were prepared by pulsed laser deposition technique equipped with a KrF excimer laser (λ=248 nm, d=20 ns, and E~1.5 J/cm²). The films were deposited on atomically stepped α-Al2O3 (0001) substrates with NiO (111) buffer layers at room-temperature. The obtained amorphous Ga2O3 thin film were subsequently solid-phase crystallized by atmospheric excimer laser annealing (ELA) process, in which KrF excimer laser beam (not focused, E~250 mJ/cm²) was irradiated on the film at room-temperature circumstances. As a result, room-temperature formation of both β-Ga2O3 (-201) / NiO (111) / α-Al2O3 (0001) and ZnO (0001) / NiO (111) / α-Al2O3 (0001) heteroepitaxial thin films was obtained. The β-Ga2O3 (-201) and ZnO (0001) films revealed ultra-flat surface well reflecting morphology of the substrates. The gas sensing properties of the heteroepitaxial ZnO thin films were evaluated with pure H2 gas at room-temperature, in which the result revealed fast response that sheet resistivity was reduced by 30% from ~1×10⁻³ to ~7×10⁻⁴ Ωcm. In addition, the optical bandgap of the obtained β-Ga2O3 (-201) film was 4.9 eV comparable to high-temperature grown films. Structural analyses of β-Ga2O3 crystallization process by ELA, and conduction property modification of both materials would also be presented.


EN16.03.16
The Sensing of Oxygen Partial Pressure in Air Based on ZnO Nanoparticles Xin Chang and Daping Chu;
Centre for Photonic Devices and Sensors, University of Cambridge, United Kingdom

Oxygen-related defects are dominant to the properties of Zinc Oxide nanoparticles (NPs) and thus making ZnO NPs a potential candidate for oxygen sensing applications. A solution-processed and highly sensitive oxygen partial pressure sensor based on ZnO NPs thin film was fabricated and characterized. The sensor was capable of measuring the oxygen partial pressure in air from 10⁻⁵ mBar to 10³ mBar and it also featured a heat-erasing capability. In the meanwhile, it was observed that the annealing temperature has a notable effect on sensor sensitivity and the highest sensitivity was realized at 600°C. In order to explain the annealing effect and understand the fundamental physics behind it, ZnO NPs were investigated on their trap states and dielectric properties. In the end, mould-guided drying technique was introduced to pattern ZnO NPs into lines in micrometer and even nanometer scale directly from its dispersion, and an oxygen partial pressure sensor was fabricated based on the patterned ZnO NPs lines, which makes it extremely promising in miniaturized and integrated sensing applications.

EN16.03.17
Gas Sensing by Nanostructured Tin Dioxide Films Decorated with Polyoxometalates Martin Vrnata¹, Jan Vlcek¹,², Masooma Ibrahim¹, Jaroslav Otta¹,², Martin Hruska¹ and Premysl Fitl¹,²; ¹University of Chemistry and Technology, Prague, Czechia; ²Institute of Physics, Czech Academy of Sciences, Czechia; ³Karlsruhe Institute of Technology - Institute of Nanotechnology, Germany

This contribution brings connection of two impressive kinds of oxide semiconducting materials for using as enhanced sensitive material for chemical gas sensing. The first kind of material is nanostructured tin dioxide (SnO₂) in form of thin film consisting of nanowires and nanoporous structures. SnO₂ and its nanostructures are well known for years as an effective material for chemiresistive gas sensor for detection of gases with redox features (H₂, hydrocarbons, vapor of alcohols etc.). The second kind of material is transition metal oxide single molecule nanocrystal (polyoxometalate) with catalytic features. Polyoxometalates consist of large number of Mo, W, V, Ta, Nb, P. As atoms with oxygen and form lacunary (vacant) molecules with features of high chemical stability and catalytic activity. They can accommodate/incorporate transition metal ions or transition metal clusters at specific sites of the rigid structure, leading to interesting molecules with specific topologies and highly symmetric environments.

In this work we present sensor structure consists of nanostructured SnO₂ decorated with polyoxometalates. As sensor substrates we use alumina plates with interdigitating platinum electrodes (50 microns between electrodes) and platinum heater element. SnO₂ thin films are prepared by thermal CVD from tin monoxide and tin acetylacetonate source material. Different polyoxometalates are subsequently applied by using wet-techniques from water solution onto the SnO₂ nanostructures. Morphology studies are performed by electron microscopy (SEM) and chemical composition analysis is done by EDX and XPS. Sensor behavior of such structures was tested as responses
to basic analytes (H₂, alkanes, alcohols and aldehydes) in concentration of up to 100 ppm in synthetic air. Sensor results from polyoxometalates decorated sensors are compared to bare SnO₂ sensors. We demonstrate that polyoxometalates significantly improve sensitivity of presented sensor structures as well as they decrease the detection limit to ppb concentrations region.

EN16.03.18
Hydrothermally and Anodized Titanium Dioxide Nanotubes Powder (TNTP) as an Antibacterial Agent under Light and Dark Conditions for Water Microbial Purification Walaa Abbas, Mohamed Ramadan, Amged Ouf and Nageh K. Allam; The American University in Cairo, Egypt

The use of titanium dioxide nanotubes in the powder form (TNTP) has been a hot topic for the past decades in many applications. The high quality of the fabricated TNTP by various synthesis routes may meet the required threshold of performance in a plethora of fields such as drug delivery, sensors, supercapacitors, and photocatalytic applications. In this research work, the TNTP were used as an antibacterial agent for water microbial purification with different synthesis techniques of the powder form as hydrothermal and rapid breakdown anodization methods. The TNTP were characterized by SEM, X-Ray Diffraction (XRD), Raman, FTIR, and UV-Visible Spectroscopy to study the effect of the structure, surface morphology, chemical composition, crystallinity and the optical properties of them. The antibacterial activity test was carried out using a viable count method against Escherichia. coli as a model of gram-negative bacteria in the presence and absence of solar radiation. Upon UV irradiation, hydrothermally synthesized-TNTP showed higher efficiency in deactivating E. coli (~96.7%) than the anodized TNTP. Several factors play a significant role in determining the antibacterial activity of TNTP. These factors including the crystalline phase, surface hydroxyls, physicochemical properties of TiO₂ as well as the experimental conditions.

EN16.03.19
Effect of Channel Morphology and Gating Medium on Tio2 Ion-Gated Transistors Arunprabaharan Subramanian, Ben George, Irina Valitova, Sanyasi Rao Bobbara, Clara Santato, Fabio Cicoira and Jo’Elen R. Hagler; Polytechnique Montréal, Canada

Nowadays transistors are used for the production of lightweight, transparent, flexible, portable and biocompatible electronics for a variety of applications, such as flexible displays, chemical or biological sensors, wearable and textile integrated systems, medical implants and artificial skins. Metal oxide ion-gated transistors (IGTs) are attractive for chemo- and bio-sensing platforms as they operate at a low voltage (e.g. below 1 V). Metal oxides are of interest as transistor channel materials in IGTs due to chemical stability and ease of processability in the air at a lower temperature. These include oxides of tin, indium, zinc, tungsten, titanium, and iron. Indium oxide-based channel material shows superior transistor performance, but the availability of indium is limited in the earth crust, so there is a necessity to explore alternative materials. Titanium dioxide is an abundant material, whose conductivity can be strongly modulated by ion-gating and is useful as an n-type semiconducting channel material for IGTs. IGTs use ionic liquids, polymer electrolytes or aqueous saline solutions as gating media to modulate the charge carrier density in the transistor channel. In this work, we investigate the role of TiO₂ film morphology (porous versus dense films) and cation size in the gating medium ([EMIM]⁺ versus Li⁺) on the electrical characteristics of IGTs. The solution processed film yields a porous structure with a mixture of anatase and rutile phases, whereas e-beam evaporated TiO₂ yields a dense and smooth film with mostly anatase phase. Electrical characteristics of dense-film IGTs gated by large-size cation gating media are relatively unaffected by scan rates in current-voltage measurements, as the ions cannot permeate the films. However, in these same films, small-size cations can permeate the films such that reducing the scan rate increases drain current and ON/OFF ratio.

References

EN16.03.20
Detection of Volatile Organic Compounds by Freestanding Aligned Ag/QR/PMMA Texture Chi-Hung Lin¹, Ming-Chung Wu¹, Tz-Feng Lin², Shun-Hsiang Chan¹, Ting-Han Lin¹, Kai Wang¹ and Chao-Sung Lai¹; ¹Chang
Gung University, Taiwan; 2Feng Chia University, Taiwan; 3Southern University of Science and Technology, China

Volatile organic compounds (VOCs) are organic chemicals having a high vapor pressure at ordinary room temperature, and they are potentially dangerous to human health once chronically breath in. Daily exposure to VOCs has serious harmful effects including a wide range of sensory irritation and chronic diseases (e.g., nervous system impairment, asthma, or potential to cancer). On the other hand, severe injury and lethal death could occur in the gas explosion and consequent fire since the VOCs concentration gets above the lowest explosion limit in air. Monitoring of VOCs and delivering of the alarm message in the very early stage therefore becomes important for modern society, especially in chemical factory management. In order to guard our homeland and eliminate accidental factors, a gas sensor is urgent to be developed as a precaution tool. High-performance VOCs sensor should be a device with real-time detection, high sensitivity, and high reproducibility. In this study, we build a high-performance freestanding aligned Ag/CdSe-Cds/poly(methyl methacrylate) (PMMA) texture to detect VOCs. The insight of this new VOCs sensing materials is based on electrospinning techniques, ultraviolet (UV)/ozone treatments, and nano-optics. The incorporation of CdSe-Cds core-shell quantum rods (QRs) and silver nanocrystals in the PMMA nanofibers amplifies the polarization response of long rods from VOCs detection so as to increase the sensitivity of VOCs sensing materials. Further, the uniaxial aligned Ag/QR/PMMA was treated by UV-ozone etching to a certain increment of surface absorption. Metal frame substrate is employed for 15 min UV-ozone etching on double-side. The higher specific surface area was successfully made on the freestanding Ag/QR/PMMA sensing materials enabling advanced VOCs sensing efficient. The advanced UV-ozone etching on the double-side of uniaxial aligned Ag/QR/PMMA efficiently enhances the extinction changes of VOCs. The freestanding Ag/QR/PMMA sensing materials has characteristics of polarization at 90° and 270°. It amplifies extinction changes in light to a significant level for the VOCs sensitivity judgment. Moreover, when the freestanding Ag/QR/PMMA sensing materials was exposed in high concentrations (10,000 ppm) of volatile organic gases, the alcohols, esters, and the aromatic can be detected instantly. The results showed that even under a low concentration (100 ppm) n-butanol atmosphere can still be detected within one minute. The freestanding aligned Ag/QR/PMMA texture is a newly designed nanocomposite device for environmental risk monitoring. It could be accepted by the market compared to the other commercial highly sensitive VOCs sensing materials.

EN16.03.21
Highly Selective and Sensitive Ammoina Gas Sensors Using Naphthalene Diimide(NDI)-Based N-Type Organic Field-Effect Transistors Byeong M. Oh, Seung Cheol Lee, Su-Kyo Jung, Gyeong G. Jeon, Sung-Ha Park, Jong H. Kim and O-Pil Kwon; Ajou University, Korea (the Republic of)

In this presentation, we report highly selective and sensitive ammonia gas sensors using highly electron deficient naphthalene diimide (NDI)-based organic field-effect transistors (OFETs). In order to control π-electron deficiency of NDI core, we designed the NDI derivatives by introducing various electron withdrawing groups (EWGs). In contrast to conventional FET gas sensors that operate through resistive mechanism, NDI-based OFETs exhibited high responsivity by showing high current increase when exposed to NH3 gas with excellent selectivity. From the optical and electrical characterizations, we revealed that the origin of high selectivity and sensitivity were the efficient radical formation between the NDI derivative and gas molecules, and degree of radical formation, respectively. Through the morphology optimization with device engineering, we achieved outstanding responsivity up to 250% current increase and sensitivity down to sub-ppm gas concentration. We suggest that employing different types of EWGs on organic n-type semiconductors can be a potential design strategy for developing highly selective and sensitive gas sensors.

EN16.03.22
Microscale Phthalocyanine Gas Sensors Prepared by Laser-Induced Forward Transfer Jaroslav Otta1,2, Joris More-Chevalier2, Premysl Fitl1,2, Martin Vrana1 and Jan Vlcek1,2; 1University of Chemistry and Technology Prague, Czechia; 2Institute of Physics of the Czech Academy of Sciences, Czechia

The miniaturization of sensors plays a significant role in the development of wireless and complex detection systems. We suggest continuous-wave laser-induced forward transfer (CW-LIFT) combined with photolithography as a suitable manufacturing process for the creation of micro-chemiresistors. The laser deposition system consisted of a CW laser with a 405 nm operating wavelength, 50 mW power source and 4x microscope objective. A donor substrate was composed of borosilicate glass, a thin layer of sputtered gold and a layer of zinc phthalocyanine. The interface of the glass substrate and sacrificial gold layer absorbed the laser energy resulting in a local thermal
transfer of the zinc phthalocyanine from the donor substrate to a receiving substrate with golden electrodes. The absorbed laser energy was controlled by altering a laser scan speed in a range of 0.1 to 5 mm/s. At the speed that produced the best results, the transferred phthalocyanine had a spatial resolution of less than 5 µm and a very high surface-to-volume. SEM scans showed the transferred zinc phthalocyanine structure with confirmation by FTIR. The response of microchemiresistors was tested on a wide variety of gasses with the highest response above 200 to 10 ppm of nitrogen dioxide. Our results showed CW-LIFT as a suitable high-resolution deposition technique for creation of micro-chemiresistors.

EN16.03.23
High-Resolution Deposition of Phthalocyanine-Fullerene Heterojunctions by Laser-Induced Forward Transfer
Jaroslav Otta1,2, Joris More-Chevalier3, Ladislav Fekete1, Premysl Fitl1,3, Martin Vrnata1 and Jan Vlcek1,2;
1University of Chemistry and Technology Prague, Czechia; 2Institute of Physics of the Czech Academy of Sciences, Czechia; 3Institute of Physics of the Czech Academy of Sciences, Czechia
Phthalocyanine-fullerene thin films, a promising material for solar cell technology and chemical sensing, are typically formed by evaporation and PLD. However, such deposition techniques require vacuum systems and do not offer high-resolution. Here, we investigate the use of continuous wave laser-induced forward transfer (CW-LIFT) as a suitable deposition technique for the formation of zinc phthalocyanine-fullerene nanocomposites. In particular, we seek to determine the laser energy range at which nanocomposites are formed with suitable morphology and composition. The laser deposition system consisted of a CW laser with a 405 nm operating wavelength, 50 mW power source and 4x microscope objective. The laser energy was controlled by altering the laser scan speed in the range of 0.05 – 5 mm/s. A donor glass substrate/sputtered gold layer interface was used to absorb the laser energy for the local thermal transfer of thin phthalocyanine and/or fullerene films to a receiver substrate. SEM scans showed that microcrystals were formed in a wide laser scan speed range. At the speed that produced the best results, the transferred nanocomposite had a spatial resolution of less than 5 µm and a very high surface-to-volume ratio. In addition, AFM showed that the surface roughness of the donor layers was homogeneous. Collectively, our results suggest that CW-LIFT is a suitable deposition technique when operated with the appropriate laser scan speed.

EN16.03.24
Nanopatterned Structures of Molecularly Imprinted Polymer Films for the Selective Detection of Endocrine Disrupting Chemicals
Jihye Lee, Sangheon Jeon, Seon Yeong Chae and Suck Won Hong; Pusan National University, Korea (the Republic of)
Molecularly imprinted polymers (MIPs) are an intriguing class of synthetic materials capable of selectively recognizing both biological and chemical molecules for a variety of high-value applications in chemical sensors, catalysis, drug delivery, antibodies, and receptors. The concept of molecular imprinting is widely known to perform a tailored recognition process by the selective adsorption of the certain molecules often observed in natural biological systems such as enzyme catalysis or antigen-antibody interactions. In principle, the MIP technique involves the imprinting process of specific molecules in a polymer matrix by chemical synthetic approaches, which provide stable cavity configurations after the simple removal of the template molecules. Here, we report a simple one-step technique to craft a set of highly ordered MIP structures in micro- and nanoscale generated from the drying-mediated self-organization in a confined geometry where the polymer solution containing molecular templates is trapped by capillary force. MIP solutions containing a crosslinking agent, photoinitiator, and molecular templates (e.g., 2,4-D) was constrained within a roll-to-flat geometry, and the capillary held solution readily induced repetitive stick-slip motions of the contact line as the roll was slowly moved over the flat substrate. As a result, we observed highly organized MIP nanopatterns with unprecedented regularity over large areas. This self-organization of MIPs by the controlled roll-print process under UV exposure can be fully utilized to produce layered architectures with the enhanced surface area. The gravimetric quartz crystal microbalance was used to evaluate the relative selectivity of the resultant MIP sensors towards 2,4-D against 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, 4-N-ethyl-6-methylsulfanyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine, and benzoic acid. Our self-organization technique is simple and cost-effective, offering a promising route to organize molecularly imprinted polymeric materials into nanoscopic sensing devices for the selective detections of endocrine disrupting chemicals.

EN16.03.25
Steam-Aided Chemical Vapor Deposition of Metal–Organic Frameworks for Chemiresistive Sensing
Jing-Kai
Huang, Lance Li and Sean Li; University of New South Wales, Australia

Suitable on-surface film deposition methods are prerequisite to incorporating metal-organic frameworks (MOFs) into functional platforms and microdevices. Heretofore, the development mostly relies on the solvent-based procedures, typically altered from powder synthesis routes, which are obstacles to the nanofabrication process. Besides, although few vapor-phase growth approaches were presented, the proposed procedures are devious and involved with a relative high-end instrument, atomic layer deposition (ALD). Here, we report a steam-aided chemical vapor deposition (CVD) approach for directly producing ZIF-67 and associated zeolitic imidazolate frameworks (ZIFs). The introduction of solvent steam, as a mediator, thoroughly prompts ZIF crystal ripening. The introduction of solvent steam, as a mediator, thoroughly prompts ZIF crystal ripening. Also, the straightforward depositing method enables the growth of highly oriented ZIF thin films by properly adjusting the growing window. With the technique, we seek to prove that the steam-assisted CVD is a microelectronics-compatible MOF thin film synthesis route by demonstrating miniature ZIF-67 chemiresistors based on a conventional microfabricating process. The ZIF-67 chemiresistors exhibit certain response to the molecules which are equipped with the ability to form hydrogen bond and penetrate into the cages of ZIF-67. The proposed steam-assisted CVD approach not only opens new avenues to explore various MOFs preparing ways but also expedite the integration of MOF materials in microelectronics and related applications.

EN16.03.26
Optical Spectroscopy and Electrical Characterization of PEI/PAA LbL Films with Embedded Ag Nanoparticles  
Rafael C. Ferreira¹, Maria H. Gonçalves¹, Matthias Hillenkamp², Osvaldo Oliveira Jr.³, Antonio Riul¹ and Varlei Rodrigues³; ¹University of Campinas, Brazil; ²Institut Lumière Matière, France; ³University of São Paulo, Brazil

The Layer-by-Layer (LbL) technique is a versatile method to modify surfaces by spontaneous adsorption of charged molecules. This technique allows assembling highly ordered nanostructured films with specific tunable properties, which makes them suitable for various applications, including catalysis, optics, biomedicine and sensors. It has been demonstrated that both sensitivity and selectivity of sensors based on polyelectrolyte LbL films can be significantly enhanced by doping them with metal nanoparticles (NPs).¹,² The underlying mechanisms for this enhancement are, however, unclear today, notably because important parameters such as nanoparticle concentration are difficult to control in wet-chemical assembly. We propose here a different approach to sample fabrication, based on the implementation of surfactant-free silver nanoparticles in prefabricated LbL films, giving us full and independent control over all sample parameters. We can then study the influence of individual parameters like NP size, composition and concentration on optical and electric properties of the nanostructured films before implementing them in sensor prototypes. LbL films composed of polyethylenimine (PEI) and poly(acrylic acid) (PAA) in (PEI/PAA)n architecture, were grown on quartz substrates and interdigitated gold electrodes. Bare Ag NPs around 3 nm diameter, fabricated in the gas phase in a magnetron cluster source are then implanted at controlled deposition energy. The first prerequisite is to verify the correct spatial dispersion of the NPs in the polymer. This is achieved by optical spectroscopy of the localized surface plasmon resonance of Ag NPs, which allows distinguishing between isolated and coupled NPs, up to the formation of (discontinuous) metallic films. Further experiments comprise in situ impedance measurements, which were performed using an impedance meter developed in our research group. The impedance measurements allow keeping track of the hybrid material ’s electrical properties during NP deposition. Thus, we observe that Ag NP deposition causes a competition between capacitive and resistive behavior. Following the electrical ac response during continuous accumulation of metal NPs within the polymer matrix gives us crucial information, not only about the NP dispersion but also on how the electrical properties of the nanostructured film can be tuned for future implementation in electrochemical sensors.

References

Acknowledgments
The authors are grateful to FAPESP (2007/01722-9, 2017/19169-6), Capes and CNPq for financial support, Microfabrication Laboratory and Electron Microscopy Laboratory in Brazilian Nanotechnology National Laboratory (LNNano/CNPEM) for the experimental support.

EN16.03.27
Fast-Response Humidity Sensor Based on Transition Metal Dichalcogenide Nanosheets and Metal Ion
Humidity sensors have been studied for decades. Most sensing elements are either ceramic or polymeric and the sensing platform is either capacitive or resistive. Recently 2D material, in particular MoS₂, based capacitive relative humidity sensors have shown much higher sensitivity than existing relative humidity (RH) sensors based on ceramics. The other major performance characteristics of RH sensors is the range that should ideally cover the entire range of non-condensing humidity percentage and the response time. Typical range for modern sensors is now 10 – 97% and response time is larger than 1 second (typically 10s).

In order to integrate the sensors in real-life applications, such as health monitoring system, the sensing needs to exhibit sub-second response time to obtain real-time information and be able to measure an extended range of humidity with high resolution in order to detect when humidity surpasses normal operating levels but also sense human presence in proximity with the system.

In this work we have studied the application of 2D materials such as MoS₂ or WS₂ for humidity sensing. For this purpose, we have developed the sensing platform based on TMDCs/metal nanoparticles composite sensing element. Both MoS₂ and WS₂ have been identified as promising candidates for sensing application and nanoparticles of metals such as Ag, Au and Cu were added to improve the sensitivity and stability of the sensor.

Solution-exfoliated MoS₂ and WS₂ nanosheets were obtained using a probe sonicator system and nanosheets with different sizes were extracted by a vacuum filter system. Humidity sensors with different nanosheet sizes were assembled and tested against the commercial humidity sensor. The devices showed good response to RH in the range of 5 - 75% and response time below 1 s. Moreover, they show excellent stability in time.

MoS₂ nanosheets with smaller size show better humidity sensing behavior than the original MoS₂ nanosheets without filtering and centrifugation, mainly due to their higher surface-to-volume ratio. We have also observed different resistance response to humidity between the MoS₂ and WS₂. Finally, the influence of metal nanoparticles on the sensing capabilities was studied.

EN16.03.28

Transparency-Based Visual Sensor for Easy-to-Use Detection of Organic Liquids Kyeong Min Song and Yeon Sik Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

With growing demand for fast and accessible testing device for health and environment monitoring, easy-to-use visual sensors has been gaining wide attention. Especially, visual based detection system for organic liquids has been gaining interest due to increase in awareness of the negative effects of the organic liquids to the health and the environment, and is increasing in demand because use in a wide variety of applications from food inspection and fuel quality control to synthesis monitoring. Currently, the most conventional visual sensors are based on colorimetric system, which produces its signal based on color change to external stimuli. However, several challenges are present for colorimetric sensors to detect liquid-phase chemicals, and needs to meet strict requirements for the sensing medium to perform liquid sensing capabilities. Therefore, development of a new visual sensing platform for detecting target liquids is highly desired.

In order for effective detection of organic liquid based on visual sensing, we took a different approach and used transparency as the visual que for the organic liquid sensing platform. The idea is to use a light scattering polymer medium that changes its transparency in response to the presence of the organic liquid. The sensing medium was designed to produce three transparency state: transparent, semi-transparent, and opaque, according to the interaction between the organic liquid and the sensing medium. The sensing medium was fabricated by engineering the shrinkage stress relaxation between the polymer matrix and the embedded particle, which produces a porous structure with micro-sized voids embedded in hollow particles. This porous structure is essential for producing the three transparency state, which is crucial for effective differentiation of various organic liquids. The advantage of the fabricated porous sensing medium is that the structure is produced by controlling polymer dynamics rather than polymer assembly, allowing use of a wide selection of polymer and control of the thickness. An array of the transparency-switching scattering medium using different polymers is able to differentiate a wide variety of organic liquids, and even liquids with similar structures and chemical properties. Furthermore, by varying the thickness of the responsive medium, the transparency-based sensing medium is able to identify the liquid composition in ternary mixture. This work shows the effectiveness of a newly designed sensing material using transparency as a visual que for organic liquid sensing.

EN16.03.30
Optical Nano-Antennas for Short Wave Infrared Sensing of Water Vapour and Aerosols in the Atmosphere
Kritika Bhattacharya, Akshita Mishra, Priya Vinayak and Madhusudan Singh; Indian Institute of Technology Delhi, India

Earth's atmosphere is a complex and dynamic system that directly impacts, and is impacted by human activity. Levels of water vapour in air and their spatial distribution determine major weather events such as the Indian monsoon. Human activity generated aerosols (especially PM2.5) have lasting impacts on human health, and their presence is in turn affected by relative humidity through the hygroscopic growth factor. Space-based sensors such as MODIS (specifically bands 20 - 22), and VIIRS (specifically I4 and M12 bands) regularly image the Earth's atmosphere in an interesting short wave infrared range (2.5-4 μm) that contains fundamental band for water (~ 2800 nm) and absorption bands for several other atmospheric gases/pollutants - O₃ (low absorption), N₂O (significant absorption), O₂ (low absorption), CO₂ and CH₄ (significant absorption for both these greenhouse gases), CO (low absorption), etc. In this work, we have designed and fabricated a bowtie nanoantenna (400 nm arm length, apex angle = 60°, thickness = 80 nm) reflectance-based sensor exhibiting a strong response in the wavelength range 2.55-2.85 μm. An array of these nanoantennas (apex to apex gap = 100 nm) was designed using finite difference time-domain (FDTD) simulations (Lumerical, using polarized light parallel to antenna axis). A hundred fold electric field enhancement in the gap, tuned to match this wavelength range (averaged efficiency ~60%, predicted using HFSS, with a 1 kΩ source impedance), resulting in maximal absorption was predicted. To fabricate the antennas, a positive photoresist (A4 (450K)) was deposited on a cleaned (RCA) silicon substrate (University Wafers). A pre-bake step was carried out at 180°C for 20 minutes. The photoresist was patterned using electron-beam lithography (eLine Plus, Raith) with a dose of 120μC/cm² to write a layout of the antenna array (Cadence Virtuoso). A post-bake step (110°C, 30 minutes) was employed before pattern development in a methyl isobutyl ketone (MIBK): isopropanol (IPA)=1:1 developer for 60 seconds. Gold (Sigma-Aldrich, 4N pure) was then deposited on the substrate through thermal evaporation (Advanced Process Technologies) at a base pressure of 4x10⁻⁶ Torr, followed by lift-off (acetone). Scanning electron microscopy (SEM) scans of the bowtie array were found to agree with the designed periodicity of 1000 nm. Fourier Transform Infrared spectroscopy (Thermo Electron Scie) measurements in the range 2.55 μm to 2.85 μm revealed a broad minimum in reflectance at ~2.75 μm, in reasonable agreement with the simulation results, which are being refined to achieve a better match with the measurements. This nanoantenna array can be tuned to a different band by changing the geometry of the antenna, and thus provides significant flexibility when compared to narrow band detectors based on InSb and HgCdTe. Space-based light-weight sensors based on these nanoantenna arrays can potentially be used for addressing several bands of interest in short wave infrared for mapping water vapour and derived aerosol content in the air column beneath a satellite in conjunction with sensors working in visible and near infrared regimes.

SESSION EN16.04: Carbon Nanotubes, Graphene and Other Carbon-Based Materials for Gas Sensors
Session Chairs: Albert Romano-Rodriguez and Thomas Thundat
Tuesday Morning, December 3, 2019
Sheraton, 3rd Floor, Berkeley AB

8:30 AM *EN16.04.01
Countering Variability of Carbon Nanotubes in Printed Gas Sensor Jin-Woo Han, Dong-Il Moon and Meyya Meyyappan; NASA Ames Research Center, United States

Despite the early promise of high sensitivity and detection limit of carbon nanotube-based gas sensors, the practical implementation has been delayed. The primary reason is the imperfection of commercially available carbon nanotube material and the variabilities involved in the sensor fabrication procedure. A key longstanding issue has been the production of tightly controlled nanotube properties such as chirality, length and diameter. In addition, placing the nanotube in a controlled volume and orientation is another challenge. As a result, the device responses often vary from device to device and batch to batch. Therefore, a successful transition of the promise of nanotechnology into practical implementation depends on how to design a device that is tolerant to inherent material and process variations and other imperfections. Herein, we present a variation-tolerant sensor design where the sensor response is defined by a statistical value of sub-sensors array in contrast to a traditional deterministic value of a single sensor. Thanks to recent development in microfabrication or inkjet printing technology, one can easily
fabricate a few hundreds of sensors in a stamp size chip. With the printed sensor chip containing multiple sub-sensor array, the sensor response can be obtained by stochastic decision, i.e. single input and multiple output (SIMO). In this work, we present the inkjet printed SIMO gas sensor. The data processing method to remove outlier data point from signal distribution is explained and the origin of outliers is investigated. The repeatability and reproducibility of SIMO sensor is demonstrated. An analytical model to support the hypothesis is addressed.

9:00 AM EN16.04.02
Carbon Black Templated Gold Nanoparticles for Detection of a Broad Spectrum of Environmental Analytes by Surface Enhanced Raman Spectroscopy Akram Abbasi, Geoffrey D. Bothun and Arijit Bose; University of Rhode Island, United States

Surface Enhanced Raman Scattering (SERS) is a powerful tool for detection of analytes at low concentrations. To enhance the Raman signal, the analyte must be in close proximity to the substrate. This often requires customization of substrate, making it useful for the detection of only a specific subset of molecules. We have produced hybrid carbon-gold nanoparticles for the detection of a broad spectrum of molecules using Surface Enhanced Raman Scattering (SERS). Carboxyl-terminated carbon black (CB) nanoparticles were coated with the cationic polyelectrolyte poly-L-lysine (PLL), and exposed to a tetrachloroauric acid solution. Gold-carbon black (Au-PLLCB) particles were formed by the reduction of gold chloride ions that concentrate on the surfaces of the PLL-coated CB templates. The Au-PLLCB particles produced strong SERS signals for 4-nitrobenzene thiol (4-NBT) in ethanol, and for Congo red, crystal violet, and nitrate ions in water. The fractal morphology of the carbon black template and the presence of PLL promote the formation of sharp gold spikes on the surface, yielding hot spots for Raman enhancement. The underlying carbon acts as an absorbent for organic molecules, allowing analytes with poor affinity for the gold surface to concentrate in regions close enough to the particle surfaces to enable detection by SERS. The morphology and chemical nature of the underlying template make the Au-PLLCB a broadly applicable type of particle for detecting of a wide range of analytes in solution.

9:15 AM EN16.04.03
A Practical Hydrogenated Graphene Gas Sensor for CO₂ & CO Monitoring Samuel Escobar, Solimar Collazo, Alexis Lavin, Leandro Paulino, Ernesto Espada, Brad Weiner and Gerardo Morell; University of Puerto Rico at Río Piedras, United States

The development of a practical gas sensor is of great interest for the monitoring of toxic and non-toxic gases that might endanger our safety and wellbeing in different settings. Hereby we present a practical gas sensor based on hydrogenated graphene for CO₂ & CO monitoring. Hydrogenated graphene was synthesized by “non-conventional” method, directly, onto an Au-pattern insulating substrate. Hydrogenated graphene was then characterized using RAMAN spectroscopy, X-ray photoelectron spectroscopy (XPS) and X-ray Diffraction (XRD). Then, the interaction of the materials with CO₂ & CO was systematically study at different PPM to determine our sensor’s detection limits. Some preliminary research reveals that the hydrogenated graphene-based sensor is capable of sensing CO₂ at the mid ppm level, while the detection limit for CO could be as low as low-ppb.

9:30 AM EN16.04.04
Graphene-Based Environmental Sensors Sensitized by Laser-Deposited Receptor Layers Raivo Jaaniso, Artjom Berholts, Tauno Kahro, Margus Kodu, Dmitri Lanevski, Indrek Renge and Pavel Rubin; University of Tartu, Estonia

As an atomically thin electric conductor, graphene is an ideal transducer of electrical signals from a molecular receptor. Concerning small gas molecules, graphene itself is a poor receptor, supporting only physical, non-specific adsorption. Monolayer graphene functionalized with nano-layers or –clusters of metal oxides (MOX) or noble metals using pulsed laser deposition (PLD) produces a sensitive chemiresistive sensor for air pollutants. The deposition of even a sub-nanometer amount on the CVD-grown graphene increases the gas sensitivity up to 2 orders of magnitude due to the formation of effective adsorption centers. Also, the selectivity can be introduced by the selection of the deposited material. For example, a layer of ZrO₂ or similar oxide lead to high selectivity towards NO₂ or O₃ with low (<10%) cross-sensitivity to other tested gases (CO, SO₂, NH₃, H₂S), whereas V₂O₅ layer leads to a similar result for NH₃ gas. Further improvement of sensitivity and recovery rate occurs when the sensor material is exposed to UV light (< 0.2 mW/mm², 365 nm). The sensitivity level of 1%/ppb was achieved. The increase of signal amplitudes in the UV
light, compared to the conductivity change in the dark state, indicates that the adsorption is photo-chemically promoted. Potential light absorbers – graphene itself, MOX, adsorbed gas molecule – were considered to establish the most plausible photochemical mechanisms. In a different approach, CVD monolayer graphene was successfully transferred to and functionalized by PLD on microheater platforms. It will be demonstrated how the pulsed or modulated heating allows achieving further gas selectivity or significantly reduced response times. The proposed sensor materials have additional merits, such as insensitivity to air humidity and long-term (> 3 years) stability in ambient air. First principle calculations of hybrid nanomaterials consisting of single-layer graphene with MOX clusters on top of it are performed for clarifying the origin of the adsorption sites.

9:45 AM EN16.04.05
Enabling In Situ Electrochemical Sensing in Water Treatment Using Electrically Conductive Water Filtration Membranes Bezawit Getachew, David S. Bergsman and Jeffrey C. Grossman; Massachusetts Institute of Technology, United States

Population growth and urbanization has increased the vulnerability of urban water systems. To maintain the quality of water supplied in the face of increased pollution, there is a need for a more proactive monitoring of contaminants within water distribution systems. Incorporating sensing capabilities into technologies that are already part of the water treatment process, such as water filtration membranes, can help meet this need. The use of water filtration membranes as simultaneous sensors also benefits from the high surface area that is inherent in membranes and reduction in mass transfer limitations that restrict the effectiveness of traditional submerged sensors. While traditional polymeric membranes cannot be exploited for sensing, recent advances in the fabrication of electrically conductive membranes present an unexplored opportunity to incorporate in situ electrochemical sensing into membrane filtration. This study discusses the design of conductive membranes for in situ electrochemical sensing using laser induced graphitization (LIG), a facile and scalable method to form porous graphitic surface on a wide range of substrates under ambient conditions. LIG is used to fabricate conductive membranes directly from polyethersulfone (PES) and graphene oxide (GO) membranes. The conductive membrane is then used for the detection of heavy metals using anodic stripping voltammetry. The membrane acts as the working electrode in a three-electrode system while filtering water spiked with Pb²⁺ standard solution. The performance of two types of conductive membranes, namely, PES and GO derived conducive membranes, is evaluated. The effect of solution conductivity, deposition time, as well as filtration rate on the detection limit are investigated. The results of this study will introduce novel sensing architectures for monitoring contaminants within water treatment systems.

10:00 AM BREAK

10:30 AM *EN16.04.06
Suspended Carbon Nanotube FETs for NO₂ Sensing—Signal Readout and Noise Christofer Hierold¹, Peter F. Satterthwaite², Sebastian Eberle¹ and Cosmin Roman¹; ¹ETH Zurich, Switzerland; ²Stanford University, United States

We report on recent investigations of signal readout concepts and advantageous biasing conditions for suspended single walled carbon nanotube field effect transistors (SWNT FETs) as functional building blocks in ultra-low power NO₂ sensors for environmental applications [1]. Advances in fabrication processes as well as better understanding of the signal characteristics of SWNT FETs has enabled the vision of using individual tube devices directly for NO₂ gas sensors. Suspended devices, which have the potential for upscaling in an industrial process flow, and the optimization of device contact architecture by selective Pt ALD help maintaining the cleanliness of the carbon nanotubes for low hysteresis, low contact resistance and improvement of the noise performance [2],[3], as well as improvement in the cross-sensitivity to humidity. Suspended devices are also attractive for self-heated, low-power architectures [4]. We will discuss signal readout options for ultra-low power sensing with carbon nanotubes. The comparison of transient (e.g. signal rise or change) and steady-state (i.e. working point related) parameters in the presence of 1/f noise allow the conclusions that due to the Langmuir binding behavior of NO₂ on carbon nanotubes, sensing using the considered transient parameters decreases response time relative to steady-state sensing. However, noise analysis further shows that with current devices, transient sensing has a lower SNR relative to steady-state sensing [5]. With improving control over fabrication processes gas sensor functional devices operating at extremely low power can be envisioned.

Acknowledgments:
Conjugated polymers have been widely investigated in thin film devices because of their low cost, flexibility, and room-temperature operation. Recently, a variety of solution-processed polymer materials have been explored for sensing toxic gases such as nitrogen dioxide based on thin-film transistors and it is particularly relevant for health and safety in work and ambient environments when NO2 concentrations reach the 1−10 ppm range. Recent efforts have been directed towards increasing sensitivities by adjusting film thickness, tailoring device structures and judicious tailoring of conjugated polymer backbones and sensing functional groups. Nevertheless, the role of molecular designs the mechanistic principles behind the interactions between the polymers backbones and the gases is less understood. In this work, ammonia and nitrogen-dioxide responsive polymer-based organic field-effect transistors (OFETs) are fabricated from diketopyrrolopyrrole (DPP)-fluorene (F) based polymers and room-temperature detection with high sensitivity and minimal current drifts entirely from the semiconductor was achieved. Six polymers (PF1-PF6) were employed as active layers to detect NO2 gas of concentrations 0.5-30 ppm. The polymer backbones were designed by coupling DPP to fluorene containing the linear n-octyl side-chains, spiro-fluorene, thiophene and N-methyl-N-phenylnaphthalen-1-amine bridges. The proportional on-current change of OFETs using these polymers reached over 200% for the DPP-fluorene polymer with thiophene-bridges over a concentration spanning 0.5-30 ppm of nitrogen-dioxide. From cyclic voltammetry studies, we found that the introduction of thiophene into the backbone raises the highest occupied molecular orbital (HOMO) levels. This work demonstrates the capability of increasing balancing current drifts with good sensitivity by modulating redox and aggregation properties of polymer semiconductors.


Peptide based molecules have shown to interact with charged molecules, like DNA and various polar molecules. However, charge transfer through peptide thin films is not favourable. As a result, fabrication of OFET using peptide molecules are not explored. We have attempted to fabricated peptide based organic field-effect transistors combining Pentacene molecules as one of the semiconductor channel materials. In this work, we fabricated \(^{\text{A}}\text{TAA-Py-Py Pentapeptide}\) - pentacene based bilayer organic thin film transistor for volatile organic compound (VOC) vapours sensor with selectivity and enhanced sensitivity. Ultra-thin \(^{\text{A}}\text{TAA-Py-Py Pentapeptide}\) molecules of different thickness were grown using spin coating on pentacene semiconducting films. The device designs are
optimized to enhance the detection performance. We have studied the morphology of the films using atomic force microscopy (AFM) and also optical properties of the films were studied using UV-Vis spectroscopy. The gas sensing performances of different thickness devices were tested for different volatile organic compound (VOC) vapours relevant to environmental monitoring, such as, ethanol, 2 propanol and acetone at room temperature (RT). It was observed that sensitivity of OFET increased when reduced the thickness of peptide film. From literature we have seen that these VOCs are generally detected at higher temperature but it is indeed interesting to emphasize that we could able to sense those gases efficiently at RT. Additionally, the OFET based devices exhibit higher selectivity, enhanced sensitivity with comparably fast response time (~ 3sec) and recovery time (~4sec). Gas sensing results confirmed that \[^{AcTAA}_{Py-Py}\] Pentapeptide based OFETs show excellent response towards ethanol gas at room temperature.

11:30 AM
EN16.04.09
Development of Chemical Sensors Using Polymer Composite Materials for Monitoring Oil Spillage Perpetual E. Idehen: The University of Manchester, United Kingdom

Detection and control of petroleum contaminants resulting from oil spillage pollution activities to the environment remain a major challenge to both developed and developing countries. Generally, the crude oil spill discharge to the environment is regulated and one of the key parameters used for compliance monitoring is the measure of oil concentration. Environmental laws require oil companies to keep oil spill total hydrocarbons concentration at 50 mg/kg soil (50 ppm). Mostly, soil analyses for oil spills use the standard gas chromatographic methods, but these methods are expensive, require high expertise and not suitable for in-situ analysis. This study was conducted to evaluate the possibility of developing low power and inexpensive chemiresistive material based sensors for in-situ detection of hydrocarbons in soils. Contaminated soils obtained at different depths from different oil spillage sites were extracted using Soxhlet technique and analysed by gas chromatography-flame ionization detector to determine types of hydrocarbons and their concentrations, as they are required to be detected by chemiresistors. The results recorded carbon numbers ranging from C\(_8\) – C\(_{36}\) with varying concentrations up to 20125 mg/kg at different sampling sites. Composites of non-conducting polymers (Poly(methyl methacrylate) (PMMA) and Polyvinyl chloride (PVC)) and conductive filler (carbon black) were prepared to make chemiresistors. The films were dried to evaporate the solvent and the morphology of the films was characterised using scanning electron microscopy (SEM). The impact of carbon concentration and geometry on the measured resistance of the polymer composite to hydrocarbons was determined. The optimum response was found to be with 10% w/w carbon black (CB) with 90% w/w polymer. Three sets of chemiresistors CB-PMMA, CB-PVC and CB-PMMA+PVA were constructed by depositing thin films of a carbon black/polymer onto interdigitated electrodes and investigated. The CB-PMMA sensors showed much higher responses when exposed to a range of hydrocarbons with varying sensitivities compared to the other two, however, the three sensors detected diesel range hydrocarbon concentrations up to Eicosane (C\(_{20}\)) more than the existing devices [3]. The sensors responses to the EPA maximum concentration (50mg/kg soil) limits are large (resistance changes), fast (90% in less than 1s), reversible and selective, hence validating high adaptability of this method. The underlying mechanism of this high sensitivity of sensors might be due to the strength of the hydrophobic interactions between the polymer and the hydrocarbons. The findings reported here expand the potential applications for inexpensive composite thin-film chemiresistor for oil spillage monitoring.

References

11:45 AM
EN16.04.10
Engineered Bacteria for Electrochemical Pollutant Detection in Water Ariel L. Furst: Massachusetts Institute of Technology, United States

Endocrine disruptors, pollutants that interfere with the normal function of hormones in the body, are found nearly
everywhere. These compounds are components of plastics, medications, and pesticides, and many have been found in high concentrations in water sources. Endocrine disruptors have been implicated in health problems, ranging from cancer to diabetes. However, due to the chemical dissimilarity of compounds that interact with a single hormone receptor, detecting endocrine disruptors in complex solutions has remained a challenge. We have developed a novel detection strategy for estrogenic compounds that is both rapid and portable. Our platform is based on *E. coli* engineered to surface express a native estrogen receptor construct. These *E. coli* enable the detection of many dissimilar compounds with inherent signal amplification from impedance measurements due to their binding to a modified electrode. We have detected sub-ppb levels of the native hormone estradiol and ppm levels of the endocrine disruptor bisphenol A (BPA) in complex solutions. As our system reports the total estrogenic activity of a sample rather than the concentration of specific components, we can measure the activity of unknown compounds, including chemicals released from a BPA-free plastic baby bottle following microwave heating. Importantly, this approach is broadly applicable to the detection of chemically diverse compounds that bind to a single receptor.

SEASON EN16.05: Advanced Architectures for Improved Gas Sensing
Session Chairs: Jin-Woo Han and Christofer Hierold
Tuesday Afternoon, December 3, 2019
Sheraton, 3rd Floor, Berkeley AB

1:30 PM *EN16.05.01
**Scalable Miniaturized Low Power Gas Sensors** Olga Casals, Cristian Fabrega and J. Daniel Prades; University of Barcelona, Spain

Our research of the last 10 years has been focused on the implementation of new approaches to improve power consumption. In this presentation we will review our main contributions in the context of the state-of-the-art.

First, we will show how power consumption in semiconductor devices can be lowered to just a few microwatts by means of the self-heating effect occurring in nanomaterials [1]. Only a decade ago, this principle was proved with fully hand-made devices [2]. Today, it is possible to achieve comparable efficiencies with devices produced in mass scale, using widely spread micro and nanofabrication techniques.

Second, we will move to light activated chemical sensors [3], where dramatic power savings can be achieved by combining the power efficiency of light emitting diodes (LED) with aggressive miniaturization efforts. Using industry standard technologies, it is possible to offer sub-milliwatt power demands in monolithic integrated microLED devices that can be produced in large amounts. We will also show how optical activation opens the door to complementary operation approaches, based on light energy harvesting that can enable virtually zero-power devices in the near future [4].

References

2:00 PM *EN16.05.02
**Material-Based Gas Sensors Research at GE—New Design Rules, Performance Capabilities and Applications** Radislav A. Potyrailo; GE Research, United States
Modern gas-monitoring requirements for numerous demanding applications push the limits of existing detection concepts to the point where we may reach their fundamental performance limits. Thus, without violating the laws of physics, chemistry, and electronics and without crossing the border into the 21st century science fantasy, we need to develop new analytical concepts and instruments. This talk will stimulate your scientific and engineering senses by (1) posing several fundamental and practical questions on principles of gas sensing and (2) by demonstrating on how modern multidisciplinary research addresses these questions in the developments of sensors with previously unthinkable capabilities. We will discuss new sensor-design criteria that allow multi-gas detection with individual sensors and the key roles of advanced sensing materials, transducers, and data analytics to achieve desired sensor performance. These developed multi-gas sensors are attractive when selectivity advantages of classic analytical instruments are cancelled by requirements for no consumables, low power, low cost, and unobtrusive form factors. We will conclude with a perspective for future needs in fundamental and applied aspects of gas sensing and with the 2030 roadmap for ubiquitous gas monitoring.

2:30 PM EN16.05.03
Eco-Friendly Transfer Printing of Electronic Devices in Nature with Adhesive Nanostructure for Sustainable Environmental Monitoring System Seonggwang Yoo, Youngkyu Hwang and Heungcho Ko; Gwangju Institute of Science and Technology, Korea (the Republic of)

The capability of monitoring, collecting, transferring, analyzing various environmental information in nature enables hyper-connected society around the rural and urban area. Among the related device fabrication technologies, the development of membrane-type electronic devices and transfer printing onto desired surfaces is very important to provide electronic functions to the desired surfaces, which is so-called ‘Stick-&-Play’ system. The transfer printing naturally confronts the controversial issues between sufficient interfacial adhesion and environmental friendliness. For example, the use of too much glue to accommodate the surface mismatch enhances the adhesion but tends to lose the latter whereas simple laminating of a planar substrate with no chemical suffers from easy delamination. In this study, we introduce a nanotubular cilia structure underneath the substrate to allow conformal wrapping on complex surfaces. After transfer printing on the polymer substrate, the nanotubular structures undergo omnidirectional conformal wrapping by flattening motion to have a large contact area and thereby enhance the interfacial adhesion of the polymer substrate. The mechanical experiments with simulations confirm that the polymer substrate with highly deformable nanotubular structure strongly adheres to the target surfaces under harsh conditions which may occur in nature, such as wind and rain. Finally, we demonstrate successful transfer printing with a temperature sensor and thin film transistors on various surfaces including an eggshell, textile, and a stone.

2:45 PM EN16.05.04
Nanowire-Based Electronic Nose for Gas Classification Albert Romano-Rodriguez1,2, Guillem Domenech-Gil1,2, Lukas Hrachowina3, Antonio Pardo1, Michael Seifner1, Isabel Gràcia4, Carles Cané4 and Sven Barth3; 1Universitat de Barcelona, Spain; 2In2UB, Spain; 3Physikalisches Institut, Goethe University, Germany; 4Institut de Microelectrònica de Barcelona-Centre Nacional de Microelectrònica, CSIC, Spain

The current concern about toxic and harmful gases is substantiate in a great number of related health problems and in the unceasing global warming. Gas sensors systems are used to survey these gas species, avoiding dangerous situations and controlling the emitting sources. A low-cost choice that offers high sensitivity performances towards several types of gases of interest are the solid-state gas sensors, including devices based in metal oxide semiconducting nanowires, presenting remarkable performance in terms of sensitivity and response time, but lacking in selectivity. To compensate the lack of selectivity of this type of sensors to discriminate between various dangerous gases, the electronic nose configuration is used and, in this work, the use of site-selective growth and in-situ integration nanowires of different materials, is proposed. Tin oxide, tungsten oxide and germanium nanowires are grown on different membranes of a single chip surface using a chemical vapor deposition method modification to characterize them later towards carbon monoxide, nitrogen dioxide and water vapor diluted in dry synthetic air. To study the sensing behavior of the sensor arrays, with various sensing patterns arising from the differences between materials, the sensors are exposed to mixtures of the mentioned gases, mimicking real ambient scenarios. Each of the studied nanowires are sensitive to all the exposed gases, compromising the ability of the fabricated sensing systems to distinguish the composition of gas mixtures. However, the measured set of responses from the different materials was studied using the well-known principal component analysis representation that allows to
distinguish between all three studied analytes by pattern recognition. Moreover, the system is able to work under high relative humidity concentration (70 %), still maintaining the sensitivity towards nitrogen dioxide, proving the potentiality of the here-proposed approach.

3:00 PM BREAK

3:30 PM *EN16.05.05
Self-Powered Sensing Based on Triboelectric Nanogenerator and Impedance Matching Effect  
Xuhui Sun; Soochow University, China

Triboelectric nanogenerators (TENGs) based on the coupling effect of triboelectrication and electrostatic induction have been developed to be a promising strategy to harvest mechanical energy and convert them to electricity. Traditional TENG-based self-powered sensing systems have been demonstrated by measuring the triboelectric effect of the sensing materials altered by the external stimulus. However, the limitations of triboelectric sensing materials and instable outputs caused by ambient environment significantly restrict their practical applications. In this talk, I will illustrate the impedance matching effect based self-powered sensing process which can avoid the external impacts. Since a TENG is intrinsically a capacitor, while connecting with an external load, the output current from the TENG will decrease with the increment of the load resistance. By using a traditional sensor as the external load of TENGs, a self-powered sensing system can be achieved through monitoring the variation in the current or voltage signals. Several powered systems will be introduced in this talk, such as real-time ultraviolet photodetector, vehicle emission testing system, self-powered weighing/pressure system, on-line ion concentration monitor, etc. This novel self-powered sensing system is not affected by working frequency and requires no external power supply, which is favorable to improve the stability and reliability for practical application.

4:00 PM EN16.05.06
Compact, Versatile and Cost-Effective Colorimetric Gas Sensors  
J. Daniel Prades, Christian Driau, Olga Casals, Ismael Benito and Cristian Fabrega; Univ of Barcelona, Spain

We report on an inexpensive and very selective gas sensor implemented by simply combining colorimetric indicators cast on top of Scotch tape, with a commercial microchip adapted here to measure optical reflectance. This sensor can be easily reproduced (leading to quantitatively consistent results), refreshed and reconfigured to sense different target gases (CO₂, NH₃) just replacing the colorimetric tape. Colorimetric methods provide many compounds and reaction mechanisms to detect a wide variety of gaseous molecules. These techniques offer unprecedented levels of selectivity and specificity towards the target species. Regarding their readout, spectrophotometers have been traditionally the technique to measure the light absorption spectra of these indicators, but they are costly and bulky. To achieve a continuous readout and compact form factors, development focused on miniaturized systems that measure color changes at specific spectral ranges. Many different configurations have been proposed so far, but most are based on confronting a narrow-spectrum light source with a photodetector. To maximize their sensitivity, enlarging the optical path from the emitter to the detector through the indicator medium is the preferred option. Therefore, the integration of the different components is challenging. Furthermore, the efforts in miniaturization complicate refreshing the indicator substances, which are prone to degradation over time. In summary, the continuous readout of colorimetric indicators still raises a set of inconveniences.

Here, we propose an approach to colorimetric detection of gases with the following advantages: it is based on easily accessible, off-the-shelf commercial components; it is compatible with a wide range of colorimetric indicators, operating at different wavelengths; it is easily resettable/refreshable with good stability in a time frame of weeks, and offers an excellent repeatability among devices. Our gas sensor is based on the MAX30105 component. This integrated microsystem encloses a set of 3 internal LEDs (red, green and infrared), a broadband photodiode, and the corresponding control, driving, acquisition and communication modules. We use this device to excite and monitor the indicator in a reflection configuration. The sensor has a cost of less than 4$ and can be easily replicated, with excellent reproducibility. The device operates at different wavelengths and with moderate power requirements (starting from a few mW). The approach has also the advantage of being easily resettable/refreshable, as the gas sensitive color indicator layer can be easily removed and replaced by a new one. This also allows for addressing other target gases, as simple as just replacing the indicator, and reusing the readout chip. Therefore, the proposed principle offers a good trade-off between cost, simplicity, convenience, and good gas sensing performance; circumventing some of the limitations of colorimetric
Earthquakes are lethal natural disasters frequently burying people alive under collapsed buildings. Tracking entrapped humans from their unique volatile chemical signature with hand-held devices would accelerate urban search and rescue (USaR) efforts. Here, a compact and orthogonal sensor array has been designed to detect the breath- and skin-emitted metabolic tracers acetone, ammonia, isoprene, CO₂ and RH, all together serving as sign of life. It consists of three nanostructured metal-oxide sensors (Si-doped WO₃, Si-doped MoO₃ and Ti-doped ZnO), each specifically tailored at the nanoscale for highly sensitive and selective tracer detection along with commercial CO₂ and humidity sensors. When tested on humans enclosed in plethysmography chambers to simulate entrapment, this sensor array rapidly detects tracers of human presence with low parts-per-billion (ppb) level accuracy and precision, unprecedented by portable detectors but required for USaR. These results were validated by bench-top selective reagent ionization time-of-flight mass spectrometry (SRI-TOF-MS). As a result, an inexpensive nanostructured sensor array is presented that can be integrated readily into hand-held or even drone-carried detectors for first responders to rapidly screen affected terrain.


Photo-Physics of FRET and PET for Highly Sensitive Detection of Nitro-Compounds Vishal Kumar and Soumitra Satapathi; Indian Institute of Technology Roorkee, India

Förster Resonance Energy Transfer (FRET) is a powerful technique used to probe close-range molecular interactions. Physically, the FRET phenomenon manifests as a dipole-dipole interaction between closely juxtaposed fluorescent molecules (10–100 Å). For instance, after photoexcitation, a fluorophore may de-excite through direct emission with a bathochromic spectral shift. However, in the presence of a nearby acceptor, the donor non-radiatively transfers energy to the acceptor molecule, resulting in quenched donor fluorescence. With the advent of genetically encoded fluorescent molecules, this method has found widespread biological applications as a spectroscopic atomic-scale ruler, biochemical reaction kinetics and chemical sensor. [1] Our effort is to employ this FRET technique to make a prototype device for highly sensitive detection of environmental pollutants. Among the most common environmental pollutants, nitroaromatic compounds (NACs) are of particular interest because of their durability and toxicity. That’s why, sensitive and selective detection of small amounts of nitroaromatic explosives, in particular, TNP, DNT and TNT has been a key challenge due to the increasing threat of explosive-based terrorism and the need of environmental monitoring of drinking and wastewater. In addition, the excessive utilization of TNP in several other areas such as burn ointment, pesticides, glass and the leather industry resulted in environmental accumulation and is eventually contaminating the soil and aquatic systems. To date, A great number of elegant methods, including fluorimetry, gas chromatography, mass, ion-mobility and Raman spectrometry have been successfully applied for explosive detection. Among these efforts, fluorescence-quenching methods based on the mechanism of FRET show good assembly flexibility, high selectivity and sensitivity. [2] Here, we report a FRET-based sensor system for the highly selective detection of NACs, such as TNP, DNT and TNT. The sensor system is composed of a copolymer Poly[(N,N-dimethylacrylamide)-co-(Boc-Trp-EMA)] (RP) bearing tryptophan derivative in the side chain as donor and dansyl tagged copolymer P(MMA-co-Dansyl-Ala-HEMA) (DCP) as an acceptor. Initially, the inherent fluorescence of RP copolymer is quenched by non-radiative energy transfer to DCP which only happens once the two molecules are within Förster critical distance (R₀). The excellent spectral overlap (I₀= 6.08×10¹⁴ nm²M⁻¹cm⁻¹) between donors’ (RP) emission profile and acceptors’ (DCP)
absorption profile makes them an exciting and efficient FRET pair i.e. further confirmed by the high rate of energy transfer from RP to DCP i.e. 0.87 ns⁻¹ and lifetime measurement by time correlated single photon counting (TCSPC) to validate the 64% FRET efficiency. This FRET pair exhibited a specific fluorescence response to NACs such as DNT, TNT and TNP with 5.4, 2.3 and 0.4 μM LODs, respectively. The detection of NACs occurs with high sensitivity by photoluminescence quenching of FRET signal induced by photo-induced electron transfer (PET) from electron-rich FRET pair to electron-deficient NAC molecules. The estimated stern-volmer constant \( (K_{SV}) \) values for DNT, TNT and TNP are \( 6.9 \times 10^3 \), \( 7.0 \times 10^3 \) and \( 1.6 \times 10^4 \) M⁻¹, respectively. The mechanistic details of molecular interactions are established by time-resolved fluorescence, steady state fluorescence and absorption spectroscopy confirmed that the sensing process is of mixed type, i.e. both dynamic and static quenching as the lifetime of FRET system (0.73 ns) is reduced to 0.55, 0.57 and 0.61 ns DNT, TNT and TNP, respectively.

In summary, the simplicity and sensitivity of this novel FRET sensor open up the possibility of designing an optical sensor of various NACs in one single platform for designing a multimodal sensor for environmental monitoring and future field-based study.

Reference
energy transduction is still being understood, the technological potential can be truly realized if multiple interactions can be detected simultaneously. This talk will focus on both the scientific understanding as well as the technological progress in the development of micro/nanostructures for physical, chemical and biological sensing. Recent results for achieving high selectivity in chemical and biological detection using multi-physics approach will be presented.

9:00 AM EN16.06.03
Humidity Sensing Behavior of Microporous Titanosilicate and Vanadosilicate Thin Films Ramona Davoudnezhad, Duygu Kuzyaka, Ibrahim Çam and Burcu Akata; Middle East Technical University, Turkey

The growing demand for environmental control for a variety of chemical molecules has led to considerable interest in the research devoted to the development of new materials for sensor devices. Since humidity is a very common component in our environment, measurements and/or control of humidity are important not only for human comfort but also for a broad spectrum of industries and technologies. The constructive design of a good humidity sensor is a rather complicated topic, because high performance humidity sensors claim many requirements, including linear response, high sensitivity, fast response time, chemical and physical stability, wide operating humidity range and low cost.

Zeolites and zeo-type materials are known for their well-defined porous structure, moisture holding capacity and ionic conduction properties. Therefore, a study is done to investigate humidity sensing properties of microporous titanosilicate and vanadosilicate thin films. Two different zeo-type materials with different type of quantum wires in their structures (i.e.,–Ti-O-Ti-O-Ti- and –V-O-V-O-V- in the structures of ETS-10 and AM-6, respectively) were produced and the humidity sensors by using these types of films were fabricated for the first time. Developed humidity sensors are examined by impedance spectroscopy method. By this means, conductive properties of the films dependent on the relative humidity will be revealed. The results showed that stable, sensitive, and cheap resistive type humidity sensors that operate in a wide range of relative humidity can be designed by using titanosilicate ETS-10 and Vanadosilicate AM-6 films.

Acknowledgment: This study is supported by Scientific and Technological Research Council of Turkey (TUBITAK), with the project number 118M631.

9:15 AM EN16.06.04
Highly Sensitive Chemical Sensors Based on InAs Nanowires David Lynall1,2, Selvakumar V. Nair2, Igor Savelyev2, Marina Blumin2, Shiliang Wang3, Zhiming Wang1 and Harry Ruda2,2,1; 1University of Electronic Science and Technology of China, China; 2University of Toronto, Canada; 3Defence Research and Development Canada, Canada

Semiconductor nanowires have received much recent attention in the fields of chemical sensing and catalysis due to their high aspect ratio. The confinement of charge carriers to one dimension is ideal for environmental charge-based detection since no classical conducting paths exist where local perturbations at the surface are not felt by the electron gas, provided the nanowire diameter is similar to or less than the electronic screening length. Such a system is realized in InAs nanowires where the high electron mobility, low effective mass, and dielectric confinement of the electron gas leads to weakened screening and high charge sensitivity [1]. Indeed, InAs nanowires have demonstrated extraordinarily high charge sensitivity at room temperature [2], and thus present an excellent material system in which to probe and study the behaviour of molecules at their surfaces. In low-dimensional systems such as InAs nanowires, surface states play a dominant role in dictating transport properties. InAs nanowires have been shown to contain high densities (~ $10^{13}$ cm$^{-2}$) of slow surface traps originating from the native surface oxide [3]. These dynamic surface state capture and emission processes exhibit time constants on the order of seconds to several hours and dictate the time-dependent conductivity of the material in response to external stimuli [4]. Dynamic capture and emission from surface states is thus the primary mechanism determining the transport and chemical sensing behaviour.

So far, nanowire-based environmental gas sensors have relied on slow, activated processes restricting their applicability to high temperatures and macroscopic adsorbate coverages (> 1 ppm). Here, we demonstrate the ppb-level detection capabilities of InAs nanowire-based chemical sensors towards volatile organic compounds (VOCs) at room temperature. The sensors are based on globally back-gated field-effect transistors with channels consisting of parallel arrays of thousands of MBE-grown InAs nanowires transferred by a mechanical contact printing method [5]. We present a model for non-equilibrium carrier dynamics based on thermally activated capture and emission from
surface states to provide insight into the chemical sensing behaviour observed in our devices and discuss factors that can be used to tune the sensitivity and dynamic range.

References:

9:30 AM EN16.06.05
Wide-Bandgap Perovskite Indoor Photovoltaic Cells for Self-Powered Sensors Ian Mathews¹, Sai Nithin Reddy Kantareddy¹, Shijing Sun¹, Mariya Layurova¹, Janak Thapa¹, Juan Pablo Correa Baena², Rahul Bhattacharyya¹, Tonio Buonassisi¹, Sanjay Sarma¹ and Ian Marius Peters¹; ¹Massachusetts Institute of Technology, United States; ²Georgia Institute of Technology, United States

Owing to their high efficiency, bandgap tunability, and potential to be fabricated at low-cost on many different substrate types, perovskite photovoltaic cells present an exciting opportunity as power sources in many autonomous systems. In this work, we evaluate their suitability as power sources for wireless sensors located in buildings and harvesting only ambient light. Wide-bandgap 1.63 and 1.84 eV perovskite photovoltaic cells are fabricated for indoor-light harvesting with measured efficiencies of 21% and 18.5%, respectively, under low-intensity compact fluorescent lighting. We increase the Br content in our (Rb0.01Cs0.05)(MAxFA1-x)0.94Pb(BrxI1-x)3 composition to produce an 1.84 eV cell, that achieves a high open-circuit voltage of 0.95 V cell under a light intensity as low as 0.16 mW/cm². To demonstrate the application of these cells as power sources for Internet of Things (IoT) nodes, three perovskite photovoltaic cells are connected in series to create a module that produces 14.5 mW output power under 0.16 mW/cm² of compact fluorescent illumination, with an efficiency of 13.2%. We create a self-powered sensor, by using this indoor IoT power module as an external power source for a semi-passive RFID temperature sensor. The combination of perovskite indoor photovoltaic modules and backscatter radio-frequency sensors is further discussed as a route to ubiquitous sensing in buildings, given the potential of all components to be manufactured in an integrated manner on plastics.

9:45 AM EN16.06.06
Ultrasonically-Exfoliated Layer-Controlled Black Phosphorus Nanosheets as High-Performance Humidity Sensors Ying-Hao Pai, Hung-Chieh Lin and Chun-Hua Chen; Department of Materials Science and Engineering, National Chiao Tung University, Taiwan

Atomically thin black phosphorus (BP), a new family member of the two-dimensional (2D) material, has attracted considerable attention in these years due to its exceptional electrical, mechanical, and surface properties offering great potential in a variety of applications. However, synthesis, dimensional control, particularly the thickness, and even the preservation of BP remain the challenges since BP is extremely sensitive to humidity, which would lead to severe structural damage. In this work, extremely-high-energy ultrasonic exfoliation was performed not only for effectively fabricating dimension-controlled BP nanosheets (~1 nm to 250 nm and ~8 nm to 10 μm in thickness and width, respectively) but for substantially reducing the risk of overexposure to harmful organic solvents. The well-clarified BP nanosheets were then made into single-nanosheet and nanoassembled chemical sensors for evaluating their performance and stability in detecting humidity.

10:00 AM BREAK
Zinc-Adeninate Metal-Organic Framework—A Versatile Photoluminescent Sensor for Rare Earth Elements in Aqueous Systems Scott E. Crawford1, Xing Yee Gan1, Peter C.K. Lemaire1, Jill Millstone1, John P. Baltrus2 and Paul R. Ohodnicki2,3; 1University of Pittsburgh, United States; 2National Energy Technology Laboratory, United States; 3Carnegie Mellon University, United States

Rare earth elements (REEs) are critically important to numerous advanced materials, including electronics, magnets, catalysts, phosphors, and others, leading to their use in applications including catalytic converters, permanent magnet based motors, turbines, rechargeable batteries, petroleum refinement, and lighting displays, among others. The attainment of a stable supply of REEs is also a vital goal of national security policies due to their use in advanced technologies, including defense systems. Yet factors including monopolistic conditions, expensive separation of co-mined REE ores, and environmental concerns as a result of REE extraction have hindered the attainment of this goal. Consequently, significant effort has been devoted to increased REE domestic production, including the extraction of REEs from coal, coal combustion byproducts, and their associated waste streams such as acid mine drainage. Analytical techniques for rapid quantification of REE content in aqueous phases can facilitate REE recovery through rapid identification of high-value waste streams. Here, the metal-organic framework BioMOF-100 is used as a fluorescent-based sensitizer for emissive REE ion detection in water, providing rapid (<10 minute) analysis times and sensitive detection (part-per-billion detection limits) for terbium, dysprosium, samarium, europium, ytterbium, and neodymium, even in the presence of acids or secondary metals in aqueous conditions or following REE extraction into organic solvents. Taken together, the BioMOF-100 system is a promising step towards the rapid, sensitive detection of valuable REEs in real-world waste streams.

A Portable, Single-Use, Paper-Based Microbial Fuel Cell Sensor for Rapid, On-Site, Water Quality Monitoring Jonghyun Cho and Seokheun Choi; State University of New York at Binghamton, United States

Water quality monitoring is essential for providing clean and safe drinking water to the public as well as for ecological safety. Recent advances in miniaturization and microbial fuel cells (MFCs) have shown great promise for the monitoring of toxic compounds in water. In this work, we demonstrate a novel paper-based, single-use, MFC-based biosensor for rapid detection of formaldehyde in water. The MFC-based biosensor was created by combining two layers of paper for a low-cost, disposable, and simple structure. *Shewanella oneidensis* MR-1 was pre-inoculated in the anodes and was left to be air-dried at room temperature for bacterial accumulation and for long-term storage and portability. When a drop of water sample (100mL) with formaldehyde was introduced to this MFC biosensor, rapid and sensitive voltage responses were obtained over a concentration range of 0.001% to 0.02%. To compensate for any external factors and variations among different devices, the inhibition ratio of each device before and after drying were obtained and compared. The inhibition ratio increased proportionally with the formaldehyde concentration giving R² of 0.908.

Due to the recent advances in rapid urbanization, industrialization, and excessive farming, providing access to clean water has become one of the greatest challenges in the coming decades for both developing and developed countries. To maintain safe water quality, there is an urgent need for a rapid and portable sensor for on-site and real-time measurements of toxic components in water. Conventional techniques for water monitoring allow for accurate and sensitive detection of various chemicals, but they are time-consuming, costly, and require a wide range of external equipment which may not be easily portable. Recently, MFCs have shown great potential as generic biosensors for water quality monitoring. MFCs utilize microorganisms to breakdown organic substrates to produce electrical energy. When these microorganisms are exposed to toxic components, their metabolic activities can be inhibited, thus decreasing their electron transfer reactions. Therefore, the changes in the output voltage or current of an MFC can be used to qualitatively or quantitatively measure toxic components in water. The paper-based MFCs proposed here have several advantages over the traditional MFCs in that they are cost-effective, flexible, biodegradable, and easily portable. They do not require any other external equipment, such as external pumps, which make these paper-based MFCs a truly stand-alone and self-sustainable device. Additionally, pre-inoculated and air-dried bacteria on the paper anode allow for long-term storage and on-site measurements. The dried bacteria can easily resume their biological activities by rehydrating them with a drop of water sample to be tested.

Formaldehyde was chosen as a model toxin because it has distinct biological toxicity and stability with other chemicals in media. The EPA has set the threshold limit for formaldehyde to be 10 ppm (equal to 0.001% v/v). As
such, the proposed MFC-based biosensor would be suitable for the monitoring of formaldehyde in water. The MFC-based biosensor was made by combining two layers of paper: one layer for the anode and the other layer for cathode and proton exchange membrane (PEM). The PEM and the boundaries of the anode and cathode were defined by printing wax onto the papers. The functional and hydrophilic areas of anode and cathode were made conductive by injecting poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). Furthermore, the cathode was treated with Ag₂O to act as a solid electron acceptor.

11:00 AM EN16.07.03
Organic Molecule Based Chemiresistive Sensor for the Detection of Hexavalent Chromium Shweta Shekar and Praveen C. Ramamurthy; Indian Institute of Science, India

The extensive use of chromium in steel manufacturing, leather tanning, metal finishing, electroplating, and alloy manufacturing has made the element commercially important. The biologically stable and environmentally non-toxic trivalent chromium is considered to be an essential nutrient in humans as it regulates the effect of insulin in lipid and carbohydrate metabolism. The other kinetically stable form of chromium, Cr(VI) is recognized as a toxic substance. However, its thermodynamic instability results in spontaneous reduction in presence of reducing agents to the ultimate trivalent chromium ion.

In the recent years, several electroactive materials have been employed to probe Cr(VI) ion. 4-dimethylaminoazobenzene, 1-(2-(1H-imidazole-1-yl)-1-(4-methoxyphenyl)ethylidene)-2-phenyl hydrazine, 2-acetylpyridine, p-(4-Acetanilidazo)calix[4]arene, glyoxal bis(2-hydroxyanil), Aurin TCA, tributyl phosphate are some of them. Poly-L-histidine has been successfully used to detect Cr(III) and Cr(VI) by electrochemical methods. Despite the presence of the above molecular designs, the quest for an efficient, portable and miniature sensing device remains unaccomplished.

The present work reports the synthesis of a guanidine based small organic molecule which has exhibited potential to detect hexavalent chromium from contaminated water samples. The chemiresistor fabricated herein has shown selectivity towards chromium over other interfering anions such as carbonate, sulfate, phosphate, fluoride and chloride. The biguanide molecule also reveals fluorescence quenching in the presence of hexavalent chromium. The bio-mimicking nature of the organic molecule presented herein is manifested by the nature of complexation of hexavalent chromium to the guanidine derivative. The thermodynamically stable chromium-histidine complex in mammalian cell shows the use of hydroxyl and amine groups acting as active sites to co-ordinate to the chromium ion. The guanidine derivative being a small molecule requires the use of conductive fillers such as multi-walled carbon nanotubes (MWCNTs) to be used as an electroactive sensing material in the chemiresistor fabricated in this work. The chemiresistor evaluation shows repeatability, reproducibility, sensitivity, selectivity and a lower limit of detection of 1 ppm.

11:15 AM EN16.07.04
Methodologies for the Clean-up of Workplace Spills Containing Engineered Nanomaterials Viridiana L. Perez, Irene Andreu, Tony Ngo, Cameron Hodgins, Matthew Bilton, Kelly Cadieux, Michael T. Paul, Tania Hidalgo Castillo, Clifton Bright Davies and Byron D. Gates; Simon Fraser University, Canada

Nanomaterials occur as a result of natural events such as forest fires, ocean spray, volcanic activity, and dust storms. Engineered nanomaterials were created to exploit their enhanced properties. They have found a myriad of applications as components of electronic devices, sensors, commodity chemicals, therapeutics and even food packaging. Their increased use on consumer products has raised health and safety concerns. However, studies on the short and long term of nanomaterials toxicity are limited due to the large variety of nanomaterials prepared and commercialized. Furthermore, their physicochemical properties have shown to largely influence their interactions with living organisms, their toxicity, accumulation and elimination pathways. The large variety of existent nanomaterials turns the investigation of their specific adverse health effects into an insurmountable task. Thus, unintentional exposure to nanomaterials is a concern for workers involved in the manufacturing and handling of nanomaterials.

The development of methodologies to protect workers health is now a necessity. Our work has focused on the development of analytical methodologies to assess the presence of engineered nanomaterials on workplace surfaces. Methodologies for detection using X-ray fluorescence spectroscopy and inductively coupled plasma mass spectrometry were used to detect traces of nanomaterials on laboratory countertops. The results of our research are intended to inform and enable scientist to continue innovating in the field of nanomaterials in a safe manner. We have shown that protecting workers from unintentional exposure can be achieved by adopting simple modifications.
Aerosols consist of two systems, solid and particles which are suspended in gas. These days, there are many harmful aerosols, which badly affect to human health such as yellow dust, air pollution, bioaerosol like a fungus, even fine particle which can deposit human’s lung. These aerosol particles have a many toxic factors which can affect to the health of humans, animal even plants. Especially, in urban areas, many pollution factors that from automobile and buildings are exist almost everywhere. Because of this, monitoring and analysis of these harmful aerosols are very important for human health in urban areas. In order to measure and monitored these aerosols, we were researching about aerosol sampling technology and analysis using by simulation. There are many aerosol sampling methods such as particle measurement using optical principle which is using optical aerodynamic to measure the relaxation time, also, scattering size of particle about light sources and measurement of scattering and absorption. In this study, Autodesk Inventor and FLUENT 16.1 will use for the design of the new aerosol sampler. The basic design of designing an aerosol sampling device is cyclone sampler which generates a cyclone inside the tube. The basic theory of this aerosol sampling device is Stokes number and Reynolds number. Using these theories, we can derive an equation which is can get a proper size of the aerosol sampling device. Also, we will use a FLUENT 16.1 program for numerical analysis and simulation for designing an aerosol sampling device as a proper size. In the experiment, we can measure the particle use a Raman spectroscopy, Ion trap mass spectroscopy, Induced Fluorescence. In this study, we will collect aerosols on the outside using by existing aerosol sampling device before the development of aerosol monitoring device, and we are planning to use an aerosol sampling device for aerosol collection, which is such as ELPI (Electrode Low Pressure Impactor), CPC (Condensation Particle Counter) and SMPS (Scanning Mobility Particle Sizer). These aerosol sampling devices are not only collecting various aerosol, but also, can evaluate a collected aerosol in real time. Therefore, we expect to collect various aerosol samples in outside conditions like an environmental condition. After this process, we expect we can get an aerosol number concentration, aerosol particle size, aerosol flow rate and so on that can use for evaluating which aerosol suspended in the environmental air. Also, it can classify sampled aerosol which aerosol is more harmful, and more badly affects to human health. Furthermore, it can not only classify sampled aerosol, but also can conjecture which aerosol is coming from which factor such as automobile or building and so on. In our plan, we expect can show the sampled aerosol in outside condition and results of classified various sampled aerosols. Through these experiments we can show various results of aerosol sampling and monitoring data on the environmental condition. In addition, according these results we will development of aerosol monitoring systems for monitoring air quality of urban areas.
The tutorial will provide an introduction to the challenges faced by nuclear materials, whether they be within or outside the core. It will discuss the materials choices that have been made historically, the impacts they endure during operation, and how these impacts have themselves impacted material design. It will cover topics such as radiation damage, property changes during operation and future materials options.

1:30 PM
**Material Choices within the Reactor Core, Radiation Damage and Its Impacts** Karl Whittle; University of Liverpool

This will cover the historical reasoning behind the choices, the changes induced by radiation damage, and how they impact the operational usage.

2:15 PM
**Characterization and Visualization of Materials from Within the Core** Karl Whittle; University of Liverpool

This will look at how nuclear materials can be characterized, what can be determined, and what the new techniques are capable of.

3:00 PM BREAK

3:30 PM
**Historical Fuel Development, Performance, and Selection** Maria Okuniewski; Purdue University

In core challenges and interdependencies associated with fuel performance.

4:15 PM
**New Materials and Their Potential for New Technologies** Karl Whittle; University of Liverpool

Taking on board the first hour, linking it with new manufacturing methods and discussing future reactor technologies and their requirements.

**SYMPOSIUM EN17**

Structure–Property Processing Performance Relationships in Materials for Nuclear Technologies
December 2 - December 5, 2019

Symposium Organizers
Chaitanya Deo, Georgia Institute of Technology
Maik Lang, University of Tennessee
Simon Middleburgh, Bangor University
Maria Okuniewski, Purdue University

* Invited Paper
8:30 AM *EN17.01.01
**Fission Products in Thoria** Robin W. Grimes¹, Navaratnarajah Kunganathan¹, Partha S. Ghosh² and Ashok K. Arya²; ¹Imperial College London, United Kingdom; ²Bhabha Atomic Research Centre, India

While fuels based on thoria have been considered as alternatives for urania for decades, there is considerably less data concerning the accommodation of fission products at the atomic scale. Here atomic scale computer simulation based on density functional theory is used to predict the energies and accommodation sites for a range of fission products and He in stoichiometric ThO₂ and hypo-stoichiometric ThO₂ₓ.

Nine sites were considered including point defects and vacancy clusters with multiple species. Neutral and all possible defect charge states up to full formal charge were investigated. For Xe and Kr, in ThO₂ₓ, the most favourable solution equilibrium site is a neutral tri-vacancy while in ThO₂ it is the di-vacancy. The most favourable solution site for I and Br is the single positively charged oxygen vacancy in ThO₂ₓ while in ThO₂, I demonstrates the same solubility in all clusters. Rb, Cs, Sr, Ba, Y and Zr are accommodated at the thorium vacancy but the charge state of the vacancy is important. Finally for He, a relationship is generated that describes the incorporation energy of the xᵗʰ He atom, Eₓ (n, m), into a cluster consisting of n thorium vacancies and m oxygen vacancies.

9:00 AM *EN17.01.02
**Radiation Effects in ThO₂** Tiankai Yao¹, Vinay S. Chauhan², Maniesha Kaur Salaken Singh³, Zilong Hua¹, Marat Khafizov², Anter El-Azab³, Matthew Mann⁴, Thierry Wiss⁵, Jian Gan¹, David Hurley¹ and Lingfeng He¹; ¹Idaho National Laboratory, United States; ²The Ohio State University, United States; ³Purdue University, United States; ⁴Air Force Research Laboratory, United States; ⁵European Commission Joint Research Centre, Germany

Oxide nuclear fuels have been widely used in light water reactors. The thermal conductivity of nuclear fuels is closely related to energy conversion efficiency as well as reactor safety margins. Understanding the mechanisms that cause the degradation of thermal conductivity in a high radiation environment is important for the design and development of new high-burnup fuels. For oxide nuclear fuels, phonon scattering by point defects, extended defects such as dislocation loops and bubbles, and grain boundaries plays a significant role in limiting the thermal transport properties. ThO₂ is an actinide-bearing material that does not contain 5f electrons and will serve as a baseline that enables the investigation of phonon transport mechanisms in defective fuel without the effects of 5f electron. In this work, defect evolution in both single crystal and polycrystalline ThO₂ has been studied by a combination of in situ ion irradiation and modeling. In addition, the effects of point defects and extended defects on the phonon transport in ThO₂ have performed on ion irradiated samples. The microstructure of pristine and ion irradiated ThO₂ has been characterized by using electron backscatter diffraction (EBSD), scanning transmission electron microscope (S/TEM), and time-domain Brillouin scattering (TDBS) techniques. The thermal conductivity before and after irradiation has been determined using laser-based modulated thermoreflectance (MTR) technique.

9:30 AM EN17.01.03
**Atypical Melting Behaviour of (Th,U)O₂, (Th,Pu)O₂ and (Pu,U)O₂ Mixed Oxides** Conor O. Galvin¹, Patrick A. Burr¹, Michael W. Cooper³, Paul Fossati⁴ and Robin W. Grimes²; ¹University of New South Wales, Australia; ²Imperial College London, United Kingdom; ³Los Alamos National Laboratory, United States; ⁴CEA, France

Numerous experimental studies have investigated the melting point of mixed oxides in the ternary UO₂–ThO₂–PuO₂ system, with significant discrepancies. In particular, a few studies have reported anomalous reduction in the melting point of mixed oxide, below that of the end members, which have variously been attributed to uncontrolled deviations of stoichiometry and limitations in the experimental setup. Here we provide a mechanistic understanding of the peculiar melting behaviour using molecular dynamics simulations, which are inherently free of the above limitations, combined with a robust pair-potential and a novel technique for calculating solidus and liquidus lines. We show that a dip in melting temperatures is indeed observed in the solidus and liquidus of the mixed oxides (Th,U)O₂, (Th,Pu)O₂ and (Pu,U)O₂ and that this is an inherent property of the solid solutions. This dip is found at
~5% additions of the oxide with higher melting point, in agreement with experimental observations. We propose that the root cause for this reduction in melting point is the formation of low-energy Frenkel pairs in the vicinity of small amounts of dissimilar cations of larger ionic radius: the random (and therefore locally heterogeneous) distribution of cations leads to a spread of Frenkel pair formation energies, depending on the local environment around the vacancy and interstitial. Overall this results in an increase in the average Frenkel pair formation energy, but a small portion of Frenkel configurations exhibit a significantly lower formation energy, which may act nucleation sites for early-onset melting.

9:45 AM EN17.01.04
Equilibrium and Irradiation-Induced Point-Defect Disorder in ThO₂ and U-Doped ThO₂—Modeling and Ion Irradiation Experiments Maniesha Kaur Salaken Singh¹, Tiankai Yao², Lingfeng He², Anter El-Azab¹ and Sanjoy Kumar Mazumder¹; ¹Purdue University, United States; ²Idaho National Laboratory, United States

As a part of EFRC Project titled ‘TETI: Thermal Energy Transport under Irradiation,’ the impact of irradiation induced defects in ThO₂ and U-doped ThO₂ is investigated. Prior to irradiation, the defect content of this material is tied to off-stoichiometry and hence it is dependent upon the U doping level and the temperature and external oxygen pressure or chemical potential. Under irradiation, non-equilibrium defects are produced by energetic particle bombardment, leading to the formation of nanoscale and sub-nanoscale defect clusters that influence thermal transport in ways that are not fully understood to the community. In this presentation we discuss our modeling results for the equilibrium and non-equilibrium defects in ThO₂ and U-doped ThO₂. A thermodynamic defect disorder model was used to investigate the off-stoichiometry behavior in ThO₂ and U-doped ThO₂ in an oxygen partial pressure and temperature environment. The model shows that while ThO₂ remains mostly hypo stoichiometric at relevant thermodynamic conditions, U doping expands the thermodynamics window over which ThO₂ becomes hyper-stoichiometric, thus illustrating the impact of 5f electrons introduced by the U doping on defect disorder. For example, U₀.₅₂Th₀.₄₈O₂₊ₓ can sustain disorder up to an oxygen off-stoichiometry content of x = 0.4 at high temperatures, up to 2000 K, and high oxygen pressures, up to 0.316 atm, whereas U₀.₂Th₀.₈O₂₊ₓ can only exist up to an oxygen off-stoichiometry content of x = 0.05. The extent of hyper-stoichiometry in the oxide reduces with increasing temperature and decreasing oxygen partial pressure values. We will also present the results of a recent cluster dynamics model of vacancy and interstitial cluster formation in ThO₂ under irradiation in conjunction with microstructure and chemical analysis of pure and ion-irradiated ThO₂ at different temperatures by EELS imaging technique in TEM. The impact of cluster composition on matrix composition is illustrated both computationally and experimentally, showing that irradiation provides a further mechanism of altering the stoichiometry of the matrix by forming clusters not commiserating with the chemical formula of the crystal.

10:00 AM BREAK

SESSION EN17.02: Accident Tolerant and Advanced Nuclear Fuels
Session Chairs: Michael Cooper and Shenyang Hu
Monday Morning, December 2, 2019
Sheraton, 3rd Floor, Hampton

10:30 AM EN17.02.01
Atomistic Level Study of Oxidation of Ce₆Si₂ as an Accident Tolerant Nuclear Fuel Surrogate Robert W. Harrison, Robert Worth, James Buckley and Tim Abram; University of Manchester, United Kingdom

Since the Fukushima accident in 2011 there has been a large international effort in the development of accident tolerant fuel and cladding materials for water cooled reactors [1]. Uranium silicide intermetallics are being considered as accident tolerant fuels (ATF) to replace UO₂ currently used in light water reactors (LWRs) [2]. Primarily U₃Si₂ is being examined due to its good thermal conductivity (~15 W/m/K at 500°C) [3], higher U metal density, (giving economic advantages by requiring lower ²³⁵U enrichments) and reduced radiation swelling compared to the higher U containing silicides such as U₃Si [4,5]. However, little is known on the oxidation behaviour of U₃Si₂ under high temperature air and steam environments which could be experienced under a loss of coolant accident (LOCA) scenario with water and/or air ingress into the fuel pin.
The oxidation process of Ce₃Si₂ (as a surrogate for U₃Si₂) has been studied to develop an oxidation mechanism. Samples were oxidised under flowing air to 750°C finding discrepancies between the terminal and theoretical mass gains for complete oxidation similar to previous works on the U₃Si₂ system. As oxidised materials were studied using scanning transmission electron microscopy (S/TEM) with energy dispersive x-ray (EDS) and energy filtered (EF)TEM mapping to elucidate the reaction products and develop a mechanism. The fate of the Ce and Si in the system will be presented and mechanistically discussed and discrepancy in the differences in mass gains revealed. The resulting composition and structure of the as-oxidised materials will also be presented, discussing potential consequences on mechanical stability of the fuel material under a LOCA scenario. The oxidation mechanism, comparison with the U-Si system and consequence of the resulting material structure on fuel performance under a LOCA will also be discussed.


10:45 AM EN17.02.02
Specific Heat Measurements on USi from 2.4 K to 398 K Jason Baker, Joshua White, Aiping Chen, Robert Roback and Hongwu Xu; Los Alamos National Laboratory, United States

The use of uranium-silicide compounds as potential nuclear reactor fuels requires knowledge of thermophysical properties as a function of temperature. At elevated temperatures, a great deal of research has been performed to understand the thermodynamic properties of U-Si compounds; however, in the low-temperature regime, only limited data are available [1-4]. Operating temperatures of nuclear reactors are high, yet important thermodynamic quantities such as Debye temperature and standard entropy (S°) can be derived from low-temperature measurements. S° is an imperative quantity in determination of the Gibbs free energy which depends on $S^\circ$ and enthalpy. Among the U-Si compounds, stoichiometric USi has typically received significantly less attention in the literature with regards to characterization; however, uranium-silicide phases used as nuclear fuels may include appreciable fractions of USi either introduced through fuel synthesis or fabrication. The potential of USi both as a nuclear fuel itself and as a fraction of other U-Si samples, implies a need to further the thermophysical understanding of this material.

Here we present investigations of the low-temperature thermal properties of USi by measuring its specific heat capacities from 2.4 to 398 K using a Quantum Design Physical Properties Measurement System (QD-PPMS). A smooth curve is observed over the entire temperature range measured, and the specific heat capacity at the maximum temperature tested (398 K) was determined to be 67.2 J mol⁻¹ K⁻¹. Additionally, the Debye temperature has been determined from fitting the low-temperature (below 30 K) specific heat capacity data as 252.3 K. Furthermore, by performing integration of the specific heat capacity over the temperature range, the standard entropy at room temperature has been determined as 88.5 J mol⁻¹ K⁻¹.


11:00 AM EN17.02.03
Fission Gas and Creep Behaviour in U₃Si₂ from DFT Calculations and Atomistic Simulations David Andersson¹, Michael W. Cooper¹, Xiang-Yang Liu¹, Benjamin Beeler², Kyle Gamble² and Giovanni Pastore²; ¹Los Alamos National Laboratory, United States; ²Idaho National Laboratory, United States

The U₃Si₂ compound has a high uranium density and thermal conductivity compared to standard UO₂ fuel and, for these reasons, it is being considered as a possible replacement fuel in the current fleet of light water nuclear reactors. It could bring significant performance and economic benefits, while the exothermic reaction with the coolant upon cladding breach is a known drawback that needs to be addressed. Material properties such as the diffusion rate of fission gas atoms and point defects must be determined in order to model the in-reactor behaviour of U₃Si₂. Here we
use density functional theory (DFT) calculations and empirical potential simulations to study diffusion of Xe and point defects in bulk U$_3$Si$_2$ as well as at grain boundaries. The DFT calculations apply the GGA+U methodology to calculate defect energies, entropies and migration barriers of point defects as well as of Xe atoms interacting with point defects. Xe and point defect diffusion rates are predicted from a point defect model parameterized by results from DFT calculations. The diffusion rate under irradiation due to ballistic damage is derived from molecular dynamics simulations based on a MEAM potential for the U-Si-Xe interactions. Molecular dynamics simulations are also used for investigating grain boundary diffusion and segregation of point defects and Xe atoms. We find that Xe diffusion in U$_3$Si$_2$ is faster than in conventional UO$_2$ nuclear fuel in the intrinsic regime, but lower in the regime where transport is dominated by ballistic mixing. The latter observation is a consequence of the high thermal conductivity of U$_3$Si$_2$ preventing high-temperature thermal spikes, which leads to transport by ballistic mechanisms being dominant. The impact of the diffusion properties on fission gas release and swelling in U$_3$Si$_2$ is investigated by parametrizing a fuel performance model in the Bison code with results from the atomic scale simulations. The results are compared to recent irradiation experiments available in the literature. Finally, we discuss the importance of bulk and grain boundary diffusion on creep rates in U$_3$Si$_2$.

11:15 AM EN17.02.04
Ceramic Oxide Coatings for Accident Tolerant Fuel Concept in Light Water Reactors Mattia Cabrioli$^{1,2}$, Matteo Vanazzi$^1$, Erkka Frankberg$^1$, Koba Van Loo$^3$, Jozef Vleugels$^3$, Konstantina Lambrinou$^4$ and Fabio Di Fonzo$^1$; $^1$Istituto Italiano di Tecnologia, Italy; $^2$Politecnico di Milano, Italy; $^3$KU Leuven, Belgium; $^4$SCK-CEN, Belgium

Accident Tolerant Fuel (ATF) concepts aim at providing radical performance and safety improvements for the Light Water Reactors (LWR) at economically attractive conditions. Coatings as near-term evolutionary option take advantage of the reliability of traditional Zirconium-based cladding materials for structural purposes, while conferring engineering of the surface properties. In particular, they are expected to reduce corrosion rates, retain structural integrity and adhesion, minimize hydrogen uptake by the cladding matrix and improve high temperature oxidation resistance.

In this work, the process of selection, design, production and testing of ceramic oxides as protective coatings for LWR fuel cladding is presented. It is worth mentioning that all these activities have been performed in the framework of the European project IL TROVATORE. In the first stage, candidate materials are selected by matching neutronic requirements and chemical stability in pressurized-water environment. This phase is followed by the production of ceramic oxides, in the form of sintered pellets or as thin films by the Pulsed Laser Deposition (PLD) technique. Specimens are then exposed to Pressurized Water Reactor (PWR) environment. Specifically, compatibility tests are performed in pure water at 360°C and saturation pressure, in order to simulate the PWR core during normal operating conditions. Mass changes are monitored during the exposure, then correlated to modifications on the surface and in the structure of the tested samples. The specific dissolution and oxidation processes related to the measured mass changes are also investigated. This initial phase allows us to simultaneously evaluate the behaviour of candidate materials as bulk oxides and coatings, hence confirming the feasibility of PLD as a viable technique to produce high-performance ceramic films, with strong adhesion and interfacial bonding. Eventually the screening phase leads us to the selection of best candidate oxide to uptake an additional phase of optimization of the coating fabrication process.

The selected material is grown on relevant substrates such as Zirconium-based alloys and AISI 316L via an optimized PLD process. The exposure of the new coated specimens to the simulated PWR ambient is performed, up to 30 days in saturated pure water at 360°C. The analysis of the mass change confirms that the coatings act efficiently as barriers against oxidation by reducing significantly the oxidation of the metal alloy. In addition, structural integrity and good adhesion to the substrates are confirmed by spectroscopic characterization and electron microscopy.

Furthermore, the improvement of tolerance against severe accidents is considered with respect to the specific case of Loss Of Coolant Accident (LOCA). Preliminary tests at high temperature (up to 1000°C) and in a controlled atmosphere are conducted in order to evaluate the performance of the selected ceramic material during accidental transients. The coatings show structural integrity and good adhesion, suggesting the high capability of protecting the underlying alloy and their potential for a relevant delay of uncontrolled oxidation of the claddings during accidental transients. On the other hand, the importance of correct alignment of the thermal expansion coefficients between coating and substrates becomes evident at higher temperatures (≥1200°C).

In conclusion, the overall results collected show that PLD ceramic coatings are capable of sustaining both normal and off-normal reactor conditions and consequently constitute a promising option for coated-cladding ATF.
concepts.

**11:30 AM EN17.02.05**

**DFT+U Point Defect Calculations of Uranium Mononitride Ground State and Metastable States**

Bryant B. Jerome and Dilpuneet S. Aidhy; University of Wyoming, United States

Uranium mononitride (UN) is a proposed nuclear fuel for upcoming generation IV nuclear reactors, due to its higher thermal conductivity, greater melting point, and higher concentration of fissile material compared to conventional oxide fuels. DFT+U is used to capture the anti-ferromagnetic ground state of UN. However, the +U correction leads to the possibility of convergence to metastable states, thereby disrupting the correct predictions of electronic-level properties, particularly point-defect energies. In this work, we provide a comprehensive analysis of ground and metastable states and the resulting defect properties using three methods, namely occupation matrix control (OMC), quasi-annealing (QA), and U-ramping. We preform each of these calculations using both the Dudarev and Liechtenstein rotationally-invariant forms of DFT+U. We find that QA and OMC reproduce the ground state, whereas U-ramping converges to metastable states as previously observed. All three methods predict the nitrogen interstitial to be the most favorable defect, whereas the uranium interstitial is the least favorable defect among the vacancies and interstitials of both elements. For example, the calculated formation energies of defects calculated using the QA method across the Dudarev form are 1.76 eV and 9.38 eV for the U vacancy and interstitial, respectively, and for the N vacancy and interstitial are 3.86 eV and 0.94 eV, respectively. The migration barriers for both the U and N vacancies are similar, i.e., ~3 eV. Finally, our results show there are significant deviations in defect formation energies among various metastable states.

**11:45 AM EN17.02.06**

**Multifunctional Nano-Ceramic Coatings—The Enabling Technology for Next Generation Nuclear Reactors (Including Fusion)**

Matteo Vanazzi, Mattia Cabrioli, Boris Paladino, Daniele Iadicicco, Erkka Frankberg and Fabio Di Fonzo; Istituto Italiano di Tecnologia, Italy

Next generation nuclear systems are meant to outperform current ones, by providing disruptive solutions in terms of non-proliferation, fuel cycle efficiency, radioactive waste management, safety and economics. However, the real occurrence of this scenario is directly linked to the availability of suitable materials for the more demanding conditions of these advanced plant concept, in terms of higher burnup and operating temperature, intense radiation fields, liquid metal or molten salt corrosion and tritium permeation. Interposing an engineered surface layer between qualified structural materials and the reactor environment makes this scenario reachable in the short term. In the last years our group developed multifunctional nanoceramic coatings by Pulsed Laser Deposition and Atomic Layer Deposition for Accident Tolerant Fuel for Light Water Reactors and as a solution to high-temperature Heavy Liquid Metal (HLM) corrosion in Generation-IV (GIV) and fusion systems. Accident Tolerant Fuel (ATF) concepts are developed by depositing on ZIRLO® and Zircaloy-4 suitable nanoceramic coatings, which are found to minimize hydrogen uptake and to improve high temperature oxidation resistance. On the other hand, in respect to GIV and fusion systems, Al₂O₃ and Y₂O₃ on AISI316, 1515-Ti and EUROFER-97, has been tested as anti-corrosion, radiation-resistant tritium permeation, insulating barriers. In particular, the compatibility in Pb and Pb-Li has been proven up to 10,000 hours. The tritium permeation reduction of these films is in the order of 10⁴-10⁵, well above the design requirements. Furthermore, Al₂O₃ coatings have been tested under heavy ions irradiation, at damage levels relevant for fission and fusion applications. The ceramic film under irradiation preserves its integrity and mechanical behaviour, evolving structurally from an amorphous to a crystalline state. To conclude, engineered coatings deposited by PLD/ALD techniques represent promising candidates to face the major issues related to future nuclear technologies and allow the design of innovative and economically attractive power plants.
Microstructure-Based Model of Gas Bubble Swelling in Polycrystalline UMo Fuels by Integrating Cluster Dynamics and Phase-Field Approaches

Shenyang Hu1, Benjamin Beeler2 and Douglas Burkes1; 1Pacific Northwest National Laboratory, United States; 2Idaho National Laboratory, United States

Experiments show that recrystallization dramatically speeds up the gas bubble swelling kinetics in UMo nuclear fuels. This implies that gas bubbles inside the recrystallization zone, which has hundred nano-meter sized grains in diameter, grow much faster than those inside coarse grains. However, the mechanism of fast gas bubble growth is not well understood. In this work, a gas bubble evolution model integrating cluster dynamics and phase field models is developed to study the effect of vacancy and interstitial clustering on gas bubble evolution and volumetric swelling kinetics in the recrystallization zone. Cluster dynamics is used to describe the evolution of interstitial loops, vacancy clusters, and dislocation density. The phase field model is used to describe the gas bubble nucleation and growth. With this integrated model, the effect of defect generation rate, defect clustering rate, defect sink strength, and interstitial emission rate from interfaces on gas bubble evolution were systematically simulated. The comparison of gas bubble size, density and volumetric swelling from simulations and experimental data demonstrate that the nucleation and growth of interstitial loops in recrystallization zone is one of key mechanisms behind the fast swelling kinetics.

2:00 PM EN17.03.02
Modeling Irradiation Induced Grain Refinement Utilizing Cahn’s Time Cone Method

Alejandro L. Figueroa1, Joshua Pribe1, Walter J. Williams1,2, Rayaprolu Goutham Sreekar Annadanam1, Edwin Garcia1 and Maria Okuniewski1; 1Purdue University, United States; 2Idaho National Laboratory, United States

Irradiation induced grain refinement is a high burnup phenomenon associated with the fuel’s response to high strain fields created through in reactor irradiation. The increase in grain boundary area from the refinement increases the nucleation rate of fission gas bubbles which leads to a sharp increase in the swelling rate of the fuel. Understanding this phenomenon will allow for more accurate fuel life predictions and can lead to more efficient fuel design. The fission process creates multi-dimensional defects, including fission products, which strain the lattice. The defects produced by this process propagate through material creating both pinning points for dislocations and grain-boundaries, as well causing dislocation propagation by acting both as a source and a climb mechanism. This increases the internal energy of the material, which provides a driving force for recrystallization. Current models of this phenomenon approach the behavior sequentially; addressing grain nucleation first, then growth of the nuclei. This approach is useful but does not fully capture the temporal inhomogeneity of the system. By utilizing Cahn’s time cone method and adapting it to a temporally inhomogeneous reactor environment the nucleation and growth of the irradiation induced grain refinement can be modeled concurrently and can provide an analytical solution to the phenomenon. To address the temporal inhomogeneity of the system, strain which affects both the nucleation and growth was defined as a function of fission density. The mobility of the system was also adapted for irradiation enhanced diffusion. Heterogenous nucleation was used as the dominant nucleation mechanism. Utilizing this technique to model irradiation induced grain refinement showed comparable results to experimental observations demonstrating that the adapted Cahn time cone method can effectively model the phenomenon, while addressing both nucleation and growth simultaneously.

2:15 PM EN17.03.03
The Effects of Fabrication Parameters on the Microstructure of Monolithic U-Mo Nuclear Fuels

Jan-Fong Jue, Dennis Keiser, Adam Robinson, Brandon Miller, Jian Gan and Glenn Moore; Idaho National Laboratory, United States

Monolithic U-Mo fuels have been down-selected for the conversion of several US high performance research and test reactors. In order to qualify this new fuel type, more than a hundred fuel plates have been fabricated and irradiated to date in the Advanced Test Reactor at Idaho National Laboratory. The size of fuel plates fabricated for these irradiation campaigns varies from 4 inches (mini-plates) to more than 40 inches (full-size plates) in length. The fabrication parameters used in fabricating mini-plates and full-size plates are very different, thus resulting in different as-fabricated microstructures. The microstructure of as-fabricated and irradiated mini-plates and full-size plates will be presented. The impact of the fabrication parameters on the microstructure and irradiation performance will be discussed.
Density Functional Theory Study of Uranium-Based Compounds

Edmanuel Torres, Thaneshwor Kaloni and Jeremy Pencer; Canadian Nuclear Laboratories, Canada

The accurate description of the electronic and thermal properties of uranium-based compounds is fundamental in the development of novel nuclear fuels. Density functional theory calculations (DFT), within the plane wave pseudopotential approach using Quantum ESPRESSO (QE), has been applied to the study of uranium-based compounds. The lack of widely accessible pseudopotentials to perform DFT studies of uranium compounds significantly limits the capability of innovation in nuclear materials. As such, we have developed a set of projector augmented-wave (PAW) pseudopotentials for uranium, oxygen, nitrogen, and carbon atoms. The pseudopotentials were optimized to be used with a low kinetic energy cutoff of 37 Ry, which is considerably lower in comparison to PAW pseudopotentials available for QE. The set of pseudopotentials is then used to perform DFT calculations of uranium-based compounds, such as uranium metal, uranium oxides (UO$_2$, UO$_3$, and U$_3$O$_8$), uranium mononitride, and uranium monocarbide. Systems with strong electron correlations were described using Hubbard corrected DFT+U calculations. As such, monitoring the occupation matrix for 5f electrons of the uranium atoms was required to avoid metastable state solutions, and therefore to obtain reasonable ground properties. The reported results are shown to be accurate in comparison to reported theoretical and experimental results. This new set of PAW pseudopotentials are thus suitable for use in modelling a variety of uranium compounds, but also have the advantage of enhanced computational efficiency, due to the reduced kinetic energy cutoff.

Defect Clustering in Irradiated Alpha Uranium—Cluster Dynamics Modeling and Ion Irradiation Experiments

Fabia Farlin Athena$^1$, Tiankai Yao$^2$, Lingfeng He$^3$, Anter El-Azab$^1$ and Sanjoy Kumar Mazumder$^1$; $^1$Purdue University, United States; $^2$Idaho National Laboratory, United States

There is limited information in the literature about defect clustering in irradiated alpha uranium in spite of the fact that defect clustering is responsible for irradiation growth of that material. The limited available data shows that two types of dislocation loops form in alpha uranium on the (010) and (100) planes, with Burgers vectors of $\sqrt{a^2+b^2} <110>/2$ and $a [100]$ respectively, under neutron irradiation. Under He ion irradiation, however, small cavities, which are assumed to be He bubbles were observed. We present a cluster dynamics model for loop formation in alpha uranium. The defect clusters considered at prismatic loops of interstitial type, those on (010) planes, and vacancy type, those on (100) planes. The dynamics model parameters were partly taken from open literature and partly fixed by molecular dynamics simulations. Cluster dynamics simulations were carried out and at different temperatures and dose rates, and the comparison with the existing neutron irradiation data for the loop size distribution and average loop size and density shows that the model is able to make reasonable predictions. We also present the results of proton irradiation of alpha uranium, where the proton beam was used to produce a microstructure dominated by dislocation loops. The formation and evolution of dislocation loops were studied by TEM technique, which provided further data for validation of the cluster dynamics model.

3:00 PM BREAK

SESSION EN17.04: Oxide Nuclear Fuels
Session Chairs: Lingfeng He and Simon Middleburgh
Monday Afternoon, December 2, 2019
Sheraton, 3rd Floor, Hampton

Structural and Microstructural Features Observed in (Ln,U)O$_{2-x}$ Systems

Gianguido Baldinozzi$^1$, Bernardo Herrero-Bocco$^{1,2}$, Fabienne Audubert$^2$, Lionel Desgranges$^2$, Luis Casillas$^1$, Maulik K. Patel$^3$, Haixuan Xu$^2$ and Kurt Sickafus$^3$; $^1$University of Paris Saclay, France; $^2$CEA, France; $^3$Linköping University, Sweden; $^4$University of Liverpool, United Kingdom; $^5$The University of Tennessee, Knoxville, United States

The majority of periodic table elements are created within the conventional uranium dioxide fuel matrix during its
time in pile. These elements are accommodated in quite different ways within the nuclear ceramic. Ba, Zr, Y and the lanthanide atoms are typically substituted within the uranium dioxide matrix. At high burnup, the number of phases that form and the differences between them can result in the development of highly complex structures and microstructures. Similar effects might be encountered in manufactured advanced actinide fuels for the transmutation of minor actinides or in fuels containing significant amounts of burnable poisons (typically Gd). Those systems constitute then a large class of compounds, generally with fluorite or fluorite-derived structures, exhibiting high radiation tolerance, possibly related to their peculiar ability to accommodate a variety of defects and to exist as nonstoichiometric compounds within a large homogeneity range. Nevertheless, a variety of behaviours and different phases is observed after quenching or annealing in several of the pseudo-binary systems of type (Ln,U)O$_2$$_x$, suggesting that the thermal history of those systems is of paramount importance. Some of these systems, like (U,Ce)O$_2$$_x$ are particularly complex, display an intriguing structural variety, and therefore present a fundamental interest. In this talk we would try to address some of those interesting structural features induced by aliovalent substitutions in UO$_2$.

4:00 PM EN17.04.02
Modeling Fission Gas Behavior in Doped UO$_2$ Michael W. Cooper$^1$, Topher Matthews$^4$, Kyle Gamble$^2$, Giovanni Pastore$^2$, Chris Stanek$^1$ and David Andersson$^1$; $^1$Los Alamos National Laboratory, United States; $^2$INL, United States

Advanced fuels are being considered for deployment in light water reactors (LWRs). Advanced fuels are designed to improve performance and fuel economics during normal operation and/or safety margins during accidents. For example, additives such as Cr$_2$O$_3$ can be used during fuel fabrication to modify the UO$_2$ microstructure. Specifically, the resultant enhanced grain size is considered to benefit pellet-clad interactions by modifying the mechanical properties of the fuel and by increasing fission gas retention, which reduces the plenum pressure. The effect of increased grain size on fission gas release can be readily captured within physics-based fission gas models, such as that implemented in the BISON fuel performance code. However, the dopant could modify the defect chemistry of UO$_2$ during reactor operation, thus altering the fission gas diffusivity and potentially undermining the enhanced fission gas retention obtain through enlarged grains. Fission gas diffusivity exhibits three diffusion regimes for reactor conditions: high T intrinsic diffusion, intermediate T irradiation enhanced diffusion, and low T athermal diffusion. In this work, we present a cluster dynamics model developed and validated for the description of irradiation enhanced diffusion in undoped UO$_2$. Large defect clusters play a crucial role in the reproduction of irradiation enhanced diffusion. For doped UO$_2$, it is assumed that the oxygen potential is controlled by the preferential reduction of Cr$_2$O$_3$ to Cr (over UO$_2$$_x$ reduction to stoichiometric UO$_2$). The resultant doped UO$_2$ Xe diffusivity is enhanced with respect to undoped UO$_2$. The enhancement in Xe diffusivity relative to undoped UO$_2$ has been implemented in BISON. The predicted fission gas release from BISON has been compared to Halden experiments.

4:15 PM EN17.04.03
Prediction of the Shape, Size and Pressure of Intragranular Fission Product Bubbles in Spent Nuclear Fuel Michael J. Rushton$^1$, Conor O. Galvin$^{1,2}$, Michael W. Cooper$^4$, Patrick Burr$^2$, Simon C. Middleburgh$^1$, William E. Lee$^{1,3}$ and Robin W. Grimes$^3$; $^1$Bangor University, United Kingdom; $^2$University of New South Wales, Australia; $^3$Imperial College London, United Kingdom; $^4$Los Alamos National Laboratory, United States

During its life in a reactor fission products build up in nuclear fuel. Some of these such as Xe, Kr and He form bubbles in the fuel. Whilst in a reactor, these have a detrimental effect on fuel performance as fission product bubbles may lead to swelling and a degradation of mechanical properties, and when released from the fuel, where the gas degrades the thermal conductance of the fuel-clad gap and leads to an increase in fuel temperature and cladding pressure. Understanding the size, shape and pressure of bubbles also allows the fission product inventory of nuclear fuel to be gauged. This information is important in developing improved fuel performance codes, pushing fuel to higher burn-up and has relevance to back-end processes such as reprocessing and ultimate disposal of spent fuel.

In this work, molecular dynamics simulations have been used to study fission product bubbles in UO$_2$. The results of this work will show the behaviour of small fission product bubbles in the range of diameters below <100nm. In particular bubble morphology is considered with both spherical and faceted Wulff shapes being compared. The effect of bubble internal pressure on morphology and its dependence on bubble size will be presented. The
simulation results will be described in terms of the bubble size and pressure distribution expected in spent fuel.

4:30 PM EN17.04.04
Effect of High Burnup Structure on Fuel Rod Performance with Burnup Extension  Jianguo Yu and Hongbin Zhang; Idaho National Laboratory, United States

The formation of high burnup structure (HBS) or rim structure is possibly the most significant restructuring processes at the rim of pellets in-pile with burnup extension in LWR and the effect of HBS on fuel thermo-physical or mechanical properties is a key requirement to ensure the successful implementation of extended burnup. There is independently experimental evidence to support that HBS concomitantly affects thermal and mechanical properties of fuel. But it is still not well understood how such HBS affects fuel thermo-physical or mechanical properties. In this work, we present results how HBS impacts the fission gas behavior of fuel rod under normal operating conditions. The fuel performance code FRAPCON-4.0 was used to simulate fission gas related properties, such as plenum pressure, fission gas release, and gap conductance. The effect of HBS under different boundary conditions, i.e. power history profiles, will also be discussed.

4:45 PM EN17.04.05
Fracture Behavior of Pure UO₂ Using Small-Scale Mechanical Testing  Brent Heuser and Shen J. Dillon; University of Illinois at Urbana Champaign, United States

Fracture of UO₂ affects fission gas release in fuels. Predicting, understanding, and controlling within UO₂ fuel pellets is of considerable practical interest. An ongoing fundamental challenge is understanding the constituent contributions form grain boundaries and the bulk to the fracture response of the polycrystal. In this work, micro-scale mechanical testing has been used to induce single grain transgranular fracture and bicrystal intergranular fracture in samples isolated from polycrystalline UO₂. The results are discussed in the context of bulk UO₂ fracture and similar measurements performed on other oxides.
annealing temperature after irradiation. The results will be discussed in regard of the role of impurities on the microstructure evolution in the first stages of irradiation in tokamak and of the impact on the swelling of the material.

Acknowledgements:
This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission. Irradiations were performed at JANNuS (Joint Accelerators for Nanoscience and Nuclear Simulation) Orsay at CSNSM (France) and Saclay at CEA (France), which are part of the EMIR French accelerators network.

8:45 AM EN17.05.02
Void Evolution in Tungsten and Tungsten-5wt.% Tantalum under In Situ Proton Irradiation Iuliia Ipatova1, Simon C. Middleburgh1, Robert W. Harrison2, Michael Rushton1, Enrique Jimanez-Melero2 and Stephen Donnelly3; 1Bangor University, United Kingdom; 2University of Manchester, United Kingdom; 3University of Huddersfield, United Kingdom

Void evolution during in-situ irradiation in polycrystalline W and W-5wt.%Ta material has been examined at 800 and 1000°C, via TEM. No dislocation loop formation was observed prior to void nucleation. The irradiated W microstructure was characterised by the presence of a population of voids, randomly distributed in the region. The number density of the voids reduces when the irradiation temperature is raised. In contrast, the excess of free vacancies in the W-5wt.%Ta material irradiated at 800°C only leads to the formation of visible voids after post-irradiation annealing of the sample at 1000°C. Solute Ta atoms also cause a significant decrease in the number density of voids when comparing the microstructure of both materials irradiated at 1000°C, and a gradual progression towards saturation at 0.2 dpa. Moreover, for the first time, we have detected a progressive transition from a spherical to a faceted shape in a number of voids present in both materials at damage levels 0.3 dpa.

9:00 AM EN17.05.03
High Irradiation Resistance of Nanocrystalline W-Based High Entropy Alloy Enrique Martinez1, Osman El Atwani1, Nan Li1, Meimei Li2, Arun Devaraj3, Kevin Baldwin1, Matthew Schneider1, Damian Sobieraj4, Jan Wrobel4, Duc Nguyen-Manh2 and Stuart Maloy1; 1Los Alamos National Laboratory, United States; 2Argonne National Laboratory, United States; 3Pacific Northwest National Laboratory, United States; 4Warsaw University of Technology, Poland; 5Culham Center for Fusion Energy, United Kingdom

A novel W-based refractory high entropy alloy with outstanding radiation resistance has been developed. The alloy was grown as thin films showing a bimodal grain size distribution in the nanocrystalline and ultrafine regimes and a unique 4 nm lamella-like structure revealed by atom probe tomography (APT). Transmission electron microscopy (TEM) and X-ray diffraction show an underlying body-centered cubic crystalline structure with certain black spots appearing after thermal annealing at elevated temperatures. Thorough analysis based on TEM and APT correlated the black spots with second phase particles rich in Cr and V. After both in situ and ex situ irradiation, these precipitates evolve to quasi-spherical particles with no sign of irradiation-created dislocation loops even after 8 dpa at either room temperature or 1073 K. Furthermore, nanomechanical testing shows a large hardness of 14 GPa in the as-deposited samples, with a slight increase after thermal annealing and almost negligible irradiation hardening. Theoretical modeling based on ab initio methodologies combined with Monte Carlo techniques predicts the formation of Cr and V rich second phase particles and points at equal mobilities of point defects as the origin of the exceptional radiation tolerance. The fact that these alloys are suitable for bulk production coupled with the exceptional radiation and mechanical properties makes them ideal structural materials for applications requiring extreme conditions.

9:15 AM EN17.05.04
Modified Deformation Behavior of Ion-Implanted Tungsten Felix Hofmann, Suchandrima Das, Hongbing Yu and Edmund Tarleton; University of Oxford, United Kingdom

Tungsten is the main candidate material for plasma-facingarmor components in future fusion reactors. During operation bombardment with high-energy fusion neutrons will create collision cascades that leave behind lattice-
Helium, injected from the plasma and produced by transmutation, strongly binds to these defects, and modifies their behavior and retention. We investigate the impact of helium-implantation-induced and self-ion-implantation-induced damage on the deformation behavior of tungsten, comparing spherical nano-indenters in unimplanted, helium-implanted and self-ion-implanted tungsten crystals of 001-orientation. Ion-implantation increases hardness and causes large pile-ups that increase with increasing implantation dose. Lattice rotations and indentation-induced residual strains beneath indents, probed using 3D-resolved synchrotron X-ray micro-diffraction, are smaller in the ion-implanted material, suggesting a more confined plastic zone. The increase in pile-up points to a reduction in strain hardening capacity or even a strain softening. Based on these results, as well as TEM observations of defects beneath indents, we hypothesize that while dislocation motion is initially obstructed by implantation-induced defects, the strength of these obstacles is reduced by the passage of dislocations. A 3D crystal plasticity finite element (CPFE) model founded on this hypothesis, with only three fitting parameters, reproduces these effects and is directly compared to the experiments. We also explore the orientation dependence of the indentation-response by considering grains with <001>, <110> and <111> out-of-plane orientations. Indents in unimplanted tungsten show little orientation dependence. In the helium-ion-implanted material, <110> and <111>-oriented grains show a much lower pile-up and hardness than <001>-oriented grains. The CPFE formulation, with all parameters unchanged except the crystal orientation, captures these orientation-dependent changes. The results suggest an orientation-independent mechanism governing the interaction of implantation-induced defects with glide dislocations, with differences in pile-up morphology arising just due to the relative orientations of the crystal slip systems, sample surface and spherical indenter tip.

9:30 AM EN17.05.05
Microstructural Features and Hydrogen Isotope Diffusion and Retention in Ion Irradiated Lithium Aluminate
Weilin Jiang and David J. Senor; Pacific Northwest National Lab, United States

As a tritium (T) production material, ⁶Li enriched tetragonal lithium aluminate (γ-LiAlO₂) has been used in support of the Tritium Sustainment Program. It also has been investigated as a candidate blanket material for fusion reactor designs. When γ-LiAlO₂ is irradiated with thermal neutrons, 2.75 MeV T and 2.05 MeV He particles from reaction ⁶Li (n, He) T will emit. These energetic particles collide with the lattice atoms and initiate damage cascades, generating point defects in the crystalline structure. The accumulation and interaction of point defects and gas species lead to the formation of extended defects and bubbles. In addition, radiolysis due to electronic energy deposition causes the material to decompose. The modified microstructure will affect T diffusion in the irradiated material.

In order to gain a physical insight into the defect production and gas species diffusion processes, ion irradiation experiments have been designed and performed in reactor-relevant conditions. Both protium and deuterium (D) have been used as surrogates for T in this study. Sequential irradiation with 90 keV He⁺ and 80 keV H₂⁺ ions as well as 120 keV He⁺ and 80 keV D₂⁺ ions with an equal ion fluence was performed over temperatures from 188 to 773 K. The ion energies were so chosen that the H or D profile peak was located at the He⁺ damage peak. The ion fluence ranged from 2×10¹⁶ to 4×10¹⁷ He⁺+H⁺ (or He⁺+D⁺)/cm². Isochronal and isothermal annealing experiments were followed up to 873 K and 60 min, respectively. The irradiated samples were characterized using a number of spectroscopy and microscopy techniques, including RBS/C, ToF-SIMS, STEM, STEM-EDS, STEM-EELS, HIM, Nano-SIMS and APT.

This presentation will report our main results from ion irradiation studies of monocrystalline γ-LiAlO₂ and polycrystalline pellets. Major conclusions from these studies include the following. Saturation stages of lattice disorder are found in γ-LiAlO₂ irradiated at 573 K. Complete amorphization with gas bubble formation starts from the surface. Cubic LiAl5O₈ precipitates surrounded by cavities form in the damage peak region. Li out-diffusion and vacuum evaporation from the sample surface occur during ion irradiation at elevated temperatures. STEM-EELS provides evidence for preferred pathways of Li diffusion along the grain boundaries. In situ HIM shows volume swelling, He bubble formation in grains and He release via grain boundaries. In situ TEM reveals a rapid formation of cavities due to radiolysis in γ-LiAlO₂ under low-energy electron irradiation. The thermal annealing data suggest that the D diffusion coefficients in the irradiated material have a value on the order of 2×10⁻¹⁰ cm²/s at 773 K. There is an exponential decay behavior of D release at room temperature from γ-LiAlO₂ pellets irradiated at 188 K; at the low temperature, D atoms appear to be immobilized in the irradiated structure. The data from this study also show significant H and D diffusion and release from γ-LiAlO₂ during irradiation at 573 K; D retention increases with increasing D⁺⁺ ion fluence and tends to saturate at 4×10¹⁷ He⁺+D⁺/cm².

9:45 AM EN17.05.06
Defects, Stoichiometry and Transport Processes in Be12X Intermetallics Robin W. Grimes1, Matthew Jackson2, Patrick A. Burr3 and Simon C. Middleburgh4; 1Imperial College London, United Kingdom; 2University College London, United Kingdom; 3University of New South Wales, Australia; 4Bangor University, United Kingdom

Be12X (X = Ti, V, Mo and W) intermetallics are a promising family of materials for the first wall and neutron multiplying applications in future nuclear fusion reactors. Due to the difficulties of working with Be they are often poorly characterized. Thus, the crystallography, elastic properties, atomic transport processes, thermodynamical stability and deviation from stoichiometry have been investigated using computer simulation based on density functional theory.

Surprisingly there has been considerable controversy regarding the structure of TiBe12, which is variously reported as hexagonal and tetragonal. Lattice dynamics simulations show the I4/mmm tetragonal phase to be more stable over all temperatures. The formation enthalpies of intrinsic point defects and the elastic constants of all the Be12X intermetallics are then predicted. Defect concentrations were shown to be dominated by antisite disorder and Be vacancies, suggesting these materials can accommodate excess X much more easily than excess Be. In Be12Ti it was found that titanium defects have much higher hopping energy than beryllium across the majority of migration pathways studied. Both beryllium vacancy and interstitial diffusion is weakly anisotropic, however, migration of beryllium divacancies is isotropic with energy equal to that of the isolated vacancy.

10:00 AM BREAK

SESSION EN17.06: Reactor Steels
Session Chairs: Marie-France Barthe and Iuliia Ipatova
Tuesday Morning, December 3, 2019
Sheraton, 3rd Floor, Hampton

10:30 AM *EN17.06.01
Influence of Irradiation Conditions on Precipitation Behavior in Fe-Cr and Ni Alloys Li-Jen Yu1, Elaina Reese1, Takuya Yamamoto2, G. Robert Odette2, Julie D. Tucker3, M. Grace Burke4 and Emmanuelle A. Marquis1; 1University of Michigan, United States; 2University of California, Santa Barbara, United States; 3Oregon State University, United States; 4University of Manchester, United Kingdom

The use of heavy ions, protons, or electrons to understand the effect of irradiation on microstructures and therefore materials properties presents many experimental benefits over the use neutrons. However, extrapolating the laboratory observations to behaviors found under neutron irradiation in reactor conditions is not a straightforward process. In particular, dose rates that are orders of magnitude apart and can play a significant role on the development of microstructures, through mechanisms that include higher point defect production and cascade mixing effects. Here, we will discuss the behaviors under ion, proton, and neutron irradiation of alloys that would normally phase decompose under thermal conditions. Specifically, using atom probe tomography to characterize microstructures at high spatial and chemical resolution, the evolution of microstructures in model ferritic Fe-Cr alloys and austenitic Ni alloys was quantified as a function of dose and dose rates. In Fe-Cr alloys, precipitation of the α’ phase is expected under long thermal annealing times. In the selected commercial Ni alloys (625, 625 Plus, and 690), the γ” phase, an ordered Pt2Mo-type phase, and in some cases the γ’ phase are expected to precipitate. Under irradiation conditions, both alloy systems exhibit different precipitation regimes that are dependent on dose rate. Generally, accelerated precipitation by radiation-enhanced diffusion is observed at lower dose rates, establishment of a steady state regime occurs at intermediate dose rates, and precipitation is entirely suppressed at higher dose rate.

11:00 AM EN17.06.02
In Situ Micromechanical Testing of Unirradiated and Ion Irradiated Reactor Pressure Vessel Steels Claudia Gaparrini1, Alan Xu2, Tao Wei2, Ken Short2, Joel Davis2, Tim Palmer2, Dhruti Bhattacharyya2, Nick Riddle2, Lyndon Edwards2 and Mark R. Wenman1; 1Imperial College London, United Kingdom; 2Australian Nuclear Science and Technology Organisation, Australia; 3Rolls-Royce, United Kingdom
Recently there has been a considerable need to extend the lifetime of the world’s pressurised water reactor (PWR) fleet from 40 to 60 or possibly 80 years. The continued safe operation of these reactors is intrinsically linked to the structural integrity of the steel used for the reactor pressure vessel (RPV). Matrix damage and solute clustering induced by neutron irradiation are considered one of the main causes of embrittlement of RPV steel. Intensive research has been ongoing to investigate embrittlement mechanisms of the low alloy ferritic RPV steel, however, testing neutron irradiated materials can take a long time and is very costly. The recent development of micro mechanical testing allows researchers to evaluate mechanical properties of ion irradiated materials which aim to simulate the damaging effects observed on neutron irradiated materials.

This work presents in situ micro tensile testing of a novel manufactured RPV steel: hot isostatic pressed (HIP) SA508 grade 3 steel. Micro tensile specimens with dimensions of $5 \times 5 \times 15 \mu m$ were manufactured using a gallium focused ion beam (FIB) and tensile testing was performed under displacement control at a rate of 20 nm/s in situ in a scanning electron microscope (SEM). Tests were performed under the same conditions on unirradiated and ion irradiated specimens which were irradiated by He$^{2+}$ ions at 5 MeV at room temperature to the damage of 0.6 dpa using a 2 MV tandem accelerator with energy degrader at ANSTO. The mechanical properties (in terms of ultimate tensile stress and 0.2% proof stress) of the unirradiated micromechanical tests agreed well with data obtained via conventional mechanical testing. The effects of ion irradiation on the mechanical properties of this RPV steel were measured as an increase of ultimate tensile stress and yield strength via micro tensile testing. The hardening of the irradiated specimens was also measured using nanoindentation performed on the top sample surface. The hardening mechanism can be correlated to the implantation induced features observed on the ion irradiated material that were resolved using a transmission electron microscope. Fine bubbles/voids with an average diameter of $1.2 \pm 0.5 \text{ nm}$ were observed.

11:15 AM EN17.06.03
Energetic Drive for Ni, Mn and Si Clustering at Dislocation Loops in $bcc$ Iron

Thomas Whiting, Daniel J. King and Mark R. Wenman; Imperial College London, United Kingdom

There are currently concerns that clusters of Cu, Mn, Ni and Si could limit the operational lifetime of reactor pressure vessels (RPVs) through reductions in fracture toughness, unaccounted for in regulatory models. As there is much debate over the origin of these clusters and whether they are radiation-enhanced or radiation-induced and whether they can be classified as discrete phases, there is an ongoing global research effort to investigate their mechanism of formation.

Using density functional theory (DFT) simulations, we have conducted investigations into the effect of strained environments on the binding energies of solutes, solute pairs, vacancy-solute pairs and dumbbells in bcc Fe to better understand the conditions that favour nucleation and growth of solute clusters as it is expected that these are dependent on both strain fields and the local chemical environment. Atom probe tomography studies have found that clusters are frequently associated with dislocation loops and grain boundaries, suggesting that these could act as nucleation sites for solute clustering. As modelling large dislocation loop sizes is computationally expensive using DFT, we have used interatomic potentials for Fe to model both small (19 atom) and large (65 atom) $<111>$ dislocation loops to identify the range of strain on the lattice. We have then used these results to parameterize DFT simulations by modelling defects in strained lattices that are typical of these loops.

Our findings show that: (1) vacancies will be dragged to these locations as vacancy formation energies are reduced by more than 1 eV when subject to large volumetric strains, (2) solutes will be dragged due to the strong solute-vacancy binding energy for Ni, Mn, Si in both first and second nearest neighbour positions, (3) solutes remain bound to vacancies even in significantly strained environments, and (4) magnetic effects are important to model the energetics of systems, particularly for complex environments such as those including self-interstitial atoms.

11:30 AM EN17.06.04
Measuring Microstructure Changes in Ion-Irradiated 316LN Stainless Steel

I-Hsuan Lo¹, Philip D. Edmondson² and Karl R. Whittle¹; ¹University of Liverpool, United Kingdom; ²Oak Ridge National Laboratory, United States

UK’s nonprescriptive regulatory system has incentivised the nuclear industry to invest in the research and development of reliable structural integrity codes since 1970’s. To support the UK structural integrity services, the
UK project on the ‘Multi-scAle INTegrity assessment for Advanced high-temperature Nuclear system (MAINTAiN)’ offers the ability to further strengthen UK’s position in structural integrity through developing a novel computer model-based assessment code. The aim is to develop the knowledge that is necessary to reliably assess the integrity of critical nuclear components that operate in extremes of high-temperature, high mechanical stress, and irradiation. To this end, a predictive three-dimensional multi-scale creep deformation model, informed by the materials' microstructure, will be established. The MAINTAiN project will provide the scientific foundation for the next generation of high temperature structural integrity assessments.

The University of Liverpool has carried out a part of irradiation damage on the dislocation creep behaviour of three materials that are of interest for the next generation of nuclear power plants: Stainless Steel Type 316LN, ODS Steel, and FeCrAl alloys.

The presentation will illustrate the details of the MAINTAiN and the latest results on the irradiation test of 316LN stainless steel. The irradiation damage was induced by self-ion implantation using the Dalton Cumbrian Facility (DCF). In order to investigate changes, this works has included high resolution transmission electron imaging and spectroscopic analysis of damage in order to investigate the changes in irradiation.

11:45 AM EN17.06.05
Irradiation Assisted Stress Corrosion Cracking in 508-304 Weldment in BWR/NWC Simulated Environment
Brent Heuser and Zhen Li; University of Illinois at Urbana Champaign, United States

Reactor pressure vessel steel SA508 (a low-alloying steel) and 304 (Fe-Cr-Ni austenitic stainless steel) are widely employed in both PWRs and BWRs. Weldments typically have high residual stress and composition gradients within the fusion zone (FZ) and heat affected zone (HAZ) that lead to greater stress corrosion cracking (SCC) susceptibility. Irradiation assisted SCC can be controlled by factors including water chemistry, localized deformation, tensile stress, radiation induced segregation and radiation damage. In particular, the redistribution of Cr, the element responsible for oxidation/corrosion resistance via chromia formation, can sensitize these alloys to SCC phenomenon. These materials can be preferentially attacked at active paths, such as GBs in the FZ and HAZ, when exposed to chemically reactive environment and to radiation.

Slow strain rate tests (SSRT) with strain rate up to $10^{-9}/s$ were applied on proton irradiated EPRI SA508-309 weldment in an autoclave system with simulated the BWR/NWC environment (10.2 Mpa, 288 °C and 2000 ppb oxygen) in order to investigate the radiation assisted SCC. The effect of radiation to induce segregation in the FZ and HAZ of SA508-309 weldment is of typical interest. In addition, SSRTs were employed on as-received SA508-309 weldment to separate the effect of irradiation from environment factors such as LWR water chemistry and applied tensile load. Moreover, SSRTs were conducted on as-received weldment at room temperature and atmosphere pressure. The yield strength and ultimate tensile strength of as-received and proton irradiated SA508-304 weldment under NWC environment is 25% lower compared to that under room temperature and atmosphere pressure. The redistribution of elements such as Cr in the grain boundary of as-received and irradiated weldment is investigated with STEM-EDS. The initiation of cracking was studied by SEM and TEM in the as-received and irradiated weldment. This talk will focus on identification of the primary factors of SCC in Fe-based weldments.

1:30 PM EN17.07.01
Studying Corrosion in Materials for Nuclear Applications Using Synchrotron-Based X-Ray Methods
Simerjeet Gill; Brookhaven National Laboratory, United States

Development of next generation materials for nuclear energy structural applications requires understanding structural changes and failure mechanisms under extreme environments. Reactions at interfaces under corrosive environments play a crucial role in material failures in current and advanced reactors.

Our research focuses on utilizing synchrotron characterization techniques such as spectroscopy, multi-modal
imaging and diffraction for characterizing material interfaces and their properties when subjected to extreme environments of high temperature and radiation fluxes present in nuclear reactors. Synchrotron based characterization studies performed for structural materials and molten salt systems, elucidating corrosion at interfaces will be presented.

X-ray absorption spectroscopy has been utilized to investigate local coordination environment, bonding dynamics and electronic properties of metal species, and their changes at elevated temperatures in molten salt systems. Using a custom-designed in situ cell, we used Ni and Co dopants in single component ZnCl₂ and ZnCl₂-KCl eutectic and studied their properties using Ni, Co and Zn K-edge spectra. The local structural changes and speciation of metallic species in molten salt systems will be discussed.

3D multi-modal imaging techniques will be discussed to provide quantitative characterization of Cr segregation at grain boundary inside the sensitized steel sample using X-ray Fluorescence. Tomographic image reconstruction of stainless steel deteriorated by IG corrosion is combined with 3D imaging of phase contrast using Differential Phase Contrast imaging. This combined structural and chemical analysis of the Cr segregation at grain boundaries allows us to understand IG corrosion in sensitized stainless steel at nanoscale.

To track degradation of materials in real time, we built and commissioned an in situ sample environment for studying interfaces under high-temperature and pressure conditions using x-ray diffraction to investigate corrosion mechanisms in cladding materials. Capabilities of the in situ sample environment will be discussed.

2:00 PM EN17.07.02
First Principles Investigation of Cr Segregation Behaviors in Ni-Cr Alloy in Molten Salt Systems Jacob Startt¹, Stephen S. Raiman² and Chaitanya Deo¹; ¹Georgia Institute of Technology, United States; ²Oak Ridge National Laboratory, United States

The development of new structural materials that can withstand the degradative and corrosive environments exhibited by molten salt systems currently stands among the most important remaining scientific targets that must be reached before viable molten salt systems can be realized at an industrial scale. In corrosion focused studies, the prevailing trend observed in the most commonly investigated alloys (such as Hastelloy N or 316 stainless steel) is the depletion and dissolution of Cr atoms near the alloy surface and along grain boundaries. The atomic level mechanisms and forces that drive the migration of Cr and its eventual removal from the surface are not well understood, and due to the harsh environments intrinsic to molten salt systems experimental efforts may struggle to observe these fundamental processes. Carefully devised computational modelling offers another avenue to study the nature of these interactions and may even help to suggest potential mechanisms and to narrow the field of possible reaction pathways for future experimental studies to investigate.

In this study, the segregation behavior of Cr near an (100) fcc Ni surface is investigated with first-principles density functional theory (DFT), first for a clean surface and then for surfaces with various salt species adsorbed above the segregating Cr atom. Surface segregation energies describe the energetics associated with the location of a solute atom near a surface (i.e. the relative energy of an atom when its located in the bulk versus in a specific surface layer).

Calculations show that under a clean surface (i.e. no adsorbed salt atoms) it is energetically favorable for the Cr atom to inhabit the 3rd or 2nd surface layer, but largely unfavorable for it to sit in the topmost 1st layer. When a Cl adatom is placed above the Cr atom, the segregation energy for the top-most layer decreases, suggesting Cl surface adsorption lowers the barrier for Cr to move to the top layer. When F or O are adsorbed to the surface, the segregation energy not only decreases but becomes significantly negative, suggesting that Cr segregation to the top layer not only becomes more favorable with these species on the surface but also actually preferred relative to a remaining in a bulk position. Further investigation into the effects of H-Cl, H-F, and H-O will also help to understand the role of H and H₂O salt impurities in the corrosion process. The additional presence of an H atom may also allow the highly electronegative surface adsorbates to increase their local electron occupation level, which would more closely resemble the charged ionic nature exhibited by the salt in a molten state. This talk will report new insights into material-salt interfaces through atomistic modeling.

2:15 PM EN17.07.03
Corrosion Mechanism of Molten Salts on Haynes 230 Alloy Studied Using In Situ Neutron Reflectometry
Joohyun Seo, Mathieu Doucet, Gabriel M. Veith, Sheng Dai and James F. Browning; Oak Ridge National Laboratory, United States

Molten salt eutectics are used as heat transfer fluid in concentration solar power systems. One of the technological challenges with such systems is the control of corrosion of the materials used for transport of the molten salts. For this reason, understanding how the interface between salts and alloys change as a function of temperature is important. In this study, we focused on the interfacial structure at the interface of KCl-MgCl$_2$ molten salt eutectic and Haynes 230 alloy using neutron reflectometry. This binary molten salt eutectic was deposited on Haynes 230 alloy to characterize the multilayer as a function of temperature. Our measurements were carried out in situ under ultra-high vacuum conditions. First, a thin film of a single Haynes 230 alloy layer was studied to characterize the alloy as a function of temperature before exposing it to molten salts. The structure of the Haynes 230 alloy film was measured between room temperature to 451 °C. Subsequent measurements were made with a thin film of salt sandwiched between two layers of Haynes 230 alloy at temperatures below the salt’s melting point with sample temperatures ranging from ambient to 383 °C. In both cases, a change in the Haynes 230 alloy structure is observed at around 160 °C. We will describe the environment chambers used for these measurements as well as our results of the behavior of the interfacial structure in these thin film systems.

2:30 PM EN17.07.04
Tritium Mobility and Local Chemistry in Fluoride Molten Salts Stephen Lam, Ronald Ballinger, Ju Li and Charles Forsberg; Massachusetts Institute of Technology, United States

Molten fluorides have been proposed for use as coolant in various advanced nuclear concepts including molten-salt reactors (MSRs), fluoride high temperature salt-cooled reactors (FHRs) and fusion devices. In these systems, significant quantities of tritium will be produced which must be captured and controlled to prevent a radioactive release. In order to efficiently remove tritium from the system, the transport and chemical properties must be well characterized and understood. Yet, difficulty in the handling of fluoride salts and tritium has resulted in relatively few experiments being conducted and large discrepancies across different studies. In this work, the transport and local chemistry of different tritium species (tritium fluoride and diatomic tritium) has been studied in the prototypical fluoride salts FLiBe (66.6-33.3 mol% LiF-BeF$_2$) and FLiNaK (46.5-11.5-42 mol% LiF-NaF-KF) using ab-initio molecular dynamics (AIMD). The methods were validated using experimentally well-characterized fluorides. Salts examined in this study include binary fluorides LiF, NaF, and NaF, and ternary fluorides LiF-BeF$_2$ and LiF-KF at various compositions. Radial distribution functions and coordination numbers from neutron diffraction, and diffusivities and activation energies from nuclear-magnetic resonance are accurately reproduced. Chemical species and structures were found by using graph-theoretic representations of the system at each time step and removing noise with probabilistic filtering methods. Over the temperature range from 873 to 1373K, the T$_2$ and TF diffusivities in FLiBe were found to be $D[\text{m}^2/\text{s}]=4.14E^{-7}\exp(-33.0[\text{kJ/mol}]/RT)$ and $D[\text{m}^2/\text{s}]=1.724E^{-7}\exp(-32.0[\text{kJ/mol}]/RT)$ respectively. At the same temperatures in FLiNaK, T$_2$ and TF diffusivities were $D[\text{m}^2/\text{s}]=1.38E^{-6}\exp(-39.0[\text{kJ/mol}]/RT)$ and $D[\text{m}^2/\text{s}]=4.94E^{-7}\exp(-41.0[\text{kJ/mol}]/RT)$ respectively. In both systems, TF exhibited 3-4 times lower diffusivity than the reduced form of tritium T$_2$. In both cases, decrease in diffusivity due to loss in mobility is attributed to TF reactivity and complexation in the salt. In FLiBe, TF was found to be bound to various BeF$_2$ molecules, while in FLiNaK, TF$_2$ complex was formed. In contrast T$_2$ molecules in both simulations were found to be stable in pure salt with limited chemical interaction in the solvent. The tritium diffusivities fall within range of experimental values and discrepancies between different experimental studies in literature were attributed to a combination of the following factors: differences in measured species (TF and T$_2$), presence of impurities (corrosion products, moisture) and differences in isotopes used (H, D, T). Large differences in tritium transport will have significant impact on assessing tritium control strategies, which typically rely on mass transport (adsorbents, permeation windows) and chemical condition (redox controls). This study provides a deeper understanding of chemical interactions and accurate chemical-transport data that can be used to predict macroscopic behavior and design engineering and control systems.

2:45 PM EN17.07.05
High Temperature Cell for In Situ Reflectometry of Molten Salts Mathieu Doucet, James F. Browning, Joohyun Seo and Gabriel M. Veith; Oak Ridge National Laboratory, United States

Next generation concentrated solar power systems and molten salts reactors have created new interest in molten salt
chemistry. The corrosion processes of the alloy used to contain the molten salts as a function of temperature remains to be fully understood. In particular, we are interested in the corrosion of Haynes 230 (approximately Ni>57 Cr22 W14) in contact with a KCl/MgCl₂ eutectic mixture for application in solar power systems. Our team has focused on studying this corrosion process in situ using neutron reflectometry. We will present the design of the high temperature cell that will enable us to perform those in situ measurements from room temperature to 850 C.

3:00 PM BREAK

SESSION EN17.08: Zirconium Cladding
Session Chairs: Simerjeet Gill and Joohyun Seo
Tuesday Afternoon, December 3, 2019
Sheraton, 3rd Floor, Hampton

3:30 PM EN17.08.02
Free-Energy Functional of the Zirconium-Hydride System from First Principle Calculations Michele Fullarton¹, Simon R. Phillpot¹, Yongfeng Zhang² and Larry K. Aagesen²; ¹University of Florida, United States; ²Idaho National Laboratory, United States

Zirconium based alloys for nuclear fuel cladding are known to precipitate hydride phases during operation. These precipitates can cause several issues including embrittlement leading to cracking and failure of the cladding. In order to predict the materials properties of the cladding the hydride phases must be accurately simulated. In this work the thermodynamic stability of phases in the zirconium-hydride system was evaluated using first principles-based methods. Cluster expansion techniques were employed to assess the stability of each phase over a range of concentrations at zero temperature. Phonon contributions for each ground state were calculated and combined with results of finite-temperature Monte Carlo simulations to create Gibbs free energies of the phases as a function of temperature and concentration. From these results a new phase diagram was generated, which will clarify discrepancies between different experimental phase diagrams. Moreover, the free energy functionals of all relevant phases were parameterized, allowing for more accuracy calculating microstructure and materials properties of cladding, for instance, in phase field simulations with INL’s MARMOT code.

3:45 PM EN17.08.03
Oxygen Stoichiometry Deviation in Amorphous ZrO₂ and Yttria-Stabilized Zirconia Simon C. Middleburgh¹, Michael Rushton¹, Iuliia Ipatova¹, Lee Evitts¹ and William E. Lee¹,²; ¹Bangor University, United Kingdom; ²Imperial College London, United Kingdom

Amorphous zirconia (a-ZrO₂) has been modelled using a combination of reverse Monte-Carlo, molecular dynamics and density functional theory together. This combination has enabled the complex chemistry of the amorphous system to be efficiently investigated. Interestingly, the a-ZrO₂ system was observed to accommodate excess oxygen readily through the formation of neutral peroxide (O₂²⁻) defects – a result that has implications not only in the a-ZrO₂ system, but also in other systems employing network formers, intermediates and modifiers. Similar conclusions are made for the yttria-stabilized zirconia system and has been corroborated with Raman spectroscopy data. These results have potential implications for materials behaviour in reactor systems: notably a mechanism for oxygen to be accommodated and transported through thin, amorphous zirconia films such as those expected at highly damaged grain boundaries - providing a mechanism for zirconium cladding corrosion.

4:00 PM EN17.08.04
Deformation and fracture of Zirconium Hydrides During Plastic Straining of Zr-4 Luca Reali, Said El Chamaa, Daniel S Balint, Mark R. Wenman and Adrian P. Sutton; Imperial College London, United Kingdom

Crack initiation in zirconium alloys is an important issue affecting the safety of nuclear reactors. Zirconium hydrides that precipitate in service are potential crack nucleation sites. In this work, the deformation and cracking of zirconium hydrides was studied during the deformation at room temperature of Zircaloy-4 samples up to fracture. Two hydrogen concentrations of 100 and 200 ppm were considered.
Hydrides precipitate both inside and at the boundary of the grains. It is expected that thicker hydrides and hydrides at the grain boundary are more prone to fracture. The main objective of this study was to better understand which of the two is the most important factor, and to identify at which point in the deformation of the alloy the first hydrides break. Micro voids thus nucleated may coalesce and be an important factor in understanding the fracture of these alloys. Scanning microscopy (SEM) images of a number of hydrides, both intergranular and intragranular, were taken at discrete increments of deformation, and the fraction of those that show evidence of fracture was estimated.

The results show that intergranular hydrides possess a lower deformability, which can be rationalised by analysing the conditions for slip transmission into and out of the hydride.

4:15 PM EN17.08.05
Hydrogen Pickup and Oxidation Kinetics of Zirconium Alloy—Dopant Effects from the Chemo-Mechanical Perspective Jing Yang, Mostafa Youssef and Bilge Yildiz; Massachusetts Institute of Technology, United States

Effect of alloying elements on zirconium alloy degradation properties has been widely studied because of its application in nuclear water reactors. It is observed in experiments that alloying element in zirconium alloy could result in different morphology of the passive film as well as different oxide film growth kinetics. The goal of this work is to study oxygen diffusion and hydrogen pickup processes in the ZrO2 passive film system under the effect of alloying elements, with varying temperature and chemical environment. In particular, we focus on the chemo-mechanical effect of Fe, Cr, Sn and Nb dopants in ZrO2 that exist in the oxide matrix as point defects from first-principles calculations. We show that the change in defect chemistry imposed by doping is strongly correlated with the valence states of the dopants. Fe and Cr, which are dominantly in +3 valence states, tend to decrease the concentration of oxygen interstitials and increase the concentration of hydrogen interstitials in ZrO2, thus suppressing oxide growth while increasing hydrogen pickup. Nb, on the other hand, is dominantly +5 and has the opposite effect. Changes in defect chemistry are accompanied by change in phase stability. We have discovered that Fe and Cr can strongly stabilize tetragonal-phase ZrO2 while Nb has a strong destabilizing effect. This effect provides insight for the different oxide film morphology of zirconium alloys with varying alloying element.

4:30 PM EN17.08.06
Influence of Boron Isotope Ratio on the Thermal Conductivity of Uranium Diboride (UB2) and Zirconium Diboride (ZrB2) Lee Evitts1, Simon C. Middleburgh1, Erofili Kardoulaki2, Michael Rushton1, Iuliia Ipatova1 and William E. Lee1,3; 1Bangor University, United Kingdom; 2Los Alamos National Laboratory, United States; 3Imperial College London, United Kingdom

Uranium diboride is being considered as an advanced fuel, while zirconium diboride remains a leading candidate for use as a burnable absorber, often coated on uranium dioxide fuel pellets. To ensure safe and efficient operation models need to be developed to enable the material to be modelled within a fuel performance code. Thermal properties of these materials are therefore investigated using density functional theory methods. It was found that the boron isotope ratio significantly varied the thermal conductivity for both materials. When compared to experimental data, the thermal conductivity for ZrB2 is well predicted, however, a significant discrepancy is observed for UB2. Potential reasons for the discrepancy, including the Hubbard factor and phonon relaxation times, are explored and discussed.
Radiation technology is widely used medical radiation therapy, radiation dosimeter, food preservation and other industrial applications. These include scientific research such as high energy physics, radiochemistry, change of material properties and so on. Radiation detection is one of important research area to safely use ionizing radiation. Several devices are investigated for radiation detection such as Silicon diode, metal-oxide semiconductor field effect transistors, thermo-luminescent dosimeters, optically stimulated luminescence dosimeters. These devices use semiconducting properties of organic and inorganic materials with electrical or optical connection for readout. In this study, we synthesized organic conjugated molecule for application to detection of gamma-ray without any readout devices. This molecule is consisted of two main parts. One is low-band gap conjugated core part, which is dithiophene moiety, for wide absorption in visible range. And the other is dicyanomethylene parts which are possible to induce band-gap change of dithiophene core part by gamma-ray. After irradiation gamma-ray with 1 Gy on film of the molecule, dark blue color is changed to yellow color due to change of band-gap from 1.74 eV to 2.16 eV. We investigate optical and electrical properties of the molecule by gamma-ray and we also discuss detail mechanism of color change and effect on the molecule by gamma-ray.

EN17.09.04
Anode Material Development for Scale-Up Oxide Reducer in Pyroprocessing Sung-Wook Kim, Min Ku Jeon, Sang-Kwon Lee and Eun-Young Choi; Korea Atomic Energy Research Institute, Korea (the Republic of)

Pyroprocessing has been investigated as an option to recycle and to manage spent nuclear fuels (SNFs) from pressurized water reactors. The oxide SNFs needs to be transformed to metallic states for electrochemical recovery of transuranic elements. In this respect, oxide reduction (OR) technique has been developed for the metal conversion. LiCl molten salt-based electrochemical reaction is the common OR technique. Conventional OR process is designed based on Li₂O recycle reaction. Li₂O is electrolyzed to form Li metal at cathode and O₂ gas at anode (2Li₂O → 4Li + O₂(g)). The Li metal subsequently reduces the oxide SNFs (e.g., UO₂ + 4Li → U + 2Li₂O) to release new Li₂O. Hence, Li₂O concentration in the LiCl salt is expected to be constant during the OR operation. Pt has been widely used as the O₂-evolving anode material because of its superior mechanical and chemical stabilities in the high-temperature oxidation environment.

Scale-up is an important issue on feasibility examination of pyroprocessing. The Pt anode, however, is not preferred in the large-scale system because it is gradually damaged upon the operation resulting in high processing cost. The Pt anode is known to have three anodic reactions depending on anode potential: Li₂PtO₃ formation (2Li⁺ + Pt + 3O²⁻ → Li₂PtO₃ + 4e⁻ at low potential), O₂ evolution (2O²⁻ → O₂(g) + 4e⁻ at medium potential), and anodic dissolution (Pt = Pt²⁺ + 2e⁻ at high potential). Only the O₂ evolution is required and thus the operation voltage of the Pt anode system should be carefully controlled (normally, ~3 V). Nevertheless, it was revealed that the side reactions cannot be avoided to induce the Pt anode deterioration, even in small-scale experiments (~15 g-UO₂). This would be due to non-uniform potential distribution across the Pt anode (by iR drop and other reasons) and local inhomogeneity of the Li₂O concentration in the salt. This should become more severe with the scale-up and it is considered that the precise control of the reaction pathway of the Pt anode would be very difficult in the large-scale equipment.

KAERI (Korea Atomic Energy Research Institute) has examined several materials to replace the Pt anode. One approach is to develop the O₂-evolving anode with better electrochemical stabilities using conductive ceramics and other noble metals. C anode was also suggested. The C anode system operates at high voltage range (>4 V) compared to the Pt anode system to decompose the LiCl salt to generate Cl₂ gas (2Cl⁻ → Cl₂(g) + 2e⁻) at the C anode. The advantages of the C anode are non-concern on the anodic reaction control and high operation current. In this presentation, the recent studies on the anode material development done at KAERI will be introduced.

EN17.09.05
Interaction Behavior between U-Zr Alloy Containing Lanthanides and Reusable Crucible Materials Seoungwoo Kuk, KyungChai Jeong, SeokJin Oh, KiHwan Kim and Jeong-Yong Park; KAERI, Korea (the Republic of)

A U-10 wt.% Zr alloy containing lanthanide elements (Nd, Ce, Pr, La) was introduced as a surrogate for transuranium alloys in metallic nuclear fuel. U-Zr alloys containing the lanthanide elements interact significantly with graphite crucibles. Conventional coating material, Y₂O₃ reduced the interaction, but partially interacted and detached from crucible after casting due to the difference in the thermal expansion coefficients of the crucible and the coating layer. The crucible was contaminated and could not thereafter be reused. Thus, it was considered a form of radioactive waste. Moreover, interacted materials could not be removed from the casting part and amounts of the
reaction reduced casting yields. Materials such as LaYO₃, SiC, TiC, and TiN along with density-improved Y₂O₃ were considered as candidates for use in the creation of a reusable crucible, which could be used to improve casting yields and to reduce radioactive wastes. The interactive behaviors of the candidate materials were considered by means of a sessile drop test. The annealing temperature was set to 1,450 °C for investigating interactions of the casting method. Microstructures of the candidate materials were observed using a scanning electron microscope (SEM), and their elemental distributions were characterized using energy-dispersive X-ray spectroscopy (EDS). Phase formations of the candidate materials were identified using an X-ray diffractometer (XRD). The material interaction was reduced by the enhanced Y₂O₃ coating and LaYO₃. A shortlist of candidate materials for use in the creation of a reusable crucible was drawn up based on the results of this research.

EN17.09.06
Reaction Characterization between Graphite Crucible and U-Zr Melt Seong-Jun Ha¹,², Jeong-Yong Park², Seoungwoo Kuk³, KyungChai Jeong², Sang Gyu Park², Young-Mo Ko³, Yoon-Myeng Woo³ and Young-Kook Lee¹; ¹Yonsei University, Korea (the Republic of); ²Korea Atomic Energy Research Institute, Korea (the Republic of)

U-Zr metallic fuels have been developed as a nuclear fuel for Sodium-cooled fast reactor because metallic fuels are related to excellent reactor safety and fuel cycle economy. In the fabrication process of U-Zr metallic fuels, the graphite crucible is commonly used for melting and casting and yttrium oxide is coated on the inner surface of the graphite crucible to prevent the reaction with melted U-Zr alloy. It is crucial to prevent the reaction between the melt and crucible for controlling the loss in the fabrication. In this study, we investigated the reactivity between uranium, zirconium and graphite crucible. The graphite crucible was used to clarify how the graphite react with melt uranium and zirconium. U-10wt.%Zr alloy was melted using injection casting apparatus which is an induction furnace. Raw materials consisting of zirconium sponge and uranium metal were charged in the graphite crucible in the order named. The materials were superheated at 1,600°C for alloying and it was cooled in the furnace after alloying. Microstructures in the surface region of the melt-residue of U-Zr alloy were characterized using Scanning electron microscopy (SEM) equipped with Energy dispersive X-ray spectroscopy (EDS). Although the graphite crucible was used for melting uranium and zirconium, the U-10wt.%Zr melt residue was fabricated without alloying between uranium and the graphite crucible. The melt residue was easily separated from the graphite crucible. However, the reaction layer was formed on the surface of U-10wt.%Zr melt residue. The reaction layer mostly consisted of carbon and zirconium. The thickness of reaction layer was about 5 μm at side region and 10 μm at bottom region. The bottom region had the thickest reaction layer among whole surface because first of all, zirconium was reacted with graphite crucible at the bottom region when the charged raw materials were heated. The thickness of the reaction layer was assumed as the depth penetrated into the U-Zr matrix from the graphite crucible depending on the volume of the zirconium, melting temperature and time. The surface of melt residue was investigated using X-ray diffractometer (XRD). As a result of XRD analysis, ZrC and U₃O₇ were detected on the reaction region. It is likely that C was contaminated from graphite crucible. The quantitative chemical composition of graphite crucible was investigated using Inductively coupled plasma-atomic emission spectroscopy (ICP-AES). As a result of ICP-AES analysis, uranium and zirconium were contaminated at contact region. On average, uranium and zirconium contents of graphite crucible were 281 and 31 ppm but it was a considerable difference according to the position. In this study, U-10wt.%Zr alloy was fabricated in the optimizing manufacturing process to examine the reactivity between uranium, zirconium and graphite crucible. The reaction layer consisted of zirconium and carbon is formed on the whole surface of the melt residue because zirconium is commonly reacted with carbon at the contact region with graphite crucible. The graphite crucible is also contaminated with uranium and zirconium when melting.

EN17.09.07
Combined Ab Initio and Empirical Model for Irradiated Metal Alloys with Focus on Uranium Alloy Fuel Thermal Conductivity Shuxiang Zhou¹,², Ryan Jacobs¹ and Dane Morgan¹; ¹University of Wisconsin-Madison, United States; ²Idaho National Laboratory, United States

High-quality thermal conductivity data is critical to the rational design of materials for applications ranging from thermoelectrics to nuclear reactors. However, such data is experimentally and computationally challenging to obtain due to any or all of cost, technical hurdles, and time requirements. The thermal conductivity of these materials can be further influenced by their working conditions, e.g. irradiation, due to the microstructure changes. Therefore, practical models and quantitative understanding of the thermal conductivity, including changes due to microstructure, is essential to support the development of new materials. In this work, we developed a computational model of thermal conductivity of irradiated metal alloys based on
density functional theory (DFT) calculations, semi-classical scattering theory, and experimental data. This approach has been applied to model the electrical and thermal conductivity of alpha uranium previously, and can be extended to model the conductivities of U-alloys like U-Zr and U-Mo. The present model incorporated the contributions of point defects (vacancies and transmutation products), grain boundaries, and noble gas bubbles (inter- and intra-granular) resulting from irradiation. The effects of point defects and grain boundaries are modeled by both DFT calculations and semi-classical scattering theory, and the effect of noble gas bubbles are modeled using empirical models. The utility of our model is demonstrated on U-Mo alloys, which are promising nuclear fuel materials for use in next generation nuclear reactors, and displays semi-quantitative agreement with experimental data with a root-mean-square error of about 0.8 W/m-K (~7% error versus experiment) over the typical operating temperature and burn-up range for U-Mo alloys. This work provides insight into the semi-quantitative relationships of the thermal conductivity changes resulting from the different irradiation-induced changes in atomic structure and microstructure over a wide range of temperatures, and shows that scattering of electrons from point defects produce the majority of the reduction of the thermal conductivity of U-Mo alloys under irradiation. As an example, at 50% U235 burn-up, the thermal conductivity decreases about 20% due to the effect of point defects, while grain boundary and gas bubble formation contribute only about another 10% decrease. Furthermore, our model can be straightforwardly applied to different irradiation conditions or microstructures by changing the values of a few corresponding parameters.

The present model both serves as a powerful tool for quantitative semi-empirical modeling of thermal conductivity in irradiated metals, and for materials design insight for the control of thermal conductivity in metal alloys in applications experiencing irradiation, such as the further development of advanced metallic U-alloy nuclear fuels.

EN17.09.08
Effects of Initial Microstructure on the Hot Extrusion Properties of Annular Fuel after Extrusion Sang Gyu Park, Seoungwoo Kuk and Jeong-Yong Park; KAERI, Korea (the Republic of)

The innovative fuel development is the development of the advanced sodium-cooled fast reactor metallic fuel concepts. The fabrication experiment seeks to investigate advanced fuel designs with the following features: decreased fuel smeared density, venting of the fission gas to the sodium coolant, reduce the FCCI (Fuel Cladding Chemical Interaction), and an advanced fabrication method that includes consideration of annular fuel and extrusion method. The one of most attractive advantage of extrusion method is save the process waste by omitting the sodium process. From the previous study, annular fuel shows the possibility of the reduction of swelling effect and then prevention of the FCMI (Fuel Cladding Mechanical Interaction). However, the fabrication technology of the annular fuel has not been developed yet. Hence, KAERI is developing the extrusion type metal fuel manufacturing technology as a part of the development of the original technology for the production of innovative metal fuel. In this study, the prototype of annular fuel has been fabricated by using Cu billet. The design of billet and annular fuel has been determined, and then and design and material for the mold has been determined by using Deform 3D program. After the mold fabrication, the prototype annular fuel has been fabricated and its texture were examined by us EBSD (Electron Back Scatter Diffraction). There are two types of billets were used for the extrusion in this study; one is drawn billet which has very fine grains(<less than 100um), and the other is casted billet that has very coarse grains (<500um). When we compared the grain size after extrusion, the microstructure of the drawn billet showed a grain size of at most 100um or more, which is relatively coarser than that of the extruded annular fuel. Therefore, it is considered that the non-anisotropic crystal tendency analyzed after extrusion production is attributed to the fact that the crystal grains used in the processing billet are already small in size. On the other hand, the texture of annular fuel from the casted billet shows very coarse and anisotropic tendency after extrusion. Therefore, the control of initial texture of billet seems the main factor for the annular fuel microstructure. The fabrication methods for the billet microstructure control will be discussed.

EN17.09.10
Determination of Dose Effects on Defect Accumulation under Irradiation in Nanoporous Gold and Niobium via Atomistic Simulations Daniel E. Vizoso1,2, Chaitanya Deo1 and Remi Dingreville2; 1Georgia Institute of Technology, United States; 2Sandia National Laboratories, United States

This study explores the radiation resistance of metallic nanofoams and nanowires via atomistic simulations. Nanostructured metals present a high density of interfaces and surfaces as sinks for radiation produced point defects and thus may offer a means to developing radiation tolerant materials. Current work in the modeling of radiation
damage in nanofoams and nanowires typically considers defect accumulation due to a small number of primary knock on atoms. For this work, dose effects have been investigated by varying the number and energies of primary knock on atoms, including the consideration of damage accumulation due to damage events with a spectrum of energies. The study investigates the impact of structural properties such as ligament length and diameter on defect accumulation mechanisms and defect properties, such as formation and binding energies as well as the relationship between energies of the primary knock on atoms and changes in mechanical properties. This analysis is performed in two different nanoporous material systems: gold and niobium. The radiation response of nanoporous gold has been studied both experimentally and computationally, although previous computational works have been limited in the doses considered. Nanoporous niobium is a material system that has been previously synthesized but not had its radiation response characterized either computationally or experimentally. The comparison of the radiation responses of nanoporous gold with that of nanoporous niobium also allows for an investigation into the differences in behavior between bcc and fcc nanoporous media. Results suggest that the presence of interfaces and surfaces in nanofoams affects the formation and migration of defect clusters leading to a more radiation resistant metallic structure.


EN17.09.11
Reusable Multifunctional 3D Graphene Electrode for Highly Efficient In Situ Extraction of Uranium from Mining and Contaminated Solution
Ahmed Elwakeil, Chao Wang and Ju Li; Massachusetts Institute of Technology, United States

The potential strategic application of uranium in nuclear power industry, as well as the environmental and human health problems caused by uranium, promotes the development of reliable methods for in situ extraction of U (VI) from different solutions. Herein, a unique multifunctional three dimensional electrodes have been fabricated by simple hydrothermal method and used as outstanding electrosorbent for uranium extraction from different aqueous solution. The electrochemical sorption method solves the conventional drawbacks of other methods by using fixed potential to guide the movement of uranium ions in the solution and increase the collision rate onto the electrode surface, resulting in faster kinetics and higher adsorption capacity, easier scaling up, and high selectivity due to specific grafted functional groups. The fabricated electrode was characterized by RAMAN, FTIR, XRD, STEM, EDS, XPS before and after uranium loading. The adsorption capacity for U(VI) ions with our multifunctional 3D electrode is estimated to be 4800 mg/g at pH 5.2 without reaching saturation exhibiting the highest reported sorption capacity compared with other electrochemical methods. The fabricated electrode can be efficiently regenerated and recycled for at least 7 times in uranium solution with concentration 40th times higher than initial concentration without any observable change in efficiency. This work represents the first application of multifunctional 3D electrode for uranium extraction from mining solution and contaminated ground water.

EN17.09.13
Glass Degradation and pH Changes in Narrow Openings of Cracks
Rama Krishna Chinnam1,2 and William E. Lee2,3; 1University of Limerick, Ireland; 2Imperial College London, United Kingdom; 3Bangor University, United Kingdom

In an earlier degradation study on partially immersed international simple glass (ISG), it was found that water near the surface of the ISG or localised variation in pH resulted in discrepancy of glass dissolution and variation in precipitates size on the glass surface. Another finding in the study was the formation of pits on the glass surface under the gel layer [1].

In continuation to the above study, new experiments were designed to understand and measure the pH changes in the localised regions of the glass. For this purpose
1. A study was performed to understand the influence of confined narrow opening on the glass degradation. This experiment helps to understand the environment between gel layer and glass, and to simulate the degradation conditions inside a glass crack.
2. A study was performed to understand the change in pH of the water inside a glass crack with access to fresh water and glass cracks without access to fresh water.
In 1st study, two ISG slides were stacked, an excessive gel layer was found at the outer rim of the interface and the gel layer was found absent at the centre of the interface with a clear boundary between the two regions. This effect was studied under the electron microscope and the TOF-SIMS to confirm the chemical composition difference between the two regions. Thus indicating that degradation in narrow openings of glass is quite different.

In 2nd study, water inside cracks with access to fresh water was found to exhibit pH 10 and pH 8. Water in the cracks with no access to fresh water was found to exhibit pH 11, pH 12 and pH 13. The change in the pH of water in cracks is related to the depth of the crack and position in the water. Thus confirming that cracks exhibit different pH conditions than surrounding water, fresh water availability and their position within water.


EN17.09.14
Investigations in the UB2-UO2 Advanced Fuel System Fabio Martini¹, Iuliia Ipatova¹, Lee Evitts¹, William E. Lee¹, Michael J. Rushton¹, Antoine Claisse² and Simon C. Middleburgh¹; ¹Bangor University, United Kingdom; ²Westinghouse Electric Sweden AB, Sweden

Uranium borides are attractive candidates for advanced nuclear fuels. In particular, uranium diboride-based fuels are expected to outperform – in terms of thermal conductivity and spatial uranium density – their currently-used counterparts based on uranium dioxide. Nevertheless, uranium diboride is expected to be less tolerant than uranium dioxide upon accidental contact with water and other oxidizers at high temperatures. The dispersion of uranium diboride in a uranium dioxide matrix is seen as a possible solution that combines the advantages of both compounds, affording a composite material that has a greater thermal conductivity and spatial uranium density than pure uranium dioxide while maintaining its resistance to oxidation.

The interface chemistry of UO2-UB2 systems has been investigated via temperature dependent atomic scale simulations.

EN17.09.15
Multifunctional Nanoceramic Barrier for DEMO Breeding Blanket Concepts Boris Paladino¹,², Daniele Iadicicco¹, Matteo Vanazzi¹,², Patricia Munoz¹, Teresa Hernandez¹, Serena Bassini¹, Marco Utili¹ and Fabio Di Fonzo¹; ¹Istituto Italiano di Tecnologia, Italy; ²Politecnico di Milano, Italy; ³CIEMAT, Spain; ⁴ENEA, Italy

The realization of the breeding blanket system represents one of the crucial points in the design of future generation fusion reactors. At the time being, issues related to materials compatibility persist. According to the most relevant design, fusion reactors will take the Tritium-Deuterium fusion as the reference reaction for power generation. Thus, the availability of Tritium to fuel the reactor core assumes relevant importance. The breeding process represents one of the main focus points of technological R&D activities and the inhibition of Tritium permeation is mandatory to achieve Tritium balance in the reactor chain: once Tritium is produced, an adequate permeation barrier is required to confine it. At the moment, two are the eligible breeding materials under investigation: a flowing Pb-16Li eutectic alloy and a pebble bed composed by sintered Lithium ceramics and Beryllium. It was demonstrated that both these two materials lead to severe corrosive attack of the steel constituting the breeding blanket modules (RAFM steel), hence threatening the mechanical integrity of the whole structure. It is thus clear that materials are proving to be one of the major bottlenecks for this technology. In order to undertake these issues, we report on multifunctional nanoceramic oxide coatings grown by Pulsed Laser Deposition (PLD) technique. Oxides were chosen because of their chemical inertia and thermodynamic stability. Among these, Aluminium Oxide and Yttrium Oxide were identified as promising candidates. Deposited films appear dense, compact and well adherent on the steel substrates, showing optimal metal-like mechanical properties combined with high hardness. Morphological and crystalline features were evaluated in the case of as-deposited and annealed samples. A deep characterization was performed by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), Fourier Transform Infrared spectroscopy (FTIR) and X-ray Diffraction (XRD). Also, coatings of these materials have been tested as Tritium permeation barriers with Hydrogen at different temperatures (from 350°C to 650°C). They showed a permeation reduction factor (PRF) up to 10⁵ at 650°C. These results have been confirmed also in the case of Deuterium permeation, both under 1.8 MeV electron irradiation and for samples that were previously irradiated with ions. In addition, to evaluate the chemical compatibility of the films with the selected breeding materials, samples have been exposed to corrosion tests (both Pb-16Li and Lithium ceramic pebbles) up to 10000 hours. No corrosive attacks on the steel substrate were detected. Finally, Atomic Layer Deposition technique has been studied and recently employed as a
complementary deposition technique to the PLD. The deposition process is still at its early stages of development, but preliminary results show that the coatings thus produced are dense, compact and defect-free. A deeper characterization of these coatings will follow. To conclude, in a DEMO-oriented perspective, oxide coatings present interesting properties as multifunctional protective barriers, proving to be one of the few possible solutions for the material-related issues of all the breeding blanket concepts currently considered.

**EN17.09.16**

**Experimental and Computational Study of Lattice Anharmonicity Effects in Oxide Nuclear Fuels** Zilong Hua¹, Amey Khanolkar¹, Marat Khafigov², Yuzhou Wang³, Chris Marianetti³, Lyuwen Fu¹ and David Hurley⁴; ¹Idaho National Laboratory, United States; ²The Ohio State University, United States; ³Columbia University, United States

Thermal transport in nuclear fuels under irradiation is directly linked to reactor efficiency and safety. An insight into the fundamental thermal transport properties of 5f-electron materials under extreme irradiation environments is central to the development of advanced nuclear fuels. Investigating the effects of lattice anharmonicity can provide a deeper understanding of the thermal properties such as thermal conductivity, heat capacity and thermal expansion, and be used to accurately model thermal transport. Here, we present the latest study on lattice anharmonicity effects in advanced oxide fuels. Time-domain Brillouin Scattering (TDBS) has been used to generate and detect lattice vibrations associated with the propagation of quasi-longitudinal and quasi-shear elastic phonon modes along the (311), (111), and (100) directions in single crystal thorium oxide (ThO₂). Measurements of the temperature-dependent change in phonon velocities have been performed at various temperatures ranging from 77 up to 350 K to experimentally obtain the Gruneisen parameter. The value is then compared with those obtained from first-principles computation using density functional theory (DFT), and more related simulation and experimental work (i.e., Boltzmann Transport Equation (BTE) modeling, inelastic neutron and x-ray scattering measurements, and the characterization of thermal conductivity, heat capacity, and thermal expansion) are underway. This study is supported by Thermal Energy Transport under Irradiation (TETI), a recently awarded Energy Frontier Research Center. The mission of the center is to provide foundational work to understand the role of 5f electrons on phonon and electron structure of related materials and how irradiation defects influence electron and phonon transport and corresponding thermal conduction.

**EN17.09.17**

**Combined Molecular Dynamics and Sol-Gel Synthesis to Investigate the Properties of the Pellet-Clad Bonding Layer** Dillon Frost¹,², Jessica Carolan-Veliscek², Conor O. Galvin¹, Edward Obbard¹, Michael W. Cooper³ and Patrick A. Burr¹; ¹UNSW, Australia; ²Australian Nuclear Science and Technology Organisation, Australia; ³Los Alamos National Laboratory, United States

The typical burnup of currently operating nuclear reactors is around 47 GWd/MTU, which coincides with the onset of permanent bonding between UO₂ fuels and zirconium alloy claddings in water cooled reactors. The bonding between pellet and cladding occurs as a result of the oxidation of Zr-alloy cladding and subsequent bonding with the UO₂ forming a solid solution of (U,Zr)O₂. The impact of this pellet-clad bonded layer increases with increasing burnup. In order to extract more energy from nuclear fuels and increase time between refuelling, operators are increasing burnups beyond 50 GWd/MTU. This research looks at the impact of urania-zirconia mixed oxides [(UₓZr₁₋ₓ)O₂] on nuclear fuels at high burnups.

The following thermophysical properties of (UₓZr₁₋ₓ)O₂ were investigated as a function of composition and temperature: lattice parameter, thermal expansion, heat capacity and thermal conductivity. A combination of molecular dynamics and experimental methods were used to provide a means of prediction and validation. Mixtures of (UₓZr₁₋ₓ)O₂, where x = 0.25, 0.50, 0.75 and 0.9, were produced using sol-gel synthesis to enhance the mixing of cations and achieve a homogeneous solid solution. The results indicate that by increasing the concentration of Zr in (UZr)O₂ mixtures the thermal conductivity is degraded slightly at room temperature, becoming negligible at temperatures at and above reactor operating temperatures. However, the formation of t-ZrO₂ on the inner surface of the cladding at moderate burnups (20 – 30 GWd/t) is a barrier to thermal transfer being that the thermal conductivity of t-ZrO₂ is 50% lower than that of UO₂. Additionally, the lower temperature access to superionic transitions due to oxygen disorder could provide some benefit under accident conditions due to the significant increase in heat capacity around 1500-2000 K. This research shows that the impact of (U, Zr)O₂ at high burnups is positive in that it does not affect the thermal conductivity of UO₂ significantly and, due to the permanent bonding of clad and fuel, could enhance thermal throughput given the thermal conductivity of the bonded layer is an order of magnitude
SiC and W-SiC functionally-graded coatings have been fabricated and exposed to deuterium (D) plasma bombardment at different surface temperatures and ion impact energies in the PISCES-E radio frequency (RF) plasma source [1] to assess their viability as a plasma-facing material (PFM) in a magnetic confinement nuclear fusion device. In situ optical emission spectroscopy (OES) revealed that CD emission, which approximates C chemical erosion, increased with ion impact energy up to 80 eV. Chemical erosion of Si was not observed spectroscopically via the SiD molecular band. Post-mortem Auger electron spectroscopy (AES) measured a <15% increase in relative Si content within the first few hundred nm of the surface. Si enrichment was likely due to preferential erosion of C atoms, as indicated by the asymmetric spectroscopic emission mentioned above. Erosion due to physical sputtering may have also been higher for C than for Si, as shown in [2]. The amount of D retained in samples due to implantation increased by a factor of ~5 between 20 eV and 50 eV, likely due to the onset of ion-induced, extrinsic trap formation. Overall retention was 1.7-2.5× higher in SiC than in W exposed to identical plasma irradiation. The pure W surface of the W-SiC functionally-graded coatings survived plasma exposure at a fluence of $10^{25}$ m$^{-2}$, as confirmed by AES measurements. Overall erosion of the W-SiC coating was around 2.3× higher than that of pure, crystalline W samples exposed to the same conditions. D retention in the W-SiC coatings exhibited combined trap behavior of both W and SiC samples, and was >10× higher than retention in SiC and W samples. High erosion and retention values may have been an artifact of the coating process, resulting in increased intrinsic trap density and reduced lattice displacement and surface binding energies.

SiC has been considered for use as a PFM in future magnetic fusion devices due to its excellent mechanical strength under neutron irradiation, high thermal strength, and low hydrogenic diffusivity. Tungsten is currently the leading PFM candidate, due to favorable thermal and mechanical properties and low erosion. However, concerns regarding its strength under intense neutron irradiation and its detrimental effect on plasma performance when eroded have led to research on other material candidates, such as SiC. Recent experiments in DIII-D showed that SiC exhibited lower levels of chemical sputtering than that of graphite (a common PFM) [3]. These results motivated further characterization of fundamental plasma-material properties in a dedicated plasma source. SiC samples (coating thickness = 100-200 µm) and W-SiC samples (coating thickness = 10 µm) were fabricated in-house via chemical vapor deposition (CVD) and RF magnetron sputtering, respectively, on ATJ graphite substrates. W-SiC coatings exhibited a stepwise concentration gradient of 100% W at the surface to 100% SiC at the coating-bulk interface. These samples, along with W and ATJ graphite reference samples, were exposed to D RF plasmas in PISCES-E at a flux of $5 \times 10^{20}$ m$^{-2}$ s$^{-1}$, $T_e$ of ~3 eV, $n_e$ of $3.5 \times 10^{16}$ m$^{-3}$, and surface temperature of 500 K. In situ OES was used to track erosion products and was quantified via the SXB/DXB method. Overall erosion was measured using a microbalance with a resolution of 0.01 mg. AES was used to measure changes in surface composition due to plasma exposure. Post-mortem thermal desorption spectroscopy resolved the major traps present in the material and estimated overall retention. Qualifying new SiC-based materials in a dedicated plasma source may demonstrate a superior alternative for next-generation fusion reactor materials.

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Structural components of nuclear reactors must fulfill a series of mechanical and stability properties according to the specific range of experimental conditions they will be submitted during the operation of the reactor. Since the beginning of the construction of generation-II Pressurized Water Reactors (PWR’s) in the 1960’s, austenitic stainless steels from the AISI 300 series have been widely used as structural components for the fuel cladding, due to their high-temperature corrosion-resistance and mechanical strength. The variation of neutron flux along the core of a nuclear reactor presents a challenge to the materials used to build the various components of the core, considering that for a non-steady flux the effects on structural properties also varies. Wiedersich, Okamoto and Lam (WOL) proposed a model to specify irradiation conditions of dose rate and temperature where significant RIS should occur, being limited by an increase in the thermal concentration of vacancies at high temperatures and recombination of vacancies with interstitials at higher dose rates. In this work, we report the formation of radiation-induced precipitation (RIP) on an AISI 316L steel under in-situ 325 keV Xe ion irradiation/implantation for three different fluxes (1, 2 and $4 \times 10^{12}$ ions.cm$^{-2}$.s$^{-1}$) up to the same total dose within a transmission electron microscope (TEM) at MIAMI facilities at the University of Huddersfield, UK. All experiments were performed at 550 °C. Statistical analysis from bright-field images under phase contrast and selected area electron diffraction (SAED) were used to characterise the precipitates formed in the samples analysed. The nucleation and growth of second phase precipitation are observed to vary significantly according to the flux the sample is submitted. An overlapping of consecutive cascades at higher fluxes is proposed to explain the different behaviours for the evolution of RIP’s, and a small deviation on the lower limit of the WOL’s model is suggested.

SESSION EN17.10: Nuclear Materials—Ceramics and Composites
Session Chairs: Remi Dingreville and Arielle Miller
Wednesday Morning, December 4, 2019
Sheraton, 3rd Floor, Hampton

8:15 AM *EN17.10.01
Radiation Damage in Ceramics—The View From Microscopy Karl R. Whittle; University of Liverpool, United Kingdom

In the continued development of materials for use within a nuclear reactor, whether it be fission or fusion based, how a material behaves under the extremes of damage radiation is a key factor in its applicability. The impacts arising from radiation induced damage are generally damaging, ranging from local damage through to full amorphisation, or the formation of new phases both by equilibrium or non-equilibrium synthesis. Such changes often have macro-scale impacts, for example a reduction in thermal conductivity, or change in a ductility. However, they key length scale at which all changes can be considered is at the nano-scale, where damage can be visualised most easily.

Using electron microscopy as a key aid in determining the impacts from damage, a range of systems, primarily ceramic in nature, will be discussed. Such materials are key components in multiple next generation reactor technologies, whether it be fission or fusion, fuel or structural in application. Regardless of the application, there are common factors that influence a response to radiation induced damage, and the examples presented here will help link the common themes, whether they be compositional or structural in nature.

8:45 AM EN17.10.02
Modelling of Crack Nucleation and Propagation in SiC/SiC Accident-Tolerant Fuel During Routine Operational Transients Using Peridynamics Thomas Haynes and Mark R. Wenman; Imperial College London, United Kingdom

Zirconium-based alloys have been successfully used for light water reactor fuel claddings since the 1960s. Despite their excellent performance during routine operation, during severe accidents such as the one which occurred at Fukushima Daiichi in 2011, they can undergo rapid exothermic oxidation. This releases hydrogen and supplies a great deal of heat, accelerating the accident. Over the last decade, there has been a concerted effort by the nuclear fission community to develop and implement accident-tolerant fuel designs. One design showing promise is SiC/SiC composite claddings. These consist of a β-phase fibre weave surrounded by β-phase SiC matrix. Despite their
strength and improved oxidation performance, the proposed claddings have a number of drawbacks. Namely their
irradiation swelling and low thermal conductivity. Their irradiation swelling saturates after a number of months in
reactor and is greater on the colder outer surface than the warmer inner surface. The thermal conductivity lower
than for zirconium alloys and is worsened by irradiation swelling.

Peridynamics is a developing non-local modelling technique which has the ability to model crack initiation,
propagation and branching. Unlike finite element analysis, the technique uses an integral formulation to determine
the forces upon material points. This means that crack patterns can be predicted without any a priori knowledge of
the loading or crack pattern.

A peridynamic model for composite SiC/SiC cladding has been developed in the Abaqus finite element code. The
material model was isotropic and considers matrix cracking and fibre pull-out. The thermal expansion, swelling and
the degradation of the thermal conductivity are modelled under typical LWR irradiation conditions. The swelling on
the outer surface is greater than the inner surface due to the lower irradiation temperature, causing a tensile stress on
the inside of the cladding. This stress increases during the decrease in power at the start of a typical pressurised
water reactor refuelling outage and causes microcracking of the matrix on the cladding inner surface. In models
without fibres, cracks would propagate through the cladding. If fibres are modelled, matrix cracking will extend to a
depth of around 20% through the cladding from the inner surface. If an inner monolith of SiC is additionally
modelled, cracking propagates through the monolith and acts as a stress raiser for matrix cracking in the composite.
If an outer SiC monolith is modelled, fibre pull-out on the inner surface of the cladding was increased by just under
70%.

9:00 AM EN17.10.03
Irradiation of Carbide Composites for Next Generation Nuclear Reactors Daniel Rutland; University of
Liverpool, United Kingdom

Future generations of nuclear reactors are required to operate at higher temperatures and under more extreme
radiation conditions than the current generation, creating a need for novel materials for use in these environments.
Silicon carbide (SiC) has a number of desirable characteristics for use in reactors but some properties can deteriorate
under irradiation. A potential option to improve the radiation resistance is to combine SiC with other carbides such
as Titanium carbide (TiC) and Zirconium carbide (ZrC).
To determine the properties of these samples, they can be exposed to high radiation environments and electron
microscopy and diffraction techniques can be used for characterisation and analysis of the materials.

Initial samples of SiC/TiC composites have been produced and irradiated in several facilities, with bulk irradiation
using 93 MeV Pb ions and in-situ irradiation using 1 MeV Kr ions. The in-situ TEM imaging indicates different
responses rates to radiation damage in the TiC phases and the SiC phases. Diffraction of these areas indicates almost
immediate amorphisation of the SiC phases, with TiC phases retaining distinct grain boundaries, which is supported
by X-Ray Diffraction (XRD) of bulk irradiated samples. The results from these samples are used to guide the
fabrication and characterisation of the next set of samples. These samples produced are SiC/ZrC and SiC/TiC
composites, each with ratios of 30:70, 50:50, and 70:30. The raw powders are milled at low-speed in inert gas,
before being sintered using spark plasma sintering (SPS) at 1600-1900 °C. The results of these samples will be
discussed in this talk.

9:15 AM EN17.10.04
Radiation Tolerance of Stabilized Alumina Coatings—An In Situ Irradiation Study Matteo Vanazzi1, Davide
Loiacono1,2, Wei Chen3, Meimei Li3, Marco G. Beghi2 and Fabio Di Fonzo1; 1Istituto Italiano di Tecnologia, Italy;
2Politecnico di Milano, Italy; 3Argonne National Laboratory, United States

Future generation nuclear reactors – either fission or fusion systems – present intrinsic benefits in terms of
economics, safety and waste management. However, to allow the deployment of these technologies, innovative
material strategies must be designed and implemented. Recently, coatings have earned great attention in the nuclear
field as a reliable cost-efficient solution. Indeed, they could tackle major issues such as corrosion, erosion,
hydrogen/tritium confinement, etc. In this framework, amorphous/nano-crystalline alumina coatings developed by
the Istituto Italiano di Tecnologia (IIT) have been extensively characterized as corrosion-resistant anti-diffusion
Alumina films have been tested under ion irradiation, proving high stability up to 150 dpa. This radiation tolerance is related to the amorphousness of the pristine material, which evolves towards a crystalline structure under irradiation. To preserve these enabling mechanisms and improve the range of operation (in terms of life time and operation temperature), the amorphous matrix must be conserved as long as possible. In this work, the stabilization of alumina by doping is evaluated under different conditions. Firstly, pure and doped materials have been compared by thermal annealing, showing a significant increase in the crystallization temperature (from 650 °C to more than 800 °C) for the stabilized alumina. Then, irradiation tests have been performed with *in situ* TEM at the IVEM-Tandem facility at ANL. Samples have been irradiated with different ions (350 KeV Kr and 500 KeV Au) up to 20 dpa. Experiments have been conducted at 600 °C - for the sake of consistency with previous ion irradiation tests - and at 800 °C, to observe the accelerating effect of irradiation on the thermally activated crystallization process. Albeit both the materials withstand the ion irradiation without delamination or structural failure, doped alumina retards the crystallization threshold even under irradiation. Moreover, at significant levels of radiation damage, the presence of doping stabilizes the low-energy metastable phases of alumina, conserving partially the pristine characteristics. This behavior, especially at the highest temperature, improves further the radiation tolerance of the material: while pure alumina suffers from voids formation after crystallization (a traditional phenomenon for the bulk oxide), no swelling appears in the doped counterpart. To conclude, *in situ* ion irradiation tests have been performed on stabilized nano-ceramic coatings. The presence of doping slows down the material evolution under irradiation, preserving the well-established properties of the pristine coating. The outcomes of these experiments represent a major step forward in the qualification process of coatings for nuclear reactors.

**9:30 AM EN17.10.05**

*Metal/Carbon Nanotube Composites Enhance Strength and Ductility, Even During Radiation Damage* Kang Pyo Seo¹, Penghui Cao², Young Hee Lee³, Michael P. Short¹ and Ju Li¹; ¹Massachusetts Institute of Technology, United States; ²University of California, Irvine, United States; ³Sungkyunkwan University, Korea (the Republic of)

The accumulation of defects during irradiation leads to material property degradation modes such as embrittlement and swelling, eventually causing material failure. Effective and efficient removal of defects is of crucial importance to design radiation damage-tolerant materials. Here, by biasing defect migration pathways via carbon nanotube (CNT) infiltration, we present a greatly enhanced damage-tolerant Al-CNT composite with defect storage measured to be one order of magnitude lower than that in pure, irradiated Al. Furthermore, extreme-value statistics (largest size) of defect clusters are significantly changed in the presence of CNT. *In situ* ion irradiation transmission electron microscopy (TEM) experiments and atomistic simulations together reveal the dynamic evolution and convergent diffusion of radiation-induced defects to CNTs, facilitating defect recombination and enhancing radiation tolerance. The occurrence of CNT-biased defect convergent migration is tuned by the thermodynamic driving force of stress gradient in Al matrix due to the CNT phase transformation. This approach to controlling defect migration using 1D interface engineering creates a new opportunity to enhance the properties of nuclear materials.

**9:45 AM EN17.10.06**

*Investigation of Helium Precipitates in Ta(Ti)/Zr(Ti) Nanocomposites* Sisi Xiang, Kelvin Y. Xie, Ian McCue and Michael J. Demkowicz; Texas A&M University, United States

Metal degradation due to implanted helium (He) is a concern in nuclear energy applications. We investigate the size and distribution of He bubbles in Ta(Ti)/Zr(Ti) composites using transmission electron microscopy. He implanted composites are compared to both the unimplanted material as well as the individual constituents of the composite. Nano-scale He bubbles form in different quantities in the two components of this composite as well as at the curved Ta(Ti)/Zr(Ti) interfaces within the materials. We discuss the consequences of our findings for the development of radiation resistant materials with complex, hierarchical microstructures.

**10:00 AM BREAK**
Wednesday Morning, December 4, 2019
Sheraton, 3rd Floor, Hampton

10:30 AM EN17.11.01
Reduced-Order Atomistic Method for Simulating High Dose Irradiation in Metal Elton Chen¹², Chaitanya Deo¹ and Remi Dingerville²; ¹Georgia Institute of Technology, United States; ²Sandia National Laboratories, United States

Atomistic modeling of irradiation damages through displacement cascades is deceptively nontrivial. Due to the high energy, high velocity nature of the atom collisions, individual cascade simulations can become very computational expensive and ill-suited for size and dose upscaling. In order to examine microstructural evolutions, and mechanical property changes due to defect accumulation, alternative methods of modeling radiation defect accumulation are needed. Originally developed for application in ceramic materials, the Frenkel Pair Accumulation (FPA) method generates point defect pairs by directly displacing atoms from its initial lattice site. The applicability of method is somewhat limited to metallic/dense materials, as it does not capture the important cascade process known as the thermal spike. The presence of the thermal spikes has shown to be influence both point defect clustering and sequential cascade overlaps. Instead, using FPA as the basis and incorporating a reduced-order approximation for thermal spike, a new method of modeling radiation damage is developed. By adopting the athermal recovery corrected (arc) formalisms, the new arc Damage Insertion (arc-DI) method is able to predict and replicate radiation events across a wide range of recoil energy. Using Cu and Nb as the case studies, arc-DI is verified against standard displacement cascades. Example applications for simulating high energy cascade fragmentation and large dose ion-bombardment are also provided for demonstration.


10:45 AM EN17.11.02
Exceptional Radiation Performance of Crystalline-Amorphous Nanocrystalline Metal Miaomiao Jin¹², Penghui Cao³ and Michael P. Short¹; ¹Massachusetts Institute of Technology, United States; ²Idaho National Laboratory, United States; ³University of California Irvine, United States

Nanostructured materials with amorphous intergranular films (AIFs) have demonstrated superior strength and ductility. The radiation performance is expected to be as high as grain boundaries, if not better, due to the large fraction of interfacial volumes, which can be efficient sinks for radiation-induced defects. Meanwhile, the concentrated solute atoms within the film can pin down interface migration. However, better understanding beyond qualitative speculation must be pursued towards the radiation behavior of such novel design for the potential deployment in nuclear applications. In this study, we examine the response of an AIF system (nanocrystalline Cu with Zr doped AIFs) under continuous irradiation with molecular dynamics (MD) simulations. The system behavior is evaluated from three perspectives: ion mixing, defect reduction, and interface evolution. We propose a diffusion model that well characterizes the cascade-driven mixing process, and the spread of Zr distribution scales linearly with the damage level. The exceptional radiation resistance of such design can be understood from three aspects: i) Zr mixing into the bulk enhances local defect annihilation, ii) Zr impedes radiation-enhanced grain growth by restraining AIFs from migration, and iii) Zr increases the interface stiffness to maintain AIF integrity. These findings suggest that the AIF-engineered system can be a promising candidate in applications where strong mechanical property, structure stability and self-healing capability of radiation damage are required.

11:00 AM EN17.11.03
Quantitative Phase Field Model for Void Nucleation and Growth under Ion Irradiation Rayaprolu Goutham Sreekar Annadanam and Anter El-Azab; Purdue University, United States

Voids develop in crystalline materials under energetic particle irradiation as in nuclear reactors. Understanding the underlying mechanisms of void nucleation and growth is of utmost importance as it leads to dimensional instability of the metallic materials. In the past decade, researchers have adopted phase field approach to study the phenomena of void evolution under irradiation. In the phase field approach, the boundary between the void and matrix is
modeled as a diffuse interface, while it is sharp in reality. This consideration of diffuse interface requires the phase field models to asymptotically match with their sharp interface counterparts in the limit of vanishing interface thickness. The asymptotic analysis of the phase field models has enabled in obtaining a quantitative vacancy-based phase field model, however, it failed to match with the sharp interface model when included interstitials concurrently with vacancies. In this communication, we introduce a thermodynamically consistent, quantitative diffuse interface formulation of type C for void evolution under irradiation, that includes vacancy, interstitial and phase field variable as order parameters. Test cases are presented to validate our new phase field model.

11:15 AM EN17.11.04
Investigation of Proton Radiation Damage Effects on the Tensile Strength of 3D Printed Acrylonitrile Butadiene Styrene Arielle J. Miller, Dharmaraj Raghavan and Grant Warner; Howard University, United States

Polymers are widely used in nuclear power plant (NPP) components and in the storage of radioactive materials. Radiation-induced polymer degradation is a known challenge to the lifetime of components. Additive manufacturing (AM) provides a cost-effective way to replace used parts to key NPP components, thereby extending the life of commercial NPP and reducing maintenance costs and reactor downtime. The radiation damage due to polymers by neutron irradiation is mainly due to secondary protons recoiled from the polymers themselves. Therefore the study of the effects of proton irradiation of polymers informs the damage study of neutron radiation and is a viable simulation of neutron damage. The radiation damage of 3D printed polymers with gamma beams has already been studied in terms of changes to mechanical properties such as tensile strength and flexural strength. The study aims to obtain an understanding of the proton radiation impact on the mechanical performance of fused filament fabrication (FF) acrylonitrile butadiene styrene (FF-ABS). The study addresses the effect of proton radiation damage at 40 MeV and high-level proton doses through experimental evaluation of both mechanical performance and material characteristic changes. Furthermore, it considers the comparison of mechanical damage caused by protons versus that caused by Co-60 gamma-ray radiation. The key components of this research are (1) material characterization to investigate irradiation damage to FF-ABS parts caused by exposure to protons with energies up to 40 MeV and a maximum dose of 1 MGy; and (2) tensile experiments to investigate the ionizing radiation effects on the mechanical properties of the FF-ABS. Preliminary results from irradiation performed at Texas A&M University Cyclotron Institute show a significant drop in tensile strength as the radiation dose increased. The molecular weight and decomposition temperatures decreased as the radiation dose increased.

11:30 AM EN17.11.05
In Situ Cantilever Testing of Radiation Damage in Tungsten for Fusion Applications James E. Darnbrough1, Markus Alfreider2, Daniel Kiener2 and David Armstrong1 ; 1University of Oxford, United Kingdom; 2Montanuniversität Leoben, Austria

Tungsten has a high melting point and low sputtering rate, this makes it ideal for use in fusion reactor walls and divertors [1]. In this environment the material is exposed to temperatures up to 1000°C and 14.1 MeV neutrons leading to 150dpa of damage in a lifetime [2]. For structural components (e.g. divertors) it is important to understand the effect that this extreme environment has on the mechanical properties throughout working lifetime. Previous work suggests that high irradiation doses can lead to embrittlement in tungsten [3]. To investigate this, Helium implantation of Tungsten with 2% Tantalum (WTa2%) (including the role of transmutants) was irradiated with He+ up to 3000appm at a temperature of 300°C [4]. The implantation was conducted using a range of energies (0.05-1.8MeV) and fluences (1-5x1015 ions/cm2) to produce a relatively flat implantation profile ~1.56μm deep.

This scale of damage therefore requires small scale characterisation to understand the mechanical properties that change during radiation damage. In this work we illustrate the use of nanoindentation and microscale cantilevers to find the changes in/to the elastic and plastic response of the material. We have developed a new geometry of cantilever in order to test material volumes that are removed from the edge of the sample. This methodology allows for observation of the elastic and plastic properties of irradiated material and opens up a wide range of possibilities for future work in terms of location specific characterisation.

[2]:- N. Baluc et al Nuclear Fusion 2007 47 pp S696-S717
[3]:- N. Yoshida Journal of Nuclear Materials 1999 266-269 pp 197-206
Additive manufacturing (AM) refers to the technique of producing complex three-dimensional objects directly from a digital model through layer-by-layer computer-controlled deposition and consolidation of feedstock powder materials. The AM technique is emerging into a mainstream manufacturing process and has the potential to find widespread application in nuclear technologies. Inconel 625 is a Ni-Cr-based alloy widely used in nuclear reactors. In this study we investigated the relations between the microstructure and associated high-temperature oxidation properties of additively manufactured IN625. Using Laser Engineered Net Shaping (LENS) technology, we fabricated 1x1x1 cm cubes from argon-atomized IN625 powders. The microstructure of these LENS-processed IN625 consisted of primary dendrites and fine cellular grains. Characterization revealed a significant microsegregation of Nb and Mo at the boundaries of the fine grains due to local rapid solidification processes. Thermogravimetric analysis was then conducted to determine the intrinsic oxidation resistance of the LENS-processed IN625 samples exposed to dry air at 800 C and 1000 C for up to 100 h. The kinetics results indicated that the LENS-processed IN625 exhibited less resistance to oxidation as compared to wrought IN625. The results will be discussed in the context of Nb and Mo microsegregation to the grain boundaries detrimentally affecting the oxidation resistance of the LENS-processed IN625.

SESSION EN17.12: Nuclear Waste Materials
Session Chairs: Kyle Brinkman and Ming Tang
Wednesday Afternoon, December 4, 2019
Sheraton, 3rd Floor, Hampton

1:30 PM *EN17.12.01
We Need More Realistic Corrosion Tests to Provide Confidence in Safety Cases for Radwaste Disposal
William E. Lee; Bangor University, United Kingdom

Understanding the behaviour of complex materials in complex environments over millennia is a challenge for both modellers and experimentalists but must happen to have confidence in the safety cases for permanent radioactive waste disposal. Current durability testing of ceramic materials (including glass, glass composite materials and cements) as hosts for radioactive wastes is based on overly simple materials and procedures including using powders or samples of defined size and shape, polished samples, distilled water, controlled flow rates, closely defined and constant temperatures, simple and inactive compositions (International Simple Glass, ISG) etc. While steps are being taken towards more realistic testing procedures to account for package corrosion products e.g. iron oxide from container, type of water in repository environments (salts), Engineered Barrier Systems (e.g. clay) and rock dissolution products etc. more is needed.

Recent work [1-2] has highlighted the need for improved standard testing procedures and modelling developments. In [1] the impact of partial water immersion on the International Simple Glass (ISG), a condition that is inevitable as a repository gradually becomes saturated with penetrating groundwater was examined. This revealed quite different degradation behaviour compared to standard tests in which the material is fully immersed. In particular, whilst in standard tests the system reaches a steady state with a very low alteration rate thanks to the formation of a protective gel layer, in partially-immersed tests this steady state could not be reached because of the continuous alteration from the condensate water film. The constant input of ions from the emerged part of the sample caused a supersaturation of the solution, which resulted in early precipitation of secondary crystalline phases. In [2] using highly radioactive 239Pu-doped and non-radioactive samples of borosilicate glass with chemical compositions and synthesis procedure similar to French standard SON68 glass showed dramatic differences in behaviour. Over 4 months the radioactive glass is fully covered by mechanically unstable alteration layer whereas the model glass remains virtually pristine. Such studies highlight the importance of understanding the evolution of (T, environment, activity) conditions with time and the inherent inhomogeneity of the wasteforms and how they change with time, and the need to work with active material.
This talk uses these, and other, data to highlight the need for improved durability testing of wasteforms.


2:00 PM EN17.12.02
Structure-Property Relationships of Copper Coating Materials for Canada’s Used Nuclear Fuel Containers
Jason Tam1, Bosco Yu1,2, Weiwei Li1, Jason Giallonardo3, Jane Howe1 and Uwe Erb1; 1University of Toronto, Canada; 2McMaster University, Canada; 3Nuclear Waste Management Organization, Canada

Nuclear energy offers many benefits including stable electricity generation and low carbon output; however, one of the major challenges of nuclear energy is the management of the used fuel. In Canada, the Nuclear Waste Management Organization (NWMO) has proposed a deep geological repository (DGR) solution where used Canada Deuterium Uranium (CANDU) fuel bundles are packaged into a used fuel container (UFC), which is then placed at a reference depth of 500 m underground in a geologically stable rock formation and surrounded by bentonite clay. The UFC consists of a structural steel containment vessel which is copper coated on the exterior surface for corrosion protection. Two methods are used to copper coat the UFC. The first method is electrodeposition (ED) process which is used to coat the shell and hemispherical factory components in a conventional manufacturing environment. After UFC is loaded with used fuel, the vessel is welded shut and the UFC corrosion barrier is completed by applying cold spray (CS) copper coating to the weld closure zone under radiological conditions. The as-deposited CS copper coating exhibits high hardness and low ductility. In order to restore ductility, local annealing (1 hour at 350°C) with a heating band is performed.

Since the Cu on the UFC are applied using two different methods, it is important to develop a better understanding of the structure-property-processing-performance relationships of these coatings. In this study, we apply various electron microscopy techniques including electron backscattered diffraction (EBSD), focused ion beam (FIB) and transmission electron microscopy (TEM) to establish the relationships between the coating processing conditions (ED, CS, annealing of CS-Cu) and microstructure of the coatings at different regions including the ED-Cu and CS-Cu interfaces, as well as the Cu particle-particle interfaces in the CS-Cu coatings. These structural characterization results will provide a basis for the ongoing mechanical and corrosion testing programs seeking to advance knowledge on strength and corrosion resistance of these Cu materials for long term storage in the repository.

2:15 PM EN17.12.03
Complexation/Speciation—New Insight Studies of the Secondary Phase Formation under Repository Conditions
Nieves Rodríguez-Villagra, L.J. Bonales and J. Cobos; CIEMAT, Spain

In a deep geological repository scenario, oxidized uranium in aqueous systems will be stabilized as UO_2^{2+} (hexavalent uranium), as a consequence of tetravalent uranium oxidation by radiolytic byproducts. Uranyl cationic species (UO_2^{2+}) in different complexation forms, such as uranyl oxyhydroxide hydrates are expected to be found at the whole pH range conditions. The importance of uranyl lies in its potential incorporation of trace radioelements onto secondary uranyl phases. In view of the difficulty of uranium chemistry in natural groundwater, it is worthy to improve speciation assessment techniques so as to characterize precipitated solid phases and understand chemical processes.

Recently Raman spectroscopy has been shown as powerful tool to analysis the speciation of various actinyl (UO_2^{2+}, NpO_2^{2+} and PuO_2^{2+}) and to determine distribution of those elements which are more likely to be stable in a near-field groundwater environment. Therefore, the aim of this work is to develop a quantitative procedure to follow uranyl speciation in aqueous solution under repository conditions, and understand the bonding, coordination and local surroundings of uranyl species, which will brings light to understand and predict the precipitated solid phases formed (solubility-limiting phases). Hydroxide and hydroxo-carbonate complexes of uranyl will be spectroscopically identified in aqueous solution in the absence and presence of carbonate. The proposed identification procedure of uranyl complexation will give a precise basis to assign better estimates of the predicted solid phase stoichiometry combining solubility analysis with speciation and precipitation of U(VI).
In this work, it is shown the use of Raman spectroscopy adapted to the empirical analysis of different nuclear applications for uranium concentrations higher than 0.05M at ambient atmosphere, i.e. monitoring tool for UO$_2^{2+}$ precipitation as a function of pH studying UO$_2$(NO$_3$)$_2$·6H$_2$O stability in aqueous solutions representative of groundwater, in particular at ionic strength I = 0.02 – 0.4 M and pH from 7 to 13.2 and to evaluate the effect of gamma radiation fields. Therefore, the obtained results will provided a complete picture of secondary phase formations, as a result of corrosion of spent nuclear fuel in a deep geological repository.

2:30 PM BREAK

3:30 PM *EN17.12.04
Radiation Tolerant Ceramics for Nuclear Waste Immobilization—Structure and Stability of Zinc Substituted Hollandites with High Cesium Loading Kyle S. Brinkman; Clemson University, United States

The radiation tolerance of nuclear waste forms is dependent on the materials resistance to defect formation and its ability to accommodate the structural distortions that arise from defect formation. This study illustrates how the radiation tolerance of hollandite can be improved thorough compositional control of cesium stoichiometry. The barium (Ba) to cesium (Cs) ratio was varied in the tunnel sites referred to as the A site of the hollandite structure. Zinc (Zn) was substituted for titanium (Ti) on the B site to achieve the targeted stoichiometry with a general formula of Ba$_x$Cs$_y$Zn$_{x+y/2}$Ti$_{8-x-y/2}$O$_{16}$ (0<x<1.33; 0<y<1.33). The tunnel cross-section depended on the average A site cation radius while the tunnel length depended on the average B site cation radius. The enthalpies of formation from binary oxides of Zn doped hollandite measured using high temperature oxide melt solution calorimetry were strongly negative, indicating thermodynamic stability with respect to their parent oxides. The formation enthalpies became more negative, indicating hollandide formation is more energetically favorable, when Cs was substituted for Ba across the range of Zn doped compositions investigated in this study. This hollandite series was exposed to heavy ion (Kr$^{2+}$) irradiation at 27 °C, 100 °C, 200 °C and 300 °C followed by characterization with grazing incidence X-ray diffraction, transmission electron microscopy, and aqueous leaching tests. The radiation tolerance increased at elevated temperatures with a critical amorphization temperature between 200 °C and 300 °C. Elemental leaching decreased with increasing cesium content. Irradiated samples exhibited twice the fraction cesium release of pristine samples.

4:00 PM *EN17.12.05
Ion Irradiation-Induced Volume Swelling and Microcracking in Multiphase Glass Ceramic and Crystalline Ceramic Nuclear Waste Forms Ming Tang$^{1,2}$; $^1$Los Alamos National Laboratory, United States; $^2$Clemson University, United States

Crystalline ceramics and glass ceramics are candidate host materials for immobilizing alkaline/alkaline earth + lanthanide + transition metal fission product waste streams from nuclear fuel reprocessing. The major phases in these multiphase borosilicate glass ceramics are powellite, oxyapatite, pollucite, celsian, and durable residual glass phases. Al$_2$O$_3$ and TiO$_2$ were combined with these waste components to produce multiphase crystalline ceramics containing hollandite-type phases, perovskites, zirconolite/pyrochlores and other minor metal titanate phases. These alternative waste form materials offer increased solubility of troublesome components in crystalline phases compared to glass. This, in turn, leads to increased waste loading. During the long term storage, radiation stability and chemical durability always are most important concerns for nuclear waste forms. The focus of this presentation is the radiation-induced volume swelling and microcracking. These radiation damage effects would affect chemical durability of nuclear waste forms. In this study, selected glass ceramic and crystalline ceramic samples are exposed to various ion beam irradiations, which are used to simulate self-irradiations in a waste form. Several individual crystalline phases and pure glass are fabricated and tested under the same ion irradiations. Specifically, light ion (Helium) irradiation is used to simulate alpha particles and ionization process; and heavy ion (Krypton) irradiation is used to simulate alpha recoil and produce displacement damage. Ion irradiation-induced microstructural modifications, volume swelling and microcracking are examined using X-ray diffraction, transmission electron microscopy, scanning electron microscopy, atomic force microscopy, and other characterization methods. Our preliminary results show that (1) similar radiation damage responses from single crystalline phases and corresponding crystalline phases in multiphase samples; (2) different crystalline phases in these multiphase waste forms exhibit different radiation-induced volume swelling and microcracks formation under the same ion irradiation damage environment, and different ion species radiations induce different volume swelling and microcracks in the same crystalline phase; (3)
helium irradiation induced volume swelling and microcracks in glass and some crystalline phases are similar to the previous results of corresponding glass and crystallines irradiated by neutron or doped by actinide.

4:30 PM EN17.12.07
Physics-Based Mesoscale Models of Ion Exchange in Hierarchical Materials Yulan Li1, Shenyang Hu1, Chuck Henager1, Theodore M. Besmann2, Agnes Grandjean3,4 and Hans-Conrad Zur Loye2; 1Pacific Northwest National Lab, United States; 2University of South Carolina, United States; 3Univ Montpellier, France; 4CEA, France

The performance of advanced nuclear wasteform materials containing radionuclide absorbing nanoparticles such as zeolite, hexacyanoferrate (HCF), and salt-inclusion materials (SIMs) depends on hierarchical microstructures as well as thermodynamic and kinetics properties of ion exchange processes. For example, the wasteform morphology including particle size and particle aspect ratio, anisotropic mobility, and electrochemical potential affect the uptake kinetics of radionuclides. A physics-based mesoscale model of ion exchange in hierarchical materials is presented that takes into account the effects on ion exchange processes of inhomogeneous microstructures, anisotropic and inhomogeneous diffusivity of charged particles, electrochemical potentials, and operational conditions. Wasteforms consisting of zeolite or SIMs particles are taken as model systems. The thermodynamic and kinetic properties of diffusive ions are assessed using atomistic simulations and thermodynamic calculations. Simulation results showed that anisotropic mobility and larger aspect ratios of particles dramatically decrease ion exchange kinetics if the migration mobility is faster along the largest dimension anisotropic particles, such as needle-shaped particles. Electric fields associated with inhomogeneous ion distributions is an additional driving force that typically increases ion exchange kinetics depending on particle aggregation and ion mobility. The capability of the model for investigating the physics and mechanisms behind ion exchange in complicated microstructures and for predicting the effects of microstructure on ion exchange kinetics will be presented.

4:45 PM EN17.12.08
Progress in Flash Sintering of UO2 Erofili Kardoulaki, Darrin Byler and Ken McClellan; Los Alamos National Laboratory, United States

Early studies on the onset of flash sintering (FS) for UO2 have identified that flash is induced by a critical field, at a critical onset time (incubation time) and they are both shown to be dependent on temperature and O/M. UO2+x has been shown to flash at lower critical fields, compared to UO2.00, and a bifurcation stability model has been used to model the Joule heating effects [1] taking place during flash onset with reasonable agreement with experimental data [2]. Densification of stoichiometric and hyper-stoichiometric UO2 has been achieved via FS and has resulted in 81% and 92% theoretical density (TD) pellets, respectively [3]. Still, the resulting microstructures were significantly cracked and featured porosity. The latest studies on FS of UO2 have concentrated on producing high density pellets with structural integrity and uniform microstructure. FS using the current control method has been implemented to minimize thermal shock and achieve control in the resultant microstructures. The current control method has been shown to produce more structurally sound pellets, although additional difficulties with FS of UO2 result from atmosphere and subsequently stoichiometry control of the pellet. More specifically, during FS of UO2+x using Direct Current (DC), an O/M gradient can develop due to the concentration of O2 close to the anode, resulting in hyper-stoichiometric material in the vicinity which can sinter at a faster rate. This produces pellets with differential densification along their length. To overcome this issue, a pseudo-Alternating Current (pseudo-AC) has been used and it has been shown to produce pellets with slightly higher densities and more homogeneous macroscopic characteristics. Finally, the pseudo-AC and current controlled methods have been applied to FS of doped UO2 and the results are compared to doped UO2 that has been sintered conventionally.

8:30 AM *EN17.13.01
Crystal Growth and Scintillation Properties of Ternary Halides for Gamma Spectroscopy Mariya Zhuravleva and Matthew Loyd; The University of Tennessee, Knoxville, United States

In this report, we will review the crystal growth and scintillation properties of simple and mixed cation and mixed anion ternary halides that belong to the ABX3, AB2X5, A4BX6 families (A – one or more alkaline metals, B – one or more alkaline earth metals, X – one or a mixture of chlorine, bromine or iodine). They are of interest for scintillation applications due to their relatively high density, congruent melting, large band gaps, and availability of a divalent lattice site to accommodate a Eu2+ luminescence activator. They have attractive spectroscopic performance that is competitive with the industry standard, NaI:Tl, or state-of-the-art SrI2:Eu and LaBr3:Ce2+ scintillators, and therefore are suitable for use in portable radiation detectors for radio-isotope identification. Details of compositional uniformity, growth defects, and gamma-ray spectroscopic performance as a function of Eu concentration, crystal volume and growth parameters are presented to provide understanding of the best achievable performance. Particular attention is paid to thermal and structural properties to design the crystal growth parameters via the vertical Bridgman method. Additionally, the potential for scale-up is evaluated by simultaneous growth of multiple large size crystals (1” – 1.5” in diameter) using the Multi-Ampoule Growth Station.

9:00 AM EN17.13.02
Robust Perovskite Single Crystal Devices for Efficient Gamma-Ray Detection Jeremy Tisdale, Michael Yoho, Shreetu Shrestha, Kasun Fernando, Sergei Tretiak, Duc Vo and Wanyi Nie; Los Alamos National Laboratory, United States

Gamma-ray detection and spectroscopy is the quantitative analysis of gamma energy spectra, and is of critical importance in many applications, such as nuclear safeguards, nuclear forensics, and many more. Recently, single-crystalline, hybrid (and inorganic) perovskites have been proposed as new semiconducting materials for gamma-ray spectroscopy. In just a few short years, early reports have shown promising results for perovskite-based semiconductor gamma detectors. Some of the most impactful results in this new application for perovskite materials include: CsPbBr3 showing gamma-ray spectra with a resolution of 3.8% at room temperature for a 662 keV 137Cs source at room temperature;1 MAPbI3 showing gamma-ray spectra with a resolution of 6.8% at a lower temperature of 2 °C for a 122 keV 57Co source;2 and MAPbBr2.94Cl0.06 showing gamma-ray spectra with a typical resolution of 12% for a 662 keV 137Cs at room temperature.3 Although first reports for this class of materials have shown significant results with high-resolution gamma detectors, many new issues have arisen for this new application of radiation sensing.

High electric field device stability and ion migration are deeply explored to understand the effects of high bias applications in hybrid perovskites and ways to suppress/eliminate the negative effects towards high-resolution, room temperature gamma-spectroscopy. In a Cr/MAPbBr2.85Cl0.15/Cr device, low electric fields (≤25 V/mm) pulses with extremely low rise times (average of 30 to 65 µs). In order to increase the rise time, the device needs to be operated at higher electric fields, (≥ 50 V/mm) which increases the rise time to an average of 15 µs. However, at high electric fields, the signals become noisy in roughly 10 seconds to 1 minute. We directly probed the cause of the noise using long-term high voltage biasing, while studying the hysteretic behavior via IV characteristics. A new Cr/MAPbBr2.85Cl0.15/Cr exhibits pure Ohmic behavior with negligible hysteresis between -200 to +200 V (E = 100 V/mm). However, after biasing the device for only 10 minutes at +200 V, a large hysteresis loop is observed. After letting the device rest in the dark for two days, the hysteresis loop becomes even larger, rather than restoring to its original properties, showing that the interfacial damage caused is non-reversible. Using the same electrodes in the device architecture allows us to use a technique termed voltage cycling to avoid permanent interfacial damage while operating the detectors. The signals from positive and negative polarity are roughly the same in the metal/semiconductor/metal device. Therefore, when noise appears, we are able to switch polarity to eliminate the noise and continue counting for gamma spectra. Cooling the detector to temperatures of -30 °C further increases the
speed of the detector pulses by about 30%. However, the standard deviation in the pulse heights and rise times are still quite large, resulting in low resolution for the detectors with about 30-35% resolution for 59.6 keV γ-rays and 20-25% resolution for 662 keV γ-rays. Further development in hybrid (or non-hybrid) perovskite materials, such as CsPbBr3 and MAPbI3, should prove beneficial, as they are more stable under high electric fields required to achieve high resolution γ-ray spectroscopy. Also, further development in areas such as interfacial engineering and pixelated detector designs will be the next required steps in investigating the improvement for single crystalline, perovskite radiation detectors.

References

9:15 AM EN17.13.03
Passive Radiofrequency Dosimeter Tag Based on Flexible Radiation-Sensitive Oxide Field-Effect Transistor
Tobias Cramer1, Ilaria Fratelli1, Pedro Barquinha2, Rodrigo Martins2, Elvira Fortunato2 and Beatrice Fraboni1; 1University of Bologna, Italy; 2Universidade Nova de Lisboa, Portugal

Distributed ionizing radiation dosimetry is crucial in diverse security areas with significant environmental and human impacts such as nuclear waste management, radiotherapy, or radioprotection devices. We present a fast, real-time dosimetry detection system based on flexible oxide thin-film transistors that show a quantitative shift in threshold voltage of up to 3.4 V/gray upon exposure to ionizing radiation. The transistors use indium-gallium-zinc-oxide as a semiconductor and multilayer dielectric based on silicon oxide and tantalum oxide. [1] Our measurements demonstrate that the threshold voltage shift is caused by the accumulation of positive ionization charge in the dielectric layer due to high-energy photon absorption in the high-Z dielectric. The high mobility combined with a steep subthreshold slope of the transistor allows for fast, reliable, and ultralow-power readout of the deposited radiation dose. The order-of-magnitude variation in transistor channel impedance upon exposure to radiation makes it possible to use a low-cost, passive radiofrequency identification sensor tag for its readout. In this way, we demonstrate a passive, programmable, wireless sensor that reports in real time the excess of critical radiation doses. [2]


9:30 AM EN17.13.04
Thermal Diffusivity Degradation and Defect Density Prediction in Self-Ion Implanted Tungsten Using Transient Grating Spectroscopy
Mohamed Abdallah Reza1, Hongbing Yu1, Kenichiro Mizohata2 and Felix Hofmann1; 1University of Oxford, United Kingdom; 2University of Helsinki, Finland

We study the degradation of thermal diffusivity in self-ion implanted tungsten, and utilise this degradation to predict point defect densities. The defect density predictions are consistent with previous transmission electron microscopy (TEM) and molecular dynamics (MD) studies of self-ion implanted tungsten. Tungsten, due to its high melting point, high thermal diffusivity and low sputtering yield, is the prime candidate for plasma facing components in future fusion reactors. Armour components in the so-called divertor, the exhaust of the fusion reactor, will receive the highest heat and radiation loads in the reactor. The damage created in the tungsten matrix as a result of intense neutron irradiation and plasma exposure decreases its thermal diffusivity, reducing its heat removal capability. Self-ion implantation is a convenient, low cost proxy to neutron irradiation to study the displacement damage created by neutrons. It efficiently singles out the displacement damage from other
effects such as transmutation. However self-ion implantation even at energies as high as 20 MeV create damage layers that are only a few microns thick. The transient grating spectroscopy method used in this study enables us to measure the thermal diffusivity of these thin layers with high accuracy. In this study, a simple kinetic theory model is used to predict the point defect densities from the measured changes in thermal diffusivity as a function of ion dose. These predictions are compared to dislocation loop and point defect densities observed in TEM and predicted by MD.

20 MeV self-ion implanted tungsten, over a dose range of 0.0001 – 10 dpa, shows a significant degradation in thermal diffusivity above doses of 0.001 dpa. This degradation progresses up to 0.01 dpa, beyond which the decrease in thermal diffusivity saturates. Full saturation is achieved by 0.1 dpa, and the thermal diffusivity ceases to deteriorate with additional implantation. The reduction in room temperature thermal diffusivity at this damage level is 55% of the value of pristine tungsten.

The extracted point defect densities from the TGS data are about 2 orders higher than anticipated when considering solely defects visible in TEM. By combining TEM observations with predictions from MD, the density of point defects associated with defect clusters too small to be seen by TEM can be estimated. Once these “invisible” defects are accounted for, the total point defect concentration agrees to within an order of magnitude with that inferred from the TGS measurements of thermal diffusivity.

The reduction in thermal diffusivity observed in this study provides a much more complete picture of the degradation of thermal diffusivity with increasing damage dose. It also suggests that the diffusivity degradation due to the displacement damage from neutron irradiation will saturate beyond 0.1 dpa, which is an important result for predicting the in-service performance of armour components in future fusion reactors. The defect prediction results demonstrate the novel capability of TGS in quantitatively determining defect densities in irradiation-damaged materials. It also shows that the finely distributed smaller defects affect material properties such as thermal diffusivity to a larger extent than the bigger dislocation loops that are visible to TEM.

9:45 AM EN17.13.05
Processing-Structure Related Performance of Irradiated Relaxor-Ferroelectric Thin Films Evelyn Chin¹, Cory D. Cress² and Nazanin Bassiri-Gharb³;¹ ¹Georgia Institute of Technology, United States; ²U.S. Naval Research Laboratory, United States

Ferroelectric (FE) materials show a spontaneous polarization, reversibly switchable with an electric field, in addition to large dielectric, pyroelectric and piezoelectric response. Such properties make them attractive for fulfilling multiple functionalities in MEMS devices as sensors, actuators, and energy harvesting units. Traditionally, lead zirconate titanate (Pb[Zr₁₋ₓTiₓ]O₃, PZT) has been the most used ferroelectric in piezoelectric MEMS. However, relaxor-FE bulk single crystals, such as (1-x)Pb(Mg₁/₃Nb₂/₃)O₃-xPbTiO₃, (1-x)PMN-xPT, exhibit even larger electromechanical response than ceramic PZT, when cut and poled along the (001) direction with compositions on the rhombohedral side of the morphotropic phase boundary (x~0.32).

Lead-based materials are often radiation-hard, and numerous studies have shown PZT’s exceptional capabilities of retaining functional response after radiation exposure. The radiation hardness enables applications in high radiation exposure environments (e.g., aerospace, medical physics, x-ray/high energy source measurement tools, continuous monitoring of nuclear power plant applications, radiation disaster relief, etc.). However, PZT films still suffer from response degradation, especially for radiation doses at, or superior to 5 Mrad(Si). The high B-site chemical heterogeneity and disorder of PMN-PT is expected to result in a more radiation-hard material than PZT. Such perceived advantages are offset by challenges in processing pore- and crack-free PMN-PT thin films. Here we report on the radiation hardness of 0.7PMN-0.3PT thin films with varying microstructures, as modified through processing parameters.

All films were deposited on platinized Si substrates through chemical solution deposition (CSD). A 0.3M precursor solution of PMN-PT was prepared through a 2-methoxyethanol route and deposited onto the substrate via spin coating. A PbTiO₃ seed layer was used to induce (100) crystallographic orientation in PMN-PT films. Heat treatment conditions were modified in order to control porosity and grain morphology. Specifically, the samples were pyrolyzed at 250 to 430 °C for 1 to 5 minutes, and annealed at temperatures of 700 to 800 °C for 1 or 2 minutes. The deposition and heat treatment process were repeated in order to obtain final film thicknesses up to 500 to 600 nm. All samples showed strong (100) perovskite orientation with Lotgering factors > 80%, as evidenced by X-ray diffraction patterns. The samples were irradiated using a ⁶⁰Co source with ionization doses ranging from 0.2 to 10 Mrad(Si). A zero-dose sample was used for aging reference and background radiation control. Dielectric, polarization, and piezoelectric responses were conducted using sputtered Pt top electrodes, before and after irradiation.
In general, higher crystallization temperatures led to larger grains and columnar grain growth. All PMN-PT samples showed degradation in dielectric and saturated polarization within 5%, and in piezoelectric coefficients within 15%, within the radiation dose range used. Some films showed improvement in response up to 5% at lower doses, possibly due to annihilation of defects through low radiation exposure. Greater radiation hardness and lower functional response was observed in films with smaller, stacked grains, compared to films with larger, columnar grains. The influence of grain microstructure and porosity on both functional response and radiation-hardness, and a phenomenological model to quantify defect-defect interactions in irradiated functional materials will be discussed.

10:00 AM BREAK

10:30 AM *EN17.13.06
Quantifying Morphological Features of Uranium Oxides for Nuclear Forensics Luther W. McDonald; The University of Utah, United States

In the past five years, it was only hypothesized that morphological features could be used as signatures for nuclear forensics. The physicochemical connection between the processing parameters such as precipitation conditions, calcination temperature, and the composition of the starting material was generally thought to affect the morphology of the resulting material. However, quantifying these features was the limitation that prevented this signature from being utilized. In the past two years, we have published multiple papers demonstrating quantitative morphological analysis of UO₂, U₃O₈, and UO₂. To move from qualitative morphological analysis to quantitative analysis, the SEM images were processed using the Morphological Analysis of MAterials (MAMA) particle segmentation software. Following particle segmentation, the MAMA software was used to calculate morphological particle attributes for each of the segments. We generally segment enough images to acquire several hundred particles for statistical analysis. Our initial studies focused on synthetic parameters from the uranyl peroxide route in which we showed quantitative differences in the particle morphology of Am-UO₃ and U₃O₈ based on the calcination temperature.

We have also shown that incorporation of impurities with the U-oxide will alter the final product morphology. For example, four impurities: calcium, magnesium, vanadium, and zirconium were separately introduced to pure uranyl nitrate hexahydrate from stock solutions. Following the addition of the impurities, the solutions were precipitated using hydrogen peroxide. Incorporation of the impurity was quantified using inductively coupled plasma mass spectrometry (ICP-MS). The uranyl peroxide precipitate was then calcined to U₃O₈ at 800°C. ICP-MS was used again, to evaluate the incorporation of the impurity in the calcined uranium oxide. SEM was used to investigate morphological changes, and SEM-Energy dispersive spectroscopy (EDS) was used to identify any concentrated regions of the impurity in the SEM images. Results will be discussed highlighting the potential of using particle morphology for nuclear forensics, but also highlighting the challenges that need to be overcome for this to be a viable signature of processing history.

11:00 AM *EN17.13.07
Non-Destructively Uncovering Aging and Irradiation Relationships for Nuclear Material Health Assessment and Forensics Michael P. Short¹, Cody Dennett¹, Saleem Aldajani¹, Benjamin Dacus¹, Caitlin Huotilainen², Ulla Ehrnsten³, M. Grace Burke³, Kudzanai Mukihawa³, Ihor Radchenko⁴, Kai Chen⁵, Ziv Ungarish⁵, Michael Aizenshtein⁵, Eyal Yahel⁵, Pål Efsing⁷, Thak Sang Byun⁸ and Joe Wall⁹; ¹Massachusetts Institute of Technology, United States; ²VTT Technical Research Centre, Finland; ³University of Manchester, United Kingdom; ⁴Xi’an Jiaotong University, China; ⁵Nuclear Research Center Negev (NRCN), Israel; ⁶Ben-Gurion University of the Negev, Israel; ⁷Vattenfall AB, Sweden; ⁸Pacific Northwest National Laboratory, United States; ⁹Electric Power Research Institute (EPRI), United States

Nuclear materials age in service, with their properties changing as a combined result of how they were produced and to what they were exposed. This aging, which can be due to a combination of thermal and irradiation origins, sometimes results in degraded performance which can lead to failure. It also often leaves fingerprints, measurable either directly or indirectly. In this talk we will explore the use of transient grating spectroscopy (TGS) as a method to both assess the health of key light water reactor (LWR) components due to spinodal decomposition, short range ordering, and phase precipitation, and to reconstruct their irradiation history. Changes in thermal, elastic, and acoustic material properties are indirectly linked to the quantities of interest, such as Charpy impact energy via surface acoustic wave peak splitting for structural materials, and irradiation dose history to reconstruct reactor usage, particularly for additively manufactured materials. This wide variety of examples highlights the vast, unexplored
space where non-destructive, indirect techniques can far more rapidly uncover new science and assist industry in nuclear materials forensic and health assessment issues.

11:30 AM EN17.13.08
Thermodynamics and Electronic Structure of Actinide Based Metal-Organic Frameworks from Density Functional Theory Calculations
Shubham Pandey1, Zhilin Jia1, Brian Demaske1,2, Otega Ejegbavwo1, Natalia Shustova1, Wahyu Setyawan2, Chuck Henager2 and Simon R. Phillpot1; 1University of Florida, United States; 2Sandia National Laboratories, United States; 3University of South Carolina, United States; 4Pacific Northwest National Laboratory, United States

Metal-Organic Frameworks (MOFs) are emerging as a novel class of hybrid materials for the purpose of radionuclide sequestration. Significant research has been reported on MOFs for applications such as gas storage, sensing and heterogeneous catalysis; however, radionuclide incorporated MOFs are relatively unexplored. The unique and desirable properties of MOF structures like high porosity, modularity, and synthetic diversity make them attractive candidate materials to contain the radionuclides present in the nuclear wastes. Density Functional Theory (DFT) calculations were used to determine the favorability of ion-exchange (at the metal node) of relevant radionuclides in various parent MOF clusters. A range of DFT methods, including various flavors of exchange-correlation functionals, DFT+$U$, relativistic effects, and magnetic effects were employed to establish robustness in results. The electronic structures of MOFs are also determined and are correlated with experimental data.

11:45 AM EN17.13.09
Nanoscale Cross-Plane Thermal Transport and Structural Characterization of Swift Heavy Ion Irradiated LiF Crystals
Ainur Koshkinbayeva1, Azat Abdullaev1, Zhanatay Nurekeyev1, Vladimir Skuratov2,3,4 and Zhandos Utegulov1; 1Nazarbayev University, Kazakhstan; 2Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, Russian Federation; 3National Research Nuclear University MEPhI, Russian Federation; 4Dubna State University, Russian Federation

Thermal transport in insulators is of great interest in high temperature nuclear reactors application. External irradiation by swift heavy ions (SHIs) such as Bi at hundreds of MeV energy is used to simulate the fission product impact in nuclear and model materials like LiF with well-known structural response to dense excitation effects [1, 2]. We report the results of color centers formation analysis in bulk lithium fluoride crystals irradiated at room temperature by 98 MeV, 244 MeV, 465 MeV and 710 MeV Bi ions at fluence $10^{11}$ cm$^{-2}$ and 710 MeV ions at fluencies ranging from $10^{10}$ to $10^{13}$ cm$^{-2}$ using optical absorption (OA) and photoluminescence (PL) spectroscopy. The irradiation of LiF samples was carried out at the U-400 FLNR JINR cyclotron (Dubna, Russia). The proliferation of ion-induced F (245 nm) and F$_2$ (445 nm) color centers were studied by OA spectroscopy. As the fluence of irradiation ions grows, the integrated absorption intensity of F-peak gradually decays, whereas that of F$_2$-peak broadens and increases, which indicates that color centers tend to aggregate. The corresponding defects densities were estimated using Smakula-Dexter formula [2]. Since F$_2$ and F$_3$ color center related bands in absorption spectra overlap, the complementary technique, PL spectroscopy, was performed. Specifically, the F$_2$ and F$_3$ color centers in irradiated LiF samples were distinguished by their characteristic peaks observed at around 530 and 670 nm, respectively. For the fluencies $10^{10}$ - $10^{13}$ cm$^{-2}$, the integrated fluorescent intensity of F$_2$ appears to dominate in the spectrum for the lower ion doses and drops to the level comparable to that of F$_3$ as the ion dose increases. Cross-plane near-surface thermal conductivity of SHI irradiated LiF crystals was characterized by picosecond time-domain thermo-reflectance (TDTR) in the thermally probed region extending down to 290 nm, where the electronic stopping / ionization processes dominate over nuclear stopping. TDTR results show that thermal transport in this sub-surface domain irradiated by 710 MeV ions with the dose of $10^{12}$ cm$^{-2}$ has degraded by the factor of $\sim$ 2 compared to non-irradiated sample. Theoretical analysis was based on Klemens analytical thermal transport model [3] by fitting into TDTR measured thermal conductivity values. Given TDTR probed sub-surface region overlapped with ionization depth determined by SRIM calculation, we conclude that defects are formed primarily by electronic energy loss / ionization. Measurement and simulation of nano-scale thermal transport degradation in irradiated LiF will be discussed with results of structural defects proliferation as determined by OA and PL measurements. Funding by MES RK grant AP05130446, state-targeted program BR05236454 and NU FDCRG grant 110119FD4501 is acknowledged.

References
SYMPOSIUM FF01

TUTORIAL: Advances in Large-Scale Synthesis of Beyond Graphene 2D Materials
December 1 - December 1, 2019

* Invited Paper

TUTORIAL
Advances in Large-Scale Synthesis of Beyond Graphene 2D Materials

Sunday Afternoon, December 1, 2019
Hynes, Level 2, Room 208

The research areas of beyond graphene 2D and layered materials remain highly active and is continuously expanding. This is particularly true with many growth techniques emerging as promising methods for controlled large scale synthesis of single monolayers and heterostructures. This tutorial will showcase the current status and future directions in the area of largescale synthesis, doping and alloying of 2D materials and van der Waals heterostructures. Specifically, this tutorial will cover the science and practice of molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD) and solution-phase processing approaches that will ultimately enable the practical development of wafer scale electronics from beyond graphene 2D and layered materials.

1:30 PM
Metalorganic Chemical Vapor Deposition of 2D Layered Materials Joan M. Redwing, The Pennsylvania State University

Metalorganic chemical vapor deposition (MOCVD) has emerged as a promising method for the synthesis of wafer-scale epitaxial films of monolayer transition metal dichalcogenides (TMDs) and related 2D materials. This tutorial will cover the science and practice of MOCVD as it pertains to the growth of van der Waals bonded chalcogenide films. Practical considerations including reactor design, precursor selection, growth conditions and substrates will be reviewed. The role of kinetics and thermodynamics in the nucleation, domain shape and lateral versus vertical growth will be discussed. Characterization techniques for wafer-scale monolayer films as well as prospects for future advances, including in situ characterization and layer-by-layer growth of heterostructures, will be detailed.

2:30 PM BREAK

3:00 PM
Molecular Beam Epitaxy of 2D Layered Materials Christopher Hinkle, University of Notre Dame
Molecular beam epitaxy (MBE) can enable high-quality 2D layered chalcogenides through the combination of high purity elemental sources and an ultra-high vacuum growth environment. This tutorial will cover the science and practice of MBE as it pertains to the growth of van der Waals-bonded chalcogenide films and their heterostructures. Fundamental nucleation and growth behavior of transition metal dichalcogenides by MBE will be discussed, focusing on important parameters to control domain orientation and grain size in MBE to achieve wafer scale grown films. This tutorial will also feature novel advances in MBE system designs and highly developed in situ materials characterization techniques to enable the fundamental understanding of the growth thermodynamics and kinetics, the structure of these van der Waal monolayers and abruptness of heterostructures.

**4:00 PM**

**Liquid Phase Exfoliation of 2D Layered Materials and Applications** Mark C. Hersam, Northwestern University

Beyond conventional crystal growth techniques, liquid phase exfoliation of 2D sheets from layered bulk crystals represents a viable solution for producing monolayer films on a wafer scale through standard processing technologies such as spin coating and roll-to-roll manufacturing. Here, we review different strategies for exfoliation of 2D and layered materials in the liquid phase and discuss important parameters that govern the thickness and lateral size of the exfoliated sheets. Practical considerations on the role of surfactants and dispersing solvent medium as well as control of concentration and viscosity of dispersed exfoliated 2D sheets will also be highlighted. This tutorial will provide practical guidelines for the process of liquid phase exfoliation that may be generalized to different types of layered materials, with a short discussion on the impact of this process on device applications.

**SYMPOSIUM FF01**

Beyond Graphene 2D Materials—Synthesis, Properties and Device Applications
December 1 - December 6, 2019

**Symposium Organizers**
Zakaria Al Balushi, University of California, Berkeley
Deep Jariwala, University of Pennsylvania
Olga Kazakova, National Physical Laboratory
Amber McCreary, National Institute of Standards and Technology

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Accurion Inc.
IOP Publishing Ltd - 2D Materials
Scienta Omicron, Inc.

* Invited Paper

SESSION FF01.01: Scalable Synthesis Approaches for 2D Integration
Session Chairs: Zakaria Al Balushi and Amber McCreary
Sunday Morning, December 1, 2019
Hynes, Level 2, Room 208
Parametric Study on Solution Crystal Growth of Hexagonal Boron Nitride  
Eli Janzen, Jiahan Li and James H. Edgar; Kansas State University, United States

Hexagonal boron nitride (hBN) has many unique properties such as a strong interaction with thermal neutrons, a wide energy bandgap (>6.0 eV), and surface phonon polaritons. These properties make it a good candidate for compact, efficient, and low-cost neutron detectors, deep UV light emitters and detectors, and infrared nanophotonic devices. Thus, high quality hBN single crystals are needed for national defense (detection and monitoring of nuclear weapons by neutron detectors), health (sterilization of surfaces by radiation from deep UV LEDs), and microscopy (deep sub-wavelength optical imaging).

Molten metal solutions in nitrogen at atmospheric pressure have proven effective in growing large, monoisotopic, high purity, and high quality hBN single crystals. Single crystals have been grown that are up to 3mm across, hundreds of microns thick, and with etch pit densities of 10^7 to 10^8 cm^-2. Monoisotopic ^10^B and ^11^B enriched hBN crystals were also grown simply by using isotopically pure boron as the source material. While epitaxial growth techniques (CVD and MBE) have also proven effective at growing hBN, these methods require more complex apparatus and processes than solution growth and require a substrate which introduces lattice constant and thermal expansion coefficient mismatches. Furthermore, they cannot produce crystals as thick as solution growth, nor readily produce monoisotopic hBN, as they require specialized chemical sources, which are rarely available and quite expensive. However, to become commercially viable, solution growth must be further refined to produce much larger crystals with lower defect densities, and lower residual impurity concentrations.

One of the primary obstacles to optimizing this process is the lack of a cohesive understanding of how the melt composition impacts hBN crystal growth. For example, several different combinations of metals (Ni, Ni/Cr, Fe, Fe/Cr), two different boron sources (pure boron powder and hot-pressed boron nitride), and other additives such as silicon have been used in varying concentrations within the melt. In each case, the crystal nucleation density, grain size area, thickness, and other characteristics have been affected by the particular composition used. However, how the melt composition affects these characteristics and what specific properties are responsible for these effects has not been thoroughly analyzed. Thus, it is difficult to explain why certain compositions of boron, metals, and nitrogen yield excellent quality crystals while others do not.

In this work, processes employing various combinations of Ni, Cr, Fe, and other additives with a boron source were systematically analyzed according to the crystal size (obtained from micrographs), defect density (determined via defect-selective etching), and quality (determined via a variety of spectrographic tools including XRD and Raman spectroscopy). Specific features of the melt were analyzed with respect to these criteria to pinpoint exactly which properties were most important in the process. For example, pure Ni and Fe both have high boron solubilities, but nitrogen solubility is negligible in pure Ni. While alloying with Cr greatly increases the nitrogen solubility, it also increases the nucleation density. Thus, relatively large hBN single crystals can be produced in pure Fe, but not pure Ni. Thick hBN layers can be produced in Ni/Cr solutions, but with small crystal grain sizes. In addition, residual impurities present in the source materials, intentionally added impurities, and the interaction of the melt with the furnace and crucible materials significantly affects the process and the crystal properties. This project gives new insights into the interplay between melt composition and hBN crystal growth and reveal new, direct pathways toward optimizing the process.

Expanding the Palette of Layered Materials and Their 2D Counterparts by Materials Chemistry Approaches  
David J. Lewis and Niting Zeng; University of Manchester, United Kingdom

Layered bulk materials have attracted much attention for various technological applications including tribology and catalysis [1]. One of the most recent applications is in their study in the two-dimensional limit i.e. atomically thick materials such as graphene. Inorganic graphene analogues such as few layer molybdenum disulphide, black phosphorus and main group chalcogenides have also been the subjects of much intense research as two-dimensional semiconductors that would be complementary to graphene in a future electronics industry [2]. We have devised top-down routes to 2D black phosphorus [3] and tin(II) sulphide [4] both of which have layer dependent band gaps.
However, these top-down processes suffer from a major drawback: often commercially available layered bulk crystals are used as feedstock and this inherently limits the palette of two-dimensional materials available for study without resorting to expensive processing via CVD.

As a solution to this, we have devised new routes based on solventless thermolysis of metal-organic precursors that can produce layered materials in bulk at relatively low temperatures and in relatively high purity. Because the precursors used are on the molecular scale, we can control the extent of doping or alloying of materials and this then widens range of layered materials available for exfoliation. I will present the synthesis of layered transition metal oxides and chalcogenides [5] and main group chalcogenide alloys [6], the latter also studied as post-processed 2D materials as an example of a new route to 2D materials with wide applicability.


8:30 AM FF01.01.03
Liquid-Phase Exfoliated Semiconducting Transition Metal Dichalcogenide 2D Nanoflakes for Large-Area Optoelectronic Applications Kevin Sivula; Ecole Polytechnique Federale Lausanne, Switzerland

Given their established robustness and favorable optoelectronic properties, the semiconducting transition metal dichalcogenides (TMDs, e.g. MoS2 and WSe2) are attractive for optoelectronic applications including solar energy conversion (photovoltaic and photoelectrochemical solar fuel production).[1] Recent advances in the liquid-phase exfoliation (LPE) of semiconducting TMDs into mono- or few-layered 2D nanoflake dispersions suggests that inexpensive roll-to-roll processing can be used to prepare TMD-based devices inexpensively over large area.[2] However, the high concentration of defects in these materials act as recombination sites for photogenerated carriers and limit the performance. In this presentation the challenges with charge transport, separation, recombination, and interfacial transfer in LPE TMD nanoflake thin film devices will be discussed with respect to the 2D flake size and defect passivation/charge extraction treatments.[3] Our results give insight into the roles of both edge and internal defects and suggest routes for improvement. Overall it is shown that LPE semiconducting TMDs with suitable defect mitigation can achieve internal quantum efficiency for photon harvesting similar to bulk single crystal samples. Specifically, we show that WSe2 nanoflake thin films achieve absorbed-photon-to-current efficiency over 50% and photocurrent densities for solar water reduction at 4 mA cm–2 under standard testing conditions.[4]


8:45 AM FF01.01.04
Large-Area Chemically Synthesized Molybdenum Disulfide with Aqueous Thermolysis Method Akira Fujimoto, Shoji Maeda, Ryota Isu, Kei-ichi Sakamoto, Kentaro Matano, Masatoshi Koyama, Yoshiyuki Harada, Kazuto Koike, Shigehiko Sasa and Mitsuaki Yano; Osaka Institute of Technology, Japan

Graphene and 2-dimensional (2D) materials such as molybdenum disulfide (MoS2) have attracted much attention in a wide range of unique electrical and optical properties. But they are basically very small flakes and difficult to control thickness. In comparison with the exfoliation method, chemical vapor deposition has a better potential for fabricating large area 2D materials, but the synthesis is still a challenge. Furthermore, MoS2 films have been prepared by dip-coating ammonium tetrathiomolybdates ([NH4]2MoS4) followed by the annealing process in the atmosphere of Ar and S in order to make up for S deficiencies [1]. The purpose of our study is to synthesize large-area high-quality MoS2 on SiO2/Si substrate by thermolysis of (NH4)2MoS4. By means of employing thioacetamide
(CH₃CSNH₂), we are trying to compensate for deficiency of S in MoS₂ thin films and to improve the crystallinity. Moreover, we are performing Raman scattering measurements in order to explore the molar concentration dependence of the chemical precursors used for the growth of MoS₂.

Aiming for chemically synthesizing MoS₂, we employed the aqueous thermolysis method. (NH₄)₂MoS₄ and CH₃CSNH₂ with the same molar concentration were mixed in deionized water and the mixture was heated at 95 degree C for 5 hours. The solution containing the synthesized MoS₂ was spin-coated onto the 90-nm SiO₂/Si substrates. We confirmed that for the thin films synthesized with the molar concentration less than or equal to 10 mM, Raman double peaks E₁2g and A₁g appeared at about 383 cm⁻¹ and 407 cm⁻¹, respectively. The E₁2g and A₁g peak positions shift to a lower wavenumber with increasing the molar concentration. The Raman peak energy difference can be used to identify the number of MoS₂ layers. We found the thickness of our MoS₂ is as thick as that of MoS₂ natural crystal. On the other hand, for the films synthesized with the larger molar concentration E₁2g and A₁g peaks did not appear and another two Raman peaks strongly appeared at around 810 and 1000 cm⁻¹ originating in MoO₃ [2]. We found a synthesis of MoS₂ using aqueous thermolysis method should be performed under the condition of a lower molar concentration of the chemical precursors.

Furthermore, as for the sample synthesized with the lower molar concentration of (NH₄)₂MoS₄ and CH₃CSNH₂, we performed Raman scattering measurement again after a week. As the result, Raman peak strongly appeared at around 810 cm⁻¹ originating in MoO₃. It is conceivable that oxidation of Mo is caused by a reaction with the residue of water after the synthesis, therefore we consider the residue of water should be evaporated completely to prevent the oxidation of MoS₂. For this purpose, we coated the solution directly on a SiO₂/Si substrate and heated at 200 degree C for 3 hours. Even in a week after the synthesis by means of this improved process, we confirmed E₁2g and A₁g double peaks appeared and Raman peaks derived from MoO₃ did not. Now we are evaluating the electrical properties of these MoS₂ thin films. Moreover, we will stack the MoS₂ thin films and graphene for the application of gas sensors, which transduces gas-molecules adsorption on the surface of these 2D materials and at the MoS₂/graphene interface into a change of the resistance.


9:00 AM FF01.01.05
Synthesis of Molecular 2D Materials via Low-Energy Electron Irradiation Induced Chemical Reactions
Andrey Turchanin1,2; 1Friedrich Schiller University Jena, Germany; 2Center for Energy and Environmental Chemistry Jena (CEEC Jena), Germany

After the demonstration of a variety of inorganic two-dimensional (2D) materials (graphene, hBN, MoS₂, etc.), molecular 2D materials have attracted a significant research interest as well. However, the direct synthesis of these materials is an exceptionally challenging task for material scientists. In this contribution, a simple and robust physical method for the synthesis of molecular 2D materials is presented based on low-energy electron irradiation induced chemical reactions in aromatic molecular layers. In this way, ultrathin (~1 nm) molecular nanosheets with adjustable chemical and physical properties called Carbon Nanomembranes (CNM) can be prepared. Moreover, the method enables the synthesis of various other 2D organic-inorganic hybrids (e.g., MoS₂-CNM, graphene-CNM lateral heterostructures, etc.) [2] or ~20 nm thick nanosheets of organic semiconductors [3]. Functional properties of these molecular 2D materials including their chemical functionalization and engineering of hybrid hierarchical structures for application in electronic and energy conversion devices will be discussed [4-5].


9:15 AM FF01.01.06
Atomically Thin Three-Dimensional Membranes of van der Waals Semiconductors by Wafer-Scale Growth
Gangtae Jin1,2, Chang-Soo Lee3, Xing Liao4, Juho Kim1,2, Zhen Wang5, Odongo Francis Ngome Okello1, Bumsu Park2, Jaehyun Park1,2, Cheolhee Han1,2, Hoseok Heo3, Jonghwan Kim1, Sang Ho Oh4, Si-Young Choi1, Hongkun Park2 and Moon-Ho Jo1,2; 1Pohang University of Science and Technology, Korea (the Republic of); 2Institute for Basic Science (IBS), Korea (the Republic of); 3Harvard University, United States; 4Sungkyunkwan University, Korea (the Republic of)
We report wafer-scale growth of atomically thin, three-dimensional (3D) van der Waals (vdW) semiconductor membranes. By controlling the growth kinetics in the near-equilibrium limit during metalorganic chemical vapor depositions of MoS$_2$ and WS$_2$ monolayer (ML) crystals, we have achieved conformal ML coverage on diverse 3D texture substrates, such as periodic arrays of nanoscale needles and trenches on quartz and SiO$_2$/Si substrates. The ML semiconductor properties, such as channel resistivity and photoluminescence, are verified to be seamlessly uniform over the 3D textures, and are scalable to wafer-scale. Additionally, we demonstrated that these 3D films can be easily delaminated from the growth substrates to form suspended 3D semiconductor membranes. Our work suggests that vdw ML semiconductor films can be useful platforms for patchable membrane electronics with atomic precision, yet in large-areas, on arbitrary substrates.

9:30 AM FF01.01.07
Wafer-Scale Hybrid Organic-Inorganic Superlattices from Monolayer 2D Polymers and Atomic Crystals Yu Zhong$^1$, Baorui Cheng$^1$, Chibeom Park$^1$, Ariana Ray$^2$, Sarah Brown$^1$, Fauzia S. Mujid$^1$, Jae-Ung Lee$^1$, Hua Zhou$^3$, Joonki Suh$^1$, Kan-Heng Lee$^1$, Andrew J. Mannix$^1$, Kibum Kang$^4$, Steven J. Sibener$^1$, David A. Muller$^2$ and Jiwoong Park$^1$; 1University of Chicago, United States; 2Cornell University, United States; 3Argonne National Laboratory, United States; 4Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Two-dimensional (2D) materials own many interesting properties due to their atom-thick characteristics and versatile heterostructures built layer-by-layer. The capability of assembling both organic and inorganic 2D materials into heterostructures will lead to the formation of artificial van der Waals solids that takes advantage of molecular functionalities brought by the organic 2D materials. Towards this end, the biggest hurdle has been the lack of a general method to synthesize organic monolayers at macroscopic dimensions and integrate them with monolayer precision. Herein, we report the general synthesis of monolayer 2D polymers, the molecular analogs of 2D atomic crystals, with wafer-scale homogeneity and the fabrication of the hybrid superlattices. For this, we develop a new interfacial synthesis technique compatible with various molecular building blocks and polymerization chemistries. This approach incorporates key features necessary for scalable and facile processing, including large-area synthesis, ambient growth conditions, and compatibility with established patterning and integration methods. Enabled by those characteristics, hybrid organic-inorganic superlattices of monolayer 2D polymers and 2D atomic crystals were fabricated with molecular precision. The employment of versatile 2D polymers allows the incorporation of functional molecular moieties into two-dimensional electronic circuits. These materials show promising applications in multifunctional 2D electronic devices.

9:45 AM BREAK

SESSION FF01.02: Chemical Vapor Deposition of 2D Materials
Session Chairs: Amber McCreary and Joan Redwing
Sunday Morning, December 1, 2019
Hynes, Level 2, Room 208

10:15 AM FF01.02.01
Controlled Growth, Transfer and Device Integration of Large Crystal Monolayer Hexagonal Boron Nitride Vitaly Babenko$^1$, Ruizhi Wang$^1$, Ye Fan$^1$, Vlad-Petru Veigang-Radulescu$^1$, Oliver Burton$^1$, Jack Alexander-Webber$^1$, Robert Weatherup$^2$ and Stephan Hofmann$^1$; 1Cambridge University, United Kingdom; 2The University of Manchester, United Kingdom

Utilisation of hexagonal boron nitride (h-BN) in applications requires further advancements in the production, processing, integration methods and also their cost reduction. We focus here on catalytic chemical vapour deposition (CVD) and discuss two very different catalysts for monolayer h-BN growth, iron and platinum, examples of a high and low precursor solubility transition metals. For Fe, we systematically explore the role of bulk dissolved species, and find that a simple pre-growth step enables us to tailor a scalable CVD process to give mm-sized h-BN domains,[1] among the largest reported to date. For Pt, we developed sequential step growth to enable independent control of h-BN nucleation and domain expansion to also give large (> 0.5 mm) h-BN domains and continuous
We show that targeted h-BN transfer methods are required for the different catalysts or even tweaked to the processing of the catalyst, whereby we develop a moisture oxidation and acid release method for the iron and a dry peeling approach for platinum. The utilisation of h-BN with graphene is demonstrated as an encapsulating layer for integration with common ALD dielectrics and in FET devices. Additionally, we demonstrate the use of monolayer CVD h-BN as an active material for room temperature single photon emission.

References

Epitaxial Growth of Layered β-In2Se3 Thin Films via Metalorganic Chemical Vapor Deposition Xiaotian Zhang, Sora Lee, Anushka Bansal, Fu Zhang, Mauricio Terrones, Thomas Jackson and Joan M. Redwing; The Pennsylvania State University, United States

2D materials have attracted wide interest because of their potential performance and diversity of function as electronic and optoelectronic materials. Growth of transition metal dichalcogenides (TMDs) such as MoS2 and WSe2 typically requires high temperatures (>700 °C) for large domain size and epitaxy. This restricts the applications of these materials, especially considering the growing interest in 2D materials integration with silicon in back-end-of-line (BEOL) applications that require processing temperature < 450 °C. In contrast, group III metal chalcogenides (indium selenide and gallium selenide) possess lower melting temperatures than TMDs and thus high crystal quality films are anticipated at lower growth temperature. In addition, depending on their stoichiometry and phase, they also have a layered structure that offers interesting physical, electronic, and piezoelectric properties down to the monolayer limit. In the case of indium selenide, there is interest in γ-InSe due to its high carrier mobility (>1000 cm2/Vs) and β-In2Se3 and α-In2Se3 which are ferroelectric phases. Despite the intriguing properties, there have been few studies thus far aimed at investigating the epitaxial growth and properties of indium selenide films.

In this study, we demonstrate the growth of β-In2Se3 thin films on various substrates in a vertical cold-wall metalorganic chemical vapor deposition (MOCVD) system at 400 °C using trimethylindium (TMIn) and hydrogen selenide (H2Se) in a H2 carrier gas. The In2Se3 films were grown epitaxially on c-plane sapphire and Si (111) surfaces. The films were identified as β-In2Se3 by both Raman and XRD. A low reactor pressure (100 Torr) and high total gas flow rate were required to suppress gas-phase reactions between TMIn and H2Se based on their Lewis acid and base properties. β-In2Se3 films were formed on both c-plane sapphire and Si (111) surfaces in this work, however, γ-In2Se3 films were synthesized on amorphous SiO2/Si substrates indicating the importance of substrate type determining the crystal structure of the films. Top-gated thin film transistors (TFTs) fabricated on β-In2Se3 thin films reasonable mobility and on/off ratio and therefore offer potential applications in electronic devices.
SrTiO$_3$ is greatest when maximum commensuration between the lattices is achieved. Therefore, a key finding of this work is that the vdW interaction between MoS$_2$ and SrTiO$_3$ substrates determines the supported crystal shapes and orientations by epitaxial relations. Controlled crystal orientations make the growth of large sheets of MoS$_2$ possible when there are multiple nucleation sites. This minimizes the number of grain boundaries and optimizes the electronic properties of the material, e.g., charge mobility, which is crucial for the application of monolayer MoS$_2$ in next-generation nanoelectronics devices.

11:00 AM FF01.02.04
Accessing High Optical and Structural Quality of CVD Grown MoS$_2$ Monolayers Shivangi Shree$^1$, Antony George$^2$, Tibor Lehner$^3$, Cedric Robert$^1$, Xavier Marie$^1$, Kenji Watanabe$^4$, Takashi Taniguchi$^4$, Ute A. Kaiser$^1$, Bernhard Urbaszek$^1$ and Andrey Turchanin$^2$; $^1$CNRS LPCNO INSA-CNRS-UPS, France; $^2$Friedrich Schiller University Jena, Institute for Physical Chemistry, Germany; $^3$University of Ulm, Germany; $^4$National Institute for Materials Science, Japan

Transition metal dichalcogenides (TMDs) are ideal for exploring fundamental physics and applied optics as they are semiconductors with a direct bandgap in the monolayer (ML) limit. Therefore, it is very important to have access to high quality and also large surface area films. Here we show that chemical vapour deposition (CVD) growth can yield high quality MoS$_2$ monolayers on SiO$_2$/Si substrates.

We show high structural quality of CVD grown MoS$_2$ MLs on SiO$_2$ [1] in 4k x 4k high-resolution transmission electron microscopy (HRTEM) images using the chromatic and spherical aberration-corrected low-voltage TEM instrument operated at 60 kV. We determine a defect concentration of $10^{13}$/cm$^2$ in as grown MoS$_2$ MLs. But we observe broad optical transitions in as-grown samples (50 meV FWHM at T = 4K) on SiO$_2$ that are not expected for high structural quality, therefore indicating detrimental ML-substrate interactions. Therefore, we lift off the CVD grown layers from the growth substrate and encapsulate them in hBN flakes, which give us access to the intrinsic optical quality of the MoS$_2$ MLs.

We compare the optical quality of MoS$_2$ MLs in three different structures: CVD grown MoS$_2$ films on SiO$_2$, exfoliated MoS$_2$ ML from bulk MoS$_2$ in exfoliated hBN and most importantly MoS$_2$ ML grown by CVD encapsulated in hBN crystals prepared by mechanical exfoliation. For the latter structure, we show (i) in photoluminescence the neutral A-exciton emission linewidth reduced to 5 meV at T = 4 K, as compare to 50 meV linewidth in the as grown CVD sample and (ii) in absorption well separated optical transitions A:2s stemming from excited states of the A-exciton Rydberg series, indicating comparable quality of our CVD MLs to exfoliated MoS$_2$ material. We optically generate valley coherence and valley polarization in our CVD grown MoS$_2$ layers, showing the possibility for studying spin and valley physics in CVD samples of large surface area.


11:15 AM FF01.02.05
High Temperature CVD of Hexagonal Boron Nitride on Sapphire Using Carbon Free Precursors Anushka Bansal, Tanushree H. Choudhury, Mikhail Chubarov and Joan M. Redwing; The Pennsylvania State University, United States

Hexagonal Boron Nitride (hBN) is a 2D, III-nitride wide bandgap semiconductor that has a structure very similar to graphene. Due to its extraordinary physical properties, such as high resistivity, high thermal conductivity, stability in air up to 1000°C, large bandgap (Eg $\sim$ 5.9 eV), hBN appears to be a promising material for emerging applications, including deep UV (DUV) optoelectronics, electron emitters and neutron detectors. There is also significant interest in monolayer and few-layer hBN as an encapsulating layer for 2D devices based on graphene and transition metal dichalcogenides.

While high quality hBN bulk crystals are available for exfoliation, the size of the crystals is limited, consequently there is continued interest in the epitaxial growth of large area hBN films using chemical vapor deposition (CVD). The low temperature (500-1000°C) CVD growth of hBN on metallic substrates such as Cu, Ni, Pt, Ru etc. has been widely studied using ammonia borane (H$_3$N-BH$_3$) and borazine (B$_3$N$_6$H$_6$) as single-source precursors. However, NH$_3$ has been used in some cases to control the N/B ratio. In addition, borazine is thermally unstable and readily reacts forming low volatility polymers. While growth on metal substrates is a viable approach, there is significant
interest in the growth of hBN on non-metallic surfaces for device applications. The growth of hBN on a sapphire substrate was initially reported by Nakamura et. al. in 1986 followed by Kobayashi et. al in 2008 and others at a growth temperature greater than 1200°C. The precursors used for these growths includes triethyl boron (B(C₂H₅)₃, TEB), trimethyl boron (B(CH₃)₃, TMB) and NH₃ as the source of N. It is well known, however, that organic sources such as TEB result in carbon incorporation which is the biggest concern for the growth of epitaxial high purity BN films.

In this work, we are studying the growth of crystalline sp² BN in a vertical cold wall MOCVD reactor using a mixture of diborane (5% B₂H₆ in H₂) and NH₃ as precursors for B and N, respectively using H₂ as a carrier gas. The growths are performed on nitrided c-plane sapphire substrates at temperatures ranging from 1100-1500°C. Diborane reacts with NH₃ at temperatures as low as room temperature to form H₃N-BH₃ and other volatile B-N species, consequently, gas phase chemistry plays an important role in this deposition process. The influence of temperature, N/B inlet gas ratio and precursor flow method (pulsed versus continuous) on the material quality, characteristics and deposition rate were studied. In the lower temperature range (<1200°C), stoichiometric sp² BN films were obtained on sapphire using a N/B ratio of ~600 under continuous precursor flow giving a growth rate of ~10 nm/hr. Sequential pulsing of the B₂H₆ and NH₃ precursors resulted in a significant increase in the growth rate (~18 nm/hr) due to a reduction in the extent of gas phase reaction. Additional studies are underway to investigate growth at higher temperatures and over a wider parameter space to ascertain the growth mechanism as a function of conditions to provide additional insights into the role of gas phase chemistry on the properties of highly crystalline sp² BN films on sapphire.

11:30 AM FF01.02.06
Catalytically Enhanced Metal Organic Chemical Vapour Deposition of WS₂ Monolayer Films Stephan Hofmann, Ye Fan, Kenichi Nakanishi, Vlad-Petru Veigang-Radulescu, Jack Alexander-Webber, Ryo Mizuta and James C. Stewart; University of Cambridge, United Kingdom

Despite an abundance of reported growth methods, a key challenge for both current research and future technologies is the efficient and scalable growth and device integration of “electronic-grade” 2D layers. Metal organic chemical vapour deposition (MOCVD) has emerged as highly suitable particularly for transition metal dichalcogenide (TMDC) layer growth [1]. However, the understanding of the MOCVD process and control over detailed TMDC micro-structure remains currently limited, and carbon contamination and long growth times are of concerns. Our motivation is to advance the understanding of the growth mechanism of TMDCs with the focus on developing improved, scalable process technology. We employ here a “deconstructed” MOCVD process for WS₂, based on a simple sequential exposure pattern using precursors with low toxicity, namely tungsten hexacarbonyl and dimethylsulfide [2]. Combined with the use of a cold-walled reactor set-up, this minimises precursor pre-reactions and warrants a substrate surface bound reaction path. We use this as model system to systematically explore each growth aspect, including different substrates and their pre-treatment. For Au support, we find a significant catalytic effect that not only allows a significant reduction of the carbon contamination but also a self-limiting behaviour to mono-layer WS₂ with reasonable crystallinity, and full coverage within 10min exposure times. We discuss in this context of overlap between MOCVD and ALD processes, and, in parallel to other 2D materials, of suitable device integration strategies [3].

References
[1] Briggs et al. 2D Mater. 6, 022001 (2019)

11:45 AM FF01.02.07
Van der Waals Epitaxial Growth of Transition Metal Dichalcogenides on Sapphire—Surface Chemistry Effect and Lessons for Other 2D Materials Assael Cohen, Kamal Ranganathan, Avinash Patsha and Ariel Ismach; Tel Aviv University, Israel

The ability to synthesize large-area and high quality atomic films is a prerequisite for their successful integration into a wide variety of novel and existing technologies. Here we show the growth of transition metal dichalcogenides (MoS₂, WS₂ and WSe₂) via modified chemical vapor deposition (CVD) methods using volatile precursors [1,2]. The use of high vapor pressure precursors allows for the controlled delivery to the growth sample [3], and therefore,
suitable for homogeneous and large-scale synthesis, as required for many applications. However, one of the problems with these precursors is the small domain size usually obtained [3]. In this scheme, a modified approach in which the metal and chalcogen precursors are delivered in a pulsed fashion is demonstrated. This approach allows to achieve a ten-fold increase in the domain size, from ~500 nm (or below) to ~10s of microns. Moreover, we demonstrate that the growth kinetics is highly dependent on the surface chemistry and by controlling it, the growth of ad-layers is inhibited and thus, more than 95% monolayer films are obtained. Another advantage of using volatile precursors is the ability to control the lateral and vertical heterostructures formation, and will be described as well. Following this work and in order to expand our growth capabilities, the growth of monochalcogenides using lessons learned while growing TMDs will be briefly described. Systematic structural, chemical, spectroscopic and electrical characterization will be shown for both systems as well. This work presents a big step towards the controlled growth of 2D materials.


SESSION FF01.03: Novel Stabilized 2D Materials and Heterostructures
Session Chairs: Zakaria Al Balushi and Deep Jariwala
Monday Morning, December 2, 2019
Hynes, Level 3, Room 312

8:00 AM FF01.03.01
In Situ Growth of Group V 2D Materials Matthieu Fortin-Deschênes¹, Robert Jacobberger², Charles-Antoine Deslauriers¹, Michael S. Arnold² and Oussama Moutanabbir¹; ¹Polytechnique Montreal, Canada; ²University of Wisconsin–Madison, United States

Although the existence of thousands of new 2D materials are being theoretically predicted [1], only a handful can be experimentally synthesized with the level of control required for their large-scale integration in future innovative devices and technologies. This is mainly due to the insufficient control over the nucleation at vdW interfaces, to the difficulty of implementing self-limiting monolayer growth in many systems and to the lack of experimental data regarding the van der Waals growth dynamics. In this talk, we will present in situ Low-Energy Electron Microscopy (LEEM) studies of the van der Waals growth dynamics of novel group V 2D materials. By combining LEEM and LEED measurements of the growth dynamics of antimonene on germanium and graphene substrates [2, 3] with semi-empirical modelling of the growth kinetics, we are able to determine the mechanisms governing the lateral and vertical growth modes of this new 2D material and to achieve a better control over the growth morphology. Moreover, we will present experimental evidence of the synthesis of a new 2D AsₓSb₁₋ₓ alloy with tunable As content. These results lay the groundwork for the implementation of novel group V 2D materials and heterostructures in electronic, optoelectronic and quantum devices.


8:15 AM FF01.03.02
Electron Beam Evaporated 2D Bismuth for Innovative Nanoelectronics Xinghao Sun¹, Wen Zhong¹, Zhaoying Dang¹, Seth Bank², Deji Akinwande², Beibei Zhu¹ and Li Tao¹; ¹Southeast University, China; ²The University of Texas at Austin, United States

Two-dimensional elemental materials (X-enes) have attracted increasing research attention due to tunable bandgap in between graphene and TMDs. As an emerging 2D X-ene, bismuthene, is expected to yield descent carrier
2D bismuth thin film is grown on Si (111) or SiO2/Si substrates in an e-beam evaporator. Before the deposition, Si (111) and SiO2/Si substrates were cleaned by ultrasonic in acetone for 5 min and rinsed by isopropyl alcohol and deionized water. Deposition of bismuth was initiated from a 99.999% pure Bi source at a rate of 0.1 Å/s under 5.0×10^-4 Pa pressure. The thickness of our Bi thin films can vary from 1-50 nm. Annealing effect is also studied via a tube furnace at 50-260°C in Ar atmosphere. Raman spectroscopy confirmed the successful growth of 2D bismuth with signatures at 70.4 cm⁻¹ (Eg) and 96.1 cm⁻¹ (A1g) which have a blue shift as thickness increases. X-ray diffraction on evaporated 20-nm thick Bi films observed expected hexagonal (001) orientation - a good crystallinity. A typical surface roughness is ~1nm indicated by atomic force microscope imaging over a 10×10μm² area, indicating a smooth surface for following device fabrication. The evaporated 2D bismuth, as the channel material, on SiO2/Si or Si (111) substrates, was then subjected to a field effect transistor fabrication process via lithography and Ti/Au electrodes evaporation. Electrical characterization, such as I-V curve for different thickness 2D bismuthene has been characterized on a Cascade® EPS150 probe station. A linear I-V curve reveals a good ohmic contact with conductivity ~3.65×10⁴ S/m for 20-nm 2D Bi and ~6.27×10⁴ S/m for 30-nm. Experimental research on photoelectric and thermoelectric behavior of e-beam evaporated 2D bismuthene has been carried out, which exhibited similar properties comparable to MBE bismuthene samples we prepared under the same material and device configuration in this study. Photoelectricity is observed under a wide range (visible to IR) laser exposure with photo responsibility ~10 A/W at unit power exposing to 800-nm laser. The Seebeck coefficient of our 2D bismuth was measured as -17.8μV/k (N type) at room temperature, which is greater than graphene. This study explored e-beam evaporation of 2D bismuth film and its material/device characterization comparable to MBE counterpart. This cost-effective method to prepare good quality bismuthene and its device holds great promise for innovative photoelectric and thermoelectric applications.

8:30 AM FF01.03.03
Chemically Tunable 2D Layered Materials via Intercalation and Deintercalation Mengjing Wang¹ and Kristie J. Koski²; ¹University of Central Florida, United States; ²UC Davis, United States

2D layered materials reside in a class of crystals consisting of weakly bonded atomic layers by van der Waals attraction. In particular, this distinct structure feature renders 2D layered materials exceptional physical and chemical properties inaccessible in bulk crystals, e.g., quantum confinement and surface effects, which offer 2D materials a wide range of applications in electronics, optoelectronics, energy storage, catalyst, and chemical sensing fields. One of the remaining challenges in the 2D material arena is to explore novel layered materials with breaking new properties. Rather than searching for new materials, we pursued developing reliable chemical routes, intercalation/deintercalation of metals, to tailor the original 2D materials with tunable chemical and physical properties. This talk will cover a series of innovative chemical intercalation/deintercalation of metals in layered crystals (chalcogenides and oxides), followed by examples of unusual phenomena introduced by intercalation, including polytypic phase transitions in metal intercalated Bi₂Se₃, and the chemo-chromism/thermochromism of MoO₃ intercalated with metal.

8:45 AM *FF01.03.04
Creating Atomically-Thin Metals for Next Generation Quantum Architectures Joshua A. Robinson; The Pennsylvania State University, United States

Quantum materials are prime candidates for next-generation energy-efficient technologies, such as topological quantum computing, quantum sensing, and neuromorphic computing. While van der Waals 2D materials exhibit a compellingly wide range of exotic and potentially useful properties such as charge density waves, topological insulator edges, and superconductivity, one can also realize these properties by stabilizing new 2D allotropes of traditionally 3D superconductors and magnets. In this talk I will discuss our pioneering work in confinement heteroepitaxy (CHet) that enables the creation of 2D forms of 3D materials (e.g. 2D-Ga, In, Sn, Ag, Au, etc.) and decouples the growth of the metals from other 2D layers, thereby enabling a new platform for creating artificial quantum lattices with atomically sharp interfaces and designed properties. As a specific example, we synthesize
plasmonic layers that exhibit >2000x improvement in nonlinear optical properties, and 2D-superconductors combined with topological insulators as the building block of next generation “2D” topological superconductors. Confinement heteroepitaxy opens up avenues for enabling a virtual “legoland” of hybrid quantum materials.

9:15 AM FF01.03.05
**Stable Silicene in Graphene/Silicene van der Waals Heterostructures**

Yuyang Zhang¹, Geng Li¹, Lihong Bao¹, Shixuan Du¹, Sokrates Pantelides² and Hong-Jun Gao¹; ¹Chinese Academy of Sciences, China; ²Vanderbilt University, United States

As a two-dimensional analog of graphene, silicene has recently been the subject of extensive research interest. The easy oxidation of silicene in air limits its applications in device design and fabrication. In this talk we report the experimental fabrication of silicene protected by a graphene overlayer. The graphene layer is grown first on a Ru(0001) substrate and silicene is grown under it by Si intercalation. By controlling the amount of silicon, ordered arrays of pseudomorphic silicene nano flakes as well as single layers and multilayers of silicene can be successfully fabricated under graphene that is epitaxially grown on Ru(0001). Density-functional-theory calculations show weak interactions between graphene and silicene layers, indicating that the fabricated structures are silicene/graphene van der Waals heterostructures. The as-prepared silicene-based structures show no observable damage after air exposure for two weeks. The vertical graphene/silicene/Ru heterostructure shows rectification behavior with an ideality factor of ~1.5 [1].

References:

9:30 AM BREAK

10:00 AM FF01.03.06
**CVD Synthesis and Properties of Bilayer Graphene and TMDs**

A T Charlie Johnson; University of Pennsylvania, United States

Two-dimensional (2D) van der Waals (vdW) materials fabricated by stacking of homogeneous or heterogeneous monolayer “building blocks” are attracting increased attention, since their unique physical and chemical properties offer great promise for use in atomically thin electronic and optoelectronic devices. For stacks of homogeneous 2D vdW materials, the number of layers plays a crucial role in the ultimate optoelectronic properties. Since the change in properties from monolayer to bilayer to trilateral is typically more significant than that resulting from additional layers, there is great interest in achieving precise control over bilayer/trilayer formation, including the stacking geometry. In this talk I will discuss how we have made progress in this area through new methods of controlling the catalytic growth substrate, in the case of graphene, and growth promoting compounds in the case of TMD materials.

10:30 AM FF01.03.07
**Tuning the Dimensionality and Optical Properties of TMDs with Substrate Directed Synthesis**

Thomas J. Kempa, Tomojit Chowdhury and Jungkil Kim; Johns Hopkins University, United States

Two-dimensional (2D) transition metal dichalcogenides (TMDs) exhibit an intriguing array of layer-, topology-, and morphology-dependent properties, which have demonstrated enormous potential in optoelectronics, energy conversion, and quantum information science. Although “top-down” approaches can be used to define crystal morphologies and dimensions, explicit synthetic control of the physical properties of TMD crystals is desirable, but also a major challenge. We demonstrate a gas-phase synthesis method that significantly transforms the structure and dimensionality of MoS₂ and other TMD crystals without lithography. Synthesis of MoS₂ on Si (001) surfaces pre-treated with phosphine (PH₃) furnishes high aspect ratio nanoribbons of crystalline 2H phase MoS₂. The widths of these nominally 1D crystals are exceptionally uniform and their edges are sharper than those of TMD crystals prepared by most other means. Notably, the widths of the MoS₂ nanoribbons can be systematically controlled between 70 nm and 500 nm by varying the concentration of PH₃ gas introduced during the Si surface treatment step. Detailed kinetic studies supported by cluster expansion and DFT calculations indicate that the structure and concentration of the underlying Si–phosphide moieties is instrumental in transforming growth of MoS₂ from a conventional 2D triangular to nominally 1D morphology. Notably, far-field and near-field photoluminescence (PL)
studies of 1D MoS$_2$ crystals show that they exhibit an emission peak which is blue-shifted by 50 meV relative to that of 2D MoS$_2$ nanocrystals. Our efforts highlight future opportunities for development of designer substrates that could mediate the synthesis of new low-dimensional crystals with prescribed structures and properties.

10:45 AM FF01.03.08
Large Scale Synthesis of MoS$_2$: One-Dimensional Nanostructures and the Precision Manipulation
Yun Huang$^{1}$, Kang Yu$^{1,2}$, Zexi Liang$^{1}$, Paulo Ferreira$^{2,1}$, and Donglei Fan$^{1,1}$; $^{1}$The University of Texas at Austin, United States; $^{2}$International Iberian Nanotechnology Laboratory, Portugal

In the family of two dimensional (2D) materials, molybdenum disulfide (MoS$_2$) has received immense attention owing to its unique electrical, catalytic, biological and mechanical properties. Herein, we report a robust and scalable approach to synthesize MoS$_2$ nanoribbons with controlled dimensions. Advanced characterizations confirm the chemistry, morphology, and crystalline structures of materials obtained at different reaction stages when synthesizing MoS$_2$, including MoO$_3$, MoS$_2$/MoO$_2$ hybrid, and MoS$_2$ nanoribbons. With the electric tweezers based on combined AC and DC electric fields, the MoS$_2$ nanoribbons can be readily manipulated with desired orientations along arbitrary trajectories, e.g. a cat drawing. Moreover, it is found that the electromechanical behaviors of the particles obtained at different stages strongly correlate with their electric properties, the demonstration of which could be utilized to monitor and understand the synthesis of targeted nanomaterials. This work could lead to a new paradigm in the large-scale fabrication of 2D materials with designed dimensions and inspire their innovative applications in nanorobotics, micro/nanoelectromechanical system devices (MEMS/NEMS), as well as molecule delivery and release.

11:00 AM FF01.03.09
Helical van der Waals Crystals with Discretized Eshelby Twist
Yin Liu$^{1}$, Jie Wang$^{2}$, Sujung Kim$^{1}$, Haoye Sun$^{1}$, Fuyi Yang$^{1}$, Zixuan Fang$^{1}$, Nobumichi Tamura$^{1}$, Ruopeng Zhang$^{1,3}$, Xiaohui Song$^{1}$, Jianguo Wen$^{2}$, Qin Yu$^{1}$, Michael Wang$^{1}$, Emory Chan$^{1}$, Dafet Jin$^{2}$, Robert O. Ritchie$^{1}$, Andrew M. Minor$^{1,3}$, Daryl Chrzan$^{1}$, Mary Scott$^{1,3}$ and Jie Yao$^{1}$; $^{1}$University of California, Berkeley, United States; $^{2}$Argonne national laboratory, United States; $^{3}$Lawrence Berkeley National Laboratory, United States

The ability to manipulate the twisting topology of van der Waals (vdW) structures enables a new degree of freedom to tailor their electrical and optical properties. In particular, the twist angle has been shown to strongly affect the electronic states, excitons and phonons of the twisted structures via interlayer coupling, giving rise to exotic optical, electric and spintronic behaviors. In twisted bilayer graphene, at certain twist angles, long-range periodicity associated with Moiré pattern introduces flat bands and highly localized electronic states, resulting in Mott insulating behavior and superconductivity. Beyond bilayer graphene, recent theoretical studies suggest these twist-induced localization and the formation of flat bands are phenomena common to various layered materials such as transition metal dichalcogenides and black phosphorus. Twisted vdW structures are usually created using transfer-stacking method, where atomic layers are mechanically exfoliated and transferred to stack with controlled twist angles in a layer-by-layer configuration. This approach, however, is not suitable to create twisted structures of a variety of layered materials with relatively strong interlayer binding. In contrast, facile bottom-up growth methods could provide an alternative means to create twisted vdW structures. Herein, we demonstrate that the Eshelby twist, associated with a screw dislocation, a chiral topological defect can drive the formation of twisted vdW structures on multiple scales ranging from nanoscale to mesoscale. In our synthesis method, axial screw dislocation was first introduced into vdW nanowires with growth direction along the vdW stacking direction (cross-plane direction), yielding vdW nanostructures with continuous twisting. Further growth on the dislocated nanowires adhered to the substrate results in the discretization of the Eshelby twist in the mesoscale structures, yielding unique twisting structures consisting of a helical assembly of nanoplates. In these mesoscale helical crystals, atomically sharp interfaces with various twist angles are created, providing an intriguing tunable platform to explore various interlayer coupling effects. Our theoretical modeling suggests that the formation of the discretized twisting results from the interplay between the interfacial energies associated with the twist interfaces and the elastic strain energy defined by the Eshelby twist. We further show that the twisting topology can be tailored by controlling the radial size of the structure.

11:15 AM FF01.03.10
Stabilization of Tellurene—A New Group VI 2D Material
Moon J. Kim$^{1}$, Wenzhuo Wu$^{2}$, Peide P. Ye$^{2}$, Robert Klie$^{3}$ and Maria K. Chan$^{4}$; $^{1}$The University of Texas at Dallas, United States; $^{2}$Purdue University, United States;
Since the discovery of graphene [1], other 2D materials such as silicene, germanene, borophene, phospherene, and various transition metal dichalcogenides (TMDs) have been explored in a great deal due to their novel structure and tunable properties. In contrast, group VI elements such as tellurium or selenium have yet to be stabilized in purely 2D forms, which may be due to its stable covalently bonded Te atomic chains that spiral along its c-axes. In this case, a typical exfoliation technique to produce 2D monolayers would not work. However, the density functional theory calculations by Zhu et al. predict that 2D atomic layers of tellurium might exist in stable 1T-like structure (a-Te), and the metastable tetragonal (b-Te) and 2H-like (g-Te) structures [2].

Here, we report the first experimental realization of a 2D group VI tellurium chalcogen, namely tellurene. Ultra-thin flakes of tellurium with controlled thickness were produced by substrate-free solution process. Each 2D tellurene flakes have thicknesses ranging from 15 to 100 nm. Tellurene flakes with a thickness smaller than 10 nm were also produced through a solvent-assisted post-growth thinning process [3]. A single atomic layer 2D tellurium was also synthesized by a wafer-bonding assisted self-assembly process, a new approach to synthesize and stabilize the low-dimensional structure. Each monolayer Te atom has four nearest neighbors within the plane with inter-atomic distances of 0.31 – 0.32 nm. Atomic-resolution chemical mapping and structural characterization via scanning transmission electron microscopy (STEM) leading to the definitive identification of single atomic layer tellurene.

First-principles calculations found tellurene to be metallic, with electronic band structures containing Dirac-cone-like features and exhibiting significant asymmetric spin-orbit band splitting. These findings enable further research into the suitability of tellurene for device applications, such as spintronics and quantum computing.


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Organic-Inorganic 2D Halide Perovskites Mercouri G. Kanatzidis: Northwestern University, United States

Two-dimensional (2D) layered halide perovskites are highly promising semiconductors for optoelectronic applications ranging from solar cells, light emitting diodes and detectors. This class of 2D materials gaining significance as they offer high synthetic versatility and allow for more specialized device implementation due to the directional nature of the crystal structure. A remarkable advantage of the 2D perovskites is the readily tunable functionality by incorporating a wide array of organic cations into the 2D framework and by controlling the slab thickness, in contrast to the 3D analogues which have limited scope for structural engineering. We present the new homologous series, (C(NH2)3)(CH3NH3)nPbnI3n+1 (n = 1, 2, 3), of layered 2D perovskites which is different from Ruddlesden-Popper type. These compounds adopt an unprecedented structure type which is stabilized by the alternating ordering of the guanidinium and methylammonium cations in the interlayer space (ACI). The these 2D perovskites combine structural characteristics from both Dion-Jacobson (DJ) and Ruddlesden-Popper (RP) structure archetypes. We also report the first examples of hybrid DJ hybrid 2D lead iodide perovskites which consist of thick perovskite slabs (n>1) with layer number (n) ranging from 1 to 5. We describe two new DJ perovskite series based on bivalent (+2) spacer cations deriving from a piperidinium (C5NH12) organic backbone. The new DJ perovskites are built from 3AMP (3AMP = 3-(aminomethyl)piperidinium) and 4AMP (4AMP = 4-(aminomethyl)piperidinium) spacers and methylammonium (MA) perovskitizers cations to form A'(MA)n-1PbnI3n+1 (A' = 3AMP or 4AMP, n = 1-4) homologous series acting as spacers. Surprisingly, a slight difference in the position of the-CH2NH3+ group on the piperidine chair (3- and 4- position with respect to the piperidine nitrogen) exerts a strong influence on the crystal structure, which is reflected on the distortion of the inorganic layers.
Emerging Neuromorphic Devices Based on Two-Dimensional Materials
Mark C. Hersam; Northwestern University, United States

The exponentially improving performance of conventional digital computers has slowed in recent years due to the speed and power consumption issues that are largely attributable to the von Neumann bottleneck (i.e., the need to transfer data between spatially separate processor and memory blocks). In contrast, neuromorphic (i.e., brain-like) computing aims to circumvent the limitations of von Neumann architectures by spatially co-locating processor and memory blocks or even combining logic and data storage functions within the same device. In addition to reducing power consumption in conventional computing, neuromorphic devices also provide efficient architectures for emerging applications such as image recognition, machine learning, and artificial intelligence. With this motivation in mind, this talk will explore the opportunities for two-dimensional materials in neuromorphic devices. For example, by combining p-type black phosphorus with n-type transition metal dichalcogenides, gate-tunable diodes have been realized, which show anti-ambipolar transfer characteristics that are suitable for artificial neurons, competitive learning, and spiking circuits [1]. In addition, by exploiting field-driven defect motion mediated by grain boundaries in monolayer MoS2, gate-tunable memristive phenomena have been achieved, which enable hybrid memristor/transistor devices (i.e., “memtransistors”) that concurrently provide logic and data storage functions [2]. The planar geometry of memtransistors further allows multiple contacts to the channel region that mimic the behavior of biological neurons such as heterosynaptic responses [3]. Overall, this work introduces new foundational circuit elements for neuromorphic computing in addition to providing alternative pathways for studying and utilizing the unique charge transport characteristics of two-dimensional materials [4].


2D Heterostructure-Based Neuromorphic Computing
Sanghoon Bae, Beomseok Kang, Chansoo Kim and Jeehwan Kim; Massachusetts Institute of Technology, United States

A current artificial intelligence (AI) system consumes massive computing resources from supercomputers to handle computing traffic inside deep neural networks (DNN). Although interesting application-specific integrated circuits (ASIC) solutions in CMOS have been introduced, we are still suffering limitations on memory footprint, in-memory computing, and on-/off-chip communication. In this regard, a novel computing architecture based on non-volatile resistive switching devices called RRAM has shown a great potential as the RRAM device can continuously tune its analog conductance under moderate voltage stimulation, and thus each device can efficiently execute the “synaptic weight” in the neural network. In addition, the RRAM based computing can accomplish considerably higher integration density compared with the current CMOS technologies and highly efficient parallel computing. Therefore, people have put intensive effort in development of the RRAM array-based system beyond the current supercomputing system [1].

Here, we propose a novel approach to demonstrate stable RRAM array based on 2D heterostructure, which enables real neuromorphic computing for the first time. 2D materials have been known to have atomically thin feature for high integration density and anisotropic ionic transport characteristic in the in-plane and the out-of-plane direction for stable switching filament formation. It makes them promising as a switching medium for neuromorphic computing. Despite of this great potential, there was no study for real neuromorphic computing demonstration using 2D materials based memristors because limited approaches exist for large scale, uniform 2D materials demonstration. Last year, we reported an interesting method for large-scale, uniform 2D materials which ensures pristine interface at interface of heterostructures [2]. With the method, we, for the first time, have realized a 2D
heterostructure memristor array having large memory window over $10^4$ and stable filament formation even after 100 times set-reset cycling test, which successfully functions to implement image recognition simulation. We strongly believe that this innovative approach can open a new opportunity for the neuromorphic computing.


**2:15 PM *FF01.04.03***

**All-Solid-State Non-Volatile Memory Gated by a Monolayer Electrolyte**

Jierui Liang¹, Ke Xu¹, Maokun Wu², Benjamin Hunt³, Wei-Hua Wang⁴, Kyeongjae Cho⁴ and Susan Fullerton¹; ¹University of Pittsburgh, United States; ²Nankai University, China; ³Carnegie Mellon University, United States; ⁴The University of Texas at Dallas, United States

A non-volatile, solid-state, one-transistor (1T) memory is demonstrated based on electric double layer (EDL) gating of a WSe₂ field-effect transistor (FET) using an electrolyte that is a single molecular layer thick. The “monolayer electrolyte” consists of cobalt crown ether phthalocyanine and lithium ions, which are positioned by field-effect at either the surface of the WSe₂ channel or a h-BN capping layer to achieve ‘1’ or ‘0’, respectively. Bistability in the monolayer electrolyte memory is significantly improved by the h-BN cap, with density functional theory (DFT) calculations showing an enhanced trapping of Li⁺ near h-BN due to a $\sim 1.34$ eV increase in the absolute value of the adsorption energy compared to vacuum. The threshold voltage shift between the two states corresponds to a change in charge density of $\sim 2.5 \times 10^{12}$ cm$^{-2}$, and an on-off ratio exceeding $10^4$ at a back gate voltage of 0 V. The on-off ratio remains stable after 1000 cycles and the retention time for each state exceeds 6 hours (max measured). When the write time approaches 1 ms, the on-off ratio remains $> 10^2$, showing that monolayer electrolyte-gated, 2D non-volatile FET can respond on timescales similar to existing flash memory. The data suggest that faster switching times and lower switching voltages could be feasible by top gating.

The research is supported by the National Science Foundation (NSF, U.S.) under Grant No. ECCS-GOALI-1408425 and DMR-CAREER-1847808. M. Wu and W. Wang acknowledge support from the National Key Research and Development Program of China with No. 2016YFB0901600 and National Natural Science Foundation of China with No. 11874223 and 51871121.

**2:45 PM FF01.04.04***

**Nonvolatile Resistive Memory Realized by the Morphological Control of Two-Dimensional Layered Double Hydroxide**

Haein Cho¹, Chan Woo Jeon², Jingon Jang¹, Il Kyu Park² and Gunuk Wang¹; ¹Korea University, Korea (the Republic of); ²Seoul National University of Science & Technology, Korea (the Republic of)

Diverse forms of two-dimensional (2D) materials have been attracting a lot of attention as emerging materials for low-power and high-performance electronic or optoelectronic devices. Layered double hydroxide(LDH) is a kind of 2D layers consisting of a positively charged metal hydroxide layer and intercalated charge-balancing anions, expressed by $[\text{M}^{2+}_{1-x}, \text{M}^{3+}_x \text{(OH)}_2]^x$ $(\text{A}^{6+})^{x/2} \cdot \text{mH}_2\text{O}^2$. In this study, we synthesized three LDH layers using three divalent cations such as Zn$^{2+}$, Ni$^{2+}$, and Co$^{2+}$ and controlled each packing density, which all were confirmed by XRD and SEM analysis. Then, we analyzed and performed the electrical properties for each LDH in a form of two-terminal vertical junction structures using Pt and FTO electrode. Interestingly, only densely-packed ZnAl-LDH based device exhibited unipolar switching behavior with $10^4$ ON-OFF ratio and acceptable stability, while all others did not show any switching feature. The potential reason for the switching success or failure might be attributed to the morphology difference in LDH layers induced by different ion components and concentrations during LDH synthesis. A potential switching mechanism can be suggested by space-charge-limited conduction (SCLC) transport and directional motion of ionic vacancy by the electric field. Our result indicates the importance of 2D LDH stacking morphology for the implementation of the nonvolatile resistive switching device.

3:00 PM BREAK

SESSION FF01.05: Advances in 2D Memory and Transistor Architecture
Session Chairs: Susan Fullerton and Amber McCreary
Monday Afternoon, December 2, 2019
Hynes, Level 3, Room 312

3:30 PM FF01.05.01
Memristive Behavior and Switching Mechanism in Transfer-Free 2D WS2/MoS2 Heterojunction Wenguang Zhang, Chunsan Deng, Sanlue Hu, Hao Wu, Jingwei Liu and Wei Xiong; Huazhong University of Science and Technology, Wuhan National Laboratory for Optoelectronics, China

The recent progress in memristor technology has made it an appealing competitor for future computing architectures and neuromorphic computing systems. However, the scale-down ability and uncertain switching mechanism are still the stumbling blocks to the development of memristor. The emerging transition metal dichalcogenides (TMDCs) has been recognized as a promising candidate for the nanoscale memristive devices owing to their flexibility, transparency and especially scale-down ability. In this work, we demonstrate a type of metal-semiconductor-metal (MSM) memristor architecture based on transfer-free WS2/MoS2 heterojunction, completely different from the conventional metal-insulator-metal (MIM) architectures using insulating metal oxides as the function layer. This MSM device is forming-free and shows a reproducible bipolar memristive behavior with $R_{ON}/R_{OFF}$ ratio up to $10^4$. Moreover, the programming voltages of this device is around 1.4 V with currents lower than 10 µA and the thickness of the function layer down to 10 nm. Finally, we discuss the switching mechanism in the WS2/MoS2 heterojunction. Different from the filament-based mechanism, the resistance switching of the WS2/MoS2 2D heterojunction memristor is mainly ascribed to the electric-field modulation of the band structure of the WS2/MoS2 heterojunction, which is promising for the development of high-speed and low-power memristors.

3:45 PM *FF01.05.02
Potential Electronic Applications of Graphene and 2D Layered Materials Hyeon Jin Shin; Samsung Electronics, Korea (the Republic of)

Two dimensional (2D) layered materials are crystalline materials with layered structures, including Graphene, h-BN, and Transition Metal Di-chalcogenides (TMD’s). We have studied 2D layered materials in two directions. For the near future application, we have been investigated 2D layered materials for Si technology to enhance their performance. To overcome performance limit for the long term downscaling of Si technology, we have focused 2D layered materials as interface materials due to the chemical inertness and their atomically thin nature. We investigated Graphene/metal hybrid interconnect. Although high quality graphene can be produced on catalyst metals, Si technologies are limited by the high temperature growth and the post transfer process. W/nanocrystalline graphene (ncG)/TiN is realized by direct growth on noncatalytic TiN, up to 12" wafer, at a low temperature of 560 °C which is below the semiconductor integration temperature. ncG acts in the interconnect not only a diffusion barrier to metal silicide formation but also a promoter of the preferential grain growth of the W layer. Overall, a significant reduction (27%) in the resistance of the interconnect is achieved by the insertion of ncG between W and TiN. This work points to the possibility of practical graphene applications via direct ncG growth that is compatible with current Si technology.[1] Also, We demonstrated that 2D layered materials are good candidates for interface materials between metal and Si to reduce the Schottky barrier heights and contact resistance in source and drain, which is one of the most critical issues for scaling down.[2,3,4] We found that 2D materials may change the pinning point of Schottky barrier and end up reducing contact resistance. We realized the lowest specific contact resistivity of 3.30 nΩcm² (n-type Si, 10^{15}/cm³) and 1.47 nΩcm² (n-type Si, 10^{21}/cm³) via Graphene and h-BN insertion in 6" wafer are approaching the theoretical limit of 1.3 nΩcm².[3] As one of the long term applications, we are developing transistors beyond the 5 nm node for high integration / high performance / low power, and beyond Si devices for optoelectronic applications in the IR domain. In pursuit of these research directions, we are studying a large area growth and doped structure growth. Recently, we grew MoS2 monolayer on 6 inch wafer within 10min by sequential growth method. [5] To explore 2D application, we examined triboelectric nanogenerator, which has been explored as one of the possible candidates for the auxiliary power.
source of portable and wearable devices. [6] We investigated the triboelectric charging behaviors of various 2D layered materials, including MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$, graphene, and graphene oxide and confirms the position of 2D layered materials in the triboelectric series. It is also demonstrated that the results are related to the effective work functions. This study provides new insights to utilize 2D layered materials in triboelectric devices, allowing thin and flexible device fabrication. [7]


4:15 PM FF01.05.03
Gate-Tunable Diodes and Switches Based on van der Waals Heterostructures of 2D and 3D Semiconductors
Jinshui Miao$^1$, Ravindra Saxena$^1$, Kiyoung Jo$^1$, Huiqin Zhang$^1$, Myung-Geun Han$^2$ and Deep M. Jariwala$^1$;
$^1$University of Pennsylvania, United States; $^2$Brookhaven National Laboratory, United States

Semiconductor p-n junction diodes and field-effect transistors are essential building blocks of electronic and optoelectronic devices. Over the past several decades, in the quest for higher performance, the dimensions of functional devices comprising 3D bulk semiconductors continue to decrease. However, the inherent scaling limitations of 3D devices such as short-channel effects, have fueled the exploration of alternative semiconductors. 2D layered materials have been a central focus of materials research for More Moore and More-than-Moore device applications because each layer of 2D materials consists of a covalently bonded and dangling-bond-free lattice and is weakly bound to neighboring layers by van der Waals interactions.$^{1,2}$ Consequently, 2D layered materials can be integrated with an array of materials of different dimensionalities to form mixed-dimensional van der Waals heterostructures without the constraints of lattice matching and processing compatibility. $^3$ Very recently, the integration of 2D materials with 3D bulk semiconductors offers promising platforms for heterojunction device applications, which allows the combination of novel properties of 2D materials with the proven merits of well-developed 3D semiconductors.$^4$

Here we have demonstrated highly gate-tunable heterojunction diodes using van der Waals assembly of 2D layered semiconductors (MoS$_2$, WSe$_2$ and InSe) and 3D bulk semiconductors (silicon and gallium nitride). The vertical stacking of these semiconductors forms a heterojunction with charge transport behavior that can be fully modulated by an applied gate electrostatic field. We observe gate-tunable current rectification with forward-to-reverse bias current ratios of up to 10$^7$. More importantly, when operated as three-terminal devices, the 2D/3D heterojunction diodes exhibit a unipolar n-type transistor behavior with current on/off ratios exceeding 10$^7$ sufficient for digital logic circuitry applications. These devices also deliver a large current density exceeding $\sim$130A/cm$^2$ which is attributed to ohmic metal contacts as well as a conductive 2D/3D junction. Our devices present new avenues for future nanoscale electronic and optoelectronic devices for both digital logic and radio frequency applications.

References

4:30 PM FF01.05.04
Electric Double Layer Gating of Two-Dimensional Field-Effect Transistors Using a Single-Ion Conductor Ke Xu, Jierui Liang, Eli Bostian, Aaron Woeppe, Hangjun Ding, Eric Beckman and Susan Fullerton; University of Pittsburgh, United States
Two dimensional (2D) van der Waals (vdW) semiconductors have recently emerged as next-generation channel materials for field effect transistors (FETs) owing to their atomically flat surface, improved electrostatic gate control and enhanced scalability [1]. Theoretical calculations have shown that elemental vdW crystals such as 2D black phosphorous (BP) and 2D arsenic can show high mobilities, layer dependent tunable bandgap along with extremely light anisotropic carrier effective masses [2]. This makes them better candidates for FETs than transition metal dichalcogenides, which are marked with stochiometric defects and much lowered mobilities [3]. BP has already been effectively utilized to fabricate high performance MOSFETs and tunneling FETs with steep subthreshold swings, high on/off ratios and low off current [4,5]. However, for practical use, deterioration under the ambient environmental conditions is still a major bottleneck that needs to be overcome before BP based electronic devices can be realized. 2D arsenic - isostructural to BP, is much more stable in ambient conditions [6]. Moreover, recent experiments have shown that 2D arsenic has superior or comparable electronic and thermal properties than other 2D materials due to the presence of highly anisotropic effective masses along the two crystal directions [6,7]. Due to its low bandgap, 2D arsenic should show ambipolar electrical conduction, however, in the literature only p-type conduction has been reported [6]. In this work, we present the first ever demonstration of ambipolar 2D arsenic FETs and analyze the device performance and transport for both electrons and holes in this material.

Flakes (exfoliated from crystals obtained from a commercial vendor) with varying thicknesses were used to fabricate a series of devices on a 300-nm-thick SiO2 dielectric grown on an n+ Si wafer. Electron dispersive spectroscopy (EDS) mapping was used to verify the composition of the material and the results showed that the obtained material was >99% pure arsenic. Angle resolved polarized Raman spectroscopy revealed a two-fold symmetry for $A_{1g}^1$ (220.1 cm$^{-1}$) and $A_{2g}^1$ (253.62 cm$^{-1}$) modes (with maximum and minimum intensities along armchair and zigzag direction respectively) further establishing the presence of the anisotropic puckered crystal structure [8]. In FET
devices, it was found that the subthreshold slope and off-state leakage current improved with decrease in thickness or decrease in source/drain voltage bias which is indicative of the layer dependent bandgap of 2D arsenic. At room temperature, on/off ratios as high as 2.5 x 10^5 and 3 x 10^2 were obtained for hole and electron conduction, respectively, with respective mobility values (for thickest to thinnest samples) ranging from 150 to 40 cm^2/Vs for holes and 175 to 10 cm^2/Vs for electrons. For thick flakes, hole and electron drive currents obtained were 30 μA/μm and 10 μA/μm respectively at |VDS| = 1 V. Low temperature transfer and output characteristics were taken, and a thermionic transport model was used to extract the Schottky barrier height at the metal/semiconductor contact. The tunability of the barrier height for both electron and hole transport was further explored by changing the applied backgate bias.

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SESSION FF01.06: Poster Session I: Beyond Graphene 2D Materials—Synthesis, Properties and Device Applications I

Session Chairs: Zakaria Al Balushi, Deep Jariwala, Olga Kazakova and Amber McCreary

Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

FF01.06.03
Substitutional Doping and Heterostructuring of Monolayer Transition Metal Dichalcogenides Inspired by Sol-Gel Technique
Tianyi Zhang, Kazunori Fujisawa, Fu Zhang, Mingzu Liu, Yu Lei, Kevin Crust, Rafael N. Gontijo, He Liu, Ana Laura Elias and Mauricio Terrones; The Pennsylvania State University, United States

Doping and heterostructuring lie at the heart of modern semiconductor technologies, which allow for the control over the functionalitites of semiconductors, and the formation of junctions that make semiconductor devices operational. Recent studies have indicated that, by substitutional doping of semiconducting 2D TMDs materials with judicious selection of dopants, a series of their physicochemical properties can be effectively modified. Furthermore, laterally stitching TMDs with dissimilar compositions enables the formation of atomically thin in-plane heterojunctions, endowing them with great potential for electronic and optoelectronic applications. In light of this, it is desired to develop a reliable doping method for TMDs that can be potentially suitable for a wide range of dopant selections, as well as an efficient route for creating in-plane heterostructures between two dissimilar TMDs. Herein, to solve this challenge, a reliable in situ substitution doping method for monolayer TMDs is reported. Specifically, a solution precursor-based chemical vapor deposition (CVD) technique is developed. By varying the composition of precursor solutions, it is demonstrated that iron (Fe)-doped WS2 and rhenium (Re)-doped MoS2 can be achieved by the developed technique. In addition, monolayer in-plane W6Mo1sS2-MoSxW1-xS2 heterostructures with molybdenum (Mo)-rich inner regions and tungsten (W)-rich outer regions is also successfully synthesized. This doping and heterostructuring method may also be extended for the incorporation of a variety of other elements into 2D TMDs. This work shed light on the design and control of the functionalities of 2D TMDs, enabling novel applications based on these 2D materials and heterojunctions.

FF01.06.05
Materials Solubility Engineered Wafer Scale Growth of High Quality Black Ti2O3 Layers
Il-Suk Kang, Kwonjae Yoo, Gyungtae Kim and Yun Chang Park; National Nanofab Center, Korea Advanced Institute of Science and Technology, Korea (the Republic of)
Black Ti$_2$O$_3$ is one of titanium oxide compounds with very stable properties in air, bio, and space environments. It also shows superconductivity in the high quality thin films which can be used for the quantum technology. High quality black Ti$_2$O$_3$ layers were successfully grown using Cu-Ti very low solubility phase and fast cooling approach from near the Cu melting temperature. Here we present the properties of ultrathin black Ti$_2$O$_3$ layers on SiO$_2$ substrate in large scale for solid state device applications.

Strikingly black Ti$_2$O$_3$ nanoparticles are known to exhibit narrow-band gap property compared to wide-band gap TiO$_2$ materials, which is suitable for photothermal applications as reported by T. Wu’s group. It was one of long seeking materials for a complement and alternative material of TiO$_2$, which can absorb sun light beyond UV range. Mao’s group also found that disordered black TiO$_2$ covered around TiO$_2$ nanoparticles, which later turned out to be as black Ti$_2$O$_3$, effectively increase solar absorption ability. However it is a difficult task to apply Ti$_2$O$_3$ nanoparticles to solid state device applications. Wafer level Ti$_2$O$_3$ thin films are required in the standard fab processing for cost effective and mass production of sensor and bio detection devices as well as photothermal conversion applications.

Wafer size Ti$_2$O$_3$ layers of about 10 nm thickness were grown using conventional thermal furnace by employing the concept of very low soluble property of Ti-Cu layers. Raman spectra with very narrow width at 274 cm$^{-1}$ in the samples grown above the growth temperatures of 1000-1090 Celsius degree indicate that the Ti$_2$O$_3$ layers are highly ordered and PL spectra show broad weak peaks near 500 nm in addition to the strong signals at near 574 nm at room temperature which is commonly observed in different forms of TiO$_2$.

We started from the Ti(20nm)/Cu(600nm) template deposited on SiO$_2$/Si wafer using sputtering evaporation method at room temperature. It is known that the Ti-Cu system has very low solubility which is difficult to make of alloy. The maximum Ti solubility in Cu is about 8% at 885 Celsius degree that can be found in the phase diagram literature. It is well known that Cu layers with less than about 1000 nm thickness dominantly form (111) crystal phase due to low surface free energy. The deposited ultrathin Ti layers are randomly arranged in a few Ti atomic layers on Cu(111). Then a few Ti atomic layers were exposed with very small amount of O$_2$ at high temperature and subsequently quenching under H$_2$ environments. This lead to the formation of Ti$_2$O$_3$ layers because of more oxidation affinity between oxygen and Ti. The Ti-Cu system under fast cooling with a little O$_2$ make the most stable Ti$_2$O$_3$ surface layers removing any other TiO$_2$ phase structures. Actually more O$_2$ with slow cooling lead to anatase TiO$_2$ layers.

The grown Ti$_2$O$_3$ layers showed the diffraction patterns of (012), (104), (110), and (113) planes from grazing incidence of X-ray diffraction measurements, which are well agreed with Ref. [1] and [2]. Detailed atomic crystal structure was also confirmed in TEM measurements. Raman spectra with very narrow width at 274 cm$^{-1}$ in the samples indicate high quality of the crystals. Raman peaks of any other TiO$_2$ structure phases are completely suppressed. XPS and AFM results will be presented.

References:


produce high yield nanocomposites associated with high quality nanosheets. There are several methodologies to obtain 2D-MoS$_2$, such as: CVD, mechanical exfoliation and ionic intercalation. One interesting approach is use liquid exfoliation and ultrasonication to obtain, in a single-step, 2D-MoS$_2$ nanosheets functionalized with a polymer (e.g. polybutadiene)[1]. The C-S bond on the edges of the sheets of the composite provides chemical stabilization of the 2D structure during exfoliation increasing the yield of the reaction.

In this study, we propose a novel and scalable single step synthetic method to exfoliate functionalize and polymerize MoS$_2$-polystyrene (MoS$_2$-PS) nanocomposites starting from bulk MoS$_2$ and the monomer (styrene). In this case, the vial containing styrene, bulk MoS$_2$, NMP and AIBN was introduced in the ultrasonic bath and kept for 6 days at 70°C. For a comparative experiment, the same reaction was carried out, but toluene was added in the mixture above. After this time, the colloidal dispersion was centrifuged at 5000rpm for 1hr and the greenish supernatant was collected for further analysis. Moreover, pure PS was synthesized with AIBN in the ultrasonic bath at 70°C. Thin film of the MoS$_2$-PS was made by casting in a wafer of monocrystalline silicon. Raman spectroscopy showed the characteristics peaks of polystyrene-, C-H bands at 3000cm$^{-1}$, C-C bands at 800cm$^{-1}$, C=C bands of the aromatic ring at 1600cm$^{-1}$, indicating polymerization. The A$_{1g}$ and E$^{1'2g}$ bands of MoS$_2$ can be located at 383.9cm$^{-1}$ and 409.1, respectively, with a frequency distance of 25.2cm$^{-1}$, whilst 26.5cm$^{-1}$ value is expected for a bulk MoS$_2$, indicating high degree of exfoliation and the peak in 630cm$^{-1}$ represents the C-S bond confirming the functionalization of the nanocomposite. XRD of the MoS$_2$-PS composites showed a broad basal plane (002) peak confirming the reduction of the initial size of bulk MoS$_2$. Also, it is possible to notice the absence of other peaks that indicates exfoliated material except for the (103) and (105) planes due to restacking. TGA allowed quantifying the amount of 2D-MoS$_2$ in the film of the nanocomposite as well as to verify the thermal stability compared to the pure PS film. In this case, TGA showed a 2.33% concentration of bounded 2D-MoS$_2$ in the PS film and the initial degradation temperature was 185°C for the MoS$_2$-PS whilst 162°C was reported for pure PS. DSC showed a shift in the glass transition temperature (Tg) from 148°C of the pure PS film to 162°C in MoS$_2$-PS. The MoS$_2$ exfoliated with toluene/NMP/styrene/AIBN was not able to form thin films indicating a low degree of polymerization which can be confirmed by a 0.52% weight loss of organic matrix in TGA and showed all characteristics of crystallographic peaks of bulk MoS$_2$ as well as the Raman modes, confirming the low degree of exfoliation of the MoS$_2$. The yield of the MoS$_2$-PS reaction was 50% for polymerization reaction and 11% for exfoliation. Therefore, this approach opens opportunities of new scalable single step synthetic routes with high degree of exfoliation. We thank FAPESP (CDMF proc. 2013/07296-2) for the financial support (2016/20493-0) CNPq and CAPES.

Weak van der Waals (vdW) interactions between the stacking layers of transition metal dichalcogenides (TMDCs) accommodate intercalation of various species from monovalent alkali, divalent alkaline earth and multivalent metal ions to organic molecules. The research over the past decades have revealed that intercalation of foreign species in the gap can drastically alter the physical properties of layered materials. Especially, controlled electrochemical intercalation can be used as a means to tune the electronic and optoelectronic properties. Among various TMDCs, MoS$_2$ is an important semiconductor with promising field-effect transistor (FET) applications. 2H to 1T' phase transition via chemical and electrochemical intercalations has previously been reported. However, many aspects of intercalation effects are still unclear and require further research. Here, the effects of alkali metal electrochemical intercalation on the transport properties of few-layered MoS$_2$ are presented. The intercalation was performed in top-contact and h-BN encapsulated edge-contact devices, which exhibit distinct behaviors. Additionally, careful magneto-transport studies were carried out on those intercalated MoS$_2$ flakes at various Li ion concentrations to investigate the effects of intercalants on the scattering mechanism and electron doping of MoS$_2$ flakes.

**FF01.06.07**
**Effects of the Electrochemical Li-Ion Intercalation on the Electronic Transport Properties Few-Layered MoS$_2$**

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**FF01.06.08**
**Quasi-2D Group-IV Monochalcogenides—A Density Functional Theory (DFT) Search**

NFN Sri Ranga Jai Likith and Cristian V. Ciobanu; Colorado School of Mines, United States

Quasi-2D materials have recently gathered significant interest since the discovery and application of transition metal dichalcogenides (TMDCs). Subsequently, the hunt for new families of quasi-2D materials has led us to group-IV
monochalcogenides. In addition to having structures very similar to black phosphorus, they have the added advantage of showing much higher carrier mobilities. In this study, we use density functional theory (DFT) to perform structural relaxation on group-IV monochalcogenides of the form AX (where A: C, Si, Ge, Sn, Pb; X: S, Se, Te) each in 6 different prototype van der Waals-layered quasi-2D structures in an attempt to find new quasi-2D group-IV monochalcogenides. We then scan the structures that remain quasi-2D after relaxation for dynamic stability. For the dynamically stable structures, we compute the piezoelectric tensor values ($e_{ij}$). We find a total of 20 quasi-2D, dynamically stable, and piezoelectrically active structures amongst the 90 structures that are studied here. In addition to helping similar future computational searches, our study also provides guidance to experimental efforts to synthesize new quasi-2D piezoelectric materials.

**FF01.06.09**

Scanning Tunneling Microscopy and Spectroscopy of Wet Chemically Synthesized Porous and Nitrogen-Sulfur-Nitrogen Functionalized Graphene Nanoribbons

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Graphene nanoribbons (GNRs) are promising candidates for semiconductor logic device applications. Lithographic edge roughness limits the utility of top-down fabricated GNRs due to carrier scattering effects. Bottom-up fabricated atomically precise GNRs can circumvent this issue. We are studying atomically precise GNRs that can be fabricated on the gram scale through wet-chemical synthesis methodology [1]. A fascinating aspect of the bottom-up GNR synthesis is the ability to tailor the atomic structure of the GNR through the choice of the starting molecules. GNR edge structure and width can be controlled with atomic precision. An unexplored class of GNRs contain atomically precise built-in pores. These GNRs contain multiple pores in a single ribbon and the electronic details of the ribbon have not been reported. In this work, we use dry contact transfer (DCT) to deposit porous GNRs onto hydrogen passivated Si(100) surfaces in UHV. These GNRs have been characterized by UHV scanning tunneling microscopy (STM) and spectroscopy (STS). STM imaging confirms the porous structure and indicates a unique electronic feature at the graphene nanopores. Intuition would suggest nanopores appearing as valleys due to the missing carbon atoms. However, STM indicates an electronically tall peak at the pore sites. STS measurements indicate a $1.62 \pm 0.11$ eV bandgap in the bulk GNR and a $2.50 \pm 0.02$ eV bandgap at the pores. These results are compared to first-principles density functional theory (DFT) simulations in which an increased local density of states at the pores is predicted. GW correction shows a $2.89$ eV bandgap. Results will also be reported for GNRs with nitrogen-sulfur-nitrogen (NSN) functionalizations. These GNRs are new chemically synthesized variations for which the fabrication procedure and electronic details have not yet been reported.

References:

**FF01.06.10**

Origins of Zero Phonon Line Emission Broadening for Hexagonal Boron Nitride Quantum Emitters in Films Grown by Chemical Vapor Deposition

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Single photon emitters in hexagonal boron nitride (hBN) have shown promising electrical and optical properties for utilization in quantum light source applications, owing to the ability of emitters to show Fourier transform-limited zero phonon line emission, which is crucial in applications in which sources of indistinguishable photons are required. Here we investigate the zero phonon line broadening mechanisms of emitters located in 5-10nm thick CVD-grown hBN, films of which can be grown scalable over large areas as needed for monolithic integration of quantum emitters in future chip-based quantum photonic systems. By comparing the lifetime-limited homogeneously broadened linewidth obtained from luminescence decay lifetime measured by time-resolved photoluminescence and low temperature spectroscopy of photoluminescence we observe that even at 4K, the linewidth of the zero phonon line is broader than the Fourier limited value by 2 orders of magnitude. Furthermore, we investigate sources of ZPL broadening, such as spectral diffusion (inhomogeneous) and thermal broadening (homogeneous) by performing spectroscopy and analyzing the Voigt profile at various temperatures (4K-300K). Our studies show at 4K the main broadening source is inhomogeneous but at higher temperatures homogenous.
broadening mechanisms (such as thermal broadening) are more dominant. By comparing the emitter luminescence linewidth for hBN films on several different substrates and excited at varying pump intensities, we can conclude that the main broadening mechanism is spectral diffusion at low temperature. Origins of this phenomenon and possible mitigation strategies will be discussed.

FF01.06.11
Spontaneous Relaxation through Graphene Suggests an Alternative Strain Relaxation Mechanism in Heteroepitaxy

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While conventional epitaxy produces high-quality epitaxial layers, the limited set of commercially available wafers restricts the number of material choice that can be grown through epitaxy. To extend the set of epi-materials, heteroepitaxy has been widely used although the epi-materials have severe lattice mismatch from wafers. The problem of heteroepitaxy of the lattice mismatched systems is that introducing dislocations is unavoidable because of the strain energy built up in epitaxial layers exceeds the threshold energy value to create dislocation. As the dislocations significantly reduce the materials’ properties, people have put intensive effort into finding a new way to resolve this issue.

Here, we introduce a new strain relaxation approach which can efficiently engineer the lattice with minimizing dislocation formation. Remote epitaxy allows single-crystalline growths on graphene-coated substrates as atomic potential field guides atomic registry through graphene while weakening binding energy of epilayer to the substrate. We discovered that this weakened interface offers a new pathway for strain relaxation during epitaxy in the lattice mismatched systems. While conventional heteroepitaxy relaxes accumulated strain energy through involving misfit dislocations, heteroepitaxy on graphene-coated substrates spontaneously relaxes its strain minimizing dislocation density. Thus, at the same thickness and misfit strain, the epilayer grown on graphene-coated substrates shows full relaxation with substantially reduced dislocations while that by conventional heteroepitaxy exhibits slight relaxation with full of dislocations. It means that full of strain relaxation at much lower thickness is available through this approach. We strongly believe that our strategy allows broadening range of available semiconductors through epitaxy, which could lead high performance electronic and photonics.

FF01.06.12
Spectral Responsivity in Black Phosphorus Photodetectors

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Black phosphorus (BP) has shown significant promise for use in infrared photodetectors due to its high carrier mobility, tunable bandgap and anisotropic properties. To date, characterization of BP detectors has been limited to the visible and NIR, or single IR wavelengths. We will present results on the optical characterization of black phosphorus photodetectors across the entire spectral range where photoresponse occurs. These devices show broadband photodetection from <400 nm to the nearly 4 um bandgap. This full spectral characterization allows us to establish a sharp contrast between the visible and infrared behavior. In the visible, a responsivity of >6 A/W can be obtained due to a large photoconductive gain, while the infrared responsivity is nearly independent of gate voltage and incident light intensity under most conditions. We attribute this to a photogating contribution from the surface oxide. Furthermore, we observe that the polarization anisotropy in responsivity along armchair and zigzag directions can be as large as 10⁵ and extends from the band edge to 500 nm. This anisotropy is much larger than that in previous reports and the result of measuring in an intensity regime where photoconductive gain is absent. This opens up significant opportunity for a number of applications including IR polarimetry. The devices were fabricated in an inert atmosphere and encapsulated by Al₂O₃ providing stable operation for more than 6 months.

FF01.06.13
Optical Devices from Covalent Functionalized, Redox-Exfoliated, Layered Transition Metal Dichalcogenides (Group IV – VII)

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Exfoliated Transition Metal Dichalcogenides (TMDs, MX₂) have attracted considerable attention for infrared optical elements due to their high refractive index and extreme nonlinearities (e.g. MoS₂, TiS₂). Multiphoton absorption,
nonlinear scattering, and nonlinear refraction are useful in technologies from reverse saturable absorption to optical limiting and gradient index coatings. Optimizing performance necessitates fabrication of dispersions, composites, and nanolaminates with high monolayer content, robust chemical stability, and high optical transmission. Energy intensive sonication methods to exfoliated TMDs limit scalable strategies to high quality films and coatings, due to poor oxidative stability, low concentration of TMDs, and a small choice of stabilizing solvents. The recently developed sonication-free, redox exfoliation approach address these challenges by drastically reducing reaction times for gram scale exfoliation of the entire TMD material space (Group IV – VII). This process provides TMDs dispersions in polar organic solvents (acetonitrile, acetone, alcohols) at high concentration (10% w/w) and with high monolayer content. The expansion of solvents and lack of additional stabilizers enables direct hybridization of Group VI 2H-MX₂ TMDs (e.g. MoX₂) via alkyl organometallic chemistry, as well as reduction of Group V 2H-MX₂ (e.g. VS₂, TaS₂, NbX₂) via amines and phosphines. This hybridization increases oxidative stability and tunes optoelectronic properties, including absorption and nonlinear response. The resulting access to surfactant free, monolayer populations enable design and fabrication of optical filters, GRIN optics, and non-linear absorbers.

FF01.06.14
The Halogen Etch for Scalable Production of Layered MXene’s Ali Jawaid¹, Asra Hassan², Dhriti Nepal¹, William Kennedy¹, Subramanian Ramakrishnan², Ruth Pachter¹ and Richard A. Vaia¹; ¹Air Force Research Laboratory, United States; ²Florida State University, United States

Layered metal carbides and nitrides (MXenes) have generated substantial research interest since their discovery in 2011. Their production requires selective etching of the A layer (A = Si, Al) from bulk MAX phases, yielding a new class of layered ceramics with excellent conductivity. HF is commonly used to selectively remove the A layer; however, its acute toxicity prevents safe, scalable MXene production. The complex, environmentally-sensitive reaction mechanism, as well as degradation processes in water and oxygen, challenges MXene yield optimization and compositional control of surface termination. On top of batch-to-batch heterogeneity, this leads to mixed surface termination (-F and -OH) that limits modification of the surface and layer properties. Here, we present an alternative method to fabricate MXenes that utilizes halogens in oxygen-free non-polar solvents for selective removal of the A layer. The etch products are stabilized and dispersed in non-polar solvents (THF, CHCl₃, DCM), leaving oxidatively robust, homogeneously halogenated surfaces (Cl, Br, I). Combined, this enables access to new chemistries for surface derivatization (organometallics), which result in uniform and tunable optical, electrical and chemical properties. The process is safe, scalable, and easily transferred across the MAX material space, giving access to previously un-explored MXene’s. The development of such alternative routes for etching and delamination are crucial for large-scale manufacturing for paints, coatings, and EMI shielding applications.

FF01.06.15
A Dielectric-Defined Lateral Heterojunction in a Monolayer Semiconductor M. Iqbal B. Utama¹,², Hans Kleemann¹,³ and Feng Wang¹,²; ¹University of California, Berkeley, United States; ²Lawrence Berkeley National Laboratory, United States; ³Technische Universität Dresden, Germany

Owing to their low dimensionality, two-dimensional semiconductors, such as monolayer molybdenum disulfide, have a range of properties that make them valuable in the development of nanoelectronics. For example, the electronic bandgap of these semiconductors is not an intrinsic physical parameter and can be engineered by manipulating the dielectric environment around the monolayer. Here we show that this dielectric-dependent electronic bandgap can be used to engineer a lateral heterojunction within a homogeneous MoS₂ monolayer. We visualize the heterostructure with Kelvin probe force microscopy and examine its influence on electrical transport experimentally and theoretically. We observe a lateral heterojunction with an approximately 90 meV band offset due to the differing degrees of bandgap renormalization of monolayer MoS₂ when it is placed on a substrate in which one segment is made from an amorphous fluoropolymer (Cytop) and another segment is made of hexagonal boron nitride. This heterostructure leads to a diode-like electrical transport with a strong asymmetric behaviour.

FF01.06.18
Joule Heating and Its Impact on Thermal Management in Few-Layer WSe₂ Arnab K. Majee, Cameron J. Foss and Zlatan Aksamija; University of Massachusetts Amherst, United States

The persistent down-scaling of nanostructures, such as electronic devices, sensors, NEMS, and nanocomposites, increases the surface-to-volume ratio and introduces atomic-scale disorder at boundaries and interfaces. To avoid
these issues, the nanoelectronics community has turned to intrinsically 2D materials platforms such as transition metal dichalcogenides (TMDs), where atomic flatness and the absence of dangling bonds prevent scattering due to surface roughness (SR), which severely limits mobility in ultra-thin body 3D silicon-on-insulator field-effect transistors (FETs). Despite immunity to SR scattering, the mobility of single layer TMDs are largely deteriorated by charge impurity scattering from the substrate [1]. Researchers have demonstrated that encapsulation of TMDs with hexagonal boron nitride significantly improves mobility [2]; however, encapsulation is expensive and time-intensive. Another route to improving mobility and boosting drive current is to replace the monolayer with few-layered (FL) TMDs. Despite recent advances on demonstrating improved electrical performance of FL TMD FETs [3], there has been less attention towards their thermal management, which is crucial for modern nanoelectronic devices.

In this work, we develop a coupled electro-thermal model for FL-WSe$_2$ stacks where we simultaneously solve for the current and Joule heating by treating the stack a resistor network. The resulting rise in temperature is obtained from a FL-TBC model [4] to shed light on self-heating and heat dissipation in such devices. We found that the distribution of current and Joule heating across layers in a FL-stack is highly non-uniform and strongly dependent on the back-gate voltage ($V_g$), in agreement with previous studies on FL graphene [5] and MoS$_2$ [6]. Interestingly, we found a similar behavior with respect to the drain-source voltage ($V_{DS}$) as well. For a given $V_g$, the current mostly flows through the top layers for small $V_{DS}$. But when $V_{DS}$ is increased, the current penetrates deeper into the stack and flows mostly through the bottom layers. We attribute the change to self-heating of these devices at large $V_{DS}$. We find that the temperature rise in the top layers is significantly larger than the bottom layers because the bottom layers have higher TBC and conduct heat more efficiently to the substrate [4,7]. The higher temperature of top layers, in turn, significantly reduces their mobility, which is strongly temperature-dependent as they are shielded by the bottom layers from substrate impurity scattering. Consequently, both the current and the dissipation hotspot move towards the bottom layers with increasing $V_{DS}$. We also uncover that, unlike monolayer FETs, a significant amount of heat is dissipated laterally through the contacts in FL devices at high $V_{DS}$ due to relatively large thermal healing lengths of the top layers.

In conclusion, we have developed a robust and detailed coupled electro-thermal model to solve for the non-uniform and layer-dependent temperature rise in response to Joule heating. Our findings help develop a deeper understanding of dissipation and thermal management in FL 2D materials and vertical heterostructures.


FF01.06.19
Transcending Graphene—The Unique Properties Atomically-Thin Graphene-Templated Metal Films Faisal Alamgir, Ali Abdelhafiz, Matthew Drexler, Dong Chan Lee and Crystal Bell; Georgia Institute of Technology, United States

We will present our results large-area, atomically-thin metal films (Pt, Pd and Cu) can be grown epitaxially on graphene (GR) using electrodeposition. We will focus particularly on Pt films that are one to several multilayers thick (Pt$_{ML}$) epitaxially grown on graphene (Pt$_{ML}$/GR). These Pt$_{ML}$/GR 2D systems have covalent bonds at the Pt$_{ML}$/GR interface and this intimacy between the layers serves to make the GR a ‘chemically transparent’ barrier that allows catalytic chemistry to take place above it, while protecting the Pt below it from loss. We will specifically show that graphene does not restrict access of the reactants for the canonical oxygen reduction reaction (ORR) but does block Pt from dissolution or agglomeration. These architectures simultaneously achieve enhanced catalytic activity and unprecedented stability, retaining full activity for ORR beyond 1000 cycles. Using x-ray photoemission/absorption spectroscopy (XPS/XAS), high resolution TEM, AFM, Raman, and electrochemical methods, we show that Pt/GR hybrid architectures induce a compressive strain on the Pt films, thereby increasing their ORR activity. Our room-temperature, fully-wetted synthesis approach, should allow for efficient charge, strain, phonon and photon transfer, between the films and their support, impacting not just the performance of catalysts, but also those of electronic, thermoelectric and optical materials.

FF01.06.20
Substitutional Re Doping of Monolayer Epitaxial WSe$_2$: Azimkhan Kozhakhmetov$^1$, Alex Vera$^1$, Michael LaBella III$^{2,3}$, Vince Bojan$^2$, Chengye Dong$^1$ and Joshua A. Robinson$^{1,4,5}$; $^1$The Pennsylvania State University, United States; $^2$Materials Research Institute, The Pennsylvania State University, United States; $^3$The Penn State Nanofabrication
Doping is one of the main cornerstones of modern semiconductor technology. Recent re-discovery of 2D transition metal dichalcogenides (TMDs) attracted great interest in semiconductor doping in such low dimensional systems. Numerous efforts have been devoted to extrinsic doping of TMDs to tune optical, electronic and magnetic properties with various synthesis methods such as chemical vapor transport, powder vaporization, and plasma treatment. Establishing controlled and reliable doping techniques are indispensable for the realization of TMD based CMOS-type devices for next-generation electronic devices. However, all previously reported studies still lack a fundamental understanding of doping mechanisms and have not been extensively examined.

In this work, we present finely controlled, scalable Re doping of monolayer epitaxial WSe₂ films on c-plane sapphire and epitaxial graphene (EG) substrates via gas source metal organic chemical vapor deposition method. The MOCVD synthesis is carried out in a vertical cold-wall CVD reactor at 800 °C using hydrogen selenide (H₂Se), tungsten hexacarbonyl (W(CO)₆) and dirhenium decacarbonyl (Re₂(CO)₁₀) in a hydrogen gas atmosphere. By controlling the partial pressure of the (Re₂(CO)₁₀) in the growth chamber we demonstrate that Re dopant concentration in the epitaxial WSe₂ lattice can be tuned from 5% down to <1%. High-resolution X-ray photoelectron spectroscopy (XPS) is used to quantify Re concentration at high doping levels. Time of flight secondary ion mass spectroscopy (ToF-SIMS) is further performed to confirm a presence of Re atoms in WSe₂ at low doping concentrations. The high concentration (5%) of Re dopant atoms leads to a formation of ReSe₂ and phase segregation from WSe₂; however, the undesired phase segregation is eliminated by reducing the Re flux during the growth which is further confirmed by Raman and photoelectron spectroscopies. Back-gated field effect transistors are constructed and demonstrate a clear trend as a function of Re concentration in WSe₂ from ambipolar conduction to degenerately n-type doping. Currently, high-resolution transmission electron spectroscopy, selective area electron diffraction, electron energy loss spectroscopy, and scanning tunneling microscopy studies are under investigation to further elucidate the effect of in-situ Re doping on atomic scale structural and electronic properties of epitaxial WSe₂.

Highly Stretchable MXene/RGO Composite Supercapacitors

MXene (Ti₃C₂TX) is a newly discovered family of 2D carbide material with superior electrical and electrochemical properties. Benefitting from its metal-like conductivity (6500 S/m), high volumetric capacitance (900 F/cm³) and stable dispersion in various solutions, MXene has been successfully adopted in various electronic and energy applications such as supercapacitors, batteries and electromagnetic shielding. However, the incorporation of MXene materials into emerging stretchable electronics and energy storage devices remained unexplored possibly due to their large mechanical modulus, low ultimate strain, and weak sheet interactions. The current study investigates the design, fabrication, and characterization of robust and highly stretchable MXene/RGO composite supercapacitors through wavy-shape design. The effect of RGO concentration is systematically studied.

In the fabrication of stretchable MXene electrodes, it was found that cracks formed during the prestrain-relax process leading to significant degradation of electrochemical performance of stretchable MXene electrode in the fully stretched state. To overcome this issue, Reduced Graphene Oxide (RGO) was added into the system to tune the mechanical properties of the MXene/RGO composite paper because of its lower mechanical modulus and stronger sheet interaction. It was found that MXene/RGO composite paper could maintain its mechanical integrity when the weight ratio of RGO increased to 50%. Mechanical strain tests revealed that elongation of MXene/RGO increased with RGO concentration and remained at a similar level when the RGO concentration was larger than 50%. The as-fabricated stretchable MXene/RGO composite paper (50% weight ratio) can maintain consistent resistance for more than 1000 stretch-relax cycles with uniaxial strains up to 250% which to our knowledge is the highest stretchability reported for a MXene composite. When tested as supercapacitor electrodes, the stretchable MXene/RGO (50% weight ratio) composite paper demonstrated high and identical specific capacitance in different strain states (e.g., 0%, 100%, 200% and 300%) for various charge/discharge rates. Symmetric supercapacitors made of MXene electrodes and PVA-H₂SO₄ gel electrolyte exhibit robust electrochemical performance in agreement with the electrode measurements.

The present study demonstrates a facile strategy to fabricate highly stretchable MXene/RGO composite.
supercapacitors. These results demonstrate the prospects of a robust, high performance and highly stretchable MXene composite in emerging applications such as wearable electronics, bioimplants, and stretchable electronics.

**FF01.06.22**

**Evidence of Spontaneous Time Reversal Symmetry Breaking in Graphene Grain Boundaries** Kimberly Hsieh, Vidya Kochat, Tathagata Biswas, Abhishek Mishra, Gopalakrishnan Ramalingam, Chandra Sekhar Tiwary, Kamanio Chattopadhyay, Srinivasan Raghavan, Manish Jain and Arindam Ghosh; Indian Institute of Science, India

Magnetism in graphene and other 2D materials has long been a holy grail for modern spintronics. The conventional routes towards inducing magnetism in graphene involve either functionalization of graphene with ferromagnetic adatoms or irradiation to generate vacancies and correlated defects. In this work, we provide direct experimental evidence for the existence of localized magnetic moments at the grain boundaries (GBs) of graphene, formed as a natural consequence of the chemical vapour deposition growth. The spontaneous breaking of time reversal symmetry at the graphene GBs is observed using low frequency 1/f noise arising from universal conductance fluctuations (UCF) via the ergodic hypothesis. The gate-tunable magnetism is attributed to the formation of localized magnetic moments at the octagon-pentagon defects of the disordered GB region, further enhanced by the inbuilt lattice strain leading to the dephasing of spins.

**FF01.06.23**

**Scanning Tunneling Microscopy Induced Polymerization of Bromoaromatic Graphene Nanoribbon Precursors** Steven Kolaczkowski1,2,3, Adrian Radocea2,1, Abigail Berg1,2,3, Kaitlyn Parsons1,2 and Joseph W. Lyding1,2,3; 1University of Illinois at Urbana-Champaign, United States; 2Beckman Institute for Advanced Science and Technology, United States; 3Nick Holonyak Jr. Micro and Nanotechnology Laboratory, United States

Both thermal and wet bottom-up chemical synthesis of graphene nanoribbons (GNRs) have been shown to create ribbons with atomic precision in widths and edges. This precision is essential in maintaining band-structure uniformity across the structure. However, both these recipes for GNR synthesis result in a stochastic distribution of ribbon length, location, and orientation, when studied on a substrate. This random distribution on the surface makes it impractical for devices to be made from these GNRs as there is no feasible scheme to attach metal contacts to the ribbons. To address this challenge, we utilize dry-contact-transfer of bromoaromatic precursors to a Au(111) surface and, through the use of electron tunneling currents induced by ultra-high vacuum scanning tunneling microscopy (UHV-STM), spatially control the precursor polymerization. Here we demonstrate that at sufficiently high scanning biases, 10,10′-dibromo-9,9′-bianthracene (DBBA) polymerizes into polyanthrylene only along the path that the STM tip traverses. These results introduce the feasibility of electron-tunneling controlled bromoaromatic monomer polymerization and, in the future, high degrees of spatial control over atomically precise GNR synthesis.

**FF01.06.25**

**Langmuir-Blodgett of Black Phosphorus Nanosheets and Devices** Jian Mao, Junjia Wang, Orlando Ortiz and Stéphane Kéna-Cohen; Polytechnique Montréal, Canada

Black phosphorus (BP), the most stable allotrope of phosphorus, has attracted considerable attention in recent years due to its extraordinary electrical and optical properties, which makes it an excellent candidate for applications in transistors, photodetectors, and lithium-ion batteries. 1 BP, like graphite, has a layered structure and can be fabricated into monolayers and nanosheets from its bulk form through micromechanical and liquid exfoliation. 2 Mechanical exfoliation (the scotch-tape method) has been predominantly used for proof-of-concept devices, 3 but it is inherently unscaleable and typically limited to sheets with lateral dimensions below ten micrometers. For practical applications, scalable approaches for fabricating BP large-area films are essential. We will present our results on the development of a Langmuir-Blodgett (LB) protocol which is developed for assembling BP nanosheets into thin films. Through functionalization, we increase the electrostatic force between BP nanosheets to avoid the overlapping of BP nanosheets during compression, which allows us to achieve large-area (centimeters), smooth, and compact BP thin films. In addition, this protocol is well-adapted to assembly thin and thick BP nanosheets as well as arsenic-BP alloy nanosheets.

The optoelectronic properties of transistors and photodiodes fabricated from the BP LB film are investigated. With suitable carrier transporting materials, The BP photodiodes exhibit a good optical response from visible to infrared region. Our work highlights the great potential of BP in applications of near- and middle- infrared detection and
imaging.


FF01.06.26
Polyaniline against Black Phosphorus Degradation—Thin Films with High Chemical and Electrochemical Stability
Jessica E. Fonsaca¹, Sergio H. Domingues², Elisa Orth¹ and Aldo J. Zarbin¹; ¹Federal University of Parana, Brazil; ²Mackenzie Presbyterian University, Brazil

Black phosphorus (BP) has begun to gain attention in 2014, when its stripping has led to 2D layers of phosphorene. The promising properties of this material have, however, been severely limited by its high instability under environmental conditions which rapidly leads to its degradation. Thus, the interest in exploring BP has been growing as well as the concern in protecting it. In this sense, we have synthesized a BP-polymeric nanocomposite, aiming to overcome BP deterioration in a novel material with synergic and enhanced properties. For this purpose, different samples have been prepared through the following steps: 1. a liquid exfoliation of BP resulting in a stable dispersion (0.025 mg mL⁻¹ in deaerated acetonitrile); 2. aniline polymerization in the dispersion of BP, resulting in BP/polyaniline (BP/PANI) nanocomposites; 3. thin film deposition of the BP/PANI nanocomposites through the liquid/liquid interfacial route developed in our research group. Raman spectroscopy showed the coexistence of the two components modes in the BP-PANI spectra, confirming the successful synthesis of the nanocomposite, with the polymer in its conducting form (emeraldine salt). Infrared spectra attested the unstable nature of BP, exhibiting bands related to modes resulting from the phosphorus oxidation, and suggested the protective role of PANI with the absence of these bands for BP-PANI. Thus, the stability of both bare and capped material was evaluated through their exposure to the same ambient conditions and evaluated through different techniques. Scanning electron microscopy (SEM) images evidenced the beginning of degradation of the uncapped material with only 3 days of exposure, showing the characteristic bubbles on BP surface. The same was observed through Raman, indicated by the gradual decrease in the intensity of BP bands that completely disappear with its total degradation (at about 15 days). BP-PANI nanocomposites, however, have taken up to 60 days for the same process to begin, indicating a material 2000% more stable than the bare one.

After establishing BP chemical stability, we evaluate the electrochemical properties of the nanocomposites targeting energy storage devices. Electrochemical response and stability of BP/PANI nanocomposites were evaluated through cyclic voltammetry (CV) and charge-discharge (CD) studies (NaCl 0.5 mol L⁻¹ pH 3), in order to evaluate energy storage properties. Films of BP-PANI were evaluated and compared to pure PANI and BP, under air and inert atm (N₂(g)). Bare BP is degraded right after the first cycle, evidencing the expected low stability. For the nanocomposites, BP has shown a high stability even after 200 CVs in the presence of O₂(g). BP integrity was confirmed through post-characterizations (Raman spectroscopy and SEM images). Finally, aiming to evaluate the performance of the materials as electrodes for sodium ion batteries, CD studies were performed. Current densities of 0.2 A g⁻¹ to 3 A g⁻¹ were applied and the capacities reached up to 120 mAh g⁻¹ at 0.5 A g⁻¹ rate. Overall, this work not only provides the synthesis of a novel nanocomposite, but also prints to an innovative route towards the development of transferable and stable thin films, suitable to build new BP-based devices operating in water and under ambient atmosphere. Authors acknowledge UFPR, CNPq, CAPES, INCT-Nanocarbon, PhosAgro/UNESCO/IUPAC, L’Oréal-UNESCO-ABC and FAPESP (SPEC project 2012/50259-8).

FF01.06.27
Low-Temperature Growth of Monolayer MoS₂ by Metal-Organic Chemical Vapor Deposition
Ji-Hoon Park, Pin-Chun Shen, Ang-Yu Lu and Jing Kong; Massachusetts Institute of Technology, United States

Molybdenum disulfide (MoS₂) is a representative material among transition-metal dichalcogenides (TMDCs). it has a direct bandgap of ~1.8 eV and advantages of high stability, fast electrical mobility, and high current on/off ratio compared to other TMDCs. The growth of MoS₂ is relatively simple and easy by using chemical vapor deposition (CVD) which is a conventional method to ensure large-area and high-quality. Metal-organic chemical vapor deposition (MOCVD) is one of the branches among various CVD methods. One of the advantages of MOCVD use
the metal-organic precursors which can be easily decomposed at low temperature. Another advantage is precise control of flow rate between two or three precursors by using the mass flow controller (MFC) system. Here, we report that monolayer MoS₂ flake and film were grown on a various substrate (SiO₂, sapphire, soda-lime-glass, and gold film/SiO₂) by using MOCVD with the modified solid bubbler system to ensure a stable supply of Mo source without the heating process of solid Mo(CO)₆. The minimum growth temperature of MoS₂ is below 400 °C which allowed its growth on the gold film. Also, the shapes of MoS₂ flake can be modified through the control of the ratio of flow rate between Mo and S source. Finally, the maximum electron mobility of MoS₂ field-effect transistor showed about 45.4 cm²V⁻¹s⁻¹ due to reducing strain or interaction between MoS₂ and the substrate.

FF01.06.28
Lithium Intercalation in Twisted Bilayer Graphene Daniel T. Larson and Efthimios Kaxiras; Harvard University, United States

Lithium atoms intercalating between layers of graphene show an energetic preference for regions of AA stacking. Thus the triangular array of AA regions in the moiré pattern of twisted bilayer graphene allows for control over the location of intercalants in layered materials and devices. We use density functional theory to directly calculate the energetics of lithium atoms between layers of graphene in commensurate supercells with twist angles of 7.3° and 2.5°. The two cells show universal behavior in the energy profile for single Li intercalants when the location of the intercalant is measured as a fraction of the distance between AA and AB regions. This behavior can be expected to persist down to angles of about 2.0°. For the 2.5° cell we demonstrate clustering of the Li atoms in the AA regions when the average Li concentration is relatively low. The Li intercalants cause a local increase in the interlayer separation as well as charge transfer to the nearest carbon atoms. These regions of localized charge hold the potential for interesting catalytic properties. The charge donated by the Li atoms also raises the Fermi level above the Dirac point and causes qualitative changes to the band structure, especially near the I-point. The combination of twisting with intercalation gives the added power of spatial control over the material properties that can be tuned by intercalation.

FF01.06.29
3D Graphene Foams—Synthesis and Properties Carolina Rojas Michea, Neida Santacruz, Frank Mendoza, Loida Rosado, Stephanie Colón, Laura Méndez, Gerardo Morell, Brad Weiner and Ana Guadalupe; University of Puerto Rico, United States

Graphene is a 2D material with diverse applications. However, there are important applications in gas and liquid media that can benefit from the unique properties of graphene but require a 3D structure able to interact thoroughly with the medium. Thereby, the systematic and reproducible fabrication 3D Graphene would enable further applications useful both for research and industrial processes, such as catalysis, energy storage, and environmental remediation. Thereby, we developed a method to fabricate 3D Graphene Foams using the Chemical Vapor Deposition technique, acetone as carbon source, and Ni foams as scaffolds. We studied how the structural properties of the 3D Graphene Foams depend on the growth parameters, such as temperature, precursor concentration, and Ni foam thickness. Through this study, we optimized the pore size and mechanical stability of the foams produced. We are also reporting on the interaction of these 3D Graphene Foams with representative gases and liquids to understand the effective surface area and surface terminations of these foams.

FF01.06.30
Synthesis, Characterization and Fabrication of Graphene/Boron Nitride Nanosheets Heterostructure Tunneling Devices Muhammad Sajjad¹, Muhammad Shehzad Sultan², Vladimir I. Makarov², Brad Weiner² and Gerardo Morell²; ¹Austin Peay State University, United States; ²University of Puerto Rico - Rio Piedras, United States

The various types of 2D heterostructure prototype devices based on graphene (G) and boron nitride nanosheets (BNNS) were fabricated to study the charge tunneling phenomenon. Specifically, G/BNNS/Metal, G/SiO₂, and G/BNNS/SiO₂ heterostructures were investigated under DC-bias conditions at room temperature. Bilayer graphene and BNNS samples were grown separately on copper foil and transferred subsequently between the substrates to fabricate 2D devices architecture. The high resolution transmission electron microscopy confirmed bilayer graphene structure and few layer BNNS sheets having an interpretable hexagonal B₃N₃ lattice. The I(V) characterizations for G/BNNS/Metal device have shown typical Schottky barrier behavior with very low forward voltage drop due to out-
of-plane tunneling and low sheet resistance of G layer. A theoretical model based on current tunneling is proposed to qualitatively describe hetero-2D G/BNNS/Metal devices behavior.

FF01.06.31
Refraction Index of Janus MoSSe Monolayer  Jing Zhang, Tianshu Zhai and Jun Lou; Rice University, United States

Janus type of two-dimensional chalcogenide monolayers are predicted to permanently polarize in the out-of-plane direction, due to the structural asymmetry therein. The aligned dipoles, which cause the spontaneous polarization, are experimentally difficult to identify as they are confined in a Van der Waals layer, unless through the detection of electromagnetic wave-dipole interaction. We measured the refraction index of Janus monolayer MoSSe in the range of visible light. Comparison of the pattern of Janus MoSSe with MoS2 and MoSe2 reveals the existence of the built-in dipoles in the Janus monolayer. The discovery indicates the great potential of Janus type of 2D chalcogenide monolayers in optical applications.

FF01.06.32
Effect of Boundaries on the Microscopic Conductivity and Photoexcited Carrier Dynamics in Vertical SnS2 Nanoflakes  Kateryna Kushnir, Binod Giri, Maryam Masroor Shalmani, Tao Yan, Alexander D. Carl, Curtis W. Doiron, Ronald L. Grimm, Pratap M. Rao and Lyubov V. Titova; Worcester Polytechnic Institute, United States

Tin disulfide (SnS2) is a two dimensional (2D) van der Waals material with a moderate band gap of ~ 2.1 eV, strong optical absorption and high carrier mobility that make it attractive for solar energy conversion applications. We have recently demonstrated that nanostructuring SnS2 in the form of vertically-aligned nanoflakes is beneficial to SnS2 photoanode performance [1]. It balances ~ 1 micron film thickness necessary for absorbing incident light with the highly exposed steps and edges suitable for photoelectrochemical applications. However, nanostructuring comes at a cost of increased carrier trapping at surface and edge states. Here we use time-resolved THz spectroscopy (TRTS) to elucidate the effect of nanostructuring on photoexcited carrier lifetime and mobility in vertically-aligned SnS2 nanoflake array synthesized using close space sublimation method.

SnS2 vertical nanoflakes were excited with 400 nm, 100 fs laser pulses, and transient photoconductivity was measured using a terahertz probe in the 0.25 – 1.70 THz frequency (or, equivalently, 1-7 meV) range. To delineate the effect of edges and surfaces, we have compared transient THz conductivity of nanoflakes to that of SnS2 single crystals grown using chemical vapor transport method. Photoconductivity in both single crystal SnS2 and vertical SnS2 nanoflakes exhibits a multi-exponential decay. The fastest components, ~2-3 ps and 10-15 ps, are much more pronounced in the nanoflakes, and are ascribed to the carrier-carrier scattering (former) and the carrier trapping at defect and edge states (latter). Finally, a much slower component, ~ 0.25-1.30 ns, corresponds to free carrier recombination, as confirmed by the time-resolved photoluminescence measurements. We find that the photoexcited carrier mobility in single crystal SnS2 as high as ~ 800 cm²V⁻¹s⁻¹. In vertical nanoflakes, intrinsic (intra-flake) mobility is comparable to the single crystal value at 330 cm²V⁻¹s⁻¹, while the long-range (inter-flake) mobility is reduced to 90 cm²V⁻¹s⁻¹ by the confining effect of nanoflake surfaces and edges. Based on experimental free carrier mobility and lifetime, we estimate the inter-flake photoexcited carrier diffusion length to be ~1 μm, in agreement with the nanoflake length that results in the best photoelectrochemical device performance.

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FF01.06.33
Nylon-6/Ti3C2Tz MXene Nanocomposites Synthesized by In Situ Ring Opening Polymerization of ε-Caprolactam and Their Water Transport Properties  Michael Carey, Zachary Hinton, Maxim Sokol, Nicolas Alvarez and Michel Barsoum; Drexel University, United States

Typically, MXene polymer composites have been limited to small scales and polymers that are soluble in aqueous solutions. This is largely due to the use of MXene in its colloidal form – where concentrations are relatively low (~10-20 mg mL⁻¹) and stability is restricted to neutral aqueous solutions or polar solvents. Additionally, synthesis generally revolves around dissolving the polymer, mixing in colloidal MXene and then solvent casting samples. In
order to make samples on an industrial scale, use of multilayer MXene and in-situ polymerization techniques is a must. Clay-reinforced nylon-6 nanocomposites (NCs), characterized by the full exfoliation of the nanofiller were introduced in the marketplace in the 1990s. Herein, we demonstrate, for the first time, a scalable technique to disperse multilayer Ti$_3$C$_2$T$_z$ MXene into nylon-6 to synthesize melt-processable nanocomposites with excellent water barrier properties (94% reduction in water vapor permeation). To intercalate the ε-caprolactam monomer, the MXene multilayers were first treated with 12-aminolauric acid, a low-cost, nontoxic, biodegradable, and long shelf life compound. Upon heating to 250 °C, in the presence of 6-aminocaproic acid, in-situ polymerization occurred, yielding melt-processable nylon-6/MXene NCs that were in turn, studied by thermogravimetric analysis, differential scanning calorimetry, X-ray diffraction, scanning and transmission electron microscopy, infrared spectroscopy, and dynamic vapor sorption analysis. Using the latter, moisture-sorption isotherms of a neat and a 1.9 vol % NC at 60 °C, were fit to the Guggenheim, Anderson, and de Boer equation. Solubility, permeation, and diffusion coefficients of water through the NCs were measured as a function of temperature and found to be the lowest ever reported for nylon-6, despite the fact that, at ~1.9 and 5.0 vol %, the MXene loads were relatively low. This record low diffusivity is ascribed to the very large aspect ratios ~ 500 to 1000 of Ti$_3$C$_2$T$_z$ flakes and their dispersion. The water permeation rate is a factor of 5 lower than the best reported in the much more mature nylon/clay field, suggesting lower values can be achieved with further optimization. Lastly infrared spectroscopy spectra of neat and NC samples suggest the surface terminations of the 12-Ti$_3$C$_2$T$_z$ flakes bind with nylon-6, limiting water adsorption sites, resulting in reduced solubility in the NC films. This facile, low cost and scalable technique allows for the complete dispersion of MXene into the polymer matrix. By building upon this knowledge and tailoring the chemistry of the surfactant, we are continuing to utilize this method in order to disperse MXene into a variety of thermoplastic and thermosetting polymeric host matrices.

**FF01.06.35**

**High-Resolution, Active-Matrix Arrays of Pressure Sensors**

Jiuk Jang$^{1,2}$, Hyobom Kim$^1$ and Jang-Ung Park$^{1,2}$;  
$^1$Yonsei University, Korea (the Republic of); $^2$Center for Nanomedicine, Institute for Basic Science (IBS), Yonsei-IBS Institute, Korea (the Republic of)

The active-matrix pressure sensors as an electronic device have become of great interests as a critical component for recently emerging electronic skin and biomedical applications for artificial intelligence and human-machine interfaces. The conventional pressure sensors still has limitations such as the narrow sensing range and low pixel density, and they confines the applicability of the device to specific area. Here, we fabricate the active-matrix arrays of pressure-sensitive monolayer MoS$_2$ field-effect transistor (FET) with air-dielectric layer, which is supported by elastomer spacer. The air-dielectric monolayer MoS$_2$ FET was acting as pressure sensor solely by incorporating air as the gate dielectric layer with elastomeric supporting spacer, and hysteresis of this pressure-sensitive transistor was very small because of the clean surface states between a MoS$_2$ channel and air. The double-layered elastomer in which the two elastomeric materials had different elastic moduli allowed a wide detectable range of pressures. By utilizing the light emission of the ML composites induced under the external stress, ZnS:Cu phosphors were implemented to the elastomer layer to induce a photocurrent effect in the MoS$_2$ FETs, resulting in the enhancement of the sensitivity at high pressure (> 0.5 MPa). Furthermore, the pressure on the 20 X 20 MoS$_2$ FETs active-matrix pressure sensor array was mapped spatially even at 10 µm of pixel resolution. Since this resolution is fine enough to measure 2D pressure distribution of the cell, we demonstrated a 2D mapping of pressure distribution during the pulsing of single cardiomyocyte in the first time. We believe this unique FET structure and its active-matrix array will contribute to future applications of prostheses, robotics and biomedical electronics.

**FF01.06.36**

**A Plausible Method of Preparing an Ideal Interface of a p-n Junction by Surface Treatment**

Imgeong Ho-Soon Yang; Pusan National University, Korea (the Republic of)

The study of p-n junctions has been of interest in condensed matter physics and materials sciences. Especially, the fabrication of a p-n junction out of atomically thin two-dimensional crystals has drawn attraction in the field of semiconductors as it allows a high-quality interface with very high electron conductivity in the absence of strong chemical bonds at the interface. Here we report an atomically thin p-n junction prepared using a Van der Waals material, SnSe whose bulk property is a p-type semiconductor. The electron band structure of SnSe has been investigated using angle-resolved photoemission spectroscopy (ARPES). By depositing metallic atom on the surface, the valence band maximum shifts towards higher binding energy as much as 0.28 eV, leading to an n-type
charge carriers in the surface. A comparison to a theoretical work suggests that this charge transfer appears only at the top-most layer, leaving the rest of the bulk to remain a p-type semiconductor. This result suggests that an atomically well-defined vertical p-n junction is fabricated in between n-type surface and p-type bulk of SnSe.

**FF01.06.37**
**Charge Transport Behavior and Ultrasensitive Photoresponse Performance of Exfoliated F16CuPc Nanoflakes** Hang Yan¹,², Yang Li²,², Jing-Kai Qin²,², PingAn Hu²,², Liang Zhen¹,²,² and Cheng-Yan Xu¹,²,²; ¹State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, China; ²Harbin Institute of Technology, China

Air-stable, photosensitive copper hexadecafluorophthalocyanine (F16CuPc) is a promising n-type semiconductor for organic electronics and optoelectronics. However, the performance of F16CuPc-based devices is significantly limited by the poor crystallinity of thin films. In this work, the charge transport and electrical contact behavior of F16CuPc nanoflakes, mechanically exfoliated from high-quality needle-like bulk single crystals, are probed by analyzing the temperature-dependent carrier mobility and conductance, where the multi-trap/release and band-like transport mechanism govern the charge transport at different temperature ranges and carrier densities. F16CuPc nanoflakes based field effect transistors (FETs) exhibit high on-state current and ON/OFF ratio, one-order magnitude than those of reported F16CuPc nanowires, thin films and nanoribbons. Besides, F16CuPc nanoflake-based phototransistors exhibit attractive photoresponse performance in the spectral range of 300−750 nm even at quite low operating source-drain voltage (~ 1V), with maximum photoresponsivity of 19 A W⁻¹, detectivity of 8×10¹² Jones, and fast response speed of 36 ms, which is attributed to the single-crystalline characteristic of nanoflakes, and the resultant efficiently exciton diffusion and charge transport. Our results demonstrate that two-dimensional organic nanoflakes with single-crystalline feature will be promising candidates for flexible electronic and optoelectronic devices.

**FF01.06.38**
**Efficient Mechanochemical Exfoliation Process of Highly Soluble Two-Dimensional MoS2 Nanoflakes** Seulgi Kim¹, Dohoon Kim¹, Jiyeon Kang¹, Dongju Lee¹ and Sungho Song²; ¹Chungbuk National University, Korea (the Republic of); ²Chungbuk National University, Korea (the Republic of)

Transition-metal dichalcogenides(TMDs), such as molybdenum disulfide (MoS₂), have attracted huge interest as two-dimensional materials because of their novel electronic and optical properties. Several methods of fabricating few-layered TMDs have been developed, however, methods for mass production of intrinsic nanoflakes of TMDs are still challenge. Mass production of two-dimensional nanoflakes is highly desirable to their practical applications. In the present work, we present facile method for fabricating MoS₂ nanoflakes by using hydrazine-assisted ball-milling via synergetic effect of chemical intercalation and mechanical peeling. The MoS₂ nanoflakes obtained through the hydrazine-assisted ball milling process have lateral size of 600 to 800 nm and thickness of 4 nm or less with high quality. The resultant MoS₂ nanoflakes form stable dispersion in various solutions that can be used for many applications. For a potential application, flexible photodetectors are prepared by solution-based process using the MoS₂ nanoflakes and the optical properties evaluated.

**FF01.06.39**
**Synthesis of Bi₂Te₃ Single Crystals by Vapor Transport and Its Potential for Thermoelectric Applications** Jihoon Ahn; Korea Maritime & Ocean University, Korea (the Republic of)

Bismuth telluride (Bi₂Te₃) has recently attracted significant attention owing to its unique physical properties as a three-dimensional topological insulator and excellent properties as a thermoelectric material. Meanwhile, it is important to develop a synthesis process yielding high-quality single crystals over a large area to study the inherent physical properties and device applications of two-dimensional materials. However, the maturity of Bi₂Te₃ vapor-phase synthesis is not good, compared to those of other semiconductor twodimensional crystals. In this study, therefore, we report the synthesis of relatively large-area Bi₂Te₃ crystals by vapor transport method, and we investigated the key process parameters for a synthesis of relatively thin and large-area Bi₂Te₃ crystals. The most important factor determining the crystal synthesis was the temperature of the substrate. A Bi₂Te₃ device exhibited a
considerable photocurrent when the laser was irradiated inside the electrode area. This indicated that the photothermoelectric effect was the main mechanism of generation of photocurrent. The estimated Seebeck coefficient of the device was $\sim 196 \mu V/K$, which is comparable to the previously reported high Seebeck coefficient of Bi$_2$Te$_3$. This synthesis method can guide the development and applications of various types of layered crystals with the space group of R-3m.

FF01.06.40
Large-Area and Plasma Doped p-Type Multilayer MoS$_2$: Photodetectors with Gate Tunable Effect Xiao-Mei Zhang; Tokyo Institute of Technology, Japan

Two-dimensional (2D) transition metal dichalcogenides (TMDCs), such as MoS$_2$, have attracted considerable attention owing to the unique optical and electronic properties related to its 2D ultrathin atomic layer structure [1]. MoS$_2$ is becoming prevalent in post-silicon digital electronics and in highly efficient optoelectronics due to its extremely low thickness and its tunable band gap ($E_g = 1–2$ eV) [2]. For low-power, high-performance complementary logic applications, both p- and n-type MoS$_2$ FETs (NFETs and PFETs) must be developed. NFETs with an electron accumulation channel can be obtained using unintentionally doped n-type MoS$_2$. However, the fabrication of MoS$_2$ FETs with complementary p-type characteristics is challenging due to the significant difficulty of injecting holes into its inversion channel [3]. Plasma treatments with different species (including CF$_4$, SF$_6$, O$_2$, and CHF$_3$) have also been found to achieve the desired property modifications of MoS$_2$ [4-5].

In this work, we demonstrated a p-type multilayer MoS$_2$ enabled by selective-area doping using CHF$_3$ plasma treatment. Compared with single layer MoS$_2$, multilayer MoS$_2$ can carry a higher drive current due to its lower bandgap and multiple conduction channels. Moreover, it has three times the density of states at its minimum conduction band. Large-area growth of MoS$_2$ films on 300 nm thick SiO$_2$/Si substrate are carried out by thermal decomposition of ammonium tetrathiomolybdate, (NH$_4$)$_2$MoS$_4$, in a tube furnace. A two-step annealing process is conducted to synthesize MoS$_2$ films. For the first step, the temperature is set to 280 °C for 30 min in an N$_2$ rich environment at 1.8 Torr. This is done to transform (NH$_4$)$_2$MoS$_4$ into MoS$_3$. To further reduce MoS$_3$ into MoS$_2$, the second step of annealing is performed. For the second step, the temperature is set to 750 °C for 30 min in a reducing atmosphere consisting of 90% Ar and 10% H$_2$ at 1.8 Torr. The grown MoS$_2$ films are subjected to out-of-plane doping by CHF$_3$ plasma treatment using a Dry-etching system (ULVAC original NLD-570). The radiofrequency power of this dry-etching system is set to 100 W and the pressure is set to 7.5 mTorr. The final thickness of the treated samples is obtained by etching for 30 s.

Back-gated MoS$_2$ PFETs were presented with an on/off current ratio in the order of $10^3$ and a field-effect mobility of 65.2 cm$^2$V$^{-1}$s$^{-1}$. The MoS$_2$ PFETs photodetector exhibited ultraviolet (UV) photodetection capability with a rapid response time of 37 ms and exhibited modulation of the generated photocurrent by back-gate voltage. This work suggests the potential application of the mild plasma-doped p-type multilayer MoS$_2$ in UV photodetectors for environmental monitoring, human health monitoring, and biological analysis.

References

FF01.06.41
Horizontal-to-Vertical Transition of 2D Layer Orientation in Low-Temperature Chemical Vapor Deposition-Grown PtSe2 and Its Influences on Electrical Properties and Device Applications SangSub Han$^{1,2}$, Jong Hun Kim$^3$, Chanwoo Noh$^2$, Jung Han Kim$^1$, Eunji Ji$^2$, Junyoung Kwon$^4$, Seung Min Yu$^5$, Tae-Jun Ko$^1$, Emmanuel E. Okogbue$^{1,3}$, Kyu Hwan Oh$^2$, Hee-Suk Chung$^4$, YounJoong Jung$^2$, Gwan-Hyong Lee$^2$ and Yeonwoong Jung$^{1,1,1}$;
Two-dimensional (2D) transition-metal dichalcogenides (2D TMDs) in the form of MX2 (M: transition metal, X: chalcogen) exhibit intrinsically anisotropic layered crystallinity wherein their material properties are determined by constituting M and X elements. 2D platinum diselenide (2D PtSe2) is a relatively unexplored class of 2D TMDs with noble-metal Pt as M, offering distinct advantages over conventional 2D TMDs such as higher carrier mobility and lower growth temperatures. Despite the projected promise, much of its fundamental structural and electrical properties and their interrelation have not been clarified, and so its full technological potential remains mostly unexplored. In this work, we investigate the structural evolution of large-area chemical vapor deposition (CVD)-grown 2D PtSe2 layers of tailored morphology and clarify its influence on resulting electrical properties. Specifically, we unveil the coupled transition of structural–electrical properties in 2D PtSe2 layers grown at a low temperature (i.e., 400 °C). The layer orientation of 2D PtSe2 grown by the CVD selenization of seed Pt films exhibits horizontal-to-vertical transition with increasing Pt thickness. While vertically aligned 2D PtSe2 layers present metallic transports, field-effect-transistor gate responses were observed with thin horizontally aligned 2D PtSe2 layers prepared with Pt of small thickness. Density functional theory calculation identifies the electronic structures of 2D PtSe2 layers undergoing the transition of horizontal-to-vertical layer orientation, further confirming the presence of this uniquely coupled structural-electrical transition. The advantage of low-temperature growth was further demonstrated by directly growing 2D PtSe2 layers of controlled orientation on polyimide polymeric substrates and fabricating their Kirigami structures, further strengthening the application potential of this material. Discussions on the growth mechanism behind the horizontal-to-vertical 2D layer transition are also presented.

**FF01.06.42**

**2D-GaN Modified by Hydrogen and Vacancies—DFT Studio**

Roberto Gonzalez-Araiza1, Oscar Martinez-Castro1, Maria G. Moreno-Armenta2, Alvaro Gonzalez-Garcia1, William Lopez-Perez2 and Rafael J. Gonzalez-Hernandez2; 1Universidad del Norte, Colombia; 2Universidad Nacional Autonoma de Mexico, United States

Similar to graphene, III-V semiconductors offer extraordinary properties on a diversity of morphologies. In the last two decades, gallium nitride (GaN) and related group III-nitrides have become key materials in light emitting diodes (LEDs) and laser diodes [1,2]. Therefore, GaN-based device technologies have improved substantially, and are still under intense investigation for improved performance. GaN crystallizes in the wurtzite structure (nonlayered). Therefore, the probability to be exfoliated with traditional methods is almost null. However, this phase of gallium nitride has been experimentally produced via encapsulation between two graphene sheets and theoretical results have predicted a stable 2D graphene–like phase for GaN, known as g-GaN in which gallium and nitrogen atoms are in the honeycomb-like hexagonal disposition. We have studied the graphene phase of gallium nitride (g-GaN) structural and electronic properties by using first-principle calculations within the framework of the Density Functional Theory (DFT). We tried two different approaches: in the first one we considered the hydrogen adsorption at different levels of coverage over each kind of atom and in the second we introduced vacancy charged defects [3].

We considered hydrogen adsorption in a range from the diluted limit, as a 1/64 of the monolayer, up to the full coverage of the monolayer. It was found that N–N distances around the gallium atom with adsorbed hydrogen were similar to the clean distances. Contrarily, Ga-Ga distances around the N atom with adsorbed hydrogen increased as the hydrogen percentage decreased. The 2D g-GaN-H configurations are the most stable, having lower formation energy. Nonetheless, the ferromagnetic system with a hydrogen atom in the gallium position presents a nonzero magnetic moment. As it could be observed in the band structure, a defect level induced by the H adatom is the source of this magnetic moment, a phenomenon which can be exploited for spintronic applications. This ferromagnetism is mainly localized in the first and second closest N atoms around the gallium atoms where adsorption occurred [4].

It was found from the second approach that the Ga-Ga (or N-N) bond lengths around the vacancy increased for the gallium vacancies and decreased for the nitrogen vacancies with respect to the bond distance without vacancy. Vacancy-induced defect levels are responsible for the total magnetic moment in g-GaN, generating a magnetic moment located at the nitrogen atoms for gallium vacancies or delocalized in the lattice for nitrogen vacancies. Thermodynamic transition levels close to the conduction band minimum are identified for both the Ga and N vacancy. In addition, N vacancy has formation energy lower than the Ga vacancy. N vacancy is the dominant defect in g-GaN and could be responsible of the n-type behavior of GaN observed experimentally. Similarly, the w-GaN, gallium vacancies have a higher formation energy than those of nitrogen. However, gallium vacancies could be
successfully grown in order to design a two dimensional $p$-type semiconductor. It is expected that the results of these studies will contribute to the analysis of hydrogen adsorption on 2D g-GaN, as well as to the design of 2D H-g-GaN and 2D g-GaN-H based devices in electronic and spintronic fields.

References

SESSION FF01.07: Nanophotonics and Optics Enabled by 2D Materials
Session Chairs: Zakaria Al Balushi and Aleksandra Radenovic
Tuesday Morning, December 3, 2019
Hynes, Level 3, Room 312

8:15 AM FF01.07.02
Tunable Luminescence in Stacked Bulk-Like Hexagonal Boron Nitride Controlled by a Twist Angle Haeyeon Lee1, Mohammed AlEzzi2, Nimisha Raghuvasahi3, Kenji Watanabe4, Takashi Taniguchi3, Slaven Garaj2, Shaffique Adam2 and Silvija Gradecak1; 1Massachusetts Institute of Technology, United States; 2National University of Singapore, Singapore; 3National Institute for Materials Science, Japan

Van der Waals (vdW) heterostructures formed by layering twisted monolayers of two-dimensional materials result in formation of Moiré superlattices, which leads to new physical phenomena, including emergence of flat energy bands or tunable conductivity. So far, Moiré superlattice physics has been explored in graphene-related system and various combinations of monolayer transition metal dichalcogenides. Hexagonal boron nitride (hBN) forms a similar honeycomb lattice as graphene, but in contrast to graphene, has a large band gap with luminescence in ultraviolet region. Because of its properties, hBN has been recently extensively used as a substrate or dielectric spacer in vdW heterostructures.

Here, we show that the optical properties of stacked bulk-like (hundreds of nanometers in thickness rather than monolayers) hBN layers are dominated by the innermost interface layers and their relative twist angles as a consequence of the Moiré superlattice formation. Both the luminescence intensity and energy can be tuned using the relative twist angle between stacked layers. hBN multilayers were exfoliated from an hBN single crystal and these were used to form twisted hBN multilayers by a dry transfer method. The relative twist angles between the stacked hBN layers were measured using electron diffraction in a transmission electron microscope (TEM) and the optical properties of the resulting structure were measured simultaneously using TEM-based cathodoluminescence (CL). We show the strong functional dependence of the luminescence properties as a function of the twist angle. Our results demonstrate a new way of controlling optical properties of thin-film materials, beyond conventionally used heterostructures.

8:30 AM FF01.07.03
Near Ultraviolet Light Electroluminescence in Hexagonal Boron Nitride Based van der Waals Heterostructures Sanghoon Chae1, Dongjea Seo2, Qingrui Cao1, Xiang Hua1, En-Min Shih1, Sunho Park3, Seungjun Lee1, Takashi Taniguchi4, Kenji Watanabe5, Junyoung Kwon5, Gwan-Hyong Lee2, Cory Dean1, David Schiminoovich1, Irving P. Herman1, Heon-Jin Choi2, Young-Kyun Kwon3, Ioannis Kymissis1, Young Duck Kim3 and James Hone1; 1Columbia University, United States; 2Yonsei University, Korea (the Republic of); 3Kyung Hee University, Korea (the Republic of); 4National Institute for Materials Science, Japan

The ability to assemble van der Waals heterostructures from two-dimensional (2D) crystals provides a wealth of new opportunities for novel optoelectronic devices. To date, most such devices have shown functionality in the infrared to visible range, whereas ultraviolet (UV) applications are less well explored. Here we describe electrically driven light emission from vertical heterostructure devices consisting of thin hexagonal boron nitride (hBN) between graphene electrodes, with additional hBN encapsulation. Upon illumination at low electric fields, optically excited
carriers tunnel and generate interlayer photocurrent through Gr/hBN/Gr heterostructures. At high electric fields, hBN shows bright light emission with a strong peak in the near ultraviolet (NUV) regime at 394 nm (3.14 eV), and stable response over a wide voltage range. Light emission is accompanied by a rapidly increasing current and appearance of new photoluminescence peaks, indicating that it is facilitated by creation of color centers, whose potential structures are explored by density functional theory calculations. Finally, we report the generation of red-green-blue (RGB) color-mixed white light by a standard down-conversion approach using phosphors. These results demonstrate the promise of hBN-based van der Waals heterostructures for light emission in the NUV to visible regime.

8:45 AM *FF01.07.04
Atomically Thin Canvas for Quantum Optoelectronics Hongkun Park; Harvard University, United States

All-optical integrated circuits have long been a major pursuit for scientists and engineers because they may allow ultra-fast computing with ultra-low power consumption. The actual realization of this dream has been very difficult, however, because photons rarely interact with each other and, even with the aid of nonlinear optical materials, interact very weakly. My research group tries to leverage the advances in photonics, plasmonics, optoelectronics, and quantum optics and develop new material and technology platforms for solid-state all-optical information processing that work all the way down to single quantum level. In this presentation, I will describe our recent efforts to realize solid-state quantum optoelectronic devices by combining atomically thin semiconductors and nanoscale photonic/plasmonic structures. In particular, I will discuss how we improve the optoelectronic properties of these atomically thin materials and how we leverage them to gain detailed insight into their optoelectronic properties. I will then discuss our efforts to realize atomically thin, electrically tunable mirrors and excitonic “drums” as well as solid-state optoelectronic devices that are built upon quantum mechanical principles.

9:15 AM FF01.07.05
Strong Light-Material Interactions in Atomically Thin Metasurfaces Huiqin Zhang1, Bhaskar Abhiraman1, Qing Zhang2, Jinshui Miao1, Kiyong Jo1, Stefano Roccasecca1, Mark W. Knight3, Artur Davoyan4 and Deep M. Jariwala1; 1University of Pennsylvania, United States; 2National University of Singapore, Singapore; 3Northrop Grumman Corporation, United States; 4University of California Los Angeles, United States

Visible spectrum band-gaps with strong excitonic absorption make transition metal dichalcogenides (TMDCs) of molybdenum and tungsten attractive candidates for investigating light-material interactions and applications as absorbing media in opto-electronics.1, 2 Further, the excitonic features become more prominent as the layers are thinned down and dominant in the monolayer limit where the TMDCs transition into direct band-gap semiconductors with strong photoluminescence. Their excitonic character and luminescence in monolayer regime has been heavily investigated in fundamental science as well as exploited for device applications.2 However, the excitonic character in TMDCs persists even for few-layer thick samples and bulk crystals which has led to recent demonstrations of some interesting photonic and light trapping phenomena. Further, TMDCs are known to have very large values of optical constants which allows strong light trapping even in ultrathin samples.3 Here, we explore the fundamental material properties of light trapping in multi-layer TMDCs (namely WS2) when coupled to plasmonic substrates. Our calculations and demonstrations are primarily in WS2 which can be easily extended to other excitonic TMDCs. We systematically demonstrate via calculations and matching experiments that the presence of strong excitonic resonances in multilayers (< 20 nm thickness) combined with surface plasmon excitations of the nearby metals can achieve strongly coupled modes with apparent voided crossings in reflectance spectra. Further, we explore additional light confinement by patterning 1D arrays of rectangular resonators of varying widths and periods (100 nm to 500 nm). We find that there is a critical thickness of TMDC (~15 nm) beyond which we observe photonic modes emerging in the TMDC/metal hybrids that are strongly dispersive as a function of resonator width. Newer and higher order modes appear with increasing TMDC thicknesses and widths. Simulated field profiles suggest that these modes are mainly plasmonic and hybrid in nature. For longer wavelengths and thicker TMDCs, guided modes emerge as well. Further, the plasmonic modes exhibit strong dependence on 1D array grating period.

Finally, we will show the detailed multi-dimensional phase diagram of geometric parameters that lead to voided crossings between various resonant photonic modes and excitons and demonstrate sensing applications in the strong coupling regime. Our work may pave the way to novel hybrid photon-polariton states that are of interest for all-optical information processing, quantum and classical computing.

References:
Two-dimensional materials are inherently anisotropic – with strong bonding in-plane and weak bonding out-of-plane. Consequently, their optical properties are birefringent, particularly at frequencies close to the energies of their optically active infrared phonons. At these frequencies, certain 2D materials support hyperbolic behaviour, where along one (two) crystal axes they behave as metals (negative dielectric function), and along the other two (one) behave as dielectrics (positive dielectric function). Typically, two of these axes are in the plane of the 2D layers, and the third is out of the plane, the most well studied example being hexagonal boron nitride (hBN). Materials which exhibit hyperbolicity can support polaritonic modes, which have a wavelength much shorter than that of light in free space. Such spatially compressed modes have important implications for infrared technology, as they may be utilized to create infrared optics that are much more compact than the current state of the art. In particular, 2D materials can be used to realize metasurfaces, capable of shaping both nearfield- and far field light waves for a broad range of applications.

Conventional metasurface designs use geometrically fixed structures, or materials with excessive propagation losses, thereby limiting their potential applications. Here we show how to overcome these limitations by demonstrating a reconfigurable hyperbolic metasurface comprising a heterostructure of isotopically enriched hexagonal boron nitride (hBN) in direct contact with the phase-change material (PCM), single-crystal vanadium dioxide (VO2). Metallic and dielectric domains in VO2 provide spatially localized changes in the local dielectric environment to tune the wavelength of hyperbolic phonon polaritons (HPhPs) supported in hBN by a factor of 1.6. In contrast, propagation was only seen above a low loss dielectric phase with non-anisotropic materials supporting surface polaritons. Using this platform, we demonstrate the first reduction to practice of in-plane HPhP refraction, and the means for launching, reflecting and transmitting of HPhPs at the PCM domain boundaries. Ultimately, this phenomenon can be used to create devices based on refractive effects, such as lensing, but on length scales far below the diffraction limit. This relies on the unique properties of the 2D materials themselves, aided by the changing dielectric function of the PCM substrate.

9:45 AM BREAK
annealing of nanocrystalline metallic films with 2DC overlayers results in a ‘surface templated epitaxial’ process where the metal films become highly textured, with micron-sized, well-faceted grains in close crystallographic registry to the 2D crystal orientation. Dewetting of the encapsulated metal film occurs through the formation of pores that can span up to 60% of the planar surface area, creating an orientated pore enabled network (OPEN) film. This process has been demonstrated for a number of mechanically-exfoliated and chemical-vapor deposited 2DCs (e.g., graphene, h-BN, and transition-metal dichalcogenides (TMDs)). In the OPEN film structure, the 2DC overlayer can remain suspended above or coat the inside of the metal pores. OPEN-TMD films exhibit appreciably distinct properties, including enhancement in photoluminescence, spatially varying surface potential, and routes for coupling surface plasmon-polaritons (SPPs) to photon emission. SPPs were found to propagate throughout the OPEN film structure following generation by either free-space laser excitation or TMD-emitted photons at the metal pore sites, enabling non-local emission at room and low temperatures. We also find a high density of single photon emitters (SPEs) across an OPEN-WSe2 film and demonstrate non-local SPE excitation at distances of at least 17 mm with minimal loss of photon purity. Our results suggest the OPEN film geometry is a versatile platform that could facilitate the use of layered materials in quantum optics systems.

Work performed at NRL was supported through Base Programs funded by the Office of Naval Research. J.JF acknowledges the NRC Research Associateship Programs for their support.

11:00 AM FF01.08.03
Near-Infrared Optical Properties and Ultra-Fast, Diffusion-Less Phase-Change Functionality of Tin Selenide (SnSe) Seong Soon Jo1, Jian Zhou1,2, Akshay Singh1, Yifei Li1, Zhongzhen Luo1, Mercouri G. Kanatzidis3, Ju Li1 and Rafael Jaramillo1; 1Massachusetts Institute of Technology, United States; 2Xi’an Jiaotong University, China; 3Northwestern University, United States

Future integrated photonic circuits need materials to perform ultra-fast and low-power optical switching. Chalcogenide phase-change materials (PCMs) and two-dimensional (2D) materials contain many promising candidates to meet this need. Among layered 2D chalcogenides, IV-VI materials are particularly interesting for their trirefringent optical properties and low-processing temperature.

Here we propose a new mechanism for optical switching in anisotropic materials, and we report results obtained for SnSe. a-SnSe has an orthorhombic crystal structure that can be visualized as a highly-distorted rock salt lattice. We present theoretical predictions that, owing to strong dielectric anisotropy, short pulses of linearly polarized light can switch between ferroelastic variants of the a-SnSe structure.[1] Switching occurs because the light field changes the potential energy landscape and eliminates the barrier for switching. We predict a critical power density of 7.7 x W/cm² for near-IR photons for a barrier-less transition. We report experimental results obtained on crystals and mechanically-exfoliated sheets. We use spectroscopic ellipsometry to measure the full optical property tensor of trirefringent a-SnSe, to test theoretical calculations and to optimize the design of optical switching, and we report preliminary results using short laser pulses to perform ferroelastic switching.

The study presented on trirefringent a-SnSe can be generalized to a class of optical martensitic transitions that we predict to be ultra-fast, barrier-less, and diffusion-less. These transitions happen at the speed of lattice vibrations and are inherently non-thermal, and therefore low-power. 2D materials are ideal for realizing the predicted phenomena and for application because the transformation strains are lower than in 3D crystal structures. Optical martensitic transitions may therefore offer an improvement on existing PCMs for photonics in terms of switching energy, speed, and device lifecycle.


11:15 AM FF01.08.04
Near-Infrared Optical Properties and Phase-Change Behavior of Transition Metal Dichalcogenides Akshay Singh1, Yifei Li1, Balint Fodor2, Laszlo Makai2, Jian Zhou1, Haowei Xu1, Austin Akey4, Sergiy Krylyuk4, Ju Li1, Albert Davydov5 and Rafael Jaramillo1; 1Massachusetts Institute of Technology, United States; 2Semilab Semiconductor Physics Laboratory Co. Ltd, Hungary; 3Xi’an Jiaotong University, China; 4Harvard University, United States; 5National Institute of Standards and Technology, United States

Transition metal dichalcogenides (TMD) exist in several polymorphs including 2H (usually semiconducting), and 1T (or 1T', semi-metallic). These polymorphs are expected to have significantly different opto-electronic properties, and phase change between these polymorphs offers a new way for controlling light. This phase change is particularly interesting for near-infrared (NIR) integrated photonics, where materials with strong light-matter
interaction are required.
We present an experimental and theoretical study of sulfides (MoS₂, TiS₂ and ZrS₂) and tellurides (MoTe₂ and Mo₁₋ₓWₓTe₂) in the NIR. Our density functional theory (DFT) calculations predict a large refractive index contrast in the 1-1.5 um spectral range (relevant for telecommunications and photonics) between 2H and 1T (or 1T') phases. We measure the complex optical constants of bulk crystals via spectroscopic ellipsometry and Fourier transform IR (FTIR) spectroscopy, and find significant differences between 2H and 1T materials. By explicitly measuring native oxide thickness using transmission electron microscopy and subsequent optical modelling, we extract true optical constants of TMDs. Further, for structural polymorphs of the same material (MoTe₂ and Mo₁₋ₓWₓTe₂ in both 2H and 1T phases), we measure a large difference in refractive index and optical loss, in agreement with our DFT calculations. Our work lays the foundation for TMDs for use as active IR materials that can be switched optically and electrically.

11:30 AM *FF01.08.05
Electronic and Optical Properties of 2D Materials and Their Heterostructures Su Ying Quek; National University of Singapore, Singapore

Two-dimensional materials are known to exhibit an amazing range of novel electronic and optical properties, as demonstrated in many state-of-the-art experiments. First principles calculations play an important role in identifying the atomic-scale origins of these properties, as well as in predicting properties of new materials. In this talk, I will draw upon examples from recent work in my group on first principles calculations in 2D materials and their heterostructures. Comparison with experiment will be made throughout the talk. Firstly, I will show convincing evidence that oxygen-related point defects are dominant in mechanically-exfoliated and chemical-vapor-deposition (CVD)-grown WSe₂ samples, in contrast to mechanically-exfoliated MoS₂ samples, where sulfur vacancies are dominant. Furthermore, based on state-of-the-art, numerically converged, GW-BSE calculations, we show that oxygen interstitials in the WSe₂ lattice (in conjunction with strain gradients) are most likely responsible for experimentally observed single photon emission in these materials.1 Secondly, I will present the electronic properties of covalently functionalized organic-MoS₂ heterostructures that have been experimentally synthesized. Interestingly, we find that local magnetic moments are present. Furthermore, while the organic molecules can either withdraw or donate electrons from the MoS₂ layer, depending on the electron affinity of the molecules, electrons are always the predominant carrier type in the MoS₂ layer. Thirdly, I will show how our recent theoretical developments have enabled the prediction of quasiparticle level alignment at organic-2D material interfaces, in good agreement with experiment.2,3 Fourthly, I will show that experimentally observed Dirac cones in black phosphorus can be explained by quantum confinement and anisotropic interlayer interactions.4 If time permits, other results, including predictions on novel materials from high throughput calculations, will be presented.


SESSION FF01.09: Atomic Scale Characterization of 2D Materials
Session Chairs: Olga Kazakova and Humberto Terrones
Tuesday Afternoon, December 3, 2019
Hynes, Level 3, Room 312

1:30 PM FF01.09.01
Chemical Identification of Interlayer Contaminants within van der Waals Heterostructures with IR Nano-Spectroscopy Jeffrey J. Schwartz1,2, Hsun Jen Chuang3, Matthew R. Rosenberger3, Saujan V. Sivaram3, Kathleen McCready3, Berend T. Jonker4 and Andrea Centrone5; 1National Institute of Standards and Technology, United States; 2University of Maryland, United States; 3U.S. Naval Research Laboratory, United States

Van der Waals heterostructures (vdWHs) consist of layers of dissimilar 2D materials that provide novel and unique and properties. vdWHs are commonly assembled in a myriad of combinations by stacking 2D materials using
polymeric stamps. However, the properties of such heterostructures frequently are degraded by contaminants, typically of unknown composition, that are trapped between the constituent layers and impede studies of the heterostructures’ intrinsic properties, thus hindering their applications.

In this work, I will introduce the photothermal induced resonance (PTIR) technique, an atomic force microscopy (AFM)-based infrared technique that enables IR spectroscopy and imaging with nanoscale resolution. I will show that PTIR enables detection and identification of contaminants down to a few amomoles.

Heterostructures comprised of WSe2, WS2, and hBN layers were found to contain significant amounts of polydimethylsiloxane (PDMS) and polycarbonate, corresponding to the stamp materials used in their construction. Notably, polymer contamination between layers occurs even when ‘dry’ fabrication methods are used. Having identified the source of the contaminants, we develop a stamp cleaning procedure that eliminates or reduces PDMS contamination within the structures below the limit of detection. Our measurements suggest that the assessment of contaminants in vdWHs should not be conducted based on AFM topographic images alone but, rather, aided by nanoscale composition-sensitive methods, such as PTIR. We believe that knowledge of the contaminant composition obtained with the methods presented here will aid better understanding of vdWH properties and guide improvements to fabrication method for producing intrinsic, contaminant-free heterostructures with precisely tuned properties.

1:45 PM FF01.09.02
Abnormal Interlayer Coupling in Janus MoSSe/MoS2 Heterostructures Kunyan Zhang¹, Yunfan Guo², Hua Wang³, Alexander Puretzky⁴, Xiaofeng Qian⁵, Jing Kong⁶ and Shengxi Huang⁷; ¹The Pennsylvania State University, United States; ²Massachusetts Institute of Technology, United States; ³Texas A&M University, United States; ⁴Oak Ridge National Laboratory, United States

Janus transition metal dichalcogenide (TMD) is a newborn of the two-dimensional (2D) materials family. Its structure is similar to TMDs such as MoS2, but one layer of the chalcogen is different from the other layer, one example being MoSSe. As the first successfully synthesized Janus TMD, MoSSe has motivated a series of theoretical investigations on the Janus TMDs. Due to the unique crystal structure of Janus TMDs, unconventional phenomena have been theoretically predicted, including out-of-plane piezoelectricity and exciton disassociation by the intrinsic out-of-plane dipole moment. However, experimental investigations are extremely insufficient in terms of the principle properties of monolayer Janus TMDs and their heterostructures with other van der Waals materials. Such properties, for example interlayer coupling and phonon properties, are essential to electronic transport and optoelectronic applications.

In this work, we study the fundamental phonon properties and interlayer coupling of Janus monolayer MoSSe and MoSSe/MoS2 heterostructures. Interlayer breathing and shear modes of high-symmetry 2H and 3R heterostackings are probed by low frequency Raman spectroscopy. The uniform selenization from MoS2 to MoSSe is confirmed by the disappearance and the emergence of signature Raman modes of MoS2 and MoSSe, respectively. Low frequency Raman modes for different stacking patterns of MoSSe/MoS2 show noticeable variations in frequencies. This observation indicates that stacking configuration leads to different layer-to-layer interactions. Unintuitively, interlayer coupling in the heterostructures is stronger than their pure MoS2 counterparts possibly due to the compressive (tensile) strain in MoSSe (MoS2) introduced during synthesis. Difference in high frequency modes between MoSSe/MoS2 and pure MoS2 is consistent with variations in the low frequency modes. Both the low frequency and high frequency Raman responses are strong evidence for the abnormally enhanced interlayer coupling. These spectroscopic features can serve as a fingerprint of stacking configurations, interlayer coupling in heterostructures, and degree of conversion in the fabrication process from TMDs to Janus TMDs.

2:00 PM *FF01.09.03
Nanoscopy of 2D Materials Aleksandra Radenovic; Ecole Polytechnique Federale Lausanne, Switzerland

The simplicity and versatility of optical microscopy make it from the start the workhorse technique in the characterization of 2D materials (1). Optical microscopy is used to locate and determine the thickness of the 2D material by measuring its optical contrast with respect to the Si/SiO2 substrate (2). Although in terms of technology, the large-area growth of 2D materials is about to be mastered soon, as-grown 2D materials still host abundant and different types of defects such as vacancies, adatoms, grain boundaries (GBs), edges, and impurities, which strongly influence their properties (3). In most cases, the presence of defects is disadvantageous. However, not all defects in 2D materials are detrimental. Some 2D materials have been shown to host defects that can serve as single-photon emitters (SPEs) at cryogenic temperatures for TMDs (4-7) and room temperature for h-BN (8). This discovery has motivated the search for single-photon sources in other 2D materials and efforts that aim to engineer the defects in
well-controlled locations either using strain-induced potential traps (9) or via quantum dot confinement (7). The advent of single quantum emitters in 2D materials offers new opportunities to construct a scalable quantum architecture. Transmission electron microscopy TEM, SPM or confocal microscopy techniques are not ideal for fast, high-throughput, in-situ imaging of defects in 2D materials with nanometer resolution. There is a clear demand for the development of advanced optical technology that images individual defects at better temporal, spectral and spatial resolutions. We have explored the single molecule localization microscopy to characterize defects in hexagonal boron nitride (10). In addition to precise location of the optically active defects we record as well their spectral properties using spectral SMLM (11).


2:30 PM *FF01.09.04
Characterization of 2D Material Heterostructures Using Nanoscale Angle Resolved Photoemission Spectroscopy (nanoARPES) Eli Rotenberg; Lawrence Berkeley National Laboratory, United States

Angle-resolved photoemission spectroscopy (ARPES) is a premier technique for determining the electronic structure, state symmetry, and many body interactions (MBIs) in correlated and topological materials. These MBIs involve exchange of momentum among electrons or with excitations such as phonons, and can therefore couple to nanoscale structures. By controlling the structure at the nanoscale, we can therefore hope to control or enhance the ground state properties of materials through nanoscale engineering. This dream has motivated the development of ARPES with nanoscale spatial resolution (nanoARPES), in order to probe these effects. MAESTRO, the Microscopic and Electronic Structure Observatory, is a new synchrotron based user facility for the study of in situ prepared materials, including oxides, 2D van der Waals material, semiconductors, metals, and surfaces. With a combination of three ARPES microscopes with complementary spatial/energy/momentum resolutions, and in situ sample preparation (molecular beam epitaxy, pulsed laser deposition, and micro-mechanical sample transfer) we are able to examine the relationship between electronic structure and topology with unprecedented spatial resolution, currently around 100nm, with 50 nm performance on the horizon.

As an example, I will show the spatially resolved electronic structure of two-dimensional metal dichalcogenide heterostructures of WS2, graphene, BN and TiO2 [1, 2]. Among the findings is a striking renormalization of the spin-orbit splitting of the WS2 valence band, which can be controlled by chemical doping or by choice of substrate. This is attributed to the impact of trion (charged exciton) formation on the self-energy of carriers in WS2. We have also observed modifications in the electronic structure of “twisted” layers of WS2 on graphene. Such twisted heterostructures are garnering a lot of attention due to the possibility of engineering novel electronic structures.

https://aip.scitation.org/doi/10.1063/1.5088968
Black phosphorus is one of the most promising 2D semiconductors because of its layer-dependent bandgap and high mobility carriers. Its corrugated crystal structure also creates a unique electronic anisotropy which may create opportunities for novel angle-dependent electronic and optoelectronic devices. Native defects and their impact on the electronic structure of 2D semiconductors are understudied, especially when compared to defects in 3D semiconductors. Additionally, the degradation of black phosphorus in air, which is likely exacerbated by defects, creates a major limitation to applications. This talk will present scanning tunneling microscopy and spectroscopy studies of surface structures in black phosphorus, including defects, nanoscale stripes, and islands. We will use a temperature-dependent study of the native defects in black phosphorus to compare defect hopping rates at different temperatures to theoretical expectations. Additionally, we will present data on nanometer-scale black phosphorus islands, created by partially sublimating the top layers of the crystal. These islands appear to lose their crystallinity as they shrink to 10s of nanometers in diameter. Finally, we will present newly observed periodic, 5 nm stripes, whose appearance depends strongly on temperature. The voltage dependence of these stripes suggests an electronic superstructure. We will present the data and possible interpretations of this new superstructure.
electronic properties of interfaces that were specifically characterized in situ. We believe that achieving control of 2D/3D interfacial structure and dynamics will facilitate systematic design of contacts, heterostructures, and coupled materials for future devices with distinct properties and applications.

4:15 PM FF01.09.07
Determining the 3D Atomic Coordinates and Crystal Defects in 2D Materials with Picometer Precision
Dennis S. Kim1, Xuezeng Tian1, Shize Yang2, Christopher J. Ciccarino3, Yongji Gong4, Yongsoo Yang1, Yao Yang1, Yakun Yuan1, Pulickel Ajayan4, Juan-Carlos Idrobo5, Prineha Narang3 and Jianwei Miao1; 1University of California, Los Angeles, United States; 2Brookhaven National Laboratory, United States; 3Harvard University, United States; 4Rice University, United States; 5Oak Ridge National Laboratory, United States

To understand the structure-property relationship of 2D materials and heterostructures at the fundamental level, defects and crystalline imperfections need to be accounted for with high precision. AET allows the determination of 3D atomic structure of crystal defects and disorder systems and has recently been advanced to capture nucleation at 4D atomic resolution. However, AET has thus far been limited to metallic nanoparticles and needle-shaped samples. We have developed scanning atomic electron tomography (sAET) to localize the 3D atomic coordinates in 2D materials and heterostructures with picometer precision. Using a Re-doped MoS2 monolayer, we demonstrated the sAET method and determined the 3D atomic coordinates with picometer precision and identified 3D crystal defects such as dopants, vacancies and atomic-scale ripples. We measured the 3D atomic displacement and the full strain tensor of the Re-doped MoS2 and observed strong correlations between local atomic strains and Re, and S vacancy concentrations. Furthermore, the experimental 3D atomic coordinates were used as direct input to DFT calculations to correlate crystal defects with the electronic band structure at the single-atom level. We observed stark differences between the band structures obtained from the experimental and relaxed atomic models. The local atomic strains from Re-dopants were found to drastically alter the overall electronic properties and was corroborated by photoluminescence spectra measurements. We also demonstrate the capabilities of the sAET method through accurate reconstructions and 3D atomic coordinate determination of a multislice simulated MoSe2-WSe2 moire patterned van der Waals heterostructure. We anticipate that sAET is not only generally applicable to the determination of the 3D atomic coordinates of 2D materials, heterostructures and thin films, but also could transform ab initio calculations by using experimental atomic coordinates as direct input to reveal more realistic physical, material, chemical and electronic properties.

4:30 PM FF01.09.08
Nanoscale Electrical Mapping of Vertically Stacked Heterostructures  Manoj Tripathi1, Xiang Zhang2, Matthew Large1, Sean P. Ogilvie1, Yuanyang Rong1, Peter Lynch1, Frank Lee1, Antonios Michail3, Konstantinos Papagelis3, John Parthenios4, Konstantinos Papagelis3, Aline Amorim Graf1, Alice King1, Jonathan Salvage5, Nicola M. Pugno6,7,8, Pulickel Ajayan2 and Alan B. Dalton1; 1University of Sussex, United Kingdom; 2Rice University, United States; 3Foundation for Research and Technology Hellas, Aristotle University of Thessaloniki, Greece; 4Institute of Chemical Engineering Sciences, Greece; 5University of Brighton, United Kingdom; 6University of Trento, Italy; 7Queen Mary University of London, United Kingdom; 8Ket Lab, Edoardo Amaldi Foundation, Italy

The stacking of heterogeneous 2D materials using transition metal dichalcogenides (TMDC) allows the development of the hybrid artificial structures for unique application of tuned physical, electrical and optical properties1. The artificial integration of heterogeneous sheets has produced abundant functionalities in the hybrid structure through interface engineering2. Hence, hetero-junction hybrids are incredibly favourable to fabricate p-n junction, tunneling FET, memory devices and other optoelectronics devices3. Some of the crucial contributions of hetero-layer devices is controlled doping, bandgap tailoring and modulation of Schottky barrier height without the implementation of conventional dopant diffusion, ion implantation and laser treatment4 that leads to crystal damage and surface defect5. Nevertheless, stacked heterogeneous structures are susceptible to mechanical strain, interfacial charge transfer and unpinning of Fermi energy level through inter-layer van der Waals interaction. Thus, it has become pivotal to decouple the contribution between the electrical and mechanical properties of the overlapped heterogenous structure to fabricate flexible electronics.

The present work demonstrates nanoscale electrical properties and interfacial characteristics of two versatile heterogeneous stacked structures beyond graphene; WS2/MoS2 and the graphene/MoS2. The interactions of the monolayer MoS2 with WS2 and graphene is collated comprehensively for the mobility of charges, doping and work function. The topping of conductive graphene over the pyramidal arrangement of MoS2 sheets up to three layers revealed the unpinning of Fermi energy level at different step-edges of the hybrid structure. Consequently, the work
function and the amount of charge transfer was found different at each layer of the hybrid structure. The nanoscale conductivity map showed the higher values of currents/area (nA/µm²) in graphene/MoS2 configuration at thicker MoS2 layers. Therefore, a transition from indirect to direct band gap in the CVD MoS2 increases the charge mobility at the interface. Finally, we deconvoluted the strain in the hybrid structure from doping by Raman correlation plots for E2g Vs A1g and G Vs 2D peaks for TMDC (MoS2 and WS2) and graphene Raman modes, respectively. This investigation will address to establish a functional method to tailor the nanoscale electrical and mechanical properties of the scalable engineered 2D heterostructure for high-performance flexible electronics.

References:

4:45 PM FF01.09.09
Direct Measurement of Gap States Energy Distribution and Fermi Level Pinning in MoS2 Monolayers and Multilayers Yossi Rosenwaks, Ronen Dagan and Yhonatan Vaknin; Tel Aviv University, Israel

Transition Metal Dichalcogenides (TMDs) are promising materials for beyond silicon electronics due to their unique electrical, including tunable band gap in the visible regime, mechanical and thermal properties. The electronic quality of such materials is highly effected by lattice impurities, such as Sulfur vacancies and other atomic defects which generates atomic gap states in TMDs, as well as the semiconductor/oxide interface imperfection. To-date, even though some recent progress has been reported, the study and understanding of gap states in TMDs materials and devices is very limited. First, reliable, sensitive and quantitative methods to measure the concentration and energy distribution of such states are not fully developed. Second, fundamental issues surrounding the origin of gap states in TMDs materials are not known, and relatively very little is reported about the effect of these states on electronic device properties.

In this work, we use Kelvin Probe Force Microscopy (KPFM) under inert atmosphere to measure the gap states concentration, their energy distribution and Fermi level pinning in MoS2 monolayers and multilayer transistors. The method is based on applying back gate voltage to a working MoS2 Field Effect Transistors in-operando. The voltage applied to the back gate induce injection of electrons/holes into the transistor channel; these charge carriers populate the gap states and consequently change the Fermi level position. The Fermi level energy is measured directly by the KPFM, and the gap states energy distribution is then extracted using the injected charge concentration obtained from the transistor capacitance as described in our previous works. We have measured the gap states of both MoS2 monolayers and multilayers exfoliated on SiO2 and found that in monolayers the Fermi level is unpinned throughout most of the energy gap, and the states distribution is fairly constant at a concentration of around 10¹⁸ cm⁻³ eV⁻¹. In samples which are several multilayers thick, the states distribution decays exponentially from the conduction band edge similar to our measured bulk samples. Gap states measurements at the interfaces of MoS2 with other dielectrics will be presented and discussed.


SESSION FF01.10: Poster Session II: Beyond Graphene 2D Materials—Synthesis, Properties and Device Applications II
Session Chairs: Zakaria Al Balushi, Deep Jariwala, Olga Kazakova and Amber McCreary
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

FF01.10.02
Piezo-Phototronic Effect Enhanced High-Performance Flexible In₇₋ₓSnₓSe Photodetector Christy Roshini Paul Inbaraj1,2,3, Roshan Jesus Mathew1,2, Raman Sankar3, Yit-Tsong Chen4, Chih-Hao Lee1 and Yang-Fang Chen3;
Piezoelectricity is widely considered to be one of the emerging research fields owing to its promising applications in diverse areas including sensors, nanogenerators, energy harvesting, and biomedical devices. Recent studies on the piezoelectricity in two-dimensional materials show remarkable features for manipulating band structure and many important physical characteristics. Here, we demonstrate the piezo-phototronic property observed in the In$_{1-x}$Sn$_x$Se flexible photodetector, where the performance of the device can be tuned by applying systematic mechanical strain. The piezoelectric property and changes in the band gap of the material were carefully studied with several spectroscopic analysis under strained conditions. Quite interestingly, we discover that in the fabricated In$_{1-x}$Sn$_x$Se device, the dark and photo drain-source current can be increased by 5-fold under a bending strain of 2.7 %, which shows a great promise for the design of high performance, multifunctional device as strain sensor and photodetector. The maximum photoresponsivity and strain sensitivity are obtained as 1037 AW$^{-1}$ and 206, respectively, which outperform the flexible devices in the same class of two-dimensional materials. In addition, we show that the few-layer In$_{1-x}$Sn$_x$Se devices can be attached on a freeform surface with high performance. Thus, our designed multifunctional device is very useful for the development of advanced applications to circumvent the requisite demand for emerging technologies.

Contact Resistance Engineering in MoS$_2$ Using Hexagonal Boron Nitride Taesoo Kim$^{1,2}$, Hyun Kim$^1$ and Young Hee Lee$^{1,3}$; 1Center for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), 16419, Korea (the Republic of); 2Sungkyunkwan University, Korea (the Republic of); 3Sungkyunkwan University (SKKU), Korea (the Republic of)

Molybdenum disulphide (MoS$_2$), one of the most widely applicable transition metal dichalcogenide (TMD) is known to have high electron mobility at room temperature as well as optical property for monolayer. The band gap of single layer MoS$_2$ shows direct transition which values ~1.8 eV [1] is believed to be the source of its rectifying behavior. MoS$_2$ shows Schottky behavior when it is electrically contacted to metal by forming Schottky barrier (SB) at metal/MoS$_2$ interface. The potential barrier at the interface is directly related to contact resistance which should be minimized to achieve lower power consumption for high device performance. Many efforts to engineer contact resistance at the metal/TMD interface such as adopting low work function metal for contact [2], doping the channel material with molecular dopant [3], transferring conductive layer at the contact/channel interface [4] and introducing thin insulating material on top of the channel [5] have been reported. In this study, we used centimetre-scale synthesized hexagonal boron nitride (hBN) on top of the MoS$_2$ channel layer in order to take advantage of absence of fermi level pinning which is considered to be a main reason of forming high Schottky barrier at the interface.

Light-Induced Local Reconfigurable Doping of 2D van der Waals Semiconductor Seung-Young Seo$^{1,2}$, Gunho Moon$^{1,2}$, Jaehyun Park$^{1,2}$ and Moon-Ho Jo$^{1,2}$; 1Pohang University of Science and Technology, Korea (the Republic of); 2Institute for Basic Science, Korea (the Republic of)

The development of fast and reliable doping techniques of two-dimensional (2D) van der Waals (vdW) semiconductors are required for next generation 2D circuit fabrication. Many attempts are being reported, but such techniques are still hard to find. Here we demonstrated that light illumination can induce chemical doping on channel of 2D semiconductor molybdenum ditelluride (2H-MoTe$_2$). Moreover, the doping carrier types are selective by controlling the light illumination conditions such as wavelength and optical intensity. We found that the channel was doped to $p$-type under visible light illumination, whereas to $n$-type under ultraviolet light illumination. This light induced doping process is fast and reliable, so it can be used to assemble various functional devices or circuit elements. As a representative example, we demonstrated that we could directly write 2D CMOS inverter consisting of $n$- and $p$-type FET channels. Moreover, this CMOS inverter can also be easily converted to a CMOS switch using
Hexagonal Boron Nitride (BN) exhibits its own unique sets of properties, such as high chemical and thermal stability, transparency to visible light, electrical insulativity, and high thermal conductivity. The latter two properties are unique because of their contradictory nature, which attracts great attention for thermal dissipation applications. Furthermore, combined with the fact that BN is transparent to visible light, it has great potential to be used as a thermal conductive layer in light entrance part of optoelectronic devices.

In order for BN to exhibit high thermal conductivity and transparency to visible light, it needs to be densely stacked and aligned along the horizontal direction to suppress backward scattering of phonons and photons. However, fabrication of this aligned structure faces several processing challenges. Although liquid-phase deposition methods such as ink-jet printing and spray coating offer good scalability, they usually lack uniformity and poor adhesion due to the coffee ring effect and BN nanosheets crumpling.

Herein, we propose a new fabrication method of high-performance BN films by combining the vacuum-filtration and transfer-printing. The process is facile, rapid, and applicable to various substrates having thickness scalability with higher functionality compared to conventional deposition techniques. Controlled vacuum-filtration enables BN nanosheets, which is immediately followed by transfer-printing based on solvent-evaporation-induced adhesion-switching between BN-membrane and BN-substrate interfaces. The fabricated BN films with a few micron thickness has compact, anisotropically aligned nanostructure, achieving an unusually high thermal conductivity over 23 W/m.K and optical transparency over 90%. Additionally, thermal dissipation effect of the BN layer characterized with simple joule heating apparatus. Finally, we report that the transfer-printed BN has an outstanding light diffusion property that optically enhances the performance of various optoelectronic applications including LEDs, thin film solar cells and organic dyes by facilitating both light out-coupling and absorption.

References:
1) Controlled Formation of Nanostructures on MoS2 Layers by Focused Laser Irradiation. R. Rani, D. Sharma, A.

FF01.10.07  
Role of Native Defects in Post-Synthesis Alloying of Transition Metal Dichalcogenides Hossein Taghinejad1, Daniel Rehn2, Ali Eftekhar1, Xiang Zhang3, Sufei Shi4, Pulickel Ajayan5, Evan J. Reed2 and Ali Adibi1; 1Georgia Institute of Technology, United States; 2Stanford University, United States; 3Rice University, United States; 4Rensselaer Polytechnic Institute, United States

Post-synthesis alloying is an important method for tailoring properties of two-dimensional (2D) transition-metal dichalcogenides (TMDs). In such a method, a binary crystal (i.e., MX2) serves as a host lattice in which the partial substitution of a native element (e.g., X) with a dissimilar counterpart (e.g., X’) yields a 2D alloy (i.e., MX’2xX2(1-x)) [1]. However, the detailed mechanism of the post-synthesis alloying in 2D TMDs is largely unknown. Here, we show that native vacancy-type defects play a major role in such an alloying scheme. In a case study, we use MoSe2 films as host crystals in which exchanging “Se” atoms with “S” atoms yields MoS2xSe2(1-x) alloys. Our study reveals that Se vacancies in host MoSe2 films (1) mediate the Se-S exchange process, and (2) further take part in the lateral diffusion of S atoms within the MoSe2 lattice. Accordingly, we show that alloying of CVD-grown MoSe2 with abundant Se vacancies is more efficient than that of exfoliated MoSe2 with fewer vacancies [2]. Practical consequences of this important conclusion will also be discussed.

Ref.  

FF01.10.08  
Ultrafast Coherent Lattice Vibrations in 1T’-MoTe2 Bulk Crystal Takumi Fukuda1, Kotaro Makino2, Yuta Saito2, Paul Fons2, Alexander V. Kolobov23, Keiji Ueno4, Richard Mondal1 and Muneaki Hase5; 1University of Tsukuba, Japan; 2National Institute of Advanced Industrial Science and Technology (AIST), Japan; 3Faculty of Physics, Herzen State Pedagogical University, Russian Federation; 4Saitama University, Japan; 5Faculty of Pure and Applied Sciences, University of Tsukuba, Japan

Following the extensive investigation of the physical properties of two dimensional (2D) graphene, attention has turned to transition metal dichalcogenides (TMDs) as 2D-materials for fundamental physics and device engineering, owing to the wide variety of possible crystal structures due to the large number of accessible chemical combinations as well as unusually long lifetime carrier transport properties. Because of the possibility low energy phase switching, TMDs can also be considered as promising candidates for high-performance phase-change materials in the next generation of nonvolatile memory. In particular, phase transitions between the monoclinic phase of 1T’-MoTe2 (being stable at room temperature, RT) and the orthorhombic phase Td-MoTe2 (being stable below 250K) structures may be useful as ultrafast symmetric switching [1], since their crystal structures are similar, except for distortions along the a- or b-axes. Very recently Zhang et al. examined photoinduced structural transitions in Td-MoTe2, showing subpicosecond lattice symmetry switching by means of second harmonic generation, although the related coherent lattice vibrations were not well observed at RT [2]. Here we investigate the dynamics of coherent lattice vibrations in the monoclinic 1T’ phase using femtosecond optical pump-probe spectroscopy at RT. Preliminary results show a total of seven coherent phonon modes, which are approximately consistent with the corresponding Raman active modes. Among these modes, however, the lowest frequency mode at 0.38 THz, unexpectedly observed at RT, is primarily thought to exist only in the Td phase along the shear layer direction. Moreover, unlike the other six optical phonon modes, the amplitude of the shear phonon mode decreases with increasing pump fluence. The shear phonon mode is key in breaking the lattice symmetry, which results in the formation of a topological Weyl semimetal phase. We argue that our data demonstrate a possible ultrafast structural modulation between 1T’ and Td phases upon excitation of a shear phonon mode at RT.

Ref.  
Highly Conductive, Flexible and Solution-Processed Two-Dimensional Titanium Carbide (MXene) Electrode for Organic Light-Emitting Diode under Alternating-Current Operation

Seokyeong Lee, Euihyuk Kim, Soyeon Baek and Cheolmin Park; Yonsei University, Korea (the Republic of)

MXenes (Ti₃C₂), a new class of the two-dimensional (2D) transition-metal carbides and nitride, are currently at the forefront of 2D materials research. MXenes are promising new materials for next generation electrodes of the other electronics, in which various properties are required, including conductivity, transparency, mechanical reliability and conformability. Among the classes of various MXene family, Ti₃C₂Tx MXene, that firstly introduced from Drexel University, exhibits metal-like conductivity and hydrophilic surface including majority terminal group (-OH). Although MXene has been widely used as an electrode in many electronic devices such as supercapacitors, sensors, and batteries, it has not been applied to light-emitting diode (LED) devices yet. Herein, we prepared MXene (Ti₃C₂) thin film electrode with transparency, high conductivity and flexible for operating Organic Light-Emitting diode. This OLED with MXene electrode are very unstable in DC (Direct Current) operation but shows stable property in AC (Alternating-Current) operation. Our AC-driven OLED based on MXene electrode shows a high performance than device made from other 2D materials capable of solution processing. Moreover, the MXene electrode prepared on the non-rigid substrate (PET) with solution-processing exhibited both physical stability and durability under mechanical deformation. Therefore, we expect that this new MXene (Ti₃C₂) electrode with solution processable 2D materials will provide tremendous potential to fabricate OLEDs toward high-performance, flexible, and transparent as well as a variety of other functionality.

Wafer-Scale MXene Electrode Array for Large-Area Flexible Electronics

Benzheng Lyu¹, Seongchan Kim¹, Hong Gi Min², Hyungseok Kang¹ and Jeong Ho Cho²; Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); Yonsei University, Korea (the Republic of)

MXene, an emerging category of two-dimensional (2D) transition metal carbides and nitrides, have the potential to be high-performance and low-cost electrodes in organic field-effect transistor (OFET), due to the water dispersibility, the high conductivity, and the work function tunability. In this manuscript, we demonstrated a large-scale and uniform MXene electrode array formation on a plastic substrate for high-performance OFETs. The work function of MXene electrode was also effectively modulated through the chemical doping with NH₃. The resulting OFETs with MXene electrodes exhibited the excellent device performances such as maximum carrier mobility of ~1 cm²/V·s and on-off current ratio of ~10⁷ for both p-type and n-type OFETs, even though all electrode and dielectric layers were fabricated using solution process onto the plastic substrate. Furthermore, the MXene electrode-based complementary logic circuits such as NOT, NAND, and NOR have been integrated using p-type and n-type OFETs. The proposed method is expected to expand the application of MXene in other OFETs-involved electronic devices such as organic light emitting display and electronic skin.

Large Scale and Low-Temperature Synthesis of WS₂ Using PECVD

Vinit K. Kanade¹, Hyeong-U Kim², Seokjun Hong¹, Chaitanya K. Kanade¹, Jae-Hyun Lee¹ and Tae Sung Kim¹; Sungkyunkwan University, Korea (the Republic of); Northwestern University, United States; Ajou University, Korea (the Republic of)

The discovery of 2D graphene has attracted many researchers to synthesize a 2D transition metal dichalcogenides (TMDCs) materials. The TMDCs represented as MX₂ (M stands for Mo or W, Nb, Ta, etc. and X= S, Se, etc.) has the covalent bonds between metal and chalcogens that form the three layers which are held together by a weak van der Waals force. The stable layered structure formations in TMDCs is achieved by the absence of out-of-plane dangling bonds. Tungsten Disulfide (WS₂) is reported as one of the promising TMDC materials due to its various application in electronics, catalysis, optical, and other fields. The synthesis of WS₂ was previously reported by multiple techniques such as mechanical exfoliation, chemical exfoliation, chemical vapor deposition, etc. The limited research in large scale and high-quality synthesis of WS₂ materials restricts the use in the widescale application.

In this work, we are reporting the synthesis of a few layers WS₂ using plasma enhanced chemical vapor deposition (PECVD) technique at relatively low temperature (300°C). The PECVD technology is utilized to grow WS₂ thin film directly on the 4-inch Si-SiO₂ wafer. The quality of a synthesized WS₂ was confirmed using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HR-
TEM), and energy dispersive spectrometry (EDS) mapping techniques. The thickness of the synthesized WS₂ film was found to be around a few nanometers and showed multilayered structure (~5-6 layers). Our unique approach shows the distinct advantage of the synthesis of WS₂ thin film with high uniformity and purity with reproducibility for mass production. Further, the WS₂ thin film was used to check the hydrogen evolution reaction (HER) catalytic performance with direct growth on the glassy carbon electrode. The PECVD synthesized WS₂ shows promising HER performance comparable with previously reported materials.

**FF01.10.12**

**A New Class of Layered Nanocrystals from Aromatic Molecular Units**

Veronica Barone and Isaiah A. Moses; Central Michigan University, United States

Novel two-dimensional(2D) materials in which simple molecular units are used as building blocks are currently being synthesized through bottom-up approaches. In this work, aromatic six-membered ring units, namely benzene, pyridine, phosphinine, arsinine, 1,3-diazine, 1,3,5-triazine and borazine are each utilized to build 2D graphene-like monolayers. Our density functional theory calculations revealed the stability of different 2D layers made out of heterocyclic molecular units, for the first time. The electronic properties of the holey materials as well as band gap tuning resulting from the different stacking of consecutive layers are also examined. This set of 2D materials presents a whole new class of layered nanostructures with great potentials for applications in areas such as catalysis, gas separation, optoelectronics, and nanoelectronics.

**FF01.10.13**

**Realization of 2D Crystalline Metal Nitrides via Selective Atomic Substitution**

Jun Cao, Tianshu Li, Hongze Gao and Xi Ling; Boston University, United States

Two-dimensional (2D) transition metal nitrides (TMNs) are emerging members in 2D family with promising potential for a range of applications. Their applications can be further extended to electronic and optoelectronic devices through the acquisition of high crystalline and large-area thin films. However, materials that meet such requirements have not been achieved using previous methods. Here, we report the synthesis of few-nanometer thin Mo₅N₆ crystals with satisfactory area and quality via chemical conversion of layered MoS₂ crystals. The structure and quality of the ultrathin Mo₅N₆ crystal are confirmed using transmission electron microscope, Raman spectroscopy and X-ray photoelectron spectroscopy. The lateral dimensions of Mo₅N₆ crystals are inherited from the MoS₂ crystals that are used for the conversion. Atomic force microscopy characterization indicates that the thicknesses of Mo₅N₆ crystal reduce to about 1/3 of the MoS₂ crystal, matching well with the crystal structure model. Electrical measurement shows the high conductivity of Mo₅N₆ (resistivity is 108.4 Ω/sq). In addition, this chemical conversion strategy is found versatile for the synthesis of various metal nitrides including W₅N₁₀, and TiN using their corresponding metal sulfides. Our strategy offers a new direction for preparing 2D TMNs with desired characteristics, opening a door for future exploration of fundamental physics and devices applications.

**FF01.10.14**

**Application of 2D Interlayer to β-Ga₂O₃ Optoelectronic Devices**

Suhyun Kim and Jihyun Kim; Korea University, Korea (the Republic of)

Recent application of mechanical exfoliation method to beta-gallium oxide (β-Ga₂O₃) has allowed various device structures through integration with different two-dimensional (2D) materials. Combining the unique properties of β-Ga₂O₃ and 2D materials can yield higher performance in (opto)electronic devices. The direct ultrawide bandgap of 4.6-4.9 eV and the superior electrical breakdown field make β-Ga₂O₃ especially advantageous for solar-blind ultraviolet (UV) photodetectors and power devices. The mechanically exfoliated β-Ga₂O₃ nanobelts can also be easily stacked on to the 2D flakes to form van der Waals heterostructures without any strain issues through dry transfer techniques just like other 2D materials; an exceptionally large lattice constant along one direction in β-Ga₂O₃ crystal structure allows easy mechanical cleavage along (100) direction. Therefore, the excellent electronic properties, high transparency or the atomic thickness of 2D layered materials such as graphene, transition metal dichalcogenides (TMDC) and hexagonal boron nitride (hBN) can be used to develop β-Ga₂O₃ device structures. In this work, a 2D material was applied as an interlayer between the electrodes and channel of β-Ga₂O₃ devices, and the UV photoresponse properties of the fabricated devices based on van der Waals heterostructure were analyzed. First, hBN can be applied to β-Ga₂O₃ metal-semiconductor-metal (MSM) type UV photodetector. hBN, which is a
2D insulating material, can be used as a thin barrier in addition to the Schottky barrier between the source electrode and the channel to lower the dark current of the photodetector. Graphene with very high electrical conductivity can also be applied as UV-transparent electrodes to enhance the photocurrent of the MSM photodetector. Graphene with very high electrical conductivity can also be applied as UV-transparent electrodes to enhance the photocurrent of the MSM photodetector. Secondly, a 2D TMDC such as molybdenum disulfide (MoS2) can be used to modify the contact properties and observe the effects on the photoresponse properties of β-Ga2O3 devices. Inserting a 2D interlayer between the metal and β-Ga2O3 would reduce the Schottky barrier and thus improve the ohmic properties of the metal contacts on β-Ga2O3. Further results and discussion will be presented in detail.

**FF01.10.15**

**Multiple Heterojunction Negative Differential Transconductance Device for Realization of Multi-Valued Logic Circuits**

Hyeonje Son1, Young Jae Kim1, Haeju Choi1, Sung Kyu Jang1, Jin-Hong Park1 and Sungjoo Lee1,2; 1Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); 2Sungkyunkwan University, Korea (the Republic of)

Recently, 2D material based multi-valued logic circuits, which can reduce power consumption and complexity of integrated circuits compared to binary logic circuits, have received significant attention in an effort to overcome fundamental limits of conventional silicon technology. Based on the development of 2D material preparation processes, heterogeneous integration of 2D materials can be simply achieved for logic gate design. However, reported three-valued NOT gates (ternary inverters) based on 2D materials require limited condition and/or complex fabrication process for obtaining distinctive three logic states. Here, we demonstrate CMOS ternary inverter circuit consisting of a series connection of three-heterogeneous 2D transistors (WSe2-MoTe2-MoS2). Due to the ambipolar nature of MoTe2 channel, which can drive both n-type transistor and p-type transistor depending on the applied gate voltage range, distinctive three logic states can be obtained by complementary operation between WSe2/MoTe2 heterojunction transistor and MoTe2/MoS2 heterojunction transistor. Furthermore, a quaternary inverter based on 2D multiple heterojunction is demonstrated by controlling trans-conductance of a part of MoTe2 channel via spatially controllable surface charge transfer doping method.

**FF01.10.16**

**MOVPE of Large-Scale WS2-Graphene and MoS2-Graphene 2D-2D Heterostructures for Optoelectronic Applications**

Annika Grundmann1, Clifford McAleese2, Ben R. Conran2, Andrew Pakes2, Kenneth B. Teo2, Michael Heuken1,3, Holger Kalisch1 and Andrei Vescan1; 1RWTH Aachen University, Germany; 2AIXTRON Ltd, United Kingdom; 3AIXTRON SE, Germany

Two-dimensional (2D-2D) heterostructures combine the unique intrinsic chemical, physical and (opto)electronic properties of different types of 2D materials. Not hampered by restrictions of lattice matching, this allows for tailored heterostructure designs for (opto)electronic devices and circuits. The semiconducting transition metal dichalcogenide (TMDC) WS2 is interesting due to its direct bandgap in the visible range in combination with a high radiative quantum efficiency. Unlike graphene, WS2 has a large optical absorption coefficient (105-106 cm⁻¹), thus its implementation is an ideal method to increase the external quantum efficiency of e.g. graphene-based optoelectronic detectors. Similarly, the TMDC MoS2 could complement graphene-based electronics by a transistor channel material that can be pinched off efficiently.

The main preparation strategy of such 2D-2D heterostructures has been sequential stacking of the layered materials using wet or dry transfer methods. However, those mostly complicated transfer processes generate defects and leave residues at the interfaces of the stacked materials. In recent years, the well-established technique of metalorganic vapor phase epitaxy (MOVPE) has been used to deposit several types of 2D materials. MOVPE enables the development of a reproducible and scalable deposition process for high-quality 2D-2D heterostructures. Here, we investigated key process parameters, including growth temperatures, pressures and growth times for the single-step deposition of WS2 and -MoS2 on CVD (chemical vapor deposition)-graphene using MOVPE.

Monolayer and bilayer/multilayer graphene films were directly grown on sapphire (0001) using an AIXTRON CCS 2D system in 19 x 2" configuration. The metal-free CVD process was carried out at 1400 °C for 6 minutes using CH4 with N2 as carrier gas. The deposition of MoS2 and WS2 on these graphene samples was performed in an AIXTRON planetary hot-wall reactor in 10 x 2" configuration. Tungsten hexacarbonyl (WCO), molybdenum hexacarbonyl (MCO) and di-tert-butyl sulfide (DTBS) were used as metalorganic precursors (avoiding toxic hydride sources) and N2 as carrier gas. All samples were characterized using Raman spectroscopy, photoluminescence spectroscopy (PL), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

WS2 was deposited for 20 h at 845 °C and 30 hPa on the different graphene samples. Deposition on monolayer
graphene results in triangular domains up to 800 nm and a surface coverage of about 64 % whereas deposition on bilayer/multilayer graphene leads to crystallites up to 1.5 µm in size and 60 % surface coverage. Extending growth to 30 h yields nearly no increase of the monolayer WS\textsubscript{2} domain size on neither monolayer nor bilayer/multilayer graphene, but an enhanced bilayer WS\textsubscript{2} nucleation. Thus, the surface coverage increases only slightly up to about 71 % for monolayer and 67 % for bilayer/multilayer graphene. A rise of the total pressure at lower growth temperature (550 °C) in 10 h processes increases the domain size from about 140 nm (30 hPa) to 660 nm (200 hPa).

Using the same initial process parameters (845 °C, 30 hPa) for MoS\textsubscript{2} growth for 24 h, we find an enhanced lateral growth rate compared to WS\textsubscript{2}. This is the same trend as previously observed for growth directly on sapphire. The MoS\textsubscript{2} monolayers are nearly fully coalesced on all graphene samples (> 98 % surface coverage). Unlike the growth of WS\textsubscript{2} on graphene or both TMDC directly on H\textsubscript{2}-desorbed sapphire, MoS\textsubscript{2} crystallites exhibit a distinct hexagonal structure when deposited onto graphene. Only MoS\textsubscript{2} crystallites from secondary nucleation, which grow on top of monolayer MoS\textsubscript{2} domains, are also of hexagonal shape. The hexagonal shape generally hints on a close-to-ideal stochiometry at the crystallite edges and the absence of a significant substrate influence. Unlike the deposition of MoS\textsubscript{2} and WS\textsubscript{2} on sapphire, MoS\textsubscript{2} and WS\textsubscript{2} domains on graphene do not show any preferred orientation.

**FF01.10.17**

**High Current Gains in Heterojunction Bipolar Transistors Based on 2D Materials**

Geonyeop Lee, Janghyuk Kim, Suhyun Kim and Jihyun Kim; Korea University, Korea (the Republic of)

Two-dimensional materials (2DM) have received great attention because of their unique electrical, mechanical and optical properties. Especially, the weak van der Waals interaction and atomically sharp interface without dangling bonds make 2DMs suitable for heterojunction devices. Therefore, 2DMs-based heterojunction devices can avoid the problems of lattice constant mismatch and show high-performance compared to those fabricated by conventional epitaxy. Studies on heterojunction-based devices based on 2DMs have mostly focused on fundamental structures such as a single p-n junction diode, but not on active devices like heterojunction bipolar transistors (HBT).

In our study, we successfully fabricated double HBTs (pnp or npn) by vertically stacking n-type or p-type 2DM flakes. P-type (Black phosphorus or WSe\textsubscript{2}) or n-type (MoS\textsubscript{2}) flakes were vertically stacked in order of npn or pnp on to SiO\textsubscript{2}/Si using a micro-manipulator. Then, electrodes (Ti/Au or Pt/Au) for the emitter, base, and collector were defined using standard e-beam lithography. The interface between each flake was clean without strain and bubbles as observed in the cross-sectional TEM images of the vertically stacked heterojunction structure. The formation of the two p-n junctions in base-emitter and base-collector was experimentally confirmed by the rectifying behavior in I-V characteristics. An npn double HBT showed excellent electrical characteristics with high current gain ($\beta = \sim 100$) which is comparable to those of conventional bipolar junction transistors. The detail of our experiment and results will be presented at the meeting.

**FF01.10.18**

**Dimensional Confinement of Magnetic Soliton Phase in Exfoliated 2D Cr\textsubscript{1/3}NbS\textsubscript{2} Thin Flakes**

Siwei Tang\textsuperscript{1}, Randy Fishman\textsuperscript{2}, Satoshi Okamoto\textsuperscript{2}, Qiang Zou\textsuperscript{2}, Anping Li\textsuperscript{2}, David Mandrus\textsuperscript{3} and Zheng Gai\textsuperscript{2}; 1Central South University, China; 2Oak Ridge National Laboratory, United States; 3The University of Tennessee, Knoxville, United States

Thin flakes of Cr\textsubscript{1/3}NbS\textsubscript{2} are fabricated successfully via microexfoliation techniques. Temperature-dependent and field-dependent magnetizations of thin flakes with various thicknesses are investigated. When the thickness of the flake is around several hundred nanometers, the softening and eventual disappearance of the bulk soliton peak is accompanied by the appearance of other magnetic peaks at lower magnetic fields. The emergence and annihilation of the soliton peaks are explained and simulated theoretically by the change in spin spiral number inside the soliton lattice due to dimensional confinement. Compared to the conventional magnetic states in nanoscale materials, the stability and thickness tunability of quantified spin spirals make Cr\textsubscript{1/3}NbS\textsubscript{2} a potential candidate for spintronics nanodevices beyond Moore’s law.

**FF01.10.19**

**Wafer Scale Large Area ReS\textsubscript{2} Photodiode by Sputtering**

Dae Young Park and Mun Seok Jeong; Sungkyunkwan University, Korea (the Republic of)

Among transition metal dichalcogenides (TMDCs), rhenium disulfide (ReS\textsubscript{2}) has unique insensitive direct bandgap from monolayer to bulk [1]. Combining with this unique property and large area film fabrication techics can
overcome the limitation of TMDCs. Herein, we synthesized polycrystalline ReS$_2$ via solid state reaction route and then sputtering target was prepared using spark plasma sintering. Uniform ReS$_2$ films were deposited on 2 inch wafer by sputtering with deposition temperature and time variations. Large area ReS$_2$ films were characterized and its morphology and thickness can be controlled systematically by changing deposition temperature and time. Basic p-n diodes with p-Si and ReS$_2$ film were fabricated and it demonstrated fast response time (7 us) and typical diode behaviors. These large area ReS$_2$ films have potential to expand the applications of TMDCs.

**FF01.10.20**

**Density Functional Exploration of Two-Dimensional Transition Metal Dichalcogenides from Fe-, Co-, Ni- and Cu-Groups** Rafael Besse$^1$, Matheus P. Lima$^2$ and Juarez L. F. Da Silva$^3$; $^1$São Carlos Institute of Physics, University of São Paulo, Brazil; $^2$Federal University of São Carlos, Brazil; $^3$São Carlos Institute of Chemistry, University of São Paulo, Brazil

Two-dimensional (2D) transition metal dichalcogenides (TMDs) exhibit unique properties which create a platform to investigate novel phenomena and point to their application in several fields, such as electronics, catalysis and energy storage [1,2]. TMDs from Ti-, V-, and Cr-groups are most easily obtained in layered crystal structures and have been extensively explored as 2D materials [3], however a large diversity of crystal structures is known for compounds with the remaining transition metals, and the exploration of the physical and chemical properties of 2D dichalcogenides based on transition metals from Fe-, Co-, Ni-, and Cu-groups has been very limited. Therefore, in order to design novel two-dimensional materials based on TMDs and explore their structural, energetic, and electronic properties, we performed an investigation of 36 $MQ_2$ compositions ($M$ = Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt, Au; $Q$ = S, Se, Te), by means of density functional theory calculations with semi-local and hybrid exchange-correlation functionals, and van der Waals (vdW) corrections. For each composition, a set of 11 crystal structures experimentally reported for TMDs, both with layered and non-layered frameworks, has been employed. We found that layered phases are energetically favored for Ni-group compositions, and the octahedral intralayer coordination is the most favored among the layered phases. The layered crystals of Fe- and Ni-group materials have weak interlayer binding, dominated by vdW interactions, whereas in the remaining materials a strong interlayer binding with non-vdW chemical bonds is observed. The electronic band gaps of the lowest energy phases were screened, and selecting the lowest energy layered structure for each compound, 17 semiconductors were identified among their monolayers, all based on the Fe- and Ni-groups transition metals. The conduction and valence band offsets of the semiconductor monolayers were obtained, and the trends originate primarily from the changes on the $M$-d and $Q$-p energy levels. Based on the band alignments, we applied the Anderson rule to classify the semiconductors heterojunctions formed with the combinations of these monolayers, which mainly fall in the type-II classification, although Ni-group layers are more prone to the formation of type-I junctions. To explore the potential of these materials for application in solar energy harvesting, the power conversion efficiencies of solar cells based on type-II heterostructures were estimated, and values comparable to and higher than those estimated for the widely studied Mo- and W-based TMDs were found. Our findings provide important information to guide the design and search for novel 2D TMDs and van der Waals heterostructures. We acknowledge financial support from grant 2017/11631-2, São Paulo Research Foundation (FAPESP). R. Besse is recipient of PhD fellowship, Grant 2017/09077-7, FAPESP.


**FF01.10.22**

**New Study of 2D Layered Structure Based 1D van der Waals Materials and Their Electrical Properties** Bum Jun Kim, Hyung Kyu Lim and Jae-Young Choi; Sungkyunkwan University (SKKU), Korea (the Republic of)

Two-dimensional (2D) materials, such as graphene and transition metal dichalcogenide (TMDs), have activated enormous interests in exploration of van der Waals (vdW) materials. One of key features of 2D materials, which enables their high performance, is dangling bond-free surfaces, since interlayer bonds in these materials are vdW rather than covalent. However, dangling bonds on edges in 2D materials still act as scattering centers and recombination centers when scaled down to less than a few tens of nanometers. In recent years, interest in 2D vdW materials has expanded to include one-dimensional (1D) vdW structures that consist of vdW bonded molecular chains. There are two types of 1D vdW structures; a true 1D structure with a pure vdW inter-chain bond and a quasi
1D structure with additional non vdW bonds among molecular chains. Unlike the 2D vdW materials that yield 2D atomic sheets upon exfoliation, 1D vdW materials produce various 1D nanomaterials such as ribbons, wires, and molecular chains. These 1D materials could contribute to many interesting physics, such as topological insulator, charge-density waves, superconductor-insulator transitions, ultralong ballistic phonon transports, low-frequency electronic noise and molecular-scale connectivity.

In this study, we synthesized a vdW 1D nanomaterials on a bulk scale stacked with chain-like 1D materials. The as-grown single crystal materials contains numerous single chains linked by vdW interactions. It was confirmed that the bundle of chains can be easily separated by mechanical exfoliation. Interestingly, the isolated 1D materials exhibit a quasi-two-dimensional layered structure. The variation of the work function depends on the thickness of the layered structure, as determined by scanning Kelvin probe microscopy (SKPM) measurements. Moreover, we implemented a field effect transistor (FET) based on nanoscale vdW 2D materials stacked with chain-like single crystal 1D materials to determine proper metal electrode.

FF01.10.23
Two-Dimensional Transition Metal Dichalcogenide(TMD)/Germanium Hybrid Photodiode Youngseo Park¹, Aujin Hwang¹, Geonwook Yoo² and Junseok Heo¹; ¹Ajou University, Korea (the Republic of); ²Soongsil University, Korea (the Republic of)

Two-dimensional (2D) transitional metal dichalcogenide (TMD) such as MoS₂ and WSe₂ has been actively researched due to superior electrical and optical properties. Heterojunction of 2D based TMD and bulk semiconductor such as Silicon (Si), Germanium (Ge), and compound semiconductors, in particular, has attracted considerable attention in recent years due to new possibilities for the next-generation nanoelectronics and optoelectronics. Ge has large absorption coefficient at near IR, widely used in optoelectronics device. Combination of TMD and Ge will have a potential to absorb a broadband light. The broadband photodiodes with photosensitivity from UV to near IR can use various applications such as color imaging, night vision and environmental monitoring. In this work, we have investigated the electrical and optical characteristics of MoS₂/p-Ge photodetector for broadband photodetection.

The fabrication starts with a deposition of 100 nm thick SiO₂ on a cleaned p-Ge substrate by PECVD method. Some portions on the substrate were exposed using a wet chemical etching process to make the junction between MoS₂ and Ge. Surface passivation of Ge was carried out in (NH₄)₂S solution (40-48 wt.% in H₂O, Sigma-Aldrich) for 30 min at 90 °C. By conventional scotch tape method, few layers of MoS₂ were mechanically exfoliated from bulk MoS₂ (Graphene Supermarket, USA), and then they were transferred onto the substrate. 5/80 nm Ti/Au was deposited on the top surface of the SiO₂ as the electrode for MoS₂ by e-beam evaporation by conventional lift-off technique. Finally, 100 nm Al was deposited on the back of Ge.

The exposed area of the MoS₂ flake is approximately 1.67 × 10⁻⁵ cm². Electrical property of the device was characterized using a semiconductor analyzer (B1500A, Keysight, USA) in a dark box. I-V curve of the MoS₂/Ge photodiode is measured from -10 V to 10 V. The device shows the excellent rectification characteristic with a rectification ratio up to approximately 10⁴ within ±10 V. Threshold voltage is 4.07 V, higher than expected, due to barrier of junction by band pinning. I-V curves are measured for voltage ranging from -10 V to 10 V under incident power densities of 5, 15, and 50 mW/cm² with 466 nm DPSS (Diode Pumped Solid State) laser in N₂ ambience. We calculated photocurrent (Iₚ) from Iₚ = Iₚ - Iₚ, where Iₚ is the current with the incident laser and Iₚ is the current in the dark box, which is 0.52, 1.31, and 2.63 nA under the incident power densities of 5, 15, and 50 mW/cm², respectively, at V = -10 V.

We calculated the responsivity (R) as a function of the wavelength, obtained from 400 nm to 700 nm with the voltage of -10 V using a monochromator. The responsivity is calculated as R = Iₚe/P, where P is the incident optical power. The responsivity shows a peak at 670 nm (174.4 mA/W). External quantum efficiency (EQE) is defined by R×hc/λ×q, where h is Planck’s constant, c is the velocity of light in vacuum, λ is the wavelength of the incident light, and q is the electronic charge. The obtained EQE peak is approximately 32.3% at 670 nm.

To confirm the response behavior about the incident light, the time-dependent current was measured under pulsed DPSS laser illumination (λ = 466 nm) with 5 mW/cm². To characterize the speed of the photodiode by rise time tₕ, we plotted the rise of photocurrent for turning on the laser light. The tₕ is 11 ms, which defines the time required for the current to increase from 10% to 90% of the average current for turning on the laser. At the falling edge, we confirm the fall time tₕ of 15 ms, which defines as opposed to tₕ.

In conclusion, we have fabricated the p-Ge/MoS₂ hybrid photodiode and characterized their electrical and optical properties. We observed the excellent rectification characteristic and the responsivity of wavelength from 400 nm to 700 nm. We will measure the responsivity of the wavelength above 1000 nm and present the corresponding
**FF01.10.24**  
**Transition Metal Dichalcogenide—Sensing Layer Heterojunctions Based Ion Sensitive Electrodes for Heavy Metal Sensing**  
Priya Vinayak, Mohammed Samim Hassan, Ajeet Singh, Sameer Sapra, Bhaskar Mitra and Madhusudan Singh; Indian Institute of Technology Delhi, India

The World Health Organization recognizes heavy metal toxicity arising from contaminated water supplies as a major challenge affecting millions of people worldwide, especially in rapidly developing economies of Asia. The maximum permissible limit for heavy metals has been identified as 3 ppm for Cd^{2+}, 10 ppm for Pb^{2+}, and 20 ppm for Ni^{2+}. Low-cost methods relying on ion exchange of Cd detection include the use of chalcogenide glasses, nanomaterials, and polymers that exhibit limits of detection (LoD) ~ 0.1-3 ppm. It is thus possible to detect Cd ions at human health-relevant ppm levels reliably, but cross-sensitivities of sensing films to other ions such as Pb, Ni, etc. complicate the analysis. Further, while combinatorial sensing of different ions by using arrayed detectors is possible, followed by principal component analysis, each detector has to be independently fabricated before system-level integration and packaging that interfaces each detector to the analyte, and readout electronics. This complication can be addressed by using a common transducing layer composed of a high mobility two-dimensional transition metal dichalcogenide (TMD). The ion exchange process at the surface of the sensing layer is expected to produce changes in local charge densities due to analyte-driven changes in the local potential. These charges can be conducted laterally to contacts by the underlying TMD layer, incorporated in the nanoscale form in a spin-coated sensing film to form ion sensitive electrodes (ISEs). In this work, we have grown proof of concept nanoscale heterojunctions composed of two dimensional n-MoSe_{2} with a vertically grown p-Cu_{2}S sensing layer using a colloidal synthesis route via defect passivation of MoSe_{2}. Cu_{2}S is chosen intentionally because the cation exchange between Cu⁺ and Cd^{2+} is known to be favored in an aqueous solution. Powder X-ray diffraction (PXRD) data reveals the growth of hexagonal 2H MoSe_{2} nanosheets and a hexagonal close-packed array of Cu_{2}S. Transmission electron microscopy (TEM) measurements were carried out on the dried sample to obtain a film thickness of approximately 1 nm. A micro glass slide was cleaned and bottom contacts (Cr (10 nm)/Au (50 nm)) were thermally evaporated through a shadow mask at a base pressure of 3.4 x 10^{-6} Torr. An ink composed of the nanoscale heterojunctions was spin-coated to form a uniform film to complete the ISE. The properties of the material have been tested by electrochemical impedance spectroscopy (EIS) measurements (with Pt as counter and Ag/AgCl as reference electrode on a PAR PMC 2000 electrochemical workstation) and open circuit potential measurements (Keithley 6514 system electrometer). A series of test solutions were prepared by spiking the electrolyte with [Cd^{2+}] in the range ~[1mM, 1nM]. Charge transfer resistance values derived by fitting Randle's equivalent circuit to the Nyquist plots were found to be approximately 5.5 kΩ near the LoD. These resistance values decrease with the increasing [Cd^{2+}] due to increasing cation exchange at the Cu_{2}S/analyte interface. Open circuit potential measurements revealed that a ~20mV/decade [Cd^{2+}] increase in potential was generated with respect to the Ag/AgCl reference electrode with increasing [Cd^{2+}]. A linear response to a logarithmic rise in [Cd^{2+}] is found for the sensing device with an estimated LoD ~0.1 ppm for this initial device. Through careful tailoring of the interface between the sensing layer and the underlying 2D TMD, the strength of the molecular interactions can be enhanced, resulting in greater sensitivity to the analyte.

**FF01.10.25**  
**A Reconfigurable Remotely Epitaxial VO_{2} Electrical Heterostructure**  
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The reconfigurability of the electrical heterostructure featured with external variables, such as temperature, voltage and strain, enabled electronic/optical phase transition in functional layers has great potential for future photonics, computing and adaptive circuits. VO_{2} has been regarded as an archetypal phase transition building block with superior metal-insulator transition characteristics. However, reconfigurable VO_{2}-based heterostructure and the associated devices are rare due to the fundamental challenge in integrating high quality VO_{2} in technologically important substrates. In this report, for the first time, we show the remote epitaxy of VO_{2} and the demonstration of a vertical diode device in graphene/epitaxial VO_{2}/single crystalline BN/graphite structure with VO_{2} as a reconfigurable phase change material and hexagonal boron nitride (h-BN) as an insulating layer. By diffraction and electrical transport studies, we show that the remote epitaxial VO_{2} film exhibits higher structural and electrical quality than direct epitaxial one. In the reconfigurable diode, we find that the Fermi level change and spectral weight shift along with metal-insulator transition of VO_{2} could modify the transport characteristics. The work suggests the
feasibility of developing single crystalline VO₂-based reconfigurable heterostructure with arbitrary substrates and sheds light on designing novel adaptive photonics and electrical devices and circuits.

**FF01.10.26**
Confinement Heteroepitaxy and Electrochemical Properties of 2D Metals
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Air-stable, crystalline, atomically-thin metals can be realized at the epitaxial graphene (EG)/silicon carbide (SiC) interface through a method termed confinement heteroepitaxy (CHet). This EG/SiC interface plays a crucial role in the creation of crystalline, 2-dimensional (2D) metals, and it provides a unique environment in which material structures with mixed interfacial van der Waals and covalent bonding can be formed. Through this thermal evaporation-based technique, intercalation of group-III elements (Ga, In) through epitaxial graphene can be achieved to create atomically-thin layers at the EG/SiC interface.

CHet is a unique EG intercalation method as it utilizes graphene defects and high-pressure (1-700 Torr) thermal evaporation. In this intercalation method, graphene defects created through exposure to O₂ plasma serve as entry points for a metal that is vaporized at high temperatures (>700°C). The defective graphene layers that result from plasma treatment correlate with the increase of the Raman D:G peak intensity ratios seen between as-grown and plasma-treated EG. During intercalation, the engineered graphene defects are shown to heal. This can be observed in the significantly decreased Raman D peak intensity measured post-intercalation. Regardless of the metal intercalated, CHet also produces a 3-4× increase in the Raman G peak intensity. This effect is attributed to plasmonic resonance. Due to their potential for high optical sensitivity and tailorability, 2D metals are promising materials for plasmonic applications.

Developing efficient photosynthetic systems that can economically convert solar energy into chemical energy on a large scale is crucial for the realization of a sustainable economy. The production of hydrogen gas by reducing water is a promising solar energy conversion technique, and it has been extensively researched in semiconductor-based photoelectrochemical devices. Semiconductors are often the foundation for solar energy-harvesting technologies because they have the ability to effectively capture photons. Due to the reflective properties of bulk metals, they are not generally used for such applications. Metals on the nanoscale, however, have proven to be effective at trapping photons due to local surface plasmon resonance. Research involving plasmon-induced charge separation for photocatalysis without the use of semiconducting materials is limited. Here, we explore how 2D allotropes of 3D metals perform as photocatalysts and how their tunable plasmonic properties can play a role in developing reaction selectivity.

In order to test the photocatalytic performance of the 2D metals realized through CHet, a white-light source is utilized in conjunction with a three-electrode system in an electrochemical cell. Because plasmons can decay via uphill electron transfer to a chemical species in direct contact, plasmon-induced charge separation (PICS) can be utilized to convert light energy into electrochemical energy. If the induced charge separation is large enough, it can generate an electronic potential that is suitable to drive the electrochemical production of fuels such as hydrogen gas. Standard measurements including electrochemical impedance spectroscopy, cyclic voltammetry, and linear sweep voltammetry completed with and without the use of light serve to elucidate the plasmonic properties of 2D metals and the role that PICS can play in catalyzing reactions that yield carbon-neutral fuels.

**FF01.10.27**
Enhancement in Photo-Detecting Performance of Multilayer MoS₂ Phototransistors by Reduction Treatment with Tannic Acid
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Recently, two-dimensional nano-materials such as graphene and transition metal dichalcogenide (TMDC) have been explored with substantial interest due to their potential in various applications including nanoelectronics, optoelectronics, and bioelectronics. One type of TMDCs, molybdenum disulphide (MoS₂) is regarded as a promising material for optoelectronic application because MoS₂ has tuneable bandgap whose range is from 1.2 eV for monolayer to 1.8 eV for multi-layer. Despite the proper band gap energy for absorbing wide-range of light covering from visible light to ultraviolet, the phototransistors based on MoS₂ channel layer have some issues regarding relatively low photoresponsivity and photosensitivity due to their low efficiency of light absorption resulting from ultrathin channel layer. In this sense, intensive efforts have been widely devoted on improving the photo-related characteristics of MoS₂ phototransistors.
In this work, we propose a simple method to enhance the photo-detecting performance of MoS2 phototransistors where the reduction treatment is introduced. The reducing agent used in this research is tannic acid (C76H52O46) which is a nature-friendly material extracted from various vascular plants. The reducing reaction by tannic acid is originated from its monomer with dozens of hydroxyl groups (-OH) which forms hydrogen bonds with oxygen. The reduction treatment is simply processed by dipping the device in tannic acid solution. During the dipping process, hydroxyl groups in tannic acid make hydrogen bonds with oxygen atoms that intrinsically exist in the lattice of MoS2 by substituting the sulfur atoms. Then, the oxygen atoms bonded with tannic acid monomers are detached from lattice of MoS2. Those broken Mo-O bonds result in increased number of sulfur vacancies which are relevant for the formation of sub-gap states in MoS2 band gap. Thus, sub-gap states formed by sulfur vacancies in MoS2 induce narrower effective optical band gap energy and light absorption capability could be improved.

The multilayer MoS2 flakes were transferred onto the thermally oxidized heavily boron-doped silicon wafers by mechanically exfoliating from a bulk MoS2 crystal. Then, titanium and gold electrode sequentially deposited by electron-beam evaporation. After completing fabrication of MoS2 transistor, the device is dipped in 0.3 M tannic acid solution for 10 min.

We have measured the electrical and photo-detecting performance of tannic acid treated MoS2 phototransistor. The improvement or degradation in electrical performance was not observed in MoS2 phototransistor after reducing treatment by tannic acid. But, the difference between dark current and photoinduced current under red, green, and blue laser illumination becomes more distinguishable because of more efficient light absorption in tannic acid treated MoS2 layer. As a result, both photoresponsivity and photosensitivity of the tannic acid treated MoS2 phototransistor were improved as compared to the device without treatment. With an intensity of 10 mW/mm², photoresponsivity increased from 126.85 A/W to 807.36 A/W under red light, from 109.00 A/W to 819.29 A/W under green light, and from 166.44 A/W to 928.25 A/W under blue light. Also, with same intensity of light, photosensitivity increased from 9.51 to 243.93 under red light, from 16.23 to 527.05 under green light, and from 26.51 to 1700.98 under blue light. Therefore, we proposed a novel method for improving the performance of MoS2-based phototransistor with simple reduction method which makes it possible to be applied in various optoelectronic applications.

**FF01.10.28**

**Nanostructuring 2D Layered Nanomaterials by Low Power Focused Laser Irradiation** Kiran S. Hazra; Institute of Nano Science and Technology, India

Optical and electronic properties of 2D nanomaterials such as Graphene, Transition metal di-chalcogenides (TMDCs), Phosphorene etc. are already emerging field of research for their wide range of applications in nano-electronics, opto-electronic, solar cell, electrochemical activity etc. We have developed a novel and easy way to create various nanostructures on wide range of 2D materials in a single step process by using simple focused laser beam of a Raman spectrometer at low power irradiation. The feature size can go down up to diffraction limit of the laser used and the shape of the etched point can be used to find the orientation of the lattice structure of the material. In this presentation we focus on various applications of such nanostructures, fabricated on 2D by simple laser irradiation technique. We will demonstrate that nanostructuring on MoS2 flake can create periodic modulation in capacitive response. Optimized geometry of these nanostructures alongwith selective deposition of Au nanoparticles demonstrate ultrasensitive SERS. These nanostructures were capable of enhancing interestingly we have found that the edges of such nanostructures are more catalytically active for electrochemical deposition of Au nanoparticles. Using this route we were also able to create nanostructures on Phosphorene flakes and rGO flakes. Controlled formation of nano-voids array on few layer BP flake induces enhanced local electric field (hot spots) at the vicinity of the nano-voids, resulting in ~30% Raman intensity enhancement. Such nano-voids induced hotspots on BP flake open up a new species of metal free SERS substrate, demonstrating pronounced enhancement in Raman signal of Rhodamine B as high as of the order of ~10⁴. Nano-patterning on rGO flakes leads to the observation of radiation pressure on solid-air interface.

The discovery of 2D layered materials has opened new frontiers in science and technology. The implication of these 2D nanomaterials in gas sensing, has gained tremendous attention owing to their outstanding virtues such as high surface to volume ratio, unique electronic and structural properties. Further, the high surface reactivity of 2D materials, offers potential for room temperature gas sensing leading to low power consumption, which is highly desirable for practical applications. Among these 2D nanomaterials, the Transition Metal Dichalcogenides (TMDC’s) such as MoS2 and WS2, have been explored for the detection of various gases including NH3, NO, NO2, etc. However, these TMDC’s are prone to degradation on exposure to ambient environment due to the significant oxygen adsorption on its surface. This limits the practicability of a sensor in real environment. The engineering of these 2D materials by incorporating another nanomaterial can provide solution to this aforesaid problem. This strategy of forming nanohybrids can not only provide the air-stability, but also improve the overall performance of the sensor.

In this work, we demonstrate the fabrication of a novel nanohybrid of Iron oxide nanoparticles (NP)- decorated WSe2 nanosheets (NS) for air-stable room temperature detection of ammonia with very high response magnitude and lowest limit of detection. The aforesaid nanohybrid was fabricated using modified co-precipitation method. At room temperature, the sensor demonstrated significant response of 510% to 3 ppm ammonia while achieving the lowest limit of detection (llod) of 50 ppb, with a response of 2.4%. The iron oxide – WSe2 nanohybrid sensor response was dramatically higher when compared to pristine WSe2, as the sensing material which exhibited only 53.5% response towards 3 ppm of ammonia, and 300ppb as llod. In addition, we observed improved recovery of the nanohybrid sensor (148s recovery time in contrast to 436s recovery time for pristine WSe2) by incorporating iron oxide nanoparticles. These findings suggest that the decoration of nanoparticles can aid in tuning the properties of 2D layered materials and hence can open up new avenues for several applications.
strategy to overcome the limits of conventional top-down technologies in the semiconductor industry. Silicene allows to reach the ultimate target for thickness scaling while combining an ultra-high carrier mobility with the unique opportunity to tune the bandgap.

However, silicene oxidizes rapidly when exposed to ambient conditions, therefore requiring a reliable passivation process. Graphene represents an ideal passivation material, due to its inertness, high flexibility and outstanding impermeability, as well as being non-Raman active in the fingerprint region of silicene, allowing a precise analysis of the structural properties of the encapsulated layer.

We report the successful passivation, for up to 48 h, of silicene by few-layers graphene (FLG) flakes. The monolayer silicene was epitaxially grown on a well-ordered Ag(111) film on mica by exposing the substrate, kept at a temperature of 530 K, to a constant flux of Si (≈ 0.02 ML/min). After the growth, silicene formation was verified via LEED analysis.

For the passivation, natural graphite was mechanically exfoliated on top of a vacuum-compatible polyimide adhesive tape and inserted into a specially designed UHV chamber. Then, FLG flakes were mechanically transferred atop of the silicene monolayer by direct exfoliation in UHV.

The encapsulating flakes allowed us to perform a subsequent ex-situ Raman characterization of the 2D silicon layer. The analysis was performed at room temperature in a back-scattering geometry using a confocal μ-Raman setup. The collected spectrum is characterized by two clear peaks located at 216 cm⁻¹ and 515 cm⁻¹, consistent, respectively, with the predicted out-of-plane and in-plane vibrational modes for silicene. Polarization-dependent measurements show that the 216 cm⁻¹ peak is related to a fully symmetrical phonon mode, a clear indication of the 2-dimensionality of the passivated silicene layer.

In Situ Monitoring of Chemical Vapor Deposition Graphene on Cu by Reflectance Contrast Using Confocal Laser Scanning Microscopy Yun Sung Woo1,2, Dong Jin Kim3,2, Chang-Won Lee4, Heejeong Jeong5 and Byung Hee Hong1; 1Korea Polytechnic, Korea (the Republic of); 2Graphene Square, Korea (the Republic of); 3Seoul National University, Korea (the Republic of); 4Hanbat National University, Korea (the Republic of); 5University of Malaya, Malaysia

In order to realize the industrialization of chemical vapor deposition (CVD) graphene, it is essential to develop a method capable of characterization in real time as well as mass synthesis. In this study, we report that the reflection mode of confocal laser scanning microscopy (CLSM) enables highly visible and distinct image of CVD-grown graphene on Cu compared to dark field optical microscopy (DM). Reflectance contrast, RC, defined as the intensity ratio of light reflected from graphene grown on Cu to bare Cu, depends on the incident laser wavelength, of which maximum was obtained at 405 nm in this experiment. Remarkably, it was observed that RC of CVD-grown graphene on Cu varies with doping and crystallinity of graphene and decreases as the intensity of D peak increases in Raman spectrum. The RC over 1 calculated using the Fresnel’s interference formula with the optical conductivity of graphene estimated by tight-binding model is in good agreement with the measured RC. Consequently, it is demonstrated that RC of CVD-grown graphene on Cu is affected by the quality of graphene related with its optical conductivity. Based on these results, we suggest that the reflection mode CLSM can be applied as a powerful tool for in-situ monitoring of CVD graphene growing on Cu by analyzing RC of graphene.

Tailoring Conduction Band Edges in Molybdenum Sulfide/Selenide Alloys Enhances CO Faradaic Efficiency in Aqueous CO2 Reduction Yi-Rung Lin1,1, Wen-Hui Cheng1,1, Matthias H. Richter1,1, Joseph S. DuChene1,1, Elizabeth A. Peterson3,3, Cora Went1, Zakaria Al Balushi1,1, Deep M. Jariwala1, Jeffrey B. Neaton3,4, Li-Chyong Chen2,2 and Harry A. Atwater1,1; 1California Institute of Technology, United States; 2National Taiwan University, Taiwan; 3University of California, Berkeley, United States; 4Lawrence Berkeley National Laboratory, United States

Selective conversion of CO2 into a single chemical product remains one of the greatest challenges in CO2 reduction. Transition-metal dichalcogenides have shown potential for electrocatalytic conversion of CO2 to CO with high selectivity in ionic liquid-based electrolytes, but in fully aqueous environments the evolution of hydrogen is commonly observed to be the dominant catalytic reaction. Despite much promise, further progress in the design of layered two-dimensional materials for the CO2 reduction reaction (CO2RR) is needed to enable the sustainable synthesis of chemical fuels from CO2 feedstocks. In this work, we demonstrate that the valence band maximum and the conduction band minimum of transition-metal dichalcogenides can be tuned via chemical alloying to form MoS2(1-x)Se2x alloys (where x ranges from 0 to 1).
The band structure of few-layered transition metal dichalcogenides was tuned by changing the chemical composition of the chalcogens (sulfur, S and selenium, Se) in the resulting alloy. Systematic studies of electrochemical CO2 reduction with various MoS2(1-x)Se2x compounds demonstrate that the distribution of chemical products generated by the electrocatalyst can be controlled by the chemical composition of the alloy. Specifically, we find that the MoS1.48Se0.52 compound exhibited the best selectivity of all studied alloys, with a Faradaic efficiency for CO production of ~27% at an applied potential of ~0.2V vs. RHE in fully aqueous 50mM K2CO3 electrolytes. In general, the alloy compounds show superior CO2RR performance relative to pure MoS2 or MoSe2-based electrocatalysts. Such a trend in synthesized MoS2(1-x)Se2x alloys is consistent with that observed from bulk crystals, indicating that chemical alloying of layered two-dimensional materials is a promising approach to tuning the selectivity of transition-metal dichalcogenides for CO2RR in aqueous electrolytes.

**Synthesis of Few-Layered ZrS2 and ZrS2xSe2-2x Nanosheets**

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Group IV transition metal dichalcogenides (TMDs) have recently drawn attention due to their predicted ultra-high charge carrier mobilities (1-3000 cm2/Vs) and bandgap in the VIS-NIR region. These materials are considered to be highly promising for high-performant FETs and ultra-responsive photodetectors, in addition to their possible use as energy materials and in catalysis. However, very little work has been reported on the synthesis of two-dimensional few-layered Group IV-TMDs. Here, we report the growth of ZrS2 and ZrS2xSe2-2x thin films over cm2 areas on SiO2/Si and Au foil starting from ZrCl4 and sulphur powder as precursors. The interest in ZrS2xSe2-2x results form the possibility to tune a low energy band gap. The synthesis has been performed via chemical vapour deposition (CVD) using a tubular furnace where thickness control has been achieved tuning the growth time. Our ZrS2 thin film has been characterized via Raman spectroscopy, which revealed two fingerprint peaks at 250 cm-1 and at 335 cm-1 corresponding to the Eg and the A1g peak respectively. HRTEM and SAED characterizations have confirmed the hexagonal crystal structure and the atomically thin thickness of 2-3 layers of individual platelets. XPS and EDX has provided evidence of the expected stoichiometry and composition. Furthermore, the material exhibits photoluminescence (PL) signal at 1.4 eV, which matches with theoretical predictions ranging from 1.2 to 2 eV for the Γ-M indirect bandgap. Annealing the ZrS2 film with Se we can achieve the synthesis of ZrS2xSe2-2x, which shows morphological characteristics similar to the starting material and Raman peaks at 250 cm-1 and 300 cm-1.

**Mechanistic Understanding of Lithium Intercalation and Phase Transformation Behavior in MoS2 at Atomic Scales**

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Design and discovery of layered materials for next-generation Lithium-ion batteries require a thorough understanding of the role of structure (bonding environment) on the energetics of Lithium (Li) intercalation and the accompanying structural accommodations. In this study, density functional theory (DFT) calculations have been used to investigate the energetics and mechanisms of lithiation/delithiation in thin films of MoS2. The work aims at presenting a comprehensive study on thermodynamics of lithiation in order to sequentially investigate the process of Li-ion intercalation between layers of MoS2 films and the resultant structural transformations.

Simulations have been performed to investigate the energetics of Li-ion binding and diffusion in the 2H and 1T phases of MoS2. Li binding is observed to be stronger in 1T phase and hence, the activation energy for diffusion is higher. Sequential insertion of Li suggests that intercalation of one Li atom in the spacing between two MoS2 layers results in easier diffusion of successive Li atoms in the same gap until all of the tetrahedral binding sites are occupied. Further lithiation results in Li intercalation into successive gaps between 2H-MoS2 layers and promotes phase transformation of adjacent 2H layers to 1T phase. Thus, partial lithiation across layers creates hybrid 2H-1T phase with a stable phase boundary perpendicular to c-direction. This 2H to 1T phase transformation of MoS2 layers between the Li layers is attributed to a change in charge density around the transition metal following ionization of Li to Li+ cation.

Such phase transformations accompanying lithiation are found to be irreversible and hence, quite detrimental to the cycling stability of batteries. With the understanding gained on the binding of Li, various combinations of transition
metals and chalcogenides are tested to identify layered materials which render or resist phase transformation during lithiation. The energetics of lithiation in the various phases of layered materials will be presented. These results parallel insights gained from in-situ TEM studies and can shed light on Li-ion intercalation/de-intercalation mechanisms in thin films of layered materials. This work is being supported by NSF grant No. 1820565. CINT is an Office of Science NSRC User Facility operated for the U.S. DOE.

**FF01.10.37**

**Evaluation of Film Quality for Various Deposition Conditions of MOCVD MoS2 Films Fabricated with a Novel Mo Precursor i-Pr2DADMo(CO)3**

Kota Yamazaki1, Yusuke Hibino1, Yuya Oyanagi1, Yuya Oyanagi1, Yusuke Hashimoto1, Naomi Sawamoto1, Hideaki Machida2, Masato Ishikawa2, Hiroshi Sudo2, Hitoshi Wakabayashi3 and Atsushi Ogura1; 1Meiji University, Japan; 2Gas-Phase Growth Ltd., Japan; 3Tokyo Institute of Technology, Japan

Molybdenum disulfide (MoS2) is a layered material that is expected to be used in various devices such as TFT due to the presence of band gap (bulk to monolayer: 1.2 to 1.8 eV[1]), high mobility (mono to multilayer: 380 to 700 cm²/Vs[1,2]), high flexibility, transparency and stability. However, establishing a film fabrication method with high quality and high productivity is a major issue for its practical applications. Therefore, we focused on cold-wall MOCVD method as a deposition technique. In this film fabrication method, utilization efficiency of the precursor is high since the reaction only occurs at the substrate. In addition, fine controllability of the film quality can be achieved by facilitating control of various deposition conditions such as supply amount of Mo and S by using the organic precursors having high vapor pressure at low temperature.

We have previously proposed i-Pr2DADMo(CO)3 as a novel Mo precursor. We have reported so far that i-Pr2DADMo(CO)3 decomposes below 300°C, and 1L MoS2 without C and N contamination can be fabricated on SiO2/Si substrate at low temperature of 250°C with the Mo precursor and sulfur source (t-C4H9)2S2[3]. In this research, with the aim of further improving the quality of the MoS2 film using i-Pr2DADMo(CO)3, various film fabrication conditions were controlled and the influence on the film quality was investigated. XPS, AFM and Raman spectroscopy were used as evaluation techniques of the samples. It was suggested that the increase of substrate temperature contributes to the expansion of the grain size through the increase of Mo migration. High substrate temperature also increases the deposition rate by accelerating the thermochemical reaction of i-Pr2DADMo(CO)3 and (t-C4H9)2S2. It was also suggested that higher deposition pressure contributes to the increase in deposition rate caused by larger degree of supersaturation. Higher deposition pressure also decreases the deposition rate caused by lower concentration of the precursor in the chamber. Thus an optimum value is considered to exist for high-quality film synthesis.

This work was partly supported by JSPS KAKENHI Grant Number 18F22879 and JST CREST JPMJCR16F4


**FF01.10.38**

**The Physical and Chemical Properties of MoS2(1-x)Te2x Alloy Synthesized by Co-Sputtering and Chalcogenization and Their Dependence on Fabrication Conditions**

Yusuke Hibino1,2, Kota Yamazaki1, Yusuke Hashimoto1, Yuya Oyanagi1, Naomi Sawamoto1, Hideaki Machida3, Masato Ishikawa2, Hiroshi Sudo2, Hitoshi Wakabayashi4 and Atsushi Ogura1; 1Meiji University, Japan; 2Japan Society for the Promotion of Science Research Fellow, Japan; 3Gas-Phase Growth Ltd., Japan; 4Tokyo Institute of Technology, Japan

The alloying of transition metal dichalcogenides (TMD) and their various properties are expected to be a significant factor for the TMDs to expand in its applications. Although TMD alloys show appealing electrical, optical, and chemical properties, the synthesis method is still at its early stage. The alloy materials under research are mostly MoS2(1-x)Se2x, Mo1-xWxS2, WS2(1-x)Se2x, and so on. There have not been many reports on the alloy that incorporate Te in the system. In the past reports, we have demonstrated that Mo-S and Mo-Te bonds can be formed in the product film, but physical structure evaluation was not sufficient. Thus in this study, the alloy films were evaluated with XRD in addition to XPS. The physical structure evaluation revealed that the as-sputtered samples, i.e. samples prior to thermal treatment, shows alloy formation depending on the sputter power of MoTe2 targets. Use of compound MoS2 target promotes layer structure formation at the sputtering stage, however, use of merely-sintered (not compound) MoTe2 target may disrupt this behavior. It was also revealed that different chalcogen composition in MoS2(1-x)Te2x requires different optimal temperature in the post-deposition thermal treatment. For the sulfurization samples, the alloy showed phase segregation, MoS2 and MoS2(1-x)Te2x, when the temperature is well over or under
400°C. In other words, when the sulfurization temperature is at 400°C, the alloy showed uniform distribution of Te and S throughout the film. On the other hand, for the tellurization samples, the alloy with no phase segregation was observed at 450°C. This shows that higher Te composition for MoS$_2$($1-x$)Te$_x$ may require thermal treatment with higher temperature.

This work was partly supported by JST CREST Number JPMJCR16F4, Japan. This work was also partly supported by JSPS KAKENHI Grant Number 18J22879.

SESSION FF01.11: Exciton Dynamics in 2D Materials
Session Chairs: Deep Jariwala and Su Ying Quek
Wednesday Morning, December 4, 2019
Hynes, Level 3, Room 312

8:00 AM FF01.11.01
Exciton Dynamics in Atomically Thin Transition Metal Dichalcogenides Samuel Brem, Simon Ovesen and Ermin Malic; Chalmers University of Technology, Sweden

Monolayers of Transition Metal Dichalcogenides (TMDs) present a giant leap forward towards the realization of semiconductor devices with atomic scale thickness. As a natural consequence of their two-dimensional character, TMDs exhibit a reduced dielectric screening, leading to the formation of unusually stable excitons. Excitons dominate the optical response as well as the ultrafast dynamics in these atomically thin materials. As a result, a microscopic understanding of excitons, their formation, relaxation and decay dynamics becomes crucial for technological applications of TMDs. A detailed theoretical picture of the internal structure of excitons and their scattering channels allows for a controlled manipulation of TMD properties enabling an entire new class of light emitters, absorbers and detectors.

We provide a fully quantum mechanical description of momentum- and energy-resolved exciton dynamics in TMD mono- and hetero-bilayers [1-3] unraveling the many-particle processes governing the ultrafast dynamics of excitons in these materials. Our approach provides novel insights into exciton-phonon and exciton-photon interaction mechanisms and the impact of dark exciton states. This includes the formation of bound excitons out of a free electron-hole gas up to their eventual radiative recombination. Furthermore, we study the formation of interlayer excitons in Van-der-Waals heterostructures, i.e. spatially separated excitons composed of electrons and holes located in different layers of two stacked TMDs.

Our theoretical model allows us to predict fundamental formation and relaxation time scales as well as spectral features accessible in ultrafast pump-probe experiments. In particular, we show that the relaxation of hot excitons throughout the Rydberg series of excited exciton states gives rise to population inversions between s- and p-type excitons resulting in transient optical gain in the THz spectrum [1]. Moreover, in a joint experiment-theory study on Van-der-Waals heterostructures [3], we demonstrate how the binding energy as well as the time resolved formation of interlayer excitons can be measured using mid infrared pulses.

[2] Ovesen, Brem et al., Communications Physics, 2(1), 23 (2019)

8:15 AM FF01.11.02
Spin-Layer Locking of Interlayer Valley Excitons Trapped in Moiré Potentials Mauro Brotons i Gisbert, Hyeonjun Baek, Dale Scerri, Alejandro Molina-Sánchez, Kenji Watanabe, Takashi Taniguchi, Cristian Bonato and Brian D. Gerardot; 1Heriot-Watt University, United Kingdom; 2Universidad de Valencia, Spain; 3National Institute for Materials Science, Japan

Semiconductor heterostructures formed by vertically stacked two-dimensional transition-metal dichalcogenides (TMDs) sustain interlayer excitons - electron-hole Coulomb bound states between electrons and holes spatially
separated in different monolayers [1, 2]. In addition, heterostructures formed by vertically stacking two different monolayer TMDs (heterobilayers) can feature a spatially periodic moiré superlattice in which a periodic potential landscape for excitons is controlled by the lattice mismatch and/or the relative angle twist between the constituent monolayers. For moiré periods larger than the exciton Bohr radius, the moiré potential minima can act as smooth quantum-dot-like confining potentials [3, 4]. Bilayer TMDs offer an additional degree of freedom to engineer the properties of moiré-trapped interlayer excitons in vertical semiconductor heterostructures. In addition to the spin-valley coupling characteristic of monolayer TMDs, bilayer TMDs also present a layer pseudospin [5]. Because the bottom layer in an AB-stacked bilayer is a 180° in-plane rotation of the top layer, AB-stacked bilayer TMDs show spin-layer locking, i.e., a spin-valley configuration that is locked to the layer pseudospin.

In this work, we exploit the spin-layer locking of bilayer 2H-MoSe2 to probe the spin-valley properties of interlayer moiré-trapped excitons in a WSe2/MoSe2 heterostructure. Low-temperature (4 K) magneto-optical spectroscopy reveals the coexistence of two species of moiré-trapped excitons with different spin-layer pairings for electrons in MoSe2. Both trapped exciton species yield narrow (< 100 meV) linewidths and saturate with increasing excitation power, hallmarks of quantum dots. Although for both species of interlayer trapped excitons the hole is localized in the WSe2 layer, the electron in bilayer MoSe2 can be localized either in the bottom or top layer. The natural AB stacking of bilayer 2H-MoSe2 gives rise to AA (AB) relative stacking between the WSe2 and the bottom (top) layer of MoSe2, respectively. Due to the spin-layer locking in bilayer MoSe2, electrons in the bottom (top) MoSe2 layer present parallel (antiparallel) spin and valley contributions, which results in an effective layer-locking of the Landé g-factors of the trapped excitons. Our results reveal that the trapped excitons present g-factors that are homogeneous across the sample and take only two values: -7.0 ± 0.6 and -15.76 ± 0.13 for Moiré-trapped excitons originating from the AA- and AB-stacked WSe2/MoSe2. Finally, helicity-resolved photoluminescence measurements confirm that the trapped excitons exhibit both strong circular and valley polarization, which indicates that the confinement potential preserves the rotational C3 symmetry and the trapped interlayer excitons inherit the spin-valley properties of the constituent monolayers.


8:30 AM *FF01.11.03
Probing and Controlling Excitons in 2D Semiconductors and Heterostructures
Tony F. Heinz1,2; 1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States

In this paper we review recent developments in our understanding of the optically excited states of monolayer semiconductors and heterostructures in the family of the transition metal dichalcogenides. In particular, we will focus on the exciton character of the excited states, discussing our current understanding of the 2-, 3-, 4-, and 5-body exciton, charged exciton, biexciton, and charged bie exciton species. We will also describe the presence of spin-forbidden dark excitons and how they may be observed optically. In addition to the range of different excitonic states, the 2D semiconductors feature strong electrostatic coupling to the external environment. We will describe the corresponding influence of external dielectric screening on the band- and exciton structure of the materials and how we can use this effect to tune locally the properties of 2D semiconductors. Finally, we will consider the new states that arise in 2D heterostructures and how they can be modified by electric fields and the relative crystallographic orientation of the component layers.

9:00 AM FF01.11.04
Local Strain Control for Active and Reversible Exciton Funneling in a Monolayer Semiconductor
Hyowon Moon1, Gabriele Grosso2, Chitalema Chakraborty1, Cheng Peng1, Takashi Taniguchi3, Kenji Watanabe3 and Dirk Englund1; 1Massachusetts Institute of Technology, United States; 2The City University of New York, United States; 3National Institute for Materials Science, Japan

The ability to control the flow of excitons underlies high-speed excitonic devices and energy transport [1,2]. Two-dimensional (2D) semiconductors are well suited for these applications in that their large exciton binding energy enables room temperature operation and their enormous stretchability provides engineerable exciton potential
surfaces [3]. Since excitons are hardly respond to in-plane electric field due to their charge neutrality, the control was limited to interlayer exciton with quantum confined Stark Effect in vertical heterostructure [4,5]. Strain-engineered bandgap modulation offers a new tool for monolayer excitons. Recent studies have observed excitonic flux in predetermined non-uniform geometries, an important remaining challenge concerns active and reversible controllability [6]. Here, we tune the bandgap of suspended 2D semiconductors dynamically by applying local strain gradient with a nanoscale tip. This method enables active and reversible control of the exciton drift over several hundreds of nanometer at room temperature through the energy gradient, which has been demonstrated by wide field imaging and time resolved photoluminescence measurement. Our results pave the way for broad applications including broadband photovoltaic devices and efficient excitonic devices.

with different dipole orientations at room temperature. Besides, these excitons persist from the bulk down to the monolayer. Here, we study the anisotropic diffusion of excitons and free carriers in ReS$_2$ with transient absorption microscopy (TAM) for thicknesses from the monolayer to the bulk.

In TAM, a 10 fs pump pulse focused to the diffraction limit generates excitons and charge carriers, a 10 fs probe pulse in the wide field then monitors their temporal and spatial dynamics. A comparison of the spatial profile of the transient absorption signal following photoexcitation allows studying the movement of excited species with a sub-diffraction-limit resolution of 10 nm.

Varying the pump and probe linear polarisations we analyse the strongly anisotropic diffusion of the two lowest exciton populations. We observe an increase in the exciton lifetime and diffusion coefficients with the number of layers, which we attribute to a decrease in surface traps as the sample thickness increases.

Directional Exciton Transport in a Monolayer WS$_2$–WSe$_2$ Lateral Heterostructure with a Wide Alloy Region

Masafumi Shimasaki$^1$, Naoki Wada$^1$, Zheng Liu$^3$, Kana Kojima$^2$, Yasumitsu Miyata$^2$, Keisuke Shinokita$^1$, Taishi Nishihara$^1$, Kazunari Matsuda$^1$ and Yuhei Miyauchi$^1$; $^1$Institute of Advanced Energy, Kyoto University, Japan; $^2$Tokyo Metropolitan University, Japan; $^3$National Institute of Advanced Industrial Science and Technology, Japan

Monolayer transition metal dichalcogenides have various intriguing optical properties mainly arising from room-temperature-stable excitons [1]. Recently, the exciton dynamics in monolayer vertical/lateral heterostructures or alloy monolayers have attracted much attention, because novel excitonic phenomena including the interlayer exciton [2], exciton dissociation [3], and exciton energy change [4] emerge owing to modulating electronic energy structures. These observations indicate that a combination of such structures potentially provides a platform for exploiting further novel exciton physics and applications.

Here, we report the exciton transport dynamics in a monolayer WS$_2$–WSe$_2$ lateral heterostructure with wide alloy region between the pure WS$_2$ and WSe$_2$ regions using photoluminescence (PL) spectroscopy. The lateral heterostructure was synthesized using a chemical vapor deposition method. It has the alloy region with the width of about 20 µm, where the composition ratio of WS$_2$ and WSe$_2$ gradually changes as a function of spatial coordinate. For the PL spectroscopy, we used the 2.33 eV or 2.22 eV continuous-wave (cw) lasers to excite the sample.

First, we conducted spectrally-resolved PL mapping on the lateral heterostructures across the wide alloy region in a confocal microscope at room temperature. The PL peak from the pure WS$_2$ region was observed at 1.94 eV and assigned to the A exciton. By scanning excitation laser spot across the alloy region of WS$_2$($1-x$)Se$_2x$ from the WS$_2$ side, the PL peak showed a gradual redshift, and finally reached to 1.70 eV that corresponds to the A exciton resonance energy in a pure monolayer WSe$_2$. The continuous shift of the exciton energies indicates formation of a built-in excitonic potential gradient across the wide alloy region, in contrast to the sharp potential change caused by lattice mismatch [5] and/or piezo effect [6] previously observed in various lateral heterostructures with sharp one dimensional interfaces.

Next, we examined the exciton transport properties in the wide alloy region at room temperature. We performed spatially- and spectrally-resolved PL measurements; note that these measurements are different from the confocal PL mapping described above. In this measurement, the excitation cw laser was tightly focused on the sample (spot size of c.a. 1.3 µm at FWHM), and the PL spectra at many points along the potential gradient direction (not only the directly excited spot) were simultaneously acquired. We found that the position showing the highest PL intensity deviated from the center of the laser excitation spot by c.a. 0.6 µm at maximum in the wide alloy region, and the direction of the deviation (exciton drift) was always along the excitonic potential gradient. This was contrast to the observations at the pure WS$_2$ and WSe$_2$ regions, where the highest PL intensity was always observed at the same position as the center of the laser excitation spot. We analyzed the spatial profile of the PL intensities using a drift-diffusion model taking the excitonic potential gradient into account, and confirmed that the potential gradient mainly causes the observed exciton drift. In the presentation, we will discuss the details of the exciton transport properties in the wide alloy region.

References:

10:30 AM *FF01.12.01
Critical Behavior and Thickness-Dependent Magnetic Order in CrI3 Cedomir Petrovic, Yu Liu, Lijun Wu, Xiao Tong, Lijun Wu and Yimei Zhu; Brookhaven National Laboratory, United States

Two-dimensional (2D) materials with intrinsic ferromagnetism provide unique opportunity to engineer new functionalities in nano-spintronics. One such material is CrI3, a 2D Ising ferromagnet in monolayer with the Curie temperature \( T_c \) of 45 K [1]. Based on critical properties and scaling analysis, CrI3 shows three-dimensional (3D) long-range magnetic coupling [2]. In systematic reduction of crystal thickness down to 50 nm bulk \( T_c \) of 61 K is gradually suppressed to 57 K, however, the satellite transition at \( T^* = 45 \) K is observed. The \( T^* \) is layer-independent and corresponds to \( T_c \) observed in the monolayer. The critical analysis around \( T_c \) reveals a crossover from 3D to 2D Ising ferromagnetism with mean field type interactions for microscale-thick crystals. This work shows that magnetic transition and critical properties can be continuously tuned on a mesoscale between monolayer and bulk crystals.

Acknowledgements

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References
freedom is correlated with the antiferromagnetic ordering. The electronic band structure is dominated by the \([P_2X_6]^{4-}\) units, contributing s- and p-atomic orbitals, while the metal d-orbitals hybridize with X(p) orbitals. Most common MPX₃ compounds have monoclinic or orthorhombic crystallographic structures with a space group C₂ or P₂₁/c symmetry, respectively.

The talk at the MRS meeting 2019 will include description of the optical and magneto-optical properties of a vast number of MPX₃ single slabs, Moiré patterns and multiple layers. The description will focus on the influence of the internal magnetism on the optical properties of the materials, e.g., degree of circular polarization in the magneto-reflectance or magneto-photoluminescence spectra. Generally, the MPX₃ family exhibit merits beyond graphene and beyond the well-known (Mo,W)X₂ compounds, owed to the tune-ability of the electronic and magnetic properties.

11:15 AM FF01.12.03
Room-Temperature Dilute Magnetic Semiconductor in V-Doped Monolayer WSe₂
Dinh Loc Duong¹,², Seok Joon Yun¹, Manh Ha Doan², Kirandeep Singh¹, Thanh Luan Phan¹, Wooseon Choi², Young Kuk Kim¹, Young-Min Kim¹,² and Young Hee Lee¹,²,³; ¹Center for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), Korea (the Republic of); ²Department of Energy Science, Sungkyunkwan University, Korea (the Republic of); ³Department of Physics, Sungkyunkwan University, Korea (the Republic of)

Diluted magnetic semiconductors such as Mn-doped GaAs are attractive materials for gate-controlled spintronic devices but the low Curie temperature of the ferromagnetic state is far from room temperature, limiting for practical applications. Here, we report the long-range ferromagnetic order occurs above room temperature in diluted V-doped monolayer WSe₂. Our unambiguous observations are based on micro magnetic domains and the well-defined structure of V-substituted W atoms, which are characterized by magnetic force microscopy and high-resolution transmission electron microscopy, respectively. Furthermore, the modulation of the magnetic domains by an electronic gate is demonstrated, indicating the capability of gate-controlled magnetic properties of the samples. Our findings open new opportunities for using two-dimensional transition metal dichalcogenides for spintronic devices.

11:30 AM FF01.12.04
Anomalous CDW Response in High Mobility Magnetic 2D Material GdTe₃
Yiping Wang¹, Shiming Lei², Leslie Schoop² and Kenneth Burch¹; ¹Boston College, United States; ²Princeton University, United States

Most known magnetic van der Waals (vdW) materials are insulating or semiconducting. It is crucial to find materials with magnetic order and high-mobility for high-speed spintronic device making. Anti-ferromagnet GdTe₃ satisfies both down to 2D limits. The mobility reaches ~28000cm²/Vs, which is among the highest in all the known vdWs. It also exhibits an incommensurate charge density wave (CDW) and becomes superconductor under pressure. Here, we report the recent Raman study of GdTe₃, we will talk about the temperature and polarization dependence of CDW.

11:45 AM FF01.12.05
Fermi Polarons and Magnetic Proximity Effects in Monolayer Semiconductor-Ferromagnet Nanostructures
Thomas Lyons¹, Jorge Puebla², Daniel Gillard¹, Prasanta Muduli³, Charalambos Louca¹, Yoshichika Otani²,³ and Alexander Tartakovskii¹; ¹The University of Sheffield, United Kingdom; ²RIKEN, Japan; ³The University of Tokyo, Japan

Conventional epitaxial ferromagnet-semiconductor multilayers have proven ripe systems for both advanced spintronics research and real-world applications in information technology. The highly ordered states inherent to ferromagnets, alongside their strong collective responses to external electromagnetic fields, makes them ideal candidates to enable control of charge and spin in closely proximitized semiconductors. Monolayers of MoSe₂ are atomically thin direct band-gap semiconductors which combine a regime of coupled spin and valley physics with an optically bright exciton ground state. As such, they are highly promising in the development of valleytronics, an analogue of spintronics which utilizes the carrier valley degree of freedom as an information carrying pseudospin. Crucially, MoSe₂ is also associated with robust chiral optical selection rules, efficiently bridging the gap between spin-valley polarization and optical addressability. By bringing MoSe₂ monolayers into contact with ferromagnetic materials, it becomes possible to bestow an additional, valley, degree of freedom onto the magnetic proximity coupled system.

Here, a monolayer of MoSe₂ is transferred directly on top of a 10nm thick film of europium sulfide (EuS), a
ferromagnetic insulator with a rock-salt crystal structure [1]. Reflectivity spectra from the sample display two clear absorption resonances ascribed to attractive and repulsive Fermi-polarons, associated with spin-based interactions between photogenerated excitons and the electron Fermi sea [2, 3]. The interfacial exchange field between the EuS and MoSe$_2$ strongly amplifies an external magnetic field, leading to robust enhancement of the repulsive polaron valley Zeeman splitting, which reaches an effective $g$-factor of 15. By tuning the external magnetic field, oscillator strength may be transferred between the two polaron resonances, culminating in a complete 100% degree of circular polarization of the attractive polaron when $B = 5T$. This indicates total spin polarization of the 2-dimensional electron gas, owing to robust paramagnetic susceptibility of the MoSe$_2$ [3, 4].

Going further, we incorporate the MoSe$_2$/EuS nanostructure into a zero-dimensional optical microcavity and observe valley selective strong light-matter coupling when $B$ exceeds 5T, corresponding to the formation of Fermi polaron-polaritons in one valley only, selectable by reversing the external magnetic field orientation. In effect, swapping sample illumination between left or right circularly polarized light switches on or off the strong light-matter coupling regime. Our findings unveil the complex interplay between nanoscale magnetism, Coulomb effects, many-body physics and the spin and valley degrees of freedom in atomically thin semiconductor-ferromagnet interfaces. In particular, we expose the enormous potential of 2D material platforms for future opto-valleytronic memories and information processing technology.

Another example is using Raman spectroscopy to probe magnetic phenomena in the antiferromagnetic metal phosphorus trichalcogenide family, including FePS$_3$, MnPS$_3$, and NiPS$_3$. Results on zone-folded phonons in FePS$_3$, the emergence of magnons in FePS$_3$ and MnPSe$_3$ with anomalous symmetry behaviors, and a two-magnon mode in NiPS$_3$ will all be discussed.

Finally, the magnetic field- and temperature-dependence of an exciting ferromagnetic 2D material, CrI$_3$, will be presented.

2:00 PM *FF01.13.02
Electrical Control of Magnetism in 2D Kin Fai Mak; Cornell University, United States

Controlling magnetism by electrical means is a key challenge to better information technology. Electrical control of magnetism has been explored in a variety of materials including dilute magnetic semiconductors, ferromagnetic metal thin films and multiferroics. The recently emerged atomically thin magnetic materials provide unprecedented opportunities to study magnetism in the 2D limit and engineer devices through van der Waals heterostructures. In particular, CrI$_3$ is a model Ising ferromagnet with intriguing layer-dependent magnetic order: whereas monolayer CrI$_3$ is a ferromagnet, bilayer CrI$_3$ is an antiferromagnet with two ferromagnetic monolayers coupled antiferromagnetically. In this talk, I will present our recent results on switching the interlayer magnetic order in CrI$_3$ bilayers by either a pure electric field or electrostatic doping and discuss possible mechanisms for the observed effects in experiment.

2:30 PM BREAK

SESSION FF01.14/FF02.06: Joint Session: Breakthroughs in Graphene and Beyond 2D Materials
Session Chairs: Zakaria Al Balushi and Chuanhua Duan
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Room 312

3:30 PM *FF01.14.01/FF02.06.01
van der Waals Layered Materials towards Room-Temperature Magnetic Semiconductors Young Hee Lee$^{1,2}$, Seok Joon Yun$^1$ and Dinh Loc Duong$^1$; $^1$Sungkyunkwan University, Korea (the Republic of); $^2$Institute for Basic Science, Korea (the Republic of)

The ferromagnetic state in van der Waals two-dimensional (2D) materials has been reported recently in the monolayer limit. Intrinsic CrI$_3$ and CrGeTe$_3$ semiconductors reveal ferromagnetism but the Tc is still low below 60K. In contrast, monolayer VSe$_2$ is ferromagnetic metal with Tc above room temperature but incapable of controlling its carrier density. Moreover, the long-range ferromagnetic order in doped diluted chalcogenide semiconductors has not been demonstrated at room temperature. The key research target is to realize the long-range order ferromagnetism, Tc over room temperature, and semiconductor with gate tunability. Here, we unambiguously observe a ferromagnetic hysteresis loop together with magnetic domains above room temperature in diluted V-doped WSe$_2$, while maintaining the semiconducting characteristic of WSe$_2$ with a high on/off current ratio of five orders of magnitude.

4:00 PM *FF01.14.02/FF02.06.02
Magic Angle Graphene—Correlations, Superconductivity and Beyond Pablo Jarillo-Herrero; Massachusetts Institute of Technology, United States

The understanding of strongly-correlated quantum matter has challenged physicists for decades. Such difficulties have stimulated new research paradigms, such as ultra-cold atom lattices for simulating quantum materials. In this talk I will present a new platform to investigate strongly correlated physics, based on graphene moiré superlattices. In particular, I will show that when two graphene sheets are twisted by an angle close to the theoretically predicted
‘magic angle’, the resulting flat band structure near the Dirac point gives rise to a strongly-correlated electronic system. These flat bands exhibit half-filling insulating phases at zero magnetic field, which we show to be a correlated insulator arising from electrons localized in the moiré superlattice. Moreover, upon doping, we find electrically tunable superconductivity in this system, with many characteristics similar to high-temperature cuprates superconductivity. These unique properties of magic-angle twisted bilayer graphene open up a new playground for exotic many-body quantum phases in a 2D platform made of pure carbon and without magnetic field. The easy accessibility of the flat bands, the electrical tunability, and the bandwidth tunability though twist angle may pave the way towards more exotic correlated systems, such as quantum spin liquids or correlated topological insulators.

SESSION FF01.15/FF02.07/MS02.08: Keynote Session: Breakthroughs in Graphene and Beyond 2D Materials
Session Chairs: Zakaria Al Balushi and Chuanhua Duan
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Room 312

4:30 PM *FF01.15.01/FF02.07.01/MS02.08.01
Keynote: Molecular Transport through Two-Dimensional Capillaries  Andre Geim; University of Manchester, United Kingdom

I will review our group’s work on the molecular transport properties of angstrom-scale channels fabricated by der Waals assembly of 2D crystals. These channels can be viewed as if individual atomic planes were extracted from a bulk crystal leaving behind two edge dislocations with an empty space in between. Gas, water, ion and proton transport have been studied in capillaries down to one atom in height.

SESSION FF01.16: Poster Session III: Beyond Graphene 2D Materials—Synthesis, Properties and Device Applications III
Session Chairs: Zakaria Al Balushi, Deep Jariwala, Olga Kazakova and Amber McCreary
Wednesday Afternoon, December 4, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

FF01.16.01
In Situ Monitoring of Graphene Growth on Cu by Reflectance Contrast Using Confocal Laser Scanning Microscopy Dong J. Kim1,2, Yeon Joon Suh1, Juhee Kim1, Mina Park1, Yun Sung Woo2 and Byung Hee Hong1; 1Department of Chemistry, Korea (the Republic of); 2Graphene Square Inc., Korea (the Republic of)

Large-area, high-quality, and continuous growth technologies for CVD graphene have been developed to meet the requirements for industrial applications. However, there has been a lack of proper methods to check the quality of graphene in a fast and non-destructive way for mass-production scale. Optical microscopy (OM) has been widely explored for imaging and characterizing CVD graphene directly on Cu. Dark field (DF) OM was employed to investigate CVD graphene grown on Cu foil using the Rayleigh light scattering from Cu steps beneath graphene, which can be adopted only for metals that generate steps with considerable height beneath graphene after growing. Moreover, the DF imaging by the weak scattered light is time-consuming and requires a sample of graphene on Cu foil to be placed over a period of time under illumination. On the other hand, confocal laser scanning microscopy (CLSM) is capable of scanning a large area in a few seconds in high-resolution, which is expected to enable the faster characterization of graphene on Cu regardless of its production scale. Thus, we demonstrate that the reflection mode CLSM can be utilized for the in-situ monitoring of the CVD-grown graphene on Cu foil as a possible quality assessment tool of mass-produced CVD graphene films. The CLSM generates the high-contrast optical images of CVD-grown graphene on Cu over a large area, in which the contrast between the graphene layer and Cu is greater for shorter incident laser wavelengths. The reflectance contrast calculated by Maxwell equation is in good agreement with the experiment as the interference of reflected light at the interface between air, graphene, and Cu.
provides a high image contrast between the areas with and without graphene. Furthermore, we found out that the quality of CVD graphene can be characterized by CLSM because the reflectance and the optical conductivity are proportional to the defect density.

**FF01.16.02**

**One-Step Synthesis and Properties of Cationic Nitrogen-Doped Graphene by Solution Plasma**  
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Control of nitrogen bonding configuration in hexagonal graphene lattice is considered as the promising strategy in realizing desired electrical, chemical, and optical properties of graphene. Three bonding configurations are typically detectable, including quaternary nitrogen (or graphitic nitrogen), pyridinic nitrogen, and pyrrolic nitrogen. However, cationic nitrogen is another possible bonding, which has been rarely investigated and not well understood in graphene chemistry. Therefore, study of graphene with cationic nitrogen doping is very challenging for further development towards this area. In this work, cationic N-doped graphene (CNG) has been synthesized via a novel method called solution plasma (SP) at room temperature and atmospheric pressure. The mixture of 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA) and dimethylformamide (DMF) was employed as carbon and nitrogen sources in synthesis. The originality of this work consists of two points as follows: 1. Combination of solution plasma and ionic liquid (EMIM DCA) allows us to achieve one-step, rapid, substrate-free synthesis of p-type graphene with cationic nitrogen doping at room temperature and atmospheric pressure. 2. Cationic nitrogen-doped graphene exhibited p-type semiconducting behavior with a low sheet resistance of 16 Ω sq⁻¹ and a high carrier concentration of 10¹⁹ cm⁻³. These fascinating electrical properties can be attributed to two important effects: (i) presence of cationic nitrogen in graphene lattice and (ii) preservation of planar structure. The combination of SP and ionic liquid shows a promising strategy in design and synthesis of NG with cationic nitrogen-doping, which cannot be achieved in other existing methods. The CNG will be enable potential use in many applications in various fields, such as sensor, electronic, and energy devices.

**FF01.16.03**

**Edge Terminations Control of Tungsten Diselenide Domains Using Chemical Vapor Deposition**  
Yoobeen Lee and Jin Seok Lee; Sookmyung Women's University, Korea (the Republic of)

Variously shaped transitional metal dichalcogenides (TMDC) domains are of significant interest since the electronic properties of pristine TMDC are strongly dependent on its size, shape, and edge structures. As the reactivity of TMDC is governable by the electronic structure at its edge, a number of attempts have been made to grow differently shaped TMDC domains and to define their edge structures. Of the various TMDC synthesis techniques, it is well-known that the chemical vapor deposition (CVD) is the most reasonable and appropriate method to produce large-scale and low-defect TMDC domains. And, many CVD parameters such as growth temperature, annealing time, and the amount of precursors affect TMDC growth.

In this study, we investigated CVD method in order to grow tungsten diselenide (WSe₂) domains of various shapes. By regulating the amount of Se powder as precursor and growth temperature during the CVD process, we synthesized hexagonal, square, circular, and triangular WSe₂ domains, and characterized their morphologies and physical properties using scanning electron microscopy (SEM), Raman spectroscopy, photoluminescence (PL) analyses, atomic force microscopy (AFM) and scanning tunneling microscope (STM). Based on the atomic configurations of WSe₂ domain edges and size distributions of the WSe₂ domains, we proposed the edge termination mechanism of anisotropic WSe₂ domains, which is strongly dependent on the amount of Se precursor and growth temperature during the CVD process.

**FF01.16.04**

**MOCVD Growth of Tungsten Ditelluride Thin Films**  
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Tungsten ditelluride (WTe₂) is a layered, type-II Weyl semimetal transition metal dichalcogenide (TMD) typically observed in a distorted 1T (1T’ phase with an orthorhombic crystal structure comprised planes of distorted triangular lattices of tungsten atoms sandwiched by tellurium atoms. The distortion pushes tungsten atoms closer together in the x-axis than the y or z-axis, generating quasi-one-dimensional chains of these atoms, leading to
strongly anisotropic electronic properties throughout the material. It has been shown to have extraordinary physical properties, such as a high magnetoresistance, anisotropic ultra-low thermal conductivity and metal-insulator transition and it also exhibits interesting quantum phenomena such as the quantum spin-Hall effect and pressure-driven superconductivity. These unique properties make WTe₂ an exciting candidate for emerging applications, including phase change memory electrodes, magnetic field sensors, biosensors, microelectromechanical systems, hard disk drives and quantum computing. While bulk crystals of the material have been available for many years, to date, thin films of WTe₂ have only recently been synthesized using techniques such as molecular beam epitaxy and powder source chemical vapor deposition (CVD) that utilize Te powder and W-feedstock. Metalorganic CVD (MOCVD) growth is also of interest as it enables precise delivery of precursors to the substrate at moderate growth pressures (100-700 Torr) but has not yet been studied in detail.

In this study, we investigate the use of MOCVD for the growth of WTe₂ on c-plane sapphire substrates. The studies were carried out in a vertical cold wall MOCVD reactor using tungsten hexacarbonyl (W(CO)₆) and diethyltelluride (DETe) as precursors for W and Te, respectively, in a H₂ carrier gas. Initial studies, carried out at 100 Torr reactor pressure using a W(CO)₆ flow rate of 1.3 x10⁻⁴ sccm and Te/W ratio of ~8000 : 1, demonstrate the growth of WTe₂ as confirmed by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The growth rate was found to decrease with increasing temperature over the temperature range from 350-600°C likely due to increased desorption of Te species from the substrate surface. Peaks at ~1340 cm⁻¹ and ~1600 cm⁻¹ were present in the Raman spectra of the films indicating the presence of carbon in the layers most likely due to the DETe source. Additional studies are underway to elucidate the growth mechanism and properties of MOCVD grown WTe₂. The synthesis of W(Se,Te)₂ alloy films via introduction of H₂Se during deposition will also be explored to explicate the consequences on phase control, oxidation stability, and the reduction of carbon contamination during growth.

**FF01.16.05**

**Integration of 2D Tungsten Disulfide on Carbon Nanotube-Coated Paper for Highly Sensitive and Flexible Gas Sensors** Lee Woo Sung and Jungwook Choi; Yeungnam University, Korea (the Republic of)

Sensitive and flexible chemical sensors fabricated by a low-cost process are promising since they can be attached on curved, complex structures, and even the human body while providing an environmental signal to the user. For this reason, many nanomaterial-based flexible sensors have been investigated. However, they required a complicated manufacturing process leading to expensive cost and labor intensity. Furthermore, their limited chemical sensitivity and mechanical flexibility pose challenges.

Here, a highly deformable chemical sensor is reported with improved sensitivity that uses the hybrid structure of multiwalled carbon nanotubes (CNTs) and 2D transition metal dichalcogenides (TMDCs) on cellulose paper. Liquid dispersions of CNTs and TMDCs (e.g., WS₂ and MoS₂) are absorbed and dried on porous cellulose paper for sensor fabrication, which is simple, scalable, rapid, and cost-effective. Owing to the flexibility of cellulose paper, the sensor enables reversible three-dimensional folding and unfolding, bending, and twisting without any degradation. At the same time, the CNTs form a percolation network and simultaneously provide gas reactivity. Functionalization of CNTs with WS₂ greatly improves the sensing response to exposure to NO₂ molecules by more than 1.5 times. The measured sensitivity toward NO₂ is 4.57% ppm⁻¹, which is much higher than that of previous paper-based NO₂ sensors. In addition, our sensor maintains high sensitivity even under severe deformation such as heavy folding and crumpling. This approach can be a suitable way for simple fabrication of highly flexible and sensitive chemical sensor which can be potentially applicable for low-cost portable device and disposable sensor.

**FF01.16.06**

**Convergent Ion Beam Alteration of 2D Materials and Metal-2D Interfaces** Zhihui Cheng¹, Hattan Abuzaid¹, Yifei Yu², Fan Zhang³, Yanlong Li², Steven G. Noyce¹, Yuh-Chen Lin¹, James Doherty¹, Chenggang Tao³, Linyou Cao² and Aaron D. Franklin¹,¹; ¹Duke University, United States; ²North Carolina State University, United States; ³Virginia Tech, United States

Tailoring the properties of two-dimensional (2D) crystals is important for both understanding the material behavior and exploring new functionality. Here we demonstrate the alteration of MoS₂ and metal-MoS₂ interfaces using a convergent Ar ion beam. Different beam energies, from 60 eV to 600 eV, are shown to have distinct effects on the optical and electrical properties of MoS₂. Defects and deformations created across different layers were investigated, revealing an unanticipated improvement in the Raman peak intensity of multilayer MoS₂ when exposed to a 60 eV Ar⁺ ion beam, and attenuation of the MoS₂ Raman peaks with a 200 eV ion beam. Scanning tunneling microscopy
(STM) was used to probe the altered 4-layer MoS$_2$ surface, showing that the MoS$_2$ crystallinity still remains. This largely intact crystallinity of the 4-layer MoS$_2$ surface is in contrast to the significantly diminished PL peak of monolayer MoS$_2$, suggesting that the defects spread throughout multiple layers rather than concentrating at the surface. Using cross-sectional scanning transmission electron microscopy (STEM), alteration of the crystal structure after a 600 eV ion beam bombardment was observed for the first time, including generated defects across layers and voids in the crystal. We show that the 60 eV ion beam yields improvement in the metal-MoS$_2$ interface by decreasing the contact resistance from 17.5 kΩ*μm to 6 kΩ*μm at a carrier concentration of $n_{2D} = 5.4 \times 10^{12}$ cm$^{-2}$.

These results advance the use of low-energy ion beams to modify 2D materials and interfaces for tuning and improving performance for application as sensors, transistors, optoelectronics, and so forth.

**FF01.16.07**

**Low-Temperature Synthesis of Transition Metal Dichalcogenides Nanowires with Increased Electron Scattering**

John M. Woods, David J. Hynek, Pengzi Liu, Min-Hui Li and Judy Cha; Yale University, United States

Transition metal dichalcogenides (TMDCs) have been widely studied for a variety of applications including catalysis for hydrogen evolution reaction, flexible optoelectronics, thermoelectrics, and battery and supercapacitor applications. Recently, tellurium-based TMDCs, such as WTe$_2$ and MoTe$_2$, are heavily studied for their desirable electrical properties, which include superconductivity down to the monolayer limit,$^{1,2}$ quantum spin Hall state in monolayer,$^3$ type II Weyl semimetallic nature,$^4$ and large magnetoresistance.$^5$ In recently published work$^6$ we report on the synthesis of single-crystalline nanowires of TMDCs (WTe$_2$, WS$_2$, WSe$_2$, and MoTe$_2$) through conversion of oxide nanowires. The synthesized WTe$_2$ nanowires may be well suited to study topological superconductivity and Majorana zero modes due to the approximation as a one dimensional system.

We perform current-dependent resistance vs. temperature measurements to characterize the transport properties of our WTe$_2$ nanowires. We find that the nanowires exhibit a resistivity that is an order-of-magnitude higher than flakes of similar thicknesses, even after removing the contributions from a tunnel barrier at the contacts. We hypothesize that this increased resistivity results from increased surface scattering of the nanowires owing to surface oxidation and increased contribution from side surfaces rather than basal planes. We investigate *in situ* passivation layer to protect the nanowires from surface oxidation. Future works to develop mitigation strategies to handle scattering at the nanowire surface will allow for investigations into the topological features of WTe$_2$.


**FF01.16.08**

**Nano-Encapsulation with 2D Materials for Ambient Operation of Field Emission Electron Devices**

Girish Rughoobur, Jiayuan Zhao, Ahmad Zubair, Lay Jain, Tomas Palacios, Jing Kong and Akintunde I. Akinwande; Massachusetts Institute of Technology, United States

The quest for transistors that operate in the THz regime is driven by the requirement for higher bandwidth to increase information bandwidth of networks. The replacement of the semiconductor transport channel with free-space is a potential path for achieving this objective. The so-called “Nano Vacuum Channel Transistors” (NVCTs) could potentially have superior performance compared to solid state devices of equivalent channel length owing to ballistic transport of electrons, shorter transit time and higher intrinsic breakdown voltage.$^1$ This is achievable as electrons are not scattered in free space (higher velocity) and there is no Avalanche carrier multiplication (no breakdown). Hence NVCTs have promise for very high Johnson Figure of Merit ($\sim 10^{14}$).$^2$

NVCTs operate by injecting electrons into the channel when electrons tunnel through the barrier as the barrier is “thinned” by the application of a gate voltage with respect to the emitter tip. This barrier height is of the order of the
electron affinity of Si ($\chi = 4.05$ eV). By scaling down all the critical device dimensions by a factor of 10, very high density (10^8 tips/cm^2), self-aligned gate field emitter arrays with low turn-on voltage (8.5 V), low operating voltage (20 V), high current density (150 A/cm^2) and long lifetime (>300 hours) have been demonstrated. However, these devices need ultra-high vacuum (UHV) for reliable operation as the field emission process is sensitive to barrier height variations induced by adsorption/desorption of gas molecules. Small changes in the barrier height lead to exponential variations in current. Poor vacuum also leads to generation of energetic ions that bombard the emitter tips, rendering the tips blunt and degrading electrical performance.

To overcome the need for UHV, we use atomically thin layers such as 2D materials to nano-encapsulate only the field emitter either in UHV or in a gas (e.g. helium) with high ionization energy. We exploit the higher transmission of smaller particles such as electrons through 2D materials compared to larger atoms/molecules such as gases. By separating the electron emission region from the acceleration region (where the electrons acquire energy), electrons can be transported in a non-ideal vacuum, if not atmospheric conditions. Furthermore, the nano-encapsulation layer can either function as an ion repeller if biased positively or can be used for secondary electron emission interface. For mechanical strength, multiple layers that are transparent to electrons while impervious to gas molecules/ions are used. In this work, we investigate the structural and electrical properties of 2D materials as nano-encapsulation layers for Si based field emission sources. The goal is to realize empty state electronics capable of functioning at higher power and harsher conditions (high radiation and high temperature) compared to solid state electronics.

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Large, Low-Aspect Ratio Vanadium Dioxide Single Crystals as Actively Reconfigurable Substrates for 2D Materials Samuel T. White1, Ellis Thompson2, Peyton Brown1, Joseph Matson1, Thomas G. Folland1, Josh Caldwell1 and Richard F. Haglund1,1; 1Vanderbilt University, United States; 2Vassar College, United States

One of the main advantages of 2D materials is that their properties are dependent on their local environment, making them inherently controllable by effects such as electrostatic gating. Furthermore, 2D materials can be transferred onto arbitrary substrates, an excellent opportunity for device engineering. In particular, stacking 2D materials on tuneable or phase-change materials (PCMs), such as those exhibiting a metal-insulator transition (MIT), provides an avenue to further control the properties of 2D materials. Among PCMs, vanadium dioxide (VO2) has received a great deal of attention for its easily-accessible critical temperature (Tc) near 70°C, rich phase diagram, ultrafast optically-induced phase transition, and large change in optical properties (both n and k) especially pronounced in the near- and mid-IR; properties with promise for a variety of applications, including sensors, photonic modulators and switches, passive thermal control films—and the modulation of hyperbolic phonon polaritons (HPH) in hexagonal boron nitride (hBN). Single crystals of VO2—while less durable and scalable than thin films—have well-defined crystal lattices, sharp phase transitions, and, when strained, striped phases of coexisting insulating and metallic domains. These are ideal for situations where sharp, lateral boundaries are required within devices. Recently, these domain walls were used to demonstrate index-based launching, reflection, and refraction of HPHPs in hBN.

Developing such applications requires robust, reproducible techniques to create VO2 in a variety of forms and to locally adjust its phase transition. High-quality VO2 crystals can be grown via a physical vapor transport method, where V2O5 precursor is vaporized, transported to a growth substrate, and reduced to VO2. The size, shape, and structure of the resulting crystals depends heavily on growth parameters and the substrate used. Moreover, the Tc, existence of intermediate phases, and pattern of coexisting domains are sensitive to the crystal morphology and substrate interaction. While much work has focused on growing nanocrystals of various sizes and shapes, we seek to grow large, low-aspect ratio crystals to support large slabs of two-dimensional materials and to facilitate optical experiments on those heterostructures.

Specifically, we grow such VO2 microcrystals on a variety of crystalline oxide substrates with good lattice match to
VO₂. We discuss the optimization of growth parameters, and use optical microscopy, Raman spectroscopy, and XRD to analyze the effect of lattice match on the orientation and morphology of the crystals. Additionally, we use FTIR to measure the optical constants of single crystal VO₂ in the M1, M2, and R phases, and investigate the possibility of patterning metallic domains in VO₂ crystals with local laser heating. On c-cut sapphire—previously used to grow epitaxial nanowires—we observe large microcrystals stabilized in the insulating M2 phase at room temperature, which we attribute to strain arising from lattice mismatch and thermal expansion. On yttrium-stabilized zirconia (YSZ) (100)—previously used as a buffer layer to grow epitaxial VO₂ thin films—we observe preferred orientation of large microcrystals, as well as formation of yttrium vanadate and zirconia due to the instability of YSZ at high temperatures. These crystals exhibit unique surface morphologies, such as terrace-like steps. We also report on the growth of single crystals on other cuts of sapphire and YSZ, and on spinel (111) (MgAl₂O₄, known to support epitaxial VO₂ thin films). Finally, we describe the creation of 2D heterostructures using these crystals, and demonstrate their applicability for infrared spectroscopy experiments.

**FF01.16.10**

**Tailoring the Electronic Structure of Transition Metal Dichalcogenides Using Rationally Designed Small Molecules**

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The exotic physical and chemical properties of layered transition metal dichalcogenides (TMDCs) make them prime candidates for use in a variety of applications including electronics, optoelectronics, valleytronics, and catalysis.[¹] The ability to rationally manipulate the electronic structure of atomically thin films of TMDCs is essential to enable their practical implementation. To achieve this goal, there are several examples of surface functionalization of TMDCs using small molecules to control the charge-carrier polarity and doping of TMDCs.[²] However, our understanding about the nature of the interaction between small molecules and the TMDCs or how the structure of small molecules impacts the properties of the TMDCs, remains limited. Here, we describe studies which rationally tune the electronic structure of MoS₂ monolayers using a library of systematically designed small molecules with different structures and redox properties. Electrical and magneto-transport measurements show a factor of ten improvement in electron mobility and carrier density of functionalized MoS₂ devices with well-defined organic reductants. To obtain a holistic description of the doping effects, a range of characterization techniques including X-ray photoelectron, photoluminescence, and Raman spectroscopies, and scanning tunneling and transmission electron microscopy, as well as secondary ion mass spectrometry are utilized.


**FF01.16.11**

**Structural Identification and Related Physical Properties of Red Phosphorus Polymorphs**

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Red phosphorus, an allotrope of phosphorus which is usually known to be amorphous, has several types of crystalline phases. The atomic structures and electrical properties of crystalline red phosphorus, however, have not been studied in detail due to the existence of various crystalline phases of complex structure. The red phosphorus polymorphs are categorized into five types, which include the amorphous phase (type-I). The crystal structures of type-IV (fibrous red phosphorus) and type-V (Hittorf’s phosphorus) have been previously revealed but those of type-II and type-III phases are yet to be identified. Here we investigate the crystal structures and electrical properties of crystalline red phosphorus polymorphs. Using chemical vapor transport method, we synthesize crystalline red phosphorus. Using Raman spectroscopy, electron diffraction, and X-ray diffraction measurements, we confirmed that synthesized red phosphorus is mainly type-II with some mixture of type-IV crystalline phases. The electron crystallography can be utilized to identify the crystal structure of type-II red phosphorus. With its semiconducting nature, the crystalline red phosphorus can be a promising material for electronic and optoelectronic applications.

**FF01.16.12**

**Spectroscopy Studies on Multi-Layer InSe with Visible Range Band Gap**

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United Arab Emirates; 2 Academia Sinica, Taiwan; 3 Laboratory for Energy and NanoScience (LENS), United Arab Emirates

Atomically thin, two-dimensional (2D) indium selenide (InSe) has attracted considerable attention owing to the dependence of its bandgap on sample thickness, making it suitable for small-scale optoelectronic device applications. In this work, by the use of Raman spectroscopy with three different laser wavelengths, including 488 nm, 532 nm, and 633 nm, representing resonant, near-resonant and conventional non-resonant conditions, a conclusive understanding of the thickness dependence of lattice vibrations and electronic band structure of InSe and InSe/graphene heterostructures are presented. Combining our experimental measurements with first-principles quantum mechanical modeling of the InSe systems, we identified the crystal structure as ε-phase InSe and demonstrated that its measured intensity ratio of Raman peaks in the resonant Raman spectrum evolves with the number of layers. Moreover, graphene coating enhances Raman scattering of few-layered InSe and also makes its photoluminescence stable under higher-intensity laser illumination. The optically induced charge transfer between van der Waals graphene/InSe heterostructures is observed under excitation of the E’ transition in InSe, where the observed mechanism may potentially be a route for future integrated electronic and optoelectronic devices.

FF01.16.13
High Electromagnetic Interference Shielding Effectiveness of Graphene Foam/Polymer Composites with Fe3O4 Nanoparticles-Intercalated 2D Ti3C2Tx
Van-Tam Nguyen1,2, Bok Ki Min1, Yoonsik Yi1, Seong Jun Kim1 and Choon-Gi Choi1,2; 1 Electronics and Telecommunications Research Institute, Korea (the Republic of); 2 University of Science and Technology, Korea (the Republic of)

Electronic devices such as personal computers, smartphones, and wearable devices with many highly sensitive precision electronic components can be malfunctioned due to electromagnetic interference (EMI). An EMI shielding is a solution to prevent electromagnetic (EM) radiation pollution but conventional metal-based EMI shielding materials cannot apply for stretchable and flexible devices. The 3D graphene foam/polymer composites have acquired noteworthy interests in flexible EMI shielding materials owing to the excellent electrical conductivity and large specific surface area. However, their shielding performance still needs further improvement to serve in real world applications.

Herein, the Fe3O4 nanoparticles intercalated 2D Ti3C2Tx (MXene) through ultrasonic method is decorated on the graphene foam that is grown on nickel skeleton by chemical vapor deposition (CVD) process, before embedding in the poly dimethyl siloxane (PDMS) matrix. After etching nickel away, the composite shows flexibility, elasticity, high conductivity, and a brilliant EM wave absorption. We propose the presence of the Fe3O4 nanoparticle intercalated MXene induces the internal multi-reflection, magnetic loss, and interfacial polarization in the graphene foam/polymer matrix resulting in the excellent EMI shielding effectiveness as high as 83.6 dB in the X-band frequency range (8.2-12.4 GHz). Consequently, the lightweight, flexible, and highly conductive graphene foam-based composite opens up the possibility to use as the high-performance EMI shielding materials applicable in the wearable electronics, flexible and stretchable electronics, etc.

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FF01.16.14
AAO Assisted MoS2-Honeycomb Structures for Highly Sensitive and Ultrafast Moisture Detection
Shuvra Mondal1,2, Seong Jun Kim1 and Choon-Gi Choi1,2; 1 Electronics and Telecommunication Research Institute, Korea (the Republic of); 2 University of Science and Technology, Korea (the Republic of)

The climate change and necessity of monitoring dynamic changes of humidity in various fields starting from food processing industry, semiconductor fabrication facility, automobile and agriculture, to more sophisticated human respiration, non-contact epidermal sensing has increased the demand for highly sensitive humidity sensor material research. Two-dimensional (2D) material like molybdenum disulfides (MoS2) is an excellent material for humidity sensing due to the presence of inherent defects, and high moisture absorption even at room temperature. However, the humidity absorption of mono or multilayer MoS2 are limited by its atomically thin layers and their relatively low
defect sites for water molecules. Humidity sensor made from pure MoS2 films suffer from low sensitivity at room temperature has been reported. Recently, research on atmospheric humidity effect on the electrical characteristics of 3D nanostructure, MoS2 nanoflakes have been studied with the aim to increase moisture absorption and broaden detection range. However, previous studies are mostly focused on top or bottom gated complex devices that have limitations like hysteresis, stability at high humidity levels, durability.

In this study, we demonstrate a simple resistive type anodic aluminum oxide (AAO) assisted MoS2 honeycomb structure for superior humidity sensing with fast response. The honeycomb structured MoS2 tubes were fabricated by filtering the (NH4)2MoS4 solution through anodic aluminum oxide (AAO) membrane by vacuum filtration method. To achieve perfectly open surfaced MoS2 honeycomb for maximum water vapor absorption site, (NH4)2MoS4 solution vacuum filtration was repeated in cycles to eliminate larger particles from the solution. Next, T-CVD annealing process was used to synthesis MoS2 tube honeycomb. In our finding, this 3D honeycomb structure based on MoS2 tubes can respond fast to humidity from atmosphere, human skin, and human breath at the range of RH 20% ~ RH 85%. The sensitivity and response speed are heavily influenced by the MoS2 tubes, due to their wider surface area and open pores for higher moisture absorption sites. From experimental result, our MoS2 honeycomb structured humidity sensor showed excellent sensitivity of ~700 (ΔI/I0) at RH 83%, with a fast response and recovery time of 0.47s and 0.81s, respectively. This study paves the way to fast humidity sensing and non-contact sensation for next generation electronic devices.

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FF01.16.15
Nanotube Templated Growth of Ultra-Narrow Transition Metal Dichalcogenide Nanoribbons Jeffrey D. Cain1,2, Amin Azizi1, Sehoon Oh1, Scott Meyer1,2, Peter Ercius2, Marvin Cohen1 and Alex Zettl1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

Recently, the concept of dimensionality has emerged as an essential parameter for tuning material properties. Coinciding with the recent rise of two-dimensional (2D) materials, there have been extensive efforts to engineering additional levels of confinement, and thus lower dimensionality, in few- and monolayer materials. The greatest successes have been achieved in the fabrication and synthesis of graphene nanoribbons (GNRs), where rational bottom-up synthesis has been accomplished using the self-assembly of molecular precursors. This has enabled the growth of GNRs with specific edge structures and atomically precise widths, as well as single GNR heterojunctions with engineered band alignment and topology. Similarly, exciting physics are expected when the 2D transition metal dichalcogenides (TMDs) are further constrained to one-dimension (1D). However, the synthesis and/or fabrication of TMD nanoribbons (NRs) has lagged far behind that of GNRs both in terms of quality and width control. In the past, most studies have relied upon top-down fabrication methods that require lithography and etching processes. This results in NRs with widths greater than 50 nm (too large to observe quantum confinement effects) and a high degree of disorder. Here, we report the growth of ultra-narrow TMD nanoribbons as templated by multiwalled carbon nanotubes. The nanoribbons are grown within the hollow cavity of the carbon nanotubes, limiting their lateral dimensions and layer number, while simultaneously stabilizing them against the environment. The result is pristine nanoribbons that reach the monolayer limit and exhibit widths that can reach below 2 nm, while maintaining a defined edge structure. High-resolution transmission electron microscopy and scanning transmission electron microscopy reveal the detailed atomic structure of the material, and density functional theory is used to explore the effects of additional levels of confinement on electronic properties. The NR-in-nanotube structure represents a unique route toward nanoribbon growth and the exploration of materials under extreme dimensional constraint.

FF01.16.16
First-Principles Investigation of Dopants and Defects in 2D Materials Anne Marie Z. Tan1, Christoph Freysoldt2 and Richard G. Hennig1; 1University of Florida, United States; 2Max-Planck-Institut für Eisenforschung GmbH, Germany

Two-dimensional (2D) semiconductor materials, such as transition metal dichalcogenides, monochalcogenides, and phosphorene have attracted extensive research interests for potential applications in optoelectronics, spintronics,
photovoltaics, and catalysis. Understanding the effect of impurities, defects, and dopants on the electronic properties is crucial for the selection of materials. Choosing suitable synthesis and processing conditions allows for some control over their concentrations, and hence to tailor the carrier concentration, character, and mobility in 2D materials. Accurate determination of defect formation energies and charge transition levels enables us to predict their effect on the electronic properties and how they respond to changes in synthesis and processing.

Density functional theory (DFT) calculations of point defects in solids is a mature field with a proven record of experimentally validated predictions. However, modeling charged defects in single-layer materials with common plane-wave DFT approaches poses additional challenges which lead to the divergence of the energy with vacuum spacing. Recently, Freysoldt and Neugebauer developed a correction scheme which employs a surrogate model to restore the appropriate electrostatic boundary conditions for charged 2D materials. We apply this correction scheme to compute the formation energies and charge transition levels associated with point defects and defect complexes in technologically relevant materials such as MoS₂, WSe₂, and phosphorene. We find that dopants can bind with intrinsic defects such as vacancies to form defect complexes under certain experimental conditions, acting as compensating defects and modifying the electronic properties of the individual defects. An example of this is the Re dopant – S vacancy complex in MoS₂ which we found to be thermodynamically favorable and which if formed in fact passivate the n-type Re dopant. By further analyzing the defect electronic structures, we also predict interesting phenomena such as Jahn-Teller distortions which occur when the defects are in specific charge states. Finally, we are developing a Python-based workflow to facilitate efficient high-throughput calculations of charged point defects in 2D materials and interfacing it with existing materials databases to create a new database of defects in 2D and layered bulk materials.

FF01.16.17
Characterization of Functionalized Chevron-Type GNR Using STM and STS Abigail Berg¹,¹, Gang Li², Kaitlyn Parsons¹,¹, Amir Taqieddin¹, Steven Kolaczkowski¹,¹, Yulin He¹,¹, Pin-Chiao Huang¹,¹, Narayana R. Aluru¹,¹, Alexander Sinitskii² and Joseph W. Lyding¹,¹,¹; ¹University of Illinois at Urbana-Champaign, United States; ²University of Nebraska–Lincoln, United States

We report results on a new class of bottom-up synthesized functionalized atomically precise graphene nanoribbons (GNRs). These new ribbons are structurally related to the established chevron GNRs but are expected to have a smaller bandgap and thus higher electrical conductivity, and the edge functionalization is expected to improve their processability for device fabrication. The GNRs were synthesized in solution via Suzuki coupling of structurally different molecular precursors and characterized by a variety of spectroscopic techniques. Dry contact transfer (DCT) was used to deposit these GNRs in UHV onto hydrogen passivated Si(100) surfaces for STM imaging and spectroscopy (STS) to elucidate the structural and electronic features of these GNRs. STS results indicate a strong variation in electronic structure along the length of the GNR. Specifically, the bandgap of the functionalized ends of the reduced chevron GNR exceeds 3.3 eV while the center of the GNR exhibits a bandgap of 2.5 eV. First principle simulations using DFT and GW of the electronic structure will also be presented.

FF01.16.18
Magnetic Iron Defect Centers in Molybdenum Disulfide Monolayers Shichen Fu¹, Kamran Shayan¹, Kyungnam Kang¹, Xiaotian Wang¹, Lihua Zhang², Xiangzhi Li¹, Xiao Tong², Siwei Chen¹, Stefan Strauf¹ and Eui-Hyook Yang¹; ¹Stevens Institute of Technology, United States; ²Brookhaven National Laboratory, United States

Transition metal dichalcogenides (TMDs) have received considerable attention over the past decade, owing to its unique thickness-dependent electrical and optical properties. Chemical vapor deposition (CVD) is required to realize the scalable fabrication of TMD devices. However, the optical emission and carrier mobility of CVD-grown TMDs remain low due to the broad emission from defect bound excitons. A wide variety of approaches has been made to alter optical and electrical properties of TMD, including the incorporation of transition metals atoms (Mn, Nb, and Re) in monolayer TMDs using substitutional doping or intercalation. Among those transition metal atoms, iron (Fe) has attracted most attention due to its predicated magnetic properties and non-degenerate ground state with non-zero spin.

Here, we systematically investigated the temperature-dependent photoluminescence (PL) and magneto-PL properties of in situ Fe doping of polycrystalline MoS₂ monolayers via CVD. First, scanning transmission electron microscopy was employed to probe the atomic structure of the Fe-doped MoS₂ monolayers. Fe atoms with lower
relative intensity were visible in the MoS\(_2\) lattice at Mo sites, suggesting a substitutional Fe-doping of MoS\(_2\) monolayers. The temperature-dependent PL studies of both bare and Fe-doped MoS\(_2\) monolayers revealed significant suppression of the broad defect-bound emission related to chalcogen vacancies. In addition, we observed the emergence of new emission peaks after Fe atoms are introduced. Since the new emission peaks were absent in bare MoS\(_2\) monolayer, we attribute the new emission peaks to the optically active Fe ion sites. The light emissions from these optically active Fe ion sites had very strong thermal stability from 4K to 300K. Magneto-PL studies provided insights into the magnetic behavior of the Fe related emissions. We found \(\sim 30\%\) circular dichroism in the Fe-related emissions even at room temperature without applying a magnetic field. Furthermore, a ferromagnetic behavior of the Fe related emissions was observed by measuring the PL circular dichroism at different magnetic fields (-6.5 T to 6.5 T) with increasing and decreasing sweeping directions. These findings are pathfinders toward enabling potential applications on minimizing bit storage for future electronics based on TMDs.


**FF01.16.19**

**Monolayer Porous Molybdenum Disulfide**

Shuai Jia, Jing Zhang, Jiangtan Yuan, Hua Guo, Weibing Chen, Zehua Jin, Pulickel Ajayan and Jun Lou; Rice University, United States

Two-dimensional porous membrane is considered as promising candidate for photocatalyst or electrocatalyst, desalination and rapid DNA sequencing. Delicate preparation, low-efficiency and absence of scalability of the current high energy electron irradiation method for nanopores creation, has pushed the community to develop easy, low-cost and scalable methods to create nanopores onto two-dimensional materials. Here, we developed an oxidation and etching method to create easily multiple nanopores onto monolayer molybdenum disulfide (MoS\(_2\)). These nanopores are triangles with straight edges and their size is tunable by changing the oxidation temperature. With much more exposed fresh edge sites which are active sites for hydrogen evolution reaction, basal plane activity of monolayer porous MoS\(_2\) is significantly enhanced compared with pristine MoS\(_2\). Our findings imply great applications potential exist in two-dimensional porous membrane and this simple, effective and scalable method to create multiple nanopores on monolayer MoS\(_2\) paves the way to the applications of two-dimensional porous membrane.

**FF01.16.20**

**EELS Study of Vertically Grown Graphene Sheets on Ge**

Nitul S. Rajput, Abdulrahman S. Al Hagri, Ru Li, Jin-You Lu and Matteo Chiesa; Khalifa University of Science and Technology, United Arab Emirates

Vertically aligned graphene nanosheet arrays (VAGNAs) are grown on Ge substrate using a PECVD process. VAGNAs have unique tip morphology and large surface area, which make them as promising candidates for different applications, such as field emitting based devices, supercapacitors and batteries. Raman study implies that our PECVD-grown VAGNAs has the features of single-layer graphene termination at the top, which is further identified by our High-Resolution Transmission Electron Microscopy (HRTEM) characterization. In addition, to extract the quality of the grown layers, we also carry out the TEM based electron energy loss spectroscopy (EELS) investigation. EELS provides intricate information such as, the hybridization states and defect types present in the grown graphene sheets. Following the experimental EELS study, we also perform first-principles calculations to evaluate the effect of different types of defects on the electronic structures of VAGNAs. Moreover, the quality of the PECVD-grown graphene sheets on Germanium substrate is further compared with the graphene grown on metal substrate fabricated using the standard CVD process.

**FF01.16.21**

**Shelf-Stable 2D MXene Nanosheets Enabled by Antioxidants**

Xiaofei Zhao, Touseef Habib, Aniruddh Vashisth,
Evan Prehn, Smit Alkesh Shah, Wanmei Sun, Yexiao Chen, Zeyi Tan, Jodie Lutkenhaus, Miladin Radovic and Micah J. Green; Texas A&M University, United States

MXenes, such as Ti$_3$C$_2$T$_x$ and V$_2$CT$_x$, are fascinating 2D nanomaterials with an attractive combination of functional properties suitable for applications such as batteries, supercapacitors, and sensors. However, fabrication of devices and functional coatings based on MXenes remains challenging as they are prone to oxidize and degrade quickly in a matter of days from reacting with water and dissolved oxygen. We examine the oxidation of Ti$_3$C$_2$T$_x$, MXene nanosheets in various media (air, water, organic solvents, and polymer composite) via multiple types of measurements to assess their shelf stability. The degree of MXene oxidation is found directly indicated by the property and structure changes such as electrical conductivity and the TiO$_2$ content which is detected by X-ray Photoelectron Spectroscopy. The oxidation rate of MXene nanosheets is observed fastest in liquid media and slowest in solid media and can be accelerated by exposure to UV light. More importantly, we demonstrate an effective method to arrest the oxidation of colloidal Ti$_3$C$_2$T$_x$ MXene nanosheets by introducing the antioxidants. The success of the method is evident as the MXene nanosheets maintain their composition, morphology, electrical conductivity, and colloidal stability. Even in the presence of water and oxygen, the electrical conductivity of Ti$_3$C$_2$T$_x$ nanosheets treated with antioxidants is orders of magnitude higher as compared to untreated ones after 21 days. The conductivity changes also reveal that the resistance to oxidation persists in the dehydrated MXenes as well. In addition, our study includes a ReaxFF molecular simulation performed to elucidate the mechanism for MXene-antioxidant interactions. Our findings have the potential to be generalized to protect more types of MXenes as well and solve the most pressing challenge in the field of MXene engineering.

**FF01.16.22**

**Catalyst-Free and Morphology-Controlled Growth of 2D Perovskite Nanowires for Polarized Light Detection**

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Two-dimensional (2D) perovskites or Ruddleson Popper (RP) perovskites have emerged as a class of material inheriting the superior optoelectronic properties of two different materials: perovskites and 2D materials. The large exciton binding energy and natural quantum well structure of 2D perovskite not only make these materials ideal platforms to study light-matter interactions, but also render them suitable for fabrication of various functional optoelectronic devices. Nanoscale structuring and morphology control have led to semiconductors with enhanced functionalities. For example, nanowires of semiconducting materials have been extensively used for important applications like lasing and sensing. Catalyst-assisted Vapor Liquid Solid (VLS) techniques, and template assisted growth, have conventionally been used for nanowire growth. However, catalyst and template-free scalable growth with morphology control of 2D perovskites have remained elusive. In this manuscript, we demonstrate a facile approach for morphology-controlled growth of high-quality nanowires of 2D perovskite, (BA)$_2$PbI$_4$. We demonstrate that the photoluminescence (PL) from the nanowires are highly polarized with a polarization ratio as large as ~0.73, which is one of the largest reported for perovskites. We further show that the photocurrent from the device based on the nanowire/graphene heterostructure is also sensitive to the polarization of the incident light with the photocurrent anisotropy ratio of ~3.62 (much larger than the previously reported best value of 2.68 for perovskite nanowires), thus demonstrating the potential of these nanowires as highly efficient photodetectors of polarized light.

**FF01.16.23**

**The Fabrication of CNT@MoS$_2$ Co-Axial Nanotube and Its Applications in Electrochemistry Field**

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Heterostructures among two-dimensional (2D) layered materials have attracted great interest due to their unique properties, and potential applications. And wrapping the 2D layered materials into one-dimensional nanotubes brings out opportunities in creating chiral tubular structures and radial heterojunctions, with more interesting functionalities and phenomena. Early efforts have focused on using a tubular template to confine the formation of another nanotube inside by capillary wetting method, such as PbI$_2$@WS$_2$ and PbI$_2$@CNT$^{[1,2]}$. But in those cases, the nanotube template ends must be open and a long-term thermal annealing process (up to 1 month) is usually carried out$^{[1]}$. For practical applications, it is more desired to have the target nanotube sitting outside the template and accessible to foreign environment.

As most of inorganic crystalline materials have rigid atomic planes, wrapping a conformal inorganic layer around
the outer surface of template (where spatial confinement is absent) turns to be rather difficult. Here, we report controlled fabrication of heterogeneous inorganic nanotubes consisting of a CNT core and crystalline MoS2 multishells with long-range continuity. Starting from a three-dimensional porous CNT sponge as template, we adopt a thiourea-assisted solvothermal method to deposit precursors and form the CNT@amorphous MoS2 structure at first. Then by high-temperature annealing process, the amorphous sheath is converted into highly crystalline multi-walled MoS2 nanotubes wrapping around individual CNTs throughout the sponge. The resulting core-shell CNT@MoS2 nanotube have a controllable layer number of outer MoS2 nanotube from 2 to 40 layers, by adjusting the precursor concentration during thiourea-thermal method. And such MoS2 nanotube shows increasing surface strain as the nanotube diameter decreasing. In this way, when used as oxygen reduction reaction (ORR) electrocatalyst, the heterogeneous inorganic nanotubes with thinner-walled (2~6 layers) MoS2 nanotube exhibits superior kinetics and lower overpotential. Besides, the stable hetero-nanotube structure endows CNT@MoS2 sponge with a specific capacity of 740 mAhg⁻¹ at 100 mAg⁻¹ and high cycling stability when used as a freestanding electrode for Li-ion batteries.


**FF01.16.24**

*Multiexciton and Excited States of Excitons in Monolayer MoS2 Observed Using Photoluminescence Spectroscopy*  
Juhi Pandey and Ajay Soni; Indian Institute of Technology Mandi, India

Two-dimensional semiconducting transition metal dichalcogenides (TMDCs) provides rich platform to study several interesting many body complexes such as excitons, trions, biexcitons and excitonic states for fundamental understanding and optoelectronic applications.¹,² Remarkably, strong Coulombic interaction with reduced dielectric screening effect in TMDCs makes experimental realization of such complexes even at room temperature which are otherwise observed at low temperatures. Further, similar to Hydrogen atoms, excitons exhibit excited states known as Rydberg states which are under scientific exploration and opens up new avenues for future quantum information processing, optoelectronic and photonics.³ Owing to weak signal from biexciton and excitonic Rydberg states in TMDCs, such complexes are less understood than excitons and trion. Further, the extent of spin orbit splitting of valence band due to d-orbital of transition metal plays an important role in observation of excitonic states. Large spin orbit splitting (> 400 meV) resulted in observation of series of Rydberg states of A exciton in ML of WS2 and WSe2 using several linear and non-linear spectroscopic techniques.⁴ On the contrary, the small spin orbit splitting ~ 150 meV in ML MoS2 provides an additional challenge in distinct realization of 2s state of A exciton (A₂s) because of the overlap with large spectral width of B exciton. Recently, A₂s state in ML MoS2 has been theoretically predicted and experimentally observed in ML MoS2 encapsulated by hBN ~ 2.1 eV using advance non-linear spectroscopic measurements.⁵ In our study, we performed temperature dependent photoluminescence (PL) studies up to 4 K to minimize spectral width of A and B excitons and accessed excitonic complexes as well Rydberg states. We discuss about the systematic observation of biexciton (~ 1.90 eV), sulfur vacancy mediated bound exciton (~ 1.90 eV), and A₂s state (~ 2.13 eV) distinct from A- trion (~ 1.92 eV), A exciton (~ 1.96 eV) and B exciton (~ 2.07 eV) in ML MoS2 using laser power dependent and temperature dependent PL spectroscopy from 4 K to 300 K. At low temperatures, the observed weak signal of excited state A₂s ultimately merges with spectral broadening of B exciton with raising temperatures.⁶ From the estimated binding energy of biexciton (~ 60 meV), we suggest that biexcitons can be stable even at room temperature.

**References**

Lateral Transition-Metal Dichalcogenide Heterostructures with Arbitrary Shapes and Band Alignments
Hossein Taghinejad1, Ali Eftekhar1, Xiang Zhang2, Sufei Shi3, Pulickel Ajayan2 and Ali Adibi1; 1Georgia Institute of Technology, United States; 2Rice University, United States; 3Rensselaer Polytechnic Institute, United States

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) with MX2 formula (M: transition metal, X: chalcogen) offer a plethora of opportunities for device engineering as well as fundamental studies. TMDs can exist in various crystalline phases including semiconducting and metallic. More importantly, the electronic bandgap of the semiconducting phase can be controlled via changing M or X elements, offering a digital portfolio of 2D materials for optoelectronic applications over a wide spectral range from visible to near infrared. In addition, this digital portfolio can be turned into an analog one through the alloying of 2D TMDs, [1, 2] a unique feature that enables the design of 2D materials with customized properties. Such a diversity of material properties renders 2D TMDs a family of unmatched qualities for the formation of heterostructures (HSs) via vertical stacking or lateral stitching of dissimilar TMDs. Unlike the diverse range of developed methods for the synthesis of vertical TMD HSs, the formation of lateral TMD HSs has been mostly limited to the edge-epitaxial growth in which a dissimilar TMD crystal (e.g., MX2) is grown on the unsaturated edge of a pre-grown TMD crystal (e.g., MX’2) to form a lateral HS (i.e., MX2-MX’2). [3] Despite the high-quality junctions, the edge-epitaxial method fails to provide a systematic control over the shape, lateral dimensions, and even the location of HSs, a set of features that are mandatory for the real-world applications.

Here we introduce an alternative method for the synthesis of lateral TMD HSs with highly controllable dimensions and shapes in predefined locations. Our method relies on combining the standard lithography with the post-growth alloying of TMDs [1] for converting a uniform MX2 monolayer into a MX2-MX’2 lateral heterostructure. We will show that the involvement of the lithography facilitates the control over the geometrical aspects of the HSs, and the post-growth alloying enables a full control over the electronic band alignment at the interface of the MX2-MX’2 HSs. Furthermore, using various spectroscopic characterizations and electrical measurements, we will demonstrate potentials of lateral TMD HSs for opto-electronic applications.


Electron Transport in Multi-Dimensional Fuzzy Graphene Nanostructures
Raghav Garg, Devashish Gopalan, Sergio de la Barrera, Thomas Nuhfer, Benjamin Hunt and Tzahi Cohen-Karni; Carnegie Mellon University, United States

Graphene, a two-dimensional (2D) allotrope of carbon, has exceptional surface-area-to-volume ratio (up to 2630 m² g⁻¹) and highly catalytic edges. To leverage these properties, efforts have been made to arrange graphene flakes in three-dimensional (3D) geometries with an eye towards integration into functional electronic devices. Electron transport mechanisms in 2D single-crystal graphene films have been extensively studied with relation to the material’s structure (e.g. edge termination, defect type and density, crystallinity, layer stacking and orientation). However, these mechanisms cannot be directly extrapolated to 3D polycrystalline nanostructures due to the added dimensionality and intricate morphology. Thus, integrating 3D arrangement of graphene flakes into functional electronic devices and developing fundamental understanding of electron transport in such structures remains an open challenge.

Here we report synthesis of a multi-dimensional graphene nanostructure: nanowire templated-3D fuzzy graphene (NT-3DFG), where each nanowire is composed of controlled 3D arrangement of graphene flakes free-standing on the surface of a one-dimensional (1D) silicon nanowire (SiNW). Such an arrangement exposes both surfaces of each graphene flake maximizing the surface-area-to-volume ratio and exposed edges. Free-standing graphene flakes form
a graphitic structure surrounding the SiNW core. Electron transport in NT-3DFG occurs through parallel channels formed by the graphitic shell (metallic transport) and the free-standing graphene (variable range hopping (VRH)). The material exhibits negative magnetoresistance from cryogenic conditions up to room temperature, which we attribute to a VRH-based interference mechanism distinct from weak localization. Our study opens new avenues for synthesizing and characterizing 3D arrangement of 2D materials to understand electron transport in multidimensional nanostructures.

**FF01.16.27**  
**Inkjet-Printed MXene/TMD Hybrid Films for Tunable Chemical Sensing at Room Temperature**  
Winston Y. Chen and Lia Stanciu; Purdue University, United States

Two-dimensional (2D) transition-metal carbides/nitrides (MXenes) have attracted great attention in energy storage and electrochemical applications because of their excellent electrical conductivity and flexible layered structures. 2D transition metal dichalcogenides (TMDs) are widely utilized in gas-sensing devices for the detection of NH₃, NO₂, H₂, and volatile organic compounds (VOCs) owing to their high specific surface area and tunable electronic structures. Therefore, hybridization of MXenes nanomaterials with TMDs, currently the main type of advanced sensing materials, is a promising approach to the manufacturing of low-cost, high-performance gas sensing devices. A wireless flexible gas sensor prepared by a simple fabrication process is appealing because it suits the needs of the internet of things (IoTs). We have been working on gas-sensing 2D materials by hybridization (and surface functionalization) of a given MXene, Ti₃C₂Tx, with a variety of TMDs (e.g., MoS₂, WSe₂). Herein, we report the results of using liquid phase exfoliation (LPE) and inkjet printing, both being the most promising cost-effective, mass-production methods, to synthesize a typical TMD/MXene nanohybrids, 2D MoS₂/Ti₃C₂Tx. The hybridization of MoS₂ and Ti₃C₂Tx films through surface modification and electrostatic interaction will be reported. The research results indicated that, even at room temperature, a MoS₂-decorated Ti₃C₂Tx gas sensor exhibited superior ability to detect extremely low concentrations (1 ppm) of VOCs, as compared to a pristine Ti₃C₂Tx (reference) sensor. Furthermore, the sensitivity of the MoS₂/Ti₃C₂Tx sensor is more than 10-fold higher than that of the pristine Ti₃C₂Tx sensor resulting from the synergetic effect of high electrical conductivity of Ti₃C₂Tx and high specific surface area of MoS₂ favoring gas adsorption. A variety of material analyzing methods will be used to elucidate the reasons behind the achievement of sensing performance by optimal decoration of MoS₂. For example, chemical bonding structures of MoS₂/Ti₃C₂Tx nanohybrids will be studied by X-ray photoelectron and Raman spectroscopies. Surface morphologies and microstructures of the hybrid materials will be analyzed by scanning electron microscopy and transmission electron microscopy.

**FF01.16.29**  
**Transferrable Ultra-Thin Organic Films for Molecular-Scale Interface Engineering**  
Shinyoung Choi, Nguyen Ngan Nguyen, Seong-Jun Yang, Kilwon Cho and Cheol-Joo Kim; Pohang University of Science and Technology (POSTECH), Korea (the Republic of)

Organic films with uniform, ultra-thin thickness can serve as building blocks to be assembled into more complex structures by sequential transfer processes. The approach provides organic interfaces engineered at the molecular-scale, which form the basis for discovery of novel organic materials and development of functional organic devices. However, transfer of such films often result in structural damages to the films, due to their weak mechanical strength. In addition, programmed organic interfaces easily deform by intermolecular diffusions. Here, we report several molecular thick C₆₀ and pentacene films with high spatial uniformity as prototypical electron acceptor and donor components, and transfer them layer-by-layer while maintaining structural integrity in the final structures. To obtain the structural stability, we integrate organic films with monolayer hexagonal boron films (ML-hBN), which act as both supporting layer for transfer and molecular diffusion blocking layer across organic interfaces. Layer-by-layer assembly of different organic films successfully generates composite films, including C₆₀/pentacene pn diode and C₆₀/pentacene vertical superlattice, where thickness and composition are modulated at the molecular-scale. Ultra-thin organic photodiodes and photoconductors have been demonstrated based on the precisely programmed organic interfaces and shown high performances.

**FF01.16.30**  
**Nanomechanical and Nanoelectrical Mappings of Buried Defects in Lateral and Vertical Van der Waals Heterostructures**  
Marta Mucientes¹, Yuzhou Zhao², Melinda J. Shearer², Robert J. Hamers², Song Jin² and Oleg V. Kolosov¹; ¹Lancaster University, United Kingdom; ²University of Wisconsin–Madison, United States
Two dimensional (2D) transition metal dichalcogenides (TMDs) have generated strong interest between a wide scientific audience due to the variety of promising applications for nanoelectronics, photonics, sensing, energy storage, and opto-electronics, to name a few. In particular, tungsten disulfide (WS₂), tungsten diselenide (WSe₂) and molybdenum disulfide (MoS₂), individually or their combination to form vertical and lateral heterostructures, present unique mechanical, electrical and optical properties, being exceptional candidates for the fabrication of opto-electronic devices. The physical properties of these structures are strongly dependent of the quality of the materials and presence of defects, limiting somehow the performance in devices.¹

We have studied the subsurface defects with diverse Scanning Probe Microscopies (SPM) based in the Atomic Force Microscopy (AFM). The combination of the AFM with ultrasonic excitation of the sample or/and the cantilever allow the mapping of the mechanical properties with nanoscale resolution – namely, Ultrasonic Force Microscopy (UFM), Waveguide UFM (W-UFM) and Heterodyne Force Microscopy (HFM), respectively.² Similarly, by the electrical excitation of the sample, we can probe the dielectric properties and materials work function, using Dielectric Electrostatic Force Microscopy (D-EFM) and Kelvin Probe Force Microscopy (KPFM).

The preliminary results of the top surface nanomechanical maps of vertical heterostructures of WS₂ and WSe₂ with pyramidal shape, show clear contrast corresponding to missing planes in the buried layers, subsurface mis-orientation of the crystallographic axis and edge dislocations. To complete the study, the pyramids have been sectioned with the Beam Exit Cross-sectional Polishing (BEXP) permitting the direct scanning of the inner part of the 3D structures, identifying the layers and revealing inhomogeneities in the layer stack via local mechanical and electrical properties mapping. For lateral heterostructures of WS₂ and MoS₂ we use nanomechanical maps to reveal the unique mechanical behaviour creating ripples at the interface of the two materials, likely corresponding with the strain produced by the lattice mismatch.³

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FF01.16.31
Double Flat Bands in Kagome Twisted Bilayers Eric Suarez¹, Roberto Hiroki Miwa² and Felipe Crasto de Lima²;
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We have studied theoretically how a generic bilayer kagome lattice behave upon layer rotation. Based on Density Functional theory calculations we developed a Tight Binding model with one orbital per site and found for low rotational angles and at low energies the same flat bands structure like in twisted bilayer graphene, moreover at high energies and due to the superstructure symmetry regions we found a characteristic three band dispersion of a kagome lattice, its width decreases for low angles confining them within a few meV, generating two sets of flat bands in different energy regions and localized in different spatial regions. The value of the magic angle is greater than in the rotated graphene bilayer which could result in a higher superconductivity temperature.

The kagome lattice arises in metal organic frameworks(MOF) where metals and organic ligands are the building blocks [1], a phenomenon as exotic as a quantum spin liquids was reported in spin 1/2 kagome-lattice antiferromagnet herbertsmithite[2].

Our tight binding parameters are based on a recent experimental measurement of a bilayer kagome compound Fe₃Sn₂ [3], the system is a soft ferromagnet with intrinsic anomalous Hall conductivity, the Dirac cones are separated by a gap of 30 meV as a consequence of the spin-orbit coupling.

One way to achieve larger magic angle is by increasing the relative value of the interlayer coupling, in MOF the effective coupling within the layer might be of the same order as the interlayer coupling, we explore also how this ratio might enhance the value of the angle at which the magic angle is obtained and eventually it might results in larger critical temperature.

PHONE:

Raman Micro-Spectroscopy with Integrated Rapid Temperature Control as a Characterization Tool for Studying Heterostructured Materials Craig Wall; Montana Instruments, United States

Tailoring 2D semiconductor heterostructures with specific bandgaps is a key aspect of leveraging new quantum materials for electronics and optoelectronics. The basic heterostructure assembly principle is simple: exfoliate, for example, a monolayer of MoS$_2$, put it on top of another mono- or few-layer crystal, c.a. WS$_2$, add another 2D crystal, and so on. The resulting heterostructure represents an artificial material assembled in a specified sequence with single layer precision, held together by van der Waals forces.

Raman micro-spectroscopy is used to characterize a variety of properties in 2D materials, including chemical, magnetic, electronic, symmetry, and layer orientation. Many interesting phenomena emerge across the 4K-500K temperature range. Often, new information about a sample can be obtained with temperature dependent measurements. We demonstrate efficient hyperspectral mapping of 2D materials with a micro-Raman spectroscopy and photoluminescence platform that maintains high spatial resolution and collection efficiency across the entire temperature range (4K – 525K). The system overcomes challenges associated with variable temperature sample drift by incorporating a low thermal mass sample stage, in-vacuum high NA objective, and coupling optics to a low astigmatism, broadband spectrograph.

The exciton recombination dynamics of stacked MoS$_2$-WS$_2$ heterostructures were previously studied at room temperature. The maximum of the valence band and the minimum of the conduction band are separated in the layers of WS$_2$ and MoS$_2$, respectively. The reported energy gap for MoS$_2$ is 2.39eV and for WS$_2$ is 2.31eV. The energy difference between the maximum valence bands of MoS$_2$ and WS$_2$ is about 350meV. Photoexcited free electron–hole pairs prefer to stay separated at layer interfaces. The excited electrons in WS$_2$ tend to accumulate in the conduction band of MoS$_2$ while holes generated in the valence band of MoS$_2$ tend to transfer to WS$_2$ at the interface. The interlayer radiative recombination of spatially separated carriers can lead to the extra peaks in the PL spectra. We observed the temperature dependence of the interlayer exciton in the hyperspectral mapping study which is at lower energy compared with pure monolayer MoS$_2$ and WS$_2$.

Growth of Nanorods of 2D Materials via a Novel Laser Treatment Technique Khaled Ibrahim, Inna Novodchuk, Kissan Mistry, Christopher Ling, Michael Singh, Michal Bajcsy, Joseph Sanderson, Mustafa Yavuz and Kevin Musselman; University of Waterloo, Canada

One-dimensional (1D) nanostructures such as nano-wires, -tubes, -rods and -fibers, have garnered great attention due to their excellent electrical, thermal, mechanical and optical properties and their suitability in a myriad of applications and devices. Applications of 1D nanostructures exist in solar cells$^{1,2}$, LEDs$^3$ and transparent conductors amongst other applications.

In this study, we demonstrate the previously unrealized ability to grow nanorods and nanotubes of 2D materials by femtosecond laser treatment of the respective flakes in solution. In as short as 20 mins, nanorods of tungsten disulfide, molybdenum disulfide, graphene, and boron nitride grow resulting in an up to 10-time increase in length. Due to the laser treatment, it was found that for some materials, notably the WS$_2$ particles reassemble to form new phases. Also resulting in the chemical modification of the nanorods with functional groups from the solvent atoms. The WS$_2$ untreated flakes are originally in the crystallographic 2H phase, the laser treatment reassemble and induces new primary bonds growing the particles into nanorods consisting of the 1T metallic crystallographic phase. Due to this transition, alongside the one-dimensional nature of the fabricated nanorods, the WS$_2$ nanorods display substantial improvements in electrical conductivity and optical transparency when employed as transparent conductors.

Room Temperature Magnetic Order in Air-Stable Ultra-Thin Iron Oxide

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Manual assembly of atomically thin materials into heterostructures with desirable electronic properties is an approach that holds great promise. Despite the rapid expansion of the family of ultra-thin materials, stackable and stable ferro/ferri magnets that are functional at room temperature are still out of reach. We report the growth of air-stable, transferable ultra-thin iron oxide crystals that exhibit magnetic order at room temperature. These crystals require no passivation and can be prepared by scalable and cost-effective chemical vapor deposition. We demonstrate that the bonding between iron oxide and its growth substrate is van der Waals-like, enabling us to remove the crystals from their growth substrate and prepare iron oxide/graphene heterostructures.

Defect Engineering in 2D Materials with Ion and Electron Beams

Paul Masih Das and Marija Drndic; University of Pennsylvania, United States

Large-scale manipulation and structural modifications of two-dimensional (2D) materials for nanoelectronic and nanofluidic applications remain obstacles to their industrial-scale implementation. Here, I will discuss how focused ion and electron beams can be utilized to engineer defects and tailor the atomic, optoelectronic, and structural properties of monolayer and heterostructure 2D materials such as graphene, phosphorene, hexagonal boron nitride, and various transition metal dichalcogenides (TMDs). A combination of aberration-corrected scanning transmission electron microscopy (AC-STEM), Raman spectroscopy, photoluminescence spectroscopy, and density functional theory (DFT) is used to study the characteristics of 0-dimensional (0D) defects and other low-dimensional nanostructures such as nanoribbons, antidot arrays, and nanoporous membranes. The results shown here lend the way to the scalable fabrication and processing of 2D nanodevices.

Large-Area Multiplexed Graphene Sensors for Detection of Ions in Electrolyte

Mantian Xue, Charles Mackin, Yiyue Luo and Tomas Palacios; Massachusetts Institute of Technology, United States

Graphene, an atomically thin material, is an excellent candidate for next generation sensing platform thanks to its unique electrical, optical, mechanical and chemical properties. Its all-surface structure gives it high sensitivity to the environment. However, it also makes graphene-based devices very sensitive to fabrication process. Small differences in graphene quality, such as surface contamination and defects, can lead to large variation in device behavior.

In this work, we developed a graphene-based sensor array functionalized with ion selective membranes (ISMs) that enables us to measure ion concentration in an electrolyte. With more than 200 functional devices per array, the system is able to detect ion concentration spanning over several orders of magnitude with a near-ideal Nernstian sensitivity, excellent selectivity, high reversibility and fast response time. The intrinsic variability in 2D material based sensor performance can be greatly mitigated by taking advantage of the large sample size and utilizing the redundancy in device response. Sensor redundancy helps to tight the 95% confidence intervals from ±50% to ±10%, while the reversibility can be increased from less than 80% to almost 95%.

This work uses an ion-selective functionalization based on a polyvinyl chloride based membrane with ionophores targeting specific ions, such as calcium, sodium and potassium. We chose these ions because their physiological importance. A material jetting 3D printer is used to print the ISMs with accurate control of the size and location. Several different ISMs can be deposited onto different regions of the sensing array, which allows for a multiplexed sensor array. By using statistical analysis techniques we are able to measure the concentration of each target ion within a complex background of interfering ions.

In summary, we developed a novel sensor platform that can simultaneously measure over 200 graphene-based multiplexed sensors to characterize the concentration of sodium, calcium and potassium ions in aqueous phase.
collecting data from a statistically significant sample size, this work presents a manufacturable and reliable technology that can be employed for a wide range of physiologic monitoring applications.

**FF01.16.37**
*Toward Disorder-Free Growth of Thin Metal Films on Graphene by Magnetron Sputtering*

Nikolaos Platsikas1, Olle Andersson1, John Arvanitidis2, Dimitrios Christofilos2, Ivan Shtepliuk1, Ivan G. Ivanov1, Rositsa Yakimova1 and Kostas Sarakinos1; 1Linköping University, Sweden; 2Aristotle University of Thessaloniki, Greece

Deposition of metal contacts on graphene is a crucial step for the fabrication of a wide array of novel optoelectronic and sensing devices. Magnetron sputtering is a state-of-the-art versatile technique for large-scale thin metal film synthesis. However, its inherent tendency for generating energetic species (both neutrals and ions) that cause ballistic defects and disorder on the surface upon which they form a film, renders sputtering incompatible with processes where graphene is used as substrate. The objective of this study is to establish the effect of sputtering conditions, during growth of thin Ag films, on the structure and electronic properties of graphene. Films are grown on monolayer graphene synthesized by SiC sublimation of C-face 4H-SiC and by CVD deposition on Cu foils. We use top-view SEM from which we establish that the produced Ag films exhibit a pronounced 3D growth morphology that can be attributed to the weak interaction between Ag atoms and graphene. We also employ micro-Raman spectroscopy and define the graphene crystalline quality and the point-defect density as a function of the deposition parameters. The energetic sputtered species cause disorder, evidenced by the appearance of the defect-related D-band and inhomogeneous broadening of the characteristic Raman peaks due to charge and local strain fluctuations. We also find that the effect of the energetic deposition flux on the pristine graphene structure and electronic properties becomes less pronounced with increasing sputtering pressure. These findings suggest that it may be possible to facilitate disorder-free growth of thin metal films on graphene by magnetron sputtering if deposition parameters (e.g., sputtering pressure, target-to-substrate distance, magnetic field configuration) are carefully adjusted in a way that minimizes the energetic input from the sputtering flux to the growing surface.

**FF01.16.38**
*First-Principle Investigation of Twisted Black Phosphorus*

Minwoong Joe, Yisehak Gebredingle and Changgu Lee; Sungkyunkwan University, Korea (the Republic of)

Black phosphorus is an intriguing material with intrinsic anisotropy induced by its unique puckered honeycomb structure. In bilayer or multi-layer black phosphorus, the system's anisotropy as a whole can be tuned by an interlayer twist angle, and thereby the material's electronic, optical, and mechanical properties. Thus, we here try to investigate the effect of interlayer twist angles or stacking orientations on twisted black phosphorus using first-principles calculations. The effects of twist angle on its band structure, phonon dispersion, mechanical property, etc. are presented. We discuss the mechanism of controlling electronic structures by twisting layers, and also, an effective way to handle the long-range Moire superlattice induced by incommensurate lattices in an arbitrary twist angle.

**FF01.16.39**
*Strain Engineering of 2D Materials for Integrated Photonic Devices*

Rishi Maiti, Chandraman Patil, Ti Xie, Haoyan Kang and Sorger Volker; George Washington University, United States

Triggered by the demands for high-performance computing requires much higher bandwidth density for inter-chip communication pushes the limit of device miniaturization. Hence, 2-dimensional (2D) materials have recently emerged as promising building blocks for photonics due to their number of fascinating features. Tuning of electronic and optical properties by engineering local strain is an exciting avenue for tailoring performance for 2D materials based integrated photonic device. Besides, continuous tuning of the strain, the ability to apply a spatially controllable strain by using a patterned substrate is even more crucial because it enables the realization of a graded bandgap semiconductor for the photonic integrated device. Here, we study the effect of large localized strain in the electronic band structure of a multilayer MoTe₂ by wrapping the 2D material around a non-planarized Silicon-on-insulator waveguide etched down to the buried oxide. Interestingly, induced tensile strain (4%) shifts the bandgap of MoTe₂ by about 0.8 eV obtained using DFT calculation, thus significantly increasing the absorption as compared to their pristine counterpart of bandgap (~1 eV). Here, the device is realized in a two-terminal in-plane electrode configuration without applying external gating, showing a high responsivity of (~0.5 A/W) and NEP of 90 pW/Hz0.5 at -2 V at 1550 nm. Our device demonstrates a response rate of ~35 MHz which is limited by the low
mobility (~1 cm²/Vs) of the MoTe₂. The integration of a few-layer MoTe₂ on Si MRR as active photodetector is envisaged to offer a potential pathway toward the realization of integrated on-chip interconnects for Telecommunication band.

**FF01.16.40**

**Enhanced Carrier Transport of MoS₂ through Metal-Semiconductor Interface Decorated by Monolayer h-BN**

Hemendra Nath Jaiswal¹, Maomao Liu², Simran Shahi², Sichen Wei¹, Fei Yao¹ and Huamin Li²; ¹University at Buffalo, United States; ²University at Buffalo, The State University of New York, United States

Two-dimensional (2D) monolayer molybdenum disulfide (MoS₂) has been demonstrated as an excellent semiconductor material for future nanoelectronics because of the suitable bandgap, good intrinsic mobility, thermal velocity, and mean free path etc. To fully explore the potential of monolayer MoS₂ for practical applications such as field-effect transistors, memories, photo-sensors, and solar cells, there is a critical need of metal-semiconductor contact engineering and optimization which can lead to the maximization of device performance. In this work, we exploited 2D monolayer hexagonal boron nitride (h-BN) as a decorating layer at the metal-MoS₂ interface, and demonstrated a significant improvement of the carrier transport through a quantum tunneling effect. Both monolayer MoS₂ and h-BN were synthesized by using two-zone chemical vapor deposition (CVD) method. The triangular domains of monolayer MoS₂ were synthesized directly on SiO₂/Si substrates and the continuous monolayer h-BN film was grown on copper foils. The field-effect transistor (FET) and transmission line measurement (TLM) devices were fabricated using electron beam lithography (EBL) and evaporation (10 nm Ti and 100 nm Au). Compared to the conventional MoS₂/Ti/Au contact where the thermionic emission is the dominating mechanism, the MoS₂/h-BN/Ti/Au contact shows the outstanding improvement of the carrier transport. For example, the on-current density was increased by two orders of magnitude, and the electron mobility was improved by ten times. These improvements can be attributed to the dominance of the quantum tunneling when the monolayer h-BN is inserted at the metal-semiconductor interface. Based on the temperature-dependent measurement, a lowering of the effective metal-semiconductor barrier height from ~60 to ~30 meV was induced by the monolayer h-BN decoration, and the reduction of the contact resistance was confirmed by the TLM technique. Our work has demonstrated the great potential of this novel contact engineering technique using the 2D monolayer insulator, which can be applied to other 2D materials and devices for broad applications.

**FF01.16.41**

**Asymmetry Behaviors on Bias Temperature Stress Instability of Multi-Layered MoS₂ FETs and Their Understanding via Extraction of Subgap Density-of-States**

Seung Gi Seo¹, Jin Heon Jeong¹, Seung Yeob Kim¹, Young Jun Byeon¹, Sungju Choi², Dae Hwan Kim² and Sung Hun Jin¹; ¹Incheon National University, Korea (the Republic of); ²Kookmin University, Korea (the Republic of)

For the newly emerging IoT sensors and display applications, low dimensional semiconductors such transition metal dichalcogenides (TMDs) can be one of appealing candidates beyond graphene because of their excellent electrical-switching-characteristics, together with novel mechanical, and optical properties. Among them, molybdenum disulfide (MoS₂) has been regarded as one of the most promising materials. Until to this date, in-depth knowledge on MoS₂ FETs in terms of electrical performance improvement, transport mechanism, back channel effects, etc have been accumulated through tremendous research activities. However, device reliability studies on MoS₂ FETs have been limitedly reported. Thus, systematic investigation on device instability of MoS₂ FETs under DC and pulsed mode operation and its comparison on instability behaviors, followed by understanding on the behind mechanism, are highly necessary in order to apply TMD FETs to next-generation display platforms which are required for ultra-high definition, mechanical flexibility, electrical stability, and others. Furthermore, for a quantitative understanding on gas adsorption effects on electrical performance of MoS₂ FETs, which are regarded as one of main factors for instability of TMDs, information on subgap density of states (DOS) in MoS₂ layers without (or with) hydrophobic polymer (CYTOP) encapsulation is one of pre-requisite parameters. On the other hand, in a recent past, trap information on MoS₂ FETs has been quantitatively analyzed by several techniques, whereas the previous reports for characterization of sub-gap traps for m-MoS₂ FETs were limitedly addressed; (i) Dₜ characterization via Terman method, (ii) shallow traps nearby conduction band (Eᵥ) via multi-frequency method, and (iii) deep level traps through hysteretic gate transfer characteristics, thereby entire characterization for sub-gap DOS was fundamentally limited by method itself and its characterization.

In this study, we investigated into device instability of MoS₂ FETs associated with series of key parameters such as
bias polarity, temperature, duty cycles, bias amplitude, and others. Asymmetry behaviors on bias stress instability under DC and pulsed mode operation were reproducibly observed and their mechanisms were systematically analyzed by using frame time dependency in pulsed mode operation, rationally supported by atomic and band models. Moreover, quantitative analysis on subgap states for MoS2 FETs before and after CYTOP encapsulation were performed by using optical charge-pumping capacitance-voltage spectroscopy. Based on extracted subgap DOS and their deconvolution with analytical model of acceptor (or donor) like states, all electrical parameters were systematically analyzed. Two times increase of field effect mobility ($\mu_F$) are strongly related with decrease of shallow-donor states ($N_{SD}$). In addition, significant improvement of subthreshold swing (SS) and hysteresis gap ($V_{HYST}$) are attributed to the reduction of tail states ($N_{TA}$), along with decrease in mid-gap states ($N_{MD}$). All systematic results in this work are highly anticipated to contribute to the understanding on device instability issues which are required for fulfilling the envisioned applications.

**FF01.16.42**

**Electronical Tuning of Complex Reflectivity with Graphene-Based Metasurface** Sangjun Han, Junhyeong Kim, Ju Young Kim, Juho Park and Min Seok Jang; KAIST, Korea (the Republic of)

In this work, we design a graphene-based metasurface for independent active modulation of amplitude and phase of mid-infrared light. This independent control over the phase and amplitude can be obtained by applying the alternating voltage to the two consecutive units of periodic graphene-gold multiscale structures (meta-atoms). In complex reflectivity plane, we are able to cover a large area of unit complex reflectivity square by only controlling the values of graphene Fermi energy in each set of meta-atoms.

The proposed structure can be analyzed with an effective surface admittance model [1]. For general multiscale structure with back-reflector, it is known that the reflectivity $r$ and the effective admittance of the metasurface $Y_S$ are related as

$$r = \frac{-Y_{Sub} - Y_0}{Y_{Sub} + Y_0 + Y_S},$$

where $Y_{Sub}$ and $Y_0$ are the admittance of the substrate and vacuum, respectively [1]. In this structure of alternating meta-atoms, the admittance of the pair (meta-molecule) is a serial connection of the half-admittances of each meta-atom $Y_{SI}$ and $Y_{S2}$: $Y_S = 2Y_{SI}Y_{S2}/(Y_{SI} + Y_{S2})$. The admittance of each meta-atom is predicted by a circuit model. The circuit model represents the effective conductivity of the meta-atom as a function of its structural parameters by taking the elements constituting the metasurface as corresponding circuit elements, and then calculating the admittance of the circuit connecting the elements. The gold bars array is represented by a serial connection of inductances and capacitances with the geometrical parameter of bars and slits. The array of graphene ribbons placed between the gold bars is treated with the effective admittance of the free-standing graphene ribbon array multiplied by the gain factor $P/g$, corresponding to the electric field amplification in the gap. In this way, we can approach the complex reflectivity of the metasurface from the viewpoint of its structural parameters, and optimize the whole structure. Further, by inducing the appropriate Fermi energy independently to each meta-atom of the metasurface, the reflected wavefront can be controlled in arbitrary manner (e.g. dynamic beam steering, focusing etc.)


**FF01.16.43**

**One-Dimensional MoS2NT-SWCNT van der Waals Heterostructures as Efficient Hole Transport Layer in Perovskite Solar Cells** Yang Qian1, Seungju Seo1, Haosheng Lin1, Yongjia Zheng1, Esko Kaupinnen2, Jing Kong3, Rong Xiang1, Il Jeon1, Yutaka Matsuo1,4 and Shigeo Maruyama1,5; 1The University of Tokyo, Japan; 2Aalto University, Finland; 3Massachusetts Institute of Technology, United States; 4Nagoya University, Japan; 5National Institute of Advanced Industrial Science and Technology, Japan

MoS2, along with other transition metal dichalcogenides (TMDCs) nanomaterials, have been demonstrated to be effective in photovoltaic (PV) devices with various functions and structures. Interestingly, the TMDC-based electronic devices can be either vertical or lateral, showing the potential of fabricating TMDC-based PV devices with different dimensionality. Recently, we have synthesized a new class of 1-dimensional (1D) van der Waals (vdW) heterostructures by chemical vapor deposition, in which MoS2 nanotube (MoS2NT) is wrapping around single-walled carbon nanotubes (SWCNT) to form a MoS2NT-SWCNT interface [1]. The application of this kind of 1D vdW heterostructures can allow us to fabricate PV devices with 1D dimensionality. In this research, we demonstrate the excellent hole-extraction ability of MoS2NT by applying MoS2NT-SWCNT to normal-type perovskite solar cells. The as-synthesized MoS2NT-SWCNT functions as both the hole transport layer...
and anode at the same time. Comparing with SWCNT, the wrapping of MoS$_2$NT around SWCNT improved the power conversion efficiency (PCE) by almost 20%, owing to the substantial enhancement of the fill factor. A PCE of 15.0% has been achieved after the application of spiro-MeOTAD. The 1D vdW heterostructures are beneficial by a closer physical distance between layers for a better hole-transport ability than 2D vdW heterostructures. In addition, the integration of different materials in one substance can also allow easier fabrication than layer-stacking, and thus reduce the size of the device and the amount of used materials. The successful application of MoS$_2$NT-SWCNT in perovskite solar cells are expected to ignite the application of 1D vdW heterostructures, as well as the application of SWCNT and TMDC based nanomaterials in PV devices.


SESSION FF01.17: Application of Contacts to 2D Materials
Session Chairs: Olga Kazakova and Hyeon Jin Shin
Thursday Morning, December 5, 2019
Hynes, Level 3, Room 312

8:00 AM FF01.17.01
Fabrication of 2D Lateral Metal/Semiconductor Junction via Selective Synthetic Integration of Transition-Metal-Carbide/Transition-Metal-Dichalcogenide Haeju Choi$^{1}$, Seunghyuk Choi$^{1}$, Chaeyeon Shin$^{1}$, Jaeho Jeon$^{1}$, Jin-Hong Park$^{1}$ and Sungjoo Lee$^{1,2}$; $^{1}$Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); $^{2}$Sungkyunkwan University, Korea (the Republic of)

For real implementation of 2D material-based nanoscale device integration, the construction of a manufacturable and highly stable metal/semiconductor building block is critically required. To develop practical 2D material-based electronic and photonic devices, the formation of 2D lateral metal/semiconductor junction structures can overcome fundamental technical obstacles such as high contact resistance and limitation of channel length scaling via conventional vertical junction structures. However, a formation method of large-scale 2D lateral metal/semiconductor junction structure with sufficient levels of controllability and quality has not been demonstrated. We herein propose the formation of a scalable 2D metal/semiconductor Mo$_2$C/MoS$_2$ lateral junction structure fabricated via selective synthetic integration of large-scale metal (Mo$_2$C)/semiconductor (MoS$_2$) junction. We demonstrate that centimeter-scale metallic 2D MXene (Mo$_2$C) can be synthesized from CVD-grown few-layer MoS$_2$ with chemical conversion using CH$_4$ and Cu catalyst. Further, a dimension-controlled Mo$_2$C/MoS$_2$ junction is fabricated by depositing a lithographically patterned SiO$_2$ masking layer. Results show that while chemical conversion to Mo$_2$C occurs in the uncovered MoS$_2$ part, the MoS$_2$ layer under the SiO$_2$ masking layer is protected from chemical conversion so that a scalable Mo$_2$C/MoS$_2$ heterostructure is integrated down to the nanometer scale, exhibiting excellent resistance of contact resistance of 2.1 kΩ μm. This proposed manufacturable and highly stable 2D material-integrated metal/semiconductor junction structure will provide a scalable building block for the implementation of 2D material-based nanoscale device integration.

8:15 AM FF01.17.02
Heterostructured Contacts to MoS$_2$ Enhance the Catalytic Efficiency of Hydrogen Production Joshua Pondick$^{1,2}$, Yu Zhou$^{1,2}$, Jose Silva$^{3}$, John M. Woods$^{1,2}$, David J. Hynek$^{1,2}$, Grace Matthews$^4$, Xin Shen$^{1,2}$, Barbara Brenna$^{5}$, Shu Hu$^{1,2}$, Moyses Araujo$^{3}$ and Judy Cha$^{1,2}$; $^{1}$Yale University, United States; $^{2}$Yale West Campus, United States; $^{3}$Uppsala University, Sweden; $^{4}$North Carolina State University, United States

Two-dimensional (2D) nanostructured transition metal dichalcogenides (TMDs) are promising candidates for catalyzing the hydrogen evolution reaction (HER). However, even though the free energy of hydrogen adsorption ($\Delta G_{\text{H}}$) is close to zero for many TMDs, experimental catalytic efficiencies have consistently fallen short of thermodynamic predictions. In order to investigate this disparity, the effect of the support substrate on the MoS$_2$-catalyzed HER was investigated. It has been demonstrated that both heterostructured contacts and the support
substrate can modulate the MoS$_2$-catalyzed HER, but it is difficult to isolate and identify the specific interfacial effects that influence the catalytic efficiency. To address this challenge, we utilized an electrochemical microreactor capable of isolating individual interfacial effects to probe the catalytic efficiencies of MoS$_2$ [1]. We show that heterostructured supports enhance the HER activity of monolayer MoS$_2$ [2]. This talk will examine two possible mechanisms to explain the modulation of the HER activities. The first mechanism is that highly conductive support substrates are better than dielectric substrates because they can effectively screen mirror charges that may form during HER. Indeed, MoS$_2$-WTe$_2$ and MoS$_2$-graphene heterostructures consistently outperformed MoS$_2$ supported on SiO$_2$ in agreement with our expectation. To further probe this mechanism, we placed MoS$_2$ on substrates with dielectric constants ranging from 4 to 300. The catalytic efficiency of MoS$_2$ decreased with increasing dielectric constant, supporting the idea that mirror charges can inhibit hydrogen production. However, the effect of substrates was proven minor compared to the effect of contact metals. Devices with Ni-graphite contacts significantly outperformed devices with Cr-graphite contacts regardless of the support dielectric constant. This suggests that the catalytic efficiency is largely determined by the second mechanism: charge injection. We attribute the increased activity of the Ni devices to lower contact resistance for electrons at the Ni-graphite interface than through the Cr-graphite interface. Thus, the enhanced HER from the MoS$_2$-WTe$_2$ and MoS$_2$-graphene heterostructures is attributed to the efficient charge injection into MoS$_2$ through large-area heterojunctions.

These results demonstrate the importance of interfacial design in TMD HER catalysts. The microreactor platform presents an unambiguous approach to probe interfacial effects in various electrocatalytic reactions.


**8:30 AM FF01.17.03**

**Conformal Wafer-Scale Formation of Patterned van der Waals (W, Mo)Te$_2$ Electrodes with Ideal Schottky Barriers**

Seunguk Song$^1$, Yeoseon Sim$^1$, Se-Yang Kim$^1$, Jung Hwa Kim$^1$, Inseon Oh$^1$, Woong Ki Na$^1$, Do Hee Lee$^1$, Jaewon Wang$^1$, Jinsung Kwak$^1$, Hyeonsik Cheong$^2$, Jung-Woo Yoo$^1$, Zonghoon Lee$^2$ and Soon-Yong Kwon$^1$; $^1$Ulsan National Institute of Science and Technology, Korea (the Republic of); $^2$Sogang University, Korea (the Republic of)

Beyond the silicon and compound semiconductor industries, two-dimensional van der Waals (2D vdW) materials have been predicted to be able to revolutionize electronics, photonics, and other industrial sectors since they possess many fascinating physical and electrical properties. However, 2D materials currently face challenges along the long-term road to commercialization, with increasing efforts being made to satisfy industrial needs. At this moment, the most critical issue for final 2D device performance is related to realizing good electrical contacts to 2D vdW semiconductors. In fact, most 3D (bulk) metals form non-Ohmic Schottky junctions to 2D vdW semiconductors, resulting in relatively high and bias-dependent contact resistances. Furthermore, the Fermi level at the metal-semiconductor junction (MSJ) is often pinned owing to several types of chemical interactions, and the Schottky-Mott rule generally provides incorrect prediction for the Schottky barrier height (SBH).

In this study, we not only performed the wafer-scale production of patterned transition metal (TM) ditellurides (e.g., WTe$_2$ or MoTe$_2$) on desired surfaces and positions with high electrical performance but also demonstrated the experimental formation of monolayer MoS$_2$ FETs containing 2D WTe$_2$/MoS$_2$ vdW MSJs with almost perfect interfaces. We have designed simple and efficient methods to grow high-quality, stoichiometric TM ditellurides with electrical performances comparable to those of mechanically exfoliated flakes. The fabricated 2D (W, Mo)Te$_2$/monolayer MoS$_2$ vdW MSJs with close-to-perfect interfaces are free from significant disorder effects and Fermi level pinning on the interface, and their SBHs largely follow the trend of the Schottky-Mott limit. For example, the measured SBH ($\approx$103.5 meV) of the WTe$_2$/MoS$_2$ interface was the lowest value experimentally observed for metal electrodes formed on monolayer MoS$_2$ and was very close to the theoretical value ($\approx$100 meV) calculated by the Schottky–Mott rule. Compared to the MSJs with conventional 3D metals, the fabricated 2D WTe$_2$/MoS$_2$ vdW MSJs exhibited a much improved electrical injection across the MSJs, which was attributed to the low SBH and depinning of the Fermi level at the interface. Employing position-controlled, patterned vdW contacts with ideal Schottky barriers provides the advantage of controlling the SBHs in a predictable manner. This ability to fabricate position-controlled, conformal vdW metals with different shapes affords new possibilities for the fabrication of multiple 2D nanoelectronics devices.
8:45 AM FF01.17.04
A New Metal Transfer Process for van der Waals Contacts to Vertical Schottky-Junction Transition Metal Dichalcogenide Photovoltaics Cora Went, Joeson Wong, Phillip Jahelka, Michael Kelzenberg, Souvik Biswas and Harry A. Atwater; California Institute of Technology, United States

Two-dimensional transition metal dichalcogenides are promising candidates for ultrathin optoelectronic devices due to their high absorption coefficients and intrinsically passivated surfaces. To maintain these near-perfect surfaces, recent research has focused on fabricating van der Waals contacts that limit Fermi-level pinning at the metal-semiconductor interface. Here, we develop a new, simple procedure for transferring metal contacts that does not require aligned lithography. Using this technique, we fabricate vertical Schottky-junction WS2 solar cells with template-stripped Ag bottom contacts, 15-nm-thick exfoliated WS2 absorber layers, and 20-nm-thick semitransparent Au transferred top contacts. Under laser illumination, we observe rectifying behavior and open-circuit voltage above 500 mV in devices with transferred contacts, in contrast to resistive behavior and open-circuit voltage below 15 mV in devices with evaporated contacts. Under one-sun illumination, we measure an open-circuit voltage of 256 mV, a short-circuit current density of 4.10 mA/cm², and a fill factor of 0.44. We calculate a power conversion efficiency of 0.46%, comparable to what others have observed in ultrathin transition metal dichalcogenide photovoltaics. Guided by device simulations that predict power conversion efficiencies close to 9%, we fabricate and characterize further-optimized devices with transparent top contacts and metal work functions that are better aligned to the multilayer WS2 conduction and valence bands. Our one-sun measurements and device simulation results indicate that this metal transfer process could enable high-specific-power vertical Schottky-junction transition metal dichalcogenide photovoltaics, and we anticipate that this technique will lead to advances for two-dimensional devices more broadly.

References:

9:00 AM FF01.17.05
Ultra Clean van der Waals Contacts Using Indium Alloys on Two-Dimensional Semiconductors Manish Chhowalla; University of Cambridge, United Kingdom

We recently reported the realization of ultra-clean vdW contacts between three dimensional metals and single layer MoS2. Using scanning transmission electron microscopy (STEM) imaging, we show that the 3D metal and 2D MoS2 interface is atomically sharp with no detectable chemical interaction, suggesting van-der-Waals-type bonding between the metal and MoS2. We show that the contact resistance of indium electrodes is ~ 800 Ω-μm – amongst the lowest observed for metal electrodes on MoS2 and is translated into high performance FETs with mobility in excess of 160 cm²-V-s⁻¹ at room temperature without encapsulation. We have extended this work to other monolayer 2D semiconductors such as MoSe2, WSe2 and their p-n interfaces. We have also studied alloying of indium contacts with other metals to engineer the work function of the electrodes for facile electron and hole injection. I will describe our efforts on making good contacts on 2D semiconductors.

9:30 AM BREAK
The Solution to the Solution—Colloidal Suspension of 3D Architectures of 2D Materials Jennifer G. DiStefano and Vinayak Dravid; Northwestern University, United States

For years, solution processing has enabled researchers to employ transition metal dichalcogenides (TMDs) in fields not accessible with traditional solid-state routes and rigid substrates. Scalable synthesis and exfoliation, chemical functionalization, and hybridization are particularly promising advantages of solution-based methods for TMDs. Colloidal suspension allows for facile assembly of TMDs, often of a desired size and thickness, onto arbitrary substrates. Exploratory biomedical applications, from diagnostics to therapy, have benefited from this unprecedented access to 2D semiconductors in solution and resultant functionalization possibilities. Solution-based hybridization between TMDs and complementary materials has enabled developments in electrocatalysis, sensing, and battery technologies, demonstrating the true breadth of diverse fields these techniques can impact. However, some of the most interesting TMD structures, including heterostructures, are barred from these modification and assembly opportunities because existing solution-based synthesis and exfoliation approaches are not compatible with complex geometries. Here we introduce a platform to successfully transfer artificial two-dimensional heterostructures synthesized with solid-state deposition to an aqueous solution. This essential transfer generates a stable solution where heterostructures can be functionalized for a variety of new applications or transferred to other substrates to create hierarchical assemblies.

Recently, we reported unique nanoparticle@TMD core-shell architectures (e.g. Au@MoS$_2$) and demonstrated their promising properties for electrocatalysis and optoelectronic devices. Subsequently, we have developed an approach to synthesize TMD core-shell heterostructures and utilize Au nanoparticles as functional vehicles to transfer these unusual structures into solution. We use a metal sulfurization process to synthesize Au@MoS$_2$@WS$_2$ structures on rigid substrates. High-resolution electron microscopy and Raman spectroscopy confirm the complete conversion to MoS$_2$ and WS$_2$ and high crystallinity of the TMDs. We then suspend these particles in water and demonstrate MoS$_2$/WS$_2$ heterostructures in solution. These core-shell heterostructures exhibit exceptional natural stability and monodispersity in solution, making them viable in many applications. Additionally, we leverage this colloidal suspension to chemically functionalize the core-shell particles and further expand application opportunities.

This presentation will also cover two of the broad future avenues enabled by this research approach. On one hand, the solution of core-shell particles itself can be employed via chemical functionalization or hybridization with other functional materials. For instance, biomedicine is one particularly ripe area for this application. These particles could be functionalized to carry chemotherapy drugs, or the TMD/plasmonic Au core hybrid could be leveraged for photothermal cancer treatment. On the other hand, this new platform allows one to conveniently transfer the particles to any substrate, including flexible substrates incompatible with high temperature synthesis. Directed assembly into artificial lattices or unique patterns will be achievable to fully exploit the interplay between the heterostructure shell and plasmonic core. Thus, by introducing a broad platform to create colloidal suspensions of artificial structures, this work opens the door for advanced engineering and utilization of TMD heterostructures.

10:15 AM *FF01.18.02
3D Printed Microsupercapacitors from 2D Material Inks Cecilia Mattevi; Imperial College London, United Kingdom

Miniaturization over three-dimensions is very attractive for future on-chip technologies where device efficiencies need to be optimized over small footprints. This is a new challenge, as device miniaturization has been focused to achieve planar-geometries primarily.

Direct Ink Writing (Robocasting), is an additive manufacturing technique that brings the possibility of fabricating architectures with programmable design in the three-dimensions (3D) at different length scales. Here, we demonstrate 3D printed electrodes for microsupercapacitors and energy conversion systems from highly concentrated, water-based 2D atomically thin material inks using robocasting. The inks are composed by highly concentrated atomically thin sheets of transition metal chalcogenides either exfoliated from bulk powders or obtained via direct synthesis in solution. By tailoring the rheology of our formulated inks, printability has been achieved along with mechanical robustness of the printed architectures.

The printed architectures, from woodpile to interdigitated electrodes, are extended over a few mm in the three-dimensions and present electrodes widths as small as 100 μm. The 3D printed microsupercapacitors show leading areal capacitance and energy density as compared to planar microsupercapacitors, and stability in different electrolytes.
All-Printed Heterostructure Devices Made with Water-Based and Biocompatible 2D-Inks
Cinzia Casiraghi; University of Manchester, United Kingdom

Solution processing of 2D materials [1] allows simple and low-cost techniques such as inkjet printing [2,3] to be used for fabrication of heterostructure of arbitrary complexity. However, the success of this technology is determined by the nature and quality of the inks used. Furthermore, these formulations must be suitable for all-inkjet printed heterostructure fabrication - the remixing of different 2D crystal gives rise to uncontrolled interfaces, resulting in poor performance and lack of reproducibility of the devices. In this work we show a general formulation engineering approach to achieve highly concentrated, and inkjet printable water-based 2D crystal formulations, which also provide optimal film formation for multi-stack fabrication [4]. Examples of all-inkjet printed heterostructures, such as arrays of photosensors [4], logic memory devices [4], capacitors [5] and transistors [5, 6] will be discussed.


Towards Large Scale Manufacturability of (Mostly) Electronic Devices with 2D Materials
Juliana Radu, Inge Asselberghs, Cedric Huyghebaert, Dennis Lin, Benjamin Groeven, Steven Brems, Devin Verreck, Quentin Smets, Tom Schram, Goutham Arutchelvan and Surajit Sutar; imec, Belgium

2D materials hold the promise for many interesting applications in electronics. In this talk, we will evaluate their potential towards continued transistor scaling and provide materials targets which enable device performance comparable or surpassing that of scaled Si transistors. While transistor scaling for digital applications is the most coveted for application, MX2 materials have lower mobility than Si when deposited on wafer. Other applications in electronic circuits which do not require very high mobility have to be considered. We will approach this from the perspective of system and device co-optimization and discuss possible applications which require transits with very low leakage.

At imec, we are building a 300mm-wafer platform 2D materials which is being used to assess experimentally the manufacturability of devices with MX2 channel. In this context, we have demonstrated full-wafer (300mm) growth of MoS2 and WS2 by MOCVD and worked on transferring these materials from the growth wafer to a device wafer. We will describe the integration flow we have developed in the imec CMOS fab.

While progress in many aspects of device fabrication with MX2 materials is encouraging, several steps still lack fundamental understanding and methods to solve them. We will outline these outstanding problems and detail current status of where potential showstoppers appear.

Additive Manufacturing of Patterned 2D Semiconductor through Recyclable Masked Growth
Yunfan Guo and Jing Kong; Massachusetts Institute of Technology, United States

The 2D van der Waals crystals have shown great promise as potential future electronic materials due to their atomically thin and smooth nature, highly tailorable electronic structure, and mass production compatibility through chemical synthesis. Electronic devices, such as field effect transistors (FETs), from these materials require patterning and fabrication into desired structures.

Specifically, the scale up and future development of “2D-based electronics will inevitably require large numbers of fabrication steps in the patterning of 2D semiconductors, such as transition metal dichalcogenides (TMDs). This is currently carried out via multiple steps of lithography, etching, and transfer. As 2D devices become more complex (e.g., numerous 2D materials, more layers, specific shapes, etc.), the patterning steps can become economically costly and time consuming. Here, we developed a method to directly synthesize a 2D semiconductor, monolayer
molybdenum disulfide (MoS2), in arbitrary patterns on insulating SiO2/Si via seed-promoted chemical vapor deposition (CVD) and substrate engineering. This method shows the potential of using the prepatterned substrates as a master template for the repeated growth of monolayer MoS2 patterns. Our technique currently produces arbitrary monolayer MoS2 patterns at a spatial resolution of 2 μm with excellent homogeneity and transistor performance (room temperature electron mobility of 30 cm2 V−1 s−1 and on–off current ratio of 107). Extending this patterning method to other 2D materials can provide a facile method for the repeatable direct synthesis of 2D materials for future electronics and optoelectronics.

SESSION FF01.19: Fundamental Limits to Transport in 2D Materials
Session Chairs: Cinzia Casiraghi and Angela Hight Walker
Thursday Afternoon, December 5, 2019
Hynes, Level 3, Room 312

1:30 PM *FF01.19.01
Approaching the Intrinsic Limit in Transition Metal Dichalcogenide van der Waals Heterostructures James Hone; Columbia University, United States

Studying the intrinsic behavior of 2D materials requires attention to both external and internal sources of disorder. This talk will first review the techniques used to create clean heterostructures with hBN to reduce environmental disorder. In graphene, ten years of progress has led to device performance now rivaling the highest-quality GaAs-based heterostructures. On the other hand, semiconducting transition metal dichalcogenides (TMDs) are also limited by atomic defects within the crystalline layers, which requires efforts in synthesis and characterization of high-purity crystals. This talk will present recent progress in synthesis of TMD crystals with dramatically lower defect density using a self-flux technique. Combining higher crystal quality and clean encapsulation allows observation of greatly enhanced optical properties, including near-unity photoluminescence quantum yield, and long excited-state lifetime in TMD heterostructures. In addition, electronic transport measurements show improved carrier mobility and reveal many new details in magnetotransport measurements, including observation of fractional quantum Hall states in monolayer TMDs. These high-quality crystals also allow studies of twisted bilayer TMDs, which show the emergence of many-body correlated states.

Sample synthesis is supported under NSF DMR-1420634
Studies of magnetotransport in monolayer WSe2 are supported under DOE SC-0016703
Studies of twisted bilayer materials are supported under DOE DE-SC0019443

2:00 PM FF01.19.02
Towards High-Mobility 2D Semiconductors Yuanyue Liu; The University of Texas at Austin, United States

One of the major challenges that limits the development of 2D semiconductors is the low mobility of electrons/holes. Here using Boltzmann transport theory with the scattering rates determined from first principles, which allows us to accurately calculate the intrinsic (phonon-limited) mobility, we will present the intrinsic mobility for a variety of 2D semiconductors, including MX2 and monoelement ones. Moreover, we will discuss how the mobilities are related with underlying physical properties, causing the mobility difference across different materials, and (if time allows) how the strain and thickness would alter the mobility.

Ref: L. Cheng, Y. Liu, JACS, DOI: 10.1021/jacs.8b07871

2:15 PM FF01.19.03
Fundamental Limits of the Open Circuit Voltage in Ultrathin Transition Metal Dichalcogenide Photovoltaics Due to Band Tailing Joeson Wong1, Cora Went1, Ben L. Cotts2, Stefan Omelchenko1, Alberto Salleo2 and Harry A. Atwater3; 1California Institute of Technology, United States; 2Stanford University, United States

Band tails are ubiquitously observed at the band-edge of a semiconductor, often characterized by an exponential
decay in absorption below the band gap. Here, we characterize for the first time these band tail states in various ultrathin (<20 nm) transition metal dichalcogenide (TMDC) photovoltaic devices using photocurrent spectroscopy. We attribute the origin of these tail states to both intrinsic disorder within the TMDC (e.g. MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$) layer as well as the surrounding electrostatic environment in the form of a built-in field. Using our experimental measurements of the band tail states, we further analyze their implications on the fundamental limits of open circuit voltage in ultrathin TMDC photovoltaics using optoelectronic reciprocity relations. We find that in addition to the external radiative efficiency of TMDCs, band tail states may reduce the achievable open circuit voltage by over 100 mV due to increased recombination and therefore sets the maximum efficiency of ultrathin TMDC photovoltaics.

2:30 PM BREAK

SESSION FF01.20: Transport in 2D Materials and Heterostructures
Session Chairs: Cecilia Mattevi and Amalia Patane
Thursday Afternoon, December 5, 2019
Hynes, Level 3, Room 312

3:00 PM *FF01.20.01
Anomalously Suppressed Lattice Thermal Conduction by Electron-Phonon Coupling in Tantalum Disulfide
Huili Liu$^{1,2}$, Chao Yang$^3$, Jiawang Hong$^3$ and Junqiao Wu$^{1,2}$; $^1$University of California, Berkeley, United States;
$^2$Lawrence Berkeley National Laboratory, United States; $^3$Beijing Institute of Technology, China

Charge and thermal transport in a crystal are carried by free electrons and phonons (quantized lattice vibration), the two most fundamental quasi-particles. Above the Debye temperature of the crystal, phonons mediated thermal conductivity ($k_L$) is typically limited by mutual scattering of phonons, which results in $k_L$ decreasing with inverse temperature, whereas free electrons play negligible role in $k_L$. We report an unusual case in a charge-density-wave single crystal, where $k_L$ is limited instead by phonon scattering with free electrons, resulting in a temperature-independent $k_L$. In this system, the conventional phonon-phonon scattering is alleviated by its uniquely structured phonon dispersions, while unusually strong electron-phonon (e-ph) coupling arises from its Fermi surface strongly nested at wavevectors where phonons exhibit Kohn anomalies. The finding reveals new physics of thermal conduction, offers a unique platform to probe e-ph interactions, and provides potential ways to control heat flow in materials with free charge carriers.

3:30 PM FF01.20.02
Thermal Conductivity of High-Quality Atomically Thin Boron Nitride and Its Thermal Expansion
Qiran Cai$^1$, Declan Scullion$^2$, Ying Chen$^1$, Elton J. Santos$^2$ and Luhua Li$^1$; $^1$Deakin University, Australia; $^2$Queen's University Belfast, United Kingdom

Heat management becomes more and more critical, especially in miniaturized modern devices, so the exploration of highly thermally conductive materials with electrical insulation and favorable mechanical properties is of great importance. Here, we report that high-quality monolayer boron nitride (BN) has a thermal conductivity ($\kappa$) of 751 W/mK at room temperature. Although smaller than that of graphene, this value is larger than that of cubic boron nitride (cBN) and only second to those of diamond and lately discovered cubic boron arsenide (BAs). Monolayer BN has the second largest $\kappa$ per unit weight among all semiconductors and insulators, just behind diamond, if density is considered. The $\kappa$ of atomically thin BN decreases with increased thickness. Our large-scale molecular dynamic simulations using Green-Kubo formalism accurately reproduce this trend, and the density functional theory (DFT) calculations reveal the main scattering mechanism. The thermal expansion coefficients (TECs) of monolayer to trilayer BN at 300 to 400 K are also experimentally measured, and the results are comparable to atomistic ab initio DFT calculations in a wider range of temperatures. Owing to its wide bandgap, high thermal conductivity, outstanding strength, good flexibility, and excellent thermal and chemical stability, atomically thin BN is a strong candidate for heat dissipation applications, especially in the next generation of flexible electronic devices.
**3:45 PM FF01.20.03**  
**Hot Electron Transfer in Graphene/WS$_2$ Heterostructures**  
Chiara Trovatello$^1$, Giulia Piccinini$^{2,3}$, Stiven Forti$^{2,3}$, Filippo Fabbri$^{2,3}$, Antonio Rossi$^{4,5,2}$, Camilla Coletti$^{2,3}$, Giulio Cerullo$^1$ and Stefano Dal Conte$^1$; $^1$Politecnico University of Milan, Italy; $^2$Istituto Italiano di Tecnologia, Italy; $^3$Istituto Nanoscienze-CNR and Scuola Normale Superiore, Italy; $^4$University of California, Davis, United States; $^5$Lawrence Berkeley National Laboratory, United States

Stacking two-dimensional (2D) materials, like graphene (GR) and single layer transition metal dichalcogenides (1L-TMDs), has opened up unlimited possibilities to design and engineer new functional 2D van der Waals heterostructures (HSs).

Here we exploit ultrafast transient-reflection spectroscopy to optically investigate the charge transfer (CT) dynamics in a large area 1L-WS$_2$/GR HS, with an unprecedented temporal resolution, i.e. sub-20fs, and across a broad energy range spectrally covering both A and B excitons of WS$_2$ (1.8-2.5eV).

When the HS is excited with a photon energy of 2eV, above the optical gap of 1L-WS$_2$ (1.98eV), the differential reflectivity signal, i.e. $\Delta R/R$, is dominated A and B excitonic features of WS$_2$. On the other hand, if carriers are photo-injected in the HS well below the WS$_2$ bandgap, e.g. with 0.8eV photon energy, only graphene is actually excited. Nevertheless, the signal across A and B peaks appears immediately after excitation. This surprising result suggests an extremely fast CT from GR to WS$_2$. Indeed, when WS$_2$ alone is excited below bandgap with the same photon energy and fluence, no transient signal is detected.

The observed ultrafast charge transfer cannot be exclusively attributed to the direct excitation of new intermediate charge transfer states arising from the overlap of the graphene and the TMD bandstructures[1]. This is indicated by the excitation fluence dependence of the transient signal, which becomes strongly nonlinear at infrared excitation energies, revealing that the mechanism behind the observed ultrafast CT from graphene to the semiconductor is hot electron/hole transfer[2].

The timescale for the hot electron transfer is expected to be extremely short, below 50 femtoseconds[2]. The rise time of the A exciton dynamics is a direct estimation of the timescale for this process, and it is related both to the hot GR Fermi-Dirac distribution thermalization and the tunneling process, i.e. the time needed for hot electrons, exclusively excited in GR, to overcome the Schottky barrier and reach the semiconductor[3]. The extracted build-up of the A exciton transient signal, measured on the HS following a sub-20fs IR excitation at 1.3eV, is faster than 20 fs. This is the first direct measurement of the hot electron/hole transfer in time-domain.

Hot electron transfer is extremely promising for charge extraction at the HS interface, making this novel 2D HS suitable for the development of broadband and efficient low-dimensional photodetectors.


**4:00 PM FF01.20.04**  
**Spectroscopic Investigation of Electron Transfer from Monolayer MoS$_2$ to Organic Conjugated Polymers**  
Christopher Petoukhoff$^2$, Sofia Kosar$^1$, Ibrahim Bozkurt$^2$, Manish Chhowalla$^3$ and Keshav M. Dani$^1$; $^1$Okinawa Institute of Science and Technology, Japan; $^2$Rutgers, The State University of New Jersey, United States; $^3$University of Cambridge, United Kingdom

Organic/2D heterostructures have emerged as promising materials for ultrathin, large-area optoelectronic devices. Both organic and 2D semiconductors lack dangling bonds at their surfaces and interact via van der Waals forces, enabling their heterostructures to form ideal interfaces without the need for energy-intensive growth processes, such as molecular beam epitaxy. As such, ultrathin optoelectronic devices have been fabricated from organic/2D heterostructures including photovoltaics, photodetectors, and field-effect transistors, demonstrating large on-off ratios and anti-ambipolar behavior in the latter. Recently, organic conjugated polymer/2D heterostructures fabricated from the polymer, PTB7, and the 2D material, MoS$_2$, have demonstrated the photovoltaic effect with record values of the photovoltaic figures of merit normalized to the device active layer thickness. Despite this, devices fabricated from organic/2D heterostructures have shown relatively low internal quantum efficiencies, suggesting non-ideal charge transport throughout their devices. Investigating charge transfer dynamics across organic/2D semiconductor interfaces at fundamental timescales is an important part of understanding how to improve the low internal quantum efficiency of these devices.
Here, we employ photoluminescence and femtosecond transient absorption spectroscopies to study the charge transfer dynamics in large-area, organic conjugated polymer/MoS2 heterostructures. The heterostructures were formed between chemical vapor deposited monolayer MoS2 thin-films and 3 different conjugated polymer films: P3HT, PCDTBT, and PTB7. These 3 polymers have been used extensively as electron donors in high-efficiency polymer:fullerene organic photovoltaics, and each form Type-II heterojunctions with MoS2. Although electron transfer was expected to occur from the polymers to MoS2, we show that electron transfer occurs in the opposite direction: from MoS2 to each of the conjugated polymers via polaron pair states. We show that electrons are transferred from MoS2 to P3HT within 9 ps, and from MoS2 to PCDTBT and PTB7 in under 120 fs. Despite this, we demonstrate that the P3HT/MoS2 heterostructure is the most efficient because the transferred charges have an order-of-magnitude increase in their lifetimes, leading to enhancement in the photoluminescence from P3HT. We propose that the differences in the lifetime of transferred charges arises from the crystallinity of the conjugated polymer films.

Influence of Interfacial Morphology on Ultrafast Charge Separation in 0D/2D Mixed-Dimensional Heterojunctions

Suyog Padgaonkar, Mark C. Hersam and Emily Weiss; Northwestern University, United States

Mixed-dimensional heterojunctions (MDHJs) combine the characteristics of component materials such as the discrete orbital energies of zero-dimensional (0D) molecules and the extended band structure of two-dimensional (2D) semiconductors. While MDHJs have shown promise for optoelectronic applications – such as photodetectors because their performance exceeds that of the individual components – increased understanding of fundamental mechanisms and time scales of charge separation at the interface would drive improved design of these systems. Here, comparison between two different type-II organic/2D MDHJs comprised of copper (Cu) and free base (H2) phthalocyanine (Pc) and monolayer MoS2 elucidates the influence of interfacial morphology on charge separation lifetimes in these systems. In particular, time-resolved optical spectroscopy reveals two ultrafast charge transfer processes from selective excitation of each component material: sub-picosecond photoinduced hole-transfer and sub-320 fs photoinduced electron-transfer processes at the interfaces of CuPc/MoS2 and H2Pc/MoS2 MDHJs. In CuPc/MoS2 heterojunctions, charge separation lasts as long as 70 ns, which is a factor of 17 longer than that in H2Pc/MoS2 heterojunctions and a factor of 40 longer than that in previously reported transition-metal dichalcogenide-based heterojunctions. Polarized Raman spectroscopy shows that preservation of the charge-separated state is attributed to the face-on orientation of CuPc on the MoS2 surface, which templates stacking of CuPc molecules and facilitates hole migration away from the interface, whereas H2Pc molecules adopt a mixed edge-on and face-on orientation. This work highlights the role of molecular structure in determining the interfacial geometry and, ultimately, charge-transfer dynamics in 0D/2D heterojunctions and suggests principles for the rational design of other organic/2D MDHJs.

Unintentional n-Type Doping on Single Layer Nb-Doped MoS2 Observed by Scanning Nonlinear Dielectric Microscopy

Kohei Yamasue and Yasuo Cho; Tohoku University, Japan

Atomically-thin layered semiconductors as exemplified by few-layer MoS2 and WSe2 are an emerging class of materials with their potential use for semiconductor devices [1, 2]. In this context, dominant carrier distribution on these materials and devices is one of the key electronic properties for understanding their electrical characteristics and improving device performance. In fact, recently, an unintentional electron doping effect in MoS2 has been reported, which suggests the difficulty in fabricating intrinsic and p-type atomically-thin MoS2 [3]. This effect is attributed to surface electron accumulation due to the formation of sulfur vacancies on the surface of MoS2 and therefore becomes dominant in atomically-thin layers due to their high surface-to-volume ratio [3]. In order to investigate the transition of dominant carrier polarity on atomically-thin MoS2 layers, here we perform the nanoscale carrier distribution imaging on atomically-thin natural and Nb-doped MoS2 including single layer areas. By using a microwave-based scanning probe microscopy method called scanning nonlinear dielectric microscopy (SNDM) [4], we actually visualize unintentional n-type transition confined on single layer Nb-doped MoS2, even though Nb-doped MoS2 is nominally expected to be p-type in contrast to natural MoS2 with n-type dominant carriers. SNDM allows nanoscale dominant carrier distribution imaging through the detection of differential capacitance induced by small ac-bias voltage (so-called dC/dV imaging). As the polarity of dC/dV is inverted depending on the polarity of dominant carriers, we can identify n- or p-type on the local area below the tip. We have already succeeded in the detection of single layer MoS2 [5], because SNDM is exceptionally sensitive to tiny dC/dV. In this
study, we used novel intermittent contact SNDM with boxcar integration, which will be described elsewhere [6], to obtain higher S/N ratio than that in the conventional intermittent contact SNDM. The samples were natural and Nb-doped MoS₂ on SiO₂/Si substrates prepared by the mechanical exfoliation with so-called Scotch tape method. The measurement was performed in air at room temperature using a commercial scanning probe microscopy system (Bruker, Icon) integrated with a lab-made SNDM setup. As expected, for natural MoS₂, n-type contrast were seen even on few-layer MoS₂ including a single layer area. In contrast, we found that single layer Nb-doped MoS₂ showed unintentional n-type contrast, while multilayer areas were seen p-type. This unintentional electron doping effect was reproducibly observed on the single layer areas of other Nb-doped MoS₂ samples. In addition, unlike the multilayer areas, those with a few to several layer number often showed negligible dC/dV signal level. These results are reasonable if considering the counter doping effect depending on the surface-to-volume (S/V) ratio discussed in Ref. [5]. The effect does not manifest for multilayers with a low S/V ratio, but, for few-layers, it is balanced with Nb-doping, and then overcompensates in single layer areas with the highest S/V ratio. This implies the difficulty in p-type conduction on our as-prepared MoS₂ samples. The results here indicate that SNDM gives direct information on nanoscale carrier distribution on the areas with different stacking layers, which will provide a clue to controlling carrier types and doping levels in atomically-thin layered semiconductors.

References:

4:45 PM FF01.20.07
Rigid-Lattice Moiré vs Atomic Reconstruction in van der Waals Heterostructures Matthew R. Rosenberger¹, Hsun Jen Chuang¹, Madeleine Phillips¹, Vladimir Oleshko², Kathleen McCreary¹, Saujan V. Sivaram¹, C. Stephen Hellberg¹ and Berend T. Jonker¹; ¹U.S. Naval Research Laboratory, United States; ²National Institute of Standards and Technology, United States

Van der Waals layered materials, such as transition metal dichalcogenides (TMDs), are an exciting class of materials with weak interlayer bonding which enables one to create so-called van der Waals heterostructures (vdWH). One promising attribute of vdWH is control over the twist angle between layers, which leads to the formation of moiré patterns that enable tuning of vdWH properties. In the case of TMD vdWH, moiré patterns have been used to explain unique optoelectronic behavior of these structures. However, the moiré theory used to explain the behavior of TMD vdWH have only considered the constituent layers as rigid lattices and have not allowed for atomic-level reconstruction, i.e. rearrangement of the atoms with the layers. The existence of atomic-level reconstruction would have a significant impact on the electronic and optoelectronic properties and would fundamentally change our theoretical understanding of these systems. Here, we present experimental proof of atomic-level reconstruction in twisted TMD vdWH, which is a significant departure from the rigid-lattice moiré theory. Using conductive atomic force microscopy (CAFM), we probe the nanometer-scale electronic behavior of twisted MoSe₂/WSe₂ and MoS₂/WS₂ heterostructures and show that, for twist angles around 1° or less, large domains of constant electronic behavior form rather than a continuously varying pattern of electronic behavior, as expected from conventional moiré theory. We find that the stacking arrangement (H-type or R-type) has a profound impact on the reconstruction behavior. We use transmission electron microscopy to corroborate the presence of atomic reconstruction, to demonstrate commensurate stacking within the reconstructed domains, and to demonstrate a transition from atomic reconstruction at small twist angles (≤ 1°) to a rigid-lattice moiré pattern for larger angles (≥ 3°). We use density functional theory (DFT) calculations to predict the low-energy stacking configurations of the heterostructures and to calculate the band structures of the low-energy stacking configurations. Agreement between CAFM and DFT enables us to assign stacking arrangements to the different reconstructed domains. Finally, we show that the difference in calculated bandgaps between heterostructures with H-type and R-type stacking agree with photoluminescence measurements of reconstructed heterostructures of both types. These results provide fundamental insight into the behavior of this exciting class of semiconductor heterostructure.
FF01.21.01
TiO₂ Nanowires/Ti₃C₂ MXene Based Multi-Functional Sensors with High Sensitivity and Ultrafast Response
Seong Jin Kim¹, Shuvra Mondal¹,² and Choon-Gi Choi¹,²; ¹Electronics and Telecommunications Research Institute, Korea (the Republic of); ²University of Science and Technology, Korea (the Republic of)

Ti₃C₂ MXene, a new class of two-dimensional transition metal carbides has attracted much attention as a sensing material due to its high surface-to-volume ratios and excellent electrical conductivity. Furthermore, the presence of surface terminated functional group such as oxide (-O) and hydroxyl (-OH) onto the Ti₃C₂ MXene provides reaction sites for water absorption. Recently, many studies have been investigated to understand the charge transfer mechanism when water molecules were sorption in MXene surface or intercalation between the MXene nanosheets for improving response speed and sensitivity. However, the electrical response to water vapor absorption that determines the performance of the humidity sensor can still be limited due to the high electrical conductivity of MXene. Therefore, it is required to study the novel MXene structure which can improve the sensor performance by maximizing the electrical charge while the water vapor or moisture is adsorbed on the film surface.

In this work, we synthesized TiO₂ nanowires/Ti₃C₂ MXene composites by facile solution process manipulating of concentration of NaOH solution. As a result, the density of TiO₂ nanowires increased in proportion to the concentration of NaOH solution and formed a network on the surface and interlayers of Ti₃C₂ MXene. The sensing performance of TiO₂ nanowires (NWs)/Ti₃C₂ MXene composites based humidity sensor was evaluated under relative humidity condition from 20 to 80 %. As a result, it showed a high sensitivity and fast response compared with pristine Ti₃C₂ MXene-based sensor. In addition, piezoresistive pressure sensor was fabricated by coating TiO₂ NWs/ Ti₃C₂ MXene on cotton fabric. Thereafter, the performance of the device evaluated over a wide pressure range of 0.33 to 63.1 kPa. As a result, our sensor showed high sensitivity of 2.5 kPa⁻¹ with excellent linearity. In addition, it exhibited an ultrafast response speed with a rise time of ~13 ms and decay time of ~17 ms. This study opens up a new avenue of two-dimensional layered hybrid materials for applications of advanced contact and non-contact electronic devices.

Acknowledgement
This work was partly supported by Electronics and Telecommunications Research Institute (ETRI) grant (19ZB1100) funded by the Korean government and Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government (MOTIE) (20181510102340, Development of a real-time detection system for unidentified RCS leakage less than 0.5 gpm).

FF01.21.02
Effect of Gamma-Ray Irradiation on MoS₂ Investigated by Raman and X-Ray Photoelectron Spectroscopy
Burcu Ozden¹, Min Khalan², Minseo Park² and Choi Wonbong³; ¹Penn State Abington, United States; ²Auburn University, United States; ³University of North Texas, United States

Recently, molybdenum disulphide (MoS₂) has attracted great attention for diverse applications due to its material properties. It is thought that these material properties soon will make MoS₂ attractive for the development of radiation-hard electronics. Therefore, for the first time, we studied the effect of gamma-ray (γ-ray) irradiation on the crystal quality of a few-layered MoS₂ by using Raman and X-ray photoelectron spectroscopy techniques. The γ-ray irradiation dose of 120 Mrad was applied to 3.2, 4.5, and 5.2 nm thick MoS₂ films which were grown on Si by using a two-step synthesis method (sputtering of Mo, followed by sulphurisation). Before γ-ray irradiation, three active Raman modes (E₁g, A₁g) was detected. After γ-ray irradiation, the Raman peaks attributed to the E₁g and A₁g modes almost disappeared. The dramatic decrease in the S2p peak accompanied by an increase in the O1s peak and the change in the Mo3d3/2 binding energy from what is known for stoichiometric MoS₂ to that for native Mo oxide was observed in the XPS spectra. In conclusion, dramatic chemical changes in the MoS₂ films after irradiation is believed to be related to the fact that S vacancies are formed due to γ-ray irradiation, which subsequently transforms
MoS₂ to a native MoOₓ.

**FF01.21.03**  
**A Semimetallic Two-Dimensional ZnSb with Remarkably High Hole Mobility**  
Wonchul Shin¹,², Chang Il Kwon¹, Jun Sung Kim¹ and In Chung¹,²; ¹Seoul National University, Korea (the Republic of); ²Institute for Basic Science (IBS), Korea (the Republic of); ³Pohang University of Science and Technology, Korea (the Republic of)

The discovery of exotic electronic properties of graphene has led to extensive research efforts to find new functional two-dimensional (2D) materials. For example, transition metal dichalcogenide (TMD) compounds are an excellent candidate for various electronic devices due to their thickness-tunable band gap. However, their relative low carrier mobility limits their applications. Recently, honeycomb-like monolayer materials composed of main group elements such as GeP³ and antimonene were reported to exhibit high carrier mobility. However, this property is only observable in epitaxially grown samples on specific substrates. Here, we present a new structure-type, metastable 2D ZnSb which exhibits remarkably high carrier mobility. The structure features unique two atom-thick Zn-Sb honeycomb layers stacked along the out-of-plane direction. This compound can be only achievable by topotactic chemical reaction we developed. Temperature-dependent electrical resistivity and Hall effect measurements on single crystalline 2D ZnSb show p-type metallic conduction with hole mobility of ~400 cm²V⁻¹s⁻¹ at room temperature. A new 2D ZnSb is readily cleavable to form a few layer-thick nanosheets by various irradiation techniques. This new phase shows completely different crystal structure and physical properties from a well-known three-dimensional semiconducting polymorph.

**FF01.21.04**  
**Ultras-Sensitive Graphene-Barristor Biosensor**  
Naebong Jeung¹, Jun-Ho Lee¹, Do-Hyun Park¹, In-Chul Choi¹, Hongjeong Yu², Hakho Lee² and Hyun-Jong Chung¹; ¹Konkuk University, Korea (the Republic of); ²Massachusetts General Hospital, United States

We present a new, highly sensitive biosensing approach using a graphene-based barristor [1]. The sensor is formed by interfacing graphene with semiconductor. The resulting Schottky barrier (between graphene and semiconductor) is highly susceptible to the device surface condition; binding of target biological molecules can turn on the device with very large signal gain. This mechanism makes the barristor far superior to conventional graphene FET sensors that are based on the charge-density modulation[2]. To prove the concept, we fabricated n-type barristor sensors and used them to detect DNA molecules. With target DNA binding, the height of the Schottky barrier increases, leading to the decrease in device currents. Even at very low DNA concentrations (~1 aM), we observed more than 40% changes in the device conductance. The technology may open up a new material and device concept for ultrasensitive biosensing.

**FF01.21.06**  
**Mass Production of 2D ZnO Nanosheets Using Recyclable AAO Template**  
Jiyu Sun and Pu-Xian Gao; University of Connecticut, United States

Two-dimensional (2D) ZnO nanostructures are becoming more popular due to their properties such as nanometer-scale thickness, high surface to volume ratio, and good mechanical stability ¹. However, current strategies are usually limited to low production rate, complicated method, and high cost. Here in this study, we report a high-yield method to synthesize large-area ZnO 2D nanosheets by utilizing recyclable anodic aluminum oxide (AAO) template. ZnO nanosheets were synthesized by microwave-assisted hydrothermal synthesis method without using seeding layer, with a large lateral size and nanometer thickness. ZnO nanosheets could be obtained by a sonication process, with a yield of 3mg/cm² in 3 hours. XRD analysis indicated the formation of ZnO nanosheets exposed with (100) facets and the successful doping of Al. During electron microscopy imaging, an ultrathin morphology was observed with good wrinkling flexibility. Besides, due to the intactness of the template after nanosheet transferring using polymer, the AAO template can be cyclically utilized as the substrate for repetitive growth of ZnO nanosheets, which further reduces the cost and waste. Various application demonstrations are conducted based on this ZnO nanosheets, including gas sensor, thermochemical CO₂ hydrogenation, and photocatalysis. Owing to its ultrathin 2D morphology with abundant amounts of active sites and defects, a higher sensitivity and a short response time toward ppb–level gas detection may be obtained, and a higher conversion efficiency of CO₂ hydrogenation is achieved ²-³. High binding energies between gas molecules and oxygen vacancies existing in the exposed ZnO (100) facets lead to large surface reconstructions, which make a contribution to the gas sensing properties and CO₂ hydrogenation.
Furthermore, the highly exposed surface of nanosheets also facilitates gas sensing and catalysis performance. The demonstrated method here enables a new path to the high-yield synthesis of 2D ZnO for applications in energy-related field and beyond.

Reference

**FF01.21.07**

**Highly Efficient Luminescence from Large Scale TMDC by Minimizing Optical Loss**

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Since the discovery of graphene in 2004, two dimensional (2D) materials have led an intensive attention because of their unique physics and new device architectures. Nevertheless, there was limitation over having large-scale, monolayer 2D materials because it is extremely difficult to control the kinetic of 2D materials during the growth. Especially, it is mandatory to have monolayer of transition dichalcogenides (TMDCs) for optoelectronic applications as multilayer 2D materials have indirect band gap which involving phonon loss. In addition, since 2D materials themselves do not have sufficient external quantum efficiency (EQE), we cannot expect highly efficient luminescence from 2D material-based optoelectronics. Thus, it has been required to develop an alternative approach for 2D materials-based optoelectronics.

Here, we propose an interesting approach for highly efficient luminescence from large scale TMDCs by effectively engineering optical loss. Last year, we reported a new approach to make large scale, monolayer of the TMDC, called layer-resolved splitting. This approach enables us to have large-scale monolayer-by-monolayer stacking with pristine interface as it does not accompany any polymer residue and chemical contamination at the interface. Therefore, it minimizes the optical loss through interface interference. In addition, we successfully engineer additional optical loss by incorporating distributed bragg reflector (DBR) structures with TMDCs since DBR has broad reflection band and phase shift of DBR is close to zero. Thus, we can observe the improvement of photoluminescence in TMDC/DBR structure using layer-resolved splitting process. We strongly believe that this process will lead a new opportunity for highly efficient 2D material-based LED optoelectronic applications.

**FF01.21.08**

**Symmetry-Dependent Electron-Phonon Coupling in Black Phosphorus Revealed by Resonance Raman Spectroscopy**

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Crystals with low symmetry and low dimensionality have drawn tremendous fundamental and practical interest, since such a strongly quantum confined anisotropic system gives rise to many novel and complicated many-body interactions. Black phosphorus (BP), a two-dimensional elemental semiconductor, is a representative member of such low-symmetric nanomaterials. With the highly anisotropic electronic structure and phonon dispersions, black phosphorus has been an excellent platform for understanding the rule of symmetry related multi-particle interactions. Here, we investigated the electron-phonon coupling in few-layer and bulk BP using polarization-dependent resonance Raman spectroscopy with 16 laser lines. The in-plane \( A_\parallel \) mode, which shows larger intrinsic resonance effect than the out-of-plane \( A_\perp \) mode when excitation polarization is along the armchair direction, demonstrating symmetry-dependent electron-phonon coupling effect in BP. This understanding is further supported by the quantum perturbation theory and first-principles calculations on the anisotropic electron distributions. Moreover, the comparison of intrinsic resonance effects along two crystalline orientations allow us to resolve the existing controversies on the physical origin of Raman anomaly in BP and its dependence on excitation energy, sample thickness, phonon modes, and crystalline orientation.

**FF01.21.09**

**Ultraclean van der Waals Contact for Spintronic Devices**

Yan Wang, Guang Yang and Manish Chhowalla; University of Cambridge, United Kingdom
Graphene has been demonstrated to be promising for spintronic devices due to its intrinsically low spin orbit interaction\(^1\). Although long spin relaxation lengths (> \(2\mu\m\)) have been experimentally achieved with graphene, the degree of polarized carrier injection is still low (< \(10\%\)) due to scattering at the contact/graphene interface\(^2\). Ferromagnetic electrodes such as cobalt are most commonly used for injecting spin-polarized electrons into non-ferromagnetic graphene. Recently, atomic resolution scanning transmission electron microscope studies on metal/2D material interfaces have revealed that defects are created during metal deposition\(^3,4\). This has led the studies of inserting tunnel barriers such as h-BN\(^5\), MgO\(^6\), and TiO\(_2\)\(^7\) between Co and graphene layers for improving the spin injection efficiency. Here, we report results from our recent work on realizing ultra-clean van der Waals contacts using Indium electrodes for spintronics. Specifically, we use 3 – 10 nm indium to achieve defect-free contact, then deposit ferromagnetic Co layers on top. Annealing of the contacts leads to ferromagnetic In/Co alloy with defect free interface with graphene that can be used to inject spin polarized carriers with high efficiency.

References:

**FF01.21.10**
*WSe\(_2\)/h-BN Heterostructure Memristor Devices Stacked by Quasi-Dry Transfer Process* Beom-Seok Kang, Chansoo Kim and Jeelwan Kim; Massachusetts Institute of Technology, United States

Memristors are a great promising candidate for a next-generation nonvolatile memory due to their small footprint, low power consumption, thus, suitable for handling tremendous data set such as learning neural-networks. At the early stage, memristor devices were fabricated with titanium dioxide (TiO\(_2\)) controlling movement of oxygen vacancies, nowadays, for improved performance and various applications, several materials such as organic polymer and ferroelectric thin film have been widely studied as been suggested as a switching medium. Recently, memristors utilizing two-dimensional (2D) layered material based memristors, which are atomically thin, flexible and easily heterogeneously integrated, for example, MoS\(_2\), MoTe\(_2\), h-BN have also shown their feasibility as they are atomically thin, flexible and easily heterogeneously integrated, successfully making 2D layered material them as a promising switching medium for atomically thin, flexible, and vertically stackable memristor.

In this study, we propose a memristor device architecture consisting of report WSe\(_2\)/h-BN heterostructure showing low leakage current, pristine interface, and, pristine interface, memristor devices. stable filament formation in switching mediums, which are key factors for stable memristor operation. Our main approach for them is engineering material combination with pristine interface. As h-BN itself has low leakage current properties and WSe\(_2\) itself has stable filament formation, we have found out that WSe\(_2\)/h-BN heterostructures have much large memory window (on/off ratio of \(\sim 10^4\)) and stable switching operation (over 100 times of repeatable cycling). Heterogenous material combination often generates interfacial issues, however, heterostructure on large area was successfully fabricated exploiting advantages of each materials; low leakage current of h-BN and repeatable switching of WSe\(_2\). These improved characteristics were also estimated with several devices fabricated in same process bawe could achieve high-quality interface by using our quasi-dry transfer process. We recently developed a quasi-dry transfer, allowing us large-scale 2D materials with pristine interface because the quasi-dry transfer does not accompany any chemical contamination at the interface during the process. Thus, we successfully engineer material combination with maintaining the properties of each material for stable switching behavior. We strongly believe that WSe\(_2\)/h-BN heterostructures by the quasi-dry transfer has a strong potential for stable memristors.
Optically Coupled 2D/Organic Synaptic Device for Simplified Weight in Neuromorphic Computing

Beom-Seok Kang1, Ji-Hye Lim2, Jin-Hong Park2 and Jeehwan Kim1; 1Massachusetts Institute of Technology, United States; 2Sungkyunkwan University, Korea (the Republic of)

Neuromorphic computing supported by synaptic devices, which mimics the structure and functions of neural networks at the hardware-level, is one of emerging candidates for the next generation cognitive computing. Although synaptic devices in artificial neural networks (ANN) feature small device footprints and reduced energy consumption, it has been challenging to find an optimal synaptic device for large-scale neuromorphic computing due to stochastic and unpredictable nature in conductance update. Also, for the synaptic device to be used as analog synaptic weight facilitating a simple multiply-accumulate (MAC) operation, it is required to have two synaptic devices to represent one weight since synaptic devices merely possesses positive conductance value, which can be expressed as weight = G+ - G-.

Here, we propose a 2D/Organic heterostructure synaptic device coupled with an optical source, which enables to solely represent each weight in neural networks without having two synaptic devices. Our key approach for the function is controlling reverse current by engineering i) symmetry of Metal-WSe2 contact and ii) input pulse characteristics and postsynaptic voltages. We have figured out that amount of photo-generated carrier diffusion is proportional to the symmetry of Metal-WSe2 contact. Less symmetric contact causes more asymmetric photo-generated carrier diffusion, making the reverse current and negative conductance possible. Also, direction of the diffusion from WSe2 to Metal is opposite to the direction of carrier injection from metal to WSe2, thus, balancing of them offers a way to control the polarity of conductance. By changing input pulses and postsynaptic voltage, we successfully balanced two types of carrier flows and gradually changed conductance states from negative to positive, which can be directly used as a weight without constituting conventional weight = G+ - G- cell. We believe that optically coupled 2D/Organic synaptic device will further revolutionize the current neuromorphic computing system in the way that it cuts the size of crossbar circuit in half and thus provides an energy-efficient platform for post von Neumann Computing.

Towards Large Scale MoTe2 Layers Grown by MBE

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MoTe2 belongs to transition metal dichalcogenides - materials, which have been intensively studied for the last few years. They provide a rare occasion to test relativistic physics with low energy excitations in condensed matter experiments. The unusual properties of the charge carriers, which are chiral, helical and have a linear E(k) dependence lead to many interesting physical phenomena such as chiral anomaly [1], extremely large positive magnetoresistance [2, 3, 4], or the planar Hall effect [1, 5]. The most commonly used methods to obtain MoTe2 layers, beside exfoliation from natural crystals [6] are the flux method [3, 4, 7] and chemical vapour transport [8]. Currently, Molecular Beam Epitaxy (MBE) technique comes into play [9, 10, 11, 12] giving the perspectives to combine different phases of MoTe2 and to grow heterostructures and hybrid structures.

In this paper we present the results of structural, optical and transport investigations of MoTe2 thin layers. The samples were prepared on Al2O3 and SI-GaAs [111B] substrates which both, at the appropriate growth temperature, allow us to obtain 2H and 1T’ polytypes of MoTe2 (as evidenced with Raman scattering) as well as other phases, e.g. Mo6Te6. Controlling the growth conditions allows to modify sample morphologies from regular 2D planes, through 3D precipitations to nanowires as studied in-situ with RHEED images, and ex-situ by TEM and SEM microscopy. Transport measurement were performed on large, millimeter-size Hall bars with metal (Ti/Au or In) contacts deposited via shadow masks. The resistance of the samples was measured in the temperature range 300 K – 1.5 K revealing either an increase of the resistivity for semiconducting samples or a very weak temperature dependence, showing significant disorder for the samples with the metallic phases. In the latter case, for high concentration (n ~ 1●1016 cm-2) several monolayer sample, the low value of carrier mobility (2 cm2/Vs) and a linear magnetoresistance up to 12 T revealed sample inhomogeneity. Furthermore, we have observed that the poor stability of the MoTe2 layers can be improved by different capping layers.


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**FF01.21.13**

**Performance Study of van der Waals Density Functionals Using Group-IV Monochalcogenides**

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Within density functional theory (DFT), several methods have been developed in order to capture van der Waals interactions. Some popular density functionals used to study systems where van der Waals forces play an important role in determining the structure are the optB86b, optB88, PBE+D2, PBE+D3, PBE+TS, and PBE+TS+SCS functionals. In this study, we screen compounds of the form AX (where A: C, Si, Ge, Sn, Pb; X: S, Se, Te) in 6 different prototype van der Waals layered quasi-2D structures by first performing structural relaxation, then checking for dynamic stability for those compounds that remained quasi-2D after the relaxation, and then computing the piezoelectric tensor values (eij) for the dynamically stable structures. We perform this screening using each of the 6 van der Waals density functionals mentioned above, and thus, compare the performance and reliability of these functionals. Our results will aid future computational studies in choosing the best van der Waals density functional based on specific needs and resources at hand.

**FF01.21.14**

**Variable Temperature STM Study of Black Phosphorus**

Ben St Laurent, Hannah Bell, Christine Caputo and Shawna Hollen; University of New Hampshire, United States

While the high carrier mobility and tunable band gap of black phosphorus make it promising for device applications, a better understanding of native defects is needed for black phosphorus to reach its full potential. The native defects, which are primarily phosphorus vacancies, alter the electronic properties and expedite the degradation of black phosphorus in air. This poster will present a series of scanning tunneling microscopy experiments studying how the surface of black phosphorus changes with temperature. Varying the temperature for imaging allows us to investigate defect mobility in the lattice. The vacancies have been theorized to be highly mobile at room temperature, but become locked into place as the temperature drops. This study has also led to the observation of 5nm stripes on the surface. These stripes are periodic, and their prominence has a strong dependence on both temperature and tunneling bias.

**FF01.21.15**

**Hyperspectral Analysis of MoS2/WS2 Heterostructures**

Peter Lisker and Erik Einarsson; University at Buffalo, United States

Hyperspectral imaging is a powerful tool to connect spectral and spatial information. Raman spectroscopy is widely used to obtain rich information about 2D materials. Here we report on the combination of these methods. We grew transition metal dichalcogenide (TMD) heterobilayers of WS2 on top of MoS2 by chemical vapor deposition (CVD). We then used Raman mapping to create a hyperspectral image of the pristine heterobilayer, in which each pixel contains an entire Raman spectrum. Principal component analysis (PCA) of the hyperspectral data revealed subtle changes in the characteristic MoS2 E1g and A1g peaks, which can be used to characterize the number of layers. Based on our analysis, we identified MoS2 monolayer regions, WS2 monolayer regions, and MoS2/WS2 heterobilayers. This not only confirmed the direct growth of heterobilayers by CVD, but also revealed that WS2 preferentially...
grows on monolayer regions of MoS2, but not on multilayer regions.

**FF01.21.16**  
**Degradation Study of WSe2 via Raman Spectroscopy and Photoluminescence Imaging** Makarand R. Wadagave and Burcu Ozden; The Pennsylvania State University, United States

Semiconducting two-dimensional materials (2DMs) such as WSe2 (Tungsten Diselenide) have attracted significant attention due to their unique optoelectronic properties. However, such materials can be vulnerable to optical degradation under ambient conditions, yet a systematic study does not exist in the literature. The degradation study of WSe2 is essential to understand the applications of these materials in non-specialized operation conditions. In this study, we investigate the degradation of free-standing WSe2 due to humidity under ambient conditions by performing Raman spectroscopy and photoluminescence imaging over a 6-month period between June 2019 and December 2019. The findings of this study will provide fundamental insight into the degradation of WSe2 and inspire their application in optoelectronics under harsh conditions.

**FF01.21.17**  
**Simple Liquid Phase Intercalation and Exfoliation of MoO3 Rods into Nanosheets and Nanotubes and Conversion to MoS2** Pavithra B and Ravishanakar Narayanan; Indian Institute of Science, India

Two dimensional (2D) nano-materials are interesting due to their distinct properties like high specific surface area which make them suitable for catalytic and many other applications. One of the well-known layered oxides, MoO3 exists in stable orthorhombic a-MoO3 structure which involves stacking of MoO6 octahedra bilayers along the [010] direction. Electronic and optical properties of layered MoO3 can be tuned via ion or molecule intercalation between the layers, followed by exfoliation to form 2D nanosheets. A simple room temperature method for the exfoliation of MoO3 has been developed, which involves the intercalation of oleylamine. Starting from MoO3 rods, different systems and morphologies like MoO(3-x) – Oleylamine hybrid, MoO(3-x) nanosheets and MoO(3-x) nanotubes have been produced. α-MoO3 rods have been synthesized by the hydrothermal method as already reported. 2D-MoO3 layers have been realized via liquid phase exfoliation of Oleylamine intercalated MoO(3-x) hybrid. Following that, exfoliated sheets roll up to form nanotubes upon removal of Oleylamine. Transmission Electron Microscope (TEM) has been extensively used to understand the morphology and structure of initial rods, the intermediate stages of intercalation, hybrid structure, completely exfoliated MoO3 sheets and tubes. Structural and compositional information have been also obtained using Scanning Electron Microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy and X-Ray Diffraction. The intercalation of Oleyamine into the Van der Waals gap of MoO3 rods results in the reduction of Mo to +5 state and creation of oxygen vacancies to produce MoO(3-x)–amine hybrid. The resulting sheets and tubes are also of non-stoichiometric, amorphous MoO(3-x). The amorphous MoO(3-x) sheets and tubes have been heated in ex situ in a furnace in both oxygen and inert atmosphere. MoO(3-x) recrystallizes to form orthorhombic, stoichiometric MoO3 at around 500°C in oxygen atmosphere. Electrochromic properties of amorphous MoO(3-x)–oleylamine hybrids were studied. Furthermore, Au/MoO3 hybrids have been obtained via the wet-chemical growth of ultrathin Au nanowires on the exfoliated sheets. We have converted the MoO3 rods into MoS2, a widely used catalytic material, by a comparatively low temperature method. Transmission Electron Microscopy study shows that the MoS2 spheres formed comprises of 4-8 ultrathin nanosheet stacked together. The mechanism of conversion from MoO3 to MoS2 has been understood by a series of time-dependent experiments. Since they contain a lot of exposed edges which are active towards catalysis, this material can act as a very good candidate as an electro-catalyst for H2 evolution reaction.

**FF01.21.18**  
**GeS Field Effect Transistor for High Temperature Applications** Srinivasa R. Tamalampudi1, Raman Sankar2, Ibraheem Almansouri3, Jin-You Lu1 and Matteo Chiesa1; 1Khalifa University of Science and Technology, United Arab Emirates; 2Academica Sinica, Taiwan; 3Laboratory for Energy and NanoScience (LENS), United Arab Emirates

Intrinsic crystal defects play a major role in tailoring the electrical and optical properties of two-dimensional (2D) materials. Here, we probe the impact of planar crystal defects on the electrical characteristics of germanium sulfide (GeS) field effect transistor (FET) at different operating temperatures varying from 300 to 575 K. Our results show that the measured mobility of the GeS field effect transistor was 0.04 × 10–3 cm2/(V s) at 300 K, and this value reached 58 × 10–3 cm2/(V s) at 575 K. It is important to note that the mobility of GeS FET at elevated temperatures
in this study is greater than the mobilities in the recently reported GeS photodetector studies. Furthermore, evidence that the threshold voltage ($V_{th}$) decreases and carrier concentration increases with increasing temperature in the GeS channel is provided. We demonstrate an Arrhenius-like relation of the carrier transport as a function of temperature, a behavior that we attribute to nearest-neighbor-hopping (NNH) conduction. The existence of planar defects is revealed using transmission electron microscopy (TEM) while density functional theory (DFT) analysis supports the hypothesis that the formation of localized energy states governs hopping conduction. This study reports hopping conduction at the temperature above 300 K for the first time, whereas previous investigations on 2D materials have reported a hopping mechanism in the low-temperature (<200 K) range. These observations give insight into the fundamental charge conduction mechanisms at high temperature in other 2D materials systems which are expected to aid in the development of applications for harsh environments.

**FF01.21.19**

**Wafer Scale Synthesis of Transition Metal Telluride Thin Films**

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Two-dimensional materials have attracted much attention over the past decade due to their unique van der Waals (vdW) interlayer bonding that gives rise to interesting physical phenomena that can be accessed through monolayer isolation and synthesis of heterostructures. Recently, transition metal tellurides of the form XTe$_2$ (X: Mo, W) have shown novel electronic properties, such as large magnetoresistance$^1$, superconductivity$^{2,3}$, quantum spin Hall states$^4$, and the predicted type-II Weyl semi-metal state$^{5,6}$, which are attractive for applications ranging from chemical sensing to quantum computing. One of the biggest challenges to vdW bonded materials is the lack of industrially scalable synthesis methods to create large scale, stable structures on substrates that are easily integrable in modern microfabrication processes.

Atomic layer deposition (ALD) is an industrially scalable technique that produces epitaxially grown films with uniform stoichiometry and thickness. In this work, ALD is used to deposit transition metal oxide films, which are then converted into wafer-scale transition metal tellurides using a vapor-phase annealing process. By controlling the reaction parameters and choice of substrates, we show that control over film morphology and phase can be achieved, leading to substantial improvements in crystalline quality. Additionally, we developed an *in situ* encapsulation layer for the synthesized transition metal tellurides and studied the effects of the encapsulation layers on growth kinetics and protection against oxidation.


**FF01.21.20**

**Slot Antennas for Graphene Mid-IR Photodetectors**

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Mid-infrared imaging has a wide range of applications, such as night vision, surveillance, and remote chemical sensing. However, the current options for mid-IR imagers leave much to be desired, with cooled detectors offering excellent performance at the cost of power, size and system complexity, while uncooled bolometers struggle with slow response times and low detectivity. Graphene is a promising alternative mid-IR sensitive optoelectronic material due to its broadband absorption, strong electrical response and wide process compatibility, but its low absorption for normally incident light poses a challenge in designing high efficiency devices. We propose to couple the graphene with metal slot antennas, compact resonators which capture specific wavelengths of light and significantly enhance the free space to graphene light coupling efficiency. Additionally, since the antennas’ footprints are much smaller than their absorption cross sections, multiple
antennas with different resonant frequencies can be placed in close proximity, allowing broadband and spectrally selective photodetection. Here we present simulations and a model confirming the validity of our approach as well as measurements of slot antennas demonstrating consistency between simulated and measured optical properties. We will also discuss how the antenna absorbers can be engineered into actual photodetectors as well as paths forward for integrating the technology with electronics. This research paves the way towards establishing graphene as a viable mid-IR sensing technology, improving upon the response time of bolometers and adding spectral selectivity while maintaining similar detectivities.

FF01.21.21
Synthesis, Crystal Growth and Characterization of Tetrel-Pnictide van der Waals Materials Justin Mark1,2, Brennan McBride1, Bingheng Ji1, Shannon Lee1,2 and Kirill Kovnir1,2; 1Iowa State University of Science and Technology, United States; 2Ames Laboratory, United States

Elemental P and As crystallize in layered structures; exfoliation of these structures using tape gave rise to novel 2D materials, phosphorene and arsenene. When pnictogens, such as P and As, are combined with light tetrels, Si and Ge, the resulting binary compounds are layered van der Waals materials. Strong covalent tetrel-pnictide bonding is found within the layer. The layers are terminated by the three-coordinated pnictogen atoms which have an electron lone pair pointed towards the electron lone pairs on atoms terminating neighboring layers. The repulsion of the electron lone pairs is responsible for the two-dimensional crystal structure with weak van der Waals type interactions between the layers. Strongly anisotropic bonding makes such materials not only easy to exfoliate but also stable against oxidation, unlike phosphorene-like materials. Strongly anisotropic and fascinating properties were predicted computationally and observed experimentally for this class of materials and their individual layers. Tetrel-pnictides have been shown to have several promising applications which include thermoelectrics, batteries, photovoltaics, optics, and superconductivity. To further expand the boundary of known tetrel-pnictide systems and their characterization, a deeper understanding of their synthesis and crystal growth is required. In this work we specifically focus on binary and ternary 2D tetrel-pnictide synthesis and characterization. Solid state synthesis involving elements, binary precursors, and metal flux has yielded several new 2D tetrel-pnictide phases, which exhibit complex structural motifs, inherently influencing their physical properties. Further complexity can be added to these structures through doping of framework atoms or cations in the layers, allowing for the tuning of desired properties.

FF01.21.22
Two-Dimensional MoTe2/Pentacene as Highly Efficient Type II Heterostructure Yu Jin Jang, Jin Cheol Park, Minh D. Tran, Meeree Kim, Hyoyoung Lee, Ji-Hee Kim and Young Hee Lee; Sungkyunkwan University, Korea (the Republic of)

Atomically-thin transition metal dichalcogenides (TMDs) have been recognized as a promising platform for the next generation photovoltaics on the basis of a tunable bandgap, large absorption coefficients, weak exciton-phonon coupling, and short distances for carrier extraction. However, photovoltaic efficiencies which have been practically obtained to date from various TMD heterostructures remained below 5% and this raises the question of a new design of two-dimensional (2D) heterostructures in terms of composition or configuration. Herein, we propose to construct a type II heterojunction between MoTe2 and pentacene as n- and p- type materials, respectively. Two semiconductors in the heterostructure produced excitons under illumination ranging from visible (Vis) to near-infrared (NIR) light and the staggered band alignment facilitated the charge separation at the interface. By carefully monitoring the ground state bleach (GSB) and photo induced absorption (PIA) signals of the heterostructure as a function of time with transient absorption spectroscopy (TAS), we found that the number of electrons and holes generated and extracted from the heterostructure was increased over the single materials and intervalley scattering occurring on longer timescales confirmed the charge transfer between two layers. This observation will provide a clue to the fabrication of 2D photovoltaic devices which breaks the efficiency limit.

FF01.21.23
Aligned Growth of Monolayer WS2 with Engineered Band Structure and Morphology Derived by Quartz Substrate Tianran Li, Jingwei Wang and Chun Cheng; Southern University of Science and Technology, China

Controlled growth of two-dimensional (2D) transition metal dichalcogenides (TMDCs) is important for the
applications in next-generation electronics and optoelectronics. Apart from the growth conditions, the growth substrate plays a crucial role such as in orientation regulation, band structure and morphology engineering. In this work, we report aligned growth of monolayer tungsten disulfide (WS₂) with engineered band structure and morphology on single crystal quartz substrate. The bandgap of epitaxial WS₂ was significantly expanded due to the built-in strain. By decreasing the temperature, the increased strain could further modulate the band structure and a direct-indirect transition in monolayer WS₂ could be achieved at liquid nitrogen temperature. Moreover, the unique lattice arrangement of quartz facilitates the anisotropic diffusion of precursor monomer and results in trapezoidal-like WS₂ which is confirmed by our density functional theory simulation. This work not only contributes to the controlled growth of TMDCs but also provide an effective approach to engineer the band structure and morphology of 2D materials.

FF01.21.24
Strong Carrier-Induced Electric Double Layer for Engineering Electronic Properties of Indium Selenide Field-Effect Transistors Chih-Yi Cheng¹, Wei-Liang Pai², Yi-Hsun Chen¹, Shao-Yu Chen¹, Raman Sankar², Fang-Cheng Chour², Chun-Wei Chen², Chi-Te Liang² and Wei-Hua Wang¹; ¹Academia Sinica, Taiwan; ²National Taiwan University, Taiwan; ³Monash University, Australia

Two-dimensional (2D) semiconductors feature high surface-to-volume ratio, offering an ideal platform for exploring unique surface and interfacial interactions [1]. An ionic liquid (IL) can be used in an electrostatic gating technique for effectively achieving high carrier density regime in 2D semiconductors by creating an electric double layer (EDL) at the semiconductor/IL interfaces [2-3]. The EDL arises when an IL gate voltage is applied and mobile ions accumulate at the interfaces, which attract charge carriers to the interface. However, it is rarely discussed whether the charge carrier confined in atomically thin 2D semiconductors can alter the electrostatic coupling at the solid/liquid interfaces. In this work, we systematically study the electrostatic coupling at the interface between the layered indium selenide (InSe) and the IL. We observe an anomalous temperature dependence of the transport behavior when the IL undergoes phase transition. Interestingly, the conductivity of the InSe devices interfaced with the IL enhances by a factor of 2 and the field-effect mobility reaches 1,200 cm²/Vs when the IL is around glass transition point (T_g). By the correlation of capacitance and transport behavior, we attribute the carrier density enhancement to a strong carrier-induced EDL when the ion motion greatly decreases around T_g. The observation of the distinct carrier-induced EDL in the InSe devices suggests novel functionalities to control the electronic transport in the 2D-semiconductor/IL hybrid systems.


FF01.21.25
Synthesis of MoS₂ on Epitaxial Graphene by Chemical Vapor Deposition Gabriel V. Soares¹,², Tais O. Feijo¹,³, João M. Lopes¹ and Claudio Radtke¹; ¹UFRGS, Brazil; ²PGMICRO-UFRGS, Brazil; ³Paul-Drude-Institut für Festkörperelektronik, Leibniz-Institut im Forschungsverbund Berlin, Germany

Stacking 2D crystals on the top of each other allows for the creation of van der Waals (vdW) heterostructures with new properties and functionalities[1]. As an example, MoS₂ (semiconductor) and graphene (conductor) can be combined to form metal-semiconductor junctions exhibiting an atomically thin Schottky barrier [2]. Moreover, the MoS₂/graphene structure can be used in hydrogen evolution reaction for clean energy applications [3]. However, before this material system can be implemented into different applications, it is mandatory to achieve its controlled synthesis at wafer-scale. For this, gaining an in-depth understanding of the mechanisms underlying 2D monolayer growth, as well as the effects of processing of the resulting heterostructure on its physico-chemical properties is crucial. The aim of this work is to investigate the basic mechanisms underlying the growth of MoS₂ by chemical vapor deposition (CVD) on epitaxial graphene (EG) on SiC, taking into account the influence of the number of graphene layers, and the MoS₂ growth temperature. MoS₂ was grown on EG templates which were synthesized via Si sublimation [4] on on-axis and off-axis SiC(0001) substrates. The use of SiC substrates with different miscuts permits to obtain different graphene coverage over the (0001) surface terraces (monolayer coverage for on-axis SiC; few-layer coverage for off-axis SiC). The MoS₂ growth is done in a CVD reactor using solid precursors of MoO₃ and S. Growth temperatures within the 500-700°C range with a fixed 40 min long temperature ramp were used.
Raman spectroscopy, Near edge X-ray Absorption Fine structure (NEXAFS), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) were used to characterize the MoS$_2$/EG/SiC(0001) samples. Interestingly, we will show that MoS$_2$ prepared on few-layer thick EG on off-axis SiC(0001) at different temperatures exhibits an improved surface morphology with the growth proceeding mostly in a layer-by-layer manner without the formation of 3D particles. The latter effect is usually observed when MoS$_2$ is performed on monolayer-thick EG, and it is probably related to a higher atomic corrugation of monolayer EG in comparison to few-layer EG. The EG corrugation as well as the MoS$_2$ crystalline structure for different samples were probed by NEXAFS measurements of the S(L) and C(K) edges. They were complemented by XPS analyses, which allowed to determine the chemical environment of C, Mo and S in the MoS$_2$/graphene heterostructures.


FF01.21.26
Rapidly Dissolvable Transient Field-Effect Transistors Based on Phosphorene Min-Kyu Song$^{1,1}$, Seok Daniel Namgung$^{1,1}$, Taehoon Sung$^{1,1}$, Jae hun Lee$^{2}$, Misong Ju$^{2}$, Ki Tae Nam$^{2}$, Yoon-Sik Lee$^{2}$ and Jang-Yeon Kwon$^{1,1}$;
$^{1}$Yonsei University, Korea (the Republic of); $^{2}$Seoul National University, Korea (the Republic of)

Transient electronics has received great attention as new generation of human implantable device that physically disappear after operation time in physiological condition. Many applications including biosensors, RF antennas and memories have been reported since its first demonstration in 2012. However, dissolution rate of silicon nanomembrane which has mostly been used as an active material in transient devices is quiet low ranging from a few days to weeks. In order to minimize physical damage caused by residue from dissolvable devices, dissolution time of the devices should be minimized. Phosphorene, atomically thin layers of black phosphorus, has been promised as a promising candidate for a new semiconductor material due to its outstanding intrinsic properties including high mobility and tunable bandgap. In addition, phosphorene is attractive for biomedical applications because of its nontoxicity of final degradation products, phosphoric acid. We found that phosphorene dissolves rapidly in physiological condition due to its high reactivity to water and oxygen. From this context, we suggested phosphorene as an active material for transient electronics. In this work, we fabricated biodegradable and biocompatible field-effect transistors based on phosphorene that rapidly disappears in biofluid within 36 hours. Combined use of phosphorene, peptide insulator, and molybdenum enables rapid dissolution of the devices. The devices exhibit high field effect mobility up to 468 cm$^2$V$^{-1}$s$^{-1}$ which is over 400 times higher than that of ZnO based field effect transistors and comparable to that of Si NM based field effect transistors.

We examined biodegradability of phosphorene using AFM and Raman spectroscopy. Dissolution rate of phosphorene was found to be 1.65 nm/hour in phosphate buffered saline (pH 7.4, 37 °C), which is about 8.8 times faster than that of Si nanomembrane in the same condition. Phosphorene with thickness of 30–40 nm disappears within 1 day due to its highly reactive nature to oxygen which has been regarded as a nettlesome barrier of phosphorene. Furthermore, we assessed the cytotoxicity of phosphorene by LIVE/DEAD viability assay to verify its feasibility to be applied in biomedical devices. After incubated with phosphorene, NIH 3T3 fibroblast cells showed viability of over 90 % up to phosphorene concentration of 50 μg/mL$^{-1}$. In conclusion, we not only realized the transient device that meets two criteria, fast dissolution and high performance, but opened new application possibility of phosphorene to bio implantable electronic devices platform.

FF01.21.27
Versatile Doping of Black Phosphorus and Functional Junction Structure Formation Jingyuan Jia and Tun Cao; Dalian University of Technology, China

Black phosphorus (BP) was recently rediscovered as being a layered two-dimensional (2D) semiconductor material that is potentially useful as the active material in future nanoscale devices. The electronic properties of atomically thin BP can be controlled by external gating or by chemical doping. Here, we demonstrate the versatile doping control of black phosphorus (BP) using an ionic liquid (EMIM:TFSI) as a surface charge acceptor for a wide range of electronic and optoelectronic device applications. BP following EMIM:TFSI doping achieves a high hole density of up to $10^{13}$ cm$^{-2}$ without impurity injection, which represents a degenerate doping level. Furthermore, this doping effect can be reversibly removed through immersion in isopropanol and the electrical performance of BP devices is
able to recover and approach the pristine state (cyclic process). Using a selective-area doping technique, both lateral junction structures and self-aligned source/drain BP field-effect transistors (FETs) are fabricated through a poly(methyl methacrylate) pattern method. The BP lateral junction devices show ideal rectifying behavior. Self-aligned BP FETs with channel lengths as low as 60 nm are presented, using a process similar to the conventional CMOS gate first process. Such FETs demonstrate the potential for fabricating nanoscale BP electronic devices.

**FF01.21.28**

**Controlled Synthesis of Vertically-Oriented MoS2 Flakes by Chemical Vapor Deposition—Morphological Evolution and Growth Mechanism**  
Talal Al Tahtamouni and Fadi Kamand; Qatar University, Qatar

Understanding the growth mechanism and morphological evolution is the key to control the growth of layered two-dimensional materials using chemical vapor deposition (CVD) approach. Herein, we report the CVD synthesis of vertically-oriented MoS2 flakes from the conventional precursors of MoO3 and S powder. Using different amounts of S powder in the CVD process, different morphologies and structures of MoS2 were obtained. A hypothesis based on two competing pathways of reactions is proposed to explain the growth mechanism and morphological evolution of the MoS2 nanostructures. In addition, catalytic activities of the vertically-oriented MoS2 flakes are tested for photoelectrochemical water splitting performance. Our results open the door to promote the process for the design of other transition metal dichalcogenide materials or complex structures in various applications.

**FF01.21.29**

**2D Transition Metal Dichalcogenides (TMDs) Nanopatterning by Block Copolymer Lithography**  
Taeyeong Yun, Inho Kim and Sang Ouk Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Structure engineering method is highly necessary for the various applications of 2D transition metal dichalcogenides (TMDs). We demonstrate edge-exposed 2D polycrystalline MoS2 nanomesh thin film through conventional block copolymer (BCP) nanopatterning. Metal nanomesh is deposited by e-beam evaporation on BCP template and then, MoS2 nanomesh thin film is directly fabricated through sulfurization of pre-deposited molybdenum nanomesh without any etching process. Our approach could be easily applicable not only to other metal sulfides and metal oxides but also to other structures of TMD thin film such as nanodots, nanorods array through various BCP nanopatterning. Because edge site of MoS2 is active for NO2 sensing, our edge-exposed MoS2 nanomesh represents 7-fold enhanced sensitivity to NO2 gas molecule compared to film structure as well as shows superior reversibility even under 80 % relative humidity environment. This structure engineering method could expand a novel applications of 2D TMD materials with optimal structure controllability.

**FF01.21.30**

**Dose-Dependent Proton Beam Irradiation Effect on WSe2 Ambipolar Field Effect Transistors**  
Jiwon Shin1, Kyungjune Cho1, TaeYoung Kim1, Jinsu Pak1, Jae-Keun Kim1, Seungjun Chung2, Woong-Ki Hong3 and Takhee Lee1; 1Seoul National University, Korea (the Republic of); 2Korea Institute of Science and Technology, Korea (the Republic of); 3Korea Basic Science Institute, Korea (the Republic of)

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) have gained significant attention as one of the candidates for next-generation semiconductor materials due to their unique mechanical and electronic properties. For applications in various integrated devices, it is important to control the properties of 2D TMDs materials. In this work, the irradiation effect of high energy proton beams on tungsten diselenide (WSe2) ambipolar field-effect transistors(FETs) were investigated. We measured the electrical characteristics of the fabricated WSe2 FETs before and after the 10 MeV proton beam irradiation with different doses of $10^{12}$, $10^{13}$, $10^{14}$, and $10^{15}$ cm$^{-2}$. For low dose conditions ($10^{12}$, $10^{13}$, and $10^{14}$ cm$^{-2}$), the threshold voltages shifted to the negative gate voltage direction, and the current in the hole and electron accumulation regimes decreased and increased, respectively. However, the trends were opposite for the high dose condition ($10^{15}$ cm$^{-2}$); the threshold voltages shifted to the positive gate voltage direction, and the current in the hole and electron accumulation regimes increased and decreased, respectively. Also, we measured the physicochemical properties of the WSe2 flakes by X-ray photoemission spectroscopy (XPS) and Raman spectroscopy. There was no noticeable difference in XPS and Raman spectra on the WSe2 flakes before and after the proton beam irradiation. These phenomena can be explained by the combined effect of proton irradiation-induced traps and the applied gate bias condition. Specifically, irradiation-induced positive oxide traps in SiO2 dielectric play a role in enhancing electron accumulation and reducing hole accumulation in the WSe2 channel, whereas the irradiation-induced holes near the WSe2/SiO2 interface act as electron trapping sites, with enhancing
hole accumulation and reducing electron accumulation in the WSe₂ channel. This study may provide a method to control the electrical properties of WSe₂ FETs through proton beam irradiation. Furthermore, it is hoped that this study will contribute to a deeper understanding of the influence of high-energy proton beams on ambipolar WSe₂-based nanoelectronic devices and be helpful for the application of the TMD-based devices in harsh radiation environments such as space.

**FF01.21.31**

Selective Defect Formation in Hexagonal Boron Nitride by Boron Gettering Chemical Vapor Deposition

Irfan Haider Abidi¹, Zhengtang Luo² and Barbaros Oezylmaz³; ¹National University of Singapore, Singapore; ²The Hong Kong University of Science and Technology, Hong Kong

Luminescent defect-centers in hexagonal boron nitride (hBN) have emerged as a promising 2D-source of single photon emitters (SPEs) due to their high brightness and robust operation at room temperature. The ability to create such emitters with well-defined optical properties is a cornerstone towards their integration into on-chip photonic architectures. Here, we report an effective approach to fabricate hBN single photon emitters (SPEs) with desired emission properties in two isolated spectral regions via the manipulation of boron diffusion through copper during atmospheric pressure chemical vapor deposition (APCVD)—a process we term gettering. Using the gettering technique we deterministically place the resulting zero-phonon line (ZPL) between the regions 550-600 nm or from 600-650 nm, paving the way for hBN SPEs with tailored emission properties across a broad spectral range. Our ability to control defect formation during hBN growth provides a simple and cost effective means to improve the crystallinity of CVD hBN films, and lower defect density making it applicable to hBN growth for a wide-range of applications. Our results are important to understand defect formation of quantum emitters in hBN and deploy them for scalable photonic technologies.

**FF01.21.32**

Broadband Photodetector Based on MoS₂ Nanostructures—2D MoS₂/1D WS₂ and 2D MoS₂/3D Polyaniline for High Photoresponsive Properties

Manika Khanuja and Nahid Chaudhary; Jamia Millia Islamia, India

2D materials emerged as a new class of high-performance semiconductors for optoelectronics but with limited photoresponsivity. Herein, we have successfully synthesized pure MoS₂ nanosheets, MoS₂-Polyaniline (PANI) hybrid structure and 2D MoS₂/1D WS₂ heterostructure for their application in photodetector. The morphology was confirmed using Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) revealing nanosheets of MoS₂, hybrid structure of MoS₂-PANI and 2D/1D MoS₂/WS₂. The interlayer spacing of MoS₂ in MoS₂-PANI hybrid structure is increased from 0.68 nm to 0.75 nm. The samples were further characterized using X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Uv-vis and Raman spectroscopy. The obtained samples were drop casted over silicon substrate followed by deposition of silver electrode to fabricate optical sensor. The fabricated optical sensors were studied at three different wavelengths of laser (λex): 635 nm (red), 785 nm (infra-red) and 1064 nm (near infra-red). The calculated photoresponsivity (Rp) of MoS₂ nanosheets was found to be 23.8 µA/W at laser wavelength of 635 nm (red), whereas MoS₂-PANI hybrid structure showed maximum (Rp) = 25 A/W at 785 nm (infra-red). The optical response of 2D MoS₂/1D WS₂ based photodetector showed (Rp) in a broadband range from the visible to the near-infrared (600-1065 nm, yield a (Rp) = 15 µA/W and high specific detectivity (D*) = 24 x 10⁶ jones at λex = 785 nm). The photoresponsive properties of all samples were also studied as a function of optical power density and follows the simple power law [1-2].

Reference:

**FF01.21.34**

Three-Dimensional Architected Graphene Lattices from Additively-Manufactured Polymer Templates

Juveiriah M. Ashraf, Jing Fu, Kin Liao, Vincent Chan and Rashid K. Abu Al-Rub; Khalifa University of Science and Technology, United Arab Emirates

Two-dimensional (2D) materials offer unique properties as atomically thin layers and, when structured to be in a three-dimensional (3D) form, they exhibit exceptional material qualities. Graphene is one such material with
exceedingly novel properties with 3D porous graphene foams adding to their functionality. However, controlled synthesis of 3D foams from 2D materials into engineered structures is currently still a challenge. With the recent advances in many key technological fields, the need for lightweight and multi-functional materials is becoming highly imperative. Triply periodic minimal surfaces (TPMS) are edge-free cellular architectures with locally net zero curvature that divide a volume into two non-intersecting spaces. Their low density and yet high surface area have enabled them to be used as lightweight cellular materials, heat sinks, catalytic converters, and feed spacers. Integrating graphene into TPMS to form 3D architected lattices of the 2D material is expected to offer unprecedented thermal, electrical, and mechanical properties that could be exploited in a spectrum of engineering applications. Since processes like chemical vapor deposition (CVD) and atomic layer deposition (ALD) are highly substrate-, temperature- and shape-specific, it is difficult to synthesize 3D foams or coat complex lattice structures of TPMS with 2D materials like graphene using these techniques. For example, there is a minimum pore size needed to create free-standing graphene after removing the metal template used in CVD processes, otherwise the graphene foam collapses. Conformal or step coverage is also an issue in most physical vapor deposition (PVD) process like thermal evaporation. In this project, a facile, scalable and lab environment-friendly, synthesis method for novel 3D graphene foams has been developed using additively-manufactured polymer-based TPMS as the initial sacrificial template. Stereolithography (SLA) was employed to 3D print high resolution Gyroid (a type of TPMS) cubes of length 2 cm, which were dip-coated with graphene oxide (GO) solution followed by drying and thermal etching of the polymer scaffold. Scanning electron microscopy (SEM) and micro computed tomography (micro-CT) scans showed high shape retention of the complex TPMS architectures and low shrinkage after burnout of the polymer template, rendering the developed coating process to be used for structures of any morphology with a large range of pore sizes. Chemical reduction of the GO foams was done by adding one volume percent of hydrazine hydrate to the starting GO solution, and this was verified by an X-ray diffraction (XRD) peak at 20° along with a Raman response at 1358 cm\(^{-1}\) (D peak), 1591 cm\(^{-1}\) (G peak) and 2696 cm\(^{-1}\) (2D peak) which correspond to reduced graphene oxide (rGO). The 3D graphene foams have been tested for their thermal, electrical and mechanical properties, and evaluated for their electromagnetic interference (EMI)/shielding capability.

**FF01.21.35**

**Thickness-Dependent Optical Bandgap and Electrical Transport Properties in InSe Thin Films Grown by Pulsed-Laser Deposition** Dingheng Zheng, Junichi Shiogai, Kohei Fujiwara and Atsushi Tsukazaki; Tohoku University, Japan

The reduction of dimensionality leads to an emergence of exotic physical properties, which are absent in the bulk form of two-dimensional (2D) layered materials [1]. Up to now, many layered materials such as graphene and chalcogenides have been reported to exhibit interesting number-of-layers dependence of electronic structures and physical phenomena [2–4], providing a rich playground to explore possibility in optical or electrical device functionality at low dimensional limit.

Layered indium selenide (InSe) is one of the potential candidates for atomically-thin optoelectronic devices because of its high mobility originating from a small effective mass of electron and a wide variation of optical bandgap by thickness tuning as exemplified in mechanically-exfoliated flakes [5]. However, such thickness dependent optical properties of InSe have not been addressed in thin film form by applying deposition techniques. In this study, we have grown layered InSe thin films on insulating Al\(_2\)O\(_3\)(0001) and InP(111) substrates by pulsed-laser deposition (PLD). By taking advantage of the precise thickness controllability of PLD, systematic thickness dependences are investigated on optical bandgap and electrical transport properties [6]. With decreasing the film thickness of InSe on Al\(_2\)O\(_3\) from 145 to 1 nm, a systematic blue shift of absorption edges from about 1.4 to 3.3 eV is observed in optical transmittance spectra. Such blue shift can be ascribed to a band structure modification with bandgap broadening, as observed in an earlier report of photoluminescence studies in exfoliated flakes [5].

For the electrical transport measurements, InSe films grown on Al\(_2\)O\(_3\) show a large resistivity beyond the measurement limit. In contrast, the films on InP exhibit a \(n\)-type conduction. The sheet conductance of InSe on InP increases with increasing the films thickness, which we ascribed to an enhanced mobility from 230 cm\(^2\)V\(^{-1}\)s\(^{-1}\) at 1 nm to 730 cm\(^2\)V\(^{-1}\)s\(^{-1}\) at 146 nm. Our demonstration of the PLD growth of layered InSe thin films and their thickness dependent optical and electrical properties should establish a platform to investigate novel device functionalities beyond graphene by applying thin film growth technique to 2D materials.

After the discovery of the extraordinary properties of graphene, two-dimensional (2D) materials have attracted a growing interest due to their unique properties such as high surface area and charge carrier mobility. Different methods have been reported to prepare these materials, such as chemical vapor deposition, mechanical, chemical and electrochemical exfoliation. Most methods have disadvantages like having multistep and expensive process and using environmentally hazardous chemicals.

In this study, we used bipolar electrochemistry concept to design a cost-efficient, eco-friendly, single step, and controllable process for exfoliating and depositing 2D materials directly on conductive substrates. This method has been used for the formation of phosphorene, graphene oxide (GO), reduced graphene oxide (rGO) and their composites. Various materials characterization techniques have been used to study the properties of deposited materials. Electrochemical impedance spectroscopy, cyclic voltammetry, and galvanostatic charge-discharge tests have been carried out to evaluate the electrochemical performance of the materials as electrodes for double layer capacitors. The results showed high areal capacitance of 1.932 mF cm⁻² for rGO and 1.550 mF cm⁻² for phosphorene at a scan rate of 2 mV s⁻¹. From the frequency point of view, the capacitors showed very fast responses and cutoff frequency as high as 1820 Hz which is promising for being used in AC filtering applications. The materials synthesis technique and characterization will be addressed in details at the conference.

**Keywords:** Bipolar electrochemistry, graphene, phosphorene, exfoliation, supercapacitor, AC filter

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**Laser-Sculptured Ultrathin Transition Metal Carbide Layers for Energy Storage and Energy Harvesting Applications**

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Ultrathin transition metal carbides with high capacity, high surface area, and high conductivity are a promising family of materials for applications from energy storage to catalysis. However, large-scale, cost-effective, and precursor-free methods are lacking to prepare ultrathin carbides. Herein, we demonstrate a direct pattern method to manufacture ultrathin carbides (MoCx, WCx, and CoCx) on versatile substrates using a CO2 laser. The Laser-sculptured polycrystalline carbides (macroporous, 10~20 nm wall thickness, ~10 nm crystallinity) show high energy storage capability, hierarchical porous structure, and higher thermal resilience than Mxenes and other laser-ablated carbon materials. A flexible supercapacitor made of MoCx demonstrates a wide temperature range (-50~ 300 °C). Furthermore, the sculptured microstructures endow the carbide network with enhanced visible light absorption providing high solar energy harvesting efficiency (~ 72 %) for steam generation. The laser-based, scalable, resilient, and low-cost manufacturing process presents an approach for construction of multi-dimensional carbides and their subsequent applications.

**Keywords:** Laser-sculptured, ultrathin, transition metal carbides, energy storage, energy harvesting, solar energy harvesting, supercapacitor

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**Interface Dynamics in Monolayer Transition Metal Dichalcogenides under Applied Bias**

Akshay A. Murthy, Teodor K. Stanev, Roberto d. Reis, Shiqiang Hao, Christopher Wolverton, Nathaniel P. Stern and Vinayak Dravid; Northwestern University, United States

Stemming from their intriguing optical and electronic properties, monolayer transition metal dichalcogenides (TMDs) and their heterostructures offer unique next-generation and flexible device architectures. These systems have been explored to construct atomically thin diodes, photovoltaic cells, and memory devices. Despite the performance and functionalities in these devices being largely dictated by interfacial charge transport, the microscopic origins of various realizable macroscopic properties in these systems remain unclear. Further, the eventual practical deployment of these devices requires monolayer TMDs to operate under prolonged applied bias, which raises some concerns over long-term stability and reliability. While pre and post-operational TEM analysis is useful for identifying structural flaws or non-uniformities, in situ TEM offers a pathway for gaining a mechanistic understanding of intermediary phenomena through direct imaging of the atomic structure when subjected to an
external stimuli. In this study, we explore the mass transport dynamics at monolayer MoS2 grain boundaries (GBs) as a function of a lateral electric field. Though these GBs offer significant potential for future memristive and light emitting structures, previous reports have also indicated that these interfaces serve as regions of localized heating and are prone to oxidation and overall damage. Because such deleterious aspects are quite disruptive to device performance, we seek to understand the localized thermal spikes and attempt to establish links between applied electric field and grain boundary-mediated atomic diffusion. The observance of this mass transport phenomena and the resultant formation of porous regions help explain the non-uniform heating profile previously exhibited along grain boundaries. Through ongoing work using this in situ biasing platform, we aim to probe various types of TMD interfaces in order to more accurately model the complex atomic scale interactions giving rise to measurable properties.

FF01.21.41
Graphene-hBN Barristor Spectroscope Tae-Young Jeong, Jun-Ho Lee, Hyun-Jong Chung and You-Shin No; Konkuk University, Korea (the Republic of)

Graphene is a zero-gap semiconductor whose Fermi energy can be adjusted by an applied electric field. When a semiconductor directly contacts with graphene, the graphene-semiconductor interface forms a Schottky barrier, which offers opportunities to control barrier height and subsequently flow of current. A barristor, utilizing these unique properties, is a device that enables a high On/Off ratio (e.g. switching ratio ~1000) by adjusting the Schottky barrier height, which has been highly challenging for conventional Graphene FETs (GFETs).

This study reports a Graphene/hBN/Metal vertical nanostructure on a SiO2/Si substrate. Conceptually, the incident light in visible frequencies with enough energy $E_{\text{incident}}$ on the Graphene/hBN junction can excite electron and hole carriers so that they can either tunnel through or overcome the given Schottky barrier. In experiment, we used an excitation laser with wavelength of 488 nm to provide the external energy on the vertical junction structure. Then we slowly varied the gate voltage and observed gradual decrease in the photocurrent. When the gate voltage reached a certain point, we observed the turn-off the photocurrent (i.e., current-off point). Using this current-off point as an indicator, we calculated the Fermi energy of graphene ($E_F$) at given gate voltage. When the lasers with different wavelengths (i.e., different energies) were used, we were also able to find different current-off point and subsequently the Fermi energies. The Fermi energy difference ($D_E$) between two experiment with different lasers was estimated (e.g., $E_F,488\text{nm}$ vs. $E_F,532\text{nm}$, $E_F,520\text{nm}$), which corresponds the energy difference the incident light. In this proof-of-concept experiment, we successfully demonstrated a new nanoscale spectroscopic device that can analyze unknown incident wavelengths.

FF01.21.42
Insights into Chemical Vapor Deposition of Hexagonal Boron Nitride (h-BN) via Thermodynamic Control for 2D Electronics Applications Ankit S. Rao, Abhishek Mishra and Srinivasan Raghavan; Indian Institute of Science, India

Hexagonal boron nitride (h-BN) has been established as the preferred substrate for nanodevices based on 2-dimensional (2D) materials owing to its atomically flat interface, excellent thermal conductivity and suitable dielectric characteristics. Thus, there is a fundamental requirement to manufacture wafer scale h-BN for large area applications and the most scalable method is chemical vapor deposition (CVD). The current approaches for CVD growth of h-BN are by and large empirical due to which there is lack of control over the deposition. Our research involves thermodynamic control of the B-N-H system by identifying the appropriate windows of process parameters for controlled growth of h-BN. The system consists of ammonia borane (BH3-NH3) as the precursor for CVD growth of h-BN over copper (Cu) substrate. Within the thermodynamic windows, the control over gas phase supersaturation would allow better kinetic control over crystal growth. Thermodynamic control is exercised over gas phase supersaturation by use of carrier gases such as hydrogen (H2) and argon (Ar) and by controlling the precursor flux via a simple vaporizer setup, which allows tuning of the supersaturation and partial pressures of the gases in the chamber.

We report control over grain size and number of layers, from multilayer films to monolayer to partially covered films with uniformity across a large area. We obtain high degree of control by regulating the supersaturation and tuning the gas phase chemistry via variation of the H2, Ar partial pressures and the precursor chemistry. The growth of h-BN layers is accompanied with undesired nanocrystalline BN (n-BN) particles due to the precursor chemistry and post-growth copper deposits which degrade the film quality and these particles show preferential nucleation at
defect sites. We observe a significant reduction in n-BN particles by reduction in the precursor partial pressure via change in the carrier hydrogen partial pressure, which indicates the effect of supersaturation on the surface chemistry. Also, preferential nucleation at location of defects is seen which can be attributed to the energetic potential difference at various sites of the surface which is of thermodynamic nature as the energy barrier for nucleation at different sites are finite at a supersaturation value. Thus, the effect of growth parameters on the quality of hBN film deposited via CVD is observed with change in partial pressures and flux of precursor. The quality of film significantly changes with change in gas phase chemistry all other parameters being same, and this can be attributed to the fact that partial pressure of reactants have an exponential effect on supersaturation. Thus, we report controllable and scalable growth of h-BN over large areas by implementing thermodynamic control.

**FF01.21.45**

**Case Study on the Stability of Exfoliated II-VI Layered Hybrid Materials**

Mengwen Yan¹, Sean Collins² and Jeremy I. Feldblyum³; ¹University at Albany, State University of New York, United States; ²University of Cambridge, United Kingdom

The successful isolation of two-dimensional (2D) materials such as graphene and MoS₂ has fueled the search for other van der Waals materials with distinct functional properties. However, reducing the dimensionality of these materials often leads to undesired structural and chemical degradation, especially in the presence of air. In this presentation, we provide a case study in the factors governing the structural and chemical stability of a new class of exfoliated 2D materials known as II-VI layered hybrids (LHs). II-VI LHs are 2D, quantum-confined semiconductors capped by organic ligands, which stabilize the bound, 2D inorganic layer. We show here that of exfoliated ZnSe(butylamine) and ZnSe(octylamine) are susceptible to oxidation, but in a manner highly dependent on a variety of factors including exfoliation conditions, ligand identity, and air exposure time. We show that appropriate selection of these parameters can kinetically stabilize these metastable 2D materials that are otherwise prone to degradation when exposed to ambient conditions.

**FF01.21.46**

**Dirac-Like Linear Bands in a Non-Honeycomb Lattice of a Surface Alloy**

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Since the discovery of graphene, fabrication of atomically thin two dimensional (2D) materials with nontrivial band topology has attracted enormous attention primarily because of their dissipationless conduction. This led to the discovery of a family of 2D quantum materials with exotic properties; for example, to mention a few are stanene, silicene, aluminene, borophene and phosphorene. In particular, the prediction of stanene, a buckled tin honeycomb layer, to be a quantum spin Hall insulator with Dirac cone-like linear energy dispersion and a large gap of 0.3 eV has stirred up efforts to realize it on substrates. Gold is an interesting substrate for stanene growth that also exhibits a Rashba spin-orbit split surface state. However, both experimental as well as theoretical studies of Sn growth on Au(111) show formation of Au-Sn surface alloy. Here, we first establish that surface alloying in Sn/Au(111) using core-level photoelectron spectroscopy, scanning tunneling microscopy and low energy electron diffraction. The composition and the surface symmetries of these surface alloys at room and elevated temperatures are AuSn with p(3x3)R150° at substrate temperature Tₛ= 300 K and Au₂Sn described by the matrix (2₁₁₃) at Tₛ = 400 K that transforms to (3√3x√3)R30° phase at 493 K. Angle resolved photoemission spectroscopy demonstrates unexpected occurrence of a linear band resembling Dirac cone at the zone-center of Au₂Sn surface alloy with the (2₁₁₃) surface structure. This band disperses linearly over a wide binding energy range starting from 1.5 eV at kₖ = 0.2Å⁻¹ to the Fermi level, where the two branches of Λ meet at the Γ point. It is also observed using a different photon energy of 23 eV (He Iβ) where the dispersion is very similar to that taken with 21.2 (He I) eV photon energy indicating that it is surface related. Moreover, as expected for a Dirac cone, it is unaffected by the variation of the azimuthal angle e.g. from the Γ-M direction to the Γ-K direction. The magnitude of the slopes (dEₚ/dkₖ) of the left and the right branches are essentially same, 6.9±0.1 and 6.9±0.1, respectively, and the calculated Fermi velocity turns out to be 1.05x10⁶ m/s, which is very similar to that of graphene (1x10⁶ m/s). Importantly, it is only for the (2₁₁₃) surface, the linear bands occur and the results of our density functional theory based calculations for different possible atomic arrangements to simulate these bands will also be discussed. Importantly, here the linear bands meet at the Fermi level at the Γ point in a non-hexagonal lattice in a surface alloy with Fermi velocity comparable to graphene, which
might have potential application is high speed electronic devices.

**FF01.21.48**

**Mechanical and Conductivity Study of the 3D Printed PBAT/PLA/Graphene Nanocomposites**

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The research focuses on ways to adjust the mechanical properties of polymers that can potentially replace non-degradable, petroleum based plastics using PBAT, PLA and H-5 graphene. PBAT and PLA are both biodegradable and highly expected with the improvements in thermal and electrical conductivities by adding graphene, in which 3D printing technique is adapted to orient the H-5 platelets into a uniform direction. In this study, the concentration of PBAT and PLA was kept as 3:1 while the graphene concentrations were changed from 8% to 20%. Mechanical properties such as impact toughness and tensile properties as well as the thermal and electrical conductivity were studied to show the performance of the blends. The results were compared with the previously hot-pressed samples with the same formulations.

The impact strength of the printed sample was observed comparable to the molded samples, while significant increases in the Young’s modulus, tensile strength and elongation at break were obtained for the printed samples during the tensile tests.

In thermal conductivity test, the testings were done in two directions: 3D print vertical direction and 3D print printing direction to compare with the molded samples. The results showed that the thermal conductivity depended a lot on the measuring direction. For the vertical direction, the thermal conductivity results were not as good as the molded ones. However, for the printing direction, the results were observed to be higher than the molded samples.

For the electrical conductivity test, both printed and molded samples initially showed extremely small conductivity. When the concentration of H-5 went to 16 percent, the value of printed samples went up to 339 s/m and approximately doubled when the concentration went to 20 percent, which is around 50 times higher than that of the molded samples.

SEM images were used to observe the graphene dispersions in the polymer blends matrix. The high magnitude images of the created nanocomposites showed that graphene particles demonstrate a constant direction, indicating the possibility of enhancement of the mechanical and electrical conductivity. From the TEM images, we can clearly see the regularized orientation of the graphene platelets, further proved the rearrangement of the directions of graphene platelets during the extruding process of 3D printing.

In conclusion, the mechanical and conductivity were enhanced during the 3D printing procedure and can meet the demands of electrical appliances. The results indicated the possibility of engineering biodegradable, high-performance polymeric materials.

**FF01.21.49**

**Transition Metal Enhanced Carrier Transport in Two-Dimensional Semiconducting Crystals**

Maomao Liu¹, Simran Shahi¹, Hemendra Nath Jaiswal¹, Sichen Wei², Fei Yao² and Huamin Li¹; ¹New York State University at Buffalo, United States; ²University at Buffalo, The State University of New York, United States

Two-dimensional (2D) semiconducting crystals such as transition metal dichalcogenides (TMDs) have been considered as promising semiconductor channel materials for future nanoelectronic devices. Theoretical models predict that among various semiconducting TMDs, WS₂ has the highest electron mobility and the best transistor performance including the highest on/off ratios and on-current densities. However, for the practical application such as complementary metal-oxide-semiconductor logic circuits, it is urgently needed to improve carrier transport efficiency along the in-plane channel and through the metal-semiconductor interface. In this work, we report a significantly improved carrier transport in few-layer WS₂ field-effect transistors (FETs) by exploiting transition metals as dopants and metal contacts. Cu was chosen due to its high diffusion coefficient and compatibility in MEMS/NEMS processing. Cu-doped WS₂ was synthesized by introducing Cu during the chemical transport interaction, and Cu-contact WS₂ devices were prepared by evaporating a 2-nm-thick Cu layer at the metal-semiconductor interface. Compared to pristine WS₂ FETs, both the Cu-doped and Cu-contact WS₂ devices show the outstanding increases in carrier mobilities, on/off ratios, on-current densities, transconductances, and subthreshold swings. The metal-semiconductor contact condition was also improved from Schottky to Ohmic due to an
outstanding reduction of the contact barrier height and thus the contact resistance. We also carried out a statistical study with over 20 devices for each kind, and the results were consistent and repeatable. Our work has demonstrated the great potential of applying transition metals to improve the carrier transport of semiconducting TMDs in various device applications.

FF01.21.50
Pristine and Metal-Doped Hexagonal Boron Nitride Films on Centimeter Scale by Atomic Layer Deposition
René Weißing, Daniel Stadler, Matthias K. Grosch, Anja Sutorius and Sanjay Mathur; University of Cologne, Germany

Hexagonal boron nitride (h-BN) with its atomically flat structure, excellent stability and large band gap energy (~ 6 eV) is an ideal insulator for 2D electronics. Fabrication of h-BN thin films is mainly limited to exfoliation of multilayer or bulk crystals, however the size of h-BN crystals are limited to few millimeters. Consequently, mechanical exfoliation and chemical transfer procedures typically deliver h-BN flakes of several tens of micrometers that come along with significant interfacial impurities, defects and low production capacity that limits the use of h-BN on large scale. Therefore, the vapor phase methods ALD and CVD are promising alternatives to grow h-BN monolayers and multilayers as demonstrated for several metallic substrates (e.g., Au, Cu, Ni, Co). Nevertheless, epilayer growth of unidirectionally aligned h-BN domains has been challenging due to excessive nucleation and 3-fold symmetry of h-BN lattice that results in twin boundaries. Therefore, we have developed vacuum-based processes to grow h-BN monolayers on centimeter scale Cu(111) substrates relevant for electronic applications. The synthetic access was achieved by two complementary half-reactions of B and N precursors (ALD) and via thermal decomposition and surface nucleation of single-source precursors such as amino boranes and borazine (CVD). We have recently investigated the growth of h-BN by CVD of solid ammonia-borane (BH3<-NH3) that sublimes at 100 °C and is thermally decomposed (dehydrogenated) on the substrate surface at elevated temperature (700-900 °C) to nucleate h-BN domains. Also, the CVD of borazine (B3N3H6) on Cu(111) showed the growth of large BN crystals that show a pronounced tendency of lateral diffusion to grow into coherent h-BN domains.

FF01.21.51
Molecular Routes to Two-Dimensional Metal Disulfides MS2 (M = Mo, W)
Veronika Brune, Matthias K. Grosch, Corinna Hegemann, Sanjay Mathur and René Weißing; University of Cologne, Germany

The ever-growing interest in van der Waals materials like two-dimensional transition metal disulfides (TMDSs) demands a matching supply of these materials. TMDS complexes containing group VI metal ions are attractive starting materials for 2D materials that offer great potential for low-power electronics, especially because of their favorable layered structures and promising electro-optical properties. For this we introduce an entirely novel class of molecular precursors: [MIV(SEtN(Me)EtS)2] (MIV = MoIV, WIV). Tungsten and molybdenum complexes of dianionic tridentate pincer type ligands (HSEt)2NMe produced air-stable monomeric disulfide complexes, [W(SEtN(Me)EiS)2] and [Mo(SEtN(Me)EiS)2], displaying W and Mo centers in distorted octahedral environment of 4 S and 2 N donor atoms. We then used these volatile and cleanly decomposing precursors in chemical vapor deposition for the creation of large area crystalline MoS2 and WS2 thin films. As-prepared films were subjected to atomic scale imaging and x-ray analysis to confirm the synthesis of phase-pure MX2 materials. New ligands presented in this work open up a new molecular route to precursor engineering for 2D transition metal disulfides and allow an efficient approach towards the synthesis of scalable van der Waals heterostructured materials.

FF01.21.52
N-Doped CVD-Grown MoSe2 Field Effect Transistors by Two-Step Doping Process
Seongin Hong¹, Haewon Cho¹, Junwoo Park¹, Jun Hong Park² and Sunkook Kim¹; ¹¹) School of Advanced Materials Science & Engineering Sungkyunkwan University, Korea (the Republic of); ¹²) School of Materials Science & Engineering Gyeongsang National University, Korea (the Republic of)

Two-dimensional (2D) layered transition metal dichalcogenides (TMDs) have been considered the next-generation semiconductor materials for potential sensor applications due to their intriguing mechanical, electrical and optical properties. Molybdenum diselenide (MoSe2), one of TMDs, has recently attracted attention for high performance photosensor applications owing to its superior photoresponsivity. In addition, since the bandgap of MoSe2 is smaller than it of MoS2, wide excitation wavelength range as well as excellent electrical conductivity can be obtained in
MoSe₂ field-effect transistors (FETs). However, chemical vapor deposition (CVD)-grown MoSe₂ FETs randomly exhibit n-type, p-type, or ambipolar characteristics due to the unexpected defect generated during the growth of MoSe₂ by uncontrolled growth condition. Here, two-step doping method with n-type doping effect was developed to achieve unipolar n-type MoSe₂ FETs and its long-term stability. After the two-step doping process on MoSe₂ FETs using oxygen plasma treatment (1st step) and Al₂O₃ layer deposition (2nd step), n-type, p-type and ambipolar MoSe₂ FETs are all converted to unipolar n-type MoSe₂ with enhanced electrical properties and stability. Field effect mobility of n-doped MoSe₂ was improved from 12.23 to 31.57 cm²V⁻¹s⁻¹, 3 times larger $I_{on}/I_{off}$ without any degradation for 21 days. The enhancement is attributed to fixed positive charges in Al₂O₃ layer and electrically-insulating oxidation on the top-surface of MoSe₂ by oxygen plasma treatment. The results suggest that the two-step methods will be a novel process to achieve n-type doping effect with high-performance and stability for various sensor applications.

**FF01.21.53**

**Tuning Band Splitting and van-Hove Singularities in Twisted-Bilayer Graphene Superlattices** Francisco Sanchez-Ochoa and Cecilia Noguez; Universidad Nacional Autónoma de México, Mexico

Twisted-bilayer graphene (TBLG) is a new kind of two-dimensional material where new physical phenomena arise because of the interlayer potential modulation as a function of the different relative orientations between layers. This arbitrary orientation in TBLG is characterized by the relative angle of rotation and the stacking pattern (AA, AB). The interlayer interaction could change the electronic band structure drastically as compared to one G layer. Here, we discuss the effective band structures calculated from the projection of supercell electronic-states on a G primitive cell. These effective band structures are obtained by unfolding the bands that are calculated using density functional theory [1]. The results show that the major changes in the electronic states of G are along the K-M path in the irreducible Brillouin zone of primitive cell; meanwhile, the other two paths Γ-K and Γ-M show a split of the π band for higher energies in the valence band. In the K-M path, we observe the appearance of electronic band gaps approaching the Fermi level when the angle between monolayers is small. These band gaps give rise to van Hove singularities in the density of states with a uniform distribution of discrete electronic states, like Rydberg-like series. These results provide the first theoretical evidence of the discretization of the band structure in a set of well-ordered electronic states and are in fair agreement with experimental observations [2–4]. These electronic states can be responsible for new conduction channels, which might be essential for the realization of new optoelectronic devices based on G [5,6].


**FF01.21.56**

**Chemiresistive Sensing of Ambient CO₂ by Metal-Organic Frameworks** Jinhu Dou and Mircea Dincă; Massachusetts Institute of Technology, United States

A growing demand for indoor atmosphere monitoring relies critically on the ability to reliably and quantitatively detect carbon dioxide. Widespread adoption of CO₂ sensors requires vastly improved materials and approaches because selective sensing of CO₂ under ambient conditions, where relative humidity (RH) and other atmosphere contaminants provide a complex scenario, is particularly challenging. This report describes an ambient CO₂ chemiresistor platform based on nanoporous, electrically conducting two-dimensional metal–organic frameworks (2D MOFs). The CO₂ chemiresistive sensitivity of 2D MOFs is attained through the incorporation of imino-semiquinonate moieties, i.e., well-defined N-heteroatom functionalization. The best performance is obtained with Cu₃(hexaiminobenzene)₂, Cu₃HIB₂, which shows selective and robust ambient CO₂ sensing properties at practically relevant levels (400–2500 ppm). The observed ambient CO₂ sensitivity is nearly RH-independent in the range 10–80% RH. Cu₃HIB₂ shows higher sensitivity over a broader RH range than any other known chemiresistor.
Characterization of the CO$_2$-MOF interaction through a combination of in situ optical spectroscopy and density functional theory calculations evidence autogenously generated hydrated adsorption sites and a charge trapping mechanism as responsible for the intriguing CO$_2$ sensing properties of Cu$_3$HIB$_2$.

**FF01.21.57**

**Electronic and Magnetic Properties of Vertically Aligned Bi-/Tri-Layered Graphene**  
Sekhar C. Ray; University of South Africa, South Africa

Saturation magnetization ($M_s$) of pristine bi-/tri-layered graphene (denoted as – FLG) is enhanced by over four (4) and thirty-four (34) times to $13.94 \times 10^{-4}$ and $118.62 \times 10^{-4}$ emu g$^{-1}$, respectively, as compared to pristine FLGs ($M_s$ of $3.47 \times 10^{-4}$ emu g$^{-1}$), via plasma-based-hydrogenation (known as graphone) and nitrogenation (known as N-graphene) reactions, respectively. However, upon organo-silane treatment on FLG (known as siliphene), the saturation magnetization is reduced by over thirty (30) times to $0.11 \times 10^{-4}$ emu g$^{-1}$, as compared to pristine FLG. Synchrotron based X-ray absorption near edge structure spectroscopy measurements have been carried out to investigate the electronic structure and the underlying mechanism responsible for the variation of magnetic properties. For graphone, the free spin available via the conversion of the sp$^2 \rightarrow$ sp$^3$ hybridized structure and the possibility of unpaired electrons from induced defects are the likely mechanism for ferromagnetic ordering. During nitrogenation, the Fermi level of FLGs is shifted upwards due to the formation of a graphitic like extra π-electron that makes the structure electron-rich, thereby, enhancing the magnetic coupling between magnetic moments. On the other hand, during the formation of siliphene, substitution of the C-atom in FLG by a Si-atom occurs and relaxes out the graphene plane to form Si–C tetrahedral sp$^3$ bonding with a non-magnetic atomic arrangement showing no spin polarization phenomena and thereby reducing the magnetization. Thus, plasma functionalization offers a simple yet facile route to control the magnetic properties of the graphene systems and has potential implications for spintronic applications.

**FF01.21.58**

**Monitoring the Low Doping Regime in Graphene—Comparison of Gated Raman Spectroscopy and Transport Measurements**  
Zhuofa Chen, Nathan Ullberg, Mounika Vutukuru, David Barton and Anna Swan; Boston University, United States

Identifying charge density fluctuations and impurities in graphene is vital for high-quality graphene-based devices. The benchmark method to determine the quality of a graphene-based device is the electrical transport measurement which requires labor-intensive and time-consuming device fabrication process. Existing optical methods using Raman spectroscopy only work for graphene with doping levels higher than $\sim 10^{12}$ cm$^{-2}$. These optical techniques include Raman G peak shift [1], Raman 2D peak shift [2], and 2D versus G frequency charge vector [3]. For high purity samples, e.g., suspended graphene, Boron nitride/graphene/Boron nitride heterostructures, and graphene deposited on octadecyltrimethoxysilane (OTMS), more precise optical methods still need to be developed to estimate the doping level of graphene. Here, we developed an optical probe that can evaluate the doping level and charge fluctuation in graphene in the range from $10^{10}$ cm$^{-2}$ to $10^{12}$ cm$^{-2}$ by using the split in the Raman 2D peak which appears at low doping levels.

Clean graphene samples were prepared on OTMS self-assembled monolayers. By comparing the Raman spatial mapping of the Raman 2D peak split with other Raman parameters (such as G peak frequency, G peak width, 2D peak frequency, 2D peak width, the 2D vs G frequency strain and charge vectors, and ratio of 2D over G peak intensity), the 2D peak split was found to have 10 times larger variation on graphene exfoliated on a OTMS treated substrate (charge density around $5 \times 10^{11}$ cm$^{-2}$), which means much higher sensitivity to charge variation.

In order to quantify the relationship between the 2D peak-split and doping level, we electrostatically biased the graphene to induce a known charge density while measuring the 2D Raman response. We fabricated Graphene Field Effect Transistors (GFETs) and measure the transport curve to find the reference charge neutrality point (CNP), the charge fluctuation and the mobility. The cleanest graphene devices on OTMS-treated substrates had an accidental doping of $3.6 \times 10^{11}$ cm$^{-2}$, a charge fluctuation of $2.2 \times 10^{11}$ cm$^{-2}$, and a mobility of $\sim 1.7 \times 10^4$ cm$^2$/Vs, as deduced from fitting two-point probe transport measurements. Electrostatically gated Raman measurements combined with transport measurements were used to correlate the 2D peak-split with the charge density on graphene with high precision. We found that the Raman 2D peak-split is inversely proportional to the charge density at low doping levels, i.e., a lower charge density results in a larger 2D peak-split [4]. The 2D peak-split can differentiate charge densities down to $2 \times 10^{10}$ cm$^{-2}$ per wavenumber of the 2D peak-split, two orders of magnitude higher precision than using G peak frequency and width, or the 2D versus G frequency charge vector [3].
In conclusion, we sought an optical probe (Raman spectroscopy) that can be used to evaluate the low charge density and the low charge fluctuations across a graphene sample without the fabrication or processing steps necessary for transport measurements. The Raman 2D peak-split was found to correlate with charge density with high precision (2×10^{10} \text{ cm}^{-2} \text{ per 2D peak-split wavenumber}). Our work provides a simple and non-invasive optical method to quantify the doping level of graphene from 10^{10} \text{ cm}^{-2} to 10^{12} \text{ cm}^{-2}, two orders of magnitude higher precision than previously reported optical methods. The 2D peak-split method provides a platform for estimating the doping levels and the quality of a graphene sample before building a high-quality graphene device.

Reference:

FF01.10.21
Characterization of Interlayer Tunneling Junctions in Two-Dimensional Material Heterostructures via High-Throughput Computations

Adam Pfeifle1, Panchapakesan Ganesh2 and Marcelo A. Kuroda1; 1Auburn University, United States; 2Oak Ridge National Laboratory, United States

Following the isolation of individual graphene layers, several other two-dimensional (2D) materials have been discovered, including boron-nitride (BN), phosphorene, and transition metal dichalcogenides (TMDs) [1]. These 2D materials lack dangling bonds allowing for their seamless stacking to create multilayered heterostructures preserving their sharp interfaces [2]. The physical properties of these multilayer structures, including out-of-plane tunneling rates, may be tailored via composition and stacking order. As thousands of 2D materials have been isolated or predicted to be stable [3], the number of heterostructures that can be formed grows very rapidly. Here we develop methodology to characterize carrier transport in heterostructures formed with 2D materials. Our approach efficiently combines high-throughput first principles calculations and ballistic quantum transport. Our workflow generates vertical heterostructures with low-strain epitaxial mismatches between layers. Their geometries and electronic properties are obtained via first principles calculations within the density functional theory. Ballistic transport methodology based on the Landauer formalism employs representations of the electronic structure formed by projections of pseudo-atomic orbitals for efficient computations [4]. In particular, we analyze the modulation of the tunneling current as a function of strain perpendicular to the basal plane [5,6] for a variety of heterostructures based on graphene electrodes, and boron-nitride or transition metal dichalcogenides as tunneling barriers. Results are rationalized in terms of composition, stacking order and orientations. For the same number of layers, BN junctions exhibit larger tunneling currents than TMDs as its smaller thickness counterweights its larger band gap. We find, however, that the interlayer tunneling current of TMDs are more susceptible to mechanical strain than BN ones. We also compare results for the case of bulk electrodes and discuss virtues and limitations of approximations employed in this description. The results of this work may prove useful to the study of novel physical phenomena such as charge and spin transport in tunneling heterostructures based on 2D materials. This work has been partially supported by the NSF DMR-1848344.

[1] Novoselov et al., PNAS 102, 10451 (2005)
8:15 AM FF01.22.01
Carrier Transport Dynamics in 2D Semiconductor High-Speed Photodetectors Exian Liu¹, Peijian Wang², Hao Zeng² and Jianbo Gao¹; ¹Clemson University, United States; ²State University of New York at Buffalo, United States

Despite that 2D semiconductors have promising optoelectronic and electronic applications, our fundamental understanding of its carrier transport dynamics is still in its infancy. In general, it remains challenging to unravel the carrier transport properties in devices since they are altered in the presence of defects/impurities or trap states. An ultrafast probe or high quantum efficiency device (the ratio between electrons collected to photon number), or both, are required to elicit carrier transport properties before significant carrier trapping into trap states and recombination occur.

In this work, we integrate black phosphorus and WS₂ in an ultra-high-speed photodetector structure with sub-25 ps response time to study the carrier transport dynamics. We elucidate the nature of transport mechanisms in different temporal regimes: pre-trapping and band-like transport in early time up to nanoseconds, followed by multiple trapping and release (MTR) hopping transport. In addition to demonstrating visible and infrared high-speed photodetectors, our study reveals the fundamental device physics, leading to device performance manipulation.

8:30 AM FF01.22.02
Highly Sensitive Broad-Spectrum Photodetector Fabricated with Integration of MoS₂ with Mo₂C Multi-Gratings Young Jae Kim¹, Jaeho Jeon¹, Chaeyeon Shin¹, Seunghyuk Choi¹, Jin-Hong Park¹ and Sungjoo Lee¹,²; ¹Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); ²Sungkyunkwan University, Korea (the Republic of)

Broad-spectrum photodetection with high sensitivity through a single photodetector device is required for optical communications, wide-spectral switches, and memory storage applications. To achieve the highly sensitive photodetection in the wide spectral range, various 2D materials and heterojunction structures have been studied, however, limited absorption rate of 2D materials have still been retained as the critical huddle to achieve a sensitive photodetection in broad-spectral range. Herein, we propose a novel 2D hybrid structure consisting of semiconducting MoS₂ film integrated with metallic Mo₂C multi-gratings of various grating periods (400, 600, 800, and 1000 nm), which provides high responsivity (R > 10³ A/W) and distinctive photodetection (light-to-dark current ratio > 10²) over a broad spectral range (405 nm – 1310 nm). The grating of metallic Mo₂C produces plasmonic resonance, which provides hot carriers to the MoS₂ channel. By adjusting the grating period of Mo₂C (400 - 1000 nm), we can control the optimal photoresponse of light, from visible to NIR. The proposed photodetector with a novel 2D hybrid structure achieved a highly sensitive and broad spectral detectable photodetector devices and pave the way to achieving innovative future photodetector applications.

8:45 AM FF01.22.03
Ambient Effects on Photogating in MoS₂ Photodetectors Peize Han¹, Eli R. Adler¹, Yijing Liu¹, Luke St. Marie¹, Abdel El Fatimy¹,², Scott Melis¹, Edward Van Keuren¹ and Paola Barbara¹; ¹Georgetown University, United States; ²Ecole Centrale Casablanca, Morocco

Transition metal dichalcogenides (TMDs) have emerged as promising materials for optoelectronic applications due to their strong light absorption, their direct bandgap for semiconducting monolayers and their suitability for flexible substrates. Although photodetectors based on TMDs have shown remarkable performance, devices with high responsivity and detectivity are usually hindered by slow response times. Here we study the photogating mechanism yielding high responsivity in MoS₂ phototransistors and we show that, for wavelengths sufficiently short to create excitons in the MoS₂, light illumination causes desorption of gas adsorbates¹,².

The search for transformative materials beyond traditional covalent semiconductors, such as Si, has led to fast growing activities on new two-dimensional (2D) semiconductors and the exciting growing development of the metal chalcogenide indium selenide, InSe. This 2D crystal exhibits strong covalent atomic bonds in the layer plane and van der Waals (vdW) attraction between the layers, enabling the isolation of high-quality stable thin films down to the atomic monolayer thickness. The science and technology of 2D InSe represent a rapidly developing and vibrant field with breakthroughs emerging from both experiment and theory. InSe has a near band edge absorption that increases with decreasing layer thickness; high photoresponsivity from the infrared (IR) to the ultra-violet (UV) spectral range; a low mass conduction band electrons and high electron mobility even in atomically thin films, larger than in Si-based field effect transistors (FETs); high mechanical strength; a strain-sensitive band structure; a density of states with 1D van Hove singularities, etc. In this talk, I will present recent research on this new 2D system [1-5] and discuss emerging activities with prospects for digital electronics and photonics.


A variety of new two-dimensional (2D) van der Waals (vdW) crystals have recently been explored following extensive studies on 2D transition metal dichalcogenides (TMDs). Amongst them, noble metals-based 2D crystals such as 2D platinum (Pt) diselenide (PtSe₂) are particularly promising owing to their distinct advantages over conventional 2D TMDs offering higher carrier mobility, superior air stability, semiconducting-to-metallic transition, and lower growth temperature. Despite these projected property and manufacturing merits, much of their electrical properties have remained largely unexplored, significantly limiting their applications for electronic devices. For example, the strong metallic nature of 2D PtSe₂ layers projects a new type of metal/semiconductor Schottky junction based on 2D/3D vdW heterostructures of “mixed dimensionality” when they are interfaced with three-dimensional (3D) semiconductors. Herein, we report a new type of 2D/3Ds Schottky junction devices based on vertically-aligned metallic 2D PtSe₂ layers integrated on Si wafers. We directly grew 2D PtSe₂ layers of controlled orientation and transport characteristics via a low-temperature chemical vapor deposition (CVD) process and investigated 2D PtSe₂/3D Si Schottky junction properties. We found a comprehensive set of material parameters which decisively confirm the presence of excellent Schottky junctions, i.e., high rectification ratio (> 10³), small ideality factor (~1.9), and temperature-dependent variation of Schottky barrier heights. Additionally, we observed strong photovoltaic effects in the 2D PtSe₂/Si Schottky junction devices and extended them to realize flexible photovoltaic devices by direct growth of 2D PtSe₂ on thin (~20 µm) Si wafer. This study is believed to significantly broaden the versatility of 2D PtSe₂ layers in practical and futuristic electronic devices.
Transition metal dichalcogenides (TMD) exist in several polymorphs including 2H (usually semiconducting), and 1T/1T' (usually semi-metallic). Our theoretical calculations and experimental measurements show that TMDs are optically-dense and can feature a difference in near-infrared (NIR) refractive index greater than 1 between phases (delta n>1), which is comparable to established phase-change materials (PCMs). Martensitic phase-change behavior has been observed in TMDs and can be triggered non-thermally, and transformation strains are expected to be low due to the layered crystal structures. We suggest that TMDs may be useful as low-power, low-fatigue active materials to control light in integrated photonic circuits.

Among TMDs, sulfides are promising for photonics applications because they present the lowest optical loss and the highest material stability. Sadly, sulfide TMDs also have higher phase-change energy barriers than selenides or tellurides. This problem may be solved by designing sulfide TMD alloys that are thermodynamically-adjacent to phase boundaries. We use density-functional theory (DFT) and related methods to calculate free energy-composition diagrams at finite temperature for polymorphs in the MoS2-TiS2-ZrS2 system. Our calculations predict that the free energy of hypothesized phase-change alloys lies slightly above the convex hull. This highlights the need to process TMD alloys at low temperature, to avoid phase separation. Low temperature processing is also essential to integrated TMD films with integrated photonic circuits.

We fabricate large-area sulfide TMD pure-phase and alloy thin films by metal sputtering followed by sulfurization in H2S-containing atmospheres in a chemical vapor deposition (CVD) furnace. This two-step method combined with combinatorial sputtering enables rapid exploration of composition space and phase boundaries. By controlling CVD furnace gas conditions we are able to lower the processing temperature for large-area alloy thin films below 600 °C. We characterize the sulfide TMD alloy films by electron microscopy, Raman spectroscopy, and infrared spectroscopy. We measure the phase boundaries, quantify the extent of phase separation, and identify optimal compositions for photonics applications.


Giant Negative Electrostriction in CuInP2S6—Linking Theory and Experiments

The scientific interest in van-der-Waals (vdW) crystal CuInP2S6 originates from its many useful material properties such as ferroelectricity. The layered structure allows for easy exfoliation into ultrathin flakes and vDW interfaces can be utilized to create heterostructures with 2D materials such as MoS2 or graphene. Most notably, electrostrictive coefficients in this material have been found to be very large and negative, meaning that the crystal expands in an electric field oriented antiparallel to the spontaneous polarization in CuInP2S6. However, the magnitude of the electrostrictive coefficient and resulting piezoelectric response has been source of confusion. The Q33 and d33 extracted from XRD data using Landau-Ginzburg-Devonshire calculations are -3.2 m4/C2 and -85 pm/V, respectively, making the electromechanical output of CuInP2S6 comparable or even outperforming ferroelectric perovskites [1]. On the other hand, d33 extracted from density functional theory (DFT) as derivative of the polarization vs. stress yields only around -16 pm/V [2]. In this work we demonstrate how the boundary conditions of DFT, in particular clamping of lattice parameters are in agreement with experimental conditions in piezoresistance force microscopy (PFM) measurements on CuInP2S6 surfaces where similar d33 values are observed. In contrast, PFM on CuInP2S6 capacitors with µm sized top electrodes resembles an unclamped setup and shows piezoresponse in agreement with the predicted -85 pm/V. Having achieved excellent agreement, we have unraveled the intrinsic
origin of the negative electrostriction, which is linked to proximate chemical interactions between the vdW layers and the resulting anharmonicity of the potential well for polar Cu displacement.


11:00 AM FF01.23.03
Lithium Intercalation as a Reversible Structural Switch in WTe2: Philipp Muscher\textsuperscript{1,2}, William C. Chueh\textsuperscript{1} and Aaron Lindenberg\textsuperscript{1,2}; \textsuperscript{1}Stanford University, United States; \textsuperscript{2}SLAC National Accelerator Laboratory, United States

WTe\textsubscript{2} is a transition metal dichalcogenide (TMD) with remarkable structural properties, featuring broken inversion symmetry, quasi 1-dimensional W-W chains and out-of-plane distortions of the covalent layers. This so-called Td structure has been linked to WTe\textsubscript{2}'s unique physical properties such as its large, non-saturating magnetoresistance and its being a topological semimetal with type II Weyl points. Here, we demonstrate fast and highly reversible lithium intercalation into WTe\textsubscript{2} using an electrochemical platform with compositional control over a single flake. Our in-situ X-ray and optical studies, combined with DFT calculations, show that lithium intercalation is a powerful tool for tuning the properties of WTe\textsubscript{2}. In particular, Li\textsubscript{0.5}WTe\textsubscript{2} is a vastly expanded form of the initial structure with a polytype that is not otherwise observed in common TMDs.

11:15 AM FF01.23.04
Manipulation of Topological Properties in Weyl Semimetal Jun Xiao\textsuperscript{1,2}, Ying Wang\textsuperscript{3}, Philipp Muscher\textsuperscript{1}, Siqi Wang\textsuperscript{4}, Edbert Sie\textsuperscript{1,2}, Clara Nyby\textsuperscript{1,2}, Xiang Zhang\textsuperscript{1} and Aaron Lindenberg\textsuperscript{1,2}; \textsuperscript{1}Stanford University, United States; \textsuperscript{2}SLAC National Accelerator Laboratory, United States; \textsuperscript{3}University of California, Berkeley, United States

Quantum materials with novel phases of matter are the key building blocks of energy efficient quantum electronics and powerful quantum computation. Exploiting control of those materials is fascinating to achieve new functionalities and information algorithm in future quantum devices. Quantum nanomaterials like layered materials, has revealed many exotic properties such as extremely large magnetoresistance (MR)\textsuperscript{1}, type-II Weyl electron transport and diverging Berry curvature\textsuperscript{2,3}. On the other hand, the nature of layered materials leads to ultra large tunability of physical properties via external stimuli.

Here we report the manipulation of topological properties in Weyl semimetal based on layered materials. With such experimental control and various characterization means, we observed substantial modulation in optical and electrical responses. The observations indicate such changes are closely associated with the variation of topological property. Our findings highlight the potential for the realization of topological devices based on layered quantum materials.


11:30 AM FF01.23.05
Modulating the Functions of MoS\textsubscript{2}/MoTe\textsubscript{2} van der Waals Heterostructure via Thickness Variation Ngoc Thanh Duong\textsuperscript{1,2}, Minhee Yun\textsuperscript{3}, Seong Chu Lim\textsuperscript{1,2} and Mun Seok Jeong\textsuperscript{1,2}; \textsuperscript{1}Sungkyunkwan University, Korea (the Republic of); \textsuperscript{2}Institute for Basic Science, Korea (the Republic of); \textsuperscript{3}University of Pittsburgh, United States

The atomically thin and dangling bond-free 2D semiconducting transition metal dichalcogenides (TMDs) provides another alternative for the post-Si technologies. In the case of a Si device, the performance is predominantly dominated by doping, which changes the Fermi level, contact resistance, threshold voltage, and electrical conductivity. Fortunately, TMDs exhibit thickness-modulated band structures. Depending on the layer thickness, the position of the Fermi level changes, which implies that the effect of doping in the TMD can be observed by controlling the number of layers.

In this study, various functions have been realized in MoS\textsubscript{2}/MoTe\textsubscript{2} van der Waals heterostructures via controlling the thickness and carrier concentration of MoTe\textsubscript{2}. Thickness-dependent work function of MoTe\textsubscript{2} was confirmed by Kelvin probe force microscope (KPFM) measurement. The 2L MoS\textsubscript{2}/Few-layer (FL) MoTe\textsubscript{2} device could transform
from a $p-n$ forward diode into a Zener diode through the electrostatic gating effect. Moreover, the multi-layer MoS$_2$/multi-layer MoTe$_2$ device can be modulated between backward diode characteristic and forward diode characteristic with a rectification ratio up to $10^3$ at room temperature. Furthermore, many-valued logic (MVL) devices, which have more than three different logic states, are expected to provide higher efficiency than binary logic devices. MVL devices can help reduce the interconnection density and the number of transistors in logic circuits. For example, to create a ternary logic circuit, more than nine single transistors are used. In addition, we introduce a multi-valued inverter composed of 2L MoS$_2$/ FL MoTe$_2$ heterostructure showing three truth states (ternary inverter). In particular, our ternary inverter can be transformed to binary using simple laser irradiation. Our work also significantly benefits the electronics research, which follows the Moore’s law and beyond.

11:45 AM FF01.23.06
Atomically-Precise Moiré Fringes in 2D van der Waals Heterostructures of Graphene and Hexagonal Boron Nitride Sanjay K. Behura$^1$, Songwei Che$^1$, Phong Nguyen$^1$, Chen Wang$^1$, Rousan Debbarma$^1$, Michael R. Seacrist$^2$ and Vikas Berry$^1$; $^1$University of Illinois at Chicago, United States; $^2$MEMC LLC, United States

The van der Waals force-bound heterostructures of isostructural and isoelectronic graphene and hexagonal boron nitride (h-BN) offer a platform for fundamental phenomena evolving from the resultant Moiré superlattices. Such phenomena in two-dimensional (2D) planar sp$^2$ lattice stacks of graphene/h-BN or graphene/h-BN/graphene or h-BN/graphene/h-BN are sensitive to their atomic-scale assembly. Current techniques rely on physical or chemical transfer of both h-BN and graphene to build the 2D sandwich heterostructure circuits. These transfer-steps not only introduce the interfacial polymeric and metallic heteroatom impurities but also creates random or mis-aligned regions in the 2D-heterostructures. Here, we report Moiré fringes in the graphene and h-BN heterostructures developed through direct stacking of graphene and h-BN via a bottom-up all-chemical vapor deposition (CVD) strategy. Polycrystalline layer of h-BN is first synthesized via a surface chemical-interaction guided process on silicon-based gate-dielectric substrate. Then the graphene layer is grown via grain-boundary diffusion of catalytically produced carbon radicals through a polycrystalline metal film on h-BN. Finally, removing the thin metal film (and any graphene on it) results in graphene/h-BN heterostructures with a sharp, defect-free, and atomically-precise interfaces; as confirmed by scanning resonant Raman spectroscopy and X-ray photoelectron spectroscopy studies. The directly-grown, van der Waals bound graphene/h-BN heterostructures exhibit Moiré fringes with a periodic pitch of $\approx 10$ Å at a rotation angle of 16$^\circ$. Further, the low-temperature transport measurements reveal the charge carrier mobility of 100 cm$^2$V$^{-1}$s$^{-1}$, 2-orders of magnitude higher than the graphene/h-BN heterostructure produced via co-segregation process. Futuristically, this all-CVD direct-growth strategy will be a transformative approach for scalable production of van der Waals heterostructures to realize complex 2D circuitry and fundamental physics phenomena.

SESSION FF01.24: Fundamental Properties in 2D Material
Session Chairs: Zakaria Al Balushi and Amber McCreary
Friday Afternoon, December 6, 2019
Hynes, Level 3, Room 312

1:45 PM FF01.24.01
Induced Atomic Ordering in Two-Dimensional Alloys Amin Azizi$^1$, Mehmet Dogan$^{1,2}$, Jeffrey D. Cain$^{1,2}$, Rahmatollah Eskandari$^1$, Xuanze Yu$^1$, Emily C. Glazer$^1$, Marvin Cohen$^{1,2}$ and Alex Zettl$^{1,2}$; $^1$University of California, Berkeley, United States; $^2$Lawrence Berkeley National Laboratory, United States

Semiconductor alloys enable fabrication of materials with continuously tunable properties such as lattice constant, bandgap, and carrier mobility, and has been a key strategy for property engineering throughout the history of semiconductor devices. However, it has long been an open question whether the atoms in the lattice of a multispecies alloy are randomly distributed or ordered in some way. The answer is fundamentally important, as the electronic, optical, thermal, and mechanical properties of alloys can be significantly affected by the presence of ordering. Ordering in semiconductor alloys has been studied, but most of the reports have been limited to reciprocal space, such as diffraction techniques. Two-dimensional (2D) materials provide an ideal playground to directly
visualize potential ordering in semiconductor alloys. However, 2D TMD semiconductor alloys reported to date have mostly been random. Here, we demonstrate experimental observation of atomic ordering in a monolayer semiconductor alloy and suggest a strategy to control ordering in 2D semiconductor alloys. Additionally, combined with theoretical calculations, we demonstrate how the induced atomic ordering can notably modify the bandgap of the monolayer alloy with respect to its random counterpart.

2:00 PM FF01.24.02
Defects and New Phases in Inorganic Two-Dimensional Materials—Insights from Multi-Scale Atomistic Simulations Arkady Krasheninnikov; Helmholtz-Zentrum Dresden-Rossendorf, Germany

As compared to bulk solids, large surface-to-volume ratio of two-dimensional (2D) materials makes many of them particularly prone to defect formation due to the interaction with the environment. At the same time, this opens new opportunities for post-synthesis introduction of impurities into these systems by, e.g., vapor deposition, development of new phases and thus tailoring their properties. In my talk, I will present the results of our recent theoretical studies of defects (native and irradiation-induced) in 2D systems obtained in close collaboration with several experimental transmission electron and scanning tunneling microscopy groups [1,2,4]. I will further discuss defect- and impurity-mediated engineering of the electronic structure of 2D molybdenum dichalcogenides by introducing transition metal atoms using ion beams and atom deposition at elevated temperatures [3]. Finally, I touch upon the intercalation of Li and other alkali metal atoms into bilayer graphene [4] and MoS₂ [5].

5. I. Chepkasov, M. Ghorbani-Asl, and A.V. Krasheninnikov, to be published.

2:15 PM FF01.24.03
Extrinsic and Dynamic Edge States of Two-Dimensional Lead Halide Perovskites Letian Dou and Enzheng Shi; Purdue University, United States

As a new family of two-dimensional semiconductor materials, organic inorganic 2D halide perovskites have drawn significant attention in the past few years. Edges of 2D halide perovskites are found to exhibit unusual properties such as enhanced photoluminescence lifetime and reduced photoluminescence emission energy. In this talk, I will present the formation mechanism and the dynamic nature of edge states on the exfoliated 2D halide perovskites thin crystals. In contrast to other 2D materials, the edge states in 2D perovskites are extrinsic and can be triggered by moisture with a concentration of as low as ~ 0.5 ppm. High-resolution atomic force microscopy and transmission electron microscopy characterizations reveal the width of the low-energy states is ~ 40 nm wide. Temperature-dependent photoluminescence study suggests the edge states are a combination of several lower-energy states. Importantly, we demonstrate that the charge carriers on the dynamically formed edge states are not only long-lived, but also highly mobile and can be conducted along the edges effectively with high mobilities of 5.4-7.0 cm²V⁻¹s⁻¹. This work provides significant insights on the origin of the edge states in 2D perovskites and provides routes to manipulate their optical and electrical properties through controlling their edges.

2:30 PM FF01.24.04
Liquid-Mediated Strain Relaxation in 2D Materials Humberto Batiz Guerrero¹,² and Daryl Chrzan¹,²;¹University of California, Berkeley, United States; ²Lawrence Berkeley National Laboratory, United States

Due to its low dimensionality, properties in 2D materials are predicted to be more sensitive to strain than in their 3D counterparts. Specifically, in the case of few-layers transition metal dichalcogenides, the direct or indirect nature of the band gap, as well as its value, can be strain engineered [1]. Recently, a solvent evaporation-mediated decoupling process was demonstrated [2]. In this process, the strain within a WSe₂ grown on amorphous silica that arises from thermal expansion mismatch is released by the evaporation of an acetone droplet that initially covers the WSe₂ sample. A model for this strain release process is proposed and studied. The model assumes that the frictional forces
between the WSe₂ film and the substrate stabilize the strain within the film. As the droplet evaporates, the triple point, i.e. where the air, acetone, WSe₂ meet, is lifted from the substrate, thereby reducing the friction force and enabling strain relaxation. Taking into account the elastic, interfacial, and substrate-film interaction energies, a functional for the energy of the system is constructed and the differential equations governing the configuration of the system are derived, with the in- and out- of-plane displacements of the film being the relevant variables. A numerical approach is used to solve the resulting highly-nonlinear equations. The dynamics of the system are computed in an adiabatic manner. In this way, it is possible to gain insight about how the process could be enhanced. Theoretical understanding of a process that allows controlled strain release can potentially allow the processing of new devices with novel and interesting optoelectronic properties.


This work was supported within the Electronic Materials Program at LBNL by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division of the U.S. Department of Energy, under Contract No. DE-AC02-05CH11231.

2:45 PM FF01.24.05
Plasmon Free Surface Enhanced Raman Spectroscopy Using Metallic 2D Materials Xiuju Song¹²³, Yan Wang⁴, Fang Zhao⁵, Jieun Yang⁶, Wenjing Zhang⁷ and Munish Chhowalla⁸¹; ¹Rutgers, The State University of New Jersey, United States; ²Shenzhen University, China; ³The University of Manchester, United Kingdom; ⁴University of Cambridge, United Kingdom; ⁵Princeton University, United States

Two dimensional (2D) materials-based plasmon free surface enhanced Raman scattering (SERS) is an emerging field in non-destructive analysis. However, impeded by the low density of states (DOS), an inferior detection sensitivity is frequently encountered due to the low enhancement factor of most 2D materials. Metallic transition metal dichalcogenides (TMDs) could be ideal plasmon free SERS substrates because of their abundant DOS near the Fermi level. However, the absence of controllable synthesis of metallic 2D TMDs has hindered their study as SERS substrates. Here, we realize controllable synthesis of ultra-thin metallic 2D niobium disulfide (NbS₂) (<2.5 nm) with large domain size (>160 μm). We have explored the SERS performance of as-obtained NbS₂, which shows a detection limit down to 10⁻¹⁴ mol/L and an enhancement factor of up to ~10⁶. The enhancement mechanism was studied in-depth by density functional theory, which suggested a strong correlation between the SERS performance and DOS near the Fermi level. NbS₂ features most abundant DOS and strongest binding energy with probe molecules as compared with other 2D materials such as graphene, 1T phase MoS₂ and 2H phase MoS₂. The large DOS increases the intermolecular charge transfer probability and thus induces prominent Raman enhancement. To extend the results to practical application, the resulting NbS₂-based plasmon free SERS substrates were applied for distinguishing different types of red wines.

References:

3:00 PM FF01.24.06
Using Computation to Resolve Discrepancies in the Reported Optical Properties of Two-Dimensional Black Phosphorous Thierry Tsafack, Stephen F. Bartolucci and Joshua A. Maurer; U.S. Army Futures Command, Combat Capability Development Command, United States
Two-dimensional black phosphorous, phosphorene, is an ideal candidate for flexible opto-electronics because it possesses a direct and tunable band gap, a high carrier mobility and a negative Poisson’s ratio. The band gap and photoluminescence emission maxima vary as a function of the number of phosphorene layers. Multiple experimental studies have reported a wide range of values for the photoluminescence emission maxima as a function of number of phosphorene layers. This disagreement limits our understanding of phosphorene’s optical properties, which are critical to many of the potential applications for this material. These discrepancies may be a result of oxidation altering the photoluminescent properties. To understand these differences, we have created computational models that allow us to understand the effects of oxidation and number of layers on the optical properties of phosphorene. Many-body perturbation theory in conjunction with both the Bethe-Salpeter-Equation (BSE) and the Green’s function screened potential (GW) have been used to derive absorption spectra that include excitonic and other many-body effects. These studies allow us to understand how oxidation level and layer number affect phosphorene’s absorption spectra, which, in turn, provides useful insights into phosphorene’s photoluminescence excitation and emission maxima.

3:15 PM BREAK

SESSION FF01.25: Novel Applications of 2D Materials
Session Chairs: Zakaria Al Balushi and Amber McCreary
Friday Afternoon, December 6, 2019
Hynes, Level 3, Room 312

3:30 PM FF01.25.01
2D Transition Metal Carbide (MXene) Thin Film for EMI Shielding and Heating Applications Chong Min Koo1,2; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Korea University, Korea (the Republic of)

MXenes are a family of 2D transition metal carbides, nitrides, and carbonitrides with the general formula Mn1XnTx (n = 1, 2, or 3; M = transition metal, e.g. Ti, Nb, Mo; X = C and/or N; T = surface termination, e.g. –OH, –F, –O). Unlike other 2D materials, MXenes offer an attractive combination of high electronic conductivity (~5000 S/cm), hydrophilicity, and processability. Transition metal carbide (MXene) have been considered as an effective EMI shielding material since we reported the outstanding EMI shielding effectiveness of MXenes (60dB at 10mm) in 2016. However, still it is lack of understanding EMI shielding behavior of MXene materials, especially, at the atom-scale thickness, because it is hard to make uniform atom-thick film. In this presentation, we present the EMI shielding behavior of MXene thin film with atom-level thickness, which was prepared through a self-assembly method. Monolayer-thick MXene film offers 20% shielding ability and a 24 layer film of 55 nm thickness demonstrates 99% shielding (20dB) and extraordinarily large specific shielding effectiveness per unit areal density (SSE/t = 3.89*106 dB cm2/g), revealing that MXene is very good for ultra-thin film shielding applications. Additionally, it will be demonstrated that, due to good shape-adaptability, easy processability and low sheet resistance, MXene thin films is very good for wearable heating device application.

3:45 PM FF01.25.02
Enhancement of the Superconducting Transition Temperature through the Formation of 2D Molybdenum Carbide/Disulfide Heterostacks Fu Zhang1, Yanfu Lu1, Wenkai Zheng2, Lavish Pabbi1, Kazunori Fujisawa1, Ana Laura Elias1, Eric Hudson1, Susan Sinnott1, Luis Balicas1 and Mauricio Terrones1, 1Pennsylvania State University, United States; 2Florida State University, United States

Two dimensional (2D) crystals beyond graphene exhibit promising functionalities in catalysts, optoelectronics and electronics. Recently, renascent transition metal carbides (TMCs, e.g. molybdenum carbide) show nontrivial superconductivity even when scaled down to few layers thin samples. Conjugation between 2D superconducting TMCs and semiconducting transition metal dichalcogenides (TMDs, e.g. MoS2) needs to be realized for the next-generation logic circuits. In this work, high quality superconducting 2D α-phase molybdenum carbide (Mo2C) flakes were synthesized on molten copper, and used to produce 2D molybdenum carbide/disulfide heterostructures having
atomically sharp interfaces through a gas phase reaction. Through aberration corrected transmission electron microscopy (AC-TEM) we found that the 2D molybdenum carbide crystal undergoes a series of structural phase-transitions between phases α-γ'-γ phases upon sulfurization. Hybrid systems, such as the γ'-phase, exhibit superconductivity with a higher critical temperature ($T_c$) than the original Mo$_2$C compound, transitioning into the metallic γ-phase upon increasing the sulfur content. This study demonstrates the stabilization of 2D γ-MoC and γ'-MoC$_{1-x}$ using Mo$_2$C as the precursor, and provides an alternative way to enhance the superconductivity molybdenum carbides via a phase-transition in the carbide (or nitride in future) systems. Such atomically sharp superconductor/semiconductor heterojunctions are critical for functional electronic components.

4:00 PM FF01.25.03
Characteristics of Gas Sensor Based on Molybdenum Disulfide/Graphene van der Waals Heterostructure
Shoji Maeda$^1$, Ryota Isu$^1$, Christopher J. Perini$^2$, Daiju Terasawa$^3$, Akira Fukuda$^3$, Masatoshi Koyama$^3$, Akira Fujimoto$^3$, Yoshiyuki Harada$^1$, Kazuto Koike$^1$, Mitsuaki Yano$^1$ and Eric M. Vogel$^2$; $^1$Osaka Institute of Technology, Japan; $^2$Georgia Institute of Technology, United States; $^3$Hyogo College of Medicine, Japan

Graphene and 2-dimensional (2D) materials such as transition-metal dichalcogenide (TMD) provide a wide range of unique electrical and optical properties. Such 2D gas-sensing materials possess structural advantages, for example, a high surface-to-volume ratio and the tunable functionality of the surface for decoration species. Therefore, they have attracted immense interest as new gas-sensing materials. In particular, the resistance of the device decreases when the n-type 2D sensing layer is exposed to reducing gases such as H$_2$. Besides, van der Waals heterostructures (vdWH) consisting of graphene and TMD [1] also are fascinating a lot of researchers working on 2D materials. A MoS$_2$/graphene vdWH is reported to show a significant change in resistance upon exposure to 1 ppm NO$_2$, originating from the modulation of the Schottky barrier height at the interface [2]. The purpose of our study is to synthesize large-area MoS$_2$ on SiO$_2$/Si substrate. Furthermore, we make the transistors and the vdWH consisting of graphene and MoS$_2$, which transduces gas-molecules adsorption on the surface and the interface into a change of the resistance.

In order to control the number of MoS$_2$ layers and grow large-area MoS$_2$, 1 nm Mo layer was deposited on SiO$_2$/Si substrates by e-beam evaporation. The Mo films were then directly sulfurized in a furnace at 900 degrees for an hour. The grown large-area MoS$_2$ films showed $E_{2g}^1$ Raman peak at 383.0 cm$^{-1}$ and $A_{1g}$ one at 406.9 cm$^{-1}$. This corresponds to a peak separation 23.9 cm$^{-1}$ of 3 layers MoS$_2$ [3]. We fabricated the MoS$_2$ transistors and examined the back-gate voltage and the drain one ($V_D$) dependences of the drain current ($I_D$). We confirmed the linearity of $V_D$–$I_D$ characteristics less than $V_D = 10$ V. Moreover, we extracted the field-effect mobility for a transistor with gate length/width = 100 μm /100 μm, but the value was much smaller than that of a previous study [4], resulting from the poor crystallinity of our MoS$_2$. However, this suggests our MoS$_2$ has a lot of adsorbed sites and is of advantage to adsorb more gas molecules.

We employed chemical vapor deposited (CVD) single-layer graphene and MoS$_2$/Graphene vdWH for gas-sensing. We put the devices on a sample stage heated at 200 degree C in a sealed test chamber and measured the resistance by flowing 1000 ppm H$_2$, 100 ppm NO and 100 ppm NH$_3$, respectively. NO gas becomes oxidizing NO$_2$ gas in the air. These flow rates of these gases and dry air gas were adjusted with a mass flow controller. In the case of CVD graphene, the change rate in resistance was just about 3 % for these gases. These results are corresponding to previous research [5]. On the other hand, the change rate in resistance of MoS$_2$/graphene vdWH was approximately 20% for H$_2$ and NO gases. Furthermore, by increasing the flow rate of the NO gas from 10 ppm through 100 ppm, a step-like change of the resistance was observed, and we confirmed the change of the resistance responded to the flow rate of NO gas. One of the mechanisms of gas adsorption for our vdWH is that MoS$_2$ acts as an adsorption layer and promotes the increase of hole concentration in graphene. Now we are making a lot of efforts to improve our vdWH and increase the Schottky barrier height, so that the resistance changes significantly by means of adsorbing gas molecules at the interface.

Two dimensional (2D) transitional metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS$_2$) have been demonstrated to be excellent semi-conductors for ultra-thin field effect transistors (FETs). However, the main challenge for improving the performance of FETs using 2D semiconductors is lowering contact resistance. Studies have shown that the creation of van der Waals contacts by dry transfer (graphene$^1$, hBN$^2$, metal$^3$) method can avoid damage to atomically thin TMD semiconductors caused by metal deposition. We recently reported the realization of ultra-clean van der Waals contact between Indium alloys and 2D materials$^4$. Here, we take advantage of the soft nature of indium to alloy it metals such as Au, Pd, Pt and Co to vary the work function so that both hole and electron injection is facilitated. We have measured the work function of the alloys using Kelvin force microscopy and correlated them with band offsets in WSe$_2$, MoSe$_2$, and mixture of WSe$_2$/MoSe$_2$ devices. Furthermore, we have systematically studied how annealing at different temperatures affects the alloy/semiconductor interface and FET performance.

References:
SESSION FF02.01: Fundamental Properties and Transport
Session Chairs: Chuanhua Duan and Slaven Garaj
Tuesday Morning, December 3, 2019
Hynes, Level 3, Room 309

8:15 AM *FF02.01.01
Non-Linear Fluidic Transport in sub-2nm Channels—Towards Artificial Mechanosensitivity
Lyderic Bocquet1,2; 1Ecole Normale Superieure, France; 2CNRS, France

It is an exciting period for *nanofluidics*, the field exploring the transport of fluids at the nanoscales. Routes now exist to fabricate individual channels with nanometric and even sub-nanometric dimensions, while new instruments have also been invented to probe transport across these channels. And indeed, a number of quite exotic properties for water and ion transport have emerged since.

In this presentation I will discuss the emergence of strongly non-linear transport in ultimate confinement. I will report experiments exploring ionic transport under combined voltage and pressure driving: both in 2D channels made of van der Waals nanostructures, and in sub-2nm carbon nanotubes. In both types of channels, strong couplings between voltage-driven and pressure-driven transport are highlighted. I will show how such phenomena can be rationalized theoretically in terms of the coupled ion dynamics and flow transport, emphasizing on the key role of surface friction on ionic transport. Beyond I will further show theoretically how the classical equivalent of Coulomb blockade does emerge for ionic transport in 1D systems, via a fractional Wien effect.

These various phenomena lead to tunable ionic transport under specific stimuli, and they allow to envision the design of artificial mechano-sensitive response, similar to those observed in biological channels.

This work was done in collaboration with T. Mouterde, A. Poggioli, A. Marcotte, N. Kavokine, A. Niguës, A. Siria, from *Micromégas* team, ENS Paris, and with A. Keerthi, S. Dar, R. Boya and A.K. Geim, from Manchester University.

References

8:45 AM *FF02.01.02
Nanofluidic Transport across Nanoporous Atomically Thin Graphene and Its Development as a Next-Generation Membrane
Rohit N. Karnik; Massachusetts Institute of Technology, United States

Nanoporous atomically thin membranes, wherein nanopores in two-dimensional materials provide pathways for rapid and selective fluidic transport, represent the ideal limit of an ultrathin membrane and have potential for improving the efficiency, selectivity, productivity, versatility, and chemical resistance for a variety of membrane separations. I will discuss our work on understanding mass transport and developing membranes that employ nanoporous single-layer graphene as the selective layer. Through controlled nucleation of defects via ion bombardment and oxidative etching, sub-nanometer pores are created in the otherwise impermeable graphene placed on a porous support. We discuss strategies for the design of defect-tolerant membranes and show that design of the porous support is critical to exploiting the selectivity of nanoporous graphene, which enables molecular sieving of gases across centimeter-scale nanoporous graphene membranes. We investigate the role of defects, illustrate methods to rapidly assess nanoscale defects in graphene, and demonstrate that the impermeability of graphene can be exploited to selectively seal defects and greatly improve its selectivity. Through these developments, we are able to realize centimeter-scale graphene membranes that show high selectivity between ions, molecules, and proteins for nanofiltration and dialysis, and ultrahigh permeance in organic solvent nanofiltration. We also demonstrate that the membranes exhibit high mechanical strength and are able to withstand applied pressures of 100 bar. These studies
illustrate the interplay between material structure and transport in nanoporous graphene and demonstrate its potential for the realization of next-generation membranes for water purification, bio/chemical separations, and other applications.

**9:15 AM FF02.01.03**

*Translocation of DNA through Ultrathin hBN/Graphene Nanoslits* Wayne Yang, Ashok Keerthi, Gangaiah Mettela, Andre Geim, Radha Boya, and Cees Dekker; 1Kavli Institute of Nanoscience, Delft University of Technology, Netherlands; 2The University of Manchester, United Kingdom; 3National Graphene Institute, United Kingdom

2D nanoslit devices, where the planes of two 2D materials such as hBN or graphene are separated by only a few nm, have attracted a lot of attention for their interesting water- and ion-transport behavior arising from their interesting confined geometry. Here, we investigate the passage of single DNA molecules through such nanoslits. These 2D nanoslits allow us to examine the entropic stretching behavior of DNA and its friction interactions of DNA with 2D materials as both are in close contact during translocation. Double-stranded (ds) DNA (which has a diameter of 2.2 nm) of 1-10kbp length in 2M LiCl salt is electrophoretically driven across a 2D nanoslit. The devices have a length of 1-2 microns, a width of 80-120nm and a height of only 3-6 nm. Upon entry into the channel, the dsDNA blocks the passage of ions leading to temporary current blockades – similar to nanopore translocations. Due to their small slit height, the entrance to the nanoslit presents a significant entropic barrier that the dsDNA must overcome in order to translocate into the slit. Shortening the dsDNA length allows the entropic barrier to be overcome and clear dsDNA translocations to be resolved. Increasing the bias voltage allows for an increased signal-to-noise ratio and well resolved dsDNA blockade current signals. Ongoing experiments are underway to investigate the role of interaction and friction between the surface of different 2D materials and the translocating biomolecules.

**References**


**9:30 AM FF02.01.04**

*Water Evaporation from Graphene Nanopores* Siyang Xiao, Quan Xie and Chuanhua Duan; Boston University, United States

Nanoporous graphene membrane has shown great potentials for various promising applications such as water desalination, biochemical separation, energy management and biosensing, owing to the atomically 2-D structure of graphene and the fast molecular transport across graphene. These features of graphene also make nanoporous graphene membrane most desirable as nanoporous membrane evaporators. The atomic thickness of graphene can minimize hydraulic resistance during evaporation and the ultra-high mechanical strength of graphene can provide excellent mechanical stability of the membrane. Therefore, nanoporous graphene membrane is expected to achieve the ultimate performance of nanoporous membrane evaporator. However, there are two major challenges that inhibit the development of nanoporous graphene membrane evaporators: 1) evaporation kinetics from single graphene nanopore remains unknown and consequently there are no rational optimization guidelines for graphene nanoporous membrane evaporators; 2) there is still no mature method to fabricate scalable graphene nanoporous membranes and integrate them as evaporators. In this work, we aim to solve the first challenge by experimentally studying evaporation from graphene membranes with single nanopores and provide insights for solving the second challenge. We used a hybrid nanochannel-nanopore design that we recently invented to conduct water evaporation measurements. This design has been proved to be able to achieve kinetic-limited evaporation regime, where evaporation flux is only limited by evaporation kinetics at liquid-vapor interface at nanopore mouth instead of liquid/vapor transport toward/away from the interface. Furthermore, such design is capable to accurately measure evaporation flux from individual nanopores. Our results show that water evaporation flux from graphene nanopores increases as pore diameter decreases, exhibiting a similar trend but higher diameter dependence than water evaporation from silicon nitride nanopores. The highest measured flux from a graphene nanopore with diameter of 73 nm is 2.1 mm/s at room temperature, corresponding to the heat flux of 480 W/cm², reaching 80% of
evaporation flux limit predicted by the classic Hertz-Knudsen theory. The enhanced evaporation from graphene nanoparticles compared to silicon nitride nanopores could be corroborated by a recent MD study which showed that the edge of graphene can facilitate evaporation due to the unique graphene-water interactions. Our findings provide new understanding of evaporation from graphene nanopores and consequently provide guidance for the design of nanoporous graphene membrane evaporators.

9:45 AM FF02.01.05
Field-Boosted Selectivity in Nanoscale Transport Ke Zhou and Zhiping Xu; Tsinghua University, China

Recent experiments have confirmed that nanoscale mass transport of gases, water and ions can be modulated by external stimuli such as pressure, temperature and the external electric field (EEF). Compared to pressure and temperature, the EEF can be applied in-situ, with remarkable stability and a wide range in amplitude control. Here, I will present two of our recent work focused on the controlled transport of hydrated ion and gas in nanochannels through the response in ionic motion under the EEF. We first demonstrate the enforcement of near-surface ion diffusion under an EEF, where their hydration shells are distorted while making contact with the surface. We find from molecular simulations a trapped/hopping scenario of diffusive ionic dynamics, where the diffusivity does not depend on their hydration radius but the corrugation of the free energy surface. As a result, the diffusion-specific selectivity can be elevated to ~10 at the expense of reduction in the mobility. The second theoretical study on the ionic liquids (ILs) confined in graphene oxide membranes suggests that the spatial distribution of cations and anions can be displaced under the EEF, modifying the absorption/desorption process and gas solubility in the composite membrane, leading to significantly enhanced gas selectivity. The findings are validated by experimental data, demonstrating separation performance that is superior to the upper bound of state-of-the-art membranes.

10:00 AM BREAK

10:30 AM *FF02.01.06
Selective Permeation of Low Dimensional Materials Hyung Gyu Park¹,²; ¹Pohang University of Science and Technology, Korea (the Republic of); ²Eawag (Swiss Federal Institute for Aquatic Science and Technology), Switzerland

Membrane technology promises to bring process intensification to various industrial processes such as chemical separation and resource purification. Membrane-participating processes can become more effective if selectivity, permeation and durability of membrane materials are improved. In this regard, mass transport phenomena under extreme confinement offered by low dimensional materials call for attention because understanding of their characteristics could help designing the membrane pores. Here, I present selective transport phenomena across 0D, 1D and 2D confined space that atomically thin orifices, nanotubes and 2D material lamellas provide, respectively. As the confinement dimension increases, mass permeation tends to decrease from ultimate permeation to fast transport to unimpeded diffusion, whereas chemical selectivity is prone to increase inherently. Nevertheless, one may tailor actual chemical selectivity through proper pore design and architectural modification. Thus obtained knowledge and pore architectures could lay the cornerstone of advancing membrane transport properties toward process intensification.

11:00 AM FF02.01.07
Electrochemical Nano-Fluidics Robert Dryfe, Pawin Iamprasertkun, Radha Boya, Ashok Keerthi and Gangaiah Mettela; University of Manchester, United Kingdom

The movement of electrolyte solutions within nanometer-scale channels is central to understanding nanofluidic phenomena. Ion transport within small (nm) scale pores is also key to electrochemical energy storage, where the energy storage process is dependent on ionic ingress into porous carbon materials [1,2]. Although very significant advances in the understanding of ion movement within electrically charged pores have been made [3], a key barrier is that porous carbon materials contain a complex distribution of interconnected pores of varying size, making it difficult to de-convolute specific size effects. A further connection between the fields of nanofluidics and electrochemistry arises because electrochemical control, based on the phenomenon of electrowetting, may be used to drive liquids into small channels [4]. We have been able to overcome this restriction by applying the nanochannel technology developed by Radha et al [5,6] in the electrochemical context, where one “wall” of the graphene channel
is used as an electrode. We are therefore able to observe the effects of differing ion sizes on electrical double-layer capacitance, additionally, the effects of such extreme confinement on electrochemical processes (both capacitive and Faradaic) can also be discerned.

References:

11:15 AM FF02.01.08
Water Filling of Isolated Single-Walled Carbon Nanotubes—Cataloguing Dependence on Diameter and Etch Technique
Samuel Faucher, Natalie Northrup, Matthias Kuehne, Daichi Kozawa, Volodymyr Koman and Michael Strano; Massachusetts Institute of Technology, United States

Single-digit nanopores, or those with characteristic dimensions less than 10 nm, can induce dramatic changes in phase behavior and transport of the fluids they confine. Isolated single-walled carbon nanotubes (SWNT) form well-characterized nanopores and have been shown to contribute to anomalous water transport and phase behavior. Here, we introduce a scanning method using Raman spectroscopy that we use to rapidly determine the filled state of isolated SWNT. By scanning large numbers of carbon nanotubes, we show that substantial changes (~3 cm⁻¹) in the Raman radial breathing mode occur only in situations consistent with fluid filling, demonstrate the relative success of wet and dry etching in opening carbon nanotube ends, and discuss the diameter dependence of water filling. Specifically, the proportion of carbon nanotubes that fill increases dramatically with nitric acid treatment, while variations in filled proportion are strong but non-monotonic with carbon nanotube diameter.

11:30 AM FF02.01.09
Two-Dimensional Materials Get Electrified in Water—Ab Initio Simulations of the Surface Reactivity of Graphene, h-BN, Their Heterostructures and Graphene Oxides in Water
Benoit Grosjean¹, Felix Mouhat¹, Anton Robert¹, Francois-Xavier Coudert², Rodolphe Vuilleumier¹ and Marie-Laure Bocquet¹; ¹CNRS and ENS Paris, France; ²PSL University, France

Currently basal planes of 2D materials like graphene (G) and hexagonal boron nitride (BN) are considered inert towards covalent addition chemistry in aqueous conditions. However recent ionic transport experiments have unveiled a considerable electrification of the water-BN surfaces [1], with a contrasting response for its water-Graphite homologue [2]. This surface charging was conjectured to originate in the differential hydroxide adsorption at the surface of these twin materials, but the considerable challenge of simulating the elusive hydroxide ion in liquid water has precluded a proper explanation up to now.

In this talk I will first show by means of ab initio simulations that 2D materials do strongly interact with the hydroxide ion from water. As a key ingredient, our ab initio simulations involve the description of the quantum nature of both the layered material and liquid water, corresponding to Ab Initio Molecular Dynamics (AIMD). A full quantum treatment is indeed required to explore the targeted interfacial chemical reactivity of liquid water, in particular to properly include dynamical proton transfers between H-bonding water molecules, a process denoted as the Grotthuss mechanism. We highlight a strong (covalent) chemisorption of the OH⁻ anion on boron-nitride, while the OH⁺ ion is only physisorbed on the graphene layer. Furthermore in its physisorbed state, the OH⁻ species retains a large surface mobility thanks to the Grotthuss mechanism, here confined at the graphene interface [3]. Building on these findings, we extended our exploration of liquid water at graphene-hBN heterojunctions. Counterintuitively, our ab initio simulations of liquid water do show that liquid water does dissociate on such borders [4], leading to the spontaneous formation of an adsorbed OH⁻ ion, while the proton is liberated in the liquid.

Finally I will extend the scope of water reactivity to activated 2D materials, like graphene oxide surfaces [5]. Our ab initio results point in particular a strong dynamical reactivity of the epoxide functions.

These different results are expected to impact strongly the ionic transport across such stacked graphitic membranes.
In spite of their difficulty, quantum insights open unprecedented avenues for the use of intertwined 2D materials for nanofluidics.[6]


11:45 AM FF02.01.10
Ionic Mobility Engineering in Sub-Nanometer Graphitic Channels  Massimo Spina, Nathan Ronceray, Mordjann Hind Soulammas, Kittipitch Yooprasertchuti and Slaven Garaj; National University of Singapore, Singapore

Nanochannels based on carbon materials have been intensively studied in the last decade because of their promising application in nanofiltration and the novel physical phenomena arising between graphitic surfaces at the nanoscale. More recently, atomically-smooth graphitic channels with sub-nm heights have been fabricated and used to investigate the physics of ions and water molecules in slits comparable to the smallest ion sizes.

In this work, we investigated ionic flow in atomically-smooth graphitic channels with height ranging from 7Å to 35nm. We show that the mobilities of ions in such confinements do not scale with hydration shell in a simple fashion, and we further explored the role of the surface charge, physical confinement and chemical interactions. Engineering ionic mobilities within the graphitic channels, we could induce strong current driven by the salinity gradient. Such osmotic power generators – driven by mobility engineering, rather than surface charge – are more resilient on the variation of chemical environment and show orders of magnitude increase in osmotic power density compared to commercial membranes.

1:30 PM *FF02.02.01
Carbon Nanotube Porins—A Versatile Biomimetic Platform for Studying Nanofluidic Transport Phenomena  Aleksandr Nov., 1,2 Lawrence Livermore National Laboratory, United States; 2University of California, Merced, United States

Controlling molecular transport on a molecular scale is important for applications ranging from membrane separations, to bioelectronic interface design. Living systems move ions and small molecules across biological membranes using protein pores that rely on nanoscale confinement effects to achieve efficient and exquisitely-selective transport. Carbon nanotube porins—pore channels formed by ultra-short carbon nanotubes assembled in a lipid membrane—can exploit similar physical principles to transport water, protons, and small ions with efficiency that rivals and sometimes exceeds that of biological channels. I will discuss the role of molecular confinement and slip flow in these pores and show how it can enhance water and proton transport efficiency and influence the mechanisms of ion selectivity in these pores. Overall, carbon nanotube porins represent simple and versatile biomimetic membrane pores that are ideal for studying nanoscale transport phenomena and building the next generation of separation technologies and biointerfaces.

2:00 PM FF02.02.02
Fast Ion Diffusion in Carbon Nanotube Channels  Steven F. Buchsbaum, Melinda L. Jue, Chiatai Chen, Eric R. Meshot, Sei Jin L. Park, April Sawvel, Edmond Lau, Tuan Anh Pham, Kuang Jen Wu and Francesco Fornasiero; Lawrence Livermore National Laboratory, United States
Many simulations and experiments have investigated pressure-driven fluid flow in carbon nanotubes (CNTs) and demonstrated enormous transport rates through these channels. Comparatively little attention has been given so far to concentration-driven transport in CNTs despite its importance in a large variety of fields. While a few studies assumed bulk/hindered diffusion for small molecules through nm-wide CNTs, other simulations have predicted self-diffusion coefficients several times larger than in the bulk, and NMR experiments supporting these claims are beginning to emerge. These large uncertainties in the magnitude of the diffusion rates through CNTs have hampered their full exploitation in nanofluidic devices.

To obtain a precise quantification of the diffusive flow in CNTs, we have fabricated membranes with a large but known number of single-walled carbon nanotubes (SWCNT) as fluid transport pathways. Contrary to previous membrane systems, this platform enables us to minimize uncertainties in the calculation of the per-pore flow rate. A series of stringent control experiments confirms that these membranes are defect free and that transport occurs only through SWCNTs. Once corrected for the boundary layer resistance at the membrane/fluid interface, our measurements indicate that the transport diffusivity of small ions in single-walled carbon nanotubes is about an order of magnitude faster than in the bulk. The dependence of the flow enhancement on the ion chemico-physical properties is also discussed. These results suggest that CNT membranes could enable dialysis process with unprecedented efficiency, shed further light onto the unique transport properties of graphitic channels, and enable a more accurate design of CNT-based fluidic systems for a broad range of applications.

References

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2:15 PM FF02.02.03
Leveraging Large-Scale Electronic Structure for Multi-Scale Models of Confined Solutions Mengyi Wang, Zhongyue Yang and Heather J. Kulik; Massachusetts Institute of Technology, United States

Water exhibits unique properties under confinement that are distinct from properties of bulk water. Atomistic modeling can provide valuable insight into differences in nano-confined (e.g., by nm-scale carbon nanotubes) water and salt solutions. However, accurate, first-principles modeling of molecular interactions is necessary to predict emergent properties. To better understand the graphene-water interface in such systems, we performed ab initio molecular dynamics on representative confined systems. We investigate the nanoscale solvation behavior of selected ions on coronene and circumcoronenes as finite graphene models. We investigate the degree of charge transfer between the ion and water with range-separated hybrid density functional theory as well as how that charge transfer fluctuates during dynamics. We also investigate how defects alter these dynamics and solvation in model systems.

2:30 PM FF02.02.04
Unraveling the Role of Many-Body Polarization Effects on the Thermodynamic and Transport Properties of Nanoconfined Water Inside Carbon Nanotubes Rahul Prasanna Misra and Daniel Blankschtein; Massachusetts Institute of Technology, United States

Extremely fast water transport and high ion selectivity in smaller-diameter carbon nanotubes (CNTs) have raised the prospect of the practical use of CNTs in membrane-based applications. Several experimental and molecular dynamics (MD) simulation studies have reported that the CNT wall behaves like a nearly frictionless surface, which results in a significant enhancement of the water flow rate through CNTs. The extent of water flow enhancement is typically quantified using the concept of a slip length, which mathematically represents the extrapolated distance relative to the wall of the CNT where the water velocity goes to zero. Although previous MD simulation studies have laid a solid foundation to uncover the molecular mechanisms responsible for the large slip lengths of water inside CNTs, the precise dependence of the slip length on the CNT diameter, chirality, and metallicity still remains unknown.

In this talk, we will discuss our results on the slip flow of water through 0.8 nm – 2 nm diameter CNTs, obtained
using classical MD simulations. The classical MD simulations are carried out using quantum mechanically-derived polarizable force fields [1] to model water-CNT interactions. Our theoretical framework can accurately model the anisotropic polarizability tensors of CNTs, including self-consistently modeling the water-CNT polarization energy, which was neglected in previous MD simulation studies. By carrying out classical MD simulations, we investigated the dependence of the water density and friction coefficient on the CNT diameter and chirality. We find that contrary to common intuition, water behaves like a compressible fluid in nanoconfinement such that many-body polarization effects result in a pronounced enhancement in both the density and the structuring of water molecules confined inside CNTs. We also obtain an anomalous maximum in the water friction coefficient for ~ 1 nm diameter CNTs, which is in good qualitative agreement with previous experimental studies which have reported pronounced water ordering and freezing-point elevation inside such narrow CNTs. Further, by carrying out MD simulations using different water models, we will highlight the roles of water-CNT and water-water interactions on the water friction coefficient inside CNTs. Finally, by carrying out MD simulation studies which have utilized a Lennard-Jones potential to model the water-CNT interactions, our findings highlight the necessity to utilize polarizable force fields to more realistically model the CNT/water interface.


2:45 PM FF02.02.05
Enhanced Electrokinetic Energy Conversion with Macroscopic Vertically Aligned BNNT Membranes
Semih Cetindag1, Aaditya Pendse2, Robert F. Praino3, Sangil Kim2 and Jerry W. Shan1; 1Rutgers, The State University of New Jersey, United States; 2University of Illinois at Chicago, United States; 3Chasm Advanced Materials, United States

Recent nanofluidic experiments with single or few nanopores in graphene, molybdenum disulfide and hexagonal boron nitride have shown unique fluidic transport properties and the potential for electrokinetic energy conversion with unprecedented power densities. In such nanopores, the high-surface charge makes possible a diffusio-osmotic mechanism for ion-selective transport, distinct from the Donnan exclusion that is typical of conventional membranes. In particular, experiments with single boron nitride nanotubes (BNNTs) have reported large surface charge in aqueous solution, and osmotic power densities up to several kW/m² when extrapolated to macroscopic membranes. However, no such macroscopic BNNT membranes have ever been fabricated, and their performance at large scales and pore densities is unknown. Thus, we seek to devise scalable means to manufacture such large-area nanotube membranes, and to investigate their fundamental mechanisms and performance for ion selectivity and electrokinetic energy conversion.

Here, we describe the fabrication of the first-ever macroscopic vertically aligned- (VA-) BNNT membranes, and our study of their ion-selectivity mechanism and osmotic-power-generation performance. The membranes are fabricated with a unique solution-based technique in which BNNTs are aligned and concentrated in a liquid oligomer with an external field, and then locked in place by in-situ polymerization. With this scalable fabrication technique, we have made VA-BNNT membranes of size 1-10 cm² and having tube densities of $10^6$-$10^8$ BNNTs/cm² and open pore densities on the order of $10^7$ pores/cm². We show that, due to the high surface charge in their pores, the BNNT membranes are highly cation-selective even when the Debye length is smaller than the inner radius of the nanotubes. Moreover, the membranes exhibit energy-conversion efficiencies of 30%, and have osmotic power densities (based on open pore area) comparable to and even exceeding that of single BNNTs, up to 7,500 W/m² at pH 11 and 1 M:1 mM KCl molarity difference. To elucidate the mechanisms for ion selectivity and osmotic-power generation, we compare the membrane performance for different salts and for few-wall and multi-wall BNNTs of different diameters. Notably, these scalably fabricated VA-BNNT membranes, with relatively large yet highly selective pores, have enhanced electrokinetic-energy-conversion performance, and may enable efficient energy harvesting from salinity gradients, as well as efficient desalination and other separations via a different mechanism than conventional membranes.

3:00 PM BREAK
3:30 PM *FF02.02.06
Observation and Spectral Assignment of Family of Hexagonal Boron Nitride Lattice Defects Daichi Kozawa¹, Ananth Govind Rajan¹, Sylvia Xin Li¹, Takeo Ichihara¹, Jamie Warner², Daniel Blankschtein² and Michael Strano¹; ¹Massachusetts Institute of Technology, United States; ²University of Oxford, United Kingdom

Atomic vacancy defects in single unit cell thick hexagonal boron nitride are of significant interest because of their photophysical properties, including single-photon emission, and promising applications in quantum communication and computation. The spectroscopic assignment of emission energies to specific atomic vacancies within the triangular lattice is confounded by the exponential scaling of defect candidates with the number of removed atoms. Herein, we collect more than 1000 spectra consisting of single, isolated zero-phonon lines between 1.69 and 2.25 eV, observing 6 quantized zero-phonon lines arising from hexagonal boron nitride vacancies. A newly developed computational framework for isomer cataloguing significantly narrows the number of candidate vacancies. Direct lattice imaging of hexagonal boron nitride, electronic structure calculations, and subsequent boric acid etching are used to definitively assign the 6 features. Systematic chemical etching supports the assignment by demonstrating the sequence of growth of successively larger vacancy centres from smaller, which include a single B vacancy and a 16-atom triangular defect. These features exhibit a range of emission lifetimes from 1 to 6 ns, and phonon sidebands offset by the dominant lattice phonon in hexagonal boron nitride near 1370 cm⁻¹. This assignment should significantly advance the solid-state chemistry and photophysics of such vacancy emitters.

4:00 PM FF02.02.07
Ion Solvation and Transport in Carbon Nanopores—Predictions from First-Principles Simulations Tuan Anh Pham, Cheng Zhan and Eric Schwegler; Lawrence Livermore National Laboratory, United States

Carbon nanopores underpin a large array of materials systems and technological applications, including supercapacitors and water desalination. In these devices, understanding of the ion behavior is essential for predicting and optimizing the performance; however, many mechanistic details remain enigmatic. These include transport and solvation properties of the ions, and how they are governed by the degree of confinement and interfacial interactions. Here, we employ first-principles simulations to unravel key features of the solvation structure of several common ions at the interface with graphitic interface, and under confinement within graphene slit pores as well as carbon nanotubes (CNTs). We find that polarizable ions generally exhibit a stronger adsorption at graphitic interfaces, and these effects are found to be significantly enhanced under confinement. In addition, we find that confinement significantly influences ion selectivity and transport, i.e., ions with a small radius are found to yield a notably larger energy barrier to reach the pore entrance. These results points to the complex interplay between confinement and specific ion effects, which has broad implications in optimizing nanopores for ion selectivity and energy storage. Comparison with available experimental data will also be discussed.

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4:15 PM FF02.02.08
Forced Convection Heat Transfer of Air Along the Longitudinal Direction of Aligned Multi-Walled Carbon Nanotube Channels Wonjae Jeon¹, Taehun Kim¹, Sung-Min Kim¹ and Seunghyun Baik¹,²; ¹Sungkyunkwan University, Korea (the Republic of); ²Institute for Basic Science (IBS), Korea (the Republic of)

Fast mass transport through carbon nanochannels has been extensively explored. However, only a few studies have investigated convective energy transport through nanochannels. The no-slip and temperature-jump conditions compete each other in nanoscale convection heat transport [1]. The fast mass transport provides an interesting opportunity to explore nanoscale convection heat transfer. Here, we report the experimental investigation of convective heat transport of air through the vertically-aligned multi-walled carbon nanotubes (VAMWNTs) [1]. The unit cell flow channel was defined as an interstitial space among four adjacent nanotubes (hydraulic diameter = 84.9 nm). The air flow was in the transition and creeping flow regime with two orders magnitude higher flow rates than the prediction of Hagen-Poiseuille theory [1]. Due to the ultrahigh microwave absorption cross-section of long nanotubes [2], rapid, selective, and volumetric heating of the VAMWNTs was realized by providing a constant heat flux using the single-mode microwave (2.45 GHz) heating system [1]. The convective heat transfer coefficient and Nusselt number were experimentally obtained [1]. The heat transfer coefficient was relatively small partly due to the temperature jump and small Reynolds number. However, the heat transfer coefficient increased significantly as
Reynolds number increased. Furthermore, the surface area available for heat transfer could be increased by 4 orders of magnitude using the aligned nanotube structure [1]. Overall, a large number of nanochannels in a given cross-section of heat sinks may enhance the total heat flow rate significantly [1]. A recent progress in our lab will also be introduced. References: [1] Nanoscale, 10, 23103 (2018) [2] J. Phys. Chem. C, 118, 13757 (2014)

4:30 PM FF02.02.09

**New Water Structure in a Geo-Inspired Nanotube and Interrelated Dynamics** Geoffrey Monet¹, Erwan Paineau², Gilberto Teobaldi³, Stéphane Rols¹ and Pascale Launois⁴; ¹Université Paris Saclay, France; ²CNRS, France; ³STFC, United Kingdom; ⁴ILL, France

Interfaces, as well as water structuration at interfaces, have a major influence in nanofluidics. Hydrophilicity and charge of the interfaces are key parameters [1,2]. Here, we would like to introduce nanochannels that are extremely interesting but less well-known than those based on carbon or on boron nitride for instance. These are imogolite-like nanotubes, inspired from alumino-silicate imogolite nanotubes discovered in soils as early as 1962 [3]. They are synthesized by soft chemistry and they are monodisperse in diameter and in chirality [4]. Their hydrophilic inner surface can be rendered hydrophobic by replacing hydroxyl groups by methyl ones [5] and their surface charge is also tunable [4, 6]. Such properties obviously make imogolite-like nanotubes ideal model systems for fundamental studies about nanoconfinement. Imogolite-like nanotubes are also becoming appealing for a wide range of potential applications, from filtration to depollution of water [7].

Here, we focus on geo-inspired alumino-germanate imogolite-like nanotubes (Ge-INT) with nominal formula GeAl₂O₃(OH)₄, which are synthesized by our team at Orsay and whose atomic structure has been recently determined [4, 8]. By carrying out inelastic neutron scattering (INS) experiments coupled to ab-initio molecular dynamics simulations, we reveal a unique structure of the water layer adsorbed inside Ge-INT [8]. Water molecules form an ordered triangular lattice on the inner surface of the nanotube, each molecule having three H-bonds with germanol groups on the surface. To the best of our knowledge, this structure differs from that of any kind of two-dimensional water, either on planar surfaces [9] or on curve surfaces of nanochannels. Detailed analysis of the vibrational density of state measured by INS shows that the dynamics of INT and water are strongly interrelated, a fully original result with respect to the available experimental literature about water in one-dimensional or two-dimensional nanopores. For instance, enhanced diffusion of water in CNTs due to phonon-induced oscillation friction has been predicted from molecular dynamics simulations [10] but it has not been complemented by experimental evidence. A new, well-defined translation vibrational mode of water molecules with respect to the nanotube wall is finally observed. Due to the peculiar bonding of water molecules with germanol groups, the evolution of the mean square displacement of water molecules as a function of temperature in Ge-INT is found to differ markedly from the ones measured for CNT [11] which are associated with frictionless water slip [12, 13]. Notably, the dynamics of INT-confined water remains harmonic from 10K to 300K, with no phase transition towards a liquid state up to room temperature.


4:45 PM FF02.02.10

**Measurement of the Single Molecule in a Nano Cage Based on Graphene Transfer** Fei Zheng; Southeast University, China
Nanopore sensing based on the blockage of ionic current caused by the steric hindrance of nanoparticles translocation has shown the promise in the detection of a single molecule and its morphology. However, due to the fast translocation velocity of nanoparticles and complicated fold morphology, it is hard to distinguish one from several molecules in the nanopore and achieve the concrete morphology. Here, we present the method to detect single DNA molecule precisely with a special nanoliter-sized cage. The fabrication of this cage is based on the transfer of thin graphene on the nanopore membrane which is laid on the Si chip. On both sides of the cage are two nanopores, one in the graphene membrane and the other in the silicon nitride membrane. The preparation method for the former nanopore is dielectric breakdown and the counterpart for the latter one is the drilling of the focus ion beam. The length of the cage depends on the depth of the silicon nitride membrane which can be manipulated by etching or drilling methods. The graphene nanopore is 10 nm and the silicon nitrogen nanopore is 100 nm, which form a current circuit in series. Attributed to the difference in size, the resistance of the graphene nanopore is relatively larger, which means the potential drop across the 10 nm nanopore can be of two order of magnitude larger than that across the 100 nm nanopore. Hence, the DNA molecule will translocate from the bulk solution to the nano cage through the graphene nanopore under sufficient electrophoresis force but will not escape from the 100 nm nanopore owing to the weak potential drop. The single molecule will be trapped in the nano cage unless a reverse voltage is applied. This method can extend the duration of blockage event and increase the accuracy of detecting single molecule. According to the value of current drop, the morphology of the single molecule can be confirmed. This method and the structure of nano cage will promote the research in the field of single molecule detection and provide inspirations for nanopore sensing.

**FF02.03.02**

**Investigation of Nitrogen Doping Effect on Electrokinetics at Graphene-Water Interface**

Takeru Okada¹, Golap Kalita², Masaki Tanemura², Ichiro Yamashita³, Fumio S. Ohuchi⁴, Meyya Meyyappan⁵ and Seiji Samukawa¹;
¹Tohoku University, Japan; ²Nagoya Institute of Technology, Japan; ³Osaka University, Japan; ⁴University of Washington, United States; ⁵NASA Ames Research Center, United States

Energy harvesting has been widely recognized as an important issue. Among the novel energy-harvesting methods, liquid-flow-induced electricity generation stands out as a mechanically non-degradable strategy that targets a variety of natural body of water as a viable energy source, such as river, currents in ocean, rain, etc. The energy harvesting by flowing water on graphene has been studied. The physical view proposed to date is still not deterministic, however, surface conditions are key factors for the understanding of the mechanism and maximizing the performance. In our strategy, the surface conditions include electrical potential at the liquid-solid interface and wettability of graphene, both of which can be tuned by heteroatom doping. In this paper, we discuss the contribution of the bonding state of nitrogen atoms in graphene. In addition, the role of the surface condition of graphene on flow-induced electricity generation is investigated.

We studied two type of nitrogen-dopant atoms with specific bonding state in graphene, thus graphitic and pyridinic nitrogen. Graphitic nitrogen is located at in-plane of graphene and pyridinic nitrogen atoms are located either above point defect or the edge due to geometrical limitation. The power generation was investigated using CVD graphene and deionized water droplets by manually dropping the droplets (0.1 ml). Both pyridinic and graphitic nitrogen dopants enhance voltage generation by water-flow. On pristine graphene, a single water droplet induces approximately 80 mV (0.89 μW). In contrast, the voltage induced at both types of nitrogen-doped graphene is approximately three times greater in magnitude (~240 mV). However, the output power from pyridinic nitrogen is almost zero because of much larger resistance increase by doping compared with graphitic nitrogen. The geometric constraints of the pyridinic nitrogen degrade graphene’s electrical conductivity. Therefore, it is found the graphitic nitrogen dopant is superior for power generation (1.3 μW) [1].
The enhancement of voltage generation by nitrogen doping is explained as follows. The electronic state of the nitrogen-doped sites is considered to have an important role. Nitrogen doping of carbon in various applications acts as an electron donor by providing the unshared electron pair of nitrogen in graphene. The local charge of graphitic nitrogen is positive and that of the surrounding carbon atoms is negative. This is explained by the electron transfer from nitrogen atom. The inside of the droplet sitting on top of graphene is affected by the negative charge on the graphene surface, leading to potential formation at the interface. The induced negative charge reduces electric double layer at the interface, resulting in the formation of steep potential \[2,3\].

In summary, we have investigated the effect of graphene doping on flow-induced power generation between graphene and water interface and found that the nitrogen-doped graphene shows enhancement of power generation. The surface charge of the nitrogen-doped graphene reduces the electric double layer thickness, resulting in the formation of a steep potential, which contributes to higher power generation.


**FF02.03.03**

**Ion Transport through 2D-Channels of Graphene Oxide Membranes with sub-nm Interlayer Spacing**

Jongwoon Kim, Seung Eun Lee and Chang-Soo Han; Korea University, Korea (the Republic of)

Over the past decade, ion sieving using carbon-based materials such as carbon nanotube, graphene and graphene oxide has been attracted attention in water purification and ion filtration. Among them, graphene oxide (GO) membranes have recently emerged as promising candidate in the industry due to their excellent mechanical property, inexpensive synthesis, controllable selectivity and easy processing. Especially, they naturally have sub-1nm interlayer spacing comparable to the dimension of molecules or ions, which is crucial factor for ion sieving. Since the ions and molecules are sieved out according to the interlayer spacing, it is important to narrow the interlayer spacing to enhance the filtration efficiency. Herein, we fabricated thermally reduced graphene oxide (rGO) membrane with different interlayer spacing ranging from 3.7 Å to 8.0 Å in a dry state. GO membranes have inherent property to swell in water, which enlarge the interlayer spacing by several angstroms in water. We found that the minimum spacing to allow the water molecules to permeate the channels was 5.7 Å. Once the GO membrane immersed in water, the interlayer spacing increased to 9.6 Å. While the untreated GO membrane with interlayer spacing of 8.0 Å in dry state (13.8 Å in water) have no selectivity in ion permeation, we found that the anions, such as SO\(_4\)\(^{2-}\) and Fe(CN)\(_6\)\(^{3-}\), was totally rejected to permeate through the thermally reduced GO membrane with interlayer spacing of 9.6 Å. On the other hand, the permeation of cations was exponentially decreased with the hydrated diameter of cations. We found that sub-nanometer interlayer spacing of reduced GO membrane can physically sieve the ions, and negatively charged oxygen-functional groups rejected the multivalent anions.

**FF02.03.05**

**Strain Engineering of Graphene Oxide Membranes for Nanofluidic Transport**

Catherine E. Machnicki, Kyung-suk Kim, Derek Stein and Ian Y. Wong; Brown University, United States

Molecular transport through atomically-thin, layered 2D materials is associated with unique physicochemical phenomena not observed in bulk solution. In particular, ion and water transport are affected by extreme confinement, and exhibit behaviors analogous to those observed in nanofluidic channels. Moreover, the surface chemistry of carbon nanomaterials such as graphene (oxide) results in distinct interfacial interactions, which may be further engineered by mechanical strain. Such controlled modulation of surface topography, colloquially referred to as wrinkling, could affect local electronic structure and chemical interaction by manipulation of lattice structure. The coupling of ionic and molecular transport with strain engineering in 2D material architectures could be leveraged for desalination, energy storage, molecular sensing and energy conversion. However, our fundamental understanding of physicochemical transport properties within strained 2D material nanofluidics remains limited. Here, we utilize strain engineering to modulate both in-plane and out-of-plane molecular transport within multilayered 2D material assemblies. We show that metal ions can intercalate between 2D materials, increasing the interlayer spacing. Furthermore, multilayer GO papers permit water and oxygen transport, but are impermeable to organic molecules, even when unfolded at large area strains. These mechanochemical mechanisms may enable new fundamental
insights into molecular transport under extreme confinement, as well as stretchable and wearable devices.

FF02.03.07
Nanofluidics in Smectite Clays Leide P. Cavalcanti\textsuperscript{1,2}, Heloisa N. Bordallo\textsuperscript{3}, Kenneth Knudsen\textsuperscript{4} and Jon O. Fossum\textsuperscript{2}; \textsuperscript{1}ISIS Neutron Source, United Kingdom; \textsuperscript{2}Norwegian University of Science and Technology, Norway; \textsuperscript{3}University of Copenhagen, Denmark; \textsuperscript{4}Institute for Energy Technology, Norway

New physical effects have been shown to be possible in “ultrasmall confined spaces” \cite{1} such as higher viscosity or higher mobility among others. Here we present clay minerals as possible materials for the study of nanofluidics. Clays are nano-silicate layered materials with structural properties that can be modified and controlled for intercalation and transport of foreign molecules in their 2D nanospace. Intercalation of water in smectite clays occurs naturally and has been extensively studied with a wide range of techniques, among them neutron \cite{2} and X-ray scattering \cite{3}. Water dynamics in smectite clay interlayers has been studied extensively. Recent experiments and simulations have shown that CO\textsubscript{2} can intercalate and flow in smectite clay interlayers provided from external bulk gaseous, liquid or supercritical CO\textsubscript{2} \cite{4}. We have demonstrated that under certain conditions of pressure and temperature, fluorohectorite smectite clays are able to capture a large amount of CO\textsubscript{2} in this way, depending on the type of charge compensating cation residing in the interlayer \cite{5,6,7}. We have investigated fluorohectorite clays with three different cations (Na\textsuperscript{+}, Ni\textsuperscript{2+} and Li\textsuperscript{+}), suggesting the formation of a stable CO\textsubscript{2} complexation with the clay interlayer cation. Thus, clays could also be used as a model for nanofluidics of CO\textsubscript{2}.

References:

FF02.03.08
Adsorption Transparency of Supported Graphene Morteza H. Bagheri\textsuperscript{1}, Rebecca T. Loibl\textsuperscript{1}, Yingchun Jiang\textsuperscript{1}, J. Anibal Boscoboinik\textsuperscript{2} and Scott N. Schiffres\textsuperscript{1}; \textsuperscript{1}Binghamton University, United States; \textsuperscript{2}Brookhaven National Laboratory, United States

The effect of graphene conformal mapping on the wetting of a surface remains a controversial topic. Many groups have studied the wetting transparency of graphene coated surfaces by measuring the water contact angle on the surface, however, airborne contamination due to the exposure of the surface during contact angle experiment can alter the hydrophilicity/hydrophobicity of the surface. Here, we explore this controversy by comparing the interaction of water molecules with a surface through measurement of the adsorption energy of the water molecules on the surface with and without graphene coatings. We find that the isotherms of water adsorbing on graphene are strongly influenced by the substrate, with the surface energy only being reduced by 10\% for Pt and Al and 30\% for Au

FF02.03.09
Developing the Performance of Devices for Nanopore Single Molecule Sensing of Biopolymers Brian Sheetz; University of Rhode Island, United States

Nanopores are nanoscale diameter holes in thin film membranes. They can deliver single-molecule sensing that provides concentrations while also profiling material properties of analytes from single molecules, to (bio)polymers such as DNA, proteins and sugars, and nanoparticles. Nanopores can be formed easily by controlled dielectric
breakdown (CDB) to match their size to the single nanometer to tens or hundreds of nanometers size of analytes. Passage of a molecule through a pore immersed in electrolyte is achieved by application of a voltage across the membrane. Detection of this molecular passage is most commonly done by Resistive Pulse Sensing (RPS)—measuring the change in pore resistance caused by the presence of an analyte in the pore. The magnitude of the resistive pulse is determined by parameters such as the molecular size and charge density. Detection is inherently single-molecule, without the need for chemical labelling steps. Nanopore DNA sequencing has leveraged this sensitivity to native molecular structure and properties. We have extended this basic DNA sequencing concept to motivate the development of nanopores for profiling a much more variable set of biopolymers, oligo- and polysaccharides. With more than 100 naturally occurring monomers and with more variable charge than DNA—and with the added complication of branching—a more sophisticated set of nanopore tools and sensing mechanisms is required. We have begun to undertake this development, which spans preliminary measurements of a diverse and challenging array of biopolymers to correlate known molecular properties to nanopore signal patterns. We will discuss development of alternative fabrication strategies for the core nanopore element, device-design considerations including microfluidics integration, and how to exploit a wider range of electrokinetic phenomena than had been pioneered for nanopore DNA sequencing. In addition, we will discuss issues in streamlining signal processing. These topics will be presented in the context of developing nanopore science for glycomics.

FF02.03.10
Permeation Characteristics of Graphene Oxide Membrane Fabricated and Modified in Various Methods
Seung Eun Lee and Chang-Soo Han; Korea University, Korea (the Republic of)

Recently, a tremendous amount of attention has been paid to the technology of desalination and air purification to solve the problem caused by severe water shortage and air pollution. Membrane separation method is one of the key technologies to solve this problem due to its energy-saving and environmentally friendliness. In this field, Graphene oxide (GO) membrane is a prominent candidate with its exceptional properties of selective separation and high permeability as to specific ions or molecules. It also has the potential to overcome the limitations of traditional membranes due to its excellent mechanical properties, chemical stability and easy fabrication process. GO membrane forms a dense structure formed by layered flakes, so that it obtains a sieving-effect. Moreover, selective permeating and rejecting effect is also obtained with its intrinsic properties. However, at the same time permeation through numerous defects is one of the major permeation paths, so the precise mechanism is not known yet. In this study, using GO membranes fabricated and modified by various methods, we tried to clarify the permeating mechanism by observing the change of properties of membranes and the permeation of ions and molecules. GO films were characterized using SEM, AFM, XRD, XPS and Raman. With these results, we observed the correlation between the properties of GO membrane and permeation characteristics and tried to figure out of the possibilities to commercialize.

SESSION FF02.04: Ultra-Thin Nanopores and Nanoporous Membranes I
Session Chairs: Radha Boya and Rohit Karnik
Wednesday Morning, December 4, 2019
Hynes, Level 3, Room 309

8:15 AM FF02.04.01
Highly Anion Selective Single-Layer Graphene and Boron Nitride
Mustafa Caglar1, Bertram T. Brown1, Inese Silkina1, Oliver Burton1, Vitaly Babenko1, Stephen Gilbert2, Alex Zettl2, Stephan Hofmann1 and Ulrich Keyser1;
1University of Cambridge, United Kingdom; 2University of California, Berkeley, United States

In the growing climate emergency the world finds itself in, sources of clean water and energy will be of critical importance in the near future. Efforts towards achieving this goal have been aplenty but a wholesome solution has yet to emerge. The potential of 2D materials are immense in this field given their thinness, mechanical strength and alterable surface chemistry. Most notably, anion selective 2D membranes - allowing passage of anions - are absent from literature. Membranes that are able to filter selectivity for both anions and cations are needed for applications ranging from blue energy to desalination. We present highly cation and anion permeable graphene and hexagonal boron nitride prepared with minimal overheads, achieving salt rejection ratios of up to 500. We characterise our
membranes using HRTEM in order to elucidate some of the mechanisms for this selectivity. By using Goldman-Hodgkin-Katz (GHK) fitting we extract permeability factors, demonstrating degrees of selectivity. Anion filtration is achieved through the use of multivalent ions but the effect is recreated in monovalent species using a low concentration background of multivalent ions. This means that as grown chemical vapour deposition (CVD) membranes could be used as highly ion selective and high flux membranes, extrinsically controlling the ability to filter for anions or cations as needed.

8:30 AM *FF02.04.02
Voltage Gated Inter-Cation Selective Ion Channels from Graphene Nanopores Joseph S. Bunch¹, Lauren Cantley¹, Jacob Swett², David Lloyd¹, David Cullen¹, Ke Zhou³, Peter Bedworth², Scott Heise², Adam Rondinone³, Zhiping Zhu⁴ and Steve Sinton²; ¹Boston University, United States; ²Lockheed Martin Space, United States; ³Oak Ridge National Laboratory, United States; ⁴Tsinghua University, China

With the ability to selectively control ionic flux, biological protein ion channels perform a fundamental role in many physiological processes. For practical applications that require the functionality of a biological ion channel, graphene provides a promising solid-state alternative, due to its atomic thinness and mechanical strength. Here, we demonstrate that nanopores introduced into graphene membranes, as large as 50 nm in diameter, exhibit inter-cation selectivity with a ~20x preference for K⁺ over divalent cations and can be modulated by an applied gate voltage. Liquid atomic force microscopy of the graphene devices reveals surface nanobubbles near the pore to be responsible for the observed selective behavior. Molecular dynamics simulations indicate that translocation of ions across the pore likely occurs via a thin water layer at the edge of the pore and the nanobubble. Our results demonstrate a significant improvement in the inter-cation selectivity displayed by a solid-state nanopore device and by utilizing the pores in a de-wetted state, offers an approach to fabricating selective graphene membranes that does not rely on the fabrication of sub-nm pores.

Nanoscale, 11, 9856 (2019)

9:00 AM *FF02.04.03
Transparent Proton Transport and Nonlinear Water Transport through Two-Dimensional Nanomesh Material Sheng Meng; Chinese Academy of Sciences, China

Molecular sieving is of great importance to proton exchange in fuel cells, water desalination, and gas separation. Two-dimensional crystals emerge as superior materials showing desirable molecular permeability and selectivity. Here we demonstrate that the experimentally fabricated graphyne membrane shows superior proton conductivity and perfect selectivity thanks to its intrinsic nanomesh structure. The trans-membrane hydrogen bonds across graphdiyne serve as ideal channels for proton transport. The free energy barrier for proton transfer across graphdiyne membrane is ~2.4 kJ/mol, nearly identical to that in bulk water (2.1 kJ/mol), enabling “transparent” proton transport at room temperature (Fig. 1). This results in a proton conductivity of 0.6 S/cm for graphdiyne membrane, four orders of magnitude greater than graphene and ten times larger than commercial proton exchange membrane nafion. Considering its ultimate pore size of 0.55 nm, graphdiyne membrane blocks soluble fuel molecules and exhibits superior proton selectivity. These advantages endow graphdiyne a great potential as proton exchange material in fuel cells, sensors and other applications. If time allowed, results about water transport and water photosplitting on 2D materials will be also discussed.

9:30 AM FF02.04.04
Optimal Transport and Colossal Ionic Mechano-Conductance in Graphene Crown Ethers Subin Sahu¹,², Justin Elenewski¹,², Christoph Rohmann¹,² and Michael Zwolak²; ¹University of Maryland, United States; ²National Institute of Standards and Technology, United States

Directly interrogating the mechanism of ion transport in sub-nanoscale pores is challenging. Thus, typically computational approaches are employed to help shed light on the processes contributing to ion translocation, which are many: steric hindrance due to van der Waal repulsion, dehydration, strong electrostatic interactions due to confinement and a reduced dielectric constant, the structural fluctuations of the pore and flexibility of the membrane, etc. Biological ion channels, for example, balance electrostatic and dehydration effects to yield large ion selectivities alongside high transport rates. These macromolecular systems are often interrogated through point mutations of their pore domain, limiting the scope of mechanistic studies. In contrast, we demonstrate that graphene crown ether pores afford a simple platform to directly investigate optimal ion transport conditions, i.e., maximum
current densities and selectivity. Crown ethers are known for selective ion adsorption. When embedded in graphene, however, transport rates lie below the drift-diffusion limit. We show that small pore strains – 1 % – give rise to a colossal – 100 % – change in conductance. This process is electromechanically tunable, with optimal transport in a primarily diffusive regime, tending toward barrierless transport, as opposed to a knock-on mechanism. Measurements of mechanical current modulation will yield direct information on the local electrostatic conditions of the pore. These observations suggest a novel setup for nanofluidic devices while giving insight into the physical foundation of evolutionarily-optimized ion transport in biological pores.

9:45 AM FF02.04.05
Ion Specific Adsorption under Nano-Confinement—Molecular Dynamics Simulations and a New Continuum Model Peiyao Wang, Dan Li and Zhe (Jefferson) Liu; The University of Melbourne, Australia

Ion partition in nanopores, such as averaged in-pore ion concentration and ion distribution, is critical for many electrolyte related applications, for example, energy storage devices, water treatment, and biology-inspired sensor. A comprehensive model that can quantitatively describe the ion partition under nano-confinement conditions is highly desirable for us to go beyond the trial-and-error experiments to achieve quantitative prediction and design for the next generation of the electrolyte related applications. However, it remains a fundamental challenge, especially in the case of ion-specific effect.

In this talk, we will present molecular dynamics (MD) simulations and a new continuum model to describe the ion partition in nanopores with ion-specific effects quantitatively. Our model system is sodium tetrafluoroborate (NaBF₄) aqueous electrolyte (0.8 M) in graphene nanoslits (varying from 1.0 nm to 4 nm). The Na⁺ and BF₄⁻ ions exhibit different dispersion interaction with graphene surface, leading to a strong specific BF₄⁻ adsorption at graphene surface. Our MD simulations systematically studied how the nano-confinement effects in graphene nanoslits could affect the ion concentration and distribution. The ion concentration in graphene slits exhibits a non-monotonous variation to slit size. The ion distribution profiles in the slit also demonstrate significant dependence on slit size.

Aiming to develop practical device design tools at a large length scale, we also developed a quantitative continuum model to describe the ion-specific adsorption under nano-confinement condition. We modified the classic Poisson-Boltzmann (PB) equation by incorporating the ion-surface effective potential, the electrostatic correlation, and the steric correlation interactions. A new model for steric correlation interaction is proposed, which takes account of the solvent structures in the graphene nanoslits. Our model quantitatively reproduces our MD simulation results very well. Our new continuum model could serve as a general approach for quantitative description of ion local distribution in nanoslit with ion-specific effect. It would be much more efficient than the MD simulations to describe the ion-specific adsorption inside complex porous structures. Besides, it could also lay a ground for the development of continuum models to quantitatively describe the charging dynamics in nanoporous materials.

10:00 AM BREAK

10:30 AM *FF02.04.06
2D Materials FET's for Bio-Sensing Nagendra B.M. Athreya, Mingye Xiong and Jean-Pierre Leburton; University of Illinois at Urbana-Champaign, United States

The last two decades have experienced rapid technological developments in the search of cheap and high accuracy devices for fast bio-molecular identification. In the realm of DNA and protein sequencing, there has been an increasing interest in the use of nanopores in solid-state materials because of their distinct advantage over biological pores in terms of flexibility in pore design and mechanical strength. Two-dimensional (2D) solid state materials such as graphene and Molybdenum di-sulphide (MoS₂) in particular have attracted attention because of their atomically thin layered structure and electrically active characteristics, predisposing them to offer single base resolution and simultaneously multiple modalities of detecting biomolecular translocation. 2D nanopore devices promise seamless integration with semiconductor electronics and are poised to revolutionize a variety of technologies such as genomics, point-of-care diagnostics and digital data storage to name a few.

The past year has witnessed significant activity to experimentally realize nanopore Field Effect Transistors (FETs)
and understand the fundamental sensing mechanism in such devices. Currently, the dominant consensus from theoretical calculations has involved the electrostatic modulation of the FET current due to the translocating biomolecules. In this talk, we review and provide insights into this sensing principle by modeling the electron flow through 2D material nanopore FETs. We describe a method to systematically characterize nanopores FETs by contrasting the changes in the FET behavior before-and-after nanopore drilling and DNA translocation. We outline measurable predictions of high-resolution FET based sensing of DNA-protein complexes and damaged DNA. We compare these FET signals to the corresponding ionic current signals calculated from all-atom Molecular dynamics simulations. Further, we also outline possible techniques to improve the detection SNR by augmenting pore and device design with statistical signal processing algorithms. Finally, we propose a scalable device design of nanopore FETs to detect and identify translocations of single-biomolecules in a massively parallel scheme.

11:00 AM *FF02.04.07
Nanoporous Graphene Membranes for Gas Separation—From Ion Gating to Molecular Tumbling De-en Jiang; University of California, United States

Although a single-layer graphene membrane with nanopores can separate gases with high selectivity by molecular sieving, the pore size is difficult to control at sub-angstrom resolution. Here we discuss two approaches to mitigate this issue via molecular dynamics simulations. First, we demonstrate that a monolayer of ionic liquid on the porous graphene allows anions to gate the pores of significantly larger in size than the gas molecules while still achieves high selectivity. Second, we propose a novel design based on the bilayer nanoporous graphene membrane which allows the effective pore size of the membrane to be continuously tunable by the offset between the two single layers. We find that skinnier and shorter molecules tumble through the elliptic-cylinder-shaped nanopore of the bilayer membrane, leading to higher entropic selectivity.

11:30 AM FF02.04.08
Gas Permeation and Separation across Selectively Etched Nanoporous Graphene Membranes Karl-Philipp Schlichting and Dimos Poulikakos; ETH Zurich, Switzerland

Gas molecules permeating across nanopores of two-dimensional materials experience the least possible resistance due to the atomic thickness of the material. However, pristine two-dimensional materials, such as graphene, are impermeable even to the smallest gases making it unsuitable for gas separation applications. The potential of two-dimensional materials for gas separation can consequently only be harnessed if the material is perforated in a precise and controlled manner. In this work, we present a novel synthesis route of nanoporous graphene membranes with a facile and dry chemical etching approach. The pore growth is initiated in a first step within the graphene lattice selectively at previously introduced atomic defects. The second process step consists of dry etching graphene selectively at the lattice defects, resulting in well-controlled, parallel pore growth yielding membranes with narrow pore size distributions. The resulting membrane performances are investigated in the context of gas separation applications and demonstrate similar selectivity but orders of magnitude higher permeance compared to other perforation techniques of two-dimensional materials.

11:45 AM FF02.04.09
Effects of Surface Trapping and Contact Ion Pairing on Ion Transport in Graphene Nanopores Jian Ma, Kin Li, Zhongwu Li, Jingjie Sha, Yunfei Chen and Lijian Zhan; Jiangsu Key Laboratory for Design and Manufacture of Micro-Nano Biomedical Instruments, School of Mechanical Engineering, Southeast University, China

Nanoporous graphene have attracted much attention in nanofluidics due to their high permeation and low resistance to ions or molecules. They have been widely used in biomolecules sensing, material separation, and energy conversion. With the help of the surface charges on the rim of nanopores, the nanopores have strong ionic selectivity, which provides a perfect platform for seawater desalination with a low-energy cost, and for energy conversion with high efficiency. The major challenge is how to fabricate nanoscale pores on pristine graphene as it cannot be permeated by all atoms including the hydrogen atom in the world. Here we presented an efficient way to produce high-density nanopores on graphene membranes with tunable size in the sub-nanometer range by plasma etching. Besides the pore size, the nanopore density is also controllable through adjusting the exposure time of the sample to argon or oxygen plasma. The plasma-treated graphene membranes can selectively transport protons, Na+ and Cl− ions. Density function theory calculations uncover that the sp2 and vacancy-type defects construct different energy barriers for different ions, which allow the defected graphene membrane to selectively transport ions.
In order to understand the mechanism of the ionic transport in graphene nanopores, we applied molecular dynamics (MD) to investigated the dynamic process of ion transport in graphene nanopores. With the advantage of the simulations, the duration time for each ion passing through the nanopore was analyzed. It is found that the formation of the contact ion pair plays a critical role in reducing the ion mobility inside a nanopore without surface charges. The mobility for both cations and anions decreases with the reduced pore size because it is easier to form the contact ion pairs inside the neutral nanopore with a smaller diameter. Inside a charged nanopore, besides the contact ion pair formation, the surface charges also play a significant role in reducing the counterion mobility through surface trapping. It is uncovered that the mobility of Na$^+$ ions increases first and then decreases with the surface charge density, while Cl$^-$ ions have the opposite trend. A modified first-passage time model is proposed to take into account the ion pair formation and the trapped ions inside a nanopore, which provides a clear picture in describing ion transport through a nanopore.

SESSION FF02.05: Ultra-Thin Nanopores and Nanoporous Membranes II
Session Chairs: Joseph Bunch and Rahul Raveendran Nair
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Room 309

1:30 PM *FF02.05.01
Theory of Nanofluidics in Ultrathin Nanopores Narayana R. Aluru; University of Illinois at Urbana-Champaign, United States

Structure, dynamics and transport of fluids in ultrathin membranes/nanopores can be vastly different from their macroscopic counterparts. For example, water transport through carbon nanotubes has been shown to exhibit flow rates which are many orders of magnitude larger compared to those obtained from classical theories. While classical theories are fast, they do not account for the microscopic mechanisms that are important in ultrathin membranes. Quantum and atomistic simulations can provide good accuracy, but they are limited in the length and time scales that can be dealt with. In this talk, we will present multiscale theories to describe fluidic behavior in ultrathin membranes. First, we will discuss multiscale approaches to calculate fluidic properties such as structure, interfacial friction, viscosity, permittivity, slip, etc. in ultrathin membranes. We will show that these properties can be vastly different when compared to their bulk counterparts. Second, we will discuss the development of nanofluidic theories incorporating microscopic physics and show that these theories can predict water flow rates which are consistent with experimental measurements. Finally, we will discuss the physics of electrical double layers (EDLs) and show that the structure and dynamical properties of ions and water in EDLs of ultrathin membranes can be different from those in larger pores/channels.

2:00 PM FF02.05.02
Rapid Water Transport in Carbon Nanomembranes Yang Yang1,2, Petr Dementyev1, Niklas Biere1, Daniel Emmrich1, Patrick Stohmann1, Riko Korzet2, Xianghui Zhang1, André Beyer1, Sascha Koch1, Dario Anselmetti1 and Armin Gölzhäuser1; 1Universität Bielefeld, Germany; 2Imperial College London, United Kingdom

A major challenge in developing 2D membranes is to create a high density of sub-nm sized channels in the material. Carbon Nanomembranes (CNMs) are 2D films fabricated by crosslinking of self-assembled monolayers. This work will present a ∼1.2 nm thin CNM made from terphenylthiol (TPT) precursors that combines high water permeance with high selectivity. TPT CNMs only allow water and helium to pass through, but stop most gases and liquids. In particular, water across with an extremely high permeance of $\sim 1.1 \times 10^{-4}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, 2,500 times faster than helium. Scanning probe microscopy revealed that these membranes consist of sub-nm channels with an areal density of $10^{19}$ m$^{-2}$. If assuming all channels are active for mass transport, we found a single-channel permeation coefficient of 66 water molecules s$^{-1}$ Pa$^{-1}$, as high as that observed for channels in carbon nanotubes and aquaporin proteins which support a single-file transport of water molecules. This suggests that the fast water flow through TPT CNMs is attributed to a dense network of sub-nm channels and a coordinated water movement per single channel. This encourages the potential use of these membranes for water purification. The versatile and flexible fabrication process also brings the possibility of tailoring CNM functions for usage in different separation systems.

**2:15 PM FF02.05.03**

**MXene Nanopores as Novel Solid-State Biosensors** Mehrnaz Mojtabavi¹, Armin VahidMohammadi², Wentao Liang³, Majid Beidaghi² and Meni Wanunu¹;¹Northeastern University, United States; ²Auburn University, United States; ³Kostas Advanced Nano-Characterization Facility, United States

Nanopore biosensor platforms, namely solid-state and biological nanopores, have been developed over the past two decades as label-free sensors of single molecules and biopolymers (DNA, RNA, and proteins). While biological pores are typically self-assembled and form a natural channel that penetrates an organic membrane, such as a lipid bilayer, in solid-state nanopores, pores are synthetically fabricated by focused electron beam ablation or by dielectric breakdown of an ultrathin solid-state membrane. Thus, solid-state nanopores are more tunable for arbitrary sizes and geometries, and further, the robust framework and mechanical stability of synthetic membranes offers the ability to perform experiments under harsh conditions (e.g., hydrostatic pressure, extreme pH, denaturing conditions, etc.).

The advent of two-dimensional (2D) materials (graphene, MoS₂, WS₂, and BN, for example) as support membranes for solid-state nanopores, offers in principle the highest detection resolution of any pores, because the thickness of these pores is about one atom thick. To further investigate the potential of 2D materials as nanopore support membranes, we have studied novel solid-state nanopores based on new 2D materials known as MXenes. MXenes are an emerging family of 2D transition metal carbides and nitrides with a general formula of $M_{n+1}X_nT_x$ (i.e. $T_iC_2T_x$), where $M$ is a transition metal, $X$ represents carbon or nitrogen ($n=1$, 2, and 3), and $T_x$ indicates different functional groups (O, OH, F) present on MXene surface. Sensing, energy storage, and water purification are among the various applications that MXenes have shown promise towards, owing to their controllable composition and surface tunability. Our initial results have shown that MXenes provide high mechanical robustness, long-time stability, and low-noise ion current recordings that are suitable for single molecule detection. Through further improvement in the fabrication process of MXene membranes, as well as harnessing of some unique MXene characteristics, we show here how MXene membranes could potentially overcome some challenges that relate to limited resolution, such as access resistance limitations, that other solid-state and biological nanopores are facing.

**2:30 PM BREAK**

**SESSION FF02.06/FF01.14: Joint Session: Breakthroughs in Graphene and Beyond 2D Materials**

Session Chairs: Zakaria Al Balushi and Chuanhua Duan

Wednesday Afternoon, December 4, 2019

Hynes, Level 3, Room 312

**3:30 PM *FF02.06.01/FF01.14.01***

van der Waals Layered Materials towards Room-Temperature Magnetic Semiconductors Young Hee Lee¹,², Seok Joon Yun¹ and Dinh Loc Duong¹;¹Sungkyunkwan University, Korea (the Republic of); ²Institute for Basic Science, Korea (the Republic of)

The ferromagnetic state in van der Waals two-dimensional (2D) materials has been reported recently in the monolayer limit. Intrinsic CrI₃ and CrGeTe₃ semiconductors reveal ferromagnetism but the Tc is still low below 60K. In contrast, monolayer VSe₂ is ferromagnetic metal with Tc above room temperature but incapable of controlling its carrier density. Moreover, the long-range ferromagnetic order in doped diluted chalcogenide semiconductors has not been demonstrated at room temperature. The key research target is to realize the long-range order ferromagnetism, Tc over room temperature, and semiconductor with gate tunability. Here, we unambiguously observe a ferromagnetic hysteresis loop together with magnetic domains above room temperature in doped V-doped WSe₂, while maintaining the semiconducting characteristic of WSe₂ with a high on/off current ratio of five orders of magnitude.
The understanding of strongly-correlated quantum matter has challenged physicists for decades. Such difficulties have stimulated new research paradigms, such as ultra-cold atom lattices for simulating quantum materials. In this talk I will present a new platform to investigate strongly correlated physics, based on graphene moiré superlattices. In particular, I will show that when two graphene sheets are twisted by an angle close to the theoretically predicted ‘magic angle’, the resulting flat band structure near the Dirac point gives rise to a strongly-correlated electronic system. These flat bands exhibit half-filling insulating phases at zero magnetic field, which we show to be a correlated insulator arising from electrons localized in the moiré superlattice. Moreover, upon doping, we find electrically tunable superconductivity in this system, with many characteristics similar to high-temperature cuprates superconductivity. These unique properties of magic-angle twisted bilayer graphene open up a new playground for exotic many-body quantum phases in a 2D platform made of pure carbon and without magnetic field. The easy accessibility of the flat bands, the electrical tunability, and the bandwidth tunability though twist angle may pave the way towards more exotic correlated systems, such as quantum spin liquids or correlated topological insulators.

SESSION FF02.07/FF01.15/MS02.08: Keynote Session: Breakthroughs in Graphene and Beyond 2D Materials

Session Chairs: Zakaria Al Balushi and Chuanhua Duan

Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Room 312

4:30 PM *FF02.07.01/FF01.15.01/MS02.08.01

Keynote: Molecular Transport through Two-Dimensional Capillaries

Andre Geim; University of Manchester, United Kingdom

I will review our group’s work on the molecular transport properties of angstrom-scale channels fabricated by der Waals assembly of 2D crystals. These channels can be viewed as if individual atomic planes were extracted from a bulk crystal leaving behind two edge dislocations with an empty space in between. Gas, water, ion and proton transport have been studied in capillaries down to one atom in height.

SESSION FF02.08: Angstrom-Scale Nanochannels and Lamellar Membranes I

Session Chairs: Lyderic Bocquet and Slaven Garaj

Thursday Morning, December 5, 2019
Hynes, Level 3, Room 309

8:15 AM FF02.08.01

Role of Hydration Shell in Engineering Ionic Mobility inside Å-Scale 2D Channels

Solleti Goutham, Ashok Keerthi, Ankit Bhardwaj, Michael Shiggins, Gangaiah Mettela, Andre Geim and Radha Boya; University of Manchester, United Kingdom

Two-dimensional (2D) materials have received widespread popularity over the past decade. Particular in the field of nanofluidic studies by reducing the dimensions from micro to sub-nano scale1 system led to emergence of new fluidic phenomena. In the view of fundamental science passive ion transport under the strong confinement will provide basic information about water-ion-material interaction. Under the strong confinement, various parameters such as hydration shell, orientation of water molecule, surface charge influence the movement of solvent and solute through nanochannels. The hydration shell of ion is of great significance to understand ion permeation and it plays a crucial role in biological and aqueous chemical systems2,3. We explore ions with increasing radii and study the influence of hydration shell on ionic transport in such confinement. Here our measurements of ion-transport through
Å-scale sized channels allow us to study the ion mobility to discern the hard versus soft ball behaviour of ions. Surprisingly we found that similar hydrated diameter size ions show asymmetric mobility behaviour. Our observations may help to enhance the cutting-edge technology in the fields of ion separation, energy conversion and novel fluidic devices.

8:30 AM *FF02.08.02
Tunable Graphene-Based Membranes Rahul Raveendran Nair; University of Manchester, United Kingdom

Permeation through nanometre-pore materials has been attracting unwavering interest due to fundamental differences in governing mechanisms at macroscopic and molecular scales, the importance of water permeation in living systems, and relevance for filtration and separation techniques. Latest advances in the fabrication of artificial channels and membranes using two-dimensional (2D) materials have enabled the prospect of understanding the nanoscale and sub-nm scale permeation behaviour of water and ions extensively. In particular, graphene oxide (GO) membrane containing 2D graphene capillaries shows unique permeation properties such as ultrafast permeation of water and molecular sieving. In my talk, I will discuss our recent results on molecular and ionic permeation properties of GO membranes and its prospect for several applications.

9:00 AM *FF02.08.03
Two-Dimensional Nanofluidics Jiaxing Huang1 and Jun Gao2; 1Northwestern University, United States; 2University of Twente, Netherlands

Electrolytes exhibit drastically different properties when confined in nanochannels. For example, in bulk solution, cations and anions simultaneously move along opposite directions to generate ionic current. However, in channels narrower than the Debye length of the electrolyte (a measure of how far electrostatic effects can persist), the surface charges on the inner walls repel ions of the same charge and attract the counterions, making them the dominating charge carriers. Such unipolar ionic transport can enhance ionic conductivity up to several orders of magnitudes. Nanochannels that enable such transport can be fabricated in bulk materials, but such “top-down” methods are rather expensive and difficult to scale up. The construction of nanofluidic channels with the 2D sheets, a “bottom up” approach, can be done simply by casting or filtration of 2D sheets dispersed in solution, as first demonstrated with graphene oxide sheets. The surface properties and the spacing of the 2D nanochannels can be conveniently controlled by modifying the starting sheets. A number of 2D materials are already available for this purpose.

The exfoliation-reconstruction strategy not only breaks down the experimental barrier of entry to study nanofluidics, but also offers a number of unprecedented opportunities. For example, one can also draw an analogy between the 2D nanofluidic films and extrinsically doped semiconductor wafers, because they both have a planar geometry and only one type of dominating charge carriers. Looking ahead, one can potentially use these lamellar films as “ionic wafers” to create ionic devices or even circuits mimicking the functions of their electronic counterparts. While the hard semiconducting wafers have to be patterned by lithography, these flexible ionic wafers can also be patterned by alternative methods such as Kirigami-like cutting techniques to define the functional elements. Some problems that should be addressed in the field will also be discussed.

9:30 AM FF02.08.04
Enhanced Water Flow through Angstrom-Channels Ashok Keerthi and Radha Boya; The University of Manchester, United Kingdom

Water conduction through porous materials and membranes plays a significant role in nature as well as water purification technologies. Flow through confined channels with dimensions below few nanometers displays a drastic enhancement in the observed water velocities. Most of these studies were with carbon surfaces (e.g., carbon nanotubes) and the enhanced flows were primarily attributed to frictionless transport of water molecules on atomically flat graphitic surface. Nevertheless, with another atomically flat material namely hexagonal boron nitride (hBN), a structurally similar but electronically dissimilar analogue of graphite, we test the water flow velocity. We investigate the link of the hydrodynamic flow to the surface friction and electronic properties of the confining materials, which remains unclear to date. Using precise angstrom scale capillaries made up of graphite and boron nitride walls, we study the water flow through them and address the effect of electronic properties and surface friction. We employ precision gravimetry to study the water flow quantitatively. Unlike graphite capillaries, which show slip
enhanced water flow, hBN capillaries showed at least two orders of magnitude lower water flux. While the velocities of water inside graphite capillaries reach up to 1 metre/second, for hBN capillaries the velocity can reach hardly 0.007 metre/second. Both the surfaces are atomically flat and even structurally similar. What contributes to this massive difference? We probe the possible reasons one by one. We have examined in detail the effects which can contribute to slip flow on two structurally similar atomically flat surfaces of graphite and hBN.

9:45 AM FF02.08.05
Molecular Dynamics Simulations on Ion Transport through Angstrom-Scale Channels Fengchao Wang; University of Science and Technology of China, China

Structural and dynamic properties of ions confined in nanoslits are crucial to understand the fundamental mechanism underlying a wide range of chemical and biological phenomena. Recently, angstrom-scale channels were fabricated using 2-dimensional materials assembled into devices with controllable size, atomically smooth inner walls, and little surface charge, which provide us a new platform to study ion transport under strong confinement. In particular, this new confining geometry allows the size exclusion effect to be unambiguously decoupled from other mechanisms. Here, we investigate ion transport through two-dimensional slits using molecular dynamics simulations. K+ and Cl– show similar ion mobilities in a bulk aqueous solution, whereas they exhibit a remarkable difference when transporting through an angstrom-scale channel. Our molecular dynamics simulations uncover that such discrepancy originates from the subtle differences in their hydration structures and preferable locations across the channel. Opposite charge causes different water dipolar orientations around ions, mediating the distance and tribological interactions between hydrated ions and channel’s walls. Hydrated Cl– ions experience a remarkable larger friction force inside the channel and consequently a smaller mobility compared with K+ ions. Ion transport also shows clear size effect. As the slit size approaches the ultimate scale, dehydration at the entry impedes the ionic conductance significantly, and even induces a complete ion rejection. We demonstrate that energy barriers required to accomplish the ion permeation can be theoretically connected to the partial dehydration process. The proposed model is further validated by simulations. Our results offer insights into the atomistic details of ion permeation, which may also shed light on developing effective ways for water filtration and desalination.

10:00 AM BREAK

10:30 AM *FF02.08.06
Graphene Oxide Membrane with Angstrom Channel Size for Selective Separation of Ions, Water and Gases Jongwoon Kim, Seung Eun Lee and Chang-Soo Han; Korea University, Korea (the Republic of)

Graphene oxide (GO) has been promising candidate material for separating water, ions and gases. Previous researchers have done great efforts to understand how GO membrane filtrates the ion and water molecules. The capability to separate the matters depends on the adsorption, diffusion and sieving diameter of the membranes. The transport mechanism through GO membrane with less 1nm interlayer spacing (wet state) becomes very complex to figure it out, because three effects should be considered. Using GO membrane with Angstrom channel size, separating results of ions, water and gases are presented and the plausible mechanisms are discussed.

11:00 AM FF02.08.07
Dipolar Graphene-Based Laminar Membranes Marcos V. Surmani Martins1,1, Seunghyun Hong2 and Slaven Garaj1,1,1; 1National University of Singapore, Singapore; 2King Abdullah University of Science and Technology, Saudi Arabia

Dipolar graphene-based interfaces are yet to be considered for the latest generation of ionic sieving membranes, while having remarkable potential related to their enhanced charge interactions, water acceptability and suppressed nonspecific adsorption of complex molecules on the solid-liquid interface (fouling). Such membrane bears resemblance to zwitterionic macromolecules that retain both positive and negative groups, which make them highly hydrophilic and electrokinetically stable at a broader range of pH and ionic strengths when compared to other conventional families of macromolecules or materials.

In this work, we investigated the ionic transport in dipolar laminar graphene oxide (GO)-based membranes, harboring both positive amid and negative covalently bonded charge groups. By controlling the content of different oxygen carrying groups, the overall ionic permeability can be tuned. Even with an enhanced hydrophilicity of the
membrane, the membranes with higher degree of reduction showed ionic permeability values lowered by an order of magnitude. Moreover, a peculiar reversed ionic selectivity among mono- and divalent ions is observed, giving us general insight into molecular interactions within GO membranes. The scalability of these membranes, combined with their chemical stability, as well as antifouling properties make them strong candidates for applications such as, biochemical separation processes, desalination and osmotic power generation.

SESSION FF02.09: Ultra-Thin Nanopores and Nanoporous Membranes III
Session Chairs: Narayana Aluru and Aleksandr Noy
Thursday Afternoon, December 5, 2019
Hynes, Level 3, Room 309

1:30 PM *FF02.09.01
Nanosculpting Two-Dimensional Materials—From Antidots and Bandgap Tinkering to Nanopores and DNA Sequencing
Marija Drndic; University of Pennsylvania, United States

Atomic-defect engineering in 2D materials provides new opportunities from condensed matter physics to molecular filtration. Introducing atomic and nm-scale vacancies in 2D materials changes their electrical and optical properties (for example the bandgap, as in antidot lattices). When 2D materials are suspended, vacancies make the membranes permeable to ions and molecules in liquid or gas phases, allowing transport studies at atomic scales. While Ohm’s law works well to describe ion current flow through nm-size holes, for sub-nm holes comprised of a handful of missing atoms, one measures non-linear current-voltage curves. Sub-nm holes allow the passage of smaller water molecules but block the larger hydrated salt ions which can be exploited for efficient water desalination. Raman and photoluminescence spectroscopy combined with aberration-corrected TEM, together with molecular-dynamics and DFT calculations, provide a comprehensive approach to characterize the holes and transport through them. Raman peak shifts can be used to quickly determine the density of vacancies, once those have been initially calibrated with electron microscopy data.


2:00 PM *FF02.09.02
Controlling Ionic and Molecular Transport through Porous 2D Membranes
Ulrich Keyser and Stephan Hofmann; University of Cambridge, United Kingdom

Thin membranes made from systems like graphene are emerging as essential building blocks for applications ranging from desalination, osmotic power production to molecular sensing. Here, we elucidate the physical interactions that govern transport of ions and macromolecules in these systems. Our quantitative measurements based on diffusion of positive and negative ions across porous 2D membranes of graphene and hexagonal boron nitride (h-BN) prove their cation selectivity in a wide pH range. The Goldman-Hodgkin-Katz equation allows us to extract the ion selectivity from current−voltage characteristics of graphene and h-BN monolayers separating reservoirs of different salt concentrations. Systematic measurements varying the Debye screening length as well as the type of ions and pH demonstrate that negative surface charge gives rise to cation selectivity. In addition, we show that the cation selectivity can be reversed into anion selectivity by the chosen ionic species. Surprisingly, h-BN and graphene membranes show very similar characteristics. The extrinsic nature of the selectivity enables to create efficient...
power conversion for streaming currents. Finally, we will discuss our recent measurements on the transport of macromolecules like DNA through pores in graphene and hBN and efforts to measure the force during translocation using optical tweezers.

2:30 PM FF02.09.03
Two-Dimensional Nanopore DNA Sequencing by Diffusion Current Measurements Wei-Lun Hsu¹, Yuji Nakagawa¹, Daisuke Egusa¹, Soumyadeep Paul¹, Ya-Lun Ho¹, Jean-Jacques Delaunay¹, Zhen Gu², Yi-Lun Ying², Yi-Tao Long²,³, Eiji Abe¹, Yoshihiro Iwasa¹ and Hirofumi Daiguji¹; ¹The University of Tokyo, Japan; ²East China University of Science and Technology, China; ³Nanjing University, China

Nanopore technology using biological pores embedded in a lipid bilayer has emerged as a rapid and inexpensive alternative to conventional DNA sequencing methods. In a similar vein, artificial solid-state nanopores possessing the advantages of mechanical strength, modifiable geometry and stable chemical properties over the biological nanopores are expected to be more favorable for biomolecule detections. However, thus far the development of solid-state nanopore technology has encountered gigantic obstacles in both spatial and temporal resolutions hindering the fulfillment of practical sequencing applications. Comparing with the gap between each DNA nucleotide (~3.4 angstroms), the thickness of conventional silicon nitride membranes is approximately two orders of magnitude greater. In this regard, two-dimensional materials nanopores have been recently employed attempting to improve the spatial resolution, whose thicknesses coincide with the distance between each nucleotide (e.g. the thickness of a monolayer molybdenum disulfide is 6.5 angstroms). Nevertheless, although these ultrathin nanopores conceptually promise high spatial resolution, the reduction of the pore length concurrently brings up two major issues: (i) the augmentation of Joule heating effects in which the imposed electric field magnitude is inversely proportional to the pore length. In consequence, the superheated solution inside the nanopore not only can give rise to the denaturation of DNA molecule properties but deteriorates the signal-to-noise ratio due to the additional thermal noise; and (ii) the presence of transport-induced-charge effects resulting in a lack of translocation events at low applied electric field but excessive translocation speed at high applied electric field yielding poor temporal resolution.

Here, we propose a novel and simple approach to effectively resolve above issues originated from the external electric field. Instead of tracing the conduction current variation, we replaced the external electric field with a solute concentration difference across a 3 nm monolayer molybdenum disulfide nanopore and detected the diffusion current variation during the diffusiophoretic translocation events of 20-mer ssDNA molecules. In this diffusion current system, Joule heat generated from the conductive ionic flux and transport-induced-charge effects due to the nanopore ion concentration polarization were simultaneously avoided. As a result, we successfully obtained four levels of current signals which are considered as the evidence of four types of nucleotides on the DNA molecules. These promising results revive opportunities for direct DNA sequencing using solid-state nanopores.

2:45 PM BREAK

3:15 PM *FF02.09.04
Light-Enhanced Blue Energy Generation Using MoS2 Nanopores Aleksandra Radenovic; Ecole Polytechnique Federale Lausanne, Switzerland

Back in 2016 [1] we reported the first measurement of osmotic power across 2D membranes, and they were an important demonstration that nanomaterials may indeed represent a revolution in this domain, with direct application envisioned for renewable energy and small portable sources of energy. Power densities achieved in MoS2 nanopore outperformed the “conventional” thicker solid-state pores by orders of magnitude and make the whole concept of using 2D-pores extremely attractive. To reach the full potential, the osmotic power generator had to operate in an alkaline environment (pH 11), pH levels that are far from the values found in estuaries. High pH was required to increase the surface charge of the MoS2. Early on, we understood the importance of the surface charge in the power generation of 2D membranes and we explored ways how to improve the performance of osmotic power generation. In this work, we demonstrate that the osmotic power can be increased five-fold using light. To enhance and modulate surface charges we have used low power densities of light (~1-3 W/m2), that should be attainable in real-world applications where the sun can act as the photon source. To exploit MoS2 photoexcitability, we selected laser sources operating at 475nm and 643nm, with photon energies above the bandgap of single-layer MoS2. Also, we investigate the role of the pore sizes and surface charges on the osmotic power generation. By introducing a
formalism based on the Dukhin number \cite{2}, we can decipher the contributions to the osmotic power from the pore and surface conductions. At the high surface charge densities, the osmotic potential in small pores is reduced, since the dominant contribution originates from the surface condition. The main message of our work concentrates on the elegant way how the two most abundant energy sources can be efficiently married in the same device paving a way for next generation of tandem blue energy/solar devices based on 2D materials.


3:45 PM FF02.09.05
Scaled-Up Fabrication of MoS2 Freestanding Membranes for Nanopore-Based Biomolecule Detection
Mohammad Amin Alibakhshi, Anthony Vargas, Zhuoyu Zhang and Meni Wanunu
1; 1Northeastern University, United States; 2Nankai University, China

Two-dimensional (2D) Materials such as graphene,\cite{1-4} molybdenum disulfide (MoS2),\cite{5-7} and tungsten disulfide (WS2)\cite{8} have gained attention as alternatives to the protein nanopores for DNA sequencing applications, and as promising candidates for harvesting osmotic gradients for blue energy.\cite{9} From a device standpoint, such measurements are not viable unless a reliable scaled-up fabrication method of the 2D freestanding membranes is available.\cite{10} In addition, reducing the low frequency noise of these devices is critical for sensitive measurements of biomolecules.\cite{6} Among the 2D materials, MoS2 has gained special attention due to its less hydrophobic nature as compared with graphene. Moreover, we have previously shown that unlike graphene, MoS2 membranes can directly grow on apertures using chemical vapor deposition (CVD) method, which eliminates the time-intensive membrane transfer process.\cite{6} Here, we take advantage of this technique and demonstrate scaled-up fabrication of high quality MoS2 membranes on apertures. The apertures with diameters in the range of 50 nm to 200 nm were fabricated in silicon nitride membranes in 4-inch wafers using electron beam lithography. By fine-tuning the growth conditions we have been able to grow freestanding MoS2 membranes on apertures in 4-inch wafers with over 60% yield, which enables fabrication of hundreds of devices in a single CVD run. Understanding the temperature profile in such a large diameter CVD tube is essential in successful growth of the MoS2 crystals. Our computational fluid dynamics simulation points to strong temperature gradients and density-driven flows that develop in the tube, which constrain the conditions under which growth occurs on the target wafer. By addressing this problem we have been able to reliably reproduce high-quality growth over large areas. We used a transmission electron microscope to drill nanopores in the freestanding membranes for conductance and noise measurements. The rms noise of the ionic current at 100 mV applied bias and 1MHz bandwidth was recorded to be typically less than 250 pA. Further, as the voltage increases the noise further increases, with large contributions from low-frequency components. Our wafer scale direct 2D materials growth method, combined with automated nanopore fabrication, for example, by feedback-controlled dielectric breakdown,\cite{11} can address the device fabrication requirements for performing challenging single-molecule sensing of biomolecules.

References
Ionic transport in atomic-layer materials has demonstrated stimulating phenomena rising from its molecular interaction caused by spatial confinement parallel to that observed in biological proteins. Exploration of steric hinderance in ionic salt molecules is made possible thanks to the various device fabrication capabilities with 2D materials. In our study, we fabricate an array of nanoporous defects in TMDs ranging from single-atom to few-nm defects using ion irradiation and investigate the ionic-transport behavior of these devices. In addition, we create individual single-atom defects using advanced aberration-corrected scanning transmission electron microscopy (AC-STEM) to understand wetting behavior and therefore surface-charge density of the individual single-atom defects in monolayer TMDs. In this talk, I will cover the device fabrication of single-atom to few-nm defects and the governing effects of non-linearity observed in ionic current-voltage relationship through these defects.

Hybrid Nanopore—Integration of MoS$_2$ and OmpG for Single Nucleotide Sensing at Picomolar Concentration

Payel Sen, Hiofan Hoi and Manisha Gupta; University of Alberta, Canada

Solid-state nanopores have been used as small molecule sensors due to its steady pore current [1]. Analytes can be detected by their translocation-based ionic blockade current through the nanopore. Biological pores have structural precision and high sensitivity to chemical and electronic modifications, but lack the necessary structural strength for good repeatability and stability of sensing which can be provided by the solid-state nanopores [1]. The drawbacks for both systems can be overcome by integrating the biological pore with the solid state pore to create a hybrid nanopore [2]. This can be achieved by insertion of a biological pore into a solid state nanopore. In this research, we have used both Silicon nitride, SiN$_x$ and Molybdenum disulphide, MoS$_2$ (2D material) as membranes for solid state pores. MoS$_2$ thickness can be controlled to monolayer and hence the pore thickness can be controlled very precisely. This lower thickness translates to a higher resolution for molecular sensing. Here, we have used OmpG, a barrel protein having an outer diameter of 3.3 nm and inner diameter of 2 nm, for the biological pore. Single OmpG pore is pulled through by applying a bias to the solid state nanopore and it is prevented from going through the pore by choosing a correct size (3.5-4 nm diameter) solid state pore, fabricated of either SiN$_x$ (50 nm thick) or MoS$_2$ (Monolayer: 0.65 nm thick) pores to form hybrid pores. One of the major advantages of OmpG nanopore is its capability of insertion in solid state pore without a guiding DNA. Additionally, the flexibility of its external loops can be fine-tuned, thus offering a good control over detection specificity. 40 pM solution of single stranded DNA oligos (each having 30 mixed nucleotides) were pulled through 2.5 nm solid state SiN$_x$ and MoS$_2$ pores and 4 nm (outer diameter) hybrid SiN$_x$ and MoS$_2$ pores, and their translocation statistics was compared. Both solid state and hybrid nanopores created using SiN$_x$ and MoS$_2$ along with OmpG were used for studying DNA translocation. In case of solid state nanopores, MoS$_2$ has the advantage of retarding nucleotide translocation by 26-fold as compared to SiN$_x$. This improves the signal to noise ratio (SNR) to 11.2 for MoS$_2$ as compared to 1.86 for SiN$_x$. MoS$_2$ also demonstrates a 12-32% of deviation around the average translocation current value for a particular nucleotide, hampering precise identification of individual species, especially those having low density. An improvement in current deviation to 2-5% is observed using the hybrid nanopores. Monolayer MoS$_2$ demonstrated a 2-8 fold reduction in deviation compared to solid state monolayer MoS$_2$, while preserving an SNR greater than 10. Hybrid monolayer MoS$_2$/OmpG pore therefore is seen to sense individual DNA nucleotides from its picomolar concentration solution with 3-7 times improved resolution than SiN$_x$ nanopore systems and greater than twice the specificity shown by solid state monolayer MoS$_2$ nanopores. Current blockade values, signal-to-noise ratio, standard deviation of current and detected single nucleotide count will be reported for solid state and hybrid SiN$_x$ and MoS$_2$ pores.

References
Dielectric breakdown (DBD) of solid-state membranes in solution has been proved to be a powerful method for fabricating nanopore, attracting plenty of research interests in solid-state nanopore sensing. Sub-2nm nanopores that are hard to process by FIB, TEM and laser can be fabricated with very high reliability and reproducibility by the DBD method, which enable the detection of the sizes and structures of small molecules. However, the position of fabricated nanopore via DBD method was stochastic.

Here in, we report a fascinating method called tip-controlled breakdown (TCBD) for fabricating single or multiple nanopores by combining atomic force microscopy (AFM) and DBD approach. During the fabrication process, a conductive AFM tip is firstly brought into contact with a graphene membrane positioned above an electrolyte reservoir filled with potassium chloride solution. Then, a voltage pulse is generated from AFM built-in voltage module to produce a local electrical field at the end of the AFM tip. Nanopores would form precisely beneath the tip due to the local electrical field effect with a complete suppression of multiple pore formation compared with DBD approaches. The diameter of nanopores was under control of voltage pulse frequency and amplitude. The experiments show that sub-2nm nanopore was fabricated with the voltage no more than 5V. Potassium chloride concentration, voltage pulse frequency and amplitude have been investigate to optimize the TCBD method. Our results demonstrate that the approach greatly accelerates the electric breakdown process, leading to an average pore fabrication time on the order of tens of milliseconds, at least two orders of magnitude shorter than achieved by classic DBD approaches. With this fast pore writing speed, over 100 pores can be fabricated within half an hour on the same membrane. Stable ionic-current blockades were observed when DNA passed through the nanopores created on the graphene membranes by TCBD approach.

Finally, combining the nano position advantages of AFM and the simplicity/low-cost of the DBD approach, the TCBD has been demonstrated to be a highly efficient, reliable and reproducible nanopore fabrication method. We anticipate TCBD has the potential to become a nanopore fabrication technique which, integrated into an optical/magnetic setup, could be used as a high-throughput and multichannel characterization technique.
graphene as wall coating. To this end, Molecular Dynamics (MD) simulations are conducted to study water flow through uncoated and coated polyamide nanoslit pores with different heights. We perform a characterization of the interfacial properties and evaluate the impact that the polymeric matrix has on water structure. The force fields employed to model the species are validated measuring the water contact angle and comparing values against experimental results. Using Non Equilibrium MD Simulations (NEMD), Poiseuille-like flow is studied. The flow is achieved by imposing body forces corresponding to values of 2.93, 5.87, 11.75 bar/nm. Viscous heating is transmitted to and conducted through the walls as in a real system. From the MD trajectories, we compute shear stress, density, temperature and velocity profiles across the channel. Using these observables, we analyze the correlation between local water structure, flow enhancement and slip length. The velocity profiles in the coated polymeric pore exhibit a parabolic shape with substantial wall slippage. Hence, our results indicate that water interactions with the underlying polyamide have a significant influence on the water flow rates in the pores. We compute flow enhancements ranging from 62 to 116 for the cases with coated pores. Equilibrium MD simulations (EMD) are performed to calculate the fluid-solid interfacial friction by using the Green-Kubo relation. The values of the friction coefficients calculated are 594 and 14.3 (kN s)/m² for uncoated and coated nanoslits. We find that the flow enhancements computed from NEMD are in line with the friction coefficients computed from EMD. Our results show that graphene coatings can enable drag reduction in polymeric nanopores. The insights reported in this study may serve as a guide in designing strategies to achieve low friction transport of water solutions in nanostructured pores. These strategies will allow the development of more efficient LOC platforms and membranes for molecular sieving and nanofiltration.

8:30 AM *FF02.10.02
Understanding the Free Space and Mass Transport in 2D Nanochannels Baoxia Mi, Sunxiang Zheng and Zhongying Wang; University of California, Berkeley, United States

Ultrathin membranes formed by stacking two-dimensional (2D) nanosheets, including graphene oxide (GO) and MoS₂ hold unique separation capabilities that enable their applications in the filtration of aqueous solutions as well as organic solvents. However, the separation capability of a layer-stacked membrane can be significantly affected by its natural tendency to swell in solutions by absorbing molecules into 2D nanochannels and forming an enlarged interlayer spacing (d-spacing). In this study, the d-spacing of a layer-stacked GO and MoS₂ membranes was experimentally quantified when the membranes were soaked in aqueous or organic solutions. We found that solvents with high dipole moments tends to cause significant swelling of GO, while non-polar solvents such as hexane and toluene only cause subtle swelling. To understand such unique swelling behavior, the solubility parameter of GO was experimentally determined to mathematically describe the affinity between GO and the testing solvents. Separation performance of the GO membrane in different organic solvents were tested to understand the mass transport in confined GO nanochannel. The layer-stacked GO membrane could achieve > 90% rejection of small organic dye molecules (e.g., rhodamine B and methylene blue) in ethanol and acetone without crosslinking due to insignificant swelling. Additionally, it was found that solvents with different polarity demonstrate very different transport resistance.

9:00 AM *FF02.10.03
Multilayered Graphene Membranes—New opportunities for Nanoionics Dan Li and Zhe (Jefferson) Liu; University of Melbourne, Australia

We have previously developed a soft chemistry approach to fabricate multilayered graphene membranes (MGMs) with their interlayer distance tuneable from 10 nm down to sub-nanometers [1]. In this talk, I will demonstrate how MGMs can provide a unique platform for nanofluidics, and particularly nanoionics research. My talk will include: (1) How experiments and simulations can be combined to quantify the nanostructure of the MGMs for nanoionics research [2]; (2) How supercapacitor and membrane experiments can be coupled to modulate ion diffusion through nano-confined electrical double layer; (3) How MGMs can serve as a model electrode to enable quantitative understanding of the ion transport in nanoporous for predictive design of capacitive energy storage devices.

References:

9:30 AM FF02.10.04
Realigning Nanochannels in Conventional Graphene Oxide Films to Achieve Enhanced Permeability and Controlled Release
Muchun Liu and Robert H. Hurt; Brown University, United States

There is great interest in exploiting van der Waals gaps in layered materials as continuous nanofluidic channels. Multilayer graphene oxide (GO) films with selective transport properties have been used for water desalination, oil-water separation, gas separation and pervaporation applications. Conventional GO membranes are often limited in practice by low permeability since the intersheet nanochannels align perpendicular to the desired overall transport direction, leading to highly circuitous fluid pathways that are orders of magnitude greater than the membrane thickness.

Here we demonstrate a novel approach to fabricate stable GO membranes with vertically aligned nanosheets spanning the membrane in the Z-direction. Compressive texturing of planar GO films tilts the nanosheets and nanochannels to near vertical directions, which are then stabilized imbedded in low-permeability polymer matrices and thin sectioned. The resulting membranes provide direct access to the entrances of intersheet nanochannels at both the top and bottom surfaces to create well-defined Z-directional fluid pathways whose length is on the same order as the micron-scale membrane thickness.

The compressive wrinkling and crumpling of graphene oxide films can also be used to control the release rates of molecular intercalants pre-loaded into GO gallery spaces. Experimental studies on rhodamine B dye, used as a model, show diffusive release rates in the rank order: planar > 1D wrinkled > 2D crumpled films. This type of fluidic-space manipulation should allow the intelligent design of 2D-material-based technologies such as time-release drug eluting coatings.

9:45 AM FF02.10.05
Potential Dependant Ionic Sieving through Functionalized Laminar MoS2 Membranes
Wisit Hirunpinyopas, Eric Prestat, Mark A. Bissett and Robert Dryfe; The University of Manchester, United Kingdom

Laminar MoS2 membranes show outstanding potential for practical applications in energy conversion/storage, sensing, and as nano-fluidic devices. The re-stacking of exfoliated MoS2 creates nanocapillaries between the layers of MoS2 nanosheets. These MoS2 membranes have been shown to possess a unique combination of ionic rejection properties, high water permeation rates, and long-term solvent stability, with no significant swelling when exposed to aqueous or organic solvents. Chemical modification of MoS2 membranes has been shown to improve their ionic rejection properties, however the mechanism behind this improvement is not well understood. In this work, we elucidate the ion-sieving mechanism by the study of potential-dependent ion transport through functionalized MoS2 membranes. The ionic permeability of the MoS2 membrane is transformed by chemical functionalization with a simple naphthalene sulfonate dye (sunset yellow) and with a resultant attenuation of permeability by at least an order of magnitude, compared to the pristine MoS2 membranes and permeability reported for graphene oxide and Ti3C2Tx (MXene) membranes. The effects of pH, solute concentration, and ionic size/charge on the ionic selectivity of the functionalized MoS2 membranes are also reported. Understanding the mechanism of ionic sieving within functionalized MoS2 membranes will enable future applications in electro-dialysis and ion exchange for water treatment technologies.

10:00 AM BREAK

10:30 AM *FF02.10.06
Nanoconfined Ionic Liquid in Nanoslites for Selectively Gas Separation
Xinsheng Peng; Zhejiang University, China

Separating CO2 from other light gases is believed to have extremely practical significance and economic benefits due to the strong demand from the industrial processes and the green-house effect. Conventional adsorption and low temperature distillation have their intrinsic drawbacks while membrane separation shows great potential. However, the trade-off between the high selectivity and permanence is still a great challenge. In this report, we prepared a high-performance CO2-phlic membrane, two-dimensional nanosheets supported ionic liquid membrane, by confining [BMIM][BF4] into the nanochannels of laminated graphene oxide membrane. The strong interaction
between graphene oxide and [BMIM][BF₄] stratifies the cation and anion of [BMIM][BF₄], and the layered anion facilitates CO₂ transportation. The resulted membrane has an excellent performance with CO₂ high permeance and good selectivity of CO₂/H₂, CO₂/CH₄, and CO₂/N₂ respectively. Moreover, it has high temperature resistance, long-term durability and high-pressure stability, which shows great potential in CO₂ separation. In addition, we found that external electric field could further facilitate selectively CO₂ transportation through nanoconfined ionic liquid.

11:00 AM *FF02.10.07
Mass Transport Enhancement in Modified Graphene Oxide Membranes  
Jae Eun Shin, Ji Soo Roh, Farhad Moghadam, Been Namkoong and Ho Bum Park; Hanyang University, Korea (the Republic of)

Graphene oxide (GO) has a heterogeneous nanostructure consisting of sp²-graphitic regions and sp³-oxidized regions. In general, the sp² domains of GO have hydrophobic nature, whereas sp³ domains represent hydrophilic nature. Oxygen moieties in GO act as a spacer to enlarge the interlayer distance between individual GO sheets within GO membrane. In general, the amount of oxygen moieties in GO sheets reaches above 80%, which acts as a hindrance for even small gas molecules, eventually leading to low gas permeability. To enhance the gas permeability in GO membranes, the sp² domains in GO sheets were precisely adjusted in this study. Commonly, sp²/sp³ ratio can be tuned by reducing GO using chemical, thermal, and electrochemical methods. However, these methods lead to much disadvantages of remaining chemical additives, structural deformation, difficulty in mass production. Above all, the sp²/sp³ ratio would not be precisely controlled using conventional reduction methods. Although the mild reduction methods have been reported to overcome these problems, there have been no systematic membrane studies using GO sheets with different sp²/sp³ ratio. Here we report a mild hydrothermal treatment to precisely control the graphitic regions in GO and also tune its electrical and molecular transport properties. The change in hydrothermal conditions, such as thermal temperature and time, significantly affects the gas separation performance as well as water and salt transport of the modified GO membranes. The high-resolution TEM images of hydrothermal treated GO membranes showed that this mild hydrothermal treatment leads to the gradual increase of sp²-graphitic regions and minimize the formation of structural defects during the reduction. Besides, the change in electrical conductivity as a function of sp² domain was correlated with gas permeability as well as water transport through the modified GO membranes, and also was elucidated using percolation theory. Then, we prepared the membrane using hydrothermal treated GOs to measure the gas permeability and selectivity, water permeability, and salt permeability and salt rejection. This work demonstrates the separation performance enhancement of GO membranes by redesigning the structure of GO and reveal the transport mechanisms through each domain in the modified GO membranes.

11:30 AM FF02.10.08
Nanoparticle Diffusion in Confined Liquid Observed by Graphene Liquid Cell Transmission Electron Microscopy  
Sungsu Kang¹², Minyoung Lee¹ and Jungwon Park¹²; ¹Seoul National University, Korea (the Republic of); ²Institute for Basic Science, Korea (the Republic of)

Nanoparticles are generally stabilized by ligands whose dimension is comparable to that of nanoparticle core. The surface ligands endow nanoparticles with unique physical and chemical properties which can modify collision dynamics and diffusive motion of nanoparticle when suspended in a confined medium. Here, we directly tracked trajectories of Au nanoparticles smaller than 5 nm in solution by graphene liquid cell transmission electron microscopy, and found that different modes of diffusion exist in the medium. Dynamics of the nanoparticles in graphene liquid cells display Brownian motion with stark deviation from the Stokes-Einstein equation. Detailed analyses of nanoparticle displacements exhibit that their distribution does not follow a Gaussian distribution, implying the existence of structural heterogeneity in liquid confined by graphene sheets. We also reveal that expansion of nanobubbles induces the superdiffusive motion of the nanoparticles at the bubble interface.

11:45 AM FF02.10.09
Fabrication of Sub-Nanometer Pores on Graphene Membrane for Ion Selective Transport  
Han Qi; Southeast University, China

The ability to sieve ions through nanopores with high throughput addresses significant importance in seawater desalination and other separation applications. In this work, it is demonstrated that plasma etching process provides an efficient method to produce high density nanopores on graphene membranes with tunable size in sub-nanometer.
Besides the pore size, nanopore density is also controllable through adjusting the exposure time of the sample to the argon or oxygen plasma. The plasma treated graphene membranes can selectively transport protons, Na\(^+\) and Cl\(^-\) ions. Density function theory calculations uncover that sp\(^3\) and vacancy-type defects construct different energy barriers for different ions, which allow the defected graphene membrane to selectively transport ions. Our study indicates that oxygen plasma etching can be used as a very convenient and efficient method for fabricating monolayer filtration graphene membrane with tunable sub-nanometer pores.

**SYMPOSIUM FF03**

**TUTORIAL: Aggregation-Induced Emission**  
December 1 - December 1, 2019

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* Invited Paper

**TUTORIAL**  
Aggregation-Induced Emission

Sunday Morning, December 1, 2019  
Hynes, Level 2, Room 206

Aggregation-induced emission (AIE) is an influential concept proposed in 2001 for describing a photophysical phenomenon, in which non-emissive molecules in solutions are induced to emit strongly when their intramolecular motion is restricted in aggregate or solid state. The conceptualization of AIE not only breaks the common belief of aggregation-caused quenching, but also provides new mechanistic insights on light emitting process of luminogenic aggregates and illuminates the path to the exploration of practically useful luminescent materials for optical, electronic, energy and biomedical applications, such as organic LEDs, solar cells, sensing, imaging and image-guided cancer therapy, etc. The AIE effect can be utilized in all applications involving aggregates.

The tutorial aims to bring the attendees updated information on the fundamental AIE research and the state-of-the-art applications of AIE luminogens. It is also designed for the experienced AIE researchers to reinforce their knowledge on the scopes of development of new generation of AIE materials, understanding of AIE mechanisms and exploration of advanced technological applications. Eight top experts from seven counties will deliver lectures and consulting sections, providing a unique platform for the attendees to learn from the professionals and foster dynamic and scientific exchange via exciting cross-disciplinary discussions. The tutorials will be conducted using interesting illustrations and simple languages, which will greatly benefit junior researchers and graduate students.

**8:30 AM**  
**AIE Research—Past, Present and Future** Ben Zhong Tang, The Hong Kong University of Science and Technology

**9:15 AM**  
**Design of Stimuli-Responsive Luminochromic Materials Based on Heteroatom-Containing AIE-Active Dyes**  
Kazuo Tanaka, Kyoto University

**10:00 AM BREAK**
10:30 AM  
Aggregation-Induced emission—Shining a Light into Polymers Andrea Pucci, University of Pisa

1:30 PM  
Aromatic Hydrocarbons as Steric Environment-Sensitive Fluorophores Gen-ichi Konishi, Tokyo Institute of Technology

2:15 PM  
Theoretical Revelation and Experimental Confirmation of the Mechanism of Aggregation-Induced Emission in Organic Materials Qian Peng, Institute of Chemistry, Chinese Academy of Sciences

3:00 PM BREAK

3:30 PM  

4:15 PM  
Promising Optoelectronic Applications of AIEgens Zujin Zhao, South China University of Technology

**SYMPOSIUM FF03**

Building Advanced Materials via Particle-Based Crystallization and Self-Assembly of Molecules with Aggregation-Induced Emission  
December 2 - December 6, 2019

**Symposium Organizers**  
Kristen Fichthorn, The Pennsylvania State University  
Bin Liu, National University of Singapore  
Ben Zhong Tang, Hong Kong University of Science and Technology  
Xin Zhang, Pacific Northwest National Laboratory

**Symposium Support**  
**Silver**  
Pacific Northwest National Laboratory

**Bronze**  
Bruker  
Oxford Instruments Asylum Research Inc.

* Invited Paper

SESSION FF03.01: Particle Aggregation I  
Session Chairs: Kristen Fichthorn and Xin Zhang  
Monday Morning, December 2, 2019  
Hynes, Level 3, Room 313

8:00 AM FF03.01.01  
Two-Dimensional Mesoporous Superlattices of Silica Cages Tangi Aubert$^{1,2}$, Kai Ma$^1$, Kwan W. Tan$^{1,3}$ and
Mesoporous silica based materials and their derivatives in the bulk, as films, and as nanoparticles have attracted a lot of attention for their application potential across different areas, e.g. in catalysis, energy, and nanomedicine. Extensive research efforts have resulted in the continuous discovery of new structures, from quasicrystalline to hierarchical structures. Among these materials, cage-type silica mesoporous materials are of particular interest for their facile pore accessibility and versatile functionalization opportunities. The formation of these advanced materials derives from the self-assembly of silica nanocages as the building blocks, following a cage-based crystallization mechanism. However, fundamental understanding of how order emerges on the way from a single cage to a 3D bulk material remains limited.

We recently developed a series of low-dimensional silica structures, with in particular the discovery of isolated pentagonal dodecahedral silica cages formed around single surfactant micelles [1,2]. Dodecahedral cages constitute the elementary building blocks in a large variety of naturally occurring and synthetic materials, including DNA and RNA cages, clathrates as well as mesoporous silica. These motifs are thus found across a wide range of length scales, in organic as well as inorganic materials. We therefore saw in this discovery an opportunity to investigate the early stages of the growth mechanisms at play in micelle directed self-assembly processes that lead to the formation of cage-type mesoporous silica with well-defined crystallographic structures.

Following a similar strategy as for the formation of nanocrystals superlattices, we assembled silica cages at an interface between two immiscible solvents. By carefully varying the synthesis conditions, we could assemble 2D superlattices with high control over the morphology, going from monolayers to multilayers of cages. While in a monolayer with honeycomb structure the silica cages do not show any orientational order relative to each other, this orientational correlation increases with increasing layer number leading to complex clathrate type structures in silica cage multilayers. Expanding the superlattices beyond 3-4 layers of cages further evidenced a relaxation of the 2D confinement, driving the assembly towards more favorable bulk structures. Thus, with this approach we can observe the emergence of the crystallographic registry as a result of the concerted self-assembly of surfactant micelles directing the silica 3D network.

Since these 2D superlattices can be coherently fabricated over macroscopic film dimensions, the resulting membranes may be of interest for a number of applications. By adopting concepts from 2D electronic materials, tuning the structure, composition and angle between heterostacks of silica cage superlattices is now paving the road for the design of advanced functional and hierarchical superstructures, with potential separation or catalytic properties not accessible via conventional bulk material syntheses.

References:

Facet-Controlled Synthesis and Aggregation of Hematite Nanoparticles Yining Wang1,2, Xin Zhang1, Meizong Zong1, Zhening Wang1, Junwu Zhu2 and Kevin Rosso1; 1Pacific Northwest National Laboratory, United States; 2Nanjing University of Science and Technology, China

Hematite with its high earth-abundance and low biotoxicity is considered to be one of the most promising candidates as a catalytic substrate in various new energy devices. In particular, controlling hematite morphology to expose certain high-energy facets appears to be a promising route to performance improvements. In this study, we describe additive-free synthesis protocols that yield diverse uniform nanoparticle morphologies by controlling the concentration of iron ions and hydrothermal temperatures. Increasing the concentration of iron ions and decreasing the hydrothermal temperature was found to systematically inhibit growth along the c-axis and facilitate growth along the b-axis, leading to the formation of bipyramids with \{111\} facets. Hematite nanostrings were achieved by the assembly of nanocubes with \{104\} facets and a secondary growth process. Growth by nanoparticle aggregation was investigated in detail sing powder X-ray diffraction (pXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and atomic force microscopy (AFM). These findings may pave the way to production of chemically pure and morphologically well-defined hematite nanoparticles, and to economically advance their practical application in energy devices.
8:30 AM *FF03.01.03
Water Adsorption Induced Organization of MgO Nanocubes into 1D and 2D Structures Oliver Diwald1, Gilles R. Bourret1, Daniel Thomele1, Michel Bockstedte1 and Johannes Bernardi2; 1University of Salzburg, Austria; 2TU Wien, Austria

Water adsorption and thin water film formation on unsupported metal oxide nanoparticles can lead to structural and microstructural transformations that arise from different processes like water-assisted self-assembly of particles or dissolution/ recrystallization processes. This presentation deals with examples where structure-property relationships have been established for MgO nanocubes and their transformation behavior in different water containing environments. We will show that water vapor can induce the self-organization of the nanocubes into regularly staggered one-dimensional structures.[1] The transformation evolves via an initial alignment of the MgO cubes, the formation of intermediate elongated Mg(OH)2 structures, and their annealing induced reconversion into 1-D structures. In the presence of water vapor the particles spontaneously orient themselves to form staggered MgO nanocube assemblies, where the cubes are offset from each other. Ab initio Density Functional Theory (DFT) modelling identifies surface energy changes associated with the cube surface hydration and hydroxylation to promote the uncommon particle assembly.[2] It will be shown how simple process steps like water adsorption via the gas phase or dissolution-recrystallization processes in condensed water can be utilized as valuable routes to generate anisotropic mesostructures. The here presented transformation mechanisms occurring inside and outside an aqueous bulk solution may pave novel routes for inducing texture in ceramics. Moreover, they point to a great test bed for new surface science concepts where the emergence of associated local structures can accommodate important new functionalities which are beneficial for catalytic activity and microstructure evolution.


9:00 AM *FF03.01.04
Unraveling Phase Transformation Pathways of Ferric Oxyhydroxide Nanocrystals in Aqueous Solution Kevin Rosso; Pacific Northwest National Laboratory, United States

Fe(III)-(oxyhydr)oxide nanocrystals are an emerging basis for cost-effective catalytic substrates, as well as a dominant class of reactive minerals in soils and sediments. In both contexts, developing a molecular-level understanding of crystallization processes that control particle phase, size, and morphology is critical. However, in aqueous solutions near ambient conditions this remains complicated by the challenge of following rapid initial precipitation, yielding the poorly crystalline metastable phase ferrihydrite (Fh), and then the slower mass transfer pathways transforming it into more stable nanocrystals such as lepidocrocite (Lp), goethite (Gt), and hematite (Hm). The slowness of the latter is linked to both the low aqueous solubility of Fe(III), which restricts the dissolution/reprecipitation pathway, and the low solid-state diffusivity of lattice iron, which restricts the topotactic pathway. Particle-based assembly has been proposed in some cases, but alone this cannot accomplish transformation without also recruiting one or both of these two slow pathways. Importantly, addition of only micromolar concentrations of Fe(II) accelerates the Fh phase transformation by several orders of magnitude.

Here we overview new observations that help unveil principles governing pathway selection and rate, and the catalytic effect of Fe(II). We report a comprehensive experimental/computational study of Fh transformation into Lp/Gt nanocrystals at circumneutral pH, with and without aqueous Fe(II), resolved at the iron site occupancy level. In the absence of added Fe(II), Fh aged over two years was periodically characterized using in situ mXRD with detailed line shape analysis, electron microscopy, and synchrotron Fe L-edge and O K-edge XAS/XMCD spectroscopy quantitatively analyzed using MRCI ab initio calculations. The results are compared to DFT calculations of relative phase stabilities and activation energies for solid-state diffusion of iron along topotactic channels. Tetrahedral Fe(III) is clearly resolved minor component of freshly precipitated Fh, diminishing concomitantly with increasing octahedral Fe(III) and decreasing net magnetic moment until the first appearance of Lp and Gt nanocrystals at ~100 d. Calculated iron diffusion activation energies although as low as 1 eV per unit cell are still too high to support topotactic transformation. Microscopic characterization is well aligned with dissolution/reprecipitation; no compelling evidence for particle-mediated transformation was found. In the presence of Fe(II), an observed ~1000x rate acceleration appears to arise from facile interfacial electron and iron atom exchange that effectively increases the activity of labile Fe(III) at Fh surfaces, resulting in rapid nucleation of Lp and Gt nanocrystal products. Both non-redox and Fe(II)-catalyzed transformation therefore can be explained on a uniform footing via dissolution/reprecipitation. The collective findings suggest the importance of transient Fe(III) species stabilized at interfaces controlling the kinetics of transformation and, in turn, nanocrystal outcomes.
Dynamically Evolving Hierarchical Structure in Clays
Michael Whittaker¹,², Benjamin Gilbert¹ and Jillian Banfield²; ¹Lawrence Berkeley National Laboratory, United States; ²University of California, Berkeley, United States

Clay minerals like montmorillonite (MMT), composed of highly anisotropic layers less than one nanometer thick and up to microns wide, are the most abundant inorganic nanomaterials on earth. Particles comprise negatively charged MMT layers separated by discrete molecular layers of water and solvated cations, creating a porous matrix that controls the fate of water, carbon dioxide, nutrients, and pollutants in myriad natural settings. Here, we show evidence of highly dynamic and coupled interactions between clay layers that are accessible through thermal fluctuations, which lead to unexpected particle arrangements and pore structures that are not predicted by current theories.

Stacks of layers exhibit aspects of plastic crystallinity in which the barriers to rotation of an individual layer are on the order of 0-5 kT per unit cell. This results in size-dependent short-range order between neighboring layers whose persistence length depends on the hydration energy of the interlayer cation and its concentration in solution. In the presence of mixed electrolytes, particles phase-separate into compositionally distinct particles with different hydration states. A free energy difference of approximately 4 kT per unit cell allows two populations to reach metastable equilibrium through the exchange of both cations and MMT layers. These dynamically rearranging particles exhibit a panoply of topological defects that contribute to the hierarchical structuring of particle aggregates. Non-ergodic evolution of the system dynamics over time produces new structures that continuously emerge over timescales spanning many orders of magnitude. This new perspective on the dynamic structure of MMT reveals potentially general aspects of colloidal interactions in layered materials, and will help improve predictions of ion exchange and fluid transport and retention in many natural systems.

SESSION FF03.02: Aggregation-Induced Emission I
Session Chairs: Ben Zhong Tang, Wenjing Tian and Xin Zhang
Monday Morning, December 2, 2019
Hynes, Level 3, Room 313

AIEgen-Based Bioprobes for Biomedical Applications
Dan Ding; Nankai University, China

We report a quantum dot-sized organic dot with aggregation-induced emission (AIE) characteristics as a promising cell tracker for noninvasive long-term tracking of adipose-derived stem cells (ADSCs) in living mice. We demonstrate that the AIE dots possess high fluorescence, strong photobleaching resistance, low in vivo toxicity, excellent retention in living ADSCs and negligible interference on the ADSC pluripotency and secretome. The AIE dots also exhibit far superior in vitro cell tracking capability as compared to the widely used commercial cell trackers of PKH26 and Qtracker 655. The in vivo studies using an ischemic hind limb-bearing mouse model reveal that the AIE dots can precisely and quantitatively report the fate of ADSCs and their therapeutic effect in vivo for 6 weeks. Moreover, we have also synthesized a far-red/near-infrared fluorescent AIEgen-based nanodot, which can efficiently generate reactive oxygen species (ROS) under light irradiation. It is found that the AIEgen-based nanodots are able to visualize tumor tissues and assess tumor margins during surgery in a tumor-bearing mouse model. More importantly, upon tumor removal followed by irradiation of the incision site with light, the AIE nanodots in the residual tumors will generate ROS, which has been demonstrated to successfully suppress the residual tumors and reduce the risk of tumor recurrence after debulking surgery.
Designing Fluorescent 2D Nanocrystals through Self-Assembly of Sequence-Defined Peptoids Chun-Long Chen; Pacific Northwest National Laboratory, United States

Two-dimensional (2D) materials have attracted intense interest due to their unique structures and novel properties for applications in molecular separation, sensing, catalysis, and biomedicine. Despite the unique advantage of the 2D nanostructure in development of functional optical crystals, 2D nanomaterials, such as graphene, graphene oxide and transition metal dichalcogenides, have limited intrinsic optical properties and surface chemistries that restrict them as efficient optical crystals for applications. For example, none them have been directly used as probes for single particle tracking within biological systems.

We recently developed a new class of highly stable and self-repairing 2D nanomembranes (2DNMs)\(^1\) from sequence-defined peptoids—a type of protein-mimetic that was invented to mimic the recognition capability of proteins and peptides. These free-standing 2DNMs are highly stable and exhibit a number of properties associated with cell membranes, including thicknesses in the 3.5 - 5.6 nm range, spontaneous assembly at interfaces, and the ability to self-repair. We further demonstrated that a broad range of functional groups can be incorporated and patterned within 2DNMs through large side-chain diversity and/or co-crystallization approaches. In this presentation, I will present our recent progress in the design and synthesis of fluorescent 2D nanocrystals by self-assembly of sheet-forming peptoids conjugated dye molecules. We demonstrated a fine tuning of optical properties of these 2D nanocrystals by varying the dye density and chemistry. The high crystallinity of these 2DNMs enabled a long-range ordering of dye molecules within 2D crystals to achieve unique optical properties, such as high photostability and quantum yield, for applications in biological imaging and molecular sensing.

References

11:15 AM *FF03.02.03
Modular Design of Peptide-AIEgens or DNA-AIEgens Bioprobes for Biosensing Applications Fan Xia and Zaiyu Wang; China University of Geosciences, China

Fluorophores probes are widely used in fields of bioimaging in cells, tissues, or animals and monitoring multiple biological processes in the complex environments. Such sensitive imaging properties allow scientists to make a direct visualization of pathological events and cellular targets. Conventional fluorescent molecules have developed for several decades and achieved great successes, however, their emissions are often weakened or quenched at high concentration or in aggregate state that might result from aggregation-caused quenching (ACQ) effect and reduce the efficiencies of their applications.

In contrast to ACQ effect, aggregation-induced emission (AIE) molecules exhibit strong fluorescence in aggregated states and possess various advantages such as low background, high sensitivity and accuracy, long-term tracking ability, and strong resistance to photo-bleaching. Therefore, those AIE fluorophores are employed as unique fluorescence molecules and excellent modular blocks for the biosensing applications in the field of ions, amino acid, carbohydrates, DNA/RNAs, peptide/proteins, cellular organelles, cancer cells and bacteria.

11:30 AM *FF03.02.04
Self-Assembly Based on AIEgens for Image-Guided Anticancer Therapy Wenjing Tian; Jilin University, China

Aggregation-induced emission luminogens (AIEgens) have attracted concentrated attention in bioimaging due to large stokes shift, fine biocompatibility and good photobleaching resistance. Recently, AIE nanoparticles, as a brand new anti-cancer treatment, can simultaneously achieve dual functions of tumor imaging and treatment, which are promising for clinical medicine. Herein, we successfully co-assembled AIEgens with an antitumor paclitaxel to form Co-NPs for cell imaging and antineoplastic activity. Besides, self-assembly nanostructured AIE photosensitizers with red light emission and high fluorescence quantum yield were prepared for photodynamic therapy. Furthermore, in order to investigate the relationship between molecular structure and photosensitization, we designed and synthesized two types of AIE photosensitizers (PSs) with asymmetrical Donor(D)-Acceptor(A) structure and
symmetric A-D-A structure. We found that the singlet oxygen yield could get double promotion by the A-D-A molecule design. It suggested that the designed materials were promising as PSs for potential clinical applications.

Reference

SESSION FF03.03: Aggregation-Induced Emission II
Session Chairs: Ben Zhong Tang, Wenjing Tian and Xin Zhang
Monday Afternoon, December 2, 2019
Hynes, Level 3, Room 313

1:30 PM *FF03.03.01
Towards Colorful, Switchable Enamine-Based Materials Olof Ramstrom1,2; 1University of Massachusetts Lowell, United States; 2Linnaeus University, Sweden

In this presentation, ways to harness the powers of enamines will be described. Different stabilized enamines have been developed and applied to configurational switching, metal coordination, and constitutional dynamics through transamination. By controlling the dynamic features, turn-on luminescence effects could be obtained both on the molecular level and when applied to materials. The results show that controllable, enamine-based materials show potential for sensing and imaging applications.

2:00 PM *FF03.03.02
Coordinating AIEgen—Single Molecular Platform Leading to Diversified Emission Yun Yan; Peking University, China

Controlling the emission color of AIEgens is very promising in creating functional luminescent materials. This is usually achieved by modifying the chemical structure of the AIEgens, which is very complicated and are often not very efficient. We show that by attaching a coordinating moiety to the AIEgen, multiple emission can be achieved by simply changing the coordinated metal ions. The metal coordination may bring up changes to (1) the conformation of the AIEgen;(2) the energy gap between HOMO and LUMO of the coordinating AIE molecule; (3) binding affinity to different chemicals. As a result, the emission color and the function of the AIE molecule can be facilely tuned by variation of the coordinating metal ions. Compared to organic synthesis, the coordination strategy is very facile and efficient. We show that by using coordinating AIEgen, we are able to obtain tunable emission and achieve one-on-multiple recognition of important chemicals.

2:30 PM FF03.03.03
Self-Assembly, Superhydrophobic Surface Formation, Solid State Emission and Mechanofluorochromism from Phenothiazine Derivatives Sivalingam Suganya and Edamana Prasad; Indian Institute of Technology Madras, India

Design of organic molecules exhibiting emission in the aggregated state is increasingly getting attention in the field of materials chemistry. Self assembly of low-molecular-weight gelators (LMWGs) in a particular solvent environment leads to the formation of luminescent gels with 3D nanostructures. Similarly, particular way of stacking by small organic molecules leads to solid state emission. If the self-assembling organogel/small molecules bear hydrophobic alkyl chains, it could be possible to develop superhydrophobic surfaces through self-assembly. Further, self-assembling systems can exhibit mechno responsive switchable fluorescence in solid state, which has wide applications in optoelectronics, sensors, memory chips and security papers. Herein, we present the synthesis and characterization of solid state emitting phenothiazine based organogel linked with poly (alkyl ether) dendron (S1) and small molecule connected with pyridine ring (S2). The hydrophobic alkyl chain present in S1 was effectively utilized to fabricate the superhydrophobic surface with a water contact angle of 157°. Further, small molecule S2
displayed a special kind of mechanofluorochromism (MFC) from cyan blue (480 nm) to green emission (535 nm) with an unusual crystal-to-crystal phase transitions. Upon photoexcitation, $S_1$ and $S_2$ exhibited twisted intramolecular charge transfer (TICT) and aggregation induced blue shifted emission. Further, single point energy calculations using Density functional theory (DFT) authenticate the MFC behavior of $S_1$ and $S_2$. The details of the work will be presented.

2:45 PM OPEN DISCUSSION

3:00 PM BREAK

SESSION FF03.04: In Situ Characterization—AFM
Session Chairs: Kristen Fichthorn and Xin Zhang
Monday Afternoon, December 2, 2019
Hynes, Level 3, Room 313

3:30 PM *FF03.04.01
In Situ Nanoelectrical, Electrochemical and Electromechanical Characterization of the Liquid/Solid Interface with Atomic Force Microscopy
Thomas Mueller, Bede Pittenger and Peter De Wolf; Bruker Nano Surfaces, United States

While in situ atomic force microscopy (AFM) studies have traditionally focused on nanoscale topographic or mechanical characterization, additional information would greatly benefit in situ studies of biocompatible devices, complex hierarchical materials and energy materials to name a few. Here we present the development of atomic force microscopy modalities for in situ and in operando electrical, electrochemical, and electromechanical studies with nanometer resolution at the electrified solid-electrolyte interface. This work builds on the recent development of an insulated nanoelectrode probe with small active Pt apex, which enables high resolution studies, as shown in the simultaneous acquisition of local EC and conductivity information at electrified solid/liquid interfaces of nanoparticle-catalysed photocathodes for water splitting. [1, 2] The range of in situ characterization is further expanded with the new Data Cube AFM modes which provide hyperspectral data comprising voltage and surface distance spectra at every pixel of the image. In particular, Data Cube SECM mode records an approach curve at every pixel thus aiding quantitative modeling of SECM signals. Further, we will show that the variable surface dwell time enables nanocontact EC studies such as local surface EC potential measurement. [3, 4] In general, Data Cube electrical modes provide comprehensive data for ex situ and in situ studies, and the opportunity to extract new kinds of maps through physical modeling of the point spectra or algorithms such as principal component analysis.

Finally, we will present in situ studies of bio-electromechanics with piezo force microscopy (PFM). Despite great interest for biomedical applications, such studies have so far been few other than pioneering work by Kalinin et al. [6, 7] and few other groups. [8] Challenges include the need for chemical compatibility, presence of parasitic electrochemical reactions, capacitive charging from electrical double layers, and de-localized electric field in conductive liquid environments, making the use of physiological conditions impractical. We will show that the use of the nanoelectrode probe mitigates these factors enabling acquisition of PFM data in conductive liquid. [9, 10] Here the use of Data Cube PFM mode not only provides added information about the contact resonance, it also provides higher sensitivity, pushing the PFM detection limit to higher ionic strength.

[1] Nellist et al., Nanotechnology 2017, 28, 095711
4:00 PM FF03.04.02
In Situ Tracing the Evolution of Protein 2D Nanostructures at Solid-Liquid Interface Shuai Zhang1,2, Harley Pyles1, David Baker1 and James J. De Yoreo2; 1University of Washington, United States; 2Pacific Northwest National Laboratory, United States

Among biomolecular composites in nature, the macromolecular-inorganic hybrid biomaterials, like bone, enamel and nacre, have the outstanding physical and biological properties. Several artificial bio-composites with the programmed macromolecular-inorganic interfaces, which are inspired by the native ones, have been reported. However, the in-situ visualizations of the synthesizing/assembly processes, with spatial resolution in nanoscale and temporal resolution in second are still rare. That makes the entropy term and kinetic possibilities are inaccessible in many cases. Hence, the dynamic information in the design and synthesis is often ignored.

In this talk, I will present the in-situ study of the evolution of 2D protein matrices (DHR-micaN)1, on the mica surface by in-situ high-speed atomic force microscopy. By tuning the electrolyte type, protein concentration, protein size and intra-protein interactions, the protein molecules can stay as the isolated monomers, condensed liquid, and the anisotropic 2D liquid crystal with smectic order. At [KCl] above 1M, the order develops from an initial 2D liquid phase through the formation of fluctuating clusters. The mica substrate also has certain role to confine the protein nanostructures aligning along pre-defined direction. Those findings have not been previously recorded, and 2D liquid crystal with smectic order had been considered as a non-existent phase in some theoretical analyses. Numerous lines of evidence imply that, besides the programmed protein-mica and protein-protein interactions, the entropic interactions, like the release of interfacial water from the surface and the proteins, also play a critical role in the assembly process.


4:15 PM FF03.04.03
Building Two-Dimensional Materials One Row at a Time—Avoiding the Nucleation Barrier Jiajun Chen1,2, Enbo Zhu3, Juan Liu4, Shuai Zhang1,2, Hendrik Heinz4, Yu Huang3 and James J. De Yoreo1,2; 1University of Washington, United States; 2Pacific Northwest National Laboratory, United States; 3University of California, Los Angeles, United States; 4University of Colorado-Boulder, United States

Assembly of 2D patterns on crystal surfaces has been widely investigated to reveal the structural and energetic relationships between the substrate and overlying architecture. Progress has been achieved in understanding and controlling their assembly, yet little is known about the mechanism by which they nucleate. Understanding the dominant pathways and formation kinetics would enable precise control over phase and morphology during synthesis of 2D materials. In our study, short peptides were selected for their ability to bind on MoS2 (0001). We studied nucleation and growth of 2D films of these peptides directly with in situ AFM and compared our results to molecular dynamics simulations. We find the peptide arrays exhibit an epitaxial relationship to the underlying hexagonal lattice, but assemble row-by-row from dimeric growth along three equivalent directions. The nuclei are ordered from the earliest stages. Although the final crystals are 2D, due to the 1D nature of the constituent rows, there is no critical size, and the nucleation rate varies linearly with concentration and is finite for all concentrations above the solubility limit. Our results verify long-standing but unproven predictions of classical nucleation theory in one dimension while revealing the key interactions responsible for ordered assembly.

4:30 PM *FF03.04.04
Supramolecular Heterostructures—Expanding Molecular Self-Assembly into 3D Vladimir Korolkov; Oxford Instruments-Asylum Research, United States

The self-assembly of two-dimensional supramolecular networks is a well-known route to control the spatial organization at the nanoscale and beyond as well as bringing new chemical functionality on the surface. With a very few exceptions, these supramolecular networks are, in almost all cases, limited to monolayer thickness. The controlled growth of sequential layers, creating an organic layered structure, has so far been much more limited. Specifically, the additional functional control, which may be achieved through the formation of heterostructures realized by placing one supramolecular layer on another and resulting in growth into the third dimension perpendicular to the substrate, has not been widely explored for these systems.

Here we report on our recent progress in engineering and characterizing organic van der Waals materials –
supramolecular heterostructures (SH) with atomic force microscopy (AFM) [1–2]. SHs are layered organic materials that are stabilized by hydrogen bonds in plane and by van der Waals interactions and/or dipolar interactions between layers. They can be formed by, for example, growing sequential layers of bi- and mono-component two-dimensional supramolecular arrays stabilized by hydrogen bonding. The heterostructures are formed on layered materials such as hexagonal boron nitride (hBN), graphite or black phosphorus by depositing layers of cyanuric acid/melamine (CA.M), 1,2,4,5-Tetrakis(4-carboxyphenyl)benzene (TCPB), trimesic acid (TMA) and terephthalyc acid (TPhA) and other molecules.

AFM has confirmed a clear epitaxial arrangement between the layers of the heterostructure, although each layer can exhibit distinct symmetries, for example hexagonal (CA.M) and TMA, square (TCP), linear (TPhA), rhombic (TCPB) arrangements.

We analyze SHs under ambient conditions using Cypher AFM and demonstrate the routine acquisition of images with 0.1 nm resolution.

The work will present examples of single molecule and sub-molecular resolution. In the latter case, we will discuss the opportunities and challenges in achieving and interpreting ultrahigh resolution AFM images of molecules in the ambient for the purpose of their unambiguous identification.

should exist: one is a non-equilibrium structure and the other is an equilibrium one. It was confirmed that the transition from PC ZnO to non-PC ZnO accompanied valence shift and structural changes. The XANES absorption edge is sensitive to valence states. In the case of mixed-valent manganates and phase mixtures, Mn^{2+}, Mn^{3+}, and Mn^{4+} were clearly determined by the shift of Mn-K absorption edge. The energy shift was 10 eV between Mn^{2+} and Mn^{4+}. Since the electronic circumstances are different between ZnO and manganates, it is not straight to determine the Zn valence in the same way as manganates. The Zn valence in ZnO powder is 2. At least, it could be claimed that the Zn valence increased to 2+δ under UV irradiation.

Photochromic ZnO nanoparticles were synthesized by using VHF plasma enhanced CVD. The changes in Zn valence and local atomic structures were investigated by XANES and EXAFS. The absorption edge energy (E_0) and the local atomic structure significantly changed under UV irradiation and heat treatment. The Zn valence of PC ZnO was 2+δ. The coordination number N and Debye-Waller factor σ^2 of PC ZnO retained under heat treatment at 420K; at 570 K, N and σ^2 drastically changed and PC ZnO transformed to non-PC ZnO. The transition from PC ZnO to non-PC ZnO accompanied valence shift and structural changes. It was concluded that PC ZnO has a non-equilibrium phase in terms of crystallinity.

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FF03.05.02 Ultra-Dense (~20 Tdot/in^2) Nanoparticle Array from an Ordered Supramolecular Dendrimer Building Block Containing a Metal Precursor Kiok Kwon^1, Bong Lim Suh^2, Kangho Park^2, Jihan Kim^2 and Hee-Tae Jung^2; ^1Korea Institute of Industrial Technology, Korea (the Republic of); ^2Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The creation of an ultra-dense, highly periodic nanoparticle array from a soft building block is one of the most important issues in the fields of material science and nanotechnology. To date, ordered structure made from block copolymer (BCP) have been primarily used as templates for fabricating highly periodic nanoparticle arrays with high areal densities. Herein, we demonstrate for the first time the use of a supramolecular dendrimer assembly for the formation of a highly ordered nanoparticle array with a high areal density of ~20 Tdot/in^2, four times larger than that of the currently reported BCP-based nanoparticle arrays. By the simple thermal annealing of a supramolecular dendrimers containing a metal precursor between two flat, solid substrates, a hexagonal array of small gold nanoparticles (with a diameter of ~1.6 nm and center-to-center distance of ~5.3 nm), oriented normal to the bottom, was achieved. Density functional theory calculations demonstrated that the gold cation strongly bound with high binding energy to the head group of the dendrimer with a tapered shape. This structure served as a building block for self-assembly into a stable cylindrical structure. The findings obtained in this study provide a new paradigm for creating highly periodic, ultra-dense nanoparticle arrays by using a supramolecular assembly. It is important to note that we studied only one dendrimer, which possessed a hexagonal cylindrical structure, while numerous other dendrimer materials, which have a large diversity in terms of phase, size, and chemistry, exist in nature. We anticipate that this study will lead to the creation of a large family of supramolecular dendrimers that can be utilized as soft templates for creating periodic, ultra-dense nanoparticle arrays.

FF03.05.03 Wet Corrosion Process—A Simple and Versatile Method to Fabricate K-Doped Titanium Oxide Nanostructures So Yoon Lee^1; ^1Shibaura Institute of Technology, Japan; ^2KU Leuven, Belgium

Up to date, nanostructured Ti-based materials have attracted considerable attention due to their unique and diverse physico-chemical properties and potential for diverse applications. Among them, nanostructured potassium (K) incorporated Ti-based oxide materials (KTiO_x) have received particular attention due to their wide range of interesting applications, e.g. in photovoltaic cells, batteries, photochromic and electrochromic devices.
photocatalysis, gas sensors, biomaterials, owing to their remarkable structural and physical properties. However, so far one of the main bottlenecks for diverse applications has been the nanostructures fabrication, which generally involves complicated process, low reproducibility and high cost for chemical modification. Since the physical properties can be greatly affected by the size and morphology of the nanostructures as well as the precise incorporated K amount, several processes had to be combined, exacerbating these drawbacks. This drawback strongly limits their fast implementation in potential applications. Hence, elaborating a process that allows easy synthesis and a simple tuning of the desired morphology and properties via a single-step process is currently one of the key issues in this research field.

We used the wet corrosion process (WCP) which was developed in my previous research to Ti metal plates. In this work, we extended our studies to different Ti-based metal substrates and systematically investigated, for the first time, the characteristics of the resulting KTiOx, depending on the initial Ti content prior to WCP. The results clearly indicate direct correlation of the nanostructures fabrication with the Ti content in the initial material. Moreover, optical properties of the KTiOx could be correlated with their structural properties. Understanding the direct relationship between the Ti content of the initial metal and the condition of WCP to control the structural and physical properties makes it possible to produce the KTiOx on demand, for various applications.

Ti-based materials are currently considered as one of the most promising candidates for multifunctional semiconductor photocatalysts. We have investigated the photocatalytic performance of KTiOx fabricated by WCP. This result can be very interesting for photoinduced catalysis.

We fabricated nanostructured KTiOx via WCP using the Ti, TAV, and TN substrates. Systematically the relation between the Ti content of the initial metal and the condition of WCP was studied, with the conclusion that these parameters strongly control the morphology and physical properties of the generated nanostructures. One-dimensional nanostructures could be obtained within a specific window of the process condition: Ti and TAV metals which contain more than 90% Ti yielded elongated nanostructures of K-incorporated titanium oxide after treatment with 10–20 mol/L-KOH solution. In contrast, TN metal with about 50% of Ti content required a KOH treatment with >20 mol/L-KOH solution indicating that the process window shifted to higher concentration. For all samples the morphology evolution as a function of the WCP condition was similar, but the precise Ti content of the initial material determined the amount of incorporated potassium as well as the KOH concentration at which elongated nanostructures were produced. In detail, we focused on Ti series to estimate the photocatalysis application.

Structural and crystalline properties of KTiOx were studied by means of X-ray diffraction, scanning and transmission electron microscopy. Chemical composition was determined by X-ray fluorescence and energy-dispersive X-ray analysis. Photocatalytic performance was investigated by studying the degradation of methylene blue, cardiogreen, and azorubine red dyes upon UV irradiation. The negatively charged crystalline KTiOx nanostructures with high surface area showed significantly higher photocatalytic degradation compared to their KTiOx counterpart.

FF03.05.05

Crystallization Pathway-Controlled Microstructural Evolution of Magnetite Mesocrystals

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Mesocrystals consisting of assemblies of smaller crystallites have received much attention because of their crystallization pathway beyond classical theory and emergent functionalities that are not present in the individual components. Of various materials, magnetite (Fe3O4) exhibiting soft magnetism has been extensively studied and utilized broadly in electronics and biomedicine for decades. Because the magnetic properties of Fe3O4 mesocrystals depend on the crystallite and particle sizes, it is necessary to understand how they are determined during the crystallization process. However, the crystallization mechanism of Fe3O4 has been addressed phenomenologically by observing just a part of the entire crystallization pathway; thus, the details of the crystallization mode remain unclear.

In this study, we suggest that nonclassical and classical pathways are concurrently involved in the formation of clustered mesocrystalline Fe3O4 nanoparticles (c-Fe3O4 NPs), and the microstructure is affected by which pathway governs the reaction overall. We note that different ferric (oxyhydr)oxide polymorphs appear separately as intermediates on each pathway and can be chemically controlled. In early stages of the reaction, we observe a nonclassical pathway on which c-Fe3O4 NPs grow by oriented attachment of primary particles that form directly from lepidocrocite. In a late stage of the reaction, we observe a classical pathway on which Fe3O4 NPs form by stepwise transformation of lepidocrocite, goethite, and Fe3O4, in that order. We present the kinetics of each pathway as a Johnson–Mehl–Avrami–Kolmogoroff (JMAK) model that describes the isothermal transformation process.
Based on this understanding, we can control the diameter and crystallite size of c-Fe₃O₄ NPs independently according to the content ratio of chemicals in a broad range. Finally, we report successful experimental implementation of the crystallite size effect on the coercivity curves as a function of diameter. Because c-Fe₃O₄ NPs represent a crystallographically ordered aggregate of spheres, we can discuss the collective coercivity behaviour, which is hard to observe in single NPs.

FF03.05.07

Two-Dimensional Metal Oxide Free-Standing Films by Self-Assembly of Nanoparticles at the Air-Water Interface for H₂S Sensing Pavithra B, Neha Sakhuja, Subhajit Kundu, Navakanta Bhat and Ravishanakar Narayanan; 1Indian Institute of Science, India; 2University of Minnesota Twin Cities, United States

Simple, scalable and inexpensive method for the synthesis of metal oxide thin films is highly demanded for the emerging applications especially in the field of sensing and nanoelectronics. We demonstrate an effective method for synthesizing polycrystalline thin films of metal oxides using a unique reaction design at the air−liquid interface. We have exploited this interface reaction design to synthesize SnO₂ and PdO thin films and engineered their properties by varying the reaction parameters. These free-standing sheets have been synthesized by one step hydrothermal reaction at the interface with surfactant-free method. The thin films formed at the interface have a lateral dimension in centimeter. A possible growth mechanism is proposed. The metal oxide particles formed in the bulk of the solution move to the interface and get trapped to form a continuous, polycrystalline film to minimize the energy of the system. Transmission Electron Microscopy (TEM) has been basically used to understand self-assembly of the particles. TEM study shows that the films are formed due to the self-assembly of oxide nanoparticles (~30 nm in size) trapped at the interface; hence are polycrystalline. X-ray diffraction, Scanning Electron Microscopy and Atomic Force Microscopy measurements have been carried out to understand the structure, morphology and thickness of the films. These films are highly stable at elevated temperatures. The properties of these thin films can be manipulated simply by changing the reactant concentration and other reaction parameters like temperature and time of reaction. We have explored thickness tunability by varying the precursor concentration which in turn affects optical and electronic properties; hence the sensing behavior. SnO₂ films showed astounding gas sensing performance towards H₂S by demonstrating 25 ppb (S = 19.3%) as the lowest limit of detection at 150°C. The sensor can operate reliably in the range of 25 ppb to 6 ppm (S=25621%) H₂S. H₂S is known to be exhaled in “Bad Breath” (also known as Halitosis). It is considered as “normal” in the range of 80–160 parts-per-billion (ppb), “weak” in the range of 160–250 ppb, and “strong” if exhaled in concentrations greater than 250 ppb. Hence, sub-ppm detection of H₂S can aid in disease diagnosis at early stage. The highly sensitive and selective detection of this sensor makes it a potential candidate for breath-based diagnostics. This class of materials synthesized in two-dimensional morphology is extremely interesting for fundamental studies as well.

FF03.05.08

Fabrication of 3D Hierarchical Structured β-Ga₂O₃ Film via Advanced Laser Sintering Method Jong Wan Ko, Jiyong Park, Jae Hyang Lee, Dong-Hyun Kim, Yong Son and Jeong Hun Lee; Korea Institute of Industrial Technology (KITECH), Korea (the Republic of)

Monoclinic β-Ga₂O₃, which has a direct wide bandgap (Eg = 4.9 eV at room temperature), has tremendous potential as an electronic device material due to its excellent physicochemical properties including chemical stability, high mechanical properties, and thermal stability. In particular, the high breakdown voltage of monoclinic β-Ga₂O₃ and its transparency in the visible light region are suggesting promising applications in many fields such as power semiconductor, electromagnetic wave shielding, ultraviolet shielding agents, gas sensors, field effect transistors, and solar cells. In previous studies, monoclinic β-Ga₂O₃ was used as a single crystalline wafer grown by the edge-defined film-fed growth (EFG) method, and as a form of thin film fabricated by various vacuum deposition methods such as magnetron sputtering, pulsed laser deposition (PLD), molecular beam epitaxy (MBE), metal-organic vapor phase epitaxy (MOVPE), metal-organic chemical vapor deposition (MOCVD) and sol-gel method. However, the EFG method can obtain β-Ga2O3 with high purity, but it requires a lot of energy in the process. β-Ga₂O₃ in the form of the thin film can be manufactured with a precise pattern, but it has disadvantages that require high-vacuum deposition equipment. These two traditional approaches have limitations on the extended use of monoclinic β-Ga₂O₃.

Recently, as the 3D printing technology in the metal and polymer fields has developed remarkably, it has brought innovation in the manufacturing field. For example, airplane parts made with powder bed fusion (PBF) type 3D printing technology can be manufactured in a lightweight structure that could not be manufactured by conventional
methods. This allowed us to improve fuel efficiency and profitability. In our work, the process screening platform was established for the fabrication of 3D hierarchical structured monochoric $\beta$-$\text{Ga}_2\text{O}_3$ using customized PBF-type 3D printer. We also developed the controlled process management system by facilitating process variables including the viscosity of $\beta$-$\text{Ga}_2\text{O}_3$ paste, one-step layered thickness, laser experimental conditions (power, scan direction, scan speed), and atmospheric condition. The sintering behavior of nano-sized $\beta$-$\text{Ga}_2\text{O}_3$ particles and hierarchical structure evolution of $\beta$-$\text{Ga}_2\text{O}_3$ layers were investigated. The analytical results (XRD, XPS, UV-vis absorbance, surface roughness, domain size, etc.) revealed that higher sintering activity led to the increased densification reaction resulting in larger domain size and fewer contents of the pore. Establishment of the optimization process of monoclinic $\beta$-$\text{Ga}_2\text{O}_3$ manufacturing by our laser sintering method ensures promising adaptability of PBF type 3D printing technology for ceramic materials.

FF03.05.09
Highly Efficient Radiation Shielding of Bismuth Nanoparticle Modified Textile Yiting Zheng and Ming Su; Northeastern University, United States

This abstract reports a new method that cotton textile modified with bismuth nanoparticle can block x-ray radiation effectively within hundreds of micro-meter thickness. Bismuth nanoparticle is grafted on the nanocellulose which is a bridge to crosslink nanoparticle on the textile. The homogenous dispersion of nanoparticles on textile fiber surface is attributed to this spatially distributed modification, which enhances the shielding efficiency to 90% for 500 mm nanoparticle modified cotton textile. The fact that the relationship between shielding rate and thickness agrees well with the Beer-Lambert law, facilitates the prediction of shielding rate in specific application. Given its low cost, light weight, structure conformability and wearability, bismuth nanoparticle modified cotton textile will find its use in a wide range of fields related to personal radiation protection.

FF03.05.10
Novel Hierarchical YBO3 :Eu Crystals Synthesized by Folic Acid Assisted Hydrothermal Process Shan Li, Yingzi Ge, Hongkun Deng and Xianwen Zhang; Hefei University of Technology, China

YBO3:Eu crystals with flower-like hierarchitecture are readily synthesized through a folic acid assisted hydrothermal process using polyborate precursors in the aqueous solution. It was found that the pH value, borate/yittrium ratio and the mass of folic acid take effects on the morphology and photoluminescence emission intensity of YBO3:Eu crystals. The product with the small flower-like hierarchitecture was obtained under the conditions of pH value at 9, borate/yittrium ratio at 2 and the mass of folic acid at 0.44g, showing the strongest photoluminescence intensity. Such a hydrothermal route using folic acid as a capping agent may provide a green and effective method for fabricating useful and complex 3D architectures of LEDs phosphors.

FF03.05.11
Hybrid Structures as Building Blocks for the Production of Advanced New Materials Gabriel D. Rocha, Marcelo A. Martinho, Marco Aurelio L. Cordeiro and Edson R. Leite; CDMF, Brazil

Polymer nanocomposites containing small fractions of nanoparticles (NPs) have the ability to produce materials with higher mechanical properties due to the combination of properties of the inorganic NPs (e.g., stiffness, thermal stability) and polymer (e.g., flexibility, ductility and processability). The mechanical properties of these nanocomposites are linked to the dispersion of NPs in the matrix. Thus, an excellent dispersion of the nanoparticles is the main hindrance in the processing of nanocomposites. One of the most promising strategy for overcoming this challenge is the use of self-assembly (SA) of hybrid structures, as macromolecules grafted on NPs, providing a simple and rapid method for constructing orderly structures with several degrees of complexity[1]. On the other hand, despite the progress in controlling the equilibrium structure of grafted NPs, these nanocomposites exhibit a low tensile strength fragility that limits the control of physical properties over macroscopic areas. This behavior is even more critical for nanocomposites with high quantity of NPs. In face of this scenario, this study aims to provide fundamental insights into the hybrid structures as a building blocks for new materials with tailored physicochemical properties, notoriously with high ratio hybrid structures/polymer matrix. Based on this, Polyethylene Glycol (PEG) at different molecular weights (PEG Mw = 3000 and PEG Mw = 6000) was used as grafting polymer on Magnetite ($\text{Fe}_3\text{O}_4$) NPs, which were synthesized in a single step-route[2]. By improving organic interactions within the hybrid structures, thin films samples with superior mechanical behavior were produced by controlled evaporation of the grafted NPs colloid, consolidation by uniaxial pressure and mild thermal treatment. All these steps were analyzed by...
Scanning Electron Microscopy (SEM) (F50 Inspect) and Transmission Electron Microscopy (Tecnai F20), where it was possible to identify the myriad of hybrid structures organization, interactions and fracture behavior. The films were also characterized by dynamic mechanical test, and through the data was possible to get some insights into the relationship of storage modulus and loss modulus with NPs size, shape, PEG density on the surface of NPs, PEG chain size, and interactions between NPs-PEG/PEG-NPs. Then, this study demonstrates the potential of hybrid structures as building block for the development of advanced materials by correlating fundamental mechanical behavior with structure assembly and the interaction within the organic grafted molecules.


**FF03.05.12**

**Preparation and Application of AIE Fluorescent Polymers for Semiconductor Laser Illumination**

Yue Ru and Chenxi Hu; Beijing Research Institute of Chemical Industry, China

Solid-state light, such as light-emitting diodes, organic light-emitting semiconductors, polymer light-emitting diodes, etc., have the advantages of small size, high luminous efficiency and long life, which are used to replace traditional lighting sources. Nakamura Shuji, Isamu Akasaki and Hiroshi Amano won the 2015 Nobel Prize for their high-efficiency Light Emitting Diode (LED). In a short period of time, LED lighting has developed into a lighting source with a market penetration rate of 31%. The market size of China alone has reached more than 200 billion yuan. However, LED has certain limitations as an illumination source. The problem of “efficiency drop” has always limited the wide application of white LEDs.

In these years, the emergence of laser diode (LD) technology has further expanded the types of new lighting sources. Compared with the LED light source, the LD light source has the following characteristics: (1) The electro-optical conversion efficiency is high. In the work of An Zhenfeng et al. [6], an LD component with an efficiency of 71% is prepared by optimizing the device structure, and usually LED The electro-optical conversion efficiency is generally about 20%; (2) the volume is smaller, the volume of the LD component is usually one percent of the LED component, and has greater advantages in terms of weight reduction and design; (3) the LD light source does not have a problem of "significant efficiency drop", and the device operation is not unstable due to working time and operating temperature. Therefore, LD light source instead of or auxiliary LED light source is expected to become a new direction of solid-state light source development.

When the LD light source is used as a white light illumination source, it is also necessary to refer to the synthesis method of the white LED light source. The commonly used methods include two categories: (1) the three primary color method (three primary color method), and the so-called three primary color method refers to the use of red, green, and blue. The LD light source of the same color emits light at the same time, and the three colors are mixed to obtain white light ; (2) the fluorescence conversion method, the LD light is irradiated on the material having photoluminescence property, and the emitted fluorescence is mixed with the original light of the light source. After getting white light. Usually use ultraviolet or blue light as the excitation source, and yellow and red phosphors as the fluorescent material.

Fluorescence conversion method is more advantageous in terms of cost and safety, and is more suitable for production as an industrial product. Therefore, the preparation of LD device by fluorescence conversion method has become a hot spot for research and enterprise development. However, most of the fluorescent conversion materials used in current laser illumination devices contain rare earth metals, which are costly and limit the further application of laser illumination devices.

In our work, a fluorescent polymer with Aggregation-Induced Emission (AIE) is prepared as a fluorescent conversion material, and the effects of different processes on its light conversion effect are explored. Controlled emission from cyan to red can be achieved through pH regulation, which is based on the principle that pH can effectively control spatial conjugate by altering the aggregation of carboxylic acid groups and hydroxyl groups The results show that using this material as a fluorescent conversion material, white light is produced after blue laser excitation, its CIE 1931 coordinates (0.365,0.335), color temperature 4177K, belongs to the neutral white area. which is expected to replace the existing fluorescent materials for semiconductor lasers.
Ohnuki\textsuperscript{1}, Shinya Yoshioka\textsuperscript{1}, Miki Sakai\textsuperscript{2} and Yukikazu Takeoka\textsuperscript{2}; \textsuperscript{1}Tokyo University of Science, Japan; \textsuperscript{2}Nagoya University, Japan

Recently, the spherical photonic crystal called a photonic ball has attracted attention [1-4]. It consists of the primary structure, which is a periodic array of colloidal particles, and the secondary structure of the spherical shape. The wavelength of reflection exhibits the red shift when the primary particles become large. An interesting optical property has been reported for photonic balls with colloidal particles larger than 350 nm\textsuperscript{1}: a ring-shaped iridescent reflection can be confirmed on the peripheral region of the photonic ball when observed using an optical microscope. On the other hand, photonic balls macroscopically have a specific color when observed by the naked eyes, despite the iridescence observed under the microscope.

The reflection mechanism of the peripheral region is divided into two opinions; one is the grating diffraction which originates from regularly arranged colloidal particles on the surface of the photonic ball [2, 3], and the other is Bragg diffraction caused by lattice planes of the face-centered cubic (fcc) [4]. The former idea can explain the iridescent reflection, but not the specific color when observed with the naked eye. However, the latter idea explains the specific color only.

Further, the reflection on the peripheral region does not form a perfect ring; there are non-reflective dark regions. The areas of the non-reflecting regions largely depend on the numerical aperture of the objective lens. With the numerical aperture increase, the reflective areas expand. For example, using an objective with the numerical aperture 0.90, the non-reflecting area disappears, and the complete ring-like reflection appears on the peripheral region.

In this study, we propose a theoretical model to explain the above complicated optical properties of the photonic ball. In this model, the reflection of Bragg diffraction by the fcc lattice planes coexists with the reflection of the grating diffraction that consists of surface particles [5]. It is confirmed that the wavelength fulfilling the interference condition of Bragg diffraction of the (220) planes simultaneously satisfies that of the grating diffraction. In addition, detailed observations with optical and electron microscopes revealed a distinctive structural difference between the reflective and non-reflective regions: the in-plane arrangement of colloidal particles on the surface is different with respect to the radial direction of the ball between the two regions. From detailed experiments and theoretical calculations, we have found that the non-reflective region does reflect light, but into a highly oblique direction which cannot be observed under the optical microscope using the objective lens with a low numerical aperture.

We have also investigated the angular dependence of the reflection, and found that the photonic ball exhibits very low iridescence macroscopically. This is because of the unique reflection mechanism where both the Bragg and diffraction grating are important. From this low iridescence, the photonic ball can be a suitable candidate for the structurally colored pigment.

References

FF03.05.14
Red/NIR-Emitting AIE Platform Based on Phenothiazine Junyi Gong\textsuperscript{1}, Xiangzhi Song\textsuperscript{2} and Ben Zhong Tang\textsuperscript{1}; \textsuperscript{1}Hong Kong University of Science and Technology, Hong Kong; \textsuperscript{2}Central South University, China

Nowadays, most of aggregation-induced emission luminogens (AIEgens) with donor (D) - acceptor (A) structures are based on propeller-shaped triphenylamine (TPA) as electron donor. After years of development, TPA-fused AIEgens are comprehensively developed with hundreds of papers published in past few years. Although there're many similarity between phenothiazine and TPA, AIEgens based on phenothiazine is much fewer than TPA based AIEgens. In this contribution, we designed and synthesized 11 PTZ derivatives through Knoevenagel Condensation. Almost all the PTZ dyes are emissive at red spectral region, above 600 nm. In addition, PTZ10 and 11 were found emissive at the NIR region with high fluorescence quantum yield in the solid state (~5 \%). Since PTZ doesn't have any rotatable elements like normal AIEgens, we investigated the exact driving force for the AIE behaviour of the PTZ dyes through quantum mechanics computation and single crystal analysis, from which the restriction of intramolecular vibration was proved to be the AIE mechanism. Moreover, we used PTZ6 which has fairly a high fluorescence quantum yield (~20 \%), to selectively track the lipid droplets of HeLa cells with vert high contrast,
demonstrating a high application potential of the PTZ dyes.

**FF03.05.15**

**Non-Aromatic Annulene-Based AIE System via Aromaticity Reversal Process**
Zheng Zhao, Zaiyu Wang, Jacky Wing Yip Lam and Ben Zhong Tang; The Hong Kong University of Science and Technology, Hong Kong

Aggregation-induced emission (AIE) is a photophysical phenomenon correlated closely with the excited state intramolecular motions e.g. rotation and vibration. Although AIE has attracted increasing attention due to their significant applications in biomedical and optoelectronics, an in-depth understanding of the excited state intramolecular motion and elucidation of the origin of the intramolecular motion are yet to be fully developed. Here we found that the non-aromatic annulene derivative of cyclooctatetrathiophene (COTh) shows typical AIE phenomenon in spite of its rotor-free structure. The underlying mechanism was systematically investigated through photoluminescence (PL) spectra, time-resolved absorption spectra, theoretical calculations, circular dichroism (CD) and circular polarized luminescence (CPL) spectroscopy as well as by pressure-dependent fluorescent spectra, which indicated that the aromaticity reversal from ground state to the excited state served as a driving force for inducing the excited state intramolecular vibration, leading to the AIE phenomenon. To our knowledge, this is the first time that aromaticity reversal is demonstrated as a reliable strategy to develop novel vibronic AIE systems. And this work also provides a new viewpoint to understand the excited state intramolecular motion behavior of lumiongens.

**FF03.05.16**

**An AIEgen with Anion-π+ Interactions for Selective Wash-Free Imaging and Photodynamic Killing of Bacteria**
Chenchen Liu, Qiyao Li, Jacky Wing Yip Lam and Ben Zhong Tang; The Hong Kong University of Science and Technology, Hong Kong

Recently, a new aggregation-induced emission (AIE) system with anion-π+ interactions was first developed and demonstrated a novel strategy to develop inherent-charged AIE luminogens (AIEgens). AIEgens with charges possess unique advantages, such as enhanced biocompatibility and subcellular targeting ability resulted from electrostatic interactions between biomacromolecules and AIEgens. Therefore, they are expected to find wide biological applications. Unfortunately, the introduction of charges to AIEgens often suffers from complicated synthetic route, tedious purification and low yield. Herein, a new AIEgen, namely TTPABQ, with anion-π+ interactions was designed and obtained via one-pot synthesis. TTPABQ possesses a high specificity to bacteria and high photostability. It can image both Gram-positive and negative bacteria in a wash-free manner. This greatly simplify the imaging process. Furthermore, TTPABQ can also work as a promising photosensitizer to kill bacteria through efficient generation of reactive oxygen species upon white light irradiation.

**FF03.05.17**

**Less is More—AIEgen Derived Core@Shell Nanoparticles for Multimodality Tumor Imaging and Synergistic Therapy**
Xuewen He; The Hong Kong University of Science and Technology, China

Multifunctional nanomaterials integrating the prominent feature of each single functional moiety offer a great potential in multimodality tumor imaging and synergistic treatment. The traditional strategy for achieving multifunctional nanoplatforms adopting one-by-one combination of different constituents, suffers from the problems of complicated structural design, sophisticated purification and natural incompatibility between several functionalities. Herein, a novel “less is more” strategy is presented to realize multifunctionality within a simple silver core/AIE (aggregation-induced emission) shell nanoparticle. Surprisingly, apart from their intrinsic AIE fluorescence (FL) and noble-metal based computed tomography (CT) properties, an extra interface with excellent photothermal (PT) and photoacoustic (PA) functions was in situ generated between the core and shell part. As a result, multifunctional nanoparticles integrated with FL, PA, CT, radiotherapy (RT) and photothermal therapy (PTT) properties were achieved and performed excellently in correlated tumor imaging and synergistic therapy.

**FF03.05.18**

**Fluorescence Sensing of Cr(VI) by Functionalized Polyquinolines Synthesized from Metal-Free Multicomponent Polymerization**
Yubing Hu and Ben Zhong Tang; The Hong Kong University of Science and Technology, China

Development of polymerization methodology to afford polymers with unique structures and advanced
Functionalities is of considerable academic significance and technological implication. Among various multicomponent reactions, the A3-coupling of aldehyde, alkyne and amine has been established as a convenient and atom-economical method to construct nitrogen-containing heterocycles. To construct novel functional polymers with well-defined structure, our group has been working on the exploration of polymerization methodology from alkyne monomers for decades. However, there is still a plenty room for improvement. For example, the development of metal-free polymerizations is highly desirable due to the high cost and biological toxicity of metal catalyst residues. It is hence desirable to develop metal-free efficient polymerization of alkynes to avoid such problems. Herein, a facile and highly efficient approach towards functionalized polyquinolines was designed and developed by formic acid-catalyzed multicomponent polymerizations of alkynes, arylamines and glyoxylates. Conjugated polyquinolines were formed in situ with high molecular weights ($M_w$ up to 16 900) in nearly quantitative yields (up to 97.5%). Fluorescence tunable polyquinolines were achieved by altering the electron-donating substituents of the alkyne derivatives. The incorporation of luminogens into the polymer backbone rendered the resulting polymers with various aggregation-induced fluorescence behaviors. The tetraphenylethene-containing polyquinolines demonstrated to be a sensitive and highly selective fluorescence sensor of Cr(VI). Compared to other metal ions including K+, Na+, Mg2+, Al3+, Fe3+, Co2+, Ni2+, Cu2+, Pb2+, Ag2+, Cd2+, Hg2+ and Cr3+, the fluorescent sensing of Cr(VI) was more specific with an emission quenching ratio of over 20-fold. After a series of mechanism studies, the fluorescence quenching effect of Cr(VI) was proved to induced by inner filter effect. Such a non-irradiation energy conversion manner ensured the flexible and straightforward technique for the detection of Cr(VI).

**FF03.05.19**
**Ratiometric Detection of Mitochondrial Thiol with a Two-Photon Active AIEgen** Yuan Gu and Ben Zhong Tang; HKUST, China

In clinical studies, thiol measurement in the whole blood is of diagnostic and prognostic significance. In addition, the detection of mitochondrial thiol is very important for investigating cellular functions or dysfunctions. Here, a ratiometric aggregation-induced emission luminogen (AIEgen) called TPE-PBP for thiol detection was developed by introducing a para-dinitrophenoxy benzyl pyridinium moiety to tetraphenylethylene. TPE-PBP exhibits excellent biocompatibility, high photostability, and large two-photon absorption cross-section. TPE-PBP emits red fluorescence in PBS buffer without thiol. Upon addition of thiol, there is a gradual blue shift of TPE-PBP’s emission with ratiometric fluorescent response because of cleavage of the dinitrophenyl ether bond by thiol followed by the self-immolation of the para-hydroxybenzyl moiety to produce a less-conjugated AIEgen. The *in vitro* quantification of thiol is enabled by the linear ratiometric fluorescence response with a very low limit of detection. Considering the high sensitivity and good selectivity towards thiol detection, TPE-PBP was also utilized to detect thiol in the blood. Furthermore, mitochondrial thiol *in vitro, ex vivo* and *in vivo* were quantitatively mapped by TPE-PBP using fluorescence microscopy under one- and two-photon conditions.

**FF03.05.20**
**Aggregation-Induced Delayed Fluorescence** Zujin Zhao; South China University of Technology, China

Purely organic luminogens with thermally activated delayed fluorescence (TADF) can harvest singlet and triplet excitons to afford high electroluminescence (EL) efficiencies for OLEDs. However, most TADF emitters have to be dispersed in host matrix to prevent aggregation-caused quenching (ACQ). The doped OLEDs of TADF emitters often encounter a knotty problem of severe efficiency roll-off as lumiance increases, which defers practical application of TADF emitters in industry. In our group, we are working on the luminogens with aggregation-induced emission (AIE), which are free of ACQ. Recently, we develop a series of novel luminogens with aggregation-induced delayed fluorescence (AIDF), which can facely solve the aggregation-caused emission quenching and/or exciton annihilation problems of current TADF emitters. They are composed by an electron-withdrawing carbonyl core and various electron-donating groups, such as phenoxyzine, phenothezine, 9,9-dimethyl-9,10-dihydroacridine, carbazole and so on. They exhibit weak emissions without delayed fluorescence in solutions but strong emissions with prominent delayed components upon aggregate formation or in neat films, exhibiting the typical AIDF characteristics. The nondoped OLEDs based on the neat films of these AIDF luminogens exhibit lowered turn-on voltages and increased lumiance (> 100000 cd m⁻²) with respect to the doped OLEDs. Thanks to the excellent exciton utilization (~100%), the nondoped devices furnish remarkable EL efficiencies of up to 72.9 cd A⁻¹, 81.8 lm W⁻¹ and 22.6%, and negligible efficiency roll-off at 1000 cd m⁻². To the best of our knowledge, these devices are the most efficient and stable nondoped OLEDs reported so far.
References


FF03.05.21

**Tracking Entry Process of Biofunctional AIEgens into Cells and Mapping Their Distribution in Organelles**

Wei He, Parvej Alam, Tszy Kin Kwok and Ben Zhong Tang; The Hong Kong University of Science and Technology, Hong Kong

Benefiting from high aggregated-state emission, superior photostability and low cytotoxicity, a variety of AIE luminogens (AIEgens) have been designed as fluorescent bioprobes for cell imaging. The entry process of AIEgens into cells has been rarely investigated although it is of fundamental importance. Herein halogen-labeled AIEgens with specific organelle targeting properties have been comprehensively designed for tracking their entry process into cell and their distribution inside the cells. Cooperatively with confocal fluorescent imaging, the techniques of time of flight secondary ion mass spectrometry (ToF-SIMS) have been applied to analyze the distribution of AIEgens during the process of bioimaging. This study will not only provide new strategies for designing biofunctional AIEgens but also bring new insight for understanding the cell entry process of AIEgens.

FF03.05.22

**Photonic Bandgap-Induced Light Extraction of Perovskite-Embedded Copolymer Particles**

Seung-Jea Lee¹, Jin Woo Choi², Santosh Kumar¹, Chang-Lyoul Lee¹ and Jae-Suk Lee¹; ¹Gwangju Institute of Science and Technology, Korea (the Republic of); ²Korea Institute of Materials Science, Korea (the Republic of)

LED with narrow full-with at half maximum (FWHM) has been studied to realize natural color mimetic displays. Due to relatively broad FWHM of organic-LEDs, perovskites have been suggested as an alternative. Even though perovskites have narrow FWHM, low stability hindered the usage of perovskites in LED fields. Color filters, such as photonic crystals, have been applied to narrowing the FWHM of emitting light based on the optical resonance at the edge of the photonic bandgap. However, angle-dependency of the photonic bandgap has been a big obstacle that should be overcome. Herein, organic-inorganic hybrid perovskite-embedded copolymer particles are prepared via self-emulsion polymerization (SEP) to increase the stability of the perovskite and improve the angle-dependency of the photonic bandgap. PbBr₂-embedded copolymer particles firstly prepared then the particles are self-assembled to polycrystalline photonic crystals. The embedded precursors are converted to perovskite using vapor-assisted solution process (VASP). The stability of the perovskite was enhanced due to the encapsulating polymers. Photoluminescence intensity increased ~12% and FWHM of the emission narrow down to ~13 nm due to the resonance effect of the photonic bandgap. Moreover, angle-dependency of photonic bandgap has been improved due to the polycrystalline structure of photonic crystals.

FF03.05.23

**Organic Polymorphs—Different Molecular Packing Induced Different Room Temperature Phosphorescent Properties**

Weilong Che¹, Yujun Xie¹ and Zhen Li¹,²; ¹Institute of Molecular Aggregation Science, Tianjin University, China; ²Wuhan University, China

The development of organic room temperature phosphorescent (RTP) materials is accompanied by opportunities and challenges. The relationship between polymorphisms and RTP properties has attracted much attention as the different molecular packings of one molecule in solid state, which exhibits significant different optical and electronic properties. Herein, we report an organic molecule BBP-BO with unique polymorphic emission properties. Two kinds of BBP-BO crystals were obtained, crystal A exhibit bright photoluminescence (PL) with a quantum yield of 11.25%, which is higher than that of crystal B (6.85%). Interestingly, Crystal A shows a distinct RTP phenomenon with a long lifetime of 17.92 ms@492 nm, but Crystal B has a relatively weak RTP phenomenon with
short lifetime of 3.49 ms@492 nm. Crystal structures analysis shows that the different optical properties of the two crystals are related to the molecular packing mode. The further exploration how molecular packing affect RTP property is essential for designing and synthesizing novel RTP materials.

**FF03.05.24**

**Theoretical Revelation and Experimental Confirmation of the Mechanism of Aggregation-Induced Emission in Organic Materials**  
Qian Peng; Institution of Chemistry, China

Better understanding of the mechanism of aggregation-induced emission can help develop novel AIE systems and exploit novel applications. Here, we have disclosed the microscopy mechanism of AIE by systematically investigating the excited-state electronic transition property, nuclear vibrational modes, the radiative and nonradiative decay rate constants, and the fluorescence quantum efficiency using the thermal vibration correlation function rate theory coupled with quantum chemistry calculations.[1] For typical AIEgens with the nature of \((\pi, \pi^*)\), we have put forward that the block of the nonradiative decay channels recovered strong emission in aggregate.[2] The nonradiative decay channels refer to the molecular vibration modes with large electron-vibration coupling value. We have found the rotational, twisting, bending and stretching vibration modes can be largely restricted in aggregate, resulting in the decrease of the nonradiative decay rate. For some hetero-AIEgens, we have proposed that the conversion from dipole-forbidden \((n, \pi^*)\) or \((\sigma, \pi^*)\) state to dipole-allowed \((\pi, \pi^*)\) state happen to induce strong emission when going from solution to aggregate. [3] Then, we have proposed some strategies to probe and verify the mechanism using the resonant Raman spectrum, isotopic effect, pressure effect, and the nanoparticle size effect and so on. Some of them have been fully confirmed by the experiments. Furthermore, the molecular design principles are raised and many unusual AIE fluorophors are designed theoretically and synthesized experimentally. [4]

References:


**FF03.05.25**

**Transformation of Waste Printed Circuit Boards (PCBs) to Value-Added Nano-Materials for a Wide Range of Applications: A Holistic View**  
Rasoul K. Nekouei, Farshid Pahlevani and Veena Sahajwalla; University of New South Wales, Australia

Every year a huge volume of electronic wastes (e-waste) are being discarded with an increasing trend due to the technological and scientific advancements. To many countries, this kind of waste is to be a major concern since various kind of materials including metals (basic and pernicious metals), polymers and ceramics are entangled elaborately and too hard to be separated readily. PCBs are considered as one of the main splits of e-wastes containing around 35% metals. The metallic portion includes Cu, Zn, Sn and Fe, making this waste stream valuable as a secondary source of raw materials after separation and purification. In this research, we focused on the metallic portion of waste PCBs to turn them into value-added nano-materials practical application including nano-fluids, wastewater purification and water splitting. The projects step is as below:

1. In the first step, we focused on presenting a feasible and novel process to enhance the amount and purity of metallic portion of the waste PCBs without further chemical or/and physical. Two milling stages including knife mill and ring mill were applied to increase the liberation degree followed by a physical flotation process using bromoform fluid for beneficiation and enrichment. To recognize the composition and metal content in each classification, the classified (using sieve shaker) powders were characterized in each stage. Eventually, the mixture
of all powder was characterized in terms of its thermal behavior and composition of exhausting gas to estimate its threat for the environment.

2. In this step, we used the classified waste PCBs as a source of initial alloying powders to synthesize a homogenous nano-structured Cu-Zn-Sn-Fe-Ni alloy via mechanical alloying. This nano-structured powder is commonly used in a range of applications where the heat transfer and conductivity play a vital role such as nanofluids or additive manufacturing. To characterize the properties of powders, various characterization methods were utilized including XRD, XPS, FESEM, EDS, HRTEM, STEM, UV–Vis and optical microscopy. Finally, as a potential application, a nanofluid solution was prepared and characterized using pH and conductivity measurements.

3. In the next step, we tried to leach all remaining metals to a solution just in one leaching step using HNO₃. One of the objectives of this stage was to minimize the leaching time, amount of acid applied and energy consumption. To achieve these targets, a multi-variant multi-response statistical method was used to optimize the leaching efficiency of major metals content. Lastly, to understand the composition and importance of the residue, the solid residue of leaching was characterized.

4. In this stage, SnO₂ quantum dots were unexpectedly formed as spontaneous precipitation with a very slow kinetic rate from the last step leaching solution. The precipitation was triggered without the use of any chemicals or surfactants. It also occurred selectively as a by-product without influencing the solubility of other metal-containing ionic species. Then, the precipitation mechanism in the solution and the measurement of the surface area and other characteristics of the QDs were identified. After calcination, the SnO₂ QDs were applied to wastewater treatment to remove methylene blue (MB) as dye pollution.

5. In the last step, the solution containing Cu²⁺, Zn²⁺, Ni²⁺, Al³⁺, and Pb²⁺ ions was exposed to three ion exchange resins (Amberlite IRA 743, Lewatit TP 208 and Lewatit TP 260) to extract and separate the metallic ions of heavy metals. In addition to the optimization of resin load, contact time and solution temperature, the thermodynamics and kinetics of the adsorption were calculated to prove the accuracy and reliability of the experiments. The preferred locations of adsorbed ions on resin beads were traced and analyzed by electron microscopy. Finally, a stripping process was applied to examine the desorption selectivity and enhance recycling efficiency.

**Molecular Face-Rotating Polyhedra Constructed through Restricting Phenyl Flipping of AIEgen** Hang Qu, Zheyu Huang, Xue Dong and Xiaoyu Cao; Xiamen University, China

Chiral cage compounds are important because they exhibit extending functions such as chiral recognition and circularly polarized luminescence. Generally, two strategies have been established to construct chiral cages: by using chiral precursors, or based on the chirality at metal centers. Inspired by mathematics, we have reported a strategy to generate emergent chirality of organic cages by assembling achiral two-dimensional truxene building blocks into chiral octahedra through dynamic imine chemistry.

Tetraphenylethylene (TPE) and Pentaphenylpyrrole (PPP) are well-known aggregation-induced emission chromophores (AIEgen) and exhibits two rotational patterns in its propeller-like P or M configurations, respectively. Through dynamic covalent chemistry, the chiral molecular Face-Rotating Polyhedra (FRP) were constructed from restricting phenyl flipping of TPE or PPP. Accompanied by the generation of chirality, strong fluorescence also emerged during cage formation. In the study of FRP, we provide the strategies to predict the shape of FRP and the number of isomers. This study provides insight into construct chiral cages by the rational design through graph theory, and might facilitate further design of cages and other supramolecular assemblies from aggregation-induced emission active building blocks.

**Chiral Molecular Face-Rotating Sandwich Structures Constructed through Restricting the Phenyl Flipping of Tetraphenylethylene** Xiao Tang; Xiamen University, China

Chiral tetraphenylethylene (TPE) derivatives, as well known AIE chromophores, have great potential in chiral recognition and circularly polarized luminescence. However, they were mainly constructed through introducing chiral substituents at the periphery of the TPE moiety, which required additional chemical modifications and limited the variety of chiralities of products. We constructed a series of chiral face-rotating sandwich structures (FRSS) through restricting the phenyl flipping of TPE without introducing any chiral substituents. In FRSSs, the TPE motifs display P or M configuration which resulted in complex pattern arrangements and a variety of chiralities. Interestingly, only four isomers, as two pairs of enantiomers, were found in the assemble system and two of them are thermodynamic products. And we also found that non-covalent repulsive interactions in vertices caused the
facial hetero-directionality of FRSs, and the hydrogen bonds between imine bonds and hydroxy groups induced excited-state intramolecular proton transfer (ESIPT) emission of FRSs. In addition, the fluorescence intensity of FRSs decreases with the addition of trifluoroacetic acid. Our study provides new insights into the rational design of chiral assemblies by means of AIEgens, such as TPE and its derivatives, through restriction of intramolecular rotation (RIR), which can be applied in luminescent materials, chiral molecular recognition or asymmetric catalysis.

Reference

FF03.05.28
Testing the Stability of Molecular Imprint Biosensors Emma Walsh¹, John Jerome², Jessica Semel², Kelvin Linskens² and Miriam Rafailovich²; ¹Newtown High School, United States; ²Stony Brook University, The State University of New York, United States

Previously it was shown that molecular imprinting (MI) technology can be used to produce biosensors with the potential for use in point-of-care diagnostics for detection of Zika virus, pancreatic cancer, polio and other antigens, etc. [1]. MI biosensors utilize a self assembling monolayer (SAM) of hydroxy-terminated alkanethiol chains on gold-coated silicon chips. The SAM crystallizes around the target analyte. Once crystallized, the monolayer retains the shape of the analyte allowing it to sensitively and selectively bind the target analyte. The analyte is measured using a simple potentiometric readout. These sensors are easy to implement and only require a simple potentiometer for detection. Hence they can be especially useful in third world areas where advanced sensing instrumentation is lacking. The sensor chips require sterile laboratory conditions for imprinting, but they can be used at point of care, which may be remotely located. In order to reach these areas, it is important to optimize the method of storage and shipping the imprinted detector.

MI sensors were fabricated as previously described [1] using hemoglobin as the target analyte and incubated at room temperature in the desiccator for up to a week while our control chips were tested fresh, without incubation. Following 72 hours of incubation, MI biosensor detected the analyte (hemoglobin) with almost no loss of sensitivity as compared to freshly prepared control sensors. However by 120 hours of incubation the biosensor no longer demonstrated a linear response to increasing concentrations of target analyte indicating that the SAM was unstable under test conditions. These data suggest that the thiols used in SAM are sensitive to moisture present under atmospheric conditions, and hence should always be stored in vacuum unless they are used within the day that they are imprinted. It is encouraging that the chips did not show deterioration within the first 72 hours when stored in a rough vacuum, similar to the one used in food storage applications, hence they could be vacuum packed and shipped overnight to the point of care. Further work is in progress to improve the vacuum conditions and extend the lifetime of the chips.

[1] Y. Wang, Y. Yu, J. Sokolov, K. Levon, and M. Rafailovich, Current Trends in Polymer Science, 18, 1, 2018

SESSION FF03.06: Particle Aggregation II
Session Chairs: Kristen Fichthorn and Xin Zhang
Tuesday Morning, December 3, 2019
Hynes, Level 3, Room 313

8:00 AM FF03.06.01
Light-Directed and Responsive Colloidal Crystals Engineered with DNA Jinghan Zhu, Haixin Lin, Youngeun Kim and Chad A. Mirkin; Northwestern University, United States

Colloidal nanocrystals are promising building blocks for the construction of hierarchical 2D and 3D components for use in optical, electronic, magnetic, and therapeutic devices. Therefore, multiple assembly techniques (e.g., entropic, depletion, electrostatic, biorecognition) have been developed to engineer hard or soft nanoparticle-based crystalline
materials. DNA-mediated crystallization, which uses DNA-grafted nanoparticles as “artificial atoms” to generate hierarchically ordered superlattices (e.g. soft colloidal crystals), has advantages over other assembly techniques because the nanoparticle core “atom” identity (nanoparticle size, shape, and composition) can be tuned independently of the DNA “bonds” (sequence, strength, length, and density). However, it still remains a challenge to pattern DNA-functionalized colloidal crystals into specific shapes while retaining crystallinity. Herein, we report on the light-induced patterning of colloidal crystals engineered with DNA. Light-responsive colloidal crystals are synthesized by incorporating azobenzene-tethered DNA as bonding elements. Here, the photo-isomerization of azobenzene molecules between the trans- (visible light) and cis-form (UV light) directly translates into a change in the DNA hybridization interactions, resulting in a reversible switching between nanoparticle binding and non-binding states. We thus utilize such light-controlled assembly and disassembly to selectively remove nanoparticles that are located outside of a desired pattern. Specifically, we assemble a crystalline thin film of DNA-grafted nanoparticles and then apply UV-light to controllably dehybridize certain DNA strands which enables their dissolution leaving behind the desired pattern. The light-responsive printing of DNA-functionalized colloidal crystals marks a significant step towards fabricating advanced “smart materials” that can be dynamically manipulated via different types of stimuli on-cue.

8:15 AM FF03.06.02
Nanocrystal Superlattices and Derivatives for Energy Applications Angang Dong; Fudan University, China

The self-assembly of colloidal nanocrystals (NCs) into superstructures provides an efficient bottom-up pathway for constructing new functional materials. Among various superstructures, NC superlattices represent an entirely new class of solid-state materials with unique collective properties and wide applications. However, conventional NC superlattices are inappropriate structural motifs for energy applications due to the impeded molecular accessibility of NCs by foreign species. In pursuit of widening the range of applications of NC superlattices, it is desirable to develop new architectures that enable full access of NC constituents while simultaneously facilitating mass transport properties. Herein, I will focus on low-dimensional, hierarchical NC superlattices with rationally designed structures and mesoscale morphologies toward high-performance energy storage and conversion. I will also spend half of the time to cover NC superlattice derivatives, especially ordered graphene-like frameworks, which are emerging as a new class of mesoporous carbon materials. By exploiting the versatile surface chemistry and self-assembly behaviors of colloidal NCs, a rich array of mesoporous graphene-based materials can be designed, which show great promise as material platform for energy applications.

8:30 AM *FF03.06.03
Programmable Metamaterials through Colloidal Crystal Engineering with DNA Chad A. Mirkin; Northwestern University, United States

Metamaterials exhibiting desirable optical phenomena require the precise assembly of nanoscale building blocks with positional and orientational control. Colloidal crystal engineering with DNA offers the ability to chemically program the structure of nanoparticle-based materials with sub-nanometer precision in three dimensions. This structural control enables the design and discovery of new materials with previously unattainable functionalities and the determination of key structure-property relationships. DNA-programmable assembly can be applied to the field of optical metamaterials to dramatically expand the range of architectures that can be synthesized by chemists and explored by theorists. Through the convergence of bottom-up DNA assembly with top-down lithographic approaches, colloidal plasmonic nanoparticles of different sizes, shapes, and compositions can be precisely placed in two and three dimensions on a surface to form optically active superlattices. Additionally, exploiting DNA’s native responsiveness to chemical stimuli provides dynamically reconfigurable superlattices that are particularly interesting as metamaterials. These large-area superlattices, which would be difficult, if not impossible, to synthesize with any other currently available top-down or bottom-up technique, enable the use of colloidal nanoparticles as metamaterial building blocks and provide a platform to investigate and design new types of light-matter interactions in nanoparticle-based metamaterials.

9:00 AM *FF03.06.04
Interfacial Structure, Interparticle Forces and Assembly Dynamics During Oriented Attachment of Nanocrystals James J. De Yoreo1,2, Guomin Zhu2,1, Lili Liu1, Jaehun Chun1, Maria Sushko1, Xin Zhang1, Sebastien
Kerisit¹, Jennifer Soltis¹, Gregory Schenter¹, Christopher J Mundy¹,² and Kevin Rosso¹; ¹Pacific Northwest National Laboratory, United States; ²University of Washington, United States

Crystallization by particle attachment is a widespread phenomenon in synthetic and natural environments. In mineral systems, this process exhibits diverse styles ranging from oriented attachment of like phases to mis-oriented aggregation of disparate phases followed by coarsening to single crystals. While descriptions of these systems must share a commonality with continuum-based DLVO-type theories for simple colloids, mineral systems present additional complexities, including face-specificity of dielectric properties, structured nanoscale interfaces, and solvent-responses of a comparable length scale. To understand the relationship between nanocrystal structure, interparticle forces and assembly dynamics, we are investigating nanocrystal assembly of titanium, iron and zinc oxides. For ferrihydrite (FeOOH) and ZnO, in situ TEM demonstrates that direction-specific forces align diffusing particles prior to contact and that attachment occurs on lattice matched faces via a sudden jump to contact. Direct AFM-based measurements of the forces between both TiO₂ and ZnO surfaces reveal orientation dependent attractive interactions exhibiting the symmetry of the underlying lattice. MD simulations indicate a combination of hydration and dispersion forces orient the particles and that barriers caused by hydration layers, cannot be overcome by simple Brownian forces in the absence of fluctuations of the layers. Classical DFT simulations suggest these barriers are greatly reduced and attractive forces increased through ion correlation interactions. Addition of organic ligands, like oxalate, to the ferrihydride system produces a dramatically different pathway and outcome: Nanoparticles of hematite (Fe₂O₃) nucleate sporadically from the ferrihydrite and, once formed, are covered with oxalate and drive all new hematite particles to nucleate within about 1 nm of the interface, after which they jump to contact. The oxalate inhibits growth and coarsening of the particles, leading to spindle-shaped aggregates of crystallographically aligned particles with a fixed and constant aspect ratio. Thus the random assembly process seen in the pure ferrihydrite system is replaced with one that is deterministic due to interface-driven nucleation.

9:30 AM *FF03.06.05
Marrying Top-Down Fabrication and Bottom-Up Assembly of Colloidal Nanocrystals to Construct Devices
Cherie R. Kagan; University of Pennsylvania, United States

We combine top-down fabrication and bottom-up assembly processes to construct artificial, meta-molecules, materials, and devices with unconventional physical properties from colloidal, metal nanocrystal (NC) building blocks. Lithographically-defined, size- and shape-engineered topographical templates are used to direct the capillary assembly of NC metamolecule oligomers. We map the evolution in optical response as we increase the number of nearest neighbor shells in close-packed spherical NC assemblies, and as we construct trimers of nanorods that assemble along the edges of equilateral triangles to form open structures.¹ ² The triangular arrangement of nanorod trimers supports strong magnetic plasmon modes in their open interior, and circumferential displacement of the nanorods generates a chiroptical response under unidirectional oblique illumination. We also combine nanoimprint lithography with solution-based deposition of NCs to form superstructures for large-area, active metamaterials. By chemically exchanging the long ligands used in NC synthesis with more compact ligand chemistries we control interparticle distance.³ This ligand-control of distance allows us to tailor a dielectric-to-metal phase transition seen by a 10¹⁰ range in DC conductivity and a dielectric permittivity ranging from everywhere positive to everywhere negative across the whole range of optical frequencies. We realize a “diluted metal” with optical properties not found in the bulk metal analog, presenting a new axis in plasmonic materials design. Using this approach, we demonstrate strong, near-infrared optical absorbers that transduce light to heat.⁴ We also demonstrate quarter-wave plates with extreme bandwidths and high polarization conversion efficiencies in the near- to-mid infrared.⁵ Finally, we exploit the distinct chemical and mechanical properties of NC assemblies, in comparison to bulk materials, to create 2D, lithographically-defined NC/bulk bimorphs, which upon ligand exchange, transform to create functional 3D architectures.⁶


10:00 AM BREAK

10:30 AM *FF03.06.06*  
**Chiral Inorganic Nanostructures and Long-Range Correlations in Particle Assemblies** Nicholas A. Kotov  
University of Michigan, United States

Early observation of strong circular dichroism for individual nanoparticles (NPs) and their assemblies have developed into a rapidly expanding field of chiral inorganic nanostructures. The chiral inorganic nanostructures encompass sophisticated constructs from metals, semiconductors, ceramics, and nanocarbons with multiple chiral geometries with characteristic scales from Ångströms to microns. Many of them are formed spontaneously from polydispersed building blocks, which enables their structural and functional engineering over a broad range geometries and optical properties. This talk will address (1) the mechanisms of chirality transfer in inorganic materials, (2) the origin of the uniquely high values of optical anisotropy, (3) the fundamental challenges of multiscale chirality observed in nanostructures, and (4) physicochemical differences/similarities with chiral supramolecular, liquid crystal, and biological systems. The analysis of phase diagrams for the assembly of chiral NPs affords understanding essential role of long-range correlations between NPs and a possibility of critical phenomena in the assembly at nanoscale that can lead to exceptionally complex assemblies from polydispersed nanocomponents exemplified by chiral hedgehog particles. The parallels with biominalized skeletons of coccoliths help understanding the need for chiral asymmetry in live matter. Simplification of the chiral assembly processes also helps accelerating the development of technologies based on chiroplasmonic, chiroexcitonic, and chiromagnetic effects observed for the individual NPs and their assemblies exemplified by the polarization vision mimicking that of some organisms.

11:00 AM FF03.06.07  
**Connecting Energetics to Dynamics in Oriented Attachment Using Real-Time Observations** Lili Liu¹, Elias Nakouzi¹, Jaehun Chun¹, Christopher J Mundy¹, Maria Suslik¹ and James J. De Yoreo¹,²  
¹Pacific Northwest National Laboratory, United States; ²University of Washington, United States

Although one-dimensional nanostructures of ZnO have been suggested to form via oriented attachment (OA), the detailed mechanism underlying this process remains unresolved as no direct observations of ZnO OA have been reported. Here we use *in situ* liquid phase (LP)-TEM to directly observe and investigate dynamic aspects of ZnO nanorod formation by OA. Detailed analysis on translational and rotational motions of ZnO particles, tracked in real time, demonstrates that aggregation-coalescence via OA event was the primary mode of ZnO particle growth, and in some cases produced chain-like ZnO nanostructures. While the particle interactions with molecular granularity suggest a qualitative difference between ZnO OA and near-OA events, our study shows that the attachment event is notably influenced by dynamic nature associated with the particle motions such as abnormal particle diffusivity and quasi-2D nature under confinement. Our study suggests a complementary aspect to obtain better understanding of the OA, as well as the current viewpoint mainly focusing on energetic considerations.

11:15 AM FF03.06.08  
**Understanding the Growth Mechanism of Anisotropic ZnO Nanorod Formation** Sukesh K. Tumram and Rajdip Bandyopadhyaya  
Indian Institute of Technology Bombay, India
Nanostructured Zinc oxide (ZnO) has great importance in many areas, such as catalysis, sensors, cosmetics and biomedical applications. In literature, ZnO nanorods (NR) are the most widely studied nanostructure. However, the mechanism of their growth into the final rod-shape is not well understood. In the present work, we have synthesized ZnO NR and studied its temporal growth mechanism, using zinc chloride as a precursor and hexamethylenetetramine (HMTA) as a reducing agent. It has been reported that, HMTA degrades into ammonia and formaldehyde at a certain temperature which subsequently provides hydroxyl ions and helps in the ZnO nanostructure formation. Hence, to understand the role of temperature, NR synthesis has been done at various temperatures, namely 65, 75, and 85 °C. It was observed that, the time required for NR formation decreased with increased in temperature, which was confirmed by nanostructure morphology at different reaction time-points. Length to diameter aspect ratio (AR) of NR is found to vary from ~1 to ~9, from the initial to final time-point (180 min). It correlates well with using ICP-AES, the utilization of Zn2+ ion in NR formation which increases with higher temperature (< 20 %, 20 % and 55 % at 65, 75, and 85 °C respectively at 180 min).

To capture the evolution of ZnO NR formation, intermediate samples were characterized by scanning electron and transmission electron microscopy. Initially, a new crystal structure- a hollow “nanocone” (NC) crystals of ZnO (AR ~1) was observed. Further, these crystals find a perfect crystalline match and self-organize with a neighboring NC, which results in the formation of a binary NC pair. Latter these pairs each grow in 1-D direction only, leading to the hexagonal ZnO NR. The NCs may have high intrinsic surface energy, which makes them find and attach to a similar crystalline surface of another NC, together forming NC pair. We have observed that this NC pair now acts as a base for NR formation because growth is occurring, only at both the ends along the length of the NC. Characterization techniques such as XRD and XPS have been done for analysing crystal size, phase formation and oxidation state respectively, for intermediate products. Synthesized ZnO NRs are presently being used in the degradation of pharmaceutical wastes in water.

Keywords: ZnO, Nanocone, Nanorod

11:30 AM *FF03.06.09
Noncovalent Self-Assembly and Formation of Active Nanostructures Hongyou Fan; Sandia National Laboratories, United States

Nanocrystals (NCs) exhibit unique size- and shape-dependent physicochemical properties arising from low dimensional quantum confinement effects and have been successfully used as building blocks for the fabrications of 2- and 3-dimensional NC arrays for the development of ‘artificial solids’ (or metamaterials) with new collective optical and electronic properties derived from the interaction or coupling of different NCs in an assembly. NC surface chemistry plays a key role in control of microstructures of the NC arrays such as mesophase. Here we report our recent progress in development of surfactant-assisted micelle confined noncovalent self-assembly and synthesis of active nanostructures. This approach is simple, general, and can be used to synthesize highly ordered nanostructures with different sizes and shapes. Through using varied surfactants and building blocks, this method provides a unique opportunity for subsequent self-assembly through hydrogen-bonding, π-π stacking, charge interactions, etc. and formation of highly ordered nanocrystal arrays with controlled mesophase, orientation, and material forms (film, powder, particle).

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.
Intrinsic Analysis of Transition Processes from the Lowest Triplet Excited State of Heavy Atom-Free Conjugated Molecular Crystals with Persistent Room Temperature Phosphorescence Shuzo Hirata; The University of Electro-Communications, Japan

Persistent room-temperature phosphorescence (RTP) under ambient conditions is attracting attention due to its strong potential for applications in bioimaging, sensing, or optical recording because materials with persistent RTP can be utilized for high contrast emission imaging independent of autofluorescence using small and cost effective photo-detectors. To extract efficient persistent RTP, the control of the radiative rate from the lowest triplet excited state ($T_1$) ($k_p$), the nonradiative rate of intramolecular vibrational relaxation at room temperature (RT) from $T_1$ ($k_{nr}(RT)$), and the triplet quenching rate at RT caused by interactions with the ambient surroundings ($k_q(RT)$) is crucial. In the last five years, $k_{nr}(RT)+k_q(RT)$ have been suppressed in a variety of heavy atom-free conjugated crystals under ambient conditions, which has allowed electrons in $T_1$ to partly access the persistent RTP pathway with small $k_p$. However, for complex conjugated crystalline systems a key strategy to suppress $k_{nr}(RT)$ and $k_q(RT)$ as well as increase $k_p$ for the efficient persistent RTP is not found yet.

Here, we investigate electronic structures controlling $k_p$, $k_{nr}(RT)$, and $k_q(RT)$ of heavy atom-free conjugated molecular crystals showing persistent RTP. For the analysis of $k_q(RT)$, high resolution optical microscopy analysis showed that, despite a favorable molecular stacking, aromatic crystals with persistent RTP are characterized by small diffusion length and significant small values of the diffusion coefficient of triplet excitons. Quantum chemical calculations reveal a large overlap between the lowest unoccupied molecular orbitals but very small overlap between the highest occupied molecular orbitals (HOMOs). Inefficient electron exchange caused by the small overlap of HOMOs prevents triplet excitons from diffusing over long distances and consequently from quenching at defect sites inside the crystal or at the crystal surface, contributing to minimization of $k_q(RT)$. For $k_{nr}(RT)$, analysis using vibrational spin–orbit coupling (SOC) at RT indicates that the large decrease of $k_{nr}(RT)$ hardly decreases before and after crystallization for the heavy atom-free conjugated crystals. Cooperative analysis using the high resolution microscope as well as the quantum chemical calculation indicated that the large decrease of $k_{nr}(RT)+k_q(RT)$ is caused by not the decrease of $k_{nr}(RT)$ but the small decrease of $k_q(RT)$ owing to the small diffusion of triplet excitons at RT. For overall electronic structures to access the persistent RTP, the localization of HOMO due to moderate charge transfer (CT) conjugated structure or π-degeneracy of three dimensional highly symmetric conjugated structures might be a key. The HOMO localization sometimes induces moderate CT character in transitions between high-order singlet excited states ($S_m$) and the ground state ($S_0$) as well. Stronger SOC between the moderate CT characteristics of the $S_m$–$S_0$ transitions and local excited characteristics of the $T_1$–$S_0$ transition contribute to the large increase of $k_p$ independent of $k_{nr}(RT)$.

This is first overall analysis of $k_p$, $k_{nr}(RT)$, and $k_q(RT)$ of heavy atom-free conjugated molecular aggregates. This knowledge of electronic characteristics, $k_p$, $k_{nr}(RT)$, and $k_q(RT)$ of conjugated molecular crystals will be important for realizing efficient persistent RTP from a variety of conjugated molecular crystals.

2:00 PM *FF03.07.02* Fluorescent Polymersomes with Aggregation-Induced Emission Min-Hui Li; Chimie ParisTech, PSL University Paris, CNRS, France

Synthetic amphiphilic polymers have been developed since last decades for the purpose of forming self-assembled polymer vesicles (polymersomes) which mimic the structures of lipid vesicles (liposomes) and the properties of cells in some extent. Polymersomes are much more stable, more robust and less permeable than liposomes due to the high molecular weight of polymers. They show high loading capacity for both hydrophobic molecules entrapped in the membrane and hydrophilic ones encapsulated in the inner aqueous compartment. Another interesting feature of polymersomes is that their properties can be finely adjusted by the rich chemical design of the amphiphilic building blocks. Stimuli-activatable functions, fluorescence-generating moieties and targeting groups can be introduced to make smart polymersomes which are currently studied as a means of drug delivery and biomedical imaging. Our group has focused, since several years, on the tailor-design of smart polymersomes based on biocompatible and biodegradable building blocks. In this communication, I will present fluorescent polymersomes with aggregation-induced emission (AIE), which are made of polycarbonates, polyesters, polyurethanes, and N-substituted poly(amino acid)s containing AIEgens. Some of these AIE polymersomes are also stimuli-activatable and can be opened under CO$_2$- and pH-stimulation. We aim to develop innovative approaches to cell/tissue imaging and controlled drug delivery with *in situ* bio-distribution tracing.
References:

2:30 PM FF03.07.03
**Novel Dinuclear Ir(III) Complexes Based on Schiff Base as AIEgens and Their Applications** Dongxia Zhu; Northeast Normal University, China

A series of dinuclear Ir(III) Schiff base complexes have been synthesized and shown to exhibit both aggregation induced emission (AIE) and piezochromic luminescence (PCL) behaviour. We employed highly flexible Schiff base ligands to construct an AIE-active molecule with strong intermolecular interactions between the aryl rings in the aggregated or crystal state. The multifunctional dinuclear Ir(III) complexes are applied in second-level anti-counterfeit trademark, data encryption device and reversible monitoring device for volatile organic compounds.

2:45 PM FF03.07.04
**Synthesis of COF and MOF Colloids in Confined Bioinspired Conditions** Carlos Franco Pujante1, David Rodriguez San Migue1, Felix Zamora2 and Josep Puigmarti-Luis3; 1ETH Zurich, Switzerland; 2Universidad Autónoma de Madrid, Spain

Covalent Organic Frameworks (COFs) and Metal-Organic Frameworks (MOFs) are versatile porous materials with promising applications in a vast number of fields. Nevertheless, the high temperatures and the hazardous solvents required for the synthesis of these materials, among the poor solubility of the starting building blocks in the reaction media have provided a poor control over the size of the crystalline domains generated and in the morphology of COF/MOF crystals. These factors have limited the processability of COF and MOF hindering the integration in functional devices, as well as preventing their use in bio-systems. Therefore, great efforts are made in the field to understand and control the growth of COF and MOF crystals at length scales spanning from the nano- to the micrometer scale.1-3 Inspired by the confined spaces employed in living systems to constrain the crystallization processes, here we report for the first time a methodology for preparing stable aqueous colloidal solutions at room temperature of crystalline COF and MOF nanoparticles. This procedure allows downsizing these porous-materials beyond the previously reported limits, being able to, for example, synthesize MIL 100(Fe) nanoparticles under 20 nm. Additionally, thanks to their nanosized shape, we demonstrate the possibility to process these materials into a variety of micro- and millimeter-sized structures. We have demonstrated that by controlling the aggregation of the colloids, two-dimensional freestanding films and three-dimensional shapes can be accomplished. Among to improve their bioavailability, these results will undoubtedly open new possibilities for the implementation of COFs and MOFs into functional devices.

3:00 PM BREAK

3:30 PM *FF03.07.05
**Aggregation Induced Emission (AIE) of Cyclometalated Iridium Complexes—Applications for Highly-Selective Sensing of Anions and Neutral Molecules** Martin R. Bryce; Durham University, United Kingdom
Cyclometalated iridium complexes are of considerable interest due to their high photoluminescence quantum yields (PLQYs) at room temperature, physicochemical stability and long (several microseconds) PL lifetimes leading to their widespread applications in organic light-emitting diodes (OLEDs), as light-emitting electrochemical cells (LECs), biological labels, chemosensors for inorganic ions, data recording and security protection devices.

We will report that efficient Aggregation Induced Phosphorescence Emission (AIPE) of an ionic di-Ir(III) complex occurs when the counterion is exchanged specifically by perchlorate in aqueous media. As a result, a rapid, highly selective “turn-on” phosphorescent response to perchlorate is observed in aqueous media. X-ray crystallography, transmission electron microscopy and theoretical calculations support the photophysical data and the sensing mechanism.[1] We have also synthesized mono-iridium(III) complexes which possess aggregation-induced emission enhancement (AIEE) and detect the explosive 2,4,6-trinitrophenol (TNP) selectively with high quenching constants in aqueous media. The sensing mechanism has been systematically investigated by mass spectrometry, \(^1\)H and \(^19\)F NMR spectroscopy and X-ray crystal structure analysis. A hydrogen bonding interaction between TNP and the ancillary ligand of the Ir complex explains the high selectivity for TNP compared to other nitro-aromatics.[2]

References

**4:00 PM *FF03.07.06*  
The Modification of the Functionality of π-Molecules through the Structural Adjustment Zhen Li\(^1,2\); \(^1\)Wuhan University, China; \(^2\)Tianjin University, China

To construct π-molecules with different structures is one of the key points in the research field of opto-electronic materials. In many cases, the molecular structure not only affects the intramolecular π-conjugation, but also the intermolecular π-π stacking, to result in the different functionalities. In this talk, some typical examples will be presented to partially demonstrate the interesting different properties with minor or even ignorable structural difference.

References
8:15 AM FF03.08.01
Diffusional Behavior of Cu Nanocluster on Amorphous Carbon Surface Che-Wei Chang1, Guan-Rong Huang2 and Yu-Chieh Lo1; 1National Chiao Tung University, Taiwan; 2National Center for Theoretical Sciences, Taiwan

Growth of metallic nanowires is of practical importance for manufacturing integrated circuits in semiconductor industries. Copper (Cu) nanowires recently have been considered one of the promising materials in commercial application because of its superior electric/thermal properties. Experimental researches have shown that Cu nanowire growing on amorphous carbon (a-C) substrates is productive, but to our best knowledge the microscopic mechanism of how a-C film morphology affects Cu cluster diffusion remains to be unclear. Our molecular dynamics (MD) simulations of Cu cluster diffusion with a time scale of 300 ns laid down a prior knowledge for nanowire growth engineering, and showed that Cu nanoclusters with diameter of 1 was locally-diffused rather than globally-diffused on a 2.0 g/cm² a-C film. This suggested that the substrate roughness is crucial to the diffusion behavior. To further clarify the mechanism, we carried out the MD simulations with different cluster sizes, diffusion paths, and surface roughness. Through trajectory analysis of MD simulations, the relation among diffusion coefficients, cluster sizes and surface roughness was built, and showed that increasing surface roughness on a-C film may localize the trajectory of Cu cluster and reduce its size dependence on Cu cluster diffusion. Therefore, our simulation results may draw a new direction in nanowire growth engineering for controlling the diffusion pattern of Cu cluster by tuning the surface roughness of a-C substrate.

8:30 AM *FF03.08.02
Oriented Attachment—An Alternative Mechanism for the Growth of Nanostructures Younan Xia; Georgia Institute of Technology, United States

I will present a number of examples, in which oriented attachment of nanoscale building blocks rather than atomic deposition is responsible for the formation of noble-metal nanostructures with well-defined and controllable morphologies or shapes. Typical morphologies include nanocubes, wavy nanowires lined with planar defects, and dendritic nanostructures. The key requirement is the formation of a large number of nanoscale building blocks at the very beginning through homogeneous nucleation and the initiation of colloidal stability due to depletion of stabilizer from the surface of the building blocks. Due to the inclusion of planar defects, such nanostructures are attractive catalytic materials for a range of reactions and applications.

9:00 AM *FF03.08.03
Atomically Precise Metal Nanoclusters—From Synthesis to Assembly Rongchao Jin1 and Xin Zhang2; 1Carnegie Mellon University, United States; 2Pacific Northwest National Laboratory, United States

A major goal in nanoparticle synthesis is to control nanoparticles with atomic precision and reveal their total structures (i.e., core plus surface ligands). This talk will present some breakthroughs in metal nanoparticle research, including the atomically precise synthesis via solution chemistry and total structure determination by X-ray crystallography, as well as the assembly/crystallization of nanoparticles into hierarchical macroscale structures. By controlling nanoparticles with atomic precision, one can now reveal the long sought-after total structures of nanoparticles at the atomic level, such as the 1 nm Au25(SR)18, 1.7 nm Au133(SR)52, 2.2 nm Au246(SR)80 and Au279(SR)84 nanoclusters (where, SR = thiolate). These perfect nanoparticles (i.e. uniform structures and no defects) serve as model systems for addressing many fundamental questions that were previously difficult or impossible to tackle, such as the origins of chirality, periodicities in nanoparticle growth, structural isomerism, metallic-to-nonmetallic transition, single-atom level doping, atomic-level details of self-assembly, and many other mysteries at the nanoscale. The attainment of atomically precise nanoparticles will offer exciting opportunities in future studies on functional materials.

9:30 AM FF03.08.04
Size-Dependent Dynamic Structures of Gold Nanoparticles in CO Yang He1, Jin-Cheng Liu2, Langli Luo3, Jun Li4, Scott X. Mao4, Chongmin N. Wang1, Yang-Gang Wang5, Junfa Zhu6 and Yingge Du1; 1Pacific Northwest National Laboratory, United States; 2Tsinghua University, China; 3Tianjin University, China; 4University of Pittsburgh, United States; 5Southern University of Science and Technology, China; 4University of Science and Technology of China, China

Particle structural stability and mobility on the substrate critically affects their catalytic performances and
aggregation propensity. Here, by using atomic resolution in-situ environmental transmission electron microscopy, we reveal size-dependent structure dynamics of single gold (Au) nanoparticles on ceria in CO oxidation environment at room temperature. While large Au nanoparticles remain rigid in the catalytic working condition, ultrasmall Au clusters lose their intrinsic structures and become disordered, featuring vigorous structural rearrangements and formation of dynamic low-coordinated atoms on surface. *Ab initio* molecular-dynamics simulations reveal that the interaction between ultrasmall Au cluster and CO molecules leads to the dynamic structural response, demonstrating that the shape of the catalytic particle in the relative environment may totally differ from the shape under the vacuum condition. The present observation provides insight on the origin of superior catalytic properties of ultrasmall gold clusters. In addition, we also demonstrate the substrate effect on the mobility of Au nanoparticles. Surface steps on ceria can pin the motion of Au clusters; while Au nanoparticles readily moves and aggregates on amorphous SiO₂ substrate.

9:45 AM  FF03.08.05
**Quantum State Manipulation of Atomically Precise Gold Nanoclusters for Self-Assembled Nanomaterials**
*Tatsuya Higaki*, Meng Zhou and Rongchao Jin; Carnegie Mellon University, United States

Particle-based crystallization (PBC) is a useful approach to build up nanomaterials with desired functionality by controlling the properties of metal nanoparticles as building elements. Atomically-precise gold nanoclusters have gained broad interest as the building unit for functional nanomaterials because of their unique quantum state and related intriguing properties. These nanoclusters exhibit non-metallic electronic structure unlike bulk or plasmonic nanoparticle of gold, and their electronic structure is very sensitive to the size and structure of nanoclusters, even to the atomic level of difference. Recent advances in controllable synthesis allow chemists to tailor the size/structure of nanoclusters with atomic precision, providing new opportunities to control the functionality at single atom level. Further improvement of the tailoring method is expected through the investigation of some fundamental questions regarding the quantum state of nanoclusters. For example, the question on the transition from non-metallic to metallic state still remains elusive due to the difficulty in atomically precise preparation of nanoclusters near the transition size region (i.e., ~2 nm). The answer to this central question has been eagerly pursued because the exploration near the critical size can give us further insights into the formation of metallic bond and the origin of surface plasmons. The critical factors to tailor the non-metallic properties also have been investigated toward the general rule on the unprecedented size dependence of the nanoclusters’ functionality. In this presentation, I will discuss the successful identification of the transition from non-metallic to metallic state for Au nanoclusters at atomic level of precision, as well as the critical factors to atomically control the non-metallic properties below the transition regime. I will first talk about the synthesis and optical properties of atomically precise Au₂₇₉(SR)₈₄. Further characterization by ultrafast spectroscopy revealed metallic state of the Au₂₇₉ particle based on its laser power dependent dynamics, which is in contrast with the nonmetallic state of the previously reported Au₂₄₆(SR)₈₀. The abrupt transition with merely 33 metal atom difference is unprecedented, and it goes against >50 years of theoretical prediction of smooth transition.

I’ll also talk about atomic tailoring of Au nanoclusters to manipulate their non-metallic properties. I have synthesized Au₃₀(SR)₁₈ with an exotic crystalline phase: hexagonal close-packed (hcp) structure. The excited state dynamics of hcp-Au₃₀ is studied by ultrafast spectroscopy, and compared with other two nanoclusters with different crystalline phases: body-centered cubic (bcc) Au₃₈S₂(SR)₂₀ and face-centered cubic (fcc) Au₃₆(SR)₂₄. The observed lifetimes of hcp-Au₃₀ and bcc-Au₃₈ are 1 ns and 4.7 μs, respectively, demonstrating that controlling the crystalline phase of Au nanoclusters has significant effects on the excited state lifetime with three-orders-of-magnitude alteration.

The discovery of the non-metal to metal transition and the crystalline phase effect has provided critical insights into the quantum state of gold nanoclusters at atomic level. Further studies toward the direction will guide one to the strategy to engineer the functionality of nanomaterials by quantum state manipulation for applications in optoelectronic, catalysis, and biomedicine, as well as quantum computing.

10:00 AM BREAK

10:30 AM *FF03.08.06
**Manipulating Fluid Behavior for Material Assembly and Crystallization**  
*Yan Li*; Peking University, China

Solution process is often used in the assembly and crystallization of molecular or ionic substance and clusters. We developed several strategies making use of the behaviors of the liquid fluids to control the assembly and
crystallization. Both the temperature gradient and composition gradient were used to manipulate the Marangoni flow of the solution. By using a top-heating-bottom-cooling (THBC) setup, a steady Marangoni flow with a single vortex was created in the thin liquid film on solid substrates to facilitate the patterning of materials. By dropping dispersions of nanomaterials in water soluble organic solvents on the surface of water, Marangoni flow formed spontaneously and pushed the nanomaterials outside to form a thin film floating on water. We also studied the behavior of water-insoluble organic droplets on water surface. The three phase contact lines are tunable and thus the self-division process of the droplets was manipulated, which were further used to assemble materials. We show with the above examples that fluidics is a powerful tool in controlling the solution-based crystallization and assembly.

11:00 AM FF03.08.07
Formation and Self-Assembly of Graphene Nanoribbons and Nanosheets in Metals with 3D Epitaxy Lourdes G. Salamanca-Riba¹, Xiaoxiao Ge¹, Christopher Klingshirn¹, Oded Rabin¹ ¹, Manfred Wuttig¹, Daniel Cole² and Christopher M. Shumeyko²; ¹University of Maryland, United States; ²U.S. Army Research Laboratory, United States

Composites consisting of carbon nanostructures, such as graphene and carbon nanotubes, and metals are desirable for power transmission lines, interconnects and heat transfer applications due to the combination of excellent charge carrier mobility, thermal conductivity and mechanical strength of the carbon nanostructures and the high density of electrons in the metal. There have been metal/nanocarbon composites made by different methods, such as, chemical vapor deposition, friction stir, ball milling, and plasma spraying that have produced materials with enhanced hardness and tensile strength. However, in many instances the electrical and thermal conductivities of the metal/nanocarbon composites deteriorate. In the case of aluminum and its alloys, for example, very frequently these fabrication methods give rise to the formation of Al₄C₃ which is the culprit in the worsening of the electrical and thermal properties of the metal. We are using electrocharging assisted process (EAP) to assemble graphene nanoribbons inside a liquid metal. EAP consists of the application of a high DC current to a mixture of liquid metal and carbon particles. The current in the EAP pulls out atoms from the carbon particles which assemble into C-C chains that eventually form ribbons. The ribbons become crystalline with the same structure as graphene nanoribbons forming a 3D network in the matrix of the metal. The EAP not only crystallizes the ribbons into graphene structures but the ribbons become nucleation sites for the metal during solidification. Raman scattering, TEM and XPS show that the carbon nanostructures have primarily sp² bonding, they have a preferred orientation with the crystalline lattice of the metal and a nanocarbon crystallite size that increases with duration of the applied current. Al-C nanocomposites prepared with the EAP have shown 5 % increase in electrical conductivity as well as increase in the local stiffness, as measured by nanoindentation, compared to the pure Al alloys. Molecular dynamic simulation shows that graphene nanoribbons block the propagation of dislocations in the aluminum. Current AFM also indicates an increase in the local current from these samples compared to the parent aluminum alloy. Funded by DOE EERE under Award No. EE0008313.

11:15 AM FF03.08.08
Multi-Component Colloidal Constructs Designed through Self-Assembly of Defective Colloidal Molecules Mehdi Zanjani and Nishan Parvez; Miami University, United States

Engineering various types of structures through self-assembly of colloidal particles is a powerful approach in material design and processing. While simple colloidal building blocks, such as spherically symmetric particles, provide a number of well-known structures, more complex building blocks are needed to create novel structures with desired functionalities and tunable properties. Multicomponent building blocks such as colloidal molecules can provide a versatile platform for engineering new structures. However, in many cases, the synthesized colloidal molecules may end up suffering from ‘defects’ that are generally deemed to be an undesirable characteristic for multicomponent building blocks.

In this study, we use computational techniques to identify, investigate, and exploit self-assembly paradigms that are made possible through the use of defective colloidal molecules. Specifically, we study how defective units, which are typically missing one or two particles compared to the regular units, can be taken advantage of in order to build finite-size constructs that would otherwise be inaccessible. We further demonstrate different types of ordered superstructures that can be assembled through engineered directional interactions between defective and regular colloidal molecules. We use Molecular Dynamics (MD) and Brownian Dynamics (BD) simulations to study the thermodynamics and kinetics of self-assembly, and investigate the phase behavior of the resulting colloidal
constructs as a function of building block size and shape. This study will generate an understanding of different possibilities for self-assembly of defective multi-component colloidal building blocks and provide guidelines for future experimental studies to target new material design approaches.

11:30 AM *FF03.08.09
Self-Assembly of Anisotropic Nanocrystals Ou Chen and Yasutaka Nagaoka; Brown University, United States

Anisotropic nanocrystals with defined surface patchiness represent a unique class of building objects for constructing high-order architectural nanomaterials. When utilizing in assembly, on the one hand, anisotropic nanocrystals can display strong asymmetric interactions induced by the patchiness that may complicate the formation of ordered structures compared to the assemblies of isotropic building blocks. The same asymmetric interactions, on the other hand, can not only result in novel translational orderings, but also induce correlations between the atomic orientations of HNCs upon crowding, thus possibly dictate and control the atomic lattices within the assembled superstructure. In this talk, I will use several types of anisotropic 'patchy' nanocrystals as examples to demonstrate how they assemble into the unprecedented superstructures through the directional interactions among the building blocks under an enthalpy-driven condition. Both translational periodicities and orientational ordering of the final superstructural materials will be discussed. The dominating driving forces lead to the obtained architectures will be identified through molecular dynamics computer simulations and experimental results.

SESSION FF03.09: Aggregation-Induced Emission IV
Session Chairs: Mingdi Yan and Xin Zhang
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Room 313

1:30 PM *FF03.09.01
Antimicrobial Nanoaggregates and Nanoclusters Mingdi Yan; University of Massachusetts Lowell, United States

The increasing prevalence of drug resistance to the majority of existing antibiotics has generated a pressing global healthcare crisis. Certain highly resistant bacteria have acquired multiple mechanisms against all available antibiotics including the drugs of last resort. We are developing new strategies to combat antimicrobial resistance, for example, nanoantibiotics in the form of nanoaggregates or nanoclusters. In one study, we developed a modular synthesis of fluoroquinolone derivatives which are propeller-shaped. Upon precipitation into water, these compounds readily assembled into amorphous nanoaggregates that displayed enhanced luminescence. Furthermore, the nanoaggregates exhibited up to 2 orders of magnitude enhancement in the antibacterial activity. In the second example, our recent work on antimicrobial gold nanoclusters will be discussed. We have shown that the cluster structure has a profound impact on the antibacterial activity of the nanoclusters. Additionally, by modulating the ligand structure and composition, Gram-negative activity against Pseudomonas aeruginosa was enabled.

2:00 PM FF03.09.02
Robust Serum Albumin-Responsive AIEgen Enables Latent Bloodstain Visualization in High Resolution and Reliability for Crime Scene Investigation Zhaoyu Wang, Ben Zhong Tang and Chenchen Liu; The Hong Kong University of Science and Technology, Hong Kong

Bloodstains provide admissible information for crime scene investigators. The ability to resolve latent bloodstains that are commonly found in real scenarios is therefore pivotal to public security. Here, we report a facile approach for invisible bloodstain visualization based on the click reaction between serum albumin and tetraphenylethene maleimide (TPE-MI), an aggregationinduced emission luminogen (AIEgen). Compared to the widely adopted methods based on the harsh catalytic oxidation activity of hemoglobin, this working principle benefits from the specificity of the mild catalyst-free thiol–ene click reaction that improves the reliability and resolution. In addition, the mild conditions preserve DNA information and bloodstain patterns, and the excellent photophysical properties of the AIEgen afford high sensitivity and stability (>1 yr). Such an excellent performance cannot be achieved by

Final Program 1/13/2020  1578
conventional AIEgens and aggregation-caused quenching luminogens with similar structures. TPE-MI outperforms the benchmark luminol-based technique in visualizing latent bloodstains as showcased in two mock crime scenes: spattered blood track and transfer blood fingerprint. This disclosed method is an advancement in forensic science that could inspire future development of technology for bloodstain visualization.

2:15 PM FF03.09.03
New Emissive Organic-Inorganic Hybrid Nanomaterials Based on Organic Fluorophores Grafted onto Nanocrystals Using Aggregation Induced Emission Effect Olivier Margeat1, Pierre-Antoine Bouit2, Jörg Ackermann1 and Muriel Hissler2; 1CINaM-CNRS, France; 2ISCR, France

Light emitting materials are nowadays important compounds in various applications and for many of them the developments of emissive organic molecules have opened new opportunities for future technologies.[1] However, even though organic materials show strong emission, their solution-processing remains challenging and morphology control as nanoparticles suffers from large distributions over size and shape.[2] A possible way to enhance the emission of organic fluorophores and to control the size of solution-processable emissive nanoparticles at the same time is their grafting onto inorganic nanoparticle surfaces. In order to avoid the classical aggregation-caused quenching (ACQ) effect [3] when high concentrations of organic ligands are present on nanoparticle surface, the opposite effect, namely aggregation-induced emission (AIE) [4] is a promising approach to generate strong light emission. Indeed, in this case, the high concentration helps to freeze the motion of the molecules to reduce the non-radiative deactivations. In this work, we thus present the synthesis of AIE nanohybrids prepared via the grafting of organic AIE ligands onto high band gap semiconductor nanoparticles. These organic-inorganic core-shell systems are composed of ZnO nanospheres as core and AIE ligands as shell. The design of the efficient AIE fluorophores is based here on hydroxy-oxophosphole luminophores, which can easily be grafted on metal oxide semiconductors. The structure-properties relationships leading to the highly emissive properties have been investigated. Thanks to theoretical calculations and XPS analyses, we could show that the electronic coupling between the ligands and the ZnO nanoparticles leads to partial charge transfer from the ligand to the ZnO core. Additionally, we showed that the grafting of these phosphole ligands onto ZnO nanoparticles introduces first a strong emission enhancement by the suppression of the hydroxyl resonator of the hydroxy-oxophosphole function that is electronically coupled to the emitting pi-system. Furthermore, the restriction of intra and inter molecular motions, through cluster formation (in solution) or highly emissive thin film processing, is found to introduce a second emission enhancement due to AIE effect. Preliminary tests in LED configuration using these AIE nanohybrids as emissive layer were obtained, that could demonstrate the potential of this new class of nanomaterials to be used as electroluminescent material by taking the advantage of combining both the AIE effect and the transport properties of the inorganic scaffold.


2:30 PM BREAK

3:30 PM *FF03.09.04
Face-Rotating Polyhedra Xiaoyu Cao; Xiamen University, China

In nature, protein subunits on the capsids of many icosahedral viruses form rotational patterns, and mathematicians also incorporate asymmetric patterns into faces of polyhedra. By taking inspiration from nature and mathematics, we used pseudo-chiral truxene (Tr) and triazotruxene (TAT) derivatives as building blocks to construct a series of molecular polyhedra with rotational patterns on faces, which we term as Face-Rotating Polyhedra (FRP). FRP represent a special form of molecular chirality. The relative stability of these polyhedra enables separation by chiral HPLC and full characterization. We also investigated the assembly process and the kinetics of interconversion of the polyhedra by a combination of chiral HPLC, CD, MS and NMR. Tetraphenylethylene (TPE) and its derivatives, as well-known AIE chromophores, have been extensively studied due to their broad applications in many fields. TPE unit exhibits either M or P configuration in its propeller
structure when the free rotation of phenyl rings was hindered, making it a possible building block for FRP. We assembled TPE units with triamine to construct cubes or sandwich-like assemblies with “emergent” chirality and fluorescence. This study provides strategies to construct FRP by means of AIEgens, which can be applied in luminescent materials, chiral molecular recognition or asymmetric catalysis.

Reference:

4:00 PM FF03.09.05
Tetraphenylcyclopentadiene-Based Hyperbranched Polymers—Convenient Syntheses From One Pot “A4 + B2” Polymerization and High External Quantum Yields up to 9.74% in OLED Devices Yujun Xie1 and Zhen Li1,2; 1Institute of Molecular Aggregation Science, Tianjin University, China; 2Wuhan University, China

Through the A4 + B2 type Suzuki-Miyaura coupling reaction, hyperbranched polymers CP1, CP2, and CP3 were easily prepared, which exhibited high luminous efficiency in solution, neat film, and solid state as well as good thermal stability. When fabricated into organic light-emitting diodes (OLEDs) with mCP as host, the device based on CP1 demonstrated the good EL performance with external quantum efficiency (EQE) up to 6.36%. While the bipolar TADF host of CzAcSF was utilized instead of mCP, the driving voltage (at luminescence of 10 cd m-2) decreased from 5.7 to 4.4 V, and the EQE further increased to 9.74%, which was the highest EQE reported for hyperbranched polymers.

4:15 PM FF03.09.06
Multiscale Morphological Visualization of Semi-Crystalline Polymer by a Polymorphic AIE Marker Michidmaa Khorloo; Hong Kong University of Science and Technology, Hong Kong

Crystalline morphologies exist in many synthetic and natural macromolecules and are believed to play an essential role in biological phenomena and materials science. Despite the high performance of fluorescence imaging in spatial morphology characterization in life science, high-contrast mapping across different microstructures in solid polymers is challenging. In this work, we demonstrated a strategy to impart aggregation-induced emission (AIE) and polymorphic characteristics in a single luminescent system, whose polymorphic crystalline states with distinct emission are generated selectively in amorphous and crystalline phases of a polymer to light up the whole morphology. High compatibility between the AIEgen and polymer matrix allows the sensitivity of the AIEgen to be visually shown as different emissions. Consequently, information of the polymer morphology (crystalline and amorphous phases) is transformed into distinct fluorescence colors, allowing a single AIE molecule as a fluorescent marker for multiscale visualization of polymer morphologies in terms of amorphous and crystalline phases distribution, quantitative polymer crystallinity measurement, and spatial morphological arrangement. The proposed strategy provides a correlation between microscopic morphologies and macroscopic optical signals, opens an avenue of fluorescence imaging in materials science.

4:30 PM FF03.09.07
Aggregation-Induced Enhancement of Phosphorescence via Molecular Self-Assembly in Small Molecule Platinum Acetylides William Mullin; Tufts University, United States

The development of rational design principles for electronic materials is crucial to ensure efficient device performance and favorable optical properties. Small molecule phosphors are becoming increasingly important for OLEDs, optical sensing, and display technology. Heavy transition metals such as palladium and platinum enhance spin-orbit coupling of chromophores by mixing the energy levels of the singlet and triplet states, allowing for faster
intersystem crossing and a population of excited triplet states. Solid-state phosphorescence, however, is susceptible to aggregation-caused quenching (ACQ) through non-radiative processes, which significantly diminish phosphorescent quantum yield of neat solids. Herein, we present progress on an approach to ameliorate this problem by utilizing structural components of the molecules themselves to suppress chromophore aggregation and prevent ACQ. Specifically, we demonstrate aggregation induced enhancement of phosphorescence using a series of ester substituted phosphorescent platinum acetylides. Perfluorinated arene pendant groups on these chromophores encourage coplanar aromatic stacking interactions between adjacent molecules, insulating excited chromophores from non-radiative quenching typically associated with aggregation of phosphors. Fluorinated compounds show strong solid-state phosphorescence, which we attribute to fluoroarene-arene stacking interactions that prevent inter-chromophore aggregation, as demonstrated through their X-ray crystal structures. In contrast, non-fluorinated compounds show very little solid-state phosphorescence, a consequence of cofacial chromophore aggregation. This work highlights the potential broad utility of the non-covalent stacking interactions of fluorinated arenes in the development of solid state phosphors.

SESSION FF03.10: Particle Aggregation IV
Session Chairs: Qian Chen, Litao Sun and Xin Zhang
Thursday Morning, December 5, 2019
Hynes, Level 3, Room 313

8:00 AM FF03.10.01
Analysis and Control of CeO2 Mesocrystal Formation in Continuous Hydrothermal Synthesis System Takaaki Tomai1, Andrzej-Alexander Litwinowicz2, Akira Yoko3, Gimyeong Seong4, Seiichi Takami5, Shunsuke Asahina6, Xiaodong Hao7 and Tadafumi Adschiri2; 1Tohoku University, Japan; 2Nagoya University, Japan; 3JEOL, Japan; 4Shaanxi University of Science & Technology, China

Mesocrystals formed from assembled nanoparticles with ordered alignment have attracted much attention as promising materials in various engineering fields, such as photocatalysis, energy storage, and optical/magnetic application including metamaterials. Hydrothermal method with flow-type reactor can produce not only nanoparticles, but also mesocrystals, continuously [1]. However, the mesocrystal structure/size is difficult to control because the structural formation mechanism of the secondary structure of nanoparticles has not been clarified. In this study, to investigate the mesocrystal formation process, we conducted time-resolved experiments in the order of seconds using flow-type hydrothermal reactor [2]. We employed L-glutamic-acid-modified CeO2 nanoparticle as the building block of mesocrystal. The cerium nitrate solution with L-glutamic acid was pumped into the flow-type reactor, continuously, and mixed with preheated water at a T-shaped mixer. The temperature and pressure in the reactor tube was maintained at 548 K and 25 MPa. The reaction time was varied by altering the length of the reactor tube. In the hydrothermal reactor, the precursor reacts to form the L-glutamic-acid-modified CeO2 nanoparticles and the produced nanoparticles assemble by the L-glutamic acid as a glue to form mesocrystals. The snapshots of the produced materials during formation process of mesocrystal were obtained by HRTEM and XRD observations for the clusters synthesized from 0.7 s to 8.0 s. Here, we found that the primary nanoparticles in the loose agglomeration order themselves to form a cubic CeO2 mesocrystal. At a reaction time of 0.7 s, the truncated octahedral CeO2 nanoparticles (ca. 20 nm) aggregated in spherical shape (ca. 72 nm) with polycrystal structure. However, the structure of the cluster changed from spherical to cubic in less than 8.0s. The diffraction pattern of the cubic clusters gives a crystalline structure resembling that of a single crystal by rearrangement of the primary building blocks. These formation dynamics can be regarded as the analogy to the conventional crystalline particle formation. In the case of crystalline particle formation, nucleation occurs from monomers via non-crystalline droplet, followed by crystal growth with monomer diffusion to the crystal surface. In the case of the mesocrystal formation in this system, non-ordered agglomeration of primary nanoparticles firstly formed, followed by orientation of primary nanoparticles and mesocrystal growth with primary particle attachment. Consequently, the agglomeration of nanoparticles can be regarded as nucleation, and the orientation and growth can be regarded as the crystal growth, which can be seen in the conventional crystalline particle formation.

Based on the idea that nanoparticles behave like monomers in conventional particle formation, we conducted size
control of mesocrystal. In conventional particle formation, the nanoparticle concentration and the solvent properties affects the nucleation and crystal growth, determining particle size. For example, using the same flow-type hydrothermal reactor, the unmodified CeO$_2$ nanoparticles became smaller with lower precursor concentrations and the addition of ethanol as antisolvent. On the other hand, in the case of mesocrystal formation from L-glutamic-acid-modified CeO$_2$ nanoparticles, the mesocrystal size also decreased with the decrease in the precursor concentration and with addition of the ethanol, antisolvent.


8:15 AM FF03.10.02
**Understanding the Formation of PbSe Honeycomb Superstructures by Dynamics Simulations** Giuseppe Soligno and Daniel Vanmaekelbergh; Utrecht University, Netherlands

PbSe honeycomb superstructures, recently obtained by the self-assembly of PbSe nanocrystals (NCs) at fluid-fluid interfaces [1], have attracted a great interest since their predicted optoelectronic properties should combine the virtues of graphene with those of semiconductors [2]. However, their formation mechanism is still far from understood [3].

With a new coarse-grained molecular dynamics model we are able to reproduce the self-assembly of PbSe NCs in honeycomb and other observed 2D superstructures [4]. Our results shed light on the superstructure formation dynamics by identifying and quantifying the key parameters that drive the NC self-assembly into one or another superstructure. In particular, we show how the obtained NC superstructure depends on an intricate interplay between the interface-adsorption forces experienced by the NCs at the fluid-fluid interface and short-range electrostatic forces between the NCs. We also show indications that our model can be applied to study the formation and stability of defects in the self-assembled superstructures.


8:30 AM *FF03.10.03
**Real Time Imaging of Dynamic Behavior of Individual PbSe Nanocrystals During Superlattice Phase Transformations** Haimei Zheng$^{1,2}$; $^{1}$Lawrence Berkeley National Laboratory, United States; $^{2}$University of California, Berkeley, United States

PbSe nanocrystals have attracted considerable attention because of their potential applications in solar cells, light emitting diodes and field effect transistors. Monodisperse nanocrystals form superlattices with emergent collective properties. Although there have been intensive studies on PbSenanocrystal superlattices, how individual nanocrystals change and how they interact with each other during superlattice transformations are largely unknown. Direct observation with high spatial and temporal resolution using transmission electron microscopy (TEM) provides the opportunity to address these questions. We developed high-resolution carbon-film liquid cells, which allow to directly observe PbSe nanocrystal superlattice transitions using TEM. A monolayer of hexagonal superlattice of oleate-capped PbSenanocrystals is used as the starting materials. During its transformation into a square lattice due to ligand displacement, we observed an unexpected phenomenon that PbSe semiconductor nanocrystals can drastically change shape depending on the chemical environment. For example, ethylenediamine (EDA) induced oleate removal increases the nanocrystal dipole-dipole interactions, triggering the large shape changes and rapid nanocrystal fusion. After the ligands are removed, PbSe nanocrystals experience drastic directional shape deformation when the spacing between two nanocrystals reaches 2–4 nm. Moreover, the deformation can be completely recovered when two nanocrystals move apart or it can be retained when they attach. We have also performed the superlattice phase transition in pure ethylene glycol (EG) and found nanocrystals maintain their original shape during self-assembly, the resulting superlattices are more uniform and less defective.
The large deformation, which is responsible for the structural defects in the epitaxially-fused nanocrystal superlattice, likely arises from inter-nanocrystal dipole–dipole interactions. This has been further testified by our molecular dynamics (MD) simulations.

References:

9:00 AM *FF03.10.04
Direct Imaging of Layer-by-Layer Growth in a Colloidal Nanoparticle Superlattice Qian Chen; University of Illinois at Urbana-Champaign, United States

Layer-by-layer growth has been a hallmark of atomic crystallization to produce flat films of semiconductors or alloys for device applications, where a new surface layer starts to develop only after the preceding layer is complete. Here we show the direct imaging of nanoparticles crystallizing in a layer-by-layer fashion to large-scale superlattices with flat surfaces, utilizing the protocols we have developed in low-dose liquid-phase transmission electron microscopy (TEM). Single-particle tracking of the real-space, real-time TEM movies not only elucidates the structure and surface morphology of the superlattice during growth, but also enables the measurement of key parameters associated with layer-by-layer growth that are otherwise inaccessible. Coupling the in-situ observation with molecular dynamics simulation, we reveal the energetic origin of the layer-by-layer growth in our system by mapping the free energy landscape. Changing the pairwise interparticle interaction leads to other atomic crystallization pathways to occur in the same system, including roughening transition and coalescence. These atom-mimicking crystal growth pathways have hardly been realized in micron-sized colloids, suggesting a fundamental importance of the length and time scale associated with nano-sized building blocks.

9:30 AM FF03.10.05
Synthesis of Cuboctahedral CeO2 Nanoclusters and Their Assembly in Cuboid Nanoparticles by Oriented Attachment Using Selective Ligand Desorption Edson R. Leite1,2, Içamira C. Nogueira3, Elson O. Longo2, Juan Andres4 and Santiago Maya-Johnson2; 1Centro Nacional de Pesquisa em Energia e Materiais (CNPEM), Brazil; 2Federal University de Sao Carlos, Brazil; 3Federal University of Amazonas, Brazil; 4Universitat Jaume I, Spain

Controlled and predictable growth through oriented attachment (OA) mechanism is still a challenge. Here, we describe a simple approach to control the OA process through selective ligand scavenging from the {100} facets of CeO2 nanoclusters. Aggregates of these nanoclusters smaller than 10 nm with controlled cuboid shape were obtained. For the synthesis of the cuboctahedral CeO2 nanoclusters, we developed a solvent-controlled synthesis approach based on a nonhydrolytic sol-gel process and used an ester aminolysis reaction to control ligand scavenging from the {100} facets. First-principle calculations allowed us to understand and interpret, at the molecular level, the effects of shape control on the growth process. Fine-tuning of the desired morphologies can be achieved by controlling the values of the surface energies, which leads to the formation of morphologies that the classic growth process does not allow. The methodology described in this work, for the controlled assembly of CeO2 nanoclusters, may be relevant for the investigation of self-assembly processes of other metal oxides as well as for other types of inorganic nanoparticles in future work, which means that it brings new insight for nanostructure design and controlled synthesis.

9:45 AM FF03.10.06
Toward Total Synthesis of Thiolate-Protected Metal Nanoclusters Jianping Xie; National University of Singapore, Singapore

Total synthesis, where desired organic- and/or bio-molecules could be produced from simple precursors at atomic precision and with known step-by-step reactions, has prompted centuries-lasting bloom of organic chemistry since its conceptualization in 1828 (Wöhler synthesis of urea). Such expressive science is also highly desirable in nanoscience, since it represents a decisive step towards atom-by-atom customization of nanomaterials for basic and
applied research. Although total synthesis chemistry is less established in nanoscience, recent years have witnessed seminal advances and increasing research efforts devoted into this field. In this talk, I will discuss our recent work on introducing and developing total synthesis routes and mechanisms for atomically precise metal nanoclusters (NCs). Due to their molecular like formula and properties (e.g., HOMO-LUMO transition, strong luminescence and stereochemical activity), atomically precise metal NCs could be regarded as “molecular metals” (or metallic molecules / molecular-like metals), holding potential applications in various practical sectors such as biomedicine, energy, catalysis and many others. More importantly, the molecular-like properties of metal NCs are sensitively dictated by their size and composition, suggesting total synthesis of them as an indispensable basis for reliably realizing their practical applications.

10:00 AM BREAK

SESSION FF03.11: Aggregation-Induced Emission V
Session Chairs: Paul McGonigal and Xin Zhang
Thursday Morning, December 5, 2019
Hynes, Level 3, Room 313

10:30 AM *FF03.11.01
Time-Resolved Spectroscopy Studies to Better Understand Aggregation Induced Emission Properties and Phenomena Lili Du and David Lee Phillips; The University of Hong Kong, China

The aggregation-induced emission (AIE) phenomenon was first reported by Tang and coworkers in 2001 and this new phenomena has been utilized to revolutionize biological and optoelectronic materials for use in various scientific fields over the past two decades. Due to the importance of AIE, thousands of publications have been reported on developing new efficient AIE luminogens (AIEgens) and implementing them for practical applications. Although conical intersection, E/Z isomerization, proton transfer, charge transfer, intra- and inter molecular restrictions have been considered as the main reasons for the phenomenon of AIE to occur in a number of different systems, there have been few direct pieces of evidence reported to support these hypotheses. The time-resolved spectroscopy techniques are considered to be powerful tools for studying and characterizing the mechanisms of AIE materials. Here, we report the use of transient absorption and time-resolved resonance Raman to study a number of TPE-based derivatives with varying structural rigidity and AIE properties. This allowed an examination of the direct correlation between the state-dependent coupling motions and inhibited fluorescence. Our new results prove the existence of photocyclized intermediates in several systems. We demonstrate that the dominant non-radiative relaxation dynamics i.e. formation of an intermediate or rotation around the elongated C=C bond, is responsible for the AIE effect, which is strongly structure-dependent but not related to structural rigidity. In addition, femtosecond transient absorption spectroscopy was also employed to demonstrate that the excited state aromaticity inversion for the non-aromatic annulene derivative of cyclooctatetraene causes the typical AIE phenomenon for this system in spite of its rotor-free structure. Therefore, results from the study of the photophysical and photochemical mechanisms of AIEgens will be instructive to guide the tailoring and further development of more efficient luminogens in the future.

11:00 AM *FF03.11.02
Excited-State Aromatic Interactions in the Aggregation-Induced Emission of Molecular Rotors Paul R. McGonigal; Durham University, United Kingdom

Small, apolar aromatic groups, such as phenyl rings, are commonly included in the structures of fluorophores to impart hindered intramolecular rotations, leading to desirable solid-state luminescence properties. However, they are not normally considered to take part in through-space interactions that influence the fluorescent output. This presentation will detail (Figure 1) the photoluminescence properties of a series of phenyl-ring molecular rotors bearing three, five, six, and seven phenyl groups around carbacyclic cores. The fluorescent emissions from some of the rotors are found to originate, not from the localized excited state as one might expect, but from unanticipated through-space aromatic-dimer states. We demonstrate that these relaxed dimer states can form as a result of intra-
or intermolecular interactions across a range of environments in solution and solid samples, including conditions that promote aggregation-induced emission. Computational modeling also suggests that the formation of aromatic-dimer excited states may account for the photophysical properties of a previously reported luminogen. These results imply, therefore, that this is a general phenomenon that should be taken into account when designing and interpreting the fluorescent outputs of luminescent probes and optoelectronic devices based on fluorescent molecular rotors. In order to gain deeper insights, we have also taken a ‘minimum modification’ strategy to modify the conjugation and geometries present for one of the rotors, sym-heptaphenylcycloheptatriene.[2]

References

11:30 AM FF03.11.03
A General Way to Build Plasma-Membrane Specific Probes with Aggregation-Induced Emission Lei Shi, Yan-Hong Liu and Kun Li; Sichuan University, China

The abnormality of plasma membrane (PM) is an important biomarker for cell status and many diseases. Therefore, visualizing PM is crucially important in the fields of physiology, pathology and pharmacology1-2. Herein, we provide an effective way to generate dyes that suitable for PM imaging with easy operation (one step), rapid staining, good biocompatibility and high-fidelity imaging. Four compounds with aggregation-induced emission (AIE) characteristics were presented by changing the length of alkane chain and electrostatic interaction to investigate the relationship between amphipathy and positive charges as well as the imaging effect including specificity, staining period and dyeing continuity and retention. Besides, the 2D/3D imaging experiments indicated the high specificity of PM and ultrafast imaging without washing (2D at the second-level, 3D around 1 hour). More importantly, the probe Pent-TMP could light up the PM in complex systems (brain tissue and live zebrafish). For the first time, we have captured single erythrocyte in brain tissue by fluorescence. Besides, Pent-TMP could stain the PM of the zebrafish in vivo which typical probes can hardly do1. With these advantages, we hope that this method of constructing ultrafast and easy-operation PM Specific Probes will be helpful to molecular design, medicine and biology.

11:45 AM FF03.11.04
Unexpected Room Temperature Phosphorescence from a Non-Aromatic, Low Molecular Weight, Pure Organic Molecule through the Intermolecular Hydrogen Bond Manman Fang1,2 and Zhen Li2,1; 1Tianjin University, China; 2Wuhan University, China

Efficient pure organic room temperature phosphorescence (RTP) materials have drawn considerable attention. So far, most pure organic RTP molecules are aromatic compounds, and nonconjugated molecules are really scarce. The only few reported non-aromatic organic phosphorescence materials are polymers without confirmed subtle structures, and there are no reports concerning non-aromatic organic small molecules with persistent RTP. Here, we report an example of a pure non-aromatic organic small molecule, cyanoacetic acid, that shows unexpected persistent RTP behavior with RTP lifetime as long as 862 ms. According to the CAA crystal and theoretical calculations, the presence of strong intermolecular hydrogen bonds is the key factor for its persistent RTP effect. This discovery demonstrates a clear relationship between the molecular structure, packing mode and RTP effect in the non-aromatic system, which will largely extend the current pure organic RTP systems to deeply investigate the origin of light emission
Exploring How Bimetallic Nanoparticles Evolve—Growth, Etching and Catalysis

Bimetallic nanoparticles are commonly used as catalysts in a broad range of industrially relevant reactions. To enable the rational design of catalysts with better performance, it is necessary that we understand the relationship between a nanoparticle’s structure and its catalytic properties. However, such insights have to be obtained from catalysts under reaction conditions because the nanoparticles can exhibit dynamical structures that do not exist outside the reactive environment. TEM has always been a powerful technique for studying the detailed structure of nanoparticles. Recent developments in in situ environmental TEM, now allow us to study nanostructures within gas and liquid environments with TEM, and probe their formation pathways during the synthesis and reaction kinetics during the catalysis in real-time with nanometer resolution.

In the first part of my talk, using in situ liquid phase TEM, I will describe how bimetallic nanoparticles with different architectures form in solution. By directly visualizing the growth and electrochemical etching of such nanoparticles, I will show how bimetallic nanoparticles form under different physical and chemical environments. Next, using in situ gas phase TEM imaging, I will discuss the catalytic performance of these bimetallic nanoparticles and describe how these nanoparticles exhibit surprising structural changes during catalytic reactions. Using Pt-Ni bimetallic nanoparticles as a model system, I will show that these nanoparticles evolve differently in reactive gas conditions depending on the starting structure of the nanoparticle.

These insights into the evolution of nanoparticles both during their synthesis and application are important for the rational design of nanomaterials with tailored properties.

Observing the Early Stages of Protein-Metal-Organic Framework Formation by Cryotransmission Electron Microscopy

Materials that combine synthetic and biological nanotechnologies are inspired by Nature’s tight control over organic-inorganic interactions, such as in biomineralization, to assemble biological nanomaterial hybrids with optimized performance. Although engineering synthetic-biological hybrids would accelerate the development of next-generation materials, there are currently no design rules to effectively create these synthetic/biomimetic systems. This is largely due to a gap in knowledge of the interface between biological-synthetic materials and the fundamental interactions that govern their formation. Here, we establish an initial understanding of the interactions between bovine serum albumin (BSA) protein and metal-organic framework ZIF8 using electron microscopy and reveal complex growth mechanisms that govern the final BSA/ZIF8 single-crystal nanomaterial. By varying the amount of BSA incorporated into an in-situ ZIF8 synthesis, we observe significant control in the final crystal size, morphology, and porosity ranging from well-faceted dense crystals to porous crystals with rough surfaces. Using time-resolved cryotransmission electron microscopy, we found that these structural differences stem from the simultaneous formation of two amorphous metastable phases and their dynamic interactions in the early stages of BSA/ZIF8 formation. One phase is characterized by well-defined primary particles (~ 8 nm) and the second phase is characterized by BSA/ZIF8-precursor clusters that aggregate into branched networks (~ 1 µm). Lattice-resolution cryoTEM demonstrates an important interplay between these two phases during crystallization and growth through particle aggregation mechanisms. Real-time observation of the transition between these phases is further probed with in-situ liquid TEM. The presence of these amorphous phases and their dynamic interactions to form the final BSA/ZIF8 crystals provides an understanding of protein-MOF crystal formation that is analogous with established biomineralization mechanisms.

Conjugated Polymer Nanowires Based Thermoelectric Materials

One-dimensional polymer nanowires with highly ordered structure have fast carrier transport which is beneficial for improving polymer thermoelectric (TE) power factors. Tuning the nanowire structure and interfaces in conjugated polymer nanowires may lead to unique density of states and thus thermoelectric transports. In this talk, I will review our recent works that involve the structure and interface manipulation of conjugated polymer nanowires for higher
thermoelectric performance, the possible TE enhancement mechanisms will be discussed as well.

2:30 PM *FF03.12.04
Exploring the Surface Effects of Sub-10-nm Materials from Atomic Scale Litao Sun; Southeast University, China

With the development of semiconductor technology, the 10 nm feature size of fabrication is already achieved. It is thus quite essential to explore more precise nanofabrication and characterization method to evaluate the shape/structure stability and possible new properties of sub-10nm material components, especially under external stimuli such as strain, electric, or thermal fields. Along with the reduction of dimensions, the surface-to-volume ratio of the materials increases. For a 10 um particle, only about 0.036% of atoms occupy the surface positions, and the percentage rise to ~36% and ~62% for a 10 nm and a 6 nm particle respectively. Furthermore, surface atoms are preferably reconstructed for adapting their geometrical and electronic structure to the environment. Thus, the surface structure begins to dominate material properties ranging from electronic and structural aspects when the characteristic dimension is reduced to sub-10 nm. Here we review our recent progress in atomic resolution nanofabrication and dynamic characterization of sub-10nm individual nanostructures and nanodevices based on the idea of "setting up a nanolab inside a transmission electron microscope".

3:00 PM BREAK

SESSION FF03.13: Aggregation-Induced Emission VI
Session Chair: Xin Zhang
Thursday Afternoon, December 5, 2019
Hynes, Level 3, Room 313

3:30 PM *FF03.13.01
Aggregation-Dependent Emissions and Cytotoxicity of AIEgens Deqing Zhang; ICCAS, China

AIEgens including silole and tetraphenylethylene show abnormal emissive behavior. They are almost non-emissive in the well-dispersed states, but their emissions are switched on upon aggregation. By taking advantage of this unusual emissive property, AIE gens have been successfully employed for chemo-/biosensing, fluorescence imaging and photodynamic therapy. In this presentation, I will show that the emission colors and efficiencies of AIEgens are affected the aggregation of AIEgens in terms of intermolecular interactions and orientations. Moreover, I will discuss the dependence of cytotoxicity on the size and surface zeta potential of aggregates of AIEgens.

References

4:00 PM *FF03.13.02
Understanding AIE with Theory and Computations Lluis Blancafort; Universitat de Girona, Spain

AIE has come a long way since its discovery almost 20 years ago. However, some questions about the basic mechanisms still remain open, and theory and computations can be very helpful in providing new fundamental insights. In this contribution we will center on how work from our group has contributed to a better understanding of the fundamental processes at the molecular level, both in solution and in the aggregate phase. We will center on two subjects: first, introduce our Restricted Access to a Conical Intersection (RACI) model to explain the photophysics/photochemistry in solution and in the crystal and discuss some examples (see for a review: Crespo-Otero et al, Chem. Asian J. 2019, 14, 700); and second, discuss some of the factors that affect morphochromism and, more in general, the emission color of AIEgens and their dependence on the aggregate form.
Mechanoluminescence (ML) is a light-emitting process induced by mechanical stimuli, such as grinding, rubbing, or shaking, which has attracted extensive attention because of its potential in displays, lighting, bioimaging, and stress-sensing applications. Regardless of its long history, which stems from the first report on sugar by Francis Bacon in 1605, reports on organic ML luminogens remain limited in number, partially because of a lack of reliable guidance and unclear inherent mechanisms. On the other hand, as the most investigated light-emitting process, photoluminescence (PL) is well-understood and has made great contributions to research involving other kinds of emitting processes, including electroluminescence (EL) and chemiluminescence (CL). Based on these success stories, and the previous reported ML luminogens, we decided to explore the unknown ML excitation process using well-understood PL as a template.

References

Highly conductive molecular wires are an important component for realizing molecular electronic devices and have to be explored in terms of interactions between molecules and electrodes in their molecular junctions. Here, we report new molecular wire junctions (e.g., Co(II)(tpyphS)2–AuNP–Co(II)(tpyphS)2) to enhance charge transport through gold nanoparticle (AuNP)-linked double self-assembled monolayers (SAMs) of cobalt (II) bis-terpyridine molecules (e.g., Co(II)(tpyphS)2). Electrical characteristics of the double-SAM devices are explored in terms of the existence of AuNP. The AuNP linker in the Co(II)(tpyphS)2–AuNP–Co(II)(tpyphS)2 junction acts as an electronic

References

8:15 AM FF03.14.02
Nanoparticle Linker-Controlled Intermolecular Charge Transports in Double Molecular Monolayers
Sohyeon Seo1 and Hyoyoung Lee1,2; 1Sungkyunkwan University, Korea (the Republic of); 2IBS, Korea (the Republic of)

Highly conductive molecular wires are an important component for realizing molecular electronic devices and have to be explored in terms of interactions between molecules and electrodes in their molecular junctions. Here, we report new molecular wire junctions (e.g., Co(II)(tpyphS)2–AuNP–Co(II)(tpyphS)2) to enhance charge transport through gold nanoparticle (AuNP)-linked double self-assembled monolayers (SAMs) of cobalt (II) bis-terpyridine molecules (e.g., Co(II)(tpyphS)2). Electrical characteristics of the double-SAM devices are explored in terms of the existence of AuNP. The AuNP linker in the Co(II)(tpyphS)2–AuNP–Co(II)(tpyphS)2 junction acts as an electronic
contact that is transparent to electrons. The weak temperature dependency of the AuNP-linked molecular junctions strongly indicates sequential tunneling conduction through the highest occupied molecular orbitals (HOMOs) of Co(II)(tpyphS)₂ molecules. The electrochemical characteristics of the AuNP–Co(II)(tpyphS)₂ SAMs reveal the fast electron transfer through molecules linked by AuNP. Density functional theory (DFT) calculations reveal that the molecular HOMO levels are dominantly affected by the formation of junctions. The intermolecular charge transport, controlled by the AuNP linker, can provide a rational design for molecular connection that achieves a reliable electrical connectivity of molecular electronic components for construction of molecular electronic circuits.

8:30 AM FF03.14.03
3D Patterning of Nanoparticles by Molecular Stamping Yan Xiong¹, Shize Yang², Ye Tian¹ and Oleg Gang¹;²;¹Columbia University, United States; ²Brookhaven National Laboratory, United States; ³Nanjing University, China

Molecular patterning of nanoparticles can allow prescribing inter-particle binding sites, and that can permit creating tailored building blocks for assembly of targeted nanoparticle clusters and large-scale periodic nano-organizations. However, establishing a platform for rational patterning of nanoparticles has been challenging. We have developed a so-called Molecular Stamping approach for 3D nanoparticle patterning by templating target particles with designed molecular patches using DNA frame. In this method, molecular stamps, located at the prescribed locations of frame, can be engaged for transferring distinctive molecules onto different sites of nanoparticle surface. Our approach allows for creating molecular patches with a single molecule control and with same or different binding affinities. We applied the developed method to generate planar and 3D arrangements of molecular patches on nanoparticles, and investigated factors affecting pattern formation and its resolution. The developed approach was used to create nanocluster architectures containing nanoparticles of different sizes and from different materials. Electron microscopy and tomography were utilized to reveal spatial arrangements of molecular patches and the factors contributing to the patterning process.

8:45 AM FF03.14.04
Nonlinear Optics with Colloidal Superparticles Having Metamaterial Shell Joong Hwan Bahng¹, Saman Jahani², Douglas G. Montjoy³, Nicholas A. Kotov² and Alireza Marandi¹; ¹California Institute of Technology, United States; ²University of Michigan, United States

Colloidal nanoparticles have become essential components to a broad spectrum of scientific fields, accredited to their superior and tunable physicochemical properties exclusive to the nanoscale dimensions. For example, their exceptional surface to volume ratio, diffusion rate and dispersion stability markedly increase their reactivity and bioavailability. In addition, the colloidal nanoparticles exhibit diverse electromagnetic responses whose modes, intensities and spectral locations are readily adjusted according to the engineering needs. As such, colloidal nanoparticles have become integral optical-actuating platforms in catalytic reactions, targeted drug delivery, in vivo medical imaging and sensing. On the other hand, their ultraviolet and visible spectrum requirement for photo-stimulation poses intrinsic limitations due to poor light penetration into the reaction media and the biological tissues. Delivering optical energy through the ambient media within its specific transparency window that could trigger the target responses may immensely broaden the scope of the operation while enhancing its procedural compatibilities and efficiencies. Hence, robust in situ colloidal optical nonlinear transducer capable of all wavelength accessibility with practical conversion efficiencies could provide important solutions to these challenges. Here, we demonstrate a versatile pathway to obtain second harmonic generation (SHG) of light with practical conversion efficiencies from dielectric ψ(2) nanostructures by configuring them into a colloidal superparticle. Through one-pot chemical synthesis, we were able to blend multiple materials types of different constitutive properties, shapes and dimensions into a single colloidal superstructure in a hierarchical manner. An array ZnO nano-rods, a ψ(2) material, are vertically aligned to construct a corrugated shell around a dielectric SiO₂ sphere. Extensive control over the chemical synthesis of the ZnO nanostructures enabled us to transform the nanotopographic landscape into a shell of optical metamaterials having 2nd order nonlinearity (ψ(2) meta-shell). Our analysis show that the ψ(2) meta-shell exhibits radial graded index and anisotropy profile in its constitutive properties. The effective optical responses from the ψ(2) meta-shell is engineered in the linear regime to maximize the optical nonlinear effects in the ψ(2) meta-shell, the site of nonlinear conversion. We have experimentally observed strong enhancement of SHG in the meta-shell superparticle. The FDTD simulation revealed 10⁴ enhancement in the conversion efficiency between the meta-shell superparticle and a ZnO nano-rod. Furthermore, the SHG generated by the meta-shell particle is highly localized within the nanoscale confines, making it a desirable platform for photo-chemistry, photo-medicine, biotechnology and bio-photonics.
While the current demonstration focuses on the second harmonic generation, our colloidal meta-shell superstructure has the ingredients necessary for a cohort of optical nonlinear conversion processes.

9:00 AM FF03.14.05
Particle Assembly as Templates for Synthesis of 3D Interconnected Nanostructures Pratibha Mahale¹, Hiu Yan Cheng², Nabila N. Nova², Parivash Moradifar², Alex Grede², Byeongdu Lee³, Shi-Ying Yu², Nasim Alem², Noel C. Giebink², John V. Badding² and Thomas E. Mallouk¹; ¹University of Pennsylvania, United States; ²The Pennsylvania State University, United States; ³Argonne National Laboratory, United States

3D chemically bonded nanostructures combine the unique properties of nanomaterials with the periodicity of interconnected structures and the form of bulk materials, giving rise to new physical phenomena. We have combined the strength of particle assembly and High Pressure confined Chemical Vapor Deposition¹ (HPCVD) to create ordered and electrically continuous 3D nanostructures of both metals and semiconductors. These structures called “metalattices”(ML)² were made possible by void-free infiltration of silica colloidal crystals using HPCVD. We use a vertical deposition technique³ to assemble monodisperse silica nanoparticles in the range of 14nm-120nm, at controlled temperature and humidity, to form 3D colloidal crystals. The arrangement of silica nanoparticles in the template has a direct effect on metalattice (ML) properties. Structural characterization of the colloidal crystal templates which were grown as micron-thick films on silicon substrates and of MLs using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) and Small Angle Xray Scattering (SAXS) shows a 3D-ordered and well connected structure. Extending this structural characterization of templates to metalattices, we are studying surface modification and spatial band gap modulation in Germanium metalattices. Germanium despite its high carrier mobility has suffered inefficiency in electronic applications due to formation of germanium oxide which is unstable and introduces defects at the interface. We use a core-shell approach to passivate Ge MLs and prevent oxide formation. A silicon shell is grown on the Ge core leading to the formation of a Si₆Ge₁ₓ alloy at the interface which acts as a passivating layer. TEM, Raman and X-ray Photoelectron Spectroscopy studies confirm the formation of the core-shell structure with polycrystalline Ge as core and amorphous Si as shell without any germanium oxide formation. Given the inherent structure of metalattices, there are different degrees of confinement at octahedral, tetrahedral and meta-bond site. We are currently studying this spatial band gap modulation using electron energy loss spectroscopy. This understanding and control of metalattice surface along with the spatial structural modulation will enhance their tunability for desired properties and will also enable their applications in opto-electronic devices.

This work was supported by the National Sciences Foundation Materials Research Science and Engineering Centers (MRSEC) under award DMR-1420620.


9:15 AM FF03.14.06
Programmable Self-Assembly of 3D Printed Particles David Doan and Wendy Gu; Stanford University, United States

Particle-based crystallization relies on the synthesis and self-assembly of large numbers of monodisperse particles with nano to microscale dimensions. The fabrication of particles with diverse structures remains a challenge. Currently, inorganic nanoparticles with simple geometries (e.g. spheres, cubes, platelets) can be fabricated through bottom-up synthesis, while microscale Janus and patchy particles can formed through templating techniques. It is of interest to form lower symmetry shapes in which the direction of particle-particle interactions can be defined arbitrarily, and particle geometry can be used to precisely tune interparticle forces such as depletion forces. For instance, particles with one or more concavities (e.g. cube with concavities on 1 to 6 faces) can be combined with convex structures (e.g. spheres) to form complex self-assembled structures in 1D, 2D or 3D networks using lock and key mechanisms.

Here, we address the challenge of fabricating colloidal particles with complex geometries by using 2-photon
lithography to 3D print microscale particles of arbitrary shapes. This method has been used to print hollow cones, spheres, cubes, tetrahedra, and dumbbells with bounding box dimensions of 5 um x 5 um x 5 um out of a fluorescent photoresist, and can be extended to other structures. In this method, a focused 780 nm laser is used to directly write a freestanding 3D structure into liquid photoresist, or within photoresist at the interface with a solid substrate. The particles are then transferred to a microfluidic cell, and in-situ fluorescence imaging is used to observe the dynamics and final configurations of the assemblies that form from these 3D printed particles. These 3D printed particles (e.g. concave particles) will be combined with traditional particles (e.g. polymer or silica spheres) to form networks of multi-particle assemblies with controlled porosity, with the ultimate goal of forming periodic lattices with millimeter dimensions.

9:30 AM FF03.14.07
New Mechanistic Insights into the Formation of Epitaxially Connected Quantum Dot Superstructures
Jessica Akemi Cimada da Silva, Unmukt Gupta, Fernando Escobedo and Tobias Hanrath; Cornell University, United States

Epitaxially connected colloidal quantum dot superlattices with long-range atomic coherence have generated significant interest by virtue of their predicted emerging electronic properties. Whereas advances in controlled assembly and attachment at fluid-fluid interfaces have enabled the formation of high-fidelity superlattices in which constituent lead salt quantum dots are registered to within a single atomic bond length, significant gaps in our understanding of the fundamental mechanism underlying this transformation persist. The transformation involves a complex choreography of a number of sub-processes including: (i) the transport of a chemical trigger from the subphase to the quantum dot surface, (ii) the formation and removal of the ligand metal chelation complex, (iii) the rotation and translation of the quantum dots from their site in the initial assembly and (iv) the irreversible formation of an epitaxial bond between proximate dots through mutually exposed facets. What is astonishing and not yet understood is how the irreversible attachment of tens of thousands proximate dots are coordinated to enable the formation of micrometer-sized grains. Our recent experiments sought to capture intermediates of this intriguing transformation and revealed the existence of transient elongated structures along the <100> axis. New insights into the underlying processing-structure relationships coupled with computational simulations provide new understanding of the transformation mechanism. Beyond the specific model system of lead salt quantum dots discussed in this work, we expect that these new mechanistic insights will also provide valuable guidance to advance controlled assembly and attachment of related nanostructures.

9:45 AM FF03.14.08
Hierarchical Nanoscale Architectures for 3D Structuring of Functional Materials
Jason Kahn¹, Yan Xiong¹, Brian Minevich¹ and Oleg Gang¹,²; ¹Columbia University, United States; ²Brookhaven National Laboratory, United States

Until recently, the vast majority of functional materials organizations at the nanoscale have been based in studies of packed nanoparticle architectures. Rationally designed, periodic structures tailored towards enhancing the local environment for chemical or biological components are far less explored, but equally important in consideration of their optical, catalytic, and enzymatic applications. The ability to separate material function from binding parameters bridges the divide between nanoparticles and a vast materials space often exhibiting anisotropic structure. A universal platform enabling novel hierarchical assemblies can be achieved utilizing DNA constructs that carry a molecular or nanoscale material object, where different units can be encoded for location within a crystalline lattice as well as for material type. Three-dimensional, hierarchical architectures allow for precise control of locally-defined material stoichiometries at the nanoscale as well as their mesoscale arrangements, encoding the position of units over multiple coordination spheres. With this capability, novel research into 3D structure-function relationships can be explored, as demonstrated optically using quantum dot organizations and chemically utilizing catalytic enzyme systems.

10:00 AM BREAK

10:30 AM FF03.14.09
Site-Selective Synthesis of Core-Shell Multi-Segment Nanowires for Nanoscale Soldering and Interconnection
Edward Fratto, Jirui Wang, Brendan Lucas, Hongwei Sun and Zhiyong Gu; University of Massachusetts Lowell, United States
One-dimensional nanowire-based structures enable sophisticated design and integration of functional electrical components for modern electronics and devices. Recent developments in nanowire miniaturization have the potential for the next level of advanced assembly and packaging, but thus far engineering of nanostructures has been limited by associated challenges of interconnection. This work presents a core/shell multi-segment nanowire which achieved macroscale interconnection via magnetically assisted assembly and soldering. Gold-nickel-gold (Au-Ni-Au) nanowires were synthesized via electrodeposition in anodic aluminum oxide (AAO) template, with nickel acting as a magnetic vehicle for assembly. Gold-selective deposition of tin was achieved via establishment of a chemisorbed nickel-protective monolayer, followed by immersing the nanowires in aqueous solution for selective chemical reduction. This resulted in seeded tin deposition along the gold tips, which were subsequently grown into a coherent shell on gold. Core-shell formation was confirmed by SEM, TEM, EDS and XRD. These “dumbbell” shaped core/shell nanowires were assembled tip-to-tip and subsequently soldered, establishing ohmic electrical and thermal interconnection. This work establishes an effective and scalable method for site-specific nanowire functionalization while simultaneously addressing miniaturization-associated assembly and packaging issues in its desired applications.

10:45 AM FF03.14.10
Patterns via Evaporative Self-Assembly and Dewetting Kibeom Nam, Dong Yun Lee, Jaebin Lee and Eonji Kim; Kyungpook National University, Korea (the Republic of)

We present applications of the flow coating methods to achieve unique and complex shapes of patterns or structures. Flow coating is one of the solution coating techniques that exploit the coffee-ring effect. The coffee-ring effect is referred to a circle of a non-volatile solute that is left by a droplet of the solvent after it evaporates from a flat surface. It can be fund after coffee drop dries on a table. This pattern originates from the capillary flow, which is induced by the different evaporation rates between the edge and center of the droplet. A flow coater is confined to the position of the droplet with the blade at a specific position, and the solute is deposited along the shore.

In this study, we combined such a simple phenomenon with different materials such as a polymer, silica particle, and organic semiconductors. Every material had proper conditions for flow coating from the solvent to the speed of the coating process. By control the factors, we could achieve various kinds of patterns without complicate process compare with other methods and determined the relationships between the control value and phenomenon. First, the relationship between stopping time of flow coater and deposition phenomenon of several times of patterning process was investigated. Stopping motion of blade of flow coater gave more deposition of solute, and it could make thick or wide patterns. The difference of pattern’s height impacted the additional patterning mechanism on the patterned surface. Height of patterns inhibited deposition of solute on its top inducing a dewetting phenomenon. We could observe a change of height with a dewetting phenomenon and the amount of deposition rate with the shape of patterns. Various kinds of non-linear dewetting induced patterns are reported in this study.

Second, the relationship between the speed of flow coater and deposition phenomenon such as height and structural morphology of the film was explained. Speed of flow coating process is one of the critical factors that can control the amount of evaporating solvent, flow coating could control the overall thickness, and it spontaneously changed along with the speed of the blade. In this study, nano-sized silica particles was deposited on the substrate, affording a closely packed, well-ordered structure. Photonic structures were achieved in the same manner. The thickness of photonic crystal was changed along with the speed and photonic property was examined.

Third, the relationship between the speed of flow coater and shear stress on the solution was determined with organic conducting materials. The flow coating system basically comes from solution shear coating method and the shearing gives shear stress on the solution. Shear stress deformed crystal structures and it made conducting property differently.

The patterns that came through flow coating had various shapes and its application and they were easy to obtain. Compared to other methods, flow coating is an important method due to the following reasons. First, lithography or nano-casting needs complex steps to achieve a photonic structure, while flow coating does not need a developed process. Second, deep coating takes a long time until the liquid evaporates to form a thick film. However, flow coating overcomes such problems and exhibits more advantages.

11:00 AM FF03.14.11
High Temperature Crystallization of Monodisperse and Optically Active Lanthanide Nanoparticulates for Noninvasive Optogenetics Eric Zhang1,2, Ashley Dickey1, Yura Bandera1,2, Isabell Foulger1, Jeffery Anker1, John Ballato1,2, Joseph Kolis1 and Stephen Foulger1,2; 1Clemson University, United States; 2Center of Optical Materials
Optogenetics is a field of study that combines optics and biology to control living tissues via light sensitive proteins (opsins) and radiative energy. Traditionally, optical fibers are used as a waveguide to introduce light pass the cranial; consequently, this has negative side effects such as localized heating and surgical scars. Here a noninvasive technique is proposed utilizing a high penetrating and low tissue attenuation x-ray excitation source and nanoparticulates that scintillates to deliver radiative energy to light sensitive proteins.

Scintillators are a class of materials that can experience a downconversion of electrons from a high energy excitation source, such as x-rays. The ideal scintillators utilized in radiation detection have a high atomic number, high density, inert, and have discrete emission behaviors suitable for its end use. Typical non-toxic and high light output scintillators that can be applied in the biomedical field are silicate materials which are synthesized at temperatures above 1000°C; as such the synthesis of sub 100 nm scintillators is a challenge not fully explored yet due to the difficulties from sintering.

Two polymorphs of the $\text{Re}_2\text{Si}_2\text{O}_7$ ($\text{Re} = \text{Y}^{3+}$ or $\text{Lu}^{3+}$) were crystallized at the nanoscale at above 1000°C while remaining monodisperse particulates. A core bishell architecture was used as a physical and chemical template composed of a $\text{SiO}_2$ core and a $\text{Re}_2\text{O}_3$ shell, followed by polymerization of a secondary pDVB shell, on the inorganic core-shell particulate. The organic coating carbonized to amorphous carbon at conventional sintering temperatures preventing particle-particle contact and was easily removed. Furthermore different lanthanide dopants ($\text{Ce}^{3+}$, $\text{Tb}^{3+}$, and $\text{Eu}^{3+}$) were incorporated into the particulates that can couple to different opsins. The sacrificial amorphous carbon process demonstrated control over structure-luminescent properties that can potentially be used for non-invasive optogenetics. The two atypical fields of organic and inorganic chemistry provided complementary abilities that were instrumental into the development of the high temperature nanoreactor and has the potential to be expanded upon to different crystals.
assembly mechanism were also discussed. The laser induced assembly not only demonstrates high positioning accuracy and wide material applicability, but also enables the alignment control of 1D nanomaterials in 3D assembly process. The laser-based strategy opens a route for advanced nano-device fabrication which will benefit numerous emerging fields including 3D electronics, integrated photonics, and MEMS/NEMS.

**11:45 AM FF03.14.14**

**From Diffusion Limited to Incorporation Limited Growth of Nanowires** [Jonas Johansson](mailto:Jonas.Johansson@lth.lth.se) and Martin H. Magnusson; Lund University, Sweden

Metal particle catalyzed semiconductor nanowire growth, or vapor-liquid-solid (VLS) growth, is a highly promising route to one-dimensional hierarchical materials. The most common catalyst particle material for III-V nanowires is gold and growth of such nanowires can be carried out in a variety of epitaxy set-ups, such as metal organic vapor phase epitaxy (MOVPE) and molecular beam epitaxy. Aerotaxy is a relatively new growth method that admits growth of nanowires without substrates, directly in the vapor phase at very high growth rates [1].

In this presentation, we propose a model for the length growth rate of nanowires grown by means of the VLS mechanism. Our model is based on deposition-diffusion-desorption-incorporation kinetics in steady state, and using this model we discuss nanowire growth in two experimentally relevant limits: mass transport limited growth and incorporation limited growth. We discuss our modelling results in view of experimental nanowire growth results with a special emphasis on the radius-independent, incorporation limited growth rate in the high pressure limit, observed under specific, extreme conditions of nanowire growth which are reached during aerotaxy growth. Based on diffusion calculations, we find it plausible that these growth rates are indeed the maximum growth rates under the given conditions.

Moreover, in the mass transport limit, our model explains nanowire growth in MOVPE. Specifically, we explain the experimental observations of the V/III ratio dependence of the nanowire growth rate, observed by Soci et al. [2]. According to our model, the higher the group V pressure, the more linearly does the growth rate depend on the group III pressure. In this well-known limit, the growth rate is proportional to the group III pressure and the surface diffusion length of group III material along the nanowire and inversely proportional to the nanowire radius. On the other hand, in the limit of low group V pressures the growth rate becomes independent on group III pressure.

If both the group III and the group V pressures are sufficiently high, the nanowire growth rate is at its maximum and is limited by the incorporation kinetics. In this regime the growth rate depends only on temperature but not on pressures. It might be that some processes operate at unnecessarily high pressures so that significantly decreasing the pressures would not lead to a decrease in the growth rate. Therefore the insights from our modeling not only provide valuable insights in mass transport limited growth, but could also be used to reduce the cost of some processes, where the aerotaxy process is one possible example.


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**SESSION FF03.15: Building Advanced Materials via Particle Aggregation and Applications**

**Session Chairs:** Mehdi Zanjani and Xin Zhang

**Friday Afternoon, December 6, 2019**

**Hynes, Level 3, Room 313**

**1:30 PM FF03.15.01**

**Hierarchical Pore Gradient Ceramic Foams for Thermal and Acoustic Superinsulation** [Ruizhe Yang](mailto:ruizhe.yang@buffalo.edu) and Shenqiang Ren; University at Buffalo, The State University of New York, United States
Light-weight aerogel materials hold great promise for thermal insulation. However, its low mechanical integrity and high-cost manufacturing hampered its progress for large-scale adoption in energy-efficient building insulations. In addition, it is indispensable for thermal management to achieve more soundproof and heat-resistant characteristics. In this study, we design and synthesize the scalable pore-gradient ceramic aerogel monoliths (PGAeros) through the biomimetic approach. The low-cost manufacturing of PGAeros is further facilitated by the in-situ gas bubble formation to support the pore gradient. The PGAeros exhibit a robust mechanical and thermal stability across a broad temperature range (0.040 W m\(^{-1}\) K\(^{-1}\), and a compressive strength of 100.56 MPa, respectively). The design of thermal regulation in such PGAeros is inherited from the human skin concept, where the pore gradient regulates the thermal management over the seasons. The integral ceramic monolith nature provides such PGAeros with robust soundproof and fire-retardant performance. The demonstration of scalable manufacturing of bio-mimetic inspired ceramic aerogel materials opens up thermal insulation applications with remarkable thermal management, high mechanical strength, low mass density, superior soundproof and fire-retardant performances.

1:45 PM FF03.15.02
Inverse Design of Colloidal Crystallization with Isotropic Pair Potentials Carl Simon Adorf, James Antonaglia, Julia Dshemuchadse and Sharon C. Glotzer; University of Michigan, United States

Colloidal and nanoparticle systems exhibit novel and unexpected phase behavior including the self-assembly of highly complex crystal structures. The inverse design of pair potential models provides a promising route for the \textit{a priori} approximation of required particle interactions for the targeted self-assembly of unique colloidal crystal structures. State-of-the-art techniques for the optimization of isotropic pair potentials tend toward overfitting, resulting in solutions with many features on different length scales that are challenging to map to mechanistic models. Here, we demonstrate how to effectively steer the optimization of pair interactions toward smooth, simple and possibly realizable solutions by amplifying relevant frequencies within the Fourier spectrum of the pair potential function. The resulting simpler functions should not only be more readily transferable to experiments, but simulated self-assembly pathways are generally also more robust and less prone to vitrification.

2:00 PM FF03.15.03
Ru,W\(_x\)O\(_y\)—A Novel Mixed Transition-Metal Oxide for Energy Storage Applications Sergio H. Domingues and Caroline B. Aquino; Mackenzie Presbyterian University, Brazil

Mixed transition-metal oxides (MTMO) are materials that its structural configuration consists in oxides with two different cations as AxBYOZ (where A and B are transition metals). This arrangement allows a several possibilities of structures and improve properties. The synergistic effect of multiple cations valences can to increase properties like, high conductivity and electrochemical activity, which contribute for uncounted applications, mainly in energy storage devices. Between metal oxides, ruthenium oxide (RuO\(_2\)) has been used, owing excellent electrochemical properties, such as wide electrical potential range, high conductivity and specific capacitance. However RuO\(_2\) shows many disadvantages, it is expensive and toxic, reducing severely its application. An interesting alternative is focused on the combination of RuO\(_2\) with other materials, like metals or oxides, decreasing amount of Ru in the oxide. In this way, we combined ruthenium with tungsten oxide (WO\(_3\)), in order to obtain a novel MTMO. WO\(_3\) is excellent candidate, due his unique properties. The development of novel MTMO structure (RuxWyOz) was based on bottom up strategy, using a modified polyol method, with a triblock polymer (Pluronic 123) as surfactant and different metal chlorides salts as precursors. Different precursors ratios were evaluated in order to obtain the better results. The nanomaterial obtained as characterized by different techniques such as: Raman and energy-dispersive X ray spectroscopy, scanning electron and atomic force microscopy. These analyses ensure the successful of material synthesized and shown the mainly properties of this new MTMO. RuxWyOz thin films were also characterized by electrochemical techniques, exhibiting superior capacitive performance when compared to control samples (RuO\(_2\) and WO\(_3\)). The results show promising application in energy storage field. Authors acknowledges Mackenzie Presbiterian University (UPM), FAPESP (2018/02142-0, 2017/21988-5 and SPEC2012/50259-8), CNPq (403544/2016-5), Materials Chemistry Group (GQM – UFPR), LNNano and INCT of Carbon Nanomaterials.

2:15 PM FF03.15.04
Shadow Boxing with Laser—Laser Damage Resistance of Three-Dimensional Photonic Crystals Lei Pan; Harbin Institute of Technology, China

The laser damage behavior of three-dimensional photonic crystals (3D-PCs) with an opal structure is investigated
using both experimental and simulation methods. Polystyrene (PS) colloidal crystals films with a reflection peak at 1064nm are used as the model material. Disordered films (DF) are fabricated with PS microspheres as contrast samples. The laser-induced damage threshold (LIDT) of 3D-PCs is tested, which is as 2.35 times high as the LIDT of DF. All laser damages are derived from defects in 3D-PCs, implying that the LIDT of ideal 3D-PCs will be significantly increased. The simulation results show that the electric field is contained in the pores of 3D-PCs while it is reduced in the PS microspheres, which may decrease the absorption of laser energy by 3D-PCs. In contrast, the electric field distribution is irregular in DF. Enhanced electric field areas are located in both the pores and microspheres of DF. Considering higher electric field intensity causes more energy absorption and higher temperature, the DF have a lower LIDT. The 3D-PCs structure uses ordered vacancy to contain and strike back laser energy and can increase the LIDT without changing the chemical composition of materials.

2:30 PM FF03.15.05
Robust Self-Assembled Nanofibers from Novel Small Molecule Amphiphiles for Heavy Metal Remediation Ty Christoff-Tempesta, Dae-Yoon Kim and Julia Ortony; Massachusetts Institute of Technology, United States

Traditional small molecule supramolecular assemblies (e.g. in natural systems like lipid membranes or those derived from peptides) generally exhibit high molecular exchange rates, molecular migration, and other dynamic instabilities. These dynamic processes may be beneficial for the application of supramolecular materials in biological environments, but the ability to increase nanostructure stability might provide a path forward for their application in non-biological applications. Here, we present the design of small molecule amphiphiles fabricated with robust intermolecular interactions which self-assemble into ultra-stable supramolecular nanofibers. These nanofibers notably maintain both the self-healing characteristics found in traditional amphiphilic systems and exhibit unique mechanical and thermal stabilities that arise from the tunable intermolecular interaction strengths within each assembly. Taking advantage of the high aspect ratio of these nanomaterials, heavy metal chelators are rationally chosen for expression in high densities on the nanofiber surfaces. We demonstrate the capacity for significant remediation of heavy metals from water using this novel class of materials with orders of magnitude improvement over macroscopic alternatives in use today.

2:45 PM BREAK

3:15 PM FF03.15.06
Direct Detection of DNA Using 3D Surface Enhanced Raman Scattering Hotspot Matrix Yongkang Wang, Xiongyu Wu, Shuyu Huang, Chao Wu and Yunfei Chen; Southeast University, China

Direct detection of DNA by surface enhanced Raman spectroscopy has shown great advantages and potentials owing to its ability to provide intrinsic chemical information of DNA molecules themselves with a high sensitivity. However, much small Raman scattering cross section of DNA molecules causes the SERS spectra hard to be collected directly and the SERS spectra were found to be dominated by the vibration of adenine. Although various methods of direct DNA detection by surface enhanced Raman scattering (SERS) have been proposed, more reliable and more stable SERS platform with higher signal-to-noise ratio still requires.

In this study, we propose an evaporative self-assembly strategy for constructing long-life 3D SERS hotspot matrix with the assistance of glycerol to improve the spectral sensitivity and reproducibility in direct DNA detection. Silver nanoparticles (AgNPs) are dispersed in mixed solvents that contain a small amount of non-volatile solvent glycerol and volatile solvent water. Additionally, Mg^{2+} is introduced to the AgNPs colloids to construct the sandwich structure (AgNPs-DNA-AgNPs) between negative charge AgNPs and phosphate backbones through electrostatic interaction. When the droplet is dried on a hydrophobic silicon substrate, water evaporates rapidly and glycerol as a non-volatile solvent creates a liquid environment that can stop the AgNPs colloids turning into the drying state. Both AgNPs and DNA will be concentrated and assembled together to form a 3D AgNPs hotspot matrix at the silicon/glycerol solid-liquid interface. Brownian dynamics simulations reveal that more hotspots turn up in the glycerol-stabilized 3D AgNPs hotspot matrix and the distances between the AgNPs in the liquid environment are not fixed but balanced in a small range by the interplay of the van der Waals attraction and the electrostatic repulsion. Two orders of magnitude extra SERS enhancement, more stable peak frequencies and narrower peak full width at half maximum (FWHM) can therefore be obtained, which enable the direct detection of both single strand DNA (ssDNA) and double strand DNA (dsDNA) with stable, reproducible and reliable signal-to-noise ratio SERS signals. Using the symmetric stretching vibration peak of phosphodioxy (PO2−) at 1087 cm\(^{-1}\) as the intensity internal standard, we are able to quantitatively determine the base content in oligonucleotides with single base sensitivity.
This fascinating evaporative self-assembly strategy opens up a novel perspective in manipulating plasmonic nanoparticles to construct the SERS platforms at solid/liquid interface. Ultrahigh spectral sensitivity and reproducibility of the glycerol-stabilized 3D SERS hotspot matrix would promote the surface enhanced Raman spectroscopy to become a more practical and reliable tool in direct DNA detection and analysis.

3:30 PM FF03.15.07
Circular Polarized Light Sensors Using Cellulose Nanocrystals Self-Assembled Membranes  
Paul Grey, Susete Fernandes, Diana Gaspar, Elvira Fortunato, Rodrigo Martins, Maria Helena Godinho and Luis Pereira; Universidade NOVA de Lisboa, Portugal

Cellulose is ubiquitous in our everyday life from our homes to our offices. Cellulose nanocrystals (CNCs) that can be obtained from different cellulose sources are rod-like nanoparticles with dimensions on the order of a few hundredth nanometer in length and a few nanometers in width. When dispersed in water CNCs behave like a lyotropic liquid-crystal and give rise to either isotropic or anisotropic suspensions. Whereas drying an isotropic suspension (low CNC concentration) yields transparent films, interesting photonic properties (iridescence) can be obtained by drying an anisotropic suspension (CNC concentration > 2 wt%), owing to a twisted ordering on the nanoscale. This ordering is due to an evaporation induced self-assembly process and is referred to as a chiral nematic structure.

In this work we report on the integration of bio-inspired chiral CNC membranes into sensing devices with distinct sensing properties for left- and right-handed circular polarized light (LCPL and RCPL, respectively). The CNC films are employed as photonic dielectrics in oxide thin films transistors and light filters in amorphous silicon photodetectors with the capability of discrimination between LCPL and RCPL signals in the visible region.

3:45 PM FF03.15.08
Fabrication of Plasmonic Multilayer on Cellulose Fibrils Applicable to Versatile Label-Free Diagnostic Platform  
Hyeok Jung Kim, Jiwoo Hyung and Hyeran Noh; Seoul National University of Science and Technology, Korea (the Republic of)

Surface-enhanced Raman Spectrometry (SERS) based on localized surface plasmon resonance can recognize strong Raman signals highly specific to a chemical molecule by great analytical performances. SERS enhancement factor (EF) majorly relies on distribution and density of hotspots regarded as nanoscale gap distances among noble metal nanoparticles; increasing EF necessitates a sophisticated nanostructure, either two-dimensional arrangement or three-dimensional (3D) structuring. Cellulose fibril substrates demonstrate so highly porous network structure that researchers have investigated it for development of cellulose-based SERS platforms. However, the perpendicular distances between the fibrils exceed upon micrometers resulting in low reducibility and EF level. While numerous ensuing researches have attempted to fabricate nanopatterned structures, these methodologies required highly pricey equipment and intricate processes.

Herein, we demonstrate 3D plasmonic nanostructure built on cellulose fibril surfaces using Layer-by-Layer technique. The fabricating procedure consists of steps alternatively dipping a cellulose substrate into each solution respectively containing positively and negatively charged materials; silver nanoparticles were synthesized via in-situ reduction method with capping negatively charged molecules, and a positively charged chitosan derivate oligomer was employed for the fabrication. Structural parameters were deliberately adjusted by the stepwise methodology and changes in chemical reagents concentration. Optical and mechanical traits, and surface chemistry of the substrates were altered with accordance to increasing generations. Transverse routes of analytes were confirmed by morphological studies associated with energy dispersive X-ray spectroscopy mapping. In the analytical application, the SERS substrate demonstrated a gainful performance with bringing about respected EF, limit detection, and reproductivity.

This 3D plasmonic structure was sophisticatedly built on the cellulose microfibrils and revealed profitable functions when applied to SERS analysis. It achieved high reproducibility and sensitivity without engaging complex and costly fabricating procedure. Thus, this Multilayered SERS platform is potentially advantageous for numerous purposes, in particular for point-of-care diagnosis.

4:00 PM FF03.15.09
Synthesis of Bacteriochlorophyll Mimicking Molecule for Disk-Coil Motif Based Self-Assembly  
Eugene N. Cho1, Junwon Choi2 and YongJoo Kim1; 1Korea Advanced Institute of Science and Technology, Korea (the
Light-harvesting complexes in nature consist of disk-coil motifs, a chlorin- or porphyrin centered molecule with functionalized alkyl chain. Of the many light-harvesting complexes, bacteriochlorophyll (Bchl) is of special interest due to its role in particular bacteria living in a low light environment. Bchl is the building block of chlorosome, a large light-harvesting antennae complex that allows the bacteria to harvest energy efficiently from the low-light environment. It is believed that Bchl gives chlorosome such high light-harvesting abilities due to the molecule self-assembling based on bchl-bchl interaction, which differs from chloroplast, the light complex in green plants that self-assembles from chlorophyll-protein interaction. In Bchl, the dominating features that allow the bacteriochlorophyll to form the light harvesting complex are believed to be the metal core of the porphyrin, OH group, and the long alkyl chain. This allows a combination of hydrogen bonds, coordination bonds, and π-π interactions to occur between the disk coil motif which enables assembly into the light-harvesting complex. Hence, studying the self-assembly behavior of disk-coil motifs is essential to reproduce the self-assembled structure of chlorosome that may govern its photosynthetic performances. In this study, we synthesized a disk-coil motif that mimics the bacteriochlorophyll molecule. The disk-coil motif was designed with a porphyrin-based disk that accommodates the key features that are believed to allow bacteriochlorophyll to self-assemble in the confined environment. From this, the self-assembly properties of this structure were studied to understand the self-assembly of disk-coil structures.

**SYMPOSIUM FF04**

Crystal Engineering of Functional Materials—Solution-Based Strategies  
December 2 - December 5, 2019

**Symposium Organizers**  
Ying Diao, University of Illinois at Urbana-Champaign  
Stephanie Lee, Stevens Institute of Technology  
Stefan Mannsfeld, TU Dresden  
Barry Rand, Princeton University

**Symposium Support**  
Bronze  
ACS Applied Materials & Interfaces | ACS Publications  
MilliporeSigma  
MSDE, Royal Society of Chemistry  
Organic Electronics (Elsevier)

* Invited Paper

SESSION FF04.01: Solution Processed Colloids and Nanocrystal I  
Session Chairs: Barry Rand and Wenhao Sun  
Monday Morning, December 2, 2019  
Hynes, Level 3, Room 311

8:45 AM FF04.01.01  
Crystal Engineering of Copper Fine Particles Prepared by Solution-Based Strategies Tetsu Yonezawa, Mai T. Nguyen and Hiroki Tsukamoto; Hokkaido University, Japan

This research is devoted for making nanoparticles and fine particles of metallic copper by solution-based strategies.
Gelatin and other polymers can work as stabilizing polymers to keep the particle surface in metallic state. These particles can be used as the materials for the inner electrode of MLCC by using a high-temperature annealing process. But in the field of printed electronics as well as organic electronics, conductive materials for low-temperature sintering are highly demanded.

In this study, crystal engineering and surface engineering was applied for copper fine particles prepared by solution-based strategies. By using polymer-stabilized metallic copper fine particles, and transition metal oxides via solution syntheses that can be scalable for mass production. Our solution-based preparation of copper fine particles was carried out by chemical reduction of CuO micro particles by using hydrazine at alkaline conditions. Because this process is a low temperature process, the particles are consisted of small grains. According to the grain boundary in the copper fine particles, the diffusion of copper atoms becomes higher. Therefore, lower temperature sintering can be carried out with these copper fine particles even the particle sizes bigger than 100 nm. This situation indicates that low temperature sintering cannot be performed only by the melting temperature depression.

More detailed analyses of copper fine particles prepared by solution-based strategies found that the surface of the particles was slightly oxidized. But the structure is not Cu2O or CuO. These slightly oxidized states can be reduced readily in the presence using some reductive organic small molecules and metallic copper surface generates during sintering. Moreover, when oxygen atoms are eliminated from the surface, re-arrangement of copper atoms carries out. This situation also proceeds necking and sintering of the particles.

We discuss in this paper that the strategy of the crystal engineering of copper fine particles for the application of electroconductive materials and dyebonding materials.

9:00 AM FF04.01.02
Fabrication and Optical Properties of Globally Ordered Polymer-Grafted Gold Nanorod Assemblies Jason K. Streit1,2, Kyoungweon Park1,2, Yoon-Jae Yi1,2 and Richard A. Vaia1; 1Air Force Research Laboratory, United States; 2UES, Inc., United States; 3Wright State University, United States

Precise, large-scale assembly of polymer-grafted nanoparticles (PGNs) has shown great promise for the scalable manufacturing of sensors, energy storage devices, and photonic elements. Different than more traditional ligand-coated nanoparticles, PGNs are stabilized by high molecular weight polymers at relatively low grafting densities. In this regard, PGNs are considered soft colloids, possessing the favorable processing properties of polymers while also retaining the ability to pack into ordered nanoparticle assemblies. Using a simple flow-coating technique, we demonstrate that large scale, highly uniform monolayer films of gold-polystyrene nanorods can be fabricated from PGN inks within a few seconds. Applying a combination of atomic force microscopy, scanning electron microscopy, and grazing incidence X-ray scattering, we observe positional and orientational order dependent on coupling between surface energy, process methodology, and the architecture of the grafted polymer canopy. More specifically, we show that globally oriented films possessing two-dimensional orientation parameters greater than 0.7 can be achieved through evaporation induced-assembly when processing at slower deposition velocities on hydrophilic surfaces. Additionally, optical extinction measurements reveal strong plasmonic coupling between the gold nanorods which can systematically be tuned by varying film morphology. With fundamental understanding of structure-processing relationships, we demonstrate polarized optical notch filters using laser-induced reshaping of resonant nanoparticle subpoulations.

9:15 AM FF04.01.03
Plasmonic and Magnetic Nanoparticles for Biomedical Application Nguyen T. Thanh; University College London, United Kingdom

The development of new chemical methods for the next generation of nanoparticles with very high magnetic moment, fine tuning Au nanorods and novel hybrid and multifunctional nanostructure is presented. Detailed mechanistic studies of their formation by sophisticated and advanced analysis of the nanostructure allows tuning of the physical properties at the nanoscale; these can subsequently be exploited for diagnosis and treatment of various diseases. The studies are conducted to provide insight for future material design approaches. It will also help to identify the critical process parameters that can be manipulated in order to obtain the suitable physical properties for the intended applications.
In collaboration with chemical engineers in designing the reactors in microfluidic systems, this allowed for the first time to detailed study the physical properties such as X-ray diffraction (XRD), magnetic moment and morphology to unravel the particle formation mechanism during co-precipitation synthesis of iron oxide magnetic nanoparticles, which is very important for their robust, reproducible formation process for cancer treatment.

References


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9:30 AM FF04.01.04
Quantitative Analysis of DNA-Mediated Solution and Surface Reductions on the Formation of Metal Nanocrystals Yiming Wang, Michael Counihan, Jeffrey Lin, Hong Yang, Joaquin Rodriguez-Lopez and Yi Lu; University of Illinois at Urbana-Champaign, United States

Predictive synthesis of metal nanocrystals with desired structures relies on precise control over the reduction pathways of metal ion precursors. Using capping ligand is an effective method to affect the reduction kinetic in nanocrystal formation. However, comprehensive understanding and predictive manipulation of reduction pathways is yet to be achieved by conventional capping ligand. DNA as one of the promising biomolecular capping ligand has been used to generate sequence specific morphologies in varies metal nanocrystals. Taking advantage of the well-defined binding mode between DNA and metal ions, we quantitatively analyzed the precise kinetic control of different DNA sequences over Ag+ reduction process and the relationship between reduction pathways and the structure of resulting nanocrystals. The complexation between DNA and Ag+ was shown to significantly affect the reduction potential of the precursor. The difference in binding equilibrium between DNA sequences and Ag+, as well as the interaction between DNA and the surface of the nanocrystals, synergistically determined the distinguishable Ag+ reduction path-ways with different DNA sequences. The DNA sequence specific control in reduction pathways also results in different mode of nanocrystal formation: layer growth, island growth, and the mixed of two. The discovery from this study demonstrates how rational design of metal-ligand interactions can be used to control precisely the growth kinetics of nanocrystals and the real potentials on using functional DNA sequences for the predictable synthesis of metal nanostructures.

9:45 AM BREAK

10:15 AM *FF04.01.05
The Solution Chemistry of CdS Pre-Nucleation Clusters Kevin Kittilstved, Fumitoshi Kato and Jillian Denhardt; University of Massachusetts Amherst, United States

The impact of defects on the photophysical and chemical properties of colloidal semiconductor quantum dots (QDs) is dominated by their large surface-to-volume ratios compared to bulk analogs. Understanding the formation mechanism of colloidal QDs is still largely unknown, however, the chemistry of well-defined molecular clusters has
revealed their ability to also serve as suitable pre-nucleation clusters in QD synthesis. This talk will highlight our recent studies in using high-resolution mass spectrometry and other spectroscopic techniques to study the solution chemistry and surface dynamics of a class of cadmium thiophenolate clusters with varying size and nuclearity (from 4 Cd ions to 17 Cd ions). The conversion of the tetrameric clusters to the heptadecameric clusters is complex involving numerous metastable intermediates including octameric and decameric clusters. We will also present synthetic design tools where we exploit this complex conversion chemistry to successfully dope Co(II) and Mn(II) ions into specific sites in the the decameric and heptadecameric clusters, including the core sites with metal sulfide bonds.

10:45 AM FF04.01.06
Silver Chlorobromide Nanocubes—A Class of Reactive Templates for Synthesis of Nanocages Sasitha C. Abeyweera and Yugang Sun; Temple University, United States

Transforming nanostructures into hollow ones represents a unique synthetic strategy for achieving new properties that do not exist in their solid counterparts, boosting applications in a broader range. The chemical nature of the reactive nanostructures (or sacrificial template nanostructures) determines the reaction kinetics of hollowing them along with the transformation of chemical compositions, which influences the controllability of synthesis. For example, uniform silver chlorobromide nanocubes can be used a class of sacrificial template nanostructures to regulate and maintain an extremely low concentration of available Ag⁺ that reacts with different thiol molecules to form silver thiolate with high controllability over the reaction kinetics. Such kinetic controllability enables the transformation of the silver chlorobromide nanocubes to hollow nanocages of silver thiolate. In contrast, the direct reaction of Ag⁺ ions with thiol molecules forms silver thiolate particles with irregular sizes and geometries. Moreover, the sacrificial silver chlorobromide nanocubes expose their surfaces to provide the heterogeneous nucleation sites for condensation of silver thiolate, further improving the controllability to benefit their transformation into hollow nanocages. Due to the improved controllability over reaction kinetics, the process of hollowing silver chlorobromide nanocubes can be terminated at any desired stage to form silver thiolate nanocages with the appropriate wall thickness. Time-dependent electron microscopic, X-ray diffraction, and UV-visible spectrometric studies reveal detailed insights into the structural evolution of crystals in terms of amount and dimensions during the hollowing transformation. This method represents scalable and versatile strategy to control the kinetics of fast reactions involved in the synthesis of colloidal nanoparticles, thus enabling the synthesis of uniform nanocages with desirable parameters. The availability of various silver-based hollow nanostructures provides the opportunity to explore potential interesting properties with real-world applications such as in electrocatalysis and photocatalysis.

11:00 AM FF04.01.07
Peptide Directed Enantioselective Morphology Evolution Pathways of Chiral Plasmonic Nanoparticles Sang Won Im, Hyo-Yong Ahn, Nam Heon Cho, Hyeohn Kim and Ki Tae Nam; Seoul National University, Korea (the Republic of)

Plasmonic chiral nanostructure has drawn significant attention due to its potential as a novel route for extraordinary optical properties such as negative refractive index and light polarization control. However, achieving chiral nanostructure remains as a challenge because of the complexity and resulting high cost of asymmetric morphology control at nanoscale. Inspired by natural process of chirality interaction between organic and inorganic materials, we reported a new pathway to control chiral morphology of gold nanoparticles. The resulted Helicoid nanoparticles were a new class of three-dimensional free-standing plasmonic chiral nanostructure, which exhibited strong chiroptical behavior such as anisotropic dissymmetry factor of 0.2. The chiral morphologies of Helicoid nanoparticles were further extended by establishing general model of chirality transfer from amino-acid or peptides to gold nanoparticles based on the concept of surface facet development pathway during nanoparticle growth. Asymmetric growth of chiral element is directed by enantioselective adsorption of amino-acids or peptides on high-Miller-index facet of nanoparticle which is formed in the course of particle growth. As the morphologies of nanoparticles are determined by exposed surface facets, we could establish nanoparticle growth pathway on stereographic projection of crystal plane by analyzing series of different surface facets Helicoid nanoparticles undergo. It was revealed that nanoparticle growth pathways not only depends on the types of seed particles and growth solution conditions, but also can be altered by interaction with amino-acids or peptides. The sequences of amino-acids or peptides determine on which step of growth pathway chiral morphologies are developed and which
high-Miller-index facets and final outline of nanoparticle are exposed. Understanding on peptide recognition and crystal growth enables design of diverse chiral morphologies and tailored optical response, and provides insight into further optical modification through coupling with molecular dipoles.

11:15 AM FF04.01.08
Room-Temperature Formation of Colloidal Alloy Semiconductor CdTeSe Magic-Size Clusters in a Single-Ensemble Form Kui Yu; Sichuan University, China

Alloy semiconductor magic-size clusters (MSCs) have been reported rarely, and little is known about their formation pathway. Here, we explored a room-temperature approach to alloy CdTeSe MSC-399, which is labelled according to the peak position of its sharp optical absorption at 399 nm. Also, we investigated its formation pathway. We mixed two binary CdTe and CdSe induction period samples at room temperature; after incubation, the evolution of MSC-399 was detected by optical absorption spectroscopy in toluene. The induction period is the prenucleation stage which occurs prior to nucleation and growth of quantum dots. We argue that substitution reactions take place after the two binary samples are mixed, which result in the formation of CdTeSe MSC-399 from its precursor compound (CdTeSe PC-399). The former is faster than the latter. Furthermore, we demonstrate that the formation of PC-399 is not via anion exchange nor addition reactions. The present study provides a room-temperature avenue to engineering alloy MSCs and an in-depth understanding of their probable formation pathway, making the synthesis less empirical. Given the complexity of the subject, it is impossible to extract complete mechanistic insight from one study. Even so, we believe that the present study is one solid piece, in a very large puzzle. Also, similar to the advance of organic chemistry, the field of colloidal nanocrystals is pressing forward and transforming from an empirical art to science.

Keywords: magic-size clusters, alloy, colloidal semiconductor nanocrystals, prenucleation stage, induction period

11:30 AM FF04.01.09
Impact of Template and Short Molecules on the Growth of Epitaxial Nanocrystal Superlattices Santanu Maiti1,2, Alexander André2, Sonam Maiti2, Martin Hodas2, Maciej Jankowski2, Marcus Scheele2, Stephan Förster1 and Frank Schreiber2; 1Forschungszentrum Jülich, Germany; 2Eberhard Karls Universität Tübingen, Germany; 3European Synchrotron Radiation Facility, France

We investigate the structure and growth of soft epitaxial nanocrystal (NC) superlattices, formed on the surface of designed templates. At first, we prepare template of ordered monolayer superlattice of PbS NCs, coupled with copper tetraaminophthalocyanines (CuTAPc) molecules [1-3]. Afterwards, we deposit as-prepared PbS NCs of different sizes on top of the templates and finally add short ligands on those adlayer assemblies. Here, we determine the structure of the templates and the adlayer NC assemblies by using grazing-incidence small angle x-ray scattering (GISAXS), grazing incidence x-ray diffraction (GIXD) and microscopy [4]. The deposited NCs self-assemble into ordered superstructures (sc, bcc) and show preferred atomic orientation with respect to the templates. After treating with short ligands, the bcc superlattices undergo a notable orientational change from [110]SL to [100]SL. This study provides new insight for designing epitaxial nanostructures of desired crystallographic orientation [5,6].

References:

11:45 AM FF04.01.10
Growth Mechanism of Colloidal PbSe Nanorods Yiteng Tang1, Liangfeng Sun1, Zhoufeng Jiang2, Chandra P. Neupane1, Haowen Xi3, Randy Ellingson1, Paul J. Roland1, Wenhui Wan4 and Yugui Yao5; 1Bowling Green State University, United States; 2B207 Research Center, China; 3University of Toledo, United States; 4Yanshan University, China; 5Beijing Institute of Technology, China

Oriented attachment of nanoparticles in a colloidal solution is one of the important processes to form larger-scale anisotropic functional nanomaterials. However, the mechanism of oriented attachment is still poorly understood.
Our recent study on the growth of colloidal PbSe nanorods proves that the oriented attachment is driven by the dipole-dipole interaction among the seed quantum dots. The dipole-dipole interaction strength depends on their separation distance as well as their orientations. Hence the one-dimensional oriented attachment can be controlled by the quantum-dot surface capping ligands used as the cosolvent in the synthesis. In particular, changing the length of the surface ligands can significantly change the dipole-dipole interaction strength. We demonstrate that the oriented attachment can be reliably turned on or off during the growth of nanocrystals by choosing the proper length of the surface ligand.

This kinetic-controlled growth of the nanorods prefers low reaction temperatures. Colloidal PbSe nanorods with length > 100 nm and diameter < 4 nm can be synthesized at 110 °C. The as-synthesized PbSe nanorods exhibit a single exponential decay and an absolute photoluminescence quantum yield more than 30%.

SESSION FF04.02: Solution Processed Colloids and Nanocrystals II
Session Chairs: Kevin Kittilstved and Jason Streit
Monday Afternoon, December 2, 2019
Hynes, Level 3, Room 311

1:30 PM FF04.02.01
Phase Modulation of Single Crystal MOFs through Growth on Self-Assembled Monolayers Marina Solomos, F. James Claire and Thomas J. Kempa; Johns Hopkins University, United States

Metal-organic frameworks (MOFs) are attractive crystalline molecular materials for enabling multifunctional properties in optoelectronic devices. Of particular interest are MOFs whose phases and properties can be dynamically and reversibly switched in response to external stimuli. We identify new MOF topologies prepared through tunable assembly of a modular cluster, Mo2(INA)4, and explore their electronic structures and redox capabilities. Several synthetic innovations allow us to prepare new MOFs from this Mo2(INA)4 cluster, including the use of self-assembled monolayers that template large-area thin film growth, and sacrificial pillaring molecules that control the ordering of two-dimensional (2D) layers within the MOF. This latter 2D phase exhibits anomalous gas adsorption characteristics, redox activity, and a significant photocurrent response. Reversible structural conversion between the multiple topologies is readily accomplished and associated with significant tuning of the MOF electronic properties. These efforts enable the development of sensors and actuators from stimuli-responsive molecular frameworks.

1:45 PM *FF04.02.02
Making New Materials from Molecular and Superatomic Building Blocks Colin Nuckolls; Columbia University, United States

This presentation will describe our research in creating electronic materials from molecular and superatomic building blocks. We are designing crystalline and self-assembled systems from these building blocks. We have created clusters of atoms that behave like the functional equivalent of atoms, but are on the nanoscale. These materials form solid solutions that show drastically enhanced electrical conductivity. Thin films of these materials have low thermal conductivity and point to a new direction to optimize thermoelectric materials. In addition, using this building blocks, we have made new materials with unusual magneto-optical properties.

2:15 PM FF04.02.03
Predicting Material Properties of Superatomic Crystals Using Molecular Dynamics Simulations Matthew Bartnof1, Qi Liang1,2 and Alan J. McGaughey1; 1Carnegie Mellon University, United States; 2Xi'an Jiaotong University, China

The large unit cell compounds Co6E6(PEt3)6 (E = S, Se, Te) and [Co6E6(PEt3)6][C60]2, and C60 are modeled using molecular dynamics simulations to understand how intermolecular and intramolecular interactions affect their macroscopic properties. These compounds are examples of superatomic crystals (SACs), a diverse family of compounds that span the periodic table. To enable study across the spectrum of SACs, the Universal Force Field
(UFF) and the Extended Charge Equilibration (EQEq) scheme are employed. The resulting zero-pressure lattice constants are within 5% of the experimentally measured results and the predicted elastic moduli encompass the experimental value. Unique trends in thermal conductivity are explained by qualitative assessments and quantitative measures of the rotational diffusion coefficient of the C$_{60}$ molecules. Large rotational diffusion coefficients, indicative of freely spinning C$_{60}$ molecules, correspond to temperature-independent thermal conductivities, while librating C$_{60}$ molecules with proportionally small rotational diffusion coefficients correspond to crystal-like thermal conductivities. Finally, equivalent point mass models of the six compounds are generated and used to assess the impact of the C$_{60}$ rotation on thermal conductivity.

2:30 PM FF04.02.04
Towards a Deterministic Pathway for Chiral Shape Formation in Nanocrystals Assaf Ben-Moshe$^{1,2}$, Allesandra Da-Silva$^{3}$, Alexander Mueller$^{2}$, Anas Abu-Odeh$^{2}$, Andrew M. Minor$^{1,2}$, Mark Asta$^{1,2}$, Wolfgang Theis$^{3}$, Peter Ercius$^{3}$ and Paul Alivisatos$^{1,2}$; $^{1}$University of California, Berkeley, United States; $^{2}$Lawrence Berkeley National Laboratory, United States; $^{3}$University of Birmingham, United Kingdom

In a seminal experiment performed in 1848 Louis Pasteur separated the two mirror-images of chiral tartaric acid salt crystals. The chirality of the molecular building blocks manifested itself in the macroscopic shape of the crystals, that exhibited a chiral arrangement of facets. Following this work, many observations of macroscopic shape chirality in crystals followed, and yet relations between molecular scale and overall shape chirality are not well understood. Such understanding is highly desirable for the deterministic synthesis of crystals with chiral shapes. Nanocrystals represent an embryonic stage of crystal growth, and allow direct high spatial and temporal resolution studies of crystal growth mechanisms and the way defects, ligands, impurities and other reaction conditions affect growth. Working with tellurium nanocrystals that exhibit both a chiral crystal structure and a chiral shape, we shed light on a general mechanism that leads materials to exhibit chiral shapes in crystallization. This mechanism has to do with a unique topology of partial dislocations that we believe can be very general in crystal growth reactions. Alongside a fundamental understanding of how chiral shapes might emerge sometimes in crystals we offer design principles to achieve these shapes with control over their handedness, and therefore chiral properties.

2:45 PM FF04.02.05
Cluster Assembly Pathways to Gibbsite Nucleation and Growth Xin Zhang, Ying Chen, Suyun Wang, Jianzhi Hu, Nancy Washton, Sebastian Mergelsberg, Carolyn I. Pearce, Zheming Wang, James J. De Yoreo, Sue Clark and Kevin Rosso; Pacific Northwest National Laboratory, United States

Gibbsite ($\alpha$-Al(OH)$_3$) is an important archetype hydroxide of aluminum in nature that also plays diverse roles across a plethora of industrial applications. In addition, gibbsite is a prominent component of high-level nuclear waste stored in large quantities at the Hanford Site, Washington and at the Savannah River Site, South Carolina, with future processing plans dependent on developing a predictive understanding of its nucleation, growth and transformation in highly alkaline solution. However, mechanisms of gibbsite nucleation and growth remain poorly understood. In this work, magic angle spinning nuclear magnetic resonance (MAS-NMR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray absorption spectroscopy (XAS), high resolution powder X-ray diffraction (XRD), and X-ray Pair Distribution Function (PDF) techniques were used to investigate the crystallization of gibbsite from amorphous aluminum hydroxide gel precursors. By focusing on understanding the role of aluminum coordination change dynamics from tetrahedral in solution to octahedral in solids and vice versa, and by quantifying intermediate polyxoaluminate cluster formation, some unifying principles governing these transformations emerge. Furthermore, various advanced techniques reveal the transformation and aggregation of aluminum clusters during the hydrothermal process, which indicate cluster assembly pathways to gibbsite nucleation and growth. These findings are important for developing new methods to morphology and size controlled synthesis of gibbsite, and may aid in the design of chemical processes for managing the aluminum inventory in nuclear waste.

3:00 PM BREAK

3:30 PM FF04.02.06
New Chemistry for Emerging Properties of Super Atomic Solids Jingjing Yang$^1$, Jake C. Russell$^1$, Songsheng Tao$^1$, Boyuan Zhang$^1$, Alexander D. Christodoulides$^2$, Qizhi Xu$^1$, Samuel Peurifoy$^1$, Amirali Zangiabadi$^1$, Evan A.
Superatomic solids are an emerging class of functional materials assembled from atomically precise clusters. Attributing to the unique properties of constituent clusters and their collective communications, superatomic solids show intriguing electronic, magnetic, and thermal properties. Previously, the assembly of atomically precise metal chalcogenide clusters combined with fullerenes resulted in electroactive superatomic crystals with high electrical conductivities up to 0.6 S/m. Here in this presentation, I would like to introduce two new chemistries for the superatomic solids that bring greatly enhanced or previously unattainable properties to this class of materials. Our first chemistry demonstrates solid solutions at the cluster level, namely superatomic solid solutions. We have mixed two metal chalcogenide clusters with similar sizes, Co₆Se₈(PEt₃)₆ and Cr₆Te₈(PEt₃)₆, with fullerene C₆₀ and demonstrate that the resultant superatomic solids maintain the structure of the original single component but with tunable cluster ratios [Co₆Se₈(PEt₃)₆]ₓ[Cr₆Te₈(PEt₃)₆]₁₋ₓ[C₆₀]ₓ (x = 0~1). We found that the superatomic solid solutions show up to 100 times enhanced electrical conductivities as well as tunable electrical and magnetic properties. Our second chemistry aims to explore the feasibility of integrating superatomic solids in devices. One key merit is the solution-processability of these materials, unfortunately, superatomic solids tend to be crystals due to the strong electrostatic interactions between the positive and negative charged clusters. Here, we show how to endow solution-processability to superatomic solids by frustrating the strong electrostatic interactions. By grafting flexible side chains to the clusters, we show that their crystallization tendency could be fully inhibited and they can be solution-processed into homogenous and amorphous thin films with arbitrary compositions that are not achievable in crystals ([Co₆Se₈(PPr₃)₆][PCBM]ₙ (x=2,3,4,5,7,9)). We then show these thin films possess high optical transparency of up to 92%, up to thousands of times higher electrical conductivities of up to 300 S m⁻¹ and several times lower thermal conductivities as low as 0.05 W m⁻¹ K⁻¹ compared to crystalline superatomic materials, as such, they are promising as solution-processable transparent conductors and thermoelectric materials (ZT=0.02 at RT).

3:45 PM FF04.02.07
Shaping Single Crystals at Low Reynolds Number
Semih Sevim, Carlos Franco, David Rodriguez San Migue, Alessandro Sorrenti and Josep Puigmarti-Luis; ETH Zurich, Switzerland

Self-assembly processes have a key role in the bottom-up fabrication of supramolecular structures and advanced functional materials. Traditionally, the control over non-covalent synthesis has relied on tailoring the building blocks for recognition and interaction, while targeting the global minimum of the free energy landscape (thermodynamic control). Recently, however, there is a growing interest in nonequilibrium approaches and methods that can potentially engender an improved spatio-temporal control over molecular self-assembly (kinetic control). Living systems, for example, master reaction-diffusion (RD) processes to finely tune the self-assembly of individual components in space and time leading to materials with structure and functions of remarkable complexity. In this communication, we will show how the unique physical conditions offered by microfluidic environments (e.g. laminar flow regime, mixing only through molecular diffusion, fine-tuning of the reactant gradients) facilitate an improved kinetic control over self-assembly, as well as they help to unveil the pathways underlying the formation of self-assembled materials. In particular, we will demonstrate how by using continuous flow microfluidic devices we have been able to isolate kinetically trapped crystal states of a coordination polymer (CP) (a result that leads to unprecedented materials’ properties), to enhance chiral induction in a supramolecular polymer, to uncover different crystallization pathways undertaken by a metal-organic framework (MOF) towards its thermodynamic product, as well as to shape MOF crystals at the millimeter length scale.

4:00 PM FF04.02.08
Reprogramming Granular Self-Assembly with the Control of Dynamic Boundaries
Utku Culha⁴, Zoey S. Davidson¹, Massimo Mastrangeli² and Metin Sitti¹; ¹Max-Planck Institute for Intelligent Systems, Germany; ²Delft University of Technology, Netherlands

Functional and complex structures can be generated during the self-assembly process via local interactions among a large set of simpler components. The ability to program the self-assembly of components enables novel bottom-up control strategies for multi-particle active systems, fabrication methods for functional materials, and exploration of fundamental physics. However, reprogramming requires multi-stability, and reversible selection of self-assembling
particle patterns which remains a challenge. We demonstrate the statistical reprogramming of two-dimensional, porous self-assembled structures by isothermal quenching of millimetric, orbitally-shaken, and magnetically repulsive particles. We select among a finite set of self-assembled patterns repeatably and reversibly by controlling the rate of change of the boundary volume. We report the transition from fluid- to solid-like states of driven granular particles during quenching to realize out-of-equilibrium self-assembly. With this method, we demonstrate the reprogrammable stiffness of granular self-assemblies. This work can extend to the tuning of mechanical, optical and electromagnetic properties of functional materials that depend on the spatial configuration of their components. The particles in the current work are morphologically and functionally symmetric; however the introduction of particle anisotropy may allow the programming of additional functionalities of the self-assembled structures.

4:15 PM FF04.02.09
An Inverse Pourbaix Approach to Predictive Hydrothermal Synthesis Wen Hao Sun1,2 and Gerbrand Ceder2; 1University of Michigan – Ann Arbor, United States; 2Lawrence Berkeley National Labs, United States

Pourbaix (E-pH) diagrams are often used to guide the hydrothermal synthesis of transition metal oxides. However, non-equilibrium oxide phases often precipitate from aqueous solution, which are difficult to anticipate from equilibrium Pourbaix diagrams. Here, we construct a theoretical framework to reveal the nanoscale and metastable energy landscapes of Pourbaix diagrams, providing quantitative insights into the size-dependent thermodynamics of metastable oxide nucleation and growth in water. We show that a thermodynamic analysis that takes into account these additional thermodynamic regimes can successfully capture which metastable MnO2 polymorphs appear during hydrothermal synthesis, and the order of their appearance. We further extend our theoretical framework to address the ‘inverse’ stability question for hydrothermal synthesis. That is, rather than plotting Pourbaix diagrams under varying solution conditions to search for a stable phase, can we instead solve for solution conditions where a target phase is stable? We demonstrate this ‘inverse’ formalism by computing the aqueous stability conditions for the relatively soluble compound LiFePO4, as a function of [Li], [Fe], [P], E, and pH.


4:30 PM FF04.02.10
Single Crystals from Solution at Room Temperature via Assembly and Epitaxy of Nanocubes Harshal Agrawal1, Biplab K. Patra1, Thomas Altantzis2, Annick De Backer2 and Erik Garnett1; 1AMOLF, Netherlands; 2University of Antwerp, Belgium

Additive manufacturing has enabled low cost, large area, and solution-based processing. Moreover, it is also possible to assemble full-scale working devices with quantum dots (QDs) as the active layer. Small fundamental building blocks (<100 nm) in the form of nanocrystals offer the unique flexibility to assemble crystals in complex shapes realizing novel functional properties via bottom-up assembly. In this work, we demonstrate the assembly of nanocubes capped with polyvinylpyrrolidone (PVP) into arbitrary patterns including curves of varying radii of curvature. We use polydimethylsiloxane (PDMS) as the flexible template to directly print and pattern the cubes at the same time on the substrate from a colloidal solution. Subsequently, we remove the ligands or use epitaxial overgrowth to convert them into single crystals. The effect of angular misalignment between adjacent cubes and the resulting crystallinity of the welded structure was investigated with high-resolution transmission electron microscopy (HRTEM). We demonstrate that single crystalline interfaces can form which are strain-free and without dislocations. The technique proposed enables room temperature fabrication of patterned single crystalline materials which makes it compatible with low heat resistant flexible polymeric substrates and roll to roll processing to enable next-generation optoelectronic devices.

4:45 PM FF04.02.11
Designed 3D Crystalline Organizations of Nano-Objects with Addressable Bonds Brian Minevich1, Jason Kahn1, Aaron Michelson1,2 and Oleg Gang1,2; 1Columbia University, United States; 2Brookhaven National Laboratory, United States

There have been significant advances in the field of self-assembly of functional, nanoscale materials into periodic
2D and 3D arrays. A number of strategies have been demonstrated for the crystallization of these materials using complementary DNA shells or other linking motifs. However, most notable methods are system-specific, dominated by particle shape, and remain challenging to obtain multiple lattices using a single set of particles. Instead, a more broadly accessible strategy for the assembly of crystalline organizations with programmable nanoscale features can be achieved using well defined DNA constructs integrated with nano-objects. Each of the integrated units can self-assemble in solution into periodic arrays, and can be probed in-situ by Small Angle X-ray Scattering (SAXS). The symmetry of the resulting crystalline assemblies is determined by the unit geometry and the pairwise DNA bonds. Due to the sequence specific nature of DNA, it is possible to encode unique bonds at these specified sites. The addressability of the inter-frame bonds provides the foundation for encoding multiple crystallographic organizations through specific sets of pair-wise bonds. We show that this strategy allows for the design and assembly of complex designed nanoscale architectures, including an analog of a perovskite’s structure, multiscale organizations, and chiral crystals.

SESSION FF04.03: Coating Methods—Functional Materials
Session Chairs: Detlef Smilgies and Samuel Thomas
Tuesday Morning, December 3, 2019
Hynes, Level 3, Room 311

8:00 AM *FF04.03.01
Solution-Crystalized Large-Area Organic Semiconductor Films and High-Performance Organic Circuits Jun Takeya; The University of Tokyo, Japan

Electronic devices in the future sustainable societies require maximum function with minimum amount of constituent materials and energy cost for production. Electronic functions are often originated from two-dimensional material properties so that device components of large area and small thickness saves material consumption. The fundamental electronic functions such as switching “zero” and “one” in the digit of information are governed only by a nanometer-scale thin layer at the very surface of the semiconductor material due to the very short penetration length of electric field. Future ten-meter scale large-area display also needs to be more “two-dimensional” to save materials and save energies to carry and equip on billboards.

This presentation focuses on recently developed ultrathin organic semiconductor single crystalline films that is suitable for large-area production with low energy consumption; the films is easily formed to large area from solution at relatively low temperature at 80 degrees centigrade. Extremely thin crystal films are controllably grown to a-few molecular layers with the thickness of only 10 nm, so that material cost can be only 0.01 USD per cm2. The talk begins with material chemistry of designing the semiconductor molecules that causes very high carrier mobility more than 10 cm2/Vs. Furthermore, Recent development of key technologies for printed integrated circuits which can provide future low-cost platforms for RFID tags and sensing circuitries. Finally, a technology for large-area light-weight display sheets will be demonstrated.

Such prospect bears increasing reality because of recent research innovations in the field of material chemistry, charge transport physics, and solution processes of printable organic semiconductors. With excellent chemical and thermal stability in recently developed new materials, we are developing simple integrated devices based on CMOS using p-type and n-type printed organic FETs. Particularly important are new processing technologies for continuous growth of the organic single-crystalline semiconductor “wafers” from solution and for lithographical patterning of semiconductors and metal electrodes. Successful rectification and identification are demonstrated at 13.56 MHz with printed organic CMOS circuits.

8:30 AM *FF04.03.02
Motion-Programmed Bar-Coating Approach for Fabricating Highly Ordered and Oriented Organic Semiconductor Thin Films Kilwon Cho; Pohang University of Science and Technology, Korea (the Republic of)

Solution-processed organic thin-film transistors (OTFTs) have received enormous interest due to their great potential for realizing low-cost, lightweight and flexible electronics applications, such as displays, wearable sensors and electronic skins. Although several novel solution-processing techniques for achieving highly-crystalline organic
Thin film transistors (TFTs) are essential building blocks in a variety of electronic devices, and play important roles in transmitting electronic information. Generally, the sequential deposition of each component such as a semiconductor layer, an insulator layer, and contact electrodes is required in TFT fabrication processes. In order to achieve high performance devices, it is necessary to control the interface between these layers, which makes the device fabrication process complicated. This difficulty is even more crucial in the case of organic TFTs (OTFTs), which are promising building blocks in printed electronic devices thanks to the soluble nature of organic semiconductors (OSCs). By utilizing the solution process, single-crystal thin films of OSCs composed of only a few molecular layers can be obtained with large areal coverage[1]. However, to obtain perfect single crystal, conditions of underlayers need to be precisely controlled. So far, there have been strict limitation on candidates for underlayers of OSCs. For example, they must satisfy the requirements such as heat tolerance, organic solvent durability and surface energy. In this study, we demonstrate water exfoliation to obtain self-standing thin films of solution-processed single-crystal OSC thin film. Furthermore, the developed transfer method allows the facile integration of OSC layer of OTFTs.

A single-crystal thin film of the analogs of our benchmarked material[2], 3,11-dinonyldinaphtho[2,3-d:2′,3′-d′]benzo[1,2-b:4,5-b′]dithiophene (C9–DNBDT–NW), was grown via continuous edge-casting method[3] on a freshly cleaved piece of natural mica. Then, the C9–DNBDT–NW/mica was carefully immersed in water. In only a few seconds, the C9–DNBDT–NW thin film was peeled off from mica substrate. The preservation of original single crystallinity during this step was confirmed by transmission electron microscope measurements. The successful exfoliation of an OSC thin film from a mica substrate can be attributed to the difference in the surface energy. C9–DNBDT–NW has a highly hydrophobic alkyl chain that stands perpendicular to the substrate, which gives a high contact angle of water of 108°, while a freshly cleaved mica has a super hydrophilic surface as indicated by a contact angle of 3°. The large difference in the surface energy allows water to infiltrate between the interface of OSC and mica.

In order to employ the exfoliated single-crystal OSC thin film as an active semiconductor layer in OTFTs, a transfer technique was developed. First, the super hydrophobic substrate on which the OSC thin film was fabricated was mounted on the destination substrate. Then, a few droplets of water were applied near the edge of the template substrate, which promotes an exfoliation of OSC thin film from the template substrate and results in perfect transfer to the destination substrate. The present transfer technique allows a wide usage for the underlayers of OSC layer. As representative examples, we demonstrated fabrication of OTFTs on (i) a highly hydrophobic surface (fluorinated polymer coated substrate), and (ii) a substrate with low thermal stability and solvent resistance (commercially available food wrap). The fabricated OTFT showed remarkably high electronic performance with a mobility up to 12 cm² V⁻¹ s⁻¹. We also demonstrated the deposition of large-area OSC thin films of 3 cm × 3 cm, which shows the scalability of the present technique. All of 100 OTFTs fabricated with photolithography process showed transistor operation with a high mobility of 10 cm² V⁻¹ s⁻¹. These results represent that the water exfoliation and the transfer method developed in this study enable an ideal production of OTFTs in printed electronic devices.

9:15 AM FF04.03.04
High Speed Real Time Single Droplet Analysis to Improve Spray Pyrolysis Deposition Process
Jonas Köhling, Kavish Tyagi and Veit Wagner; Jacobs University Bremen, Germany

Spray pyrolysis is a cheap, scalable process for deposition of thin functional layers that can be used in electronic or optic applications. Temperature is one of the crucial parameters that influence the properties of the thin layer. Deposition properties change around the Leidenfrost temperature where smoother films are obtained at higher temperatures. Leidenfrost temperature depends mainly on the solvent and the substrate. Other deposition parameters like the droplet lifetime, droplet movement and evaporation rate are usually neglected.

In this work we follow a new real time approach to determine the microscopic properties and the interaction of small droplets (smaller than 80 µm) on hot surfaces on a timescale below 1 ms. A uniform distribution of small droplets are produced by an ultrasonic atomizer and transported by an inert carrier gas onto the temperature controlled substrate. The behavior of the droplets at the surface is monitored by a high speed camera with up to 10,000 frames per second. Droplet properties are automatically extracted by a computer algorithm and statistically analyzed. For time-dependent properties the droplets are being automatically tracked on the surface. The findings enable to obtain physical parameters of the droplets during their lifetime. Furthermore, they help to optimize parameters of the spray pyrolysis deposition process, e.g. for thin film zinc oxide deposition used in thin film transistors.

9:30 AM FF04.03.05
Eliminating the Aging Effect in Organic Semiconductor Thin-Film Transistors
Jing Wan, Yang Li, Randall Headrick, Adam C. Whalley and Jonathan Hollin; University of Vermont, United States

The pen-writer solution deposition method is used to deposit 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) organic semiconductor thin films and also polymer dielectric layers. The performance of top-contact bottom-gate C8-BTBT transistor is found to improve with time in ambient air, which is consistent with passivation of shallow traps during exposure to air. In addition, severe non-ohmic injection and large contact resistance resulted from gold penetration during the evaporation process are observed with these top-contact transistors. This aging effect can be eliminated in the bottom-contact geometry when gold was deposited first without the penetration issue and contact resistance was reduced an order of magnitude by treating the gold electrode with pentafluorobenzethiol (PFBT). An optimized geometry is obtained by using pen-written Cytop™ dielectric in a top-gate bottom-contact structure, which exhibits a near-intrinsic average saturation mobility of 4.73 cm²/V-s with C8-BTBT thin films deposited at high writing speed (25mm/s) and contact resistance down to 5.52*10² W.cm. We will report temperature-dependent carrier transport results for the high mobility C8-BTBT top gate transistors.

9:45 AM FF04.03.06
Understanding of Structure-Property Relationship Enables Blade-Coated Amorphous In2O3 Thin-Film Transistors at Low Temperatures
Ahmad R. Kirmani, Emily F. Roe and Lee Richter; National Institute of Standards and Technology, United States

Metal oxide thin-film transistors (MOTFTs) are expected to play a vital role in enabling printed transparent and flexible electronics, given their excellent charge transport, wide bandgaps and solution processability. Compatibility with plastic electronics, however, strictly requires MOTFTs to be processed at low temperatures in a scalable fashion, a necessity that has so far been a challenge. Herein, we explore blade-coating of indium oxide (In2O3) TFTs via sol-gel and combustion chemistries using 2-methoxyethanol (MeOEt) as the processing solvent. Blade coating is an established prototyping technique for slot-die coating. We find that the sol-gel chemistry enables amorphous In2O3 TFTs annealed at 200°C with moderate electronic mobility (ca. 1 cm²V⁻¹s⁻¹). Subtle increase in annealing temperature to 212°C preserves the amorphous state whilst increasing the mobility (ca. 5 cm²V⁻¹s⁻¹). Films coated using combustion synthesis are found to bypass the electronically-active amorphous state leading to an early onset of crystallization. This behavior is expected given the lowered nucleation barrier thanks to the added fuel in the combustion ink. Paradoxically, blade-coated combustion TFTs are found to possess poor charge transport at low temperatures of 200-250°C. Small-angle X-ray scattering evidence suggests that early nucleation during combustion leads to formation of nanocrystalline domains that are deleterious to charge transport. Our results highlight that surprisingly it is not crystallization, rather the absence of it that is required to fabricate high-mobility, low-temperature In2O3 FETs using blade coating.
10:00 AM BREAK

10:30 AM *FF04.03.07
Solution-Processed High Temperature Organic Semiconductors and Devices Jianguo Mei; Purdue University, United States

High-temperature operation (i.e., beyond 150°C) is of great interest for many electronics applications. To achieve charge transport characteristics for organic semiconductors at elevated temperatures is fundamentally challenging. We report a general strategy to make thermally stable high-temperature semiconducting polymer blends, composed of interpenetrating semicrystalline conjugated polymers and high glass-transition temperature insulating matrices. When optimized, such polymer blends can display a temperature-insensitive charge transport behaviors. Further, We employ polyimide substrates, polyimide dielectrics, and a polyimide-based semiconducting blend to achieve flexible and thermally-robust transistors. An in situ temperature-dependent charge transport study was used to demonstrate that these devices can operate in extremely high temperatures and can sustain prolonged baking. Our devices maintained stable charge-transport characteristics with charge mobilities of 0.20 cm²/V s, ION/IOFF of 10⁴, threshold voltage of 3 V, and operational voltage of 10 V when baked at 195 °C for 2 h.

11:00 AM FF04.03.08
Femtoliter Meniscus-Guided Crystallization for 3D Printing Mojun Chen, Jihyuk Yang and Ji Tae Kim; The University of Hong Kong, Hong Kong

3D printing, one of the most disruptive technologies to emerge in recent years, has attracted increasing attention due to its potential impact on science, industry, and society. Winning high-quality materials is one of the most important challenges in modern 3D printing technology. To this end, beyond exterior shaping, 3D printing techniques that can also engineer crystallinity or molecular orientation are in a great demand. Here, we have developed a new method to incorporate solution-mediated crystallization into nanoscale 3D printing. The key idea is to exploit a femtoliter solution meniscus formed on a nanopipette to guide evaporation-induced crystallization in mid-air. Evaporative loss of solvent rapidly creates a supersaturated concentration field of solutes inside the femtoliter meniscus, leading to the nucleation and growth of nanocrystals. Furthermore, omnidirectional guiding of the meniscus with moving the nanopipette realizes freeform 3D nanostructures with excellent crystallinity. By employing this method, we have successfully demonstrated nanoscale 3D printing of two promising material systems: (1) organic-inorganic metal halide perovskites and (2) self-assembled peptides. In this talk, we will present the theoretical and experimental results including examples of 3D printed crystalline structures and discuss prospects of our work for potential applications in electronics and optoelectronics.

11:15 AM FF04.03.09
Controlled Synthesis and Transport of Micro- and Nanostructured Thin Films Using Microreactor-Assisted Nanomaterial Deposition Process Chih-Hung Chang, Zhongwei Gao and Yujing Zhang; Oregon State University, United States

Microreactor-Assisted Nanomaterial Deposition (MAND) process combines the merits of microreaction technology and solution phase synthesis of nanomaterials. This technique uses continuous flow microreactors for the synthesis, assembly and deposition of nanomaterials. MAND processes control the heat transfer, mass transfer and reaction kinetics using well-defined microstructures of the active unit reactor cell that can be replicated to produce higher chemical production volumes. This important feature opens a promising avenue in developing scalable nanomanufacturing. Furthermore, the continuous flow microreactor opens up the opportunity to conveniently assemble unique nanostructures and nanostructured thin films. In this presentation, we will report our recent progress in using continuous microreactors to achieve controlled synthesis and transport of reactive building blocks for the fabrication of micro- and nanostructured thin films of inorganic compound semiconductors such as metal oxides and metal chalcogenides and organic-inorganic hybrid materials like metal organic frameworks along with the applications of these functional materials.

11:30 AM FF04.03.10
Nickel-Rich Cathode Material Synthesized by Flame Spray Pyrolysis Yujia Liang, Jinhup Han, Kyojin Ku, Eungje Lee and Joseph Libera; Argonne National Laboratory, United States
Process scaling-up is an essential step to apply laboratory innovations into mass-manufacturing. Unfortunately, the small scale of laboratory synthetic routes makes them difficult to be scaled-up due to the significant difference of transport phenomena between the two scales and the resultant kinetics dilemma during scaling up. Development of the scalable process is a promising strategy to address that issue. Among those scalable processes, the ones based on aerosol science and technology are intrinsically easier to be scaled-up by simply increase the feed solution concentration or reduce the residence time. The product morphology, composition, and crystallinity can be designed a priori. Currently, three aerosol processes, spray pyrolysis, spray drying, and flame spray pyrolysis, are widely used to fabricate metals, composites, and oxides.

To meet the demands of the US Department of Energy (DOE) on the high energy density battery materials and large scale synthesizing, Argonne National Laboratory has built a state-of-art facility based on flame spray pyrolysis. Feed solutions containing salts are continuously atomized and fed into self-supported flame. Particle formation by gas-to-particle route is completed within milliseconds. A scalable process has been developed to manufacture nickel-rich cathode materials at a scale of 20 g/h. The synthesized materials displayed excellent battery performance in terms of cycling stability and rate performance. This solution-based synthetic strategy is a promising method to tackle the bottleneck of increasing production rate.

11:45 AM FF04.03.11
Flexible Thermochromic Smart Films by IPL Sintering of VO₂ Nanoparticle Ink Kwang-Seok Kim, Siwhan Lee, Ji Won Youn and Dae Up Kim; Korea Institute of Industrial Technology, Korea (the Republic of)

Large-area fabrication of vanadium dioxide (VO₂) on polymeric substrates has been a great challenge to manufacture the flexible thermochromic smart films which control the influx of radiant heat transfer by attaching to pre-installed windows. These smart window films are promising for applications in building windows and automotive glasses to improve the energy efficiency. However, the formation of VO₂ layer on flexible substrates has been rarely reported due to the high temperatures of VO₂ growth process. Herein, we demonstrate the fabrication of VO₂ layers from hydrothermal synthesized VO₂ nanoparticle ink using multi-step intense pulsed light (IPL) sintering. IPL irradiation rapidly triggers the evaporation of organic vehicles and the formation larger VO₂ clusters, and improves significantly the crystallinity and thermochromic performance of VO₂ granular films. These films exhibit visible light transmittance of 65.7%, excellent infrared modulation at 2000 nm of 43.8%, and salient solar modulation efficiency of over 12%. IPL sintering of VO₂ nanoparticles effectively enhances the crystallinity and stoichiometry of VO₂ layers on a polyethylen terephthalate substrate. It is believed that the proposed strategy provides new insight into the manufacturing of flexible thermochromatic smart films for energy saving.

SESSION FF04.04: Solution Processed Inorganic and Hybrid Semiconductors
Session Chairs: Jianguo Mei and He Wang
Tuesday Afternoon, December 3, 2019
Hynes, Level 3, Room 311

1:30 PM *FF04.04.01
Changing the Dimensions of Organic Metal Halide Semiconductors Michael L. Chabinyc; University of California, Santa Barbara, United States

Hybrid organic metal halides, such as CH₃NH₃PbI₃, have garnered significant attention because they are earth-abundant, solution-processable materials that can be used to form solar cells with high power conversion efficiency (>20%). Despite their high performance in lab-based devices, there are significant questions about the phase behavior of these materials and their resulting properties. For example, an interesting feature of these compounds is the ability to form layered Ruddlesden-Popper phases with quantum confinement by introduction of mixed organic cations. We will present our work on understanding the electronic properties of 3D and 2D Pb- and Bi-based systems. The microstructure of thin films of layered Ruddlesden-Popper compounds, (CH₃(CH₂)₃NH₃)n(CH₃NH₃)ₙ₋₁PbI₃n₋₁⁺ (n = 1, 2, 3, 4) suggests that they are not phase pure with varying composition depending on the growth conditions used. While these compounds are structurally disordered, apparent from quantitative analysis of grazing incidence X-ray scattering and electron microscopy, they surprisingly still have sharp band edges. Recent results on the optoelectronic properties of these materials will be discussed.
Lead halide-based perovskite nanocrystals are promising as optoelectronic materials for their easy tunable optical range, high absorption coefficient and photoluminescence quantum yield and solution processible preparation. However, ionic properties of the halide-based perovskite nanocrystals have a stability problem against humidity, heat, and long-term light irradiation. Especially the perovskite nanocrystals consisting of iodide as anion, which have larger ionic radius and lower electronegativity than chloride and bromide, show low crystalline phase stability and photoluminescence quantum yield without any surface post treatments. In order to enhance the stability of the materials and also tune the optical range up to near infrared region, it is necessary to introduce elements with low ionic radius and high electronegativity

Herein we report new perovskite nanocrystals substituted with the lead cation with iso-valent tin cations which have low ionic radius and high electronegativity for high stability issue. The tin cation can control the distortion of the metal halide octahedron and make the strong bond with iodide in nanocrystals. To control the activity of two different metal cations and enhance the stability of the nanocrystals, we use phosphine as a functional group of base ligands rather than alkyl amine ligands. Considering the pKa of the conjugate acid of the phosphine and amine as Brønsted bases, the phosphine is weaker Brønsted base than amine. And phosphine ligands are expected to have lower reaction constant for the acid-base reaction with oleic acid which is used for acid ligands for synthesis of perovskite nanocrystals. This results in the tuning the reaction between the oleate and metal cation to change the activity of the metal cation. Therefore, base ligands having phosphine as a head group are used to finely control the activity of the metal cation via acid-base reaction with acid ligands.

This results demonstrate that the acid-base reaction between ligands should be considered to control the activity of the precursor of the nanocrystals. Furthermore, the phosphine ligands as base ligands can control the activity of two different metal cations to mediate the growth of the alloyed perovskite nanocrystals via acid-base reaction. It is highly expected that the stable Pb-Sn alloyed iodide perovskite nanocrystals can be useful for various optoelectronic applications in the near future.

Reference:

Hybrid organic-inorganic perovskites have been of paramount interest for solution-processible solar cells, reaching photon conversion efficiencies larger than 23%. We will study in detail the effect of different processing routes, including use of different coating and annealing methods, antisolvent drip, as well as mixtures of organic cations, halogen anions, and metal cation additives. We have performed in-situ time-resolved x-ray scattering experiments during processing, that provide detailed information about the emergence and disappearance of different crystalline phases, and how these affect the final film morphology. Our method allows us to assess, how different material composition and processing conditions influence the crystallization process and we can correlate these findings with the resulting photon conversion efficiency of the films.

Mechanisms Study of Meniscus-Guided Perovskite Deposition for Photovoltaics Devices Xiaoyu Deng, Stephanie Guthrie, Luke Huelsenbeck, Gaurav Giri and Joshua Choi; University of Virginia, United States

In order to realize scalable fabrication of perovskite optoelectronic devices, large area deposition techniques such as solution shearing must be realized and perfected. However, the mechanisms of fabrication processes are still not well studied in different solution shearing regimes. By monitoring the precursor species during crystallization process using In-situ Grazing Incidence Wide-Angle X-ray Scattering, the crystallization process in low shearing speed meniscus regime is proven to happen under lower supersaturation. The low supersaturation contributes to the bigger crystal size of thin film while high speed shearing results in thin films with small size crystals. Photodetectors with perovskite thin films coated at low shearing speed meniscus regime show much higher internal quantum efficiency because of the larger crystal domain size and uniform orientation inside of domains. This shows continuing study and rational design of the crystallization process is needed to push perovskite technology toward useful applications.

Size-Dependent Phase Stability and Optical Properties of CsPbX₃ (X = Br, I) Nanocrystals Ruoxi Yang and Liang Z. Tan; Lawrence Berkeley National Laboratory, United States

Cesium lead halide perovskites are promising candidates for photovoltaic and light-emitting diode applications. Bulk CsPbX₃ however, are structurally unstable, transforming into an orthorhombic phase at room temperature. Improved thermal stability can be achieved in nanocrystal form with stability and optoelectronic properties dependent on the size of the nanocrystal.

Using first-principles calculations, we investigate phase stability and optoelectronic changes as a function of varying nanocrystal size. The stabilization of the CsPbI₃ cubic phase against the orthorhombic phase at nanocrystal dimensions of a few nanometers is explained by the competition between short-range bond formation and long-range electrostatic forces. We demonstrate lattice constants and band gap scaling behavior with nanocrystal size, explaining discrepancies between experiments and simple quantum confinement models previously proposed.

We also show that superlattices of CsPbBr₃ nanocrystals preserve the photoluminescence signature of the constituent nanocrystals, while undergoing structural changes that give rise to new photoluminescence peaks. With
multi-scale modeling, we predict the rate of these changes and simulate their optical properties.

4:15 PM FF04.04.08
Room Temperature Synthesis, Self-Assembly and Anion Exchange of Nano to Micron Scale Lead Chalcogenide Particles  
**Swapnil D. Deshmukh, Kyle Weideman and Rakesh Agrawal; Purdue University, United States**

Lead chalcogenides are one of the important class of semiconducting materials. PbS and PbSe have shown promising performance in the field of photovoltaic devices when synthesized in the form of quantum dots with power conversion efficiencies exceeding 11% while PbSe and PbTe in the pure and alloyed form are one of the best performing thermoelectric materials with the figure of merit (zT) greater than 2. These materials promise further scope in performance improvement by introducing controlled nano-structuring of material for device fabrication which is realized via solution chemistry.

In this work, we have synthesized lead chalcogenide materials via solution processing route at ambient reaction conditions using lead halide and pure chalcogen precursors. Unlike traditional syntheses routes, we have demonstrated phase pure, carbonaceous impurity free particle synthesis using a highly volatile organic mixture of amine and thiol. For these syntheses, we have observed instantaneous reactions with simultaneous self-assembly yielding nano to micron scale structures from PbS nanoparticles. These assembly sizes were further controlled such that the desired quantum confinement yielding specific optical bandgap of PbS nanoparticles is achieved in sub-micron structures. Similar controlled nano to micron scale structures for PbSe and PbTe materials were also synthesized and then studied using cross-sectional FIB milling and TEM/STEM analysis to understand the different interiors in the structures. Along with the size of the structures, the morphology and shape of the structures were also manipulated giving highly faceted cubic structures in addition to original spherical assemblies.

Similar to morphological evolution, compositional variation was also achieved at room temperature using this new solution route. Homogeneous alloys of PbSSe in the form of nanoparticles and self-assemblies were obtained via reaction and room temperature anion exchange strategy respectively. This alloy formation approach was further extended in the case of PbSeTe material where a homogeneity in alloy formation was realized by gradual diffusion of chalcogens in the structure as a function of heat treatment.

4:30 PM *FF04.04.09
Solution Processing of Metal-Halide Perovskite Films—Insight from In Situ X-Ray Diffraction  
**Michael F. Toney; SLAC National Accelerator Laboratory, United States**

Hybrid organic-inorganic metal-halide perovskites have excited the photovoltaic community due to their high light to power conversion efficiencies. One surprising aspect of HOIPs is that they are synthesized with solution processing and under mild conditions (e.g., 100°C annealing). Understanding the role of processing on crystallization pathways of HOIPs can provide insight into developing new processing strategies. In this talk I will show our recent results on the HOIP formation mechanisms during solution processing. We have investigated the film formation of Cs-FA-containing perovskites during in situ spin coating, blade coating, and the subsequent thermal annealing using X-ray scattering. Different processing approaches such as anti-solvent [chlorobenzene (CB)] and compressed-gas N2 treatments were applied during film casting. I will show how these different processing routes affect the competition between the formation of the non-perovskite δ-phase and perovskite α-phase during film formation and subsequent annealing. I will also discuss the formation of MAPbI3 films from the single-step deposition of lead chloride and three equivalents of methylammonium iodide (PbCl2 + 3(CH3NH3I)). We use X-ray scattering and absorption to determine the film formation mechanisms, revealing the importance of a self-regulating mechanism that slows the film growth. This work provides insight into optimizing processing conditions and realizing enhanced optoelectronic properties in HOIPs.
**FF04.05.01**

**Monitoring Solid State Reactions at the Nanoscale in Binary Nanocrystal Superlattices to Access Tunable Multinary Metal Oxides** Chethana Janardhana Gadiyar and Raffaella Buonsanti; Ecole polytechnique fédérale de Lausanne, Switzerland

Multinary metal oxides (MO) are the key active materials in a range of energy applications, from batteries to fuel cells, from water oxidation catalysts to light absorbing photoanodes for artificial photosynthesis. The synthesis of compositionally homogenous and morphologically-controlled films is crucial to understand how composition and structural parameters impact performance.

Here, we discuss our work on using colloidal nanocrystals (NCs) as nanoscale precursors to access tunable multinary MOs of interest as light absorbers for water splitting. We have already demonstrated that copper vanadates with variable grain size can be obtained when reacting copper NCs of different sizes with a molecular vanadium precursor.[1] By reacting two NC seeds (Cu +WO₃) with a molecular vanadium precursor, Cu₂V₂O₇/WO₃ heterostructures were also synthesized, thus increasing the level of complexity achievable by our NC-seeded growth.[2] To further advance the understanding of the solid state reactions occurring between NCs, we are now taking advantage of the formation of ordered binary NC superlattices.[3] The idea is to use in-situ electron microscopy to monitor the transformation of CuO NCs and Fe₂O₃ NCs towards copper ferrites.[4] We show that Fe₂O₃-Cu NC in AlB₂ and NaCl superlattices can be obtained by properly tuning the NC size, ligand shell and solvents. We use a combination of electron microscopy techniques together with elemental compositional mapping and X-ray techniques, like GIWAXS and GISAXS, to study the growth of compositionally homogenous copper ferrite from the reaction of the two components in the superlattice. We believe that this knowledge can guide the development of a general synthesis procedure for achieving ternary MO films with tunable composition and morphology.


**FF04.05.02**

**Tuning the Synthesis of Platinum–Copper Nanoparticles with a Hollow Core and Porous Shell for the Selective Hydrogenation of Furfural to Furfuryl Alcohol** Shuangshuang Huang; Wuhan University, China

In this work, we report the synthesis of Pt–Cu nanoparticles with hollow core and porous shell based on self-assembly of ultrasmall particles. At the initial stage, Pt–Cu cage frames with porous outermost shells were formed. These pores on the shells served as tunnels to afford getting across by residual Pt and Cu ions in the solution. These Pt and Cu ions then mostly deposited on the inside shells to thicken the width of the shells, leading to the smaller dimension of the hollow core. By carefully governing the reaction conditions, the thickness of the shell and the size of the hollow core could be precisely tuned. Furthermore, we compared the catalytic performance of Pt–Cu nanoparticles with hollow-core structures and Pt–Cu nanoparticles without a hollow-core structure for the selective hydrogenation of furfural to furfuryl alcohol. It is found that the Pt–Cu nanoparticles with a hollow-core structure exhibited an over 4-fold increase in catalytic activity, compared to Pt–Cu nanoparticles without a hollow-core structure. In particular, these Pt–Cu with hollow-core nanoparticles achieved almost 100% selectivity toward furfuryl alcohol, which cannot be obtained using bimetallic Pt–Cu nanoparticles without hollow-core structure.

**FF04.05.03**

**Decreasing Structural Disorder of ZrO₂ Nanocrystal by Ligand Exchange—A PDF and Theoretical Analysis** Edson R. Leite¹,², Içamira C. Nogueira³, Adalberto Fazzio¹, Gabriel Schleder³, Gustavo Azevedo⁴ and Querem Rebelo³; ¹Centro Nacional de Pesquisa em Energia e Materiais, Brazil; ²Federal University de Sao Carlos, Brazil; ³Federal University of Amazonas, Brazil; ⁴Centro Nacional de Pesquisa em Materiais e Energia, Brazil; ⁵Federal University of Western Para, Brazil

In this work, we report the synthesis of Pt–Cu nanoparticles with hollow core and porous shell based on self-assembly of ultrasmall particles. At the initial stage, Pt–Cu cage frames with porous outermost shells were formed. These pores on the shells served as tunnels to afford getting across by residual Pt and Cu ions in the solution. These Pt and Cu ions then mostly deposited on the inside shells to thicken the width of the shells, leading to the smaller dimension of the hollow core. By carefully governing the reaction conditions, the thickness of the shell and the size of the hollow core could be precisely tuned. Furthermore, we compared the catalytic performance of Pt–Cu nanoparticles with hollow-core structures and Pt–Cu nanoparticles without a hollow-core structure for the selective hydrogenation of furfural to furfuryl alcohol. It is found that the Pt–Cu nanoparticles with a hollow-core structure exhibited an over 4-fold increase in catalytic activity, compared to Pt–Cu nanoparticles without a hollow-core structure. In particular, these Pt–Cu with hollow-core nanoparticles achieved almost 100% selectivity toward furfuryl alcohol, which cannot be obtained using bimetallic Pt–Cu nanoparticles without hollow-core structure.
Nanocrystals (NCs) present unique physicochemical properties arising from their size and the presence of ligands. Comprehending and controlling the ligand–crystal interactions as well as the ligand exchange process is one of the central themes in NC science nowadays. However, the relationship between NC structural disorder and the ligand exchange effect in the NC atomic structure is not yet sufficiently understood. Here we combine pair distribution function analysis (PDF) from electron diffraction data (ED), extended X-ray absorption fine structure (EXAFS), and high-resolution transmission electron microscopy (HRTEM) as experimental techniques and first-principles density functional theory (DFT) calculations to elucidate the ligand exchange effects in the ZrO$_2$ NC structure. In our work, we have demonstrated that the combination of advanced characterization techniques (EXAFS and PDF from ED) with theoretical DFT calculations is a powerful tool to reveal the nature of NC structures. We presented the unprecedented result that the ligand exchange process causes a decrease in the static structural disorder of the ZrO$_2$ NCs, mainly due to strain rearrangement caused by solvothermal treatment at elevated temperatures and not due to the type of functional organic group (R) present in the X$_2$- type ligand. These results have a direct impact on NCs manipulation processes involving ligands, properties associated with their structural disorder degree, and the development of functional nanomaterials, especially for functionalities where the structural disorder located on the surface plays an important role in the physicochemical properties, such as in mechanical, photoluminescence, electronic transport, and catalytic properties.

FF04.05.04
Understanding the Electrochemically Mediated Growth of Crystalline III-V Semiconductors Using InAs as a Platform Yorick Bleijii, Marco Valenti, Mark Aarts, Loreta A. Muscarella and Esther Alarcon-Llado; AMOLF, Netherlands

III-V semiconductors have promising composition and size dependent optoelectronic properties for a variety of applications in nanophotonics and high speed electronic devices. Due to their increasing demand, large-scale production of the III-V semiconductors is required. New growth techniques have been proposed to tackle the resource- and energy-intensive techniques which are currently used. One of the proposed techniques is electrochemical mediated crystal growth, which has already been demonstrated for the III-V semiconductor growth at ambient conditions. One advantage of using electrochemical mediated growth is the possibility of controlling the crystal growth with the applied potential.

In this work, we assess via Raman spectroscopy the voltage effects on crystal quality in InAs grown at ambient conditions directly onto Indium foils. We find that the average crystal correlation size is not affected by using more cathodic potentials up to a critical potential. Beyond that critical value, the average correlation length decreases, following the phonon confinement model. This decrease can be explained by an increase in the nanostructured roughness and or porosity of the grown InAs crystals. Gas evolution of hydrogen and or arsenic and the overgrowth of As can induce this nanostructured roughness and or porosity. Therefore, we find that the crystal structure of the electrochemically grown InAs can be modified with applied potential, giving rise to the possibility to fine-tune optoelectronic properties at ambient conditions.

FF04.05.05
Excimer Laser Annealing of Sol-Gel Metal-Oxide Thin Films Christina Koutsiaki, Nikolaos Kalfagiannis and Demosthenes Koutsogeorgis; Nottingham Trent University, United Kingdom

Over the last decade, the transition from conventional vacuum based thin film deposition techniques to solution processes has remarkably empowered the evolution of a novel manufacturing scheme that involves state-of-the-art applications, such as flexible and high-performance electronics. Besides time and cost-efficiency included in their major advantages, solution processes additionally present an outstanding compatibility with a plethora of materials; small molecules, polymers and colloids, to name a few. Amongst them, metal oxides (MOs) constitute an attractive research field, as their significantly enhanced optoelectronic properties, concomitantly with high optical transparency and mechanical stability render them as highly promising, especially in delivering trend-of-the-future applications (e.g. IoT) into high throughput manufacturing.

“Sol-gel” is established as one of the currently favorable solution processes, as it uniquely links metal oxides to solution processing. This deposition of organometallic precursors via wet techniques, followed by a subsequent thermal treatment, prevails the formation of high quality, uniform and homogenous metal oxide thin films. Nevertheless, considering its demanding high processing temperatures (>250 °C), this post-deposition treatment remains challenging, as it constitutes a major obstacle that hinders the integration of temperature-sensitive materials.
(plastic) and thus large-scale manufacturing. Therefore, a breakthrough method of converting as-deposited organometallic precursors into uniform MO thin films with tunable morphological and chemical structure is essential.

A radically new idea for the processing of metal oxides is the implementation of a combination of solution-processing and laser annealing techniques. These methods marry two important attributes that are currently absent from the existing state-of-the-art commercial technologies, namely scalable manufacturing and high temperature annealing via ultra-fast laser post-processing. Because of the temporal nature of the laser-annealing step (typically nanoseconds), efficient conversion of the printed metal oxide precursor can be achieved even when the layer is deposited atop temperature-sensitive substrates such as plastic. There is currently no other method that combines these two highly attractive attributes while being compatible with existing manufacturing processes.

The applicability of this approach has already been demonstrated [S. Dellis et al. J. Mater. Chem. C] by the successful In(NO₃)₃ conversion into high quality In₂O₃ thin films, leading to the realization of high performance (μ>13 cm²/Vs) Thin Film Transistors (TFTs). We now expand the method to a pallet of metal-oxides of different opto-electronic nature (conductors, semiconductors and dielectrics) in an effort to develop a platform for a new era of metal-oxide based printable and flexible devices, on the route towards mass production of modern electronics. In particular, an extensive study regarding the optoelectronic response of three highly promising metal oxides such as ITO, In₂O₃ and Al₂O₃ after laser annealing is presented, shedding light onto the precise mechanism under which the photochemical conversion of their organometallic precursors occurs. Optical, structural and electrical behavior of the above-mentioned thin films will be reported, including their implementation in TFT manufacturing.

FF04.05.06
Residual Stress Reduction in the SiC Crystal Grown via Top Seeded Solution Growth Method Yunji Shin, Si-Young Bae, Myung-Hyun Lee and Seong-Min Jeong; Korea Institute of Ceramic Engineering and Technology (KICET), Korea (the Republic of)

During the last two decades, silicon carbide (SiC) has been widely studied for power electronics application because of its superior physical and chemical properties especially under high power and high frequency. For the reliable performance of SiC devices, control of the crystal quality related to polytype, defect density and residual stress, are very important. Thus, both thermodynamic and kinetic factors must be considered during SiC growth process. Despite the big advancement in SiC technologies, there still remain some open questions. For instance, the fabrication of high quality SiC wafers is still topical, because the commercialized crystal growing technique, physical vapor transport (PVT) method, could not easily grow high quality SiC crystal. As an alternative method growing SiC crystal, top seeded solution growth (TSSG) method has recently studied by many researchers. This method has a big advantage growing SiC crystal at low temperature and a big potential getting a high quality SiC crystal with low dislocation density. However, the thermal stress, which is the most important issue in TSSG, still exists without a key solution. During TSSG process over 1900°C, a seed crystal always experiences an abrupt temperature change when it reached the melt surface. Consequently, residual stress could remain after crystal growth, which brings about the deformation or the crack of the crystals in the subsequent processes. The melt droplet, which is often observed on the as-grown surface after process due to the surface tension, was benefited to reduce the residual stress locally but resulted in the generation of micropipes. Therefore, it is even more problematic in epitaxy growth and device performance.

Note that such stress is mostly caused by the differences in the thermal expansion coefficients between graphite and SiC material. Thus we consider that some kind of buffer layer would be helpful to reduce the thermoelastic stress. In the present study, we will discuss the recent progress on TSSG method for growing SiC crystal from the basic to the recent progress focused on the thermoelastic stress relaxation on the entire grown surface.

FF04.05.07
Intense Pulse Light Sintering Mechanism of Solution-Processed Indium-Tin-Oxide Thin Film Inyoung Kim; Korea Institute of Machinery and Materials (KIMM), Korea (the Republic of)

Solution-processed metal oxide films have shown stunning properties of high charge carrier mobility, high electrical conductivity, large dielectric constants, or optical transparency in the application of flexible solar cells, thin film transistors, light emitting devices and various sensors. However, their high annealing temperatures are still incompatible with flexible polymeric substrates even though various chemical approaches have been studied to reduce the annealing temperature. In this study, we adopted intense pulse light sintering for solution-processed indium tin oxide films instead of thermal annealing. Multi-pulses of intense light consisting of 5 on/off pulses for 2
ms were repeatedly irradiated on the films. The electrical sheet resistance of indium tin oxide film decreased effectively as the pulse number increased. However, the decreased sheet resistance tended to return back before the microstructure of film was stabilized. After the full densification, the sheet resistance did not change again, and the solution-processed indium tin oxide film showed a sheet resistance of 95 Ω/sq and a high optical transparency of 98 %. The intense pulse changed the chemical organization of oxide bonding from M-OH to oxygen deficient M-O-M structure, which was a critical factor to complete the photonic sintering of metal oxide films.

**FF04.05.08**

**Self-Assembly of Quantum Dot Gold Heterostructural Nanocrystals into Orientational Ordered Superlattices**

Hua Zhu1, Zhaochuan Fan2, Yasutaka Nagaoka1, Dennis Eggert3,4, Yuzi Liu4, Ruipeng Li5, Zhongwu Wang5, Michael Gruenwald2 and Ou Chen1; 1Brown University, United States; 2University of Utah, United States; 3Heinrich Petter Institute-Leibniz Institute for Experimental Virology, Germany; 4Max Planck Institute for the Structure and Dynamics of Matter, Germany; 5Argonne National Laboratory, United States; 6National Synchrotron Light Source II, Brookhaven National Laboratory, United States; 7Cornell High Energy Synchrotron Source, United States

The self-assembly of nanocrystals into ordered superlattices is a powerful strategy for the production of functional nanomaterials. While much progress has been made assembling nanocrystals with homogeneous composition into superlattices with novel structures and properties, high-quality multicomponent nanocrystals and their ordered assemblies are rarely reported. Besides, controlling the orientations of nanocrystals in superlattices also remains a challenge. Here, we combine experiments with computer simulations to study the self-assembly of two unique quantum dot–gold (QD-Au) heterostructural nanocrystals (HNCs), namely heterodimers and satellites. Assembly of the heterodimers results in a superlattice with long-range orientational alignment of dimers while the assembly of satellites results in a close-packed superlattice with pronounced orientational orders. Molecular dynamics simulations of a coarse-grained model suggest that anisotropic interactions between the QD and Au is responsible for superlattice formation. We also demonstrate experimentally that the degree and type of orientational alignment can be controlled by changing ligand populations. This study provides guidance for the design and fabrication of nanocrystal superlattices with enhanced structural control and potential optoelectronic properties.

**FF04.05.09**

**Crystal Engineering of Chromium Molybdate Cluster Coordinated with Lanthanides as Potential Photoluminescence Materials**

Arunachalam Ramanan and Shilabh Tewari; Indian Institute of Technology Delhi, India

Lanthanide ion-based coordination solids are majorly sought after for their distinctive optical properties’ applications in OLEDs, lasers and sensors. Recent trends include incorporating suitable ligands to increase the quantum efficiency of parity forbidden f-f transitions through synergetic effects while simultaneously preventing the coordination of solvent molecules that can quench emissive processes. In our work, we employed the well-known Anderson-Evans cluster, \([\text{CrMo}_6\text{O}_{24}]^{n-}\), a molecular cluster, that exhibits ruby–like red emission and its optically inactive analogue, \([\text{AlMo}_6\text{O}_{24}]^{n+}\), as inorganic ligands to coordinate with optically active lanthanide ions (Ln=Sm, Eu, Tb, Dy). We have successfully synthesized the whole series of closely related structures with the general composition, \([\text{Ln(OH)}_2]_3\{X(\text{OH})_6\text{Mo}_6\text{O}_{24}\}\cdot n\text{H}_2\text{O}\) with varying dimensionality; the difference in supramolecular aggregation of the same set of molecular species appears to depend on the size of the lanthanide ions. Photophysical properties were dominated by Ruby-like emission in chromium analogues while characteristic emissions of lanthanide ions were observed in the aluminium counterparts. Our results strongly suggest a possible energy transfer between lanthanide ions to chromium levels resulting in the quenching of lanthanide emission in lanthanide coordinated chromium molybdates. We have also succeeded in preparing new analogues wherein more than one lanthanide ions are present in the same crystal as well as hybrid inorganic-organic solids based on these molecular building blocks. The structural features of the system change when a competing organic ligand is added to it leading to another series of photoluminescent materials. In this talk, we discuss the structural landscape, stability and photoluminescent behaviour of all the materials with an emphasis on structure-property correlation.

**FF04.05.10**

**Surface Conversion Growth of ZnO@ZIF-8 Core-Shell Nanowires and Their Application as Water Splitting Photoanode**

Alejandro G. Galan, Andrew Gallant, Del Atkinson and Dagou Zeze; Durham University, United Kingdom

Surface conversion growth of ZnO@ZIF-8 core-shell nanowires and their application as water splitting photoanode
The evolution of nanomaterials over the last few decades has prompted widespread research on their integration into a range of applications resulting from their outstanding physical, optical and electric properties. Nanowires (NWs) have been at forefront of these developments due to the variety of semiconductor materials, highly controllable growth coupled with the large surface to volume ratio and the high aspect ratio. ZnO in particular is highly researched due to its wide band gap (3.37 eV) and high exciton binding energy (60 meV) that confers interesting piezoelectric and optoelectronic properties. In recent years, research interest in metal-organic frameworks (MOFs) has developed rapidly. MOFs are a zeolite-like nanomaterial that have been extensively studied due to their remarkably high surface area, enabling catalytic and gas storage properties. MOFs are reticular nanomaterials formed by transition metal cations coordinated by multidentate organic linkers. This combination results in a crystalline material with a flexible structure. Among the many existent MOF families, the zeolitic imidazolate frameworks (ZIF) are one of the most researched because of their exceptional thermal and chemical stability. ZIF-8 is a standout MOF comprised of zinc as transition metal nuclei and imidazolate linkers as the coordinating agent.

Here, these different forms of nanoscale materials prompted the idea for synergetic combination to create novel nanocomposite materials that exploit the individual outstanding properties, in this case for ultimate application in hydrogen production. In this work, the idea is the realisation of the integration of ZnO NWs and ZIF-8 to form a core-shell structure in which ZnO is the core and ZIF-8 is the shell around it (ZnO@ZIF-8) via a low-cost and fast production processes. A two-step wet-chemistry process is used to grow the ZnO NWs: first, a thin ZnO seed layer is deposited using atomic layer deposition. Then, the sample is introduced in a solution containing the Zn precursor and a hydroxide source. The shell is grown by means of surface conversion of the ZnO NWs. For this, we introduce a novel method based on spin coating. A methanol solution containing the imidazole linker is spin coated on top of the NWs and, afterwards, the sample is heated above the melting point of the imidazole so the surface reaction with the ZnO NWs can take placing, thus using the ZnO NWs as sacrificial pattern to grow the ZIF-8 shell. The cheap and easy route to grow the core-shell structure through this process is remarkable, especially considering that the most commonly used alternative is a hydrothermal growth that requires the use of a pressure vessel, water/dimethylformamide mixtures and long reaction times. In our case, only few droplets of a methanol solution are required to obtain comparable results.

This work presents the structural analysis and the optoelectronic characterisation of these nanocomposite materials and aims to show the first results using ZnO@ZIF-8 structures as a photoanode for the photoelectrocatalytic (PEC) water splitting of water. Electron microscopy and x-ray analysis are used to study the structure of the NWs and the core-shell structure, while voltammetry and optical methods are sued to study the optoelectronic properties. Different NW and shell growth conditions are compared to demonstrate the control over the growth of the NWs and the MOF shell in relation the long-range homogeneity and shell thickness. It is shown that the shell thickness is a critical factor that can directly influence the performance of the photoanode by controlling the electrolyte diffusion time to the ZnO NW core. The effectiveness of the core-shell structure as photoanode is compared to as-grown ZnO NWs. The PEC tests also show that the presence of the shell in the core-shell structure passivates the surface states of the ZnO core, improving its stability over time, and protecting it from photocorrosion.

**FF04.05.11**

*Au-Pt-Pd Radially-Assembled Nanospheres as Multi-Functional SERS Sensors for Rapid Detection of Pesticides Residues* Yu-Cheng Chu, Fang-Ching Chang, Jing-Wen Huang and Chun-Hua Chen; National Chiao Tung University, Taiwan

In this work, a series of novel Au-Pt-Pd ternary self-assembled porous nanospheres with featured building segments and radially distributed composition have been successfully synthesized via a facial solution approach with tri-block copolymer F127 as soft templates and applied as surface enhanced Raman scattering (SERS) chemical sensors for identifying trace amount of pesticides. Based on our previously developed techniques used for synthesizing Pt-Pd binary self-assembled nanoparticles arrays[1], in this work, to further enhance the SERS performance, Au was mainly selected and has been successfully introduced as the third active component to form the Au-Pt-Pd ternary self-assembled porous nanospheres. By adjusting the amounts of the Au precursors and F127, two unique presentative Au-Pt-Pd nanospheres respectively with spherical-like and petal-like building segments were achieved. The decoration of tiny Au nanoparticles on the surface layer of the preformed Pt-Pd nanospheres could effectively enhance the SERS hot spots via increasing coupling modes for generating large local electromagnetic fields without crushing the specialized, transparent porous architectures. The liquid penetrable copolymer networks in the synthesized Au-Pt-Pd nanospheres could effectively enhance the ability to absorb target molecules and the
consequent SERS performance. Also, the extremely uniform dimension and morphology of the synthesized Au-Pt-Pd nanospheres are essential for having steady SRES signals. It was found that the petal-like Au-Pt-Pd nanospheres exhibit a lower limitation approaching 50 ppb in detecting malachite green oxalate (MGO) and show promising potential in sensing pesticides such as thiabendazole directly on apple skins. The unique architectures as well as the active chemical composition of the present ternary Au-Pt-Pd nanospheres improve the molecular detection limitation and also show high potential for practical applications in the fields of biochemistry, chemical analysis, food safety and environmental monitoring.


FF04.05.12
Rapid Synthesis of Copper Nanowires with High Aspect Ratios in Ascorbic Acid Aqueous Solution Hiroki Oikawa, Shun Yokoyama, Kenichi Motomiya and Hideyuki Takahashi; Tohoku University, Japan

Many efforts have been made to produce low cost, flexible and high performance transparent conductive materials, replacing high cost, brittle and high performance Indium tin oxide (ITO) films. Cu nanowires (NWs) with high aspect ratios are promising materials as an alternative to ITO because of their high performance, low cost and flexibility. To take the lower limitation, the process of Cu NWs synthesis is required to be low-cost and environmentally-friendly. Cu NWs are usually synthesized via chemical reduction as this method often requires high temperature, high pressure, organic solvent and toxic reagent\(^1\), resulting in high cost. Recently, we have developed a low-cost and environmentally-friendly synthesis method in which aqueous copper complexes are reduced to Cu NWs by using ascorbic acid in acidic region near room temperature under atmosphere. Cu atoms were produced by reduction of the Cu complexes using ascorbic acid, forming decahedral Cu seeds. Subsequently, PVP bound to the newly formed (100) planes of the seeds rather than the (111) planes, and Cu atoms were continuously deposited on the (111) facets along the [110] direction, leading to the Cu NW synthesis\(^2\). It is noted that the particle size depends strongly on the driving force for the reduction. As ascorbic acid is a mild reducing agent, the driving force is smaller than that of commonly employed reducing agents. As a result, Cu seeds become larger, leading to low aspect ratios. Besides, the small driving force caused long reaction time (48 hours or more), limiting practical use of Cu NWs. The rapid synthesis of Cu NWs with high aspect ratios requires large driving force. In this study, we reported the rapid synthesis of Cu NWs with high aspect ratios based on the environmentally-friendly method. The driving force is the difference between the half-cell reactions potential of ascorbic acid and Cu complex. The redox potential of ascorbic acid changed depending on pH, enhancing the driving force in alkali region. In addition, easily reducible Cu complexes also increase the driving force. Thus, we precisely controlled pH values in the synthesis and changed Cu complexes to increase the reduction potential, leading to Cu NWs with high aspect ratios in short reaction time (1h). Detailed results and discussion will be introduced in our presentation. Part of this work has been supported by the Grant-in-Aid for Scientific Research (B) (18H03416)

Reference


FF04.05.13
Synthesis of Ga-Doped ZnO Nanocrystals Using Esterification Reaction for High-Performance Transparent Conductive Films Takuya Endo, Shun Yokoyama, Kenichi Motomiya and Hideyuki Takahashi; Tohoku University, Japan

Transparent conductive films are currently used in various optical devices such as solar cells and smartphones. Indium tin oxide (ITO) is widely used as a high performance transparent conductive film, but it is toxic and expensive rare metal. Fabrications of ITO layer on substrates usually require a sputtering system with high material loss and high vacuum environment. Metal doped ZnO nanocrystals are promising materials as an alternative to ITO because of its low cost, high transparency and low resistivity. Besides, metal doped ZnO film can be fabricated on substrates by sintering metal doped ZnO nanocrystals without material loss and high vacuum environment. In order to make high-performance ZnO transparent conductive film, ligand on crystal surfaces and crystal size controls are needed to facilitate the sintering to become bulk ZnO at low temperatures. In addition, precise metal doping is required to optimize carrier concentration and mobility in ZnO for high conductivity. These control methods about
ZnO nanocrystal have been studied using thermal decomposition method as a typical synthesis method[1]. As the synthesis method often requires high reaction temperatures and toxic reagents, we developed the synthesis of ZnO nanocrystals via esterification reaction between zinc carboxylate and alcohols at low temperature. In this study, we changed surface ligands and crystal size of ZnO nanocrystal synthesized from the esterification method[2]. We precisely controlled the amount of Ga doping into ZnO. Finally, we fabricated Ga-doped ZnO films and discuss the effect of ligand, crystal size and Ga doping on performances of the film. In the esterification between zinc oleate and oleyl alcohol, oleic acid remained on ZnO nanocrystal. Low molecular zinc carboxylates and alcohols were used to change surface ligand from oleic acid to low molecular carboxylic acids. Although low molecular carboxylic acids also work as a surface ligand, the steric hindrance of the carboxylic acid modified ZnO nanocrystals decreased, leading to bigger nanocrystals. The size was decreased by decreasing the amount of zinc carboxylate to prevent nucleus growth. The sintering of low molecular carboxylic acid modified ZnO nanocrystals with small size were facilitated at low temperatures. Metal carboxylates react with alcohols to form M-OH species with the ester, and then H2O molecule is dehydrated by condensation to form a metal oxide. When a different element is doped, two different M-OH species formed with the ester react to form M-O-M1-OH species, and then H2O molecule is dehydrated, finally produces the doped metal oxide. The amount of Ga doping into ZnO were precisely controlled by changing the amount of Ga carboxylate. We will present details of these controls and performance of ZnO conductive films.

Part of this work has been supported by the Grant-in-Aid for Scientific Research (B) (18H03416).

Reference

FF04.05.14
Overcoming the Charge Carrier Mobility Limitation of Inorganic p-Channel Thin-Film Transistors
Seonjeong Lee, Hanju Lee, Yena Ji and Kihyon Hong; Chungnam National University, Korea (the Republic of)

P-channel thin film transistors (TFTs) are essential components of complementary circuits, displays and flexible electronics. However, development of high performance p-channel TFTs has been delayed due to the charge carrier accumulation, large effective mass/low conductivity of semiconductor, and device optimization issues. Although tremendous efforts have been devoted to improve the device performance, the field effect mobility of p-channel TFTs still remained 0.01 ~ 5 cm²/Vs.

Recently, Electrolyte gated transistors (EGTs) have attracted attention for switching devices due to their low operating voltage and great device performance. We have employed EGT structure into p-channel TFTs to improve the electrical performance of devices. During the operation, EGT form high capacitance (> 1 uf/cm²) electrical double layer (EDL) and 3-dimensional hole transport channel. Thus, the huge amounts of charge carriers can be accumulated in the channel region and we can expect realization of the high performance p-channel TFTs. Using this EGT structure, we successfully demonstrated p-channel TFTs with ultra-high mobility exceeding 100 cm²/Vs and low operating voltage of ~ 0.5 V. As a semiconductor, copper iodide (CuI) was employed due to its small effective hole mass and high Hall mobility. For electrolyte gating, polymer electrolyte was used as a gate insulator. All the fabrication processes were conducted by low temperature (< 100 °C), solution process. We also examined the electrical and mechanical stability of CuI-TFTs. Finally, we demonstrated complementary inverters by the combination of CuI- and ZnO-TFTs and the circuits exhibited low operation voltage (0.7 V) and high voltage gain value of 18.

FF04.05.15
High-Performance, Solution Processed Vertical Thin-Film Transistors with p-Type CuSCN Semiconductor
Yena Ji, Hanju Lee, Seonjeong Lee and Kihyon Hong; Chungnam National University, Korea (the Republic of)

Copper(I) thiocyanate (CuSCN) has wide optical band gap (Eg = 3.5 ~ 3.9 eV), making it transparent in the optical spectrum, high charge carrier mobility, and solution processability. Due to these advantages, it has been used as a p-type semiconductor in thin film transistors (TFTs) and hole transport materials in organic/inorganic solar cells. Especially, high Hall mobility (10 ~ 70 cm²/Vs) of CuSCN allows for the possibility of realization of high performance p-channel TFTs. However, previously reported CuSCN-TFTs showed low field effect mobility in the range of 0.01 ~ 0.5 /Vs. This low mobility might be originated from the hole accumulation issue, non-stoichiometry of CuSCN and charge carrier scattering effect in the channel regions.
In this work, to realize high mobility CuSCN-TFTs, we introduced vertical structure and chlorine doping method. For vertical structured TFTs, the channel length (L) is defined as the thickness of CuSCN film. Comparing to the conventional planar structure, the L can be reduced from the several tens of micrometers to nanometer scale. Thus, employing vertical structure can minimize the charge carrier scattering effect in the channel region and our device exhibited high mobility about 3 /Vs with low operation voltage of 1V. This mobility value is 10 times higher than those of TFTs with conventional planar structure. To more improve the device performance, we doped SnCl into CuSCN. Our XPS and UPS analysis revealed that by the doping of SnCl, the Cl induces additional p-type doping effect with formation of acceptor states. The work function of material increased by 0.20 eV and the mobility of device also increased up to 4.13 cm²/Vs. Using this high performance CuSCN-TFTs, we could successfully demonstrate resistor-loaded inverters. The inverter was completely switched with in 1V of V_in variation. The dynamic response of the inverter was measured and it worked well at 500 Hz without a large rise-fall delay.

**FF04.05.16**

**Electrically Annealed and Densified Solution-Deposited Piezoelectric Thin Films** Rajinder S. Deol, Nitika Batra, Pranjal Rai, Henam Sylvia Devi, Bhaskar Mitra and Madhusudan Singh; Indian Institute of Technology Delhi, India

Sensors and actuators in various industrial, lab and environmental monitoring applications often require deposition of piezoelectric thin films like lead zirconium titanate (PZT). Such films require deposition temperatures (~600°C), are incompatible with traditional silicon-based foundries, and the high temperatures of deposition present unique process challenges. In recent years, several new classes of piezoelectric films such as sputtered lead-free potassium sodium niobate (KNN) and AlN have been developed. In the former case, owing to the differential response of potassium and sodium to needed annealing steps, and the result stoichiometric shifts near the (K:Na)=50:50 morphotropic phase boundary and the high temperature of annealing (~ 600-800°C) has created challenges to widespread adoption of KNN. In contrast, sol-gel based methods coupled with simple deposition methods such as spin-coating, dip-coating and printing offer process simplification at lower temperatures. However, the resulting amorphous films exhibit low values of d₃₃, resulting in inferior overall performance. In this work, we have examined the possibility of using high in-plane electric fields to modify the packing density of the material. A concentrated KNN sol (50:50) was synthesized using the sol gel method. Powder X-ray diffraction (XRD) measurements on the dried sol films reveal an amorphous product. Oxide substrates (University Wafers) were cleaned (RCA) and metal bottom contacts were deposited using successive DC sputtering (Cr/100Å) and RF sputtering (Au/500Å) at a base pressure of 2 x 10⁻⁶ Torr. The metal was patterned using maskless lithography (Intelligent SF100 Express) and etched (Sigma Aldrich CAS: 7681-11-0) with two electrode spacings of ~ 10μm. Films of KNN were deposited via drop casting of concentrated sol (~10 μL) onto the two electrode lateral structures and dried at 90°C prior to measurements. Energy dispersive X-ray fluorescence (EDX) reveals (K:Na)=50:50, which was confirmed using X-ray Photon Spectroscopy (XPS) surface survey measurements. The lateral devices were biased on a probe station (Cascade Microtech) with a Keithley 2450 source meter at 10V. Under the microscope, we observed sporadic possible reflow of the dried film on the positive pad, along with a 300% increase in the spot temperature estimated using a non-contact IR thermometer. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements were used to gather information about the morphology of the film in the vicinity of the device, which shows cracks in shapes that closely resemble calculated electric field patterns (COMSOL), which predict a maximal electric field of ~330 kV/cm with the averaged field far away from the device subsiding to ~100 kV/cm. The resistance between the electrodes increased by ~44% as a result of the annealing, attesting to changes in local thickness due to crack formation. Post-annealing EDX measurements showed a ~16% reduction in the volatile potassium content suggesting a local migration of ions, resulting in a stoichiometric shift to (K:Na)=44:56. SEM and AFM measurements of the annealed film were combined to estimate a volume reduction of ~4.8% over an area of 100 μm². We are currently developing the above process in combination with successive spin-coating of sol on annealed films and reannealing to develop densified films of KNN suitable for measurements of relevant electromechanical coefficients.

**FF04.05.17**

**Sol-Gel Processed Mg Doped SnO₂ Thin-Film Transistors** Changmin Lee, Seunghyun Ha, Hyunjae Lee, Won-Yong Lee and Jaewon Jang; Kyungpook National University, Korea (the Republic of)

We demonstrate sol-gel processed Mg-doped SnO₂ thin film transistors (TFTs) with high performance and improved stability. To improve the performance of tin oxide, which is unstable at a high negative threshold voltage,
magnesium is used to suppress oxygen vacancy formation. As the Mg doping concentration increases, the oxygen deficiencies decrease, resulting in a negative shift in the threshold voltage and improved stability in negative bias stress environments. In this experiment, Mg-doped (0 to 1 wt%) tin oxide TFTs are fabricated. The tin oxide prepared from a synthesized solution of tin (II) chloride dehydrate precursor and ethanol has a mobility of 13.84 cm²/Vs and -32.13 V threshold voltage shift under negative bias stress. On the other hands, the SnO₂ TFTs doped with 0.5 wt% Mg also show a mobility of 4.23 cm²/Vs and a noticeable -6.98 V threshold voltage shift under negative bias stress. Our results suggest that sol-gel processed Mg-doped SnO₂ TFTs are a promising candidate for use in high stability and high-performance applications in transparent devices.

**FF04.05.19**

*Understanding the Effect of Capping Ligand Ratio in Colloidal Synthesis of Two-Dimensional TMDCs – Stoichiometric Differences Based on Surface and Defect States*

Meeree Kim¹² and Hyoyoung Lee¹²; ¹Institute for Basic Science (IBS), Korea (the Republic of); ²Sungkyunkwan University, Korea (the Republic of)

Colloidal synthesis and surface stabilization of nanocrystals (NCs) have been well-developed and established experimentally over the past 30 years. The role of surface increases as the size of materials shrinks, and this fact shines a spotlight on the surface ligands attached on the colloidal NCs. Ligands form a ‘capping’ layer on the surface which saturate dangling bonds and stabilize surface energy, and affect to the reaction mechanism in synthesis by kinetic and thermodynamic controls. However, detailed understandings on the ligand chemistry of NCs at the atomic level were largely focused on the ionic II-VI (CdSe, CdS) and IV-VI (PbS, PbSe) semiconducting NCs. Surface ligands are classified as L-, X- or Z-type depending on the number of electrons involved in ligand-NC bonds and the identity as electron donor or acceptor. Recent studies have shown that different types of ligands stabilize each facet of ionic NCs, resulting in mixed surface ligands during the synthesis (intentionally or not). In this study, we investigate the influence of molar ratio between X- and L-type ligands on the synthesis of colloidal transition metal dichalcogenides (TMDCs). Two-dimensional (2D) TMDCs have been considered to be attractive for numerous applications because of their broad range of properties from metals to insulators. However, wet chemical synthesis of 2D TMDCs is challenging because of their additional covalency requiring a high growth temperature, and even complicated by large anisotropy in layered structure. Ideally, layered TMDCs have no dangling bonds on the basal plane (001) and therefore their ligand chemistry is largely expected to rely on only edge sites (110), (100). Reflecting the ligand chemistry of ionic NCs, we control the molar ratio between different types of ligands (X-type and L-type; halides and amines), and monitor how the surface composition changes accordingly. Stoichiometric differences and oxidation states shift in overall TMD NCs show a correlated tendency, resulting in different surface states of colloidal TMDC NCs. Based on the observations, we conclusively demonstrate that the appropriate ligand ratio is required to synthesize the desired colloidal TMDC NCs, introducing an effectiveness of ligand control in colloidal synthesis of 2D TMDCs.

**FF04.05.20**

*Surface Coating of Cu Nanowires with ZnO Using Aqueous Ammine-Hydroxo Zinc Complexes for Stable and High-Performance Transparent Conductive Films*

Shun Yokoyama¹, Kenichi Motomiya¹, Balachandran Jeyadevan² and Hideyuki Takahashi²; ¹Tohoku University, Japan; ²The University of Shiga Prefecture, Japan

Many efforts have been made to produce low cost, flexible and high performance transparent conductive materials, replacing high cost, brittle and high performance Indium tin oxide films. Random networks of metal nanowires (NWs) possess optically transparent holes between nanowires and good electrical conductivity arose from metallic contacts between nanowires. Among metal nanowires, Cu has a disadvantage of low stability but is a top candidate due to its low cost. To take the cost advantage, synthesis and fabrication processes of Cu NW networks must be low cost and environmentally friendly. In addition, the surface must be modified with stable layers to avoid surface oxidation. Recently, we synthesized Cu NWs with different aspect ratios using an environmentally friendly synthetic method¹. However the surface easily oxidized, hindering NW performance.

In this study, we reported the surface coating of Cu NWs with ZnO layer based on aqueous solution processes for stable and high-performance transparent conductive films. To make transparent conductive films made of Cu NWs, a vacuum filtration and transfer method was used. The synthesized Cu NWs were deposited on a membrane filter and filtered under vacuum. Subsequently, the Cu NWs were transferred onto a glass substrate by pressing the filter against the glass substrate. After deposition of Cu NWs on the filter, aqueous ammine-hydroxo zinc complexes were employed to be absorbed on Cu NW surfaces. Although the complex easily converted to ZnO with heat treatment at low temperature, the complexes did not remain on Cu NW surfaces. As the complex condition and reactions
between Cu NW surfaces and the complexes dramatically changed depending on pH and zinc concentrations, we identified complexes using ESI-TOFMS and evaluated the surface reactions using surface analyses at different conditions. As a result, the ammine-hydroxo zinc complexes sufficiently remained on the Cu NW surfaces with appropriate conditions and then changed to thin ZnO layers. The thin ZnO layers on the Cu NWs improved the stability of Cu NWs under air without significant decreases in Cu NW performances such as transmittance and sheet resistance. In our presentation, detailed results and discussion will be introduced.

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Reference

FF04.05.21
Templated Growth of Two-Dimensional ZnO Nanoplates by the Hydrothermal Method toward Creating a Photocatalytic Surface Shota Sakurai1, Shinji Nozaki2 and Junghyun Cho1; 1Binghamton University, The State University of New York, United States; 2The University of Electro-Communications, Japan

Two-dimensional (2-D) nanomaterials have recently received a considerable attention because of their unique characteristics, which were not seen in their bulk or 1-D nanomaterials. Zinc oxide (ZnO) is one of the most industrially-promising materials because it is chemically stable, non-toxic and available at low cost. To synthesize the 2-D ZnO platelets, ZnO must grow in the a-axis direction, while suppressing its growth in the c-axis direction, which is often preferred in the ZnO growth. To control the growth direction, a seed layer plays an important role. In this study, we prepared a seed layer by spin-coating and high-temperature post annealing of the r-plane (1-102)-oriented aluminum oxide (Al2O3) thin films on Si (111) substrate. Then, ZnO nanoplates were hydrothermally grown on the seed layer in the a-axis direction with various growth parameters. Since a lattice mismatch between a-plane (11-20) of ZnO and r-plane of Al2O3 is only 1.53%, ZnO grows epitaxially along the a-axis. Such nanoplates contained a high concentration of the surface defects and were off-stoichiometric, thereby making them attractive as very effective photocatalytic surfaces for degradation of organic contaminants. In addition, these vertically-stacked ZnO nanoplate surfaces showed the electrical properties that strongly depend on the presence of oxygen and temperature. As a result, the templated growth of the 2-D ZnO nanoplates shows the great potential to form functional surfaces that can be very sensitive to external stimuli such as light and environment by controlling the concentration and type of defects. This presentation will highlight a current research progress made to the control of these defects to tailor the photocatalytic properties of the nanoplate-stacked surfaces.

FF04.05.22
Discovery and Liquid Exfoliation of 1D Materials Sudong Chae1, Seungbae Oh1, Kyung Hwan Choi2 and Jae-Young Choi1,2; 1Sungkyunkwan University, Korea (the Republic of); 2Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of)

For decades two-dimensional (2D) van der waals(vDw) materials, which have been isolated as one atomic sheet from their layered-bulk materials, are intensively studied due to their excellent and unique properties such as high mobility, flexibility, and two-dimensional quantum effects. In recent years, interest in 2D vDw materials has expanded to include a new type of nanomaterials, one-dimensional (1D) materials which are isolated as one molecular chain from their chained-bulk inorganic materials. The 1D bulk materials consist of chain-shaped inorganic molecule units which are assembled by weak physical interactions such as van der Waals or ionic bonding in their bulk materials. The inorganic molecular chain itself have a dimension of smaller than 1 nm in a diameter thus produce flexible characteristic even though they have inorganic compositions.

Here in, we synthesized new 1D materials [1,2](LiMo3Se3, V2Se9, Nb2Se9) and developed liquid-phase based exfoliation techniques for them which makes 1D bulk materials as an inorganic molecular chain. These include survey of solvents[3,4], design of dispersant[5] and ion exchange chromatography[6], and provides essential information on the material surface for additional stripping strategy design. The result of liquid exfoliation, colloidal nanomaterial, can be applied to various fabrication techniques for future applications.[7]

Crystallization Temperature Investigation of Cu₂ZnSnS₄ by Using Differential Scanning Calorimetry (DSC)
Jiayao Xu; The Hong Kong Polytechnic University, China

The Cu₂ZnSnS₄ (CZTS) powder was systematically investigated by energy dispersive X-Ray spectroscopy (EDX), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Ramam spectrometer, and further studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA). The Ramam and XRD results showed that the sample is a structure of Kesterite type under a condition of Cu-rich and Zn-poor with few impurity phases. The DSC results show that incubation time, peak time and end time of crystallization are all reduced with the increasing temperature; and the temperature of 550 °C will be more suitable for annealing treatment of CZTS. A CZTS film is also fabricated and annealed at 550 °C to confirm the result of the research. The systematic investigation of CZTS by using differential scanning calorimetry provided a fundamentally dynamic reference for the temperature selection of anneal during the fabrication of CZTS.

Photochemistry and the Role of Light in Submerged Photosynthesis of ZnO Nanorods
Lihua Zhang, Melbert Jeem and Seiichi Watanabe; Hokkaido University, Japan

Recently, metal oxide nanoparticles have gained much attention owing to their anticipated properties and application in different areas, such as photoelectron devices, sensors, catalysts, and photovoltaic devices. Among these metal oxides, zinc oxide is one of the most important natural n-type semiconductors with a direct wide band gap in the near-UV spectral region (3.36 eV at room temperature). The optical and electrical properties of ZnO are affected by many factors, such as the structure, size, shape, and defect concentration, which makes ZnO a very important and interesting subject to examine the controlled growth of novel materials. Recent work showed that metal oxide nanoparticles could be synthesized by a new pathway: submerged photosynthesis of crystallites (SPSC). In the SPSC method, the initial metal is surface treated by a submerged liquid plasma process, which creates a metal nano oxide semiconducting layer with surface protrusions. After that, the growth of metal oxide NCs is assisted by a ‘photosynthesis’ reaction, where the metal surface is irradiated with ultraviolet light in water. Thus, the SPSC process requires only light and water and does not require the incorporation of impurity precursors. Moreover, this method is applicable at low temperature and at atmospheric pressure, producing only hydrogen gas as the by-product. These characteristics give rise to the potential application of SPSC as a green technology for metal oxide nanocrystallites synthesis. Therefore, SPSC method is applied for ZnO nanorods synthesis in this work, and the photochemistry reactions and the role of light in the SPSC process are studied.

We carried out surface microstructural analysis and monitored the pH and temperature change of the water during the process. Based on this analysis, ZnO nanocrystallites formation mechanism was clarified. Furthermore, the effect of light irradiation during the process was elucidated by contrast experiments under dark conditions. The results show that both photoinduced reactions and hydrothermal reactions contribute to the SPSC process. The former generates OH radicals, which are one of the main sources of OH⁻ at the crystal tips, whereas the latter involve the ZnO growth reactions. Furthermore, ZnO nanocrystallites can be obtained under both light irradiation and heating in dark conditions, in which ZnO growth and corrosion reactions occur simultaneously. Light irradiation makes ZnO growth dominant and the water pH close to neutral, whereas thermal energy makes ZnO corrosion dominant and the water pH increases. The role of light in SPSC process is to enhance ZnO apical growth at relatively lower temperature by preventing the pH of water from increasing, revealing the environmentally benign characteristics of the present process.

Solutional Nanoparticle Syntheses of Layered Ternary Copper Selenides of Mo/W
Minyuan M. Li and Sergei A. Ivanov; Center for Integrated Nanotechnologies, Los Alamos National Lab, United States
Two-dimensional materials, especially transition metal chalcogenides MX₂, remain a dominant topic in novel material chemistry and physics. As we explore their layered ternary analogs with the formula Cu₂MX₄ (M = Mo/W, X = S/Se), we found few reports on the fabrication and characterization of those ternary selenides. Here we describe a solution processing method towards phase-pure nanoparticles and associated synthetic controls available in our method.

**FF04.05.26**
How do Surfaces Explain Growth Mechanisms and Growth Modes of KTa₁₋ₓNbxO₃ Nanoparticles? Tiffany Ly¹, Jianguo Wen² and Laurence D. Marks¹; ¹Northwestern University, United States; ²Argonne National Laboratory, United States

Predictable and consistent synthetic control of nanoparticle sizes, shapes, and properties through synthesis can be guided by comprehensive thermodynamic and kinetic models for nanoparticle growth. Establishing these models requires not only understanding how different growth mechanisms affect the size and morphology of nanoparticles, but also what factors determine the kinetic rates of these growth mechanisms and the resulting growth regimes. Here, electron microscopy characterization of hydrothermally grown solid solution KTa₁₋ₓNbxO₃ nanoparticles and density functional theory calculations revealed an intricate story, where complex relationships between several properties—including surface segregation, strain, and adsorption chemistry—affect and explain the surface behavior and growth regimes of the nanoparticles. Comprehensive study of these relationships informs mathematical models for predicting nanoparticle growth. In this case, these properties manifested in two surface composition dependent growth modes, where nanoparticles with tantalum-rich surfaces grew via step-flow growth to form smooth facets, while those with niobium-rich surfaces grew in a different growth mode to form rougher surfaces. Understanding how such properties affect growth mechanisms allows for further manipulation of nanoparticle growth, as demonstrated by the effects of adding potassium halide on KTa₁₋ₓNbxO₃ nanoparticle phase, composition, and morphology.

**FF04.05.27**
Characterization of Flash Lamp Cured, Sol-Gel Derived Tantalum Oxide Films Christopher Beale¹, Stefanie Hamacher¹, Oumaima Bensaid², Alexey Yakushenko², Dirk Mayer¹, Bernhard Wolfrum¹,³ and Andreas Offenhäusser¹; ¹Forschungszentrum Jülich GmbH, Germany; ²is it fresh GmbH, Germany; ³Technische Universität München, Germany

Prior attempts at reducing the crystallization temperature of metal oxide films have succeeded via chemical solution deposition and photochemical solution deposition [1]. These methods include seeding solutions with crystalline nanoparticles in order to reduce the activation barrier for nucleation and crystal growth, or incorporating photosensitive compounds into the solution and thereby reducing the crystallization temperature during exposure to continuous UV irradiation. In one study, a xenon flash lamp was utilized to obtain nanocrystalline thin films by the use of a metal β-diketonate solution [2]. Thus, the aim of this study is to determine whether such solutions can be used to obtain tantalum oxide films with a xenon flash lamp, and how future studies could allow for crystallization from the amorphous state via pulsed laser irradiation, or from the solution state via seeding or the incorporation of photosensitive tantalum complexes [1].

In this investigation, the characteristics of a photosensitive, tantalum β-diketonate sol-gel ink were studied as a function of flashes from a xenon flash lamp at room temperature. The ink was printed on quartz substrates for UV-Vis spectrophotometry in order to follow the absorption versus flash lamp exposure, and on interdigitated electrodes in order to follow the capacitance versus flash lamp exposure. The results indicate that the UV-Vis absorption spectrum is similar to those found for tantalum oxide films obtained by photo-irradiation [3], [4], and the interdigitated electrode capacitance increases with the number of xenon flash lamp flashes. An increase in capacitance hints at oxide densification and formation [5], thus allowing for a photopatternable material. The amorphous film could be subsequently heat treated to achieve polycrystalline films [6], or exposed to pulsed laser irradiation to similarly achieve high temperatures [1]. The photosensitivity of the ink also allows for future investigations involving low temperature crystallization via photochemical solution deposition, as has been performed for lead-titane based precursors, among others [1]. Moreover, the air stable solution would further increase the ease of manufacturing and allow for it to be implemented into a roll-to-roll manufacturing line [7].


**FF04.05.28**

*Nanoscale V₂O₃ Films Prepared by Magnetron Dc Sputtering Technique—Metal-Insulator Phase Transition and Magnetic Ordering*  
*Ivan Castillo, Karuna K. Mishra and Ram S. Katiyar; University of Puerto Rico, Rio Piedras Campus, San Juan, United States*

Vanadium sesquioxide, a transition metal oxide, is an important metal transition insulator (MTI) material for its potential applications in novel electronic and memory devices. thin films of ~230 nm thick were grown on Si/Pt substrate using a D.C magnetron sputtering system deposited at substrate temperature 450°C in a controlled atmosphere of 35:2.5 sccm of Ar:O₂. X-ray diffraction studies confirm the formation of corundum rhombohedral phase. EDAX analysis and X-ray photoelectron spectroscopy were carried out to identify the elemental compositions and their chemical states. Magnetization studies down to 5 K were measured to predict the paramagnetic to ferromagnetic transition around 53 K. Out of 7 expected Raman active modes, Raman active modes located at 242 and 500 cm⁻¹ were observed at ambient phase. Temperature dependent Raman spectroscopic studies carried out in the temperature range of 80-300 K to identify the low temperature metal-insulator transition at 153 K. A possible coexistence and hysteresis of metal and insulator phases are evident from the intensity analysis. These results will be presented in detail at the meeting.

**FF04.05.29**

*Fundamental Understanding of Polymorph Formation via Structural Evolution and H₂ Storage Properties in Nanohybride of Magnesium Borohydride Supported by Reduced Graphene Oxide*  
*Sohee Jeong and Jeffrey Urban; Lawrence Berkeley National Laboratory, United States*

Magnesium borohydride (Mg(BH₄)₂, abbreviated MBH) have received tremendous attention as a promising onboard hydrogen storage media due to its excellent hydrogen storage capacity and high volumetric density. While each polymorph of MBH — alpha (α), beta (β), and gamma (γ) — is interesting, their synthetic homogeneity is not well developed owing to complex structures and similar thermodynamic properties of the polymorphs. Here, we demonstrate effective synthetic strategies to obtain pure polymorphic phases of MBH nanomaterials supported by reduced graphene oxide (MBHG) under mild conditions (60 – 190 °C under low vacuum, 2 Torr). Different polymorphs of MBH are obtained from the different starting materials dried in two different ways (under Ar or vacuum) via the phase evolution, which mechanism elucidated by computational analysis. Specifically, we selectively synthesize thermodynamically stable phase (α-MBH) and metastable phase (β-MBH) from γ-MBH within the explored temperature ranges (150 °C to 180 °C). The relevant underlying phase evolution mechanism is analyzed by theoretical thermodynamics and kinetic nucleation modeling. Furthermore, the resulting MBHG composites were found to have an oxidational resistivity, structure stability, and expression of partially reversible [BH₄]⁻ species during de(re)hydrogenation processes, offering a potential for realizing hydrogen storage cyclability.

**FF04.05.30**

*Liquid Phase Deposition and Properties of Ni Doped ZnO for Magnetic Application*  
*Vitaly Bondarenko, Konstantin Yanushkevich and Eugene Chubenko; BSUIR, Belarus*
The ZnO films were deposited on n+-type antimony doped silicon (111) substrate (0.01 Ω×cm) using an electrochemical deposition from aqueous solution containing zinc nitride, nickel nitride and isopropyl (IP). Deposition was carried out in galvanostatic mode at current densities of 15 – 30 mA/cm² and at temperature of 80 °C. The structure and optical properties was correspondingly studied by Raman and photoluminescence spectroscopy.

According to Raman spectra the obtained films consist of ZnO doped with Ni atoms. Existence of ZnO was verified by a typical number of Raman modes for ZnO, such as E1, A1 and et. al. Nickel doping was indicated by an increase in the intensity of the 1050 cm⁻¹ Raman spectra band and smoothing of the band at 1150 cm⁻¹. The observed intense photoluminescence band in visible range on all spectra corresponds to radiative transitions through three main group of deep levels in the band gap of semiconductor ZnO: a oxygen atoms in zinc interstitial (2.28 eV or 523 nm); a complex of an oxygen vacancy and zinc interstitial (2.16 eV or 576 nm) and oxygen vacancy (2.00-1.62 eV or 640-765 nm).

ZnO films were created by standard solution (without IP). Films with arrays of crystals on them were obtained for the solution with IP. The surface density of ZnO crystals on the ZnO film surface depends on the current density and increase with increasing current density. The size of crystal also increases by increasing deposition time. For example, at current density of 15 mA/cm² and deposition time 30 min continuous ZnO film with thickness of 7 um with an array of crystals of approximately 30 x 30 um in size and thickness of 7 um on it was obtained.

Based on the data extracted from the photoluminescence spectra of annealed samples, the number of such defects as oxygen atoms in zinc vacancies are significantly reduced and the emission peak redshifts. At the same time, annealing of samples prepared with the addition of 5 vol.% IP leads to a blueshift due to the annihilation of oxygen vacancies.

After annealing, the mode at 280 cm⁻¹ appeared on all Raman spectra. This mode stand for the mute B1low mode, the display of which in an optical spectra is related to the disorder of the crystal lattice. But, this Raman mode doesn’t presented for samples that was preparing from solutions with isopropyl.

This work was supported by the Belarus Government Research Programs “Photonics, opto- and microelectronics”, Grant 2.1.02, “Physical materials science, novel materials and technologies”, Grant 1.15.

FF04.05.31
Formation of Layered Structures in Biogenic Magnesium Calcite Single Crystals via Spinodal Decomposition of Mg-ACC Precursor Alex Katsman and Boaz Pokroy; Technion–Israel Institute of Technology, Israel

Some calcitic biominerals have been shown to be formed through the crystallization of a Mg-rich amorphous calcium carbonate (Mg-ACC) precursor. That non-classical crystallization pathway allows the formation of out-of-equilibrium supersaturated solid solutions (such as high-Mg calcite) as well as the formation of intricate rounded crystal shapes. Formation mechanisms of multiscale biogenic single crystal structures at ambient temperatures, in conditions of limited solid phase diffusion, remain largely incomprehensible. Based on experimental results, we develop a model describing the formation of the brittle star Mg-calcite nanostructure from an amorphous Mg-ACC precursor to a Mg-calcite nanostructure containing periodic layers with varying concentrations of coherent Mg-rich nano-inclusions. The amorphous ACC precursor can exist as a gel or as a liquid depending on amount of Mg and acidic proteins present in the system. The formation route is rationalized in a two-step model: the first step involves spinodal decomposition of a liquid or gel-like Mg-ACC precursor into Mg-rich nanoparticles and a Mg-depleted amorphous matrix. The second step is the crystallization of the decomposed Mg-ACC precursor. The crystallization probably starts in the Mg-depleted matrix. We consider two possible crystallization routes leading to the layered structure formation. In the first route, crystallization front faces Mg-rich nano-domains and alternatively repels them to amorphous phase or embeds epitaxially to the crystalline matrix, depending on the local effective viscosity varying with the density of nano-domains. In the second route, the crystallization of Mg-depleted ACC matrix is accompanied by the exclusion of Mg ions into a diffusion zone adjacent to the crystallization front; after crystallization of a certain layer, the Mg concentration ahead of the layer exceeds the critical value above which the Mg-ACC matrix becomes unstable against spinodal decomposition. A secondary spinodal decomposition will then start and result in the formation of additional Mg-rich nano-domains. As a result, the density of Mg-rich nano-domains changes periodically and forms periodic layered structure inside magnesium calcite single crystals. The model was supported by our experimental results in synthetic Mg-calcite, which suggest a spinodal decomposition in the amorphous precursor. These new insights have significant implications for fundamental understanding of the role of Mg-ACC material transformation during crystallization and its subsequent stability.
SESSION FF04.06: Solution Processed Organic Semiconductors
Session Chairs: Ji Tae Kim and Hanying Li
Wednesday Morning, December 4, 2019
Hynes, Level 3, Room 311

8:15 AM FF04.06.01
Twisted Crystals of Chiral and Achiral Functional Materials David B. Amabilino and C. Elizabeth Killalea;
University of Nottingham, United Kingdom

The formation of twisted crystals of a family of low molecular weight organic dye molecules from solutions of the
compounds has been discovered. This phenomenon is fascinating because the chirality arises over the lengthscale of
microns, which is not accessible by simply relying on chiral materials (where helical pitch is short) or by twisting
fragile macroscopic organic crystals. The properties of this new kind of material are potentially unique for a range of
optoelectronic applications.

The twisting occurs across a broad range of compounds based on the diketopyrrolopyrrole family, substituted at the
core of the molecule or at the terminus. Chiral side chains induce single handed crystals with very regular pitch
related with the thickness of the objects. Achiral sidechains result in the formation of twisted crystals of more varied
morphology, and a variety of twisted crystal types depending on the constitution of the side chain.

Electron and atomic force microscopy have been used to understand the morphology of the materials, and single
crystal diffraction and scanning tunnelling microscopy reveal the nature of interactions between the molecules and
their long range packing. Circular dichroism has been used to demonstrate the huge optical activity of the twisted
crystals compared with the solution phase systems, thereby demonstrating the interest for chiroptical phenomena.

8:30 AM *FF04.06.02
Crystal Engineering for Oligoacenes John Anthony; University of Kentucky, United States

The precise nature of intermolecular interactions, both in solution aggregates and in the solid state, plays a key role
in the electronic and photonic properties of any material. We developed a reliable functionalization strategy that
allowed the tuning of the solid-state order of a variety of aromatic chromophores, and established a rough set of
guidelines to predict how functional group size impacts crystal packing. For this talk, I will discuss several
refinements of our models, including (1) the use of computational screening to reduce the time and effort required to
engineer the crystal packing of new semiconductors for electronic and photonic applications, (2) the impact of
disorder on electronic properties, and how functionalization can diminish or enhance several types of disorder, and
(3) efforts to minimize dynamic disorder, and minimize phonon modes that are disruptive to charge transport.

9:00 AM FF04.06.03
Controlling Solid-State Packing and Spectroscopy of Conjugated Molecules Using Discrete Non-Covalent
Interactions of Pendants Samuel W. Thomas; Tufts University, United States

Despite the importance of conjugated materials in organic optoelectronic devices, the rational design of their
properties as solid state ensembles is currently not possible. The current design paradigm of conjugated materials
uses long, often branched alkyl side chains to impart solubility to otherwise insoluble conjugated backbones that are
responsible for the key optoelectronic properties of these materials. This talk will summarize work in which discrete
non-covalent interactions between pendants and conjugated backbones can dictate the conformations, and resulting
spectroscopic characteristics, of conjugated molecules in the solid state. In particular, intra- and intermolecular
arene-fluoroarene stacking interactions twist phenylene-ethyne linkages as revealed by X-ray crystallography.

The weak nature of this interaction results in surprising sensitivity to seemingly insignificant changes in chemical
structure that impact interaction strengths and the resultant conformations of these solids. This non-covalent control
over solid state conformation and spectroscopy extends to a wide variety of conjugated materials, including
organometallic phosphors. Mechanofluorochromism—the reversible change in photoluminescence upon application
of force—is a shared feature of many of these solids. The temperatures at which the force-induced phases revert to
the thermodynamically favored crystalline states is tunable over a wide range by changing the lengths of alkyl
substituents. Overall, this collection of materials opens a new path forward to controlling the properties of solid conjugated materials, for which rational design is most difficult, yet critically important for future technological development.

9:15 AM FF04.06.04
Crystal Engineering of Solution-Processable Organic Semiconductors to Enhance Optoelectronic Properties
Kai o. Zong¹, Yichen Ma¹, Kamran Shayan¹, Jack Ly², Emily Renjilian¹, Chunhua Hu³, Stefan Strauf¹, Alejandro Briseño² and Stephanie Lee¹; ¹Stevens Institute of Technology, United States; ²University of Massachusetts Amherst, United States; ³New York University, United States

Control over the out-of-plane molecular orientation of solution-processed organic semiconductors is a long-standing challenge in the organic electronics field. We present a generalizable strategy to orient the nucleation of small-molecule organic semiconductors during solution-phase deposition using nanoconfining scaffolds. Employing a simple dip coating process, triisopropylsilylethynyl-derivatized acene molecules were deposited onto nanoporous anodized aluminum oxide (AAO) and Si scaffolds exhibiting cylindrical pores with average diameters ranging from 60 – 500 nm. Preferentially oriented nuclei were found to form within the pores such that the fast growth direction (i.e. the π-stack direction) aligned with the long axes of the pores. Well oriented vertical crystal arrays with the π-stack direction of organic semiconductor crystals perpendicular to the substrate surface were found to form on both scaffolds. By varying the dip coating speed, the diameters and heights of these crystals on scaffolds were tunable over ranges of 100 – 600 nm and 0.8 to 6.7 m respectively. Photoluminescence (PL) experiments further revealed an eight-fold enhancement of the PL signal from vertical crystal arrays compared to horizontal crystals deposited on flat SiO₂ substrates due to waveguiding along the crystal length. This strategy is suitable for continuous deposition methods that will enable the large-area manufacturing of flexible and inexpensive optoelectronic devices.

9:30 AM FF04.06.05
2D Organic Semiconductor Monolayer for the Ohmic Contact Field-Effect Transistor Applications
Paddy K. L. Chan; University of Hong Kong, Hong Kong

In the organic field-effect transistors (OFETs), the charge accumulation region is usually within several nanometers from the dielectric surface. For small-molecule organic semiconductor material with monolayer thickness, all the molecules in the monolayer organic crystals are in principle contributed in forming the conductive channel. A meniscus-guided solution-processing method is employed to grow monolayer crystals of C₁₀-DNTT with single-crystalline domain size as large as millimeters. The intrinsic field-effect mobility of >12 cm²V⁻¹s⁻¹ is achieved. More importantly, the ultrathin thickness minimizes the charge injection barrier for the top-contact electrodes, allowing an ohmic hole injection and a low contact resistance (Rc×W) of 75 ohm-cm. Such low contact resistance not only allows short channel devices but also ensures low voltage drops at the metal/semiconductor interface, allowing the device to operate even at VDS = -1 mV. It opens a new direction of low-power OFET that operates at pico-watts, which can only be achieved by high-mobility short-channel OFETs with very low contact resistance. The physics origin of forming such low contact resistance OFETs will also be discussed.

9:45 AM BREAK

10:15 AM FF04.06.06
A Framework for Screening the Kinetic Stability of Packing Polymorphs
Lynn Loo; Princeton University, United States

The weak intermolecular forces inherent to organic semiconductors give rise to polymorphism, or the ability for these materials to adopt multiple solid-state packing arrangements. And since the details of intermolecular packing can substantively influence charge transport, the ability to predict which of the available polymorphs is preferentially accessible and stable should shed light on charge transport characteristics. In this talk, I will discuss a simple framework that directly correlates the presence of short intermolecular contacts with polymorphic stability. Quantification starts with assessing whether intermolecular contacts within a crystal structure are smaller than the
sum of the van der Waals radii of the same atoms. Polymorphs with such short intermolecular contacts are substantially more resistant to polymorphic transformation while those without exhibit an added degree of freedom for molecular rearrangement; the said polymorph can thus be easily destabilized with post-deposition processing. Starting with a series of core-chlorinated naphthalene diimide derivatives, we show this framework to be widely applicable to a wide range of molecular semiconductors, and even extending to pharmaceutics and biological building blocks. In this era of machine learning and materials by design, this framework can help refine computational predictions by identifying the polymorphs that are practically stable [1].


10:45 AM FF04.06.07
Enhancement of Charge Transfer in Thermally-Expanded and Strain-Stabilized TIPS-Pentacene Thin Films
Yang Li1, Jing Wan1, Detlef M. Smilgies2 and Randall Headrick1; 1The University of Vermont, United States; 2Cornell University, United States

We present an extensive study of the optical and electronic properties and the phase transition in 6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) thin films utilizing in situ x-ray diffraction, polarized optical spectroscopy, terahertz spectroscopy and ab initio density functional theory. The influence of molecular packing on the properties are reported for thin films deposited in the temperature range from 25°C to 140°C, and for films that are strain-stabilized at their as-deposited lattice spacings after cooling to room temperature. Anisotropic thermal expansion causes relative displacement of neighboring molecules while maintaining a nearly constant stacking distance. This leads to a large blueshift in the absorption spectrum as the temperature increases. The blueshift is a signature of charge transfer excitations, which depend sensitively on the alignment of the nodes of the frontier molecular orbitals with those on neighboring molecules. This effect is correlated with an enhancement of the field-effect transistor mobility in strain-stabilized thin films. These results suggest approaches to improve carrier mobility in strained thin films and for optical monitoring of electronic changes.

11:00 AM FF04.06.08
Molecular-Bilayer Organic Semiconductors—High Layered Crystallinity for Innovative Solution Processing
Tatsuo Hasegawa; University of Tokyo, Japan

High performance organic thin-film transistors (OTFTs) are attainable with molecular materials that show high degree of layered crystallinity, because the feature is best suitable to obtain two-dimensional channel layers interfaced with gate-dielectric layers. Here we present and discuss that some asymmetric rod-like organic molecules, composed of p-conjugated backbones linked with relatively long alkyl chains, provide molecular-bilayer-type organic semiconductors that involve intralayer herringbone-type molecular packing [1-5]. The materials exhibit considerably high layered crystallinity, allowing to realize innovative solution processing for obtaining extremely uniform channel semiconductor layers [6,7]. Based on ab initio quantum chemical calculations, we discuss that the high layered crystallinity are strongly enhanced by the intermolecular attractive forces between alkyl chains [3]. Based on molecular dynamics study, we show that the molecules are self-organized at around air-liquid interface via intermediate liquid-crystal phases, which eventually leads to the large-area single-crystal film growth [8]. We also demonstrate that the formation of single molecular bilayers becomes possible by using frustration effects for the alkyl chains [7].


11:15 AM FF04.06.09
Solvent-Free Coating of Organic Semiconductor Thin Films with Large-Area Single-Crystalline Domains
Yu
Organic semiconductors (OSCs) have been the cornerstone of organic electronics in a variety of applications, including photovoltaics, thin-film transistors (OTFTs) and electrochromics. Although OSCs promise to be lower in cost, more flexible and compatible with roll-to-roll processing compared to inorganic semiconductors, they suffer from a lack of long-range order, especially when deposited from solution over large areas. Defects, such as grain boundaries and dislocations, in as-cast OSC films, have been widely recognized to impede charge transport. While the introduction of an external field during solution processing, such as that during blade coating, has resulted in high quality millimetric single-crystalline domains and ribbons, these techniques still face formidable drawbacks because they employ chlorinated organic solvents that pose significant health and environmental hazards, and are often trapped in the resulting OSC films.

Herein, we introduce a scalable, solvent-free technique to prepare single crystalline OSC films with low defect densities over several centimeters. This approach leverages the liquid crystallinity of OSCs; depositing the OSCs at temperatures within their smectic window over a metal frame forms a freely suspended membrane. Given the elasticity of the smectic phase and that the OSCs are individually mobile at the surface, the resulting membrane – comprising of OSC molecules preferentially aligned with their long axis normal to the surface – is defect-free and uniform across its entire area. Transferring this membrane onto desired substrates and cooling it slowly from its smectic phase into its crystal phase preserves this high quality assembly. In the particular example of an equimolar blend of dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) and didodecyl[1]-benzothieno[3,2-b][1]benzothiophene (C12-BTBT), we have produced BTBT cocrystalline films with single-crystalline domains that span ca. 30 mm laterally. Varying the deposition temperature and coating speed produces membranes that are 20 nm to a few hundreds of nanometers thick.

To assess the electrical properties of these single crystalline films, we fabricated OTFTs by transferring the OSC membranes to heavily n-doped silicon wafers with a 100 nm thick SiO2 as the gate dielectric and cooling them slowly into their crystalline phase. Evaporation of gold contacts defined individual transistors with a channel width of 200 mm and a channel length of 500 mm. We chose a particularly large channel length of 500 mm to demonstrate the uniformity and quality of our films over large areas. Such devices exhibit an average hole mobility of 8.5 ± 2.3 cm²/V.s⁻¹ and an average on/off ratio that exceeds 10⁶, independent of device location across the entire film. This solvent-free scalable approach of producing single crystalline OSC films at wafer dimensions (ca. 50 mm) should be amenable for broad applications in organic electronics.

Molecular and Supramolecular Engineering of Thienoacenes for Improved Charge Transport

Yves H. Geerts; Univ Libre de Bruxelles, Belgium

A large diversity of π-systems exist, nearly all transport electrical charges but only a few molecular structures qualify as best-performing organic semiconductors with μ ≥ 10 cm²/V.s. But charge carrier mobility is more a material than a molecular property. One has, thus, to consider supramolecular order at all length scales. The best organic semiconductors self-organize into large plate-like monocrystals as evidenced in recent papers. Due to their electronic properties but also to their favorable crystalline morphology, thienoacenes derivatives exhibit record charge carrier mobility above 10 cm²/V.s. We will report our latest results on the molecular and supramolecular engineering of BTBT semiconductors, including: design by theory, synthesis, crystal engineering, calculation and observation of crystal morphology, and processing into single crystal thin films for transistor fabrication.
**Desalination** Ryan Andris, Phillip Ridley and Ekaterina Pomerantseva; Drexel University, United States

Nanowire morphology combined with one-dimensional (1D) diffusion pathways is advantageous for the enhanced electrochemical performance of materials in a wide range of applications. In this work, we for the first time report the performance of highly ordered Na-2x3 and Na-2x4 tunnel manganese oxide (TuMO) nanowires with 1D crystallographic channels for the hybrid capacitive deionization (HCDI) of water. TuMOs are a family of relatively low cost, sustainable, and highly electrochemically active materials. In addition, the size of the tunnel opening can be modified by altering the nature of the stabilizing ion and hydrothermal treatment parameters of the precursor materials. The Na-2x3 and Na-2x4 tunnel dimensions refer to the number of MnO₆ octahedra on perpendicular sides of the tunnel walls, and the ordered nature of these structures is revealed via scanning transmission electron microscopy (STEM). Thus, TuMOs provide a unique platform to investigate the relationship between the size of the 1D diffusion channels and their electrochemical performance, including potential selectivity for removing various ions from aqueous solutions.

The homogeneity of tunnel sizes was achieved through improving crystallinity of the layered Na-birnessite precursor material via extended aging and control over the pH of the solution during hydrothermal treatment. The Na⁺ ions that stabilize the tunnels have increased radii in basic solutions that result in increased tunnel dimensions [1]. In addition, a study that investigated ion transport properties demonstrated that sodium preferentially diffuses into the larger tunnel sizes [2]. Therefore, the ion removal performance of Na-2x3 and Na-2x4 TuMO nanowires is investigated in a variety of solutions to gain insight into relationships between cation hydrated radii, charge, and electrode ion removal capacities.

NaCl, KCl, MgCl₂ solutions, and mixtures of all three were analyzed. In sodium chloride solutions, the Na-2x3 and Na-2x4 electrodes demonstrated ion removal capacities as high as 20 mg g⁻¹. Previous research conducted on TuMOs with an irregular distribution of tunnel sizes and incomplete formation of tunnel walls demonstrated higher ion removal capacities up to 45 mg g⁻¹. This data indicates that structural defects can be a vital factor in determining performance [3]. In addition, the highly ordered nanowires showed capacity retention as high as 90% after 20 cycles compared to 100% in the disordered material. To further understand the relationship between tunnel size and HCDI performance, both Na-2x3 and Na-2x4 tunnel structures were tested with a mixed ion solution containing all three chloride salts: NaCl, KCl and MgCl₂. Our results indicate that Na-stabilized TuMO electrodes may preferentially remove ions with larger hydrated radii from solution as demonstrated by a 40% drop in concentration of potassium ions compared with a 50% drop in concentration of magnesium ions. Interestingly, we observed that the concentration of sodium ions in mixed solution increased after cycling, indicating that stabilizing Na⁺ ions can be released from the structural tunnels of TuMO electrodes. This result suggests that there is interesting ion dynamics between stabilizing sodium ions and ions electrochemically removed from the mixed solution. In summary, this work contributes to the overall scientific understanding between ion transport and tunnel structure within manganese oxide materials used as electrodes in HCDI for water desalination.

References:

2:00 PM FF04.07.02
**Understanding Electrical Conduction Mechanisms in Polycrystalline Indium Antimonide Nanowires Grown in Flexible Polycarbonate Membrane Pores** Abhay P. Singh and Usha Philipose; University of North Texas, United States

A dense array of vertically aligned indium antimonide (InSb) nanowires with high aspect ratio (diameter ~150-200 nm, length 20 µm) were grown in the pores of a track-etched polycarbonate membrane via a one-step electrochemical method. There are several reports on InSb nanowire growth in the pores of mechanically rigid, nano-channel alumina template (NCA), where nanowire growth occurs in the pores of the NCA. However, non-uniform pore size across the thickness of the template and the roughness within the pore tubules translate to the nanowires, resulting in them having non-uniform diameters and rough surfaces. In contrast, InSb nanowires grown in polycarbonate (PC) membranes appear to have uniform diameters and smooth surfaces. However, transmission electron microscopy images show that despite their smooth surfaces, InSb nanowires grown in PC membranes are
polycrystalline and in some cases even amorphous. A possible nanowire growth mechanism explaining the variation in crystallinity based on the template type will be presented in this work. The electronic quality of the nanowires was assessed by fabricating a back-gated InSb nanowire field effect transistor (NWFET), with a channel length of 1 µm. Analysis of the transport measurements show the nanowires have high resistivity (4 Ω cm), and a majority hole carrier concentration of the order of $10^{16}$ cm$^{-3}$.

2:15 PM FF04.07.03
**Electrochemical Nanofabrication with Pulsed Electrical and Mechanical Techniques Using Scanning Probes**
Mark Aarts$^1$, Alain S. Reiser$^2$, Ralph Spolenak$^2$ and Esther Alarcon-Llado$^1$; $^1$AMOLF, Netherlands; $^2$ETH Zürich, Switzerland

Bottom-up fabrication holds great commercial potential due to the cost-effectiveness of saving material. Solution-based fabrication methods are particularly attractive due to their scalability, low cost, and mild operating conditions. In this respect, electrodeposition using scanning probe microscopy provides a unique platform. Scanning probes allow for additive nanoscale manufacturing under ambient conditions, and additionally provide 3-dimensional spatial freedom which enables the fabrication of structures that are hard to realize in conventional cleanroom environments.

We report on the direct writing of Copper and Cobalt nanostructures using pulsed mechanical and electrical techniques in both an Atomic Force Microscope (AFM) and a Scanning Tunneling Microscope (STM). We demonstrate the writing of arbitrary structures beyond the sizes characteristic of single clusters and with lateral dimensions down to tens of nanometers, which can be read in-situ using the scanning probe. The extent of the deposition is interpreted based on the charging dynamics of ions in the liquid, determined by fundamental constants of the electrolyte such as the concentration, dielectric constant, and diffusion coefficient.

Due to the wide variety of electrochemical deposition and conversion processes, the technique of controlled electrochemical deposition with a scanning probe can be extended to different materials and morphologies. As such, we envision this technique to enable the manufacturing and rapid prototyping of novel devices at the nanoscale such as optical resonators, magnetic elements, and semiconductor devices.

2:30 PM BREAK

3:30 PM *FF04.07.04
**Solution-Grown Organic Single-Crystalline Heterojunctions**
Hanying Li; Zhejiang University, China

Organic heterojunctions are widely used in electronics and well ordering in the molecular packing inside the heterojunctions is highly desired. However, it is still challenging to interface organic single crystals to form single-crystalline heterojunctions. In this work, two novel methods will be introduced to describe how to prepare, from solutions, single-crystalline heterojunctions. On one hand, organic single-crystalline planar heterojunctions are grown in a single step from a mixed solution of p-type and n-type molecules. Based on crystallization of six organic semiconductors from a droplet on a substrate, two distinct crystallization mechanisms have been recognized in the sense that crystals form at either the top interface between the air and solution or the bottom interface between the substrate and solution. The preference for one interface rather than the other depends on the semiconductor-substrate pair and, for a given semiconductor, it can be switched by changing the substrate, suggesting that the preference is associated with the semiconductor-substrate molecular interaction. Furthermore, simultaneous crystallization of two semiconductors at two different interfaces to reduce their mutual disturbance results in the formation of bilayer single crystals interfaced together for organic heterojunctions. On the other hand, single crystals are prepared in organogels of a typical conjugated polymer. Instead of pure crystals, crystals containing the gel nanofibers are obtained. Essentially, nanofiber networks are incorporated into growing crystals and penetrate through the crystals, resulting in a crystal/gel-network interpenetrating composites. Based the two types of single-crystalline heterojunctions, charge transport and charge transfer process are studied. Hence, by demonstrating these two solution methods for the preparation of single-crystalline heterojunctions, this work should greatly harvest the highly ordered organic crystalline materials for high performance electronics.

4:00 PM FF04.07.05
Solution-Based Growth of Co- and Cu-Doped ZnO NWs with Controllable Optoelectronic Properties

Aswathi K. Sivan1, Alejandro G. Galan2,3, Lorenzo di Mario1, Andrew Gallant2, Del Atkinson2, Dagou Zeze2 and Faustino Martelli1; 1Istituto per la Microelettronica e i Microsistemi (IMM), Italy; 2Durham University, United Kingdom; 3Istituto di Struttura della Materia-CNR, Italy

The application of nanoscale oxide semiconductors for optical applications is growing, which drives research that seeks to modify and tune the electronic behaviour for technological applications. ZnO is a wide bandgap (3.37 eV) semiconductor with a large exciton binding energy (60 meV) at room temperature, making it a good candidate as a transparent conductive oxide and as part of optoelectronic-based or piezoelectric devices. For ZnO nanowires (NWs), the options for growth are vast, including pulsed laser deposition (PLD), chemical vapour deposition (CVD), molecular beam epitaxy (MBE) or chemical synthesis. Among them, the latter represents a cheap and simple route towards the production-scale synthesis of high quality single crystal ZnO NWs. Typically, the chemical route is a two-step process: first, a seed layer is deposited followed by the NW growth using chemical bath deposition (CBD). The CBD process allows tuning of the electronic properties via the introduction of doping agents to the growth solution that can be incorporated within the ZnO NW lattice during growth.

In this work, the optical properties of Co and Cu-doped ZnO NWs were studied by photoluminescence (PL) and fast-transient absorption spectroscopy (FTAS) with temporal resolution of 50 fs using a pump-probe method. The doping levels used were 1%, 5%, 10% and 20% in order to study how the doping levels affected the optoelectronic properties of ZnO NWs. The NWs were around 4 µm long and 120 nm in diameter.

For undoped NWs, the FTAS measurements show a sharp absorption bleaching at 3.3 eV with bandgap value comparable to those largely reported in the literature. As the cobalt doping was increased, a red-shift in the bandgap bleaching appeared (resulting in bandgap reductions from 3.3 eV to 2.95 eV), we also see that the bandgap bleaching has become broader. Co-doping modifies both spectral and dynamic properties of the ZnO NWs. The defect band became more prominent with increasing doping levels. This may be attributed to the modification of surface states in the presence of Co. Thy dynamics of bandgap bleaching also becomes faster with increasing Co doping. In the case of Cu-doped samples, a similar red-shift was obtained for the bandgap bleaching. The crystallinity and crystalline structure of the NWs was also demonstrated by x-ray diffraction and transmission electron microscopy to show that the original wurtzite phase of the ZnO NWs was maintained after doping. These experiments prove that by including a certain amount of dopant species, the optoelectronic properties of the ZnO NWs can be tuned, opening up a host of new and improved applications in which bandgap engineering and defect states control are key, such as selective gas sensing or photoelectrochemical water splitting.

Mechanistic Understanding of Ultrathin Single Crystalline Pt Nanowire

Debadarshini Samantaray and Ravishanakar Narayanan; Indian Institute of Science, India

Wet chemical synthesis provides a simple yet scalable route to synthesize nanomaterials with controlled size and shape. Tuning size and shape of nano crystal often leads to enhancement of various properties which could be very different from their bulk counterpart. Many exciting properties of the nanocrystals arise due to their higher surface area, hence shows excellent catalytic property. Noble metal nanowires are extremely important from fundamental and application point of view. However, anisotropic growth (1D here) in case of high symmetry material (specifically FCC crystal like Au, Ag, Pt) is not trivial to achieve. But, in these systems the inherent symmetry can be broken by using suitable capping agent or template. Though ultrathin Au nanowire of 2nm diameter has been synthesized and studied extensively, achieving Pt nanowire of such dimension remains challenging due to its intrinsic isotropic nature. Herein, we report synthesis and mechanism of formation of ultrathin Pt nanowire which has been achieved via a simple solvothermal method without making use of any special atmosphere.

As synthesized Pt nanowires have a diameter of 2-3 nm and lengths in microns. HRTEM images of these wires confirm that these are single crystalline in nature and interestingly the growth direction is <110> which is different from that of Au nanowire, where the growth direction is <111>. Theoretical calculation suggests the nature of binding of capping agent could be responsible for such type of growth direction. To understand the formation and growth mechanism of these nanowires, several control experiments have been performed. TEM analysis of the quenched samples at an earlier stage reveals that initially bigger particles (7-8 nm) form which eventually break down to smaller monodispersed particles of size 2-3 nm. The breaking of larger particles to smaller ones (in
presence of excessive capping agent) can possibly be attributed to digestive ripening. Further these monodisperse particles could undergo oriented attachment to form the 1D structure. It has been observed that the presence of capping agent plays a critical role in the kinetics of the reaction.

Since these nanowires are only few atoms thick, they show very interesting electrical transport property. Thermal stability of these wires has been studied by in situ TEM heating as well as ex situ heating. Moreover, these wires show superior thermal stability as compared to Au nanowire of similar dimension and hence can be used as a promising candidate for interconnects. These wires have been further converted to bimetallic nanowires like PtPd and PtCu by using Pt nanowire as template. Electrocatalytic studies on these single crystalline bimetallic nanowire shows better performance.

4:30 PM FF04.07.07
Pt-Based Nano-Dendrites as Highly Active and Stable Oxygen Reduction and Methanol Oxidation Bifunctional Catalysts Wenjuan Lei, Menggang Li, Yongsheng Yu, Weiwei Yang and Frances M. Ross; 1Harbin Institute of Technology, China; 2Massachusetts Institute of Technology, United States

Platinum (Pt) has been proven to be the most efficient candidate for the cathode catalyst of proton exchange membrane fuel cells (PEMFCs). However, the intrinsically sluggish kinetics and ultrahigh price of Pt severely limit the widespread application of PEMFC technology. Incorporating Pt with less expensive transition metals to form stable bimetallic PtM alloys, where M = Fe, Co, Ni, Cu, etc., has been considered as an effective approach to address these issues. This not only largely reduces Pt consumption but also enhances the activity of Pt-based electrocatalysts due to possible synergistic effects and electronic and lattice shrinking/strain effects. In addition, a nanodendrite (ND) structure with open skeletons can endow Pt-based electrocatalysts with higher atomic utilization and higher active surface area. Therefore, the design and synthesis of PtM alloys with highly open structure is crucial for fuel cells reaction applications.

Here, we report a highly universal approach for preparing PtM bimetallic NDs with M = Fe, Co and Ni by solution phase synthesis. By reacting Pt(acac)2 and M(acac)x at elevated temperature, we achieve NDs with a fcc crystal lattice. The as-prepared PtM NDs have a polycrystalline structure and are rich in steps and kinks on the surface, which ensure the PtM alloy has excellent bifunctional catalytic properties in acidic electrolytes for both the oxygen reduction reaction (ORR) and the methanol oxidation reaction (MOR). The ORR and MOR activities of the PtM NDs both show a sequence of PtCo/C > PtFe/C > PtNi/C > Pt/C. We conclude that the development of a novel strategy to prepare various types of bimetallic or ternary and Pt- or Pd-based alloy NDs can advance fuel cell applications by improving electrocatalytic performance.

4:45 PM FF04.07.08
Block Copolymer-Directed Hierarchically Structured Materials from Transient Laser Heating Kwan W. Tan; Nanyang Technological University, Singapore

Hierarchically porous structured materials with multifunctional properties and higher order complexities are highly desirable for many applications such as separation and energy storage. Here we describe the generation of hierarchically porous organic and inorganic structures coupling block copolymer self-assembly with spatially- and temporally-controlled laser irradiation. A simple and rapid laser irradiation of block copolymer-directed hybrid films with a continuous wave laser in the sub-millisecond timescales enabled synthesis of 3D mesoporous polymer structures and shapes. Backfilling the polymer template with amorphous silicon followed by pulsed laser annealing enabled transient melt transformation of amorphous precursors into 3D mesoporous crystalline silicon nanostructures. Mechanistic studies on laser-induced crystalline silicon nanostructure formation during the nanosecond silicon melt-crystallization process and polymer template stability at temperatures above 1200 degrees Celsius are highlighted.
**FF04.08.02**  
Extended Carrier Lifetime of Faceted PbS Quantum Dots in Superlattice Film Formed by Sedimentation Method  
Kohki Mukai, Ryota Kimura, Shunta Sugisaki, Takuya Sugimoto and Masanobu Fujishima; Yokohama National University, Japan

In this paper, we report the successful fabrication of a superlattice film composed of PbS colloidal quantum dots (QDs) with three-dimensionally-coincident crystal orientations. Semiconductor solar cells using QD superlattice has been expected to realize energy conversion efficiency of 70% or more owing to the intermediate energy bands. The chemically synthesized colloidal QDs self-form densely-packed structures when they are deposited on a substrate in solvent. However, since the QDs can move freely on the substrate, grain size of the packed structures is on the order of micrometers. Long carrier transportation is effective to improve energy conversion efficiency of solar cells. We have proposed a method to realize a large area superlattice structure by restricting the free motion of QD using pyramidal microhole array as a template produced by anisotropic wet etching. In this study, faceted QDs of truncated octahedral shape were prepared and deposited on the template of Si(100) substrate. During the deposition, facets of neighboring QDs came into contact with each other. The three-dimensional crystal orientation alignment was confirmed by X-ray pole figure mapping. QD superlattice film with aligned crystal orientation are expected to further improve carrier transportation. We found that emission lifetime of QDs became longer after the formation of superlattice film, and that the usage of template extended the lifetime of the film especially at the excited states. The emission decay curves were double exponential at the excited state, one of which was a few nanoseconds and the other was several tens of nanoseconds or more. The results suggested that two type regions, where the intermediate bands were formed or not, were mixed in the film.

**FF04.08.03**  
Programmed Twisting of Phenylene–Ethynylene Linkages from Aromatic Stacking Interactions  
William Mullin; Tufts University, United States

Control over the conformation and packing of conjugated materials is an unsolved problem that prevents the rational design of organic optoelectronics, such as preventing self-quenching of luminescent molecules. Exacerbating this challenge is a general lack of widely applicable strategies for controlling packing with discrete, directional non-covalent interactions. Here, we present a series of conjugated molecules with diverse backbones of three or four arenes that feature pentafluorobenzyl ester substituents. Nearly all the compounds reveal intramolecular stacking interactions between the fluoroarene (ArF) side-chains and nonfluorinated arenes (ArH) in the middle of the chromophores; a twisted PE linkage accompanies each example of this intramolecular ArF–ArH stacking. Furthermore, these molecules can resist dramatic changes to emission upon transition from organic solution to thin film when ArF rings prevent interchromophore interactions. Not only does this design paradigm apply to fluorophores, but we also demonstrate its utility in inducing solid state phosphorescence in platinum acetylide small molecules. By broadening the structural space of conjugated backbones over which ArF–ArH stacking can twist PE linkages reliably and prevent self-quenching of solids with simple synthetic approaches, this work suggests fluorinated benzyl ester substituents adjacent to phenylene ethynylene linkages as supramolecular synthons for the crystal engineering of organic optoelectronic materials.

**FF04.08.04**  
High-Stability Photocatalyst Based on Methylammonium Lead Tribromide Perovskite Single Crystals  
Xingmo Zhang, Feng Li and Rongkun Zheng; The University of Sydney, Australia

Hydrogen (H₂) production using the suitable semiconductors through photocatalytic water splitting process is a much sought-after technology to reduce the greenhouse gases and to further contribute to clean solar hydrogen energy production [1][2]. To date, it is still a big challenge to search for a stable semiconductor photocatalyst responding to wide-ranged light illumination. Recently, methylammonium lead halide perovskites have emerged as promise candidates for varieties optoelectronic devices, because of their low-cost, large carrier mobilities, long carrier life time and tuneable bandgap [3]. Moreover, recent advancements have demonstrated that their extraordinary optical and electrical properties make this class of perovskites a promising mediums for the high-performance photocatalysts beyond the optoelectronic device technologies. However, Most of the present works regarding the perovskite photocatalysts usually employed the hybrid perovskites in the form of thin polycrystalline...
films [4][5], and little effort is paid to apply the perovskite single crystals on photocatalysis, which is aiming at splitting water and generating H₂. Here we synthesized MAPbBr₃ single crystals by Inversed Temperature Crystalization (ITC) method and used them to fabricate the photocatalyst for water splitting with simple device structure, which exhibits high photocurrent, high H₂ evolution activity, and good stability.

Reference

FF04.08.05
Fluorescent One-Dimensional Molecular Crystals for a Novel Emissive Chemosensor Yuri Banno, Kanae Kitao and Norifumi Fujita; Meijo University, Japan

Contamination of the drinking water by heavy metal ions is a frightful problem for present and future generations. These contaminants are difficult and expensive to detect and remove and their lethal effect on the human health is of a long term and it’s impossible to trace it immediately. The permissive concentrations for the water in the environment are specified in 10⁻⁶ mol/L to 10⁻⁹ mol/L by WHO, whereas the detection limits of general chemosensors were around 10⁻⁷ mol/L. Thus, the detection properties leave something to be desired. To aim at development of molecular crystal-based chemosensor for highly ion-sensitive materials for optode, curcumin was chosen as molecular core structure because of its high absorbance and emission properties and fine coordination properties with heavy metal ions. We synthesized curcumin-based mesogenic molecules with hydrophobic tethers (1) and hydrophilic tethers (1′). Upon addition of heavy metal ions to the oligomeric assembly of 1 in the solution, UV/vis absorption spectra were more obviously changed than those of monodispersed state. The fluorescent quenching of the assembly was also detected efficiently upon metal ion addition, suggesting that the oligomeric 1D molecular crystals contribute to high detection properties for optode. For metal ion sensing properties of oligomeric 1′ will also be discussed.

FF04.08.06
Formation of Multiple Cocrystal Stoichiometries in Solution Edward Van Keuren, Andrew Fitzgerald and Scott Melis; Georgetown University, United States

The study of cocrystal formation has seen a great deal of attention in the past decade. Cocrystals have important applications as pharmaceutical compounds and in the development of organic electronics. However, for a given set of coformers, different cocrystal stoichiometries may exist, and multiple polymorphs are also more likely than in single component crystals. We have recently developed a model to describe the equilibrium formation of multiple stoichiometries under various crystallization conditions such as evaporation. By tracing the path through the phase diagram, we can identify the conditions under which individual stoichiometries will form. We present work on applying this model to explain the spatial distribution of different cocrystal stoichiometries in a drying film due to the changes in concentration along the contact line.

FF04.08.07
In Situ Studies on the Kinetic Controlled Morphology Development of Conjugated Polymer Films Processed by Blade Coating Yeon-Ju Kim¹, Jong-Jin Park¹, Kyoungtae Hwang¹, Detlef M. Smilgies², Aram Amassian² and Dong-Yu Kim¹; ¹Gwangju Institute of Science and Technology, Korea (the Republic of); ²Cornell University, United States; ³King Abdullah University of Science and Technology, Saudi Arabia
The thin-film morphology of conjugated polymers regulated by coating conditions can significant impact on electrical properties in organic field-effect transistors. Here, we analyze thin-film morphology of blade-coated poly [N,N’-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5’-(2,2’-bithiophene)] (P(NDI2OD-T2)) thin-films varying with the solvent and coating temperature. In order to achieve P(NDI2OD-T2) thin-films revealing large polymer domain, elongated packing structure and predominant face-on orientations, the consideration of pre-aggregation of P(NDI2OD-T2) in solution and the amount of thermal energy from coating temperature is crucial during film formation. The direct investigation of evolution of film formation is highly desirable with in situ measurements. By combining in situ UV-Vis spectroscopy and in situ grazing incidence wide angle X-ray scattering, we observed five stages which appear during blade coating. The insight will offer fundamental understanding of the relationship between film morphologies and charge transport properties as well as a potentially powerful method to control film microstructure of various organic electronics.

FF04.08.08
Dynamic Crystallization Behavior of Metal-Organic Framework Particles in a Polymeric Capsule
Liihan Chen, Sanfeng He and Tao Li; ShanghaiTech University, China

As a new class of crystalline porous materials, metal-organic frameworks (MOFs) have attracted broad attention for their fascinating chemistry as well as potential industrial applications as sorbent materials. However, the stability of MOFs towards water vapor and acid containing environments has been continuously criticized over the past decade and may well be one of the major bottlenecks for its many industrial deployments. Understanding the mechanism of the MOF degradation process may help us find the key towards increasing MOF stability in aggressive environments. In this talk, I will present our recent finding on the dynamic crystallization behavior of MOF particles confined in a polymeric capsule. By compartmentalizing MOF components within a polymeric boundary, the dissolution and crystallization processes are occurring simultaneously which led to a significantly extended MOF’s longevity under aggressive conditions. Such strategy may be extended as a universal method to improve the stability of MOF materials for industrial applications.

FF04.08.09
Green Sensitive Phototransistor Based on Solution Processed Two-Dimensional n-Type Organic Single Crystal
Jin Hong Kim and Soo Young Park; Seoul National University, Korea (the Republic of)

Two-dimensional (2D) organic crystals are receiving tremendous attention in next generation phototransistors for high-performing image sensor due to their potential color selective absorption and favorable electrical properties. However, organic crystals showing selective absorption in visible region have not been reported yet. Recently, we developed green color absorbing 2D single crystalline n-type material, 2F-4-TFPTA, which exhibited field effect electron mobility of up to 0.9 cm² V⁻¹ s⁻¹. 2F-4-TFPTA could form bilayer thick self-assembled 2D morphology due to the brickwork molecular packing structure with balanced intermolecular interactions along the two principal in-plane directions in the crystal. Based on the excellent optical and electrical properties, 2F-4-TFPTA single crystal exhibited decent photoresponsivity of 3.6 × 10³ A W⁻¹ under green LED irradiation and fast response time of less than 85 ms.

FF04.08.10
Lead Free Perovskite Single Crystal—Crystal Growth and Insight into Structural and Optoelectronic Properties
Naveen K. Tailor and Soumitra Satapathi; Indian Institute of Technology Roorkee, India

Lead halide semiconductors with perovskite crystal structure and APbX₃ stoichiometry [A = MA+, FA+, Cs+; X = I⁻, Br⁻, Cl⁻ or mixtures there of] have recently become perhaps the most intensely studied class of inorganic optoelectronic materials. These materials are now widely used in light-emitting diodes, lasers, photo-detectors as well as in X-ray and gamma-ray (γ-ray) detectors. In these applications large single crystals (SCs) grown by precursors solutions of perovskites are mostly utilized because of low trap density and less grain boundary. Therefore, the rapid emergence of halide perovskites based single crystalline materials for wide variety of as mentioned applications has drawn much research attention in recent years. Though lead-based perovskites single crystals have made a significant contribution in the various applications in the photodetector and imaging application, many challenges are yet to be overcome. Limitations of lead perovskites such as toxicity of lead, easy decomposition in the presence of moisture, heat, and photo instability make them non eco-friendly and are eventually restricting their further development and commercialization potential. Moreover, Pb can accumulative in
the human body causing several physiological disorders such as abdominal pain, constipation, and headaches. It is more important now to develop lead free and stable perovskite materials.

In our present study, we have reported the lead free perovskite single crystals grown by the slow cooling method. The synthesis, crystal growth, and detailed structural and optoelectronic characterization have been carried out by Optical microscopy, EDXA, single crystal XRD, UV-Vis, PL, Raman and TCSPC. The synthesized single crystals have orthorhombic structure and Pnma space group and the corresponding lattice parameters and reciprocal lattice parameters are calculated. The I-V characteristics and impedance spectroscopy of this lead free single crystal are also discussed. With all the measured characteristics, we can conclude that our synthesized lead free inorganic halide perovskite based single crystalline material is very interesting and potential candidate for the optoelectronics and photodetector applications.

FF04.08.11
Electrochromic Naphthalene Diimide-Based One-Dimensional Molecular Crystals in Organogels Yoko Maeda and Norifumi Fujita; Meijo University, Japan

Electrochromism (EC) in which the color tone changes reversibly by voltage application is well studied in various fields ranging from inorganic to organic, and polymer chemistries. Among them, organic EC materials possess a lot of advantages such as low environmental impact, easy to design, and rich properties in multicolor. In this research, we have focused on EC supramolecular gel materials which can gelate solvents and prevent from leakage of electrolytes solution. An amphiphilic naphthalene diimide derivative (1) having long alkyl chains and a pyridinium ion was synthesized for one-dimensional (1D) crystal. 1 has fine self-assembling and gelation properties through noncovalent interactions such as π–π interaction and van der Waals interaction. When a voltage was applied to 1 gel on an ITO electrode, the gel showed EC properties in which the color tone reversibly changed from pale yellow to deep brown for at least 3 times. EC properties of polymer blend film prepare from 1D molecular crystals of 1 and conventional polymers will also be discussed.

FF04.08.12
Physical Solution Blending of Diketopyrrolopyrrole- and Thiophene-Based Semiconducting Polymers for Highly Stretchable Organic Thin-Film Transistors Chun Yan Gao1, Hyoung Jin Choi1, Yun Hi Kim2 and Hoichang Yang1; 1Inha University, Korea (the Republic of); 2Gyeongsang National University, Korea (the Republic of)

There are many efforts to achieve flexible or stretchable electronics based on organic semiconductors. A certain decrease in the π-conjugated structure of semiconducting polymer chains can drastically degrade the π-overlap driven chain rigidity and conductivity, which are important factors to enhance the intra- and inter-molecular charge-carrier transport in organic electronics. Diketopyrrolopyrrole (DPP)-based semiconducting copolymers can yield excellent charge-carrier mobilities in solution-based organic thin film transistors (OTFTs) ranged from 0.01 to 6.2 cm²V⁻¹s⁻¹, due to well-defined conjugated structures. However, the poor ductile conjugated structures of these DPP-based copolymers are hard to be used as semiconducting materials for flexible or stretchable devices. Here, we simply prepare solutions including a minor portion of high electric performance P29-diketopyrrolopyrrole-selenophene-vinylene-selenophene (P29-DPP-SVS) copolymers and a major portion of flexible regiorandom poly(3-hexyl thiophene)s (rr PHT) dissolved in chloroform respectively, and develop self-assembled structures of the P29-DPP-SVS in the semiconductor/semiconductor polymer blends to improve the ductility of film. On polymer-treated gate dielectrics, these blend films are spun-cast from the solutions optionally pretreated to induce better self-assembled structures of the semiconducting polymer in spun-cast films. The semiconducting polymer blend films show greatly improvement in stretchability of the resulting OTFTs, and they can show enhanced charge-carrier mobility and on/off current ratio values in OTFTs including a hole transport layer between Au electrodes and the blend films. These phenomena indicate that the simple blending of the semiconductor polymers can achieve unexpected high π–π stacking and stretchable structures in the spun-cast films, which improving the electrical properties and flexibility in the OTFTs.

FF04.08.13
Local Temperature Reduction Induced Crystallization of MASnI3 and Achieving a Direct Wafer Production Zhun Yao and Shengzhong (Frank) Liu; School of Materials Science & Engineering, China
Despite the rapid advancement of perovskite solar cells, the fundamental drawback of toxicity in lead based materials has largely limited their large-scale development and application. Hence, we developed a local temperature reduction induced crystallization (LTRIC) method to directly obtain a lead-free perovskite wafer (CH3NH3SnI3), which is 110 mm-thick, in an oil bath. The XRD diffraction peaks of the MASnI3 wafer are indexed to (001) and its parallel crystal planes, demonstrating its high orientation. The UV-vis-NIR discloses that the absorption onset of the MASnI3 wafer is red-shifted to 1015 nm, corresponding to a narrow bandgap of 1.21 eV.

SESSON FF04.09: Solution Processed Polymers
Session Chairs: Ying Diao and Stefan Mannsfeld
Thursday Morning, December 5, 2019
Hynes, Level 3, Room 311

8:15 AM FF04.09.01
Characterizing a Novel Series of Coordinated Polymers Using Low-Frequency Raman Spectroscopy
Tal Ben Uliel¹, Eliyahu Farber², Yaakov R. Tischler¹ and David Eisenberg²; ¹Bar Ilan University, Israel; ²Technion–Israel Institute of Technology, Israel

Coordinated polymers are an important class of designer materials for broad set of applications including energy research and nano-patterning, where single atom substitution can have a dramatic impact on both structure and function. For our research, we have synthesized a novel series of coordinated polymers, which consisted of alkaline earth metals and nitrilotriacetic acid, in particular Ba-NTA, Sr-NTA, Ca-NTA, and Mg-NTA, and we used Raman spectroscopy, in particular low frequency (LF) Raman spectroscopy, as a sensitive and a nondestructive method for characterizing the materials based on their vibrational resonances. Since vibrational modes can originate both from the atomic vibrations of molecular bonds and from more distributed phonon modes of nanoscale structures and crystals, atomic mass changes can have a strong influence the observed vibrational spectra, as described by the harmonic oscillator model. Our goal was to study the effect of one atom replacement on the shift of the related Raman band. According to single crystal x-ray diffraction (XRD) measurements, Ba-NTA and Sr-NTA have the same crystalline structure despite their different central metals, while Mg-NTA and Ca-NTA have different crystalline structures. Raman measurements of the chemical fingerprints region (i.e. above 200 cm⁻¹) exhibited high similarity, however for the Raman band associated with vibration of the Metal-Oxygen bond, the lightest metals exhibited the highest frequency Raman shifts. This is expected since the lighter metals form the shortest bonds and consequently their vibrational energies are higher according to the harmonic oscillator model. We found the LF-Raman spectral range, which captures the inter-molecular interactions, to be more sensitive to differences between the compounds. Despite the Ba-NTA and Sr-NTA being highly similar and presenting almost identical regular chemical fingerprint Raman spectra, expanding the measurements to the LF-Raman region enabled us to distinguish between them. In addition, we conducted polarized LF-Raman measurements of Ba-NTA single crystals, which provided additional information on the assignment of specific LF-Raman bands to specific vibrational modes and crystallographic planes as determined by XRD.

8:30 AM FF04.09.02
Using PRISM Theory and Molecular Simulations to Understand the Complex Interplay of Solvent and Polymer Architecture on Structure and Thermodynamics in Polymer Solutions
Arthi Jayaraman; University of Delaware, United States

My research group has focused recent efforts into using molecular simulations and liquid state theory in an integrated fashion to better understand and predict effects of polymer design on the resulting macromolecular material structure and thermodynamics. In this talk I will present these efforts in the context of polymer solutions. I will describe how we have used coarse-grained models, Polymer Reference Interaction Site Model (PRISM) theory and molecular dynamics (MD) simulations to study structure and effective interactions in polymer solutions with linear, cyclic and bottle-brush polymer architectures.

9:00 AM FF04.09.03
A Density Functional Theory Study on Why Pristine PEDOT is Oxidized to 33.3%
Donghyun Kim and Igor
Poly(3,4-ethylenedioxythiophene) (best known as PEDOT) is one of the most important and most studied conducting polymers due to its superior features such as high electronic and ionic conductivities, versatile optical properties, as well as stability against oxidants and air-humidity. Owing to these properties, PEDOT has been utilized for various applications such as photovoltaic cells, supercapacitors, organic electronic ion pumps, light-emitting diodes and electrochromic displays, field effect transistor and many others. While a number of papers that address various aspects of structural, optical, electronic and transport properties of PEDOT have been published, a few studies have so far focused on its polymerization mechanisms. Moreover, a theoretical understanding of thermodynamics and kinetics of the polymerization of PEDOT is completely missing. For example, it is generally accepted that PEDOT polymerizes into relatively short oligomers consisting of 10-20 monomer units. Factors that limit the chain length are not understood, and, to our knowledge, have never been discussed in the literature. Another important property of PEDOT is its oxidation level. In contrast to most other conjugated polymers, a pristine (i.e. as polymerized) PEDOT is heavily oxidized (p-doped). In most studies the oxidation level of pristine PEDOT is typically found to be 33%, i.e. one charge per three monomer unit. Currently, the understanding of this “magic number” of 33% is not available. Apparently, understanding of the factors that determine and limit the oxidation level during polymerization is instrumental for design and improvement of charge storage material and devices such as supercapacitors and batteries with the enhanced performance.

Motivated by the need for theoretical understanding of the thermodynamics and kinetics of the oxidative polymerization, we performed step-by-step density functional theory calculations of the oxidative polymerization of PEDOT:TOS. Using the density functional theory, we calculated the Gibbs free energy for the conventional mechanism that consists of polymerization of a neutral PEDOT oligomers first, followed by their oxidation (doping). We also corroborated the feasibility of alternative mechanism of polymerization in which already oxidized oligomers are used as reactants, leading to doped(oxidized) oligomers as products during polymerization. Our study, for the first time, provides a theoretical insight into PEDOT polymerization, which has been completely missing so far. Our focus of our study is understanding of the maximum oxidation level that can be achieved during polymerization. Our calculations provide a theoretical explanation of “the magic number” of 33% for the oxidation level typically reported for the pristine (i.e. as polymerized). Another result of our study is that the proposed alternative mechanism is likely to be more feasible for longer PEDOT oligomers (chain length N>6).

9:15 AM FF04.09.04
Conjugated Carbon Cyclic Nanoring as Additives for Intrinsically Stretchable Semiconducting Polymers
Jaewan Mun and Zhenan Bao; Stanford University, United States

Molecular additives are often used to enhance dynamic motion and tune microstructures of polymeric chains, which subsequently alter the functional and physical properties of polymers. However, controlling chain dynamics and microstructures of semiconducting polymer thin films, and understanding the fundamental mechanisms of such changes is a new area of research. Here, cycloparaphenylenes (CPPs) are used as conjugated molecular additives to tune the dynamic behaviors of diketopyrrolopyrrole-based (DPP-based) semiconducting polymers. It is observed that the addition of CPPs results in significant improvement in the stretchability of the DPP-based polymers without adversely affecting their mobility. Specifically, the DPP-based polymer thin films originally form cracks at 15% strain, while the addition of 5 wt% CPP improves the stretchability to 105% strain, which arises from enhanced polymer dynamic motion and reduced long-range crystalline order. The polymer films retained their fiber-like morphology and short-range ordered aggregates, which lead to high mobility. Fully stretchable transistors are subsequently fabricated using CPP/semiconductor composites as active layers. These composites are observed to maintain high mobilities when strained and after repeated applied strains. Interestingly, CPPs are also observed to improve contact resistance and charge transport of the fully stretchable transistors. In summary, the above results collectively indicated that controlling the dynamic motion and crystalline structures of polymer semiconductors proved to be an effective way to improve their stretchability.

9:30 AM FF04.09.05
Dynamic-Template-Directed Crystallization of 2D Conjugated Polymer Thin Films and Their Distinct Electronic Properties
Prapti Kafle, Fengjiao Zhang, Noah B. Schorr, Kai-Yu Huang, Joaquín Rodríguez-López and Ying Diao; University of Illinois at Urbana-Champaign, United States
Solution-processable polymeric semiconductors have received an increasing attention in the past two decades due to their wide range of potential applications in large-area, low-cost, flexible devices. In recent years, studies pertaining to 2D films of these semiconductors are gradually emerging owing to the development and wide recognition of 2D inorganic materials which exhibit incredible properties compared to their bulk counterparts. Analogous to the phenomenon observed in inorganic materials, reducing the dimension of polymer semiconductors films to 2D could potentially give rise to unique optoelectronic and mechanical properties. Moreover, the molecular level ultrathin body of the 2D conjugated polymer films can be incorporated in field effect transistors (FETs) to develop highly sensitive sensors for biologically relevant molecules. Despite their growing interest and utilization of a wide variety of solution processable methods, crystallization of these polymers into 2D films over large area still remain challenging. This is partially due to one dimensional nature of their intermolecular interactions as well as high conformational degrees of freedom of the polymer chains. Because 2D charge transport demands highly ordered 2D films, novel methods that enhance 2D polymer crystallization are needed. So far, fundamental questions of how electronic structure and charge transport properties depend on the number of molecular layers are still unclear. Methods for fabricating 2D layers with controlled morphology will lay the foundation for understanding these questions.

In this talk, we present dynamic-template integrated meniscus-guided coating as a new technique to fabricate 2D films of conjugated polymers over centimeter length scale using a wide processing window. Using two different polymeric systems, DPP2T-TT and PII2T, we demonstrate enhanced 2D crystallization on dynamic template leading to highly ordered and aligned 2D layer with edge-on pi-pi stacking. This is in contrast to 1D fiber network morphology obtained on static substrates. Our results show that while static substrates favor ordering of alkyl side chains in 2D films, dynamic template enhances ordering of the conjugated backbone with favorable interaction between the polymer backbone. As a result, charge transport was observed only in 2D films printed on dynamic template but not in monolayer films coated on solid substrates. In addition, we also observed a change in molecular packing from edge-on to bimodal when the film reaches a critical thickness of ~25 nm as well as an abrupt increase in J-aggregation, absorption coefficient and decrease in band gap and HOMO level until the critical thickness. This phenomenon was independent of the substrate and possibly arisen from straightened polymer backbone. Furthermore, we also observed an abrupt increase in hole mobility with film thickness reaching a maximum of 0.7 cm²V⁻¹s⁻¹ near the critical thickness which further corroborates with the drastic increase backbone planarity as film thickness increases. Finally we also fabricated chemical sensors using bilayer polymer films which demonstrated ultrahigh sensitivity < 1 ppb to breath biomarkers.

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In the past two decades, significant progress has been made in the fabrication of polymer-based devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) or organic photovoltaics (OPVs), predominantly due to important improvements of existing materials and the creation of a wealth of novel compounds. Many challenges, however, still exist: from achieving reliable device fabrication, increasing the device stability and, more fundamentally, gaining a complete understanding how structural features over all length scales affect important optoelectronic and photophysical processes in such polymers, including charge transport, charge generation, and general photovoltaic processes. Here we demonstrate how classical polymer science tools can be used to elucidate the structure development of semiconducting polymers from the liquid phase, how such knowledge can be exploited to manipulate their phase transformations and solid-state order and, in turn, their electronic features and device performances. To exemplify our approach, we discuss bulk heterojunction solar cells, which are comprised of active layers that are generally comprised of a complex phase morphology where intermixed and neat phases of the donor and acceptor material co-exist. We show that the fate of photogenerated electron/hole pairs – whether they will dissociate to free charges or geminately recombine– is determined at ultrafast times, despite the fact that their actual spatial separation can be much slower. The local arrangement of the donor and acceptor plays a critical role in this phenomena as we demonstrate on a series of donor polymer:fullerenes binaries by combining 2D-NMR data with time-resolved ultra-fast spectroscopy results as well as detailed structural data. We discuss that similar considerations apply also to other functional blends, such as semiconducting polymer:dopant systems that can lead to highly conductive systems. The spatial arrangement of the polymer with the dopant, which is dictated by
the blends phase behavior, strongly affects charge transport in analogy to the photovoltaic donor:acceptor systems. We will conclude with providing a tentative picture of the complex correlation of structure and electronic landscape for the understanding of organic photovoltaic cells as well as doped, conducting “plastics” of metallic-type transport – and beyond.

10:45 AM FF04.09.07
Organic Semiconductor/Dielectric Composites for Flexible Field-Effect Transistors Tomasz Marszalek1,2, Ke Zhang1, Paul Blom1 and Wojciech Pisula1,2; 1Max Planck Institute for Polymer Research, Germany; 2Lodz University of Technology, Poland

Plastic transistors do not only create an interesting field of science but also belong to a highly promising technology for future electronic devices, especially for field-effect transistors. Thereby, conjugated small molecules or polymers are used as organic semiconductors for solution deposition onto flexible substrates. The deposition methods are based on roll-to-roll printing such as inkjet or gravure, while the substrate consists of thermoplastic polymers such as PEN, PET or PMMA. The benefits of such printed organic transistors in comparison to their traditional silicon counterparts are mechanical flexibility and low cost fabrication. To reduce the production costs, new processing concepts are required. One approach is focused on the deposition of the substrate polymer together with the organic semiconductor from the same solution or melt. During solvent evaporation or after post-treatment a vertical phase separation between the isolating polymer and the semiconductor occurs1,2. In the final bilayer structure, the semiconductor crystallizes on top of the polymer layer ensuring a charge carrier transport in the transistor. As further key factors, the molecular order, organization and film microstructure of the organic semiconductor are crucial for the charge carrier transport3.

This work acknowledges the Foundation for Polish Science financed by the European Union under the European Regional Development Fund (POIR.04.04.00-00-3ED8/17-00)


11:00 AM FF04.09.08
Leveraging Molecularly Doped Semiconducting Polymers as Functionally Graded Organic Thermoelectric Materials Tengzhou Ma, Ban Dong and Shrayesh Patel; University of Chicago, United States

With the ability to modulate electronic properties through molecular doping coupled with ease in processability, semiconducting polymers are at the forefront in enabling organic thermoelectric (OTE) devices for thermal energy management. The challenge lies in the judicious control of thermoelectric transport properties: electronic conductivity (σ), Seebeck coefficient (α), and thermal conductivity (κ). One approach considers functionally graded materials (FGMs) where one locally tunes the material properties across an operational temperature gradient. While FGMs has shown to improve the performance of inorganic thermoelectric materials, similar concepts have not been considered in the field of molecularly doped organic semiconductors. Here, we present the fabrication, structure and transport characteristics of poly[2,5-bis(3-tetradecylthiophen-2-yl) thiieno [3,2-b]thiophene] (PBTTT) thin film (ca. 30nm) with compositional functional grading control of the molecular dopant, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ). By using an in-house designed vapor doping process, we specifically fabricate a double – segmented PBTTT thin film consisting of two segments with different doping levels of F4TCNQ. Electrical conductivity and structural characterizations (X-ray scattering and Raman spectroscopy) indicate the existence of an interface region of ca. 1000 mm between the two segments within which the F4TCNQ concentration, polymer morphology, and conductivity gradually vary. The measured effective Seebeck coefficients at two sides of the two segments and across the interface match with known models describing transport in graded thermoelectric systems. Our results demonstrate the first successful fabrication and characterization of functionally graded organic thermoelectric materials, and thus providing guidelines to further develop more complex FGMs leveraging high mobility organic semiconductors and molecular doping.

11:15 AM FF04.09.09
A Stretchable Semiconducting Polymer Blend Film Including Regioregularity-Driven Phase-Separated
Domains of Poly(3-hexylthiophene)s Chun Yan Gao, Mingyuan Pei, Hyoung Jin Choi and Hoichang Yang; Inha University, Korea (the Republic of)

It has been known that poly(3-hexylthiophene) (PHT), constituted of asymmetric 3-hexyl thiophene repeat units, is a benchmark semiconducting polymer for solution-processed organic electronics. High regioregular (RR) PHTs with a backbone rigidity due to the strict head-to-tail manners approach tends to grow into an ordered domain of π–π overlapping chains in spun-cast films, facilitating the charge-carries to move along the intra- and inter-chains to yield high hole mobilities. Generally, conjugated semiconductors can't have both high electrical performance and flexibility. In order to obtain a flexible device with high optoelectrical properties, researchers have proposed many approaches. For example, semiconducting RR PHTs were chemically modified with thiophene segments generated better π-conjugated and deformable film structures and some semiconducting polymers were physically blended with elastomers or amorphous polymers to achieve stretchable semiconducting films, etc. However, most of these strategies to realize stretchable organic semiconducting films suffer from limitations of available materials and tedious fabrication processes.

Here, via simple blending a high-RR PHT (with a regioregularity of 97%) with the chemically identical but regiorandom (rr) PHT (55%) without any assistance, the RR PHT chains from the rr PHT media and develop highly conjugated nanodomains in both solution and film. In the spun-cast blend film, the rr PHT matrix imparts enough deformability of the channel layer required for stretchable organic thin film transistors (OTFTs), compared to neat RR PHTs and blends with a deformable polymer. OTFTs including RR PHT/rr PHT blend film showed excellent hole mobility (μ) values up to 0.13 cm2 V-1 s-1, surpassing that of the best RR PHT films (0.026 cm2 V-1 s-1) fabricated by ultrasound solution pretreatment. Furthermore, a 50% stretched RR PHT/rr PHT film maintains ~55% of its μ value at no strain, while RR PHT film shows a sudden decrease in μ even at 10% stretch. The simple blending approach imparts deformability to π-conjugated polymer films for application in stretchable OTFTs.

11:30 AM *FF04.09.10
A Molecular Route to Control Morphology in Solution-Processed Polymer Solar Cells Ellen Moons; Karlstad University, Sweden

The fabrication of polymer solar cells involves coating processes from a solution of electrically conducting donor and acceptor molecules, resulting in the photoactive layer. During the solvent evaporation, structures with a variety of length scales can be formed, the control of which is key to the high performance recently achieved for polymer solar cells. These structures are initiated through molecular self-assembly in which molecular interactions between donor, acceptor, and solvent have an important role. The choice of coating technique and post-fabrication annealing steps also have a significant effect on the final film morphology.

We will present one route towards estimating the molecular interactions between donor and acceptor molecules. With the help of a large set of solvents, the Hansen Solubility Parameters (HSP) of donor and acceptor are determined separately. Their distance in Hansen space presents an estimate for the mutual miscibility of donor and acceptor. From the HSPs, the Flory-Huggins interaction parameters can be determined, leading to a general strategy to control the donor/acceptor system's tendency to phase separate.

Soft X-ray based spectro-microscopy techniques provide excellent nanoscale resolution and chemical contrast to resolve the nanostructure of the donor/acceptor bulk heterojunction, as well as the composition of the domains, for systems where the acceptor is a fullerene derivative. However, the transition to non-fullerene acceptors brings along new challenges for morphology studies, because orthogonal photon energies that correspond to X-ray absorption resonances for donor and non-fullerene acceptor molecules are more difficult to find. Taking advantage of distinct functional groups on the non-fullerene acceptor molecules, new strategies for the imaging of the nanoscale morphology are being developed, such as AFM-IR spectro-microscopy.

We will present results from our multi-disciplinary effort to generate fundamental understanding about how molecular interactions drive the structure formation at different length scales in solution-borne polymer blend systems and how these processes can be manipulated by external stimuli. We aim to use this knowledge to formulate general design principles for polymer-polymer structures, as well as to apply these to guide the development of novel materials with structures that are tailor-made to improve properties and functionality of optoelectronic devices.
Emerging Approaches to Measure Orientational Order in Organic Semiconductors
Dean M. DeLongchamp; National Institute of Standards and Technology, United States

Organic semiconductors typically exhibit a rich variety of ordered phases. Orientation occurs during processing, often by passing through lyotropic liquid crystalline phases, and dried films exhibit orientation at many length scales. Liquid crystallinity appears almost ubiquitous in organic semiconductors we have studied, including behaviors similar to nematics, smectics, or sanidics. Uniaxial orientation where the conjugated plane exhibits a preferential “face on” or “edge on” orientation is the most commonly characterized aspect of orientational order, and mature techniques such as near edge X-ray absorption fine structure (NEXAFS) spectroscopy and grazing incidence X-ray diffraction (GIXD) are frequently employed to measure it. Significant challenges remain, even for this seemingly simple aspect of orientational order. For example, these approaches are often found to be insufficient when films exhibit a complex depth profile of orientation, composition, or both.

As the materials diversity of organic semiconductors increases thanks to achievements in synthetic chemistry, and as the complexity of formulation, blending, and coating increases as process design knowledge matures, there is a commensurate need for more advanced approaches to characterizing orientational order. Biaxial orientation is increasingly observed, where “face on” or “edge on” preferences are combined with an in-plane preference imparted by a substrate or processing vector. Domain-relative orientations are also been observed, with correlations in domain-to-domain orientation thought to influence charge transport.

I will describe some emerging approaches to measure orientational order in organic semiconductors. Resonant soft X-ray reflectivity (RSoXR), a method capable of measuring thin film depth profiles using the spectroscopic principles of NEXAFS, will be discussed. I will also summarize progress on in-situ spectroscopic and scattering-based structure measurement techniques that are combined with ex-situ probes including imaging and image analysis to determine how orientation originates during the processing of organic semiconductors. These new measurements will support science-based approaches for orientation control and optimization, helping to maintain the rapid pace of organic semiconductor technology development in an era where increasing complexity renders matrix-style empirical approaches too inefficient to contemplate.

Key Roles of Structural Order and In-Plane Alignment of (Semi)-Conducting Polymers on their Optical and Charge Transport Properties
Laure Biniek; CRNS, University of Strasbourg, France

This presentation focuses on recent advances in growth control and oriented crystallization of (semi)-conducting polymers for organic electronic applications. The performance and lifetime of organic electronic devices are critically dependent on the morphology of the active layers and structural order of the materials. For instance both molecular and crystalline orientations of the polymers determine optical and charge transport properties in thin films since these properties are by essence highly anisotropic.

Particular emphasis will be given to the progress made in high-temperature rubbing of conjugated polymers films. This effective large scale alignment method can orient a large palette of semiconductors with α- or ρ-type character without the use of alignment substrate. High degrees of crystallinity and in-plane alignment can be obtained which provide well-defined electron diffraction patterns essential for structure refinement. The concurrent roles of polymer molecular weight distribution and rubbing temperature (T_R) on the in-plane orientation are rationalized for P3HT and PBTTT. Correlations are drawn between nanomorphology/crystallinity on one side and charge transport and optical properties on the other side. It is shown that the exciton bandwidth in P3HT crystals is determined by the length of the average planarized chain segments in the crystals. The high alignment and crystallinity observed for T_R > 200 °C cannot translate to high hole mobilities parallel to the rubbing because of the adverse effect of amorphous interlamellar zones interrupting charge transport between crystalline lamellae of semi-crystalline P3HT.
opposite, hole mobilities along the polymer chains of rubbed PTB7 films are observed to be 6 times higher than the non-rubbed films.\textsuperscript{3} This is due to the smectic-like character of this alternated donor-acceptor copolymer. Interestingly high-Tr rubbing and post annealing process of PTB7 provide well-defined electron diffraction pattern. Combined with DFT calculation, this helps refining the structure and the chain conformation of this benchmark electron donor polymer for OPV application.

In a second part of this presentation, we show that soft doping of aligned P3HT yields highly oriented conducting polymer films with anisotropic charges and thermal conductivities. The thermoelectric properties are enhanced along the rubbing direction. The unique in-plane orientation in such conducting polymer films helps rationalizing the mechanism of redox doping.\textsuperscript{4}

References.

2:45 PM FF04.10.03/EN12.14.03
Real-Time Structural Evaluation of Naphthyl End-Capped Oligothiophenes in Organic Thin-Film Transistors During Deposition
Mathias Huss-Hansen\textsuperscript{1}, Peter Siffalovic\textsuperscript{2}, Nad’a Mkyvková\textsuperscript{2}, Jakub Hagara\textsuperscript{2}, Martin Hodas\textsuperscript{3}, Frank Schreiber\textsuperscript{3}, Eva Majková\textsuperscript{2}, Jakob Kjelstrup-Hansen\textsuperscript{4} and Matti Knaapila\textsuperscript{1}; \textsuperscript{1}Technical University of Denmark, Denmark; \textsuperscript{2}Slovak Academy of Sciences, Slovakia; \textsuperscript{3}University of Tuebingen, Germany; \textsuperscript{4}University of Southern Denmark, Denmark

The electrical properties of organic thin film transistors (OTFTs) are strongly influenced by the structural characteristics and thin film morphology. Understanding the growth dynamics that lead to preferential molecular orientation and changes in crystal structure remain an important factor in the design of new high-performance OTFTs as well as in their fundamental studies. In this contribution, we have investigated the thin film growth behavior of 5,5′-Bis(naphth-2-yl)-2,2′-bithiophene (NaT2) and 5,5″-bis(naphth-2-yl)-2,2′:5′,2″-terthiophene (NaT3) during the deposition process using real-time grazing incidence X-ray diffraction (GIXRD) \textit{in situ}. The thin films were prepared by vacuum sublimation atop various substrates, including monolayer graphene on 90 nm SiO\textsubscript{2}, in a custom-built ultra-high vacuum (UHV) chamber with a 360° cylindrical beryllium window that allows for \textit{in situ} X-ray measurements within realistic deposition time scales. The crystal structure analysis revealed that the preferred orientation of the molecules were dictated by the substrate and that the unit cell underwent significant changes when transitioning from monolayer to multilayer structure. The changes of the unit cell were not readily observed when measuring thin films of corresponding thicknesses \textit{ex situ}, suggesting that the molecules undergo further re-organization/relaxation upon terminating the deposition. From the evolution of the crystal structure, a connection to the film growth mode and kinetics is made. These findings are rationalized based on the surface energies of the studied substrates and supplemented with AFM and helium ion microscopy. Finally, the crystal structure and morphology are correlated with charge transport properties of the final thin films.

3:00 PM BREAK

3:30 PM *FF04.10.04/EN12.14.04
Semiconducting Polymers for High Performance Organic Transistor Applications Iain McCulloch; King Abdullah University of Science and Technology, Saudi Arabia

The evolution of organic electronics has now reached the commercial phase, with the recent market introduction of the first prototypes based on organic transistors and organic solar cell modules fabricated from solution. Understanding the impact of both the organic semiconductor design and processing conditions, on both molecular conformation and thin film microstructure has been demonstrated to be essential in achieving the required optical and electrical properties to enable these devices. Polymeric semiconductors offer an attractive combination in terms of appropriate solution rheology for printing processes, mechanical flexibility for rollable processing and applications, but their optical and electrical performance requires further improvement in order to fulfil their
potential. Synthesis of conjugated aromatic polymers typically involves carbon coupling polymerisations utilising transition metal catalysts and metal containing monomers. This polymerisation chemistry creates polymers where the aromatic repeat units are linked by single carbon-carbon bonds along the backbone. In order to reduce potential conformational, and subsequently energetic, disorder due to rotation around these single bonds, an aldol condensation reaction was explored, in which a bisisatin monomer reacts with a bisoxindole monomer to create an isoindigo repeat unit that is fully fused along the polymer backbone. This aldol polymerization requires neither metal containing monomers or transition-metal catalysts, opening up new synthetic possibilities for conjugated aromatic polymer design, particularly where both monomers are electron deficient. Polymers with very large electron affinities can be synthesised by this method, resulting in air stable electron transport, demonstrated in solution processed organic thin film transistors. We present an electrical, optical and morphology characterisation of polymer thin films, illustrating structure-property relationships for this new class of polymers.

4:00 PM  *FF04.10.05/EN12.14.05*
**Charge Transport in Conjugated Polymers and the Importance of Order—From Atomic to Mesoscale**  
*Alberto Salleo; Stanford University, United States*

Carrier mobility in conjugated polymers continues to increase with recent reports of field-effect mobilities exceeding 10 cm²/Vs. Charge transport is intrinsically dependent on processes occurring across multiple length scales. In order to access order parameters at the molecular scale we use charge modulation spectroscopy combined with theory. Furthermore, we study the mesoscale organization of polymers using a new technique in the transmission electron microscope. These techniques are used on homopolymers and donor-acceptor copolymers. Such multiscale studies of microstructure are instrumental in guiding our understanding of charge transport in conjugated polymers.

4:30 PM  *FF04.10.05/EN12.14.06*
**Charge Transfer State Lifetimes in P3HT:F4TCNQ Co-Processed Films**  
*Bharati Neelamraju, Kristen Watts, Jeanne Pemberton and Erin L. Ratcliff; University of Arizona, United States*

Doping is a fundamental strategy to increase the carrier density and conductivity of organic electronic layers for opto-electronic devices. The model system for p-doping is poly(3-hexylthiophene (P3HT) with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ), whereby increases in conductivity occur through integer charge transfer (ICT) to form mobile carriers in the P3HT. Extensive work in the organic electronics field has revealed the interplay between film microstructure, the opto-electronic properties, and conductivity.

This talk asks the simple question: How stable are ICT states in doped films? An alternate undesired reaction pathway is formation of a partial charge transfer complex (CPX), which results in a localized, trap-like state for the hole on P3HT. Starting first with our recent observation that both ICT and CPX states exist simultaneously in a single film, this talk will focus on thermodynamic and kinetic pathways that lead to conductivity loss in F₄TCNQ-doped P3HT films. Both reaction chemistries and microstructural effects will be discussed.

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**SYMPOSIUM FF05**

Advanced Atomic Layer Deposition and Chemical Vapor Deposition Techniques and Applications  
December 2 - December 6, 2019

**Symposium Organizers**  
Stacey Bent, Stanford University  
Karen Gleason, Massachusetts Institute of Technology  
David Munoz-Rojas, LMGP Grenoble INP/CNRS  
Kevin Musselman, University of Waterloo
SESSION FF05.01: Theoretical and Experimental Advances in ALD/CVD Chemistry I
Session Chairs: David Bergsman and Graziella Malandrino
Monday Morning, December 2, 2019
Hynes, Level 3, Room 310

8:15 AM WELCOME AND INTRODUCTION

8:30 AM FF05.01.01
DFT Study on Atomic Layer Deposition of Cobalt and Ruthenium on NHx-Terminated Nitrogen Plasma Treated Metal Surfaces Ji Liu and Michael Nolan; Tyndall National Institute, Ireland

Cobalt (Co) and Ruthenium (Ru) are used as a seed layer for metallization of interconnects, where atomic layer deposition (ALD) is applied to achieve conformality and precise thickness control at the atomic scale. Plasma-enhanced ALD (PE-ALD) is used for low-temperature thin film growth by alternating exposures of metal precursors and plasma reactants. During the PE-ALD growth of metals, N-plasma, for example, NH3 or a mixture of N2 and H2, has been developed to avoid surface metal oxidation. In this presentation, we study the PE-ALD growth of Co and Ru by first principle calculations. Experimentally known surfaces were constructed including (001), (101), and (100). The (001) surface with a hexagonal structure is the most stable surface and the (100) surface with a zigzag structure is least stable but with high reactivity. The two surfaces were chosen to study the surface saturation coverage by considering individual adsorption and co-adsorption of NH and NH2. On the (001) surface, the saturation coverage for NH is 1ML on Ru and 5/9ML on Co. For NH2, the saturation coverages are 5/9ML on both Co and Ru surfaces. Additionally, NH2 is unstable under high coverage by either desorbing from the metal surface or dissociating into NH. The calculated dissociation barrier for NH2 dissociation on both Co and Ru surfaces is 0.71eV. On the (100) surface, the saturation coverages are 2ML for NH and 1 ML for NH2 on both Ru and Co surfaces. The larger saturation coverage on (100) surfaces is attributed to the unique trench structure, which provides more available surface sites than that of (001) surfaces. We also consider co-adsorption of NH and NH2 on (001) and (100) surfaces. The results are analyzed with ab initio thermodynamics by calculating the Gibbs energy. Both the ultra-high vacuum (UHV) condition and standard ALD operating condition are used to elucidate the effect of pressure and temperature on the termination of metal surfaces.

The adsorption and reaction of metal precursors (CoCp2 and RuCp2) on NHx-terminated metal surfaces was investigated with inclusion of van der Waals corrections. Two possible adsorption structures, namely the precursor parallel and perpendicular to the NHx-terminated surfaces, were considered. The adsorption and reaction of metal precursors are classified into four steps: adsorption, pre-reaction, proton transfer, and ligand desorption. The barrier for proton transfer is calculated using climbing image nudged elastic band (CI-NEB) method. After desorption of Cp ligand, the Co or Ru metal binds to the N atom that transferred the H atom to the Cp ligand. The remaining Cp ligand will be consumed in the second half cycle with the help of the N-plasma. After a full cycle, the surface is an NHx-terminated metal surface and ready for the next cycle. In addition, the NHx-covered SiO2 surfaces are examined to investigate the initial nucleation process. This work will be important to reveal the mechanism and feasibility of atomic layer deposition of metals using N-plasma.
References

8:45 AM FF05.01.02
Multi-Scale Modelling and Experimental Analysis of ALD Alumina—Interplay of Process Dynamics, Chemistry and Interfacial Phenomena Giorgos Gakis¹, Emmanuel Scheid², Hugues Vergnes³, Andreas Boudouvis¹, Brigitte Caussat¹ and Constantin Vahlas⁴; ¹National Technical University of Athens, Greece; ²LAAS, France; ³Institut National Polytechnique de Toulouse, France; ⁴CNRS, France

Under optimized conditions, atomic layer deposition (ALD) allows processing of films with high uniformity and conformity on 3D surfaces. These characteristics make ALD an appropriate tool to produce ultra-thin films for a variety of applications in microelectronics, optoelectronics, catalysis, renewable energy and more. Nonetheless, ALD processes still suffer from some non-uniformity of the deposited films on large area wafers, from initial substrate inhibited island growth and from the formation of an interfacial layer with uncontrollable characteristics. In order to overcome such drawbacks, the thorough understanding of the phenomena and mechanisms involved during the ALD process is essential. In this work, we present a framework for the integrated study of the ALD of Al₂O₃ from TMA and H₂O on Si, using a commercial ALD reactor.

The framework consists of a combined computational and experimental approach. A three-dimensional Computational Fluid Dynamics (CFD) model is built for the ALD reactor, designed to treat large area 20 cm substrates. The model aims to investigate the effect of the reactor geometry and process parameters on the gas flow and temperature fields, and on the species distribution on the heated substrate surface. We couple this model to a surface chemistry one, which considers adsorption, desorption and reactions on the substrate surface. We combine it with ellipsometry measurements to access the limiting mechanisms, the competition between surface phenomena and their effect on ALD growth. This integrated (surface chemistry/kinetics and CFD) approach reveals a direct link between film uniformity and deleterious transport phenomena due to gas flow recirculation and low temperature zones in the reactor.

We also develop a computational model based on geometric principles to study the initial nucleation and growth steps of the Al₂O₃ film. Using XRR measurements, we evidence a substrate inhibited growth regime, attributed to the low reactivity of the HF-cleaned Si surface, together with an island growth mode for Al₂O₃. Due to these phenomena, 25 ALD cycles are needed to produce a continuous film. Our computational model, numerically reproduces these findings and allows deriving the film nucleation mechanisms and the phenomena leading to island growth.

We call for a complete range of techniques, including TEM, XPS, EDX and ToF-SIMS to get insight to the morphology and chemical nature of the deposited film. We also precisely analyze the chemical composition of the (Al, O, Si) interfacial layer to get insight in the mechanisms of its formation. We show that Si oxidation occurs during the island growth, catalyzed by the presence of Al, while it is also fed by species interdiffusion through the film.

In order to enhance the initial surface reactivity, we implement an in situ plasma N₂-NH₃ pretreatment of the HF-cleaned Si substrate prior to ALD. We use STEM coupled to EDX to show that the initial deposition is clearly increased on the pretreated surfaces, resulting in a linear ALD regime even after 5 ALD cycles. Furthermore, a Si₃N₄H layer is formed by the N₂-NH₃ plasma pretreatment, which acts as a barrier layer, reducing the oxidation of the Si substrate beneath it.

This integrated analysis provides a general framework for the study of the mechanisms and phenomena involved during the ALD process as well as the non-ideal aspects leading to the drawbacks of ALD. This can lead to the determination of adequate surface pretreatments, able to combat the witnessed drawbacks during metal-oxide ALD on Si, thus paving the way for the effective production of nanometric thin films with sharp interfaces for microelectronic and other applications of the future.

9:00 AM *FF05.01.03
CVD and ALD Processes from an Ab Initio Perspective Ralf Tonner; University of Marburg, Germany

Progress in thin-film deposition methods often depends on our understanding of the underlying elementary steps at the level of atomic and electronic structure. For key questions, theoretical investigations can help by complementing the experimental investigations. Nevertheless, the goal for theoretical approaches is to move beyond interpretation of already available data and provide predictions and guidance for future investigations. Predictive computations
require high accuracy which directly leads to \textit{ab initio} methods like density functional theory (DFT) or wave function-based methods combined with methods for larger length and time scales.

For CVD, the low-temperature growth of GaP on H/Si(001) by metal-organic vapor phase epitaxy (MOVPE) is taken as an example to highlight the strengths (and limitations) of these \textit{ab initio} approaches. For the first step - the gas phase decomposition of precursors - we find very high barriers for several reactions proposed earlier for tert-butylphosphine (TBP) and triethylgallane (TEGa) and unusual $\beta$-H elimination reactions relevant for ligand design.\cite{1} DFT approaches including methods for treating dispersion interactions (DFT-D) are in good agreement with gold-standard quantum chemical coupled-cluster methods. This lends confidence for using these methods to reveal characteristics of surface adsorption for TBP – accurate enough to predict the outcome of growth experiments and ex-situ scanning tunneling microscopy measurements. Unusual electronic vacancy stabilization effects are revealed by theory to lead to non-statistical growth in the nucleation phase.\cite{2}

In a joint endeavor of experiment and theory, we could further reveal the thermodynamic and kinetic reasons for the unexpected structure of GaP/Si interfaces. Intermixing models established previously are not sufficient to explain the pyramidal structure observed experimentally. Instead, relative facet stabilities and ad-atom mobility in the interface region needs to be quantified to find a rationale for the atomically-resolved measurements.\cite{3} Further fruitful experiment-theory collaborations resulted in transfer of these ideas and approaches towards modelling of CVD of boron carbides.\cite{4}

Recently, the insight gained from \textit{ab initio} CVD modelling are transferred to ALD research. We will present initial results focusing on surface chemistry in ALD and AS-ALD of prototype systems. The specific angle taken is based on electronic structure analysis conducted with our recently proposed energy decomposition analysis for extended systems (pEDA) giving quantitative insight in surface-adsorbate bonding crucial for the growth mechanism.\cite{5}


\[9:30 AM FF05.01.04\]

\textbf{Development of Selenium Containing Single Source Precursors for the AACVD of SnSe and ZnSe Thin Films}

\textbf{Emily Taylor}1,2, Ibrahim Ahmet3 and Andrew Johnson1; 1University of Bath, United Kingdom; 2Centre for Sustainable Chemical Technologies, United Kingdom; 3Helmholtz-Zentrum Berlin, Germany

Whilst heavy chalcogenide containing materials play an important role in a number of opto and thermo electric materials, the development of single source precursors containing elements such as Se and Te has been hindered by the inherent weakness of the elemental bonds. Without the use of expensive techniques or phosphorus containing precursors, metal selenide deposition commonly results in poorly orientated, polyphasic thin films.\cite{1} Aerosol Assisted Chemical Vapour Deposition (AACVD) circumvents the need for volatile materials and uniquely allows access to kinetically stable phases which are typically inaccessible through high temperature deposition techniques.\cite{2}

Based on our work on the development of thioureide complexes for the AACVD of metal sulphide thin films, such as SnS and ZnS, we describe here our initial studies into the synthesis, characterisation and utilisation of the seleno analogues (selenoureides) for the deposition of SnSe and ZnSe thin films.\cite{3, 4}

We have successfully deposited uniform, thin films of phase- pure SnSe which display temperature dependent orientation at temperatures as low as 200 °C. Highly orientated ZnSe polycrystalline thin films at low temperatures have also been produced utilizing the same ligand system.

Vanadium dioxide ($\text{VO}_2$) is a strongly correlated oxide widely studied for applications in electronics due to its metal-insulator transition at approximately 68°C. While thin films and nanostructures of VO$_2$ have been grown on common rigid substrates like sapphire, TiO$_2$, Si and Ge, further expansion of the scope of their application lies in their growth on transferable or flexible substrates making it easier to integrate them into devices. In this work, we report the epitaxial growth of VO$_2$ nanowires on h-BN substrates by chemical vapor transport. We observe that nucleation and growth of VO$_2$ on h-BN proceeds very differently than that on c-plane sapphire: higher nucleation unexpectedly occurs on the h-BN surface and growth tends to proceed outward i.e. toward and beyond the edges of the h-BN substrate. We study the resulting epitaxial strain in h-BN by mapping a shift in a characteristic h-BN Raman peak. We further reveal that the temperature-driven phase transition of VO$_2$ on h-BN proceeds via a single phase boundary which is drastically different from that on substrates such as SiO$_2$ and sapphire, suggesting the presence of weak bonding at the VO$_2$/h-BN interface. Such growth of single crystal VO$_2$ nanostructures not only provides an ideal system to study properties of VO$_2$ based heterostructures but may also be extended to other flexible, transferable substrates.

**10:00 AM BREAK**

**10:30 AM *FF05.01.06***

*Design Rules for Atomic Layer Deposition Precursors and Why You Should Break Them*  
Sean T. Barry; Carleton University, Canada

Atomic layer deposition processes are fundamentally controlled by surface-gas phase reactions, and so depend to a great degree on the nature of the precursor. There are many general rules for the design of precursors: they should have strong metal-ligand bonds to prevent thermolysis, but these bonds should react to allow chemisorption of the precursor to the surface. The precursor should be low molecular weight, since (to ideal assumptions) vapour pressure is related to the inverse of molecular weight, and should be designed to minimise intermolecular interactions. The precursor needs steric protection to assist with self-limiting monolayer formation, but the metal centre must be accessible to reaction with both the surface and the second reactant. Many of these design rules are in opposition to each other, and so a balance must be struck.

When comparing families of precursors, a simple Figure of Merit has allowed us, in a straightforward manner, to compare and diagnose precursor performance. Using examples from across the periodic table, this presentation will demonstrate how a Figure of Merit can highlight when these design rules succeed and when they fail. For example, a molybdenum diimide dimer shows similar volatility to a variety of its base-stabilized monomers but has superior thermal stability. This ultimately makes the dimer a better precursor candidate. In this case, the coordination base in the monomers can be thermally reactive, leading to a low-temperature decomposition route. Similarly, a gold(I) precursor candidate shows its best performance with a ligand with an intermediate steric bulk, mainly due to stabilization of the precursor thermally.

**11:00 AM FF05.01.07***

*Influence of Precursor Chemistry on Phase, Morphology and Composition of CVD Grown Metal Oxide and Noble Metal Nanostructured Films*  
David Graf, Michael Frank, Lasse Jurgensen, Aida Jami, Isabel Gessner and Sanjay Mathur; University of Cologne, Germany

The proper selection of tailored precursors plays a crucial role in chemical vapor deposition techniques for the fabrication of high-performance functional nanostructured films. Metal alkoxides are most suitable precursor class for depositing well-defined metal oxide thin films on various substrates with different surface chemistry and complexity, due to their high volatility and defined decomposition mechanism. We demonstrated the strong
influence of the alkyl function in vanadium(IV) alkoxides on phase and morphology. Phase selective chemical vapor deposition of thermochromic vanadium dioxide was achieved by deploying homogeneous and monomeric [V(OBu)t] as a precursor. The produced thin films of monoclinic VO₂ (M1) exhibited a small hysteresis at lower temperatures (63°) in the reversible thermochromic metal-to-semiconductor transition (MST), due to the anisotropic one-dimensional growth. In contrast, use of trimeric [V(OEt)] generated conductive thin films of crystalline vanadium sesquioxide with a flower-like morphology. The in-situ reduction mechanism of the V(IV) precursor to V₂O₃ was elucidated by in-operando mass spectrometry. Moreover, novel volatile and stable heteroleptic bimetallic alkoxides ([LaFe(OBu)₄(L)] and [LaSn(OBu)₄(L))] with L = trifluoro-butenone-tert-butyl amine) as well organometallic noble metal complexes ([M(COD)(L))] COD = Cyclooctadiene; M = Rh, Ir) were synthesized by using tailored multidentate enamino ligand (L) systems. The interdependence of the organic backbone, choice of donor atoms and denticity in the ligand systems on the reactivity, stability and volatility of the resulting precursors were investigated by single crystal structure analysis, NMR-spectroscopy and thermogravimetric measurements (TGA-DTA). Chemical vapor deposition of LaFe(OBu)₄(L) and LaSn(OBu)₄(L) revealed the selective conversion into perovskite LaFeO₃ and pyrochlore Sn₃La₃O₇ thin films, respectively, which shows superior gas sensing characteristics in terms of sensitivity towards sulfur-containing gases (LaFeO₃) and selectivity towards hydrogen (Sn₃La₃O₇). The decoration of noble metals on nanostructured metal oxides was performed in a second CVD step by using our developed heteroleptic janus-type precursors [M(COD)(L)] enhanced their (photo-)catalytic as well gas sensing performance.

11:15 AM FF05.01.08
Reactivity of Atomic Layer Deposition Precursors with OH/H₂O-Containing Metal Organic Framework Materials Kui Tan¹, Stephanie Jensen², Liang Feng³, Jing Li⁴, Hongcai J. Zhou⁴, Timo Thonhauser³ and Yves Chabal¹; ¹The University of Texas at Dallas, United States; ²Wake Forest University, United States; ³Texas A&M University, United States; ⁴Rutgers, The State University of New Jersey, United States

The ability to incorporate metal atoms into nanoporous materials such as metal organic frameworks (MOFs) in a well-controlled fashion provides new opportunities to prepare functionalized and modified materials for potential applications such as catalysis and gas separation. There are however new challenges that need to be overcome such as understanding the reaction mechanisms in order to develop structural and process optimization. MOFs possess three-dimensional structures, with complex pore architecture, leading to a number of possible processes (gas transport, adsorption and reaction) that are much more complex than on flat surfaces. To address these issues, we have combined in-situ infrared spectroscopy, X-ray-photoelectron spectroscopy and ab initio calculation to study the reaction of a number of common ALD precursors --trimethylaluminium (TMA), diethylzinc (DEZ), titanium tetrachloride (TiCl₄)-- with several Zr-MOFs containing hydroxyl (OH) and water (H₂O) groups. Differentiating reaction with OH and H₂O groups is particularly interesting since their reactivity highly depends on both the chemical and structural (i.e. steric) environments. We find that the OH groups in the Zr₆(μ₃-OH)₄(μ₃-O)(OH)₄(OH)₂, cluster node do not all react at similar rates (i.e., the reaction pathway and energetics are highly dependent on their location, accessibility and chemical environment). For different OH-containing MOFs without H₂O groups, the activation temperatures for the TMA reaction with bridge OH of Zr₆ clusters decrease with their node connectivity, and are 250 °C, 150 °C and 24 °C for UiO-66-NH₂, Zr-abc and MOF-808, respectively. Interestingly, the amine group in UiO-66-NH₂ is found to act as a catalytic active site by anchoring TMA molecules and facilitating their reaction with nearby hydroxyl groups, which is not observed in un-functionalized UiO-66. This synergistic effect between -NH₂ and -OH is fully elucidated by first-principles calculations. In addition, we find that TMA easily reacts with water adsorbed on the external surfaces of wet MOFs crystals at room temperature, forming a thick Al₂O₃ blocking layer on the periphery of MOFs crystals. These findings provide a basis for the design and synthesis of new MOFs structures requiring ALD for new applications.

11:30 AM FF05.01.09
Enumeration as a Computational Strategy for Automating the Design of CVD and ALD Precursors Simon D. Elliott, David J. Giesen, H. S. Kwak and Mathew D. Halls; Schrödinger Inc, United States

Chemical vapor deposition (CVD) and surface-limited variant atomic layer deposition (ALD) are strongly dependent on the chemistry of the precursors that are used, affecting yield/througput, stoichiometry, impurities and process temperature. In metalorganic precursors, the central question is therefore the choice of ligands that surround the metal center. Heteroleptic precursors (containing more than one type of ligand) are one way to compromise between conflicting chemical requirements, such as surface reactivity versus thermal stability in the gas-phase. A well-known
example is the Zr precursor that combines cyclopentadienyl and amido ligands (ZyALD(TM), Air Liquide), used commercially in fabrication of DRAM memory for electronics.

However to date we have barely 'scratched the surface' of the vast chemical space of possible heteroleptic precursors. As an example to illustrate the magnitude of the design problem, 715 chemically-distinct heteroleptic complexes can be formed by combining four of 10 ligands around a tetravalent metal center, and 8,855 complexes can be formed from a library of 20 ligands. Clearly, an exhaustive experimental analysis is not possible. Instead we look to computational screening to narrow down the search to the most promising options. Here we present a computational approach for screening metal precursors with respect to a property that is crucial for CVD and ALD: thermal stability. The computational strategy is illustrated on the example of Zr precursors for zirconium nitride, a material that is deposited as a hard coating to protect industrial parts in corrosive environments.

CVD precursors should decompose unimolecularly at elevated temperature in the reactor and we therefore seek complexes with moderately low energies for homolytic bond dissociation (i.e. into a pair of radical fragments). ALD on the other hand requires the gas-phase stability of precursors to be as high as possible, as this dictates the upper temperature limit for ALD. Such stability should be balanced against the requirement of high reactivity of ligands towards the growing surface in ALD.

We first enumerate over ligands. Even a small ligand library of just six O-free, N-bearing ligands (amines, amidinates, cyano and guanidinate, with various alkyl groups) gives $6^4=1296$ possible complexes. However, 94% of these can be neglected as symmetrically equivalent or over-coordinated, leaving 81 for optimization with density functional theory (DFT). To study thermal stability requires a second phase of enumeration, over the 1280 different bonds that can be broken in these complexes (612 C-C and C-N bonds, 446 C-H bonds and 222 metal-ligand connections), yielding a set of radical fragments that are also computed at the DFT level. It is clear that every step in this computational workflow requires robust and efficient automation.

DFT reveals that the lowest bond dissociation energies are obtained for cleaving intact ligands from the metal, ranging 133-471 kJ/mol (compared to higher energies for ligand decomposition by abstracting radicals: 198-371 kJ/mol for the ethyl radical, 233-401 kJ/mol for methyl and 310-463 kJ/mol for the hydrogen atom). The least thermally stable complexes are found to be zirconium amides with bidentate amidinates/guanidinates, and so we predict that these would be the best CVD precursors. We observe very little steric effect when replacing methyl groups with ethyl groups. By contrast, cyano groups have a stabilizing influence, suggesting that they would be useful as spectator ligands in heteroleptic precursors for ALD. On the basis of this sample system, we discuss the general requirements for chemical enumeration software and the limits faced by automation.

**SESSION FF05.02: Theoretical and Experimental Advances in ALD/CVD Chemistry II**

**Session Chairs:** Sean Barry and Ralf Tonner  
**Monday Afternoon, December 2, 2019**  
**Hynes, Level 3, Room 310**

1:30 PM FF05.02.01  
**Atomic Layer Deposition of Zinc-Doped Alumina at Room-Temperature for Organic Opto-Electronics**  
Sabrina M. Wack, Shiv Bhudia, Noureddine Adjeroud, Jérôme Guillot and Renaud Leturcq; Luxembourg Institute of Science and Technology, Luxembourg

We investigate a new process for the low-temperature atomic layer deposition (ALD) of high-quality insulating layers based on alumina. In organic opto-electronics, alumina thin films play a major role as insulating material (gate dielectric), passivation layer or encapsulation layer (gas permeation barrier). Atomic layer deposition (ALD) is known for growing amorphous alumina with high density and high electrical quality, but the deposition conditions usually require either a temperature above 100°C or highly oxidative condition (oxygen plasma or ozone) to obtain a reasonable deposition rate and high material quality. A method for producing high quality alumina below 60°C using low oxidative conditions would be highly welcome for the highly sensitive materials used in organic electronics.
By incorporating zinc as dopant during the deposition of alumina, we demonstrate the ALD of high-quality alumina films at room-temperature, while keeping a single ALD cycle below 1 minute. The resulting material shows physical properties very close to alumina grown above 80°C. The films with 5% Zn content are amorphous, with a density above 3 g/cm³, and a dielectric constant of 7.7 ± 0.4. The gas permeation rate though the zinc-doped alumina thin films has also been investigated, showing gas barrier performances comparable to alumina deposited above 80°C. In order to understand the role of zinc doping in the deposition mechanism, we have performed in-situ mass measurements using a quartz crystal microbalance, and have analysed high resolution X-ray photoemission spectra. They reveal that zinc might help the growth of alumina at low temperature by avoiding trapping of water molecules on the surface.

1:45 PM FF05.02.02
Hydrogen-Free CVD of WSe2 Monolayers from Inorganic-Se Precursors Mauro Och¹, Pawel Palczynski¹, Giulia Z. Zemignani¹,², Evgeny Alexeev³, Alexander Tartakovskii³ and Cecilia Mattevi¹; ¹Imperial College London, United Kingdom; ²Politecnico di Milano, Italy; ³The University of Sheffield, United Kingdom

Chemical Vapour Deposition (CVD) of Transition Metal Dichalcogenides (TMDs) is a promising fabrication technique that can enable both scalable synthesis and high crystal quality, both required for applications of TMDs in monolayer form. The state-of-the-art of CVD of WSe2 often relies on the use of large quantities of H2 gas as reducing agent for Se0, which represents a hazard in research laboratories and for the future industrial upscaling. Furthermore, metal-organic CVD (MOCVD) syntheses employ H2Se along with hydrogen gas, increasing the potential hazard of the process. Here, we present a H2-free low pressure CVD of WSe2 based on the chalcogen precursor chemistry. We discovered that ZnSe, containing already reduced Se (Se-2), allows the fabrication of large WSe2 monolayer flakes as well as thin films with grain size up to 100 µm. The uniqueness of this inorganic Se-precursor have been demonstrated by performing synthesis from Se powder and other inorganic Se compounds (Cu2Se, CdSe and Na2Se), which did not lead to evidence of WSe2. The chemical reaction steps have been identified and will be discussed. In addition, since our W- and Se-precursors possess similar volatilities we have simplified our CVD setup from a two-zone furnace, usually used for TMDs growth, to a single-zone furnace. The growth temperature has been selected according to vacuum TGA data, whereas the other growth parameters, i.e. pressure, growth time and quantities have been optimised to yield mono- and few-layered WSe2 crystals. The synthesized material possesses optical properties comparable to exfoliated crystals, assessed by room temperature (RT) and low temperature PL measurements on WSe2 deposited onto SiO2. The RT-PL peaks exhibit FWHM of ~50 meV, while low T PL shows a defect-bound exciton signal similar to mechanical exfoliated crystals. XPS analysis demonstrate high chemical purity of the synthesized material, and absence of Zn in the flakes.

2:00 PM *FF05.02.03
Engineering of Molecular Architectures of Metal Precursors for Vapor Phase Routes to Energy Harvesting and Energy Conversion Systems Nishant Peddagopu¹,², Anna Pellegrino¹,² and Graziella Malandrino¹,²; ¹Universita' degli Studi di Catania, Italy; ²INSTM, Italy

Nanostructured advanced materials require challenging synthetic methods ultimately suited for large scale fabrication of materials with specifically designed properties. Vapor phase routes are appealing synthetic approaches following a bottom-up building strategy, but for the synthesis of multicomponent nanostructures and films, the availability of suitable precursors is of crucial importance.

The various vapor routes require precursors with different properties, thus in conventional Metalorganic Chemical Vapor Deposition (MOCVD), the metal sources must be thermally stable and volatile, liquid assisted MOCVD processes require soluble complexes and atomic or molecular layer deposition (ALD, MLD) routes need volatile and reactive sources.

With this perspective, the presentation will focus on metal adducts bearing linked β-diketonate (β-dik) and ancillary Lewis ligands L of general formula “M(β-dik)nL”. The relationships involving the molecular architectures and mass transport properties of the adducts in function of the metal nature (M= alkaline, alkaline-earth and rare-earth metal) will be discussed. The effects due to the nature of the β-diketonate (1,1,1,5,5,5-hexafluoroacetylacetone or 2-thienoyl trifluoroacetonate) moiety as well as of the ancillary ligand L [L= monoglyme (dimethoxyethane), diglyme (bis(2-methoxyethyl)ether), triglyme (2,5,8,11-tetraoxadodecane), tetraglyme (2,5,8,11,14-pentaoxapentadecane), tmeda (N,N,N',N'-tetramethylethylenediamine], on mentioned properties will be addressed as well.

The perspectives of applications of these precursors to MOCVD and MLD of advanced materials for energy harvesting and energy conversion are presented.
In regard to energy harvesting applications, novel lithium precursors will be described for the MOCVD of LiNbO₃ thin films. As energy conversion systems, alkaline earth fluorides such as MF₂ (M: Ca, Sr) and the multicomponent MREF₄ (M: Na,K; RE: Y,Gd) are studied as materials for the production of new and more efficient photovoltaic (PV) devices due to their efficient hosts behavior for upconversion (UC) or downconversion (DC) processes. Finally, a case study of application of MLD to the fabrication of inorganic/metalorganic hybrid system will be commented.

Part of this work is supported by the European Community under the Horizon 2020 Programme in the form of the MSCA-ITN-2016 ENHANCE project, Grant Agreement N.722496.

2:30 PM FF05.02.04
Chemical Vapor Deposition of Cuprous Halide Thin Films Christina M. Chang¹, Luke M. Davis¹,² and Roy Gordon¹,¹; ¹Harvard University, United States; ²Tufts University, United States

Metal halide compounds tend to possess large bandgaps, optical transparency, ion conductivity, and semiconducting or dielectric properties. Thin films of metal halides are thus promising for use in a wide range of applications, from optical coatings and imaging devices to optoelectronic devices like photovoltaics. To be useful in many of these applications, the metal halide thin films must meet several requirements, including continuity, purity, and smoothness. Chemical vapor deposition (CVD) is one of the main techniques used in industry to fabricate device-quality films of other materials, because of its molecular-level control of the fabrication process. However, research efforts in the development of a CVD process to deposit continuous metal halide thin films have met several reactivity challenges. The few known metal halide CVD and ALD processes have been confined almost entirely to metal fluorides, and have typically required ancillary metal halides as the halide source. A more general route to metal halide vapor deposition, such as one using the hydrogen halides (HX) as the halide source, would be of considerable interest. Some researchers have succeeded in producing discontinuous “islands” of metal halides (e.g., CuCl, CuI) using HX as a precursor, but continuous thin films of metal chlorides, bromides, and iodides have remained elusive.

In response to this challenge, we have developed a pulsed chemical vapor deposition method that produces continuous CuBr thin films by reaction between HBr gas and vinyltrimethylsilane(hexafluoroacetylacetonato)copper(I). CuBr films were grown in a custom-built, hot-walled ALD reactor, at a range of substrate temperatures, between 65 and 135 °C. Rutherford backscattering (RBS) was used to quantify and confirm the 1:1 Cu:Br stoichiometry, and the RBS peak shapes indicate compositional uniformity throughout the film. γ-phase CuBr was confirmed by X-ray diffraction. Scanning electron microscopy was used to characterize the morphology of the films resulting from a variety of temperature and substrate conditions. We have found that the substrate surface can strongly influence film morphology, and that appropriate substrate choice can enable device-quality film continuity. Whereas CuBr islands were produced when grown on oxide surfaces such as SiO₂, we found that continuous CuBr films could be produced on other surfaces, such as glassy carbon, silicon nitride, or platinum.

To the best of our knowledge, these results constitute the first continuous, non-fluoride metal halide thin films deposited by CVD using the hydrogen halide as the vapor source. Our method provides a reaction pathway that may offer a more general route to CVD of metal halide thin films.

2:45 PM FF05.02.05
Facile Synthesis of Nickel Sulfide Millimeter Long Nano-Arrows (NiS₂) Using Chemical Vapor Deposition Pola Shriber¹, Rimon Tamari², Maria Tkachev¹, Sharon Bretler², Louisa Meshi² and Gilbert D. Nessim¹; ¹Bar Ilan University, Israel; ²Ben-Gurion University of the Negev, Israel

Transition metal sulfides, and in particular nickel sulfides with various compositions and phases, are gaining attention due to their potential application in practical devices.¹⁻³ We have previously demonstrated the bottom-up synthesis of bulk metal sulfides using atmospheric pressure chemical vapor deposition (AP-CVD), with elemental sulfur as a precursor.⁴ The method we developed allows us to synthesize a wide range of materials; by tuning precursors and process parameters, we can somehow control the morphology, stoichiometry, and structure of the synthesized materials. Here, we present the synthesis of arrow-like structures of nickel sulfide using chemical vapor deposition. To the best of our knowledge, these arrow-like morphologies (with pyramidal termination) were not reported before. A carpet of
long nickel sulfide arrows grew on a nickel foil. The arrows are up to 2 mm long with a high aspect ratio and a diameter of a few microns. XRD examination of the samples indicates Ni$_3$S$_2$ stoichiometry although detailed EDAX along the arrow indicates slight changes in stoichiometry as a function of the position in the arrow (closer or farther from the tip).

We will discuss the synthesis and the growth mechanism of these original structures based on extensive characterizations such as HRSEM, EDS, FIB, and HRTEM.

References:

3:00 PM BREAK

3:30 PM *FF05.02.06
Prospects for Nanostructuring Ultrathin Organic and Hybrid Films via Molecular Layer Deposition
David S. Bergsman$^{1,2}$, Richard G. Closser$^3$, Christopher J. Tassone$^1$, Bruce M. Clemens$^2$, Dennis Nordlund$^3$ and Stacey F. Bent$^2$; $^1$Massachusetts Institute of Technology, United States; $^2$Stanford University, United States; $^3$SLAC National Accelerator Laboratory, United States

Molecular layer deposition (MLD) is an increasingly popular process for the growth of organic and coordination polymer ultrathin films. This vapor-phase, layer-by-layer technique, which relies on the same principle of self-limiting surface reactions as atomic layer deposition, has shown promise for the development of many applications that require conformal organic-containing coatings. However, in many technologies, such as membranes, catalysts, and semiconductor devices, there is a growing need for ultrathin films with precisely controlled pore structure and crystallinity. Despite recent developments in MLD, there is still a significant gap in our understanding of the fundamental mechanisms that affect film structure, such as the origin of the film growth rate or their molecular-level properties. In this presentation, we present results of our recent studies to understand such mechanisms and discuss prospects for better controlling film structure moving forward.

First, we discuss our exploration of the growth behavior of MLD films by examining trends in film properties as a function of backbone flexibility [1]. Our results suggest that changes in growth rate between the most rigid and most flexible backbones (4 Å/cycle vs 1 Å/cycle) are not caused by differences in length of molecular precursors, chain orientation, or film density, but are instead caused by an increased frequency of terminations in the more flexible chemistries. These terminations likely result from monomers reacting with more than one functional group on the underlying surface, which reduces the total number of available reactive sites. We further elaborate on the relationship between the number of reactive sites and the film growth rate by modeling growth behavior after an intentional reduction in the number of reactive sites [2]. We show that terminations caused by dual-reacting monomers reduce the film growth rate; however, the adsorption of monomers likely reintroduces reactive sites, preventing the complete cessation of film growth. We also present diffraction and infrared absorption data, which suggest that films consist of a mixture of upward growing chains and horizontally aligned layers of paracrystalline polymer segments [1]. Combined, these results provide a clearer picture of the disordered nature of MLD and provide insight for the design of future ultrathin film synthesis chemistries. We conclude by highlighting recent work to create structured ultrathin films and propose several avenues of research to create films with precise morphological control.

Gallium oxide (Ga$_2$O$_3$) possesses an extremely wide bandgap around 5 eV and has attracted more attention for applications to power devices and optoelectronic devices. Ga$_2$O$_3$ exhibits five polymorphs of α, β, γ, δ, and ε phases. Among these polymorphs, only metastable-phase orthorhombic ε-Ga$_2$O$_3$ exhibits large spontaneous polarization and ferroelectricity. [2, 3]

The polarization of ε-Ga$_2$O$_3$ is expected to lead to two-dimensional electron gas (2DEG) induced at ε-(Al$_x$Ga$_{1-x}$)$_2$O$_3$/ε-Ga$_2$O$_3$ hetero-structure interface, like conventional AlGaN/GaN-type high electric mobility transistor (HEMT). Furthermore, the ferroelectricity of ε-Ga$_2$O$_3$ expected to be ferroelectric devices, such as ferroelectric field effect transistor (FeFET). It has been reported an epitaxial growth of ε-Ga$_2$O$_3$ thin films by physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques. Among various growth techniques, we have focused on mist CVD for the epitaxial growth of ε-Ga$_2$O$_3$ thin films. Also, we previously reported that orthorhombic ε-(Al$_x$Ga$_{1-x}$)$_2$O$_3$ and ε-(In$_x$Ga$_{1-x}$)$_2$O$_3$ alloy films were epitaxially grown via mist CVD. [4, 5]

To achieve ε-Ga$_2$O$_3$ based device applications, such as HEMT and FeFET, high crystal quality ε-Ga$_2$O$_3$ thin films with smooth film surface are essential issues of the crystal growth. In this study, we report on investigations to improve crystal quality and to obtain a smooth surface using mist CVD. In the mist CVD, gallium (III) acetylacetonate is generally utilized as Ga precursor dissolved in a water solution. We have previously demonstrated that controlling the Ga/O ratio by varying the Ga precursor concentration in the solution enables smooth film surface under stoichiometric conditions [6], indicating that chemical reactions under the growth of ε-Ga$_2$O$_3$ film can be controlled in the mist CVD process like other CVD techniques.

Besides, we performed two approaches to improve the crystal quality of ε-Ga$_2$O$_3$ thin films using mist CVD; use of carbon-free gallium (III) chloride as CVD precursors and a surfactant effect of heavy atom addition in a precursor solution.

We obtained ε-Ga$_2$O$_3$ thin films grown on epitaxial substrates using gallium (III) chloride with higher crystal quality than that using gallium (III) acetylacetonate, considering incorporation of impurities, such as carbon was reduced.

The surfactant effect can be expected to enhance the migration of atoms on the film surface in the growth process. We utilized bismuth atom as a surfactant and the precursor was bismuth basic nitrate dissolved in the starting solution with gallium precursors. FWHMs of XRC for (004) ε-Ga$_2$O$_3$ with and without Bi precursors were estimated as 0.13 and 0.43, respectively, indicating that the crystal quality was drastically improved by only containing Bi precursors in the starting solution. Furthermore, the RMS roughness calculated from AFM was also improved 1.0 nm to 0.4 nm by using Bi precursors. Thus, we assumed that the Bi-assisted growth of ε-Ga$_2$O$_3$ thin films in the mist CVD method to improve the crystal quality and the surface morphology. We believe that our results in the mist CVD will be useful in the development of device applications.

Atomic layer deposition (ALD), self-limiting version of CVD, is a very attractive method due to superior characteristics of conformal deposition, precise thickness and composition control, and pinhole-free thin films. The advantages make ALD used widely in various applications such as microelectronics, photovoltaics, and energy storage systems. One of the most widely used and studied ALD materials is alumina which has great mechanical, optical, and electrical properties and functions as high-k dielectrics, chemical protection layers, and encapsulation layers for flexible devices. However, because of the brittle nature of the ALD alumina, cracks in the ALD alumina layer in flexible devices occur commonly by bending. Considering the mechanical problem, it is most important to measure precisely mechanical properties of the ALD alumina. Despite the importance, studies on intrinsic mechanical properties of the ALD alumina have been very insufficient. Previous works measured mechanical properties of the ALD alumina by using indirect methods such as nanoindentation, nanobeam bending, and bulge test, which are difficult to obtain accurate mechanical properties due to substrate effect or complicated calculation. In this study, we conducted tensile tests on ALD alumina thin films on the water surface without substrate and obtained stress-strain curves and intrinsic tensile properties of the ALD alumina itself directly and easily. Deposition temperatures of the ALD alumina for tensile tests were 80, 100, 150, 200, and 250 °C, and deposition temperature effect on the tensile properties were investigated. The tensile properties such as Young’s modulus and strength were increased with the increase of deposition temperature up to 200 °C, and then the tensile properties were reduced again. We proposed the defect generation mechanism related to impurities and hydroxyl groups, where the major defects in the ALD alumina thin film are changed, depending on deposition temperature. The defect generation mechanism was verified by the composition, roughness, and density of the ALD alumina measured by XPS, AFM, and XRR, respectively. The deposition temperature effect on tensile properties of ALD alumina was explained successfully by using the mechanism.

4:30 PM FF05.02.09
Characterizing Ultra-Thin Layers Using High Resolution Low Energy Ion Scattering (LEIS) Thomas Grehl1, Philipp Brüner1 and Nathan Havercroft2; 1IONTOF GmbH, Germany; 2ION-TOF USA, Inc., United States

Layers of only a few atomic layers are often deposited by ALD, intending high control over the properties of the film. In these cases, the characterization of the early stages of film growth is crucial to optimize the process and quality of the film. For example, the initial thickness distribution before layer closure, created by the nucleation process, will often remain after the film is complete. To analyze these early stages of growth requires very surface sensitive analytical techniques with excellent detection limits. Specifically for area selective deposition, the demand for characterization increases even further. The deposition process becomes more complex, involving etching steps to remove nucleation on blocked areas. In this case, means of characterization are required which determine the effects of etching steps on the growing film, possible contamination and the level of success of the blocking.

A technique specifically suited for these application is Low Energy Ion Scattering (LEIS). By scattering noble gas ions from the surface of the sample, the mass of the atoms in the outer atomic layer is determined non-destructively. Due to specific charge exchange processes, the peaks in the scattering spectrum correspond only to the outer atomic layer, making LEIS the most surface sensitive technique to determine the elemental composition of a surface. In addition, information from deeper layers is available in two ways: First of all, features in the spectrum contain information about the first few nm of the sample – especially for heavier elements, the in-depth distribution can be determined non-destructively. For more complex systems or light elements, sputter depth profiling can be applied as well.

We will highlight the very special analytical possibilities of LEIS in the context of thin film analysis. Examples from industrial as well as academic collaborations will demonstrate typical analytical tasks. These include compositional analysis of the outer layer to determine residues of the precursor (e.g. fluorine), layer thickness evolution with varying process parameters, and core-shell nanoparticle analysis with respect to shell closure.

SESSION FF05.03: Theoretical and Experimental Advances in ALD/CVD Chemistry III
Session Chairs: Kevin Musselman and Greg Randall
Tuesday Morning, December 3, 2019
Hynes, Level 3, Room 310
Off-stoichiometric copper chromium delafossites demonstrate the highest values of electric conductivity among the non-doped p-type transparent conducting oxides. Values of electrical conductivity beyond $100 \text{ S/cm}$ are measured, this is only one order of magnitude lower than the actual n-type standard semiconductors. Values for carrier concentration beyond $10^{21}/\text{cm}^3$ are determined for the as deposited films. However, a good understanding of the doping source and conduction mechanism is required in order to tailor the optoelectronic properties towards values required in industrial applications. Controlled annealing was performed on the as deposited samples. A dramatic five order of magnitude decrease for the conductivity was measured, without observing any significant phase changes or alteration of average chemical environment. The thermal treatment proves itself as a useful tool for: first, tailoring the electric properties (such as electrical conductivity or Fermi level) ; second, investigating the source of the high level of doping on this material. High resolution Helium Ion Microscopy, Secondary Ion Mass Spectroscopy and Transmission Electron Microscopy and Positron Annihilation Spectroscopy were used to investigate the fine morphological and structural changes in $\text{Cu}_{0.66}\text{Cr}_{1.33}\text{O}_2$ upon annealing processes. The results indicate the chained copper vacancies as source of p-type doping and suggest furthermore that the changes in electrical conductivities within the off-stoichiometric copper-based delafossites are triggered by atomic rearrangements. This process, similar with an Oswald ripening mechanism, is based on the dissolution of the chains of vacancies into single Copper vacancies migrating to grain boundaries. A significant rearrangement of copper and chromium atoms after thermal treatments is revealed. The inhomogeneous distribution observed in the as-deposited high conductive thin films evolves to a uniform atomic dispersion within the annealed low conductive samples.

Acknowledgements:
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Vapor deposition (VD) techniques have been highly successful in a wide variety of nanotechnological applications. However, films prepared by current VD methods are easily either highly continuous or have difficulties in functionalizing surfaces far out-of-sight, and therefore scaling them down to complex nanostructures can be challenging. It has been shown that with capillary condensation (CC) it is possible to coat and fill nanostructures selectively and controllably from the vapor phase.[1]

CC is a phenomenon of gas-to-liquid condensation inside nanocavities below the saturation point of the condensate. Because CC scales negatively with the surface feature size, it is possible to coat or fill selectively those surfaces and spaces which have been considered to be the hardest to reach, for example complex nanopores, ledges, and particle interstices.[1] First a reagent is allowed to reach a gas-liquid equilibrium at a predefined partial pressure. Then it is fixed into solid phase by a chemical reaction.

CC based methods are capable of bypassing and reversing many traditional problems related to VD, such as limited scalability in nanostructures, low control over spatial selectivity, sensitivity to gaseous inhibitors, and sometimes high process complexity and harsh conditions.[1] Due to the simplicity of CC, the process is easy to apply with no prior expertise in simple reactors which vary from a closed container with overpressure venting[2], to self-built reactor line for high process control with manual[1] or computer-assisted controls[3], or likely even established iCVD reactors[4] if the parameters were optimized below supersaturation. CC has been utilized for processes with polyacrylates and polystyrene on various substrates with UV initiation[1], silicon on carbon with thermal initiation[2] and silica on titania with chemical initiation[3].

In the presentation we explore principles and applications for CC based coating methods. We also show early results on how the fillings could be used as nanotemplates for inorganic material deposition during Vapor Phase Infiltration.[5] Studying the fundamentals of CC based methods could create a foundation for a novel VD paradigm for toposelective vapor deposition in nano- and micron-scaled structures. Additionally, CC based processes could be attractive also for industry due to their simplicity.


Advanced technologies in electronics, energy production, and energy storage require increasingly robust protection against destructive environmental conditions, such as high humidity, condensation, reactive gases and organic contaminants. At the same time, conventional encapsulants can interfere with performance, due to modified surface roughness or changes in optical, mechanical or thermal properties of the substrate.

Chemical vapor deposition of conformal films addresses many of the challenges with changes in substrate properties. The relatively low thickness and high conformality of vapor-deposited coatings allows for minimal alteration in substrate properties while ensuring a high level of protection.

GVD Corporation is developing a vapor-deposited, multilayer gas barrier coating for environmental protection specifically for flexible substrates. GVD’s approach combines its proprietary method for vapor deposition of polymers, called iCVD, and plasma enhanced chemical vapor deposition into a single, streamlined process. The coating takes advantage of fine thickness control to achieve the barrier properties of brittle materials in flexible films. To maximize the commercial potential of this technology in advanced applications, like elastomeric seal protection and solar cell encapsulation, GVD has optimized the process for barrier performance and film deposition rate. The impact of coating uniformity, chemical structure and multilayer stack design will be discussed.
**9:30 AM FF05.03.05**

*In Situ Characterization of Metal Oxide Films Produced Using Atmospheric Pressure Spatial ALD*  
Alexander Jones, Kissan Mistry, Manfred Kao, Mustafa Yavuz and Kevin Musselman; University of Waterloo, Canada

Metal oxide films are a common component in modern electronic devices, from cell phones to photovoltaics. Atmospheric Pressure Spatial Atomic Layer Deposition (AP-SALD) is a novel technique for producing these films, retaining the high conformity and precise thickness control of conventional ALD, but without expensive vacuum chambers or time-consuming purge cycles. Where conventional ALD may take hours to produce a 100 nm Al2O3 film, our AP-SALD system can produce the same film in under twenty minutes. It is beneficial to couple AP-SALD with characterization tools that can quantitatively determine the properties of a film as it is being deposited in real time. Thus, the properties of the film can be optimized immediately via the deposition parameters such as precursor concentrations, deposition speed, reactor head height, or temperature. Using a combination of reflectance spectrometry and a novel flexible printed circuit board (PCB) our group was able to characterize how doped and undoped ZnO films change during depositions under various conditions. This allows for observation of film nucleation mechanisms, and determining the thickness, optical band gap, resistivity, refractive index, and uniformity of the films while they are forming. Notably, analytical models (Cauchy, Tauc-Lorentz, Drude-Lorentz) are used to determine the optical properties, with a feed-forward neural network providing initial guesses for those models.

**9:45 AM FF05.03.06**

*Nanometal Interconnection Layers Deposited via Site-Specific Chemical Vapor Deposition for High Conductivity Copper-Carbon Nanotube Hybrids*  
Anthony P. Leggiero1, Dylan J. McIntyre1, Erin D. Loughran1, Shannon Driess1, Cory D. Cress2, Ivan Puchades1 and Brian Landi1; 1Rochester Institute of Technology, United States; 2U.S. Naval Research Laboratory, United States

Carbon nanotubes (CNTs) hold great theoretical promise as electrical conductors due to a combination of high conductivity, flexure tolerance, tensile strength, and a low thermal coefficient of resistivity (TCR). However, the resistive junctions between individual carbon nanotubes and bundles of CNTs, along with misalignment within bulk structures presents a unique challenge in the translation of the individual electrical conductivity to bulk applications. One strategy currently under investigation to alleviate these issues is to integrate CNTs with traditional metallic conductors yielding a hybrid material which combines the metal’s high conductivity with the low density and TCR of CNTs. Copper has traditionally been chosen to produce such composites, although the metal has limited interaction with the underlying carbon nanotubes.

In this study, site-selective chemical vapor deposition (CVD) is used to deposit nanometal interconnection seeds onto a porous, low-density (0.12 g/cm3, ~9 mg/m) CNT template. This site-specific method utilizes localized changes in the resistance within the bulk CNT template to preferentially deposit an organometallic precursor at thermally active sites. The deposited seeds act as interconnections sites with an electrodeposited copper metal overcoating. Group 10 elements like nickel, palladium and platinum exhibit more favorable wetting characteristics with the CNTs, allowing for more efficient interaction between the copper overcoat and the underlying CNTs. The deposited mass and distribution of seeds may be tuned through process parameters including precursor temperature, current density, time, etc., allowing for sparse depositions of seeds localized to hot spots (<20% w/w metal) as well as high densities of seeds leading to interconnection of the deposited nanometal network (>80% w/w metal). These nanometal seeds can be deposited throughout the carbon template in relatively short periods of time (~1 hour) compared to previous techniques such as electroplating (>10 hours). The morphology of depositions from various seeding metals have been investigated using scanning electron microscopy. In an example study with a low mass (~20% w/w) of deposited platinum seeds, alteration of electroplating rate allowed for the tuning of properties such as electrical conductivity, specific conductivity, density and TCR. Conductivity as high as 31.3 MS/m and TCR as low as 0.97 x 10^-3 K^-1 were achieved at 94.4% w/w total metal mass through modification of deposition and plating parameters. These values are increasingly competitive with traditional copper, which has an electrical conductivity of 58 MS/m and TCR of 3.83 x 10^-3 K^-1 at room temperature. Overall, the present results demonstrate the potential of site-specific CVD towards the enhanced nanometal interconnection of carbon conductors (NICCs).

**10:00 AM BREAK**
10:30 AM FF05.04.01
Atomic Level Selective Surface Treatment by Down-Stream Plasma Generated Organic Radicals in Semiconductor Device Fabrication Xinliang Lu1, Haochen Li1, Hua Chung1, Michael Yang1, Ting Xie1, Qi Zhang1, Shawming Ma1, Il-Kwon Oh2 and Stacey F. Bent2; 1Mattson Technology Inc, United States; 2Stanford University, United States

With continuous CD scaling of semiconductor devices, surface and interface engineering plays an increasingly important role in semiconductor device fabrication, and atomic level surface treatment has been incorporated in thin film deposition, lithography and etch processes. Radicals are highly reactive yet do not damage materials surfaces, thus have become popular precursors in emerging atomic surface engineering applications.

In the present study, a high flux of methyl radicals is generated in a down-stream plasma setup in combination with optimized gas flow, pressure and plasma source power. Methyl radicals from the down-stream plasma source can be applied for treatment of semiconductor, dielectric and various metal surfaces. Surface methyl group coverage can be controlled by methyl radical exposure time and substrate temperature, as evident in surface infrared (IR) characterization and surface contact angle measurement.

Methyl groups on semiconductor and dielectric materials surfaces are stable upon air exposure. Sub-monolayer methyl group coverage can passivate silicon and silicon germanium surfaces, effectively eliminate native oxide growth, and thus alleviate issues with tedious queue-time control in semiconductor fabrication flows. In addition, surface methylation offers unique materials protection against chemical corrosion, including a complete stop of silicon loss in aqueous tetramethylammonium hydroxide (TMAH), a significant reduction of silicon oxide loss in aqueous HF and KOH, and a significant reduction of silicon nitride loss in aqueous H3PO4 solutions.

Low-k, silicon oxide and silicon nitride films are subject to carbon loss upon exposure to oxygen-based dry etch chemicals, etc. The surface methylation process can be adopted to restore carbon content in the surface region of low-k materials, as indicated by a recovery in X-ray photoelectron spectroscopy (XPS) carbon intensity and surface wetting angle.

Various metal materials are incorporated in semiconductor devices as work function, interconnect liner and conductor materials, respectively. Surface chemistry of hydrocarbons on different metal surfaces has been well studied [1]. Methyl radicals break down to carbon residues on reactive metal surfaces (e.g. Co). In comparison, surface methyl groups can be converted to volatile hydrocarbon products on clean metal surfaces with moderate reactivity (e.g. Cu), and thus contamination of the metal surfaces can be negligible in this methyl radical process. Overall, a selective surface methylation process is feasible on patterned wafers with exposed dielectric and copper surfaces. The selective surface methylation process can be inserted into standard back-end-of-line (BEOI) dual damascene interconnect fabrication process flow, leading to a reduction in effective capacitance with no increase of Cu line and via resistance.

The selective surface methylation pretreatment process can be further extended to area-selective chemical vapor deposition (CVD) and ALD, particularly for selective dielectric materials deposition on metallic surfaces. In our exploratory studies, ZnO ALD is carried out on silicon oxide surfaces with and without surface methylation pretreatment, and film growth is characterized by surface IR, transmission electron microscopy (TEM), XPS, X-ray fluorescence (XRF) and atomic force microscopy (AFM). In absence of surface methylation treatment, dielectric films can be deposited readily on silicon oxide surfaces. After a methylation pretreatment, however, silicon oxide surface exhibits an incubation period in ZnO ALD cycles. We propose that the dielectric film deposition on silicon oxide surface can be further suppressed with a periodic surface methylation treatment. Subsequently, a novel selective ALD process can be developed to deposit dielectric thin film on top of Cu interconnect structures vs dielectric materials in BEOI integration scheme.


10:45 AM OPEN DISCUSSION

11:00 AM FF05.04.03
Area-Selective Atomic Layer Deposition of 2D WS₂ Nanolayers
Shashank Balasubramanyam, Mark Merkx, Erwin Kessels, Adrie Mackus and Ageeth A. Bol; Eindhoven University of Technology, Netherlands

With continued downscaling of device dimensions, ultra-thin two dimensional (2D) semiconductors like WS₂ are considered as promising materials for future applications in nanoelectronics. At these nanoscale regimes, device fabrication with precise patterning of critical features is challenging using current top-down processing techniques. In this regard, area-selective atomic layer deposition (AS-ALD) has emerged as a promising candidate for bottom-up processing to address the complexities of nanopatterning. Till date, AS-ALD of metals¹ and dielectrics² have been successfully demonstrated. However, AS-ALD of 2D materials has remained elusive. In this contribution, we demonstrate area-selective deposition of 2D WS₂ nanolayers by using a three-step (ABC-type) plasma-enhanced ALD process.

AS-ALD of WS₂ was achieved by using acetylacetone (Hacac) inhibitor (A), bis(tertbutyllimido)-bis(dimethylamido)-tungsten precursor (B), and H₂S plasma (C) pulses. This process resulted in immediate growth on SiO₂ while a significant nucleation delay was observed on Al₂O₃, as determined from in-situ spectroscopic ellipsometry and ex-situ X-ray photoelectron spectroscopy measurements. The surface chemistry of this selective process was analysed by in-situ Fourier transform infrared spectroscopy. The analyses revealed that the inhibitor adsorbed on the Al₂O₃ surface, blocking precursor adsorption, while little or no inhibitor adsorption was detected on the SiO₂ surface where WS₂ was readily deposited. Furthermore, the area-selective growth was demonstrated on SiO₂ samples with patterned Al₂O₃ on top.

To improve the crystallinity, the AS-ALD WS₂ films were annealed at temperatures within the thermal budget of industrial semiconductor processing (≤ 450°C). The annealed films exhibited sharp Raman peaks, which is a fingerprint of highly crystalline WS₂. Furthermore, Raman line scans over the patterns showed very sharp peak intensity transitions at the SiO₂-Al₂O₃ interface which confirmed that annealing had no impact on selectivity. To summarize, this work pioneered the combination of two key avenues in atomic-scale processing: area-selective growth and ALD of 2D materials. It is expected that the results of this work will lay the foundation for area-selective ALD of other 2D materials.

Area-Selective Deposition Using Atomic-Layer-Deposited Carbon, Fluorine-Free SiOₓ as an Inhibitor
Taewook Nam, Inkyu Sohn, Seunggi Seo, Tatsuya Nakazawa and Hyungjun Kim; Yonsei University, Korea (the Republic of)

In area-selective atomic layer deposition (AS-ALD), the chemisorption of a precursor and reactant can be promoted or suppressed depending on the terminal groups of the substrate. For instance, nucleation and growth of an ALD film will be suppressed when the surface reaction sites are fully terminated with -CH₃ or -CF₃ groups, which have low reactivity with precursors or reactants. These chemical species that hinder the reaction on the substrate surface are called inhibitors, among which self-assembled monolayers (SAMs) have been widely studied because of their excellent inhibitor characteristics. However, the formation of a SAM on the surface of a substrate with excellent packing density requires extremely long times, which renders it not applicable to large-scale fabrication processes. Furthermore, chemisorption of a SAM requires the use of a specific substrate depending on the SAM head group, and carbon- or fluorine-containing byproducts with deleterious effects on devices can be produced during post-processing. Thus, the development of a simple approach for the fabrication of inhibitors without carbon and fluorine is required.

Hydrogen-terminated species are alternative candidates as inhibitors. The adsorption of a precursor or reactant can be inhibited when the substrate surface contains H-terminated reaction sites, which are formed by H₂ plasma treatment or hydrofluoric acid dipping. However, these processes may induce damage on the substrate or device, and complete passivation of the surface reaction sites is not ensured. Moreover, H-terminated species has poor stability and can be easily oxidized in ambient condition after only a few hours of exposure, loosing its inhibitor characteristic.

In this study, we firstly report the use of atomic layer-deposited SiOₓ as an inhibitor for AS-ALD. Unlike the traditional hydrophilic SiO₂, the SiOₓ formed by ALD using an aminodisilane precursor i.e., 1,2-bis(diisopropylamino)disilane, showed excellent hydrophobicity, even though the film was only one nanometer thick. From a thorough analysis of the film, including X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FT-IR), we confirmed that this peculiar hydrophobicity is caused by the presence of SiH₃ species, not by surface carbon from incomplete ALD reaction or by hydrocarbon from the air. The excellent stability of the SiOₓ film was also demonstrated. Thus, it retained its hydrophobicity over a month and after
exposure up to 350 °C in dry gas or at 250 °C in the ambient atmosphere. The ALD growth inhibition was confirmed by comparing the deposition of ALD Pt on the bare substrate and on the SiO$_x$-deposited substrate; the nucleation of Pt starts on the bare Si substrate after the 100th cycle of ALD, whereas no Pt growth was observed on the SiO$_x$-deposited substrate. On the SiH$_x$-terminated surface, the suppression of chemisorption was confirmed by using first-principle calculation. Although the ALD-based inhibitor covers all the substrate regardless of the material present on its surface, the reaction sites can be generated by the combination with a functional metal oxide, TiO$_2$. Using the photocatalytic effect of TiO$_2$, the inhibited sites can be easily changed to reactive sites, enabling the subsequent chemisorption of a precursor/reactant. From these results, we are certain that an ALD-based inhibitor deposition technique can be a promising method for the next generation of AS-ALD.

11:30 AM *FF05.04.05
CVD Polymers on Heterogeneous Substrates for Energy Storage and Area-Selective Applications Kenneth K. Lau; Drexel University, United States

To form uniform and conformal polymer thin films, particularly with nanometer resolution, chemical vapor deposition (CVD) is an attractive approach. Specifically, initiated and oxidative chemical vapor deposition (iCVD, oCVD) are widely used to cleanly deposit a variety of polymers. Polymers – such as acrylates, methacrylates, vinyls, ethers, silicones, and fluorocarbons – are cleanly deposited by iCVD through an array of heated filaments that thermally activates an initiator for polymerization. Conjugated (conducting) polymers – like thiophenes, pyrroles, and anilines – are easily deposited by oCVD using an oxidizing agent that oxidizes the monomer to create polymerizable species.

This talk will focus on our recent efforts in using iCVD and oCVD to apply thin polymer films on heterogeneous/textured (physical or chemical) substrates. Physically heterogeneous substrates, e.g. nanoporous particles, networks and membranes, are commonly found in gas separation, biomolecular sieving, sensors, water/oil repellency, catalysis, energy capture, and energy storage. Likewise, chemically heterogeneous substrates, i.e. surface chemical patterns or chemically disparate surfaces, are common in many areas, including integrated circuits, sensors, biology, and 3D batteries. Our work aims to fundamentally understand the chemistry and physics of iCVD and oCVD that would allow us to precisely control polymer growth on physically and chemically heterogeneous substrates. Such working knowledge enables us to apply these CVD techniques in energy storage and area-selective applications, which will be highlighted.

SESSION FF05.05: Deposition of Organic and Hybrid Materials I
Session Chairs: Anna Maria Coclite and David Munoz-Rojas
Tuesday Afternoon, December 3, 2019
Hynes, Level 3, Room 310

1:30 PM FF05.05.01
iCVD and oCVD Thin-Film Multilayer Coatings for Board-Level and Wafer-Level Protection Scott Morrison and William S. O'Shaughnessy; GVD Corporation, United States

Circuit boards and integrated circuits require protection from both RF interference as well as against the physical probing used in reverse engineering. Typical conformal coatings such as urethane or parylene have been used for environmental protection of circuit boards, but are too thick to be applied at the wafer level. In addition, the standard coatings are purely dielectric in nature and do not have any conductive aspect which could be used for either anti-tamper or RF shielding applications.

This paper describes a multi-layer coating which combines both dielectric and conductive characteristics. The dielectric material is a highly cross-linked polysiloxane polymer fabricated using a hot-filament CVD process referred to as iCVD, or “initiated chemical vapor deposition”. The iCVD process was invented at MIT by Prof. Karen Gleason and accommodates a wide range of off-the-shelf monomers and precursors. In iCVD, a gas or mixture of gases is introduced into a reactor under mild vacuum in the vicinity of an array of heated filament wires. The gas decomposes into reactive species – radicals – that serve as monomer units. These units then migrate to a cold surface (e.g., the surface of an electronic device) on which they combine and grow into a conformal polymer
thin film. That is, the monomer units successively add to one another, forming the dielectric polymer. The conductive film within the multilayer coating is pure poly(ethylene-3,4-dioxythiophene) polymer [PEDOT] deposited using a coating process referred to as oxidative chemical vapor deposition (oCVD). The oCVD method combines the clean, solventless character of chemical vapor deposition (CVD) with the versatility of radical-based chemistry techniques used in bulk polymer processing. This deposition process produces pure, mechanically-flexible coatings of intrinsically-conductive PEDOT; these PEDOT coatings are conformal to the topology of the substrate and renders surfaces electrically conductive. The novelty of the oCVD process is in the highly-conformal deposition of the polymers, which show conductivities up to $10^3$ S/cm. oCVD coatings are suitable for conformal coverage of even the most complicated surface topologies, including foams, fibers, and fabrics.

The ‘as-deposited’ multilayer coating can provide protection against RF interference. However, if the dielectric and PEDOT layers are selectively patterned then the coating can be used as an active anti-tamper coating. In this paper, the deposition processes are described in detail. The properties of the individual films are presented, along with the results of multilayer and patterning tests.

1:45 PM FF05.05.02
Direct Transfer of Graphene on Paper Surface Using Hydrophobic Primer Layer Deposited by iCVD
Emre Citak1, Mehmet Gursoy1, Huseyin Sakalak2, Bilal Istanbullu2 and Mustafa Karaman1; 1Konya Technical University, Turkey; 2Selcuk University, Turkey

With its superior physical properties and band structure, the graphene has become one of the most attractive materials of recent years. Among many graphene synthesis techniques, CVD is considered as the most important and efficient method to synthesis high quality and large area graphene for high-tech applications. In CVD-grown graphene is typically produced by decomposing a hydrocarbon gas on the surface of a transition metal catalyst. However, synthesized graphene must be transferred from the catalyst surface to desired surfaces for final product application. In the typical CVD-grown graphene transfer process, firstly, graphene on the catalyst surface is coated with a support layer to prevent disintegration of as-deposited graphene layers. After that, graphene is separated by selective etching of the catalyst using solvents. Usually, rigid materials such as silicon and glass are used as substrate. Recently, paper has an important place as a substrate in high-tech applications as compared with rigid substrates due to its lightweight, flexible, biocompatible and foldable structure. However, in the transfer of graphene on the paper, the presence of solvents can lead to damages on paper surface. In this study, paper surface was functionalized with hydrophobic thin films using initiated chemical vapor deposition (iCVD) to make an graphene transfer feasible. For this purpose, two different fluoropolymers, namely poly(hexafluorobutyl acrylate) (PHFBA) and poly(perfluorodecyl acrylate) (PFDA) were deposited on the paper surface by iCVD. Graphene layers were transferred on the encapsulated papers and their electrical conductivity performances were tested. When PHFBA film was used as a prime layer, the better conductivity performance was obtained from graphene-on-paper. Our results showed that, PHFBA thin film is more suitable for graphene transfer due to its very smooth surface structure. As-transferred graphene layer on PHFBA coated paper surface showed high conductivity, even after repeated folding and flattening cycles.

2:00 PM *FF05.05.03
Benchtop Evaporative iCVD Coater for Nanoglue Bonding
Greg Randall; General Atomics, United States

Initiated chemical vapor deposition (iCVD) enables high-purity polymer coatings at room temperature through a reactor design that segregates the high temperature initiation (e.g. $T>200^\circ$C) and surface polymerization reactions. A complex interplay between mass transport, thermal management, and surface adsorption under vacuum drives continuous flow iCVD reactor design. This talk reviews a simplified evaporative iCVD reactor that can be assembled with off-the-shelf parts in a chemical fume hood. Aspects of steady transport and reaction rates are compromised for ease-of-use and low cost. However, the simple evaporative iCVD coater is capable of providing coatings suitable for testing and for some applications, e.g. gluing small parts together with submicron glue thicknesses. Along with the evaporative iCVD reactor process design, I detail a case study where it is used to achieve sub-micron thick glue coatings on laser compression target materials (Cu, Si, CH, Al, Mo, LiF, quartz). These glued foil stacks are compressed or shocked by a laser impact in order to probe materials science at extreme pressure and/or strain rate. Sub-micron glue thicknesses are particularly important in the design and interpretation of these modern high energy density materials science experiments because the experimental foils are thin ($O[10 \mu m]$) and thick glue layers can seed instabilities and shock reflections.
Thermo-Responsiveness Linked to Deposition Conditions in Initiated Chemical Vapor Deposition of Smart Hydrogel Thin Films for Sensor Applications

Fabian Muralter¹, Alberto Perrotta¹, Oliver Werzer² and Anna Maria Coclite¹; ¹Graz University of Technology, Austria; ²University of Graz, Austria

With initiated Chemical Vapor Deposition (iCVD), it is possible to deposit smart hydrogel thin films conformally into 3D-nanostructures for sensor applications. In this contribution, we report on the thin film synthesis of such a thermo-responsive co-polymer by iCVD for the first time: namely, poly(N-vinylcaprolactam) cross-linked with di(ethylene glycol) divinyl ether; short p(NVCL-co-DEGDVE). In water, the transition of the polymeric system between a swollen state below to a shrunken state above the corresponding lower critical solution temperature (LCST) is investigated by spectroscopic ellipsometry (SE). By water contact angle (WCA) measurements and nano-indentation experiments, we show that the transition is accompanied by a change in wettability and elastic modulus. As previously shown for other polymers, the amount of cross-linking is successfully used to tune the temperature-responsive behavior of the deposited pNVCL-based systems. Higher swelling and LCST, higher surface rearrangement and lower stiffness are achieved in less cross-linked polymers. Interestingly, pNVCL is also reported to show decreased transition temperatures for higher molecular weight systems. Thus, by changing the filament temperature during iCVD, it is possible to lower the LCST by almost 20°C, without changing the (nominal) composition and, thus, the maximum swelling. Overall, maximum swelling degrees of the polymer below the transition temperature of up to 250% of the dry thickness are achieved and the LCST can be tuned in the range of 16-40°C. For probing the applicability in sensor setups, these polymers are also investigated in terms of swelling in humid environment (relative humidity, RH). There, three regions could be identified: First, in rather dry environment (up to ~40% RH), the material responds by mainly filling open porosity, but not showing a temperature-responsive behavior. Second, up to ~80% RH, the response in swelling is close to linear to the measured RH. Third, in very humid environment, the swelling is highly non-linear and temperature-dependent. Moreover, the film thickness approaches the value that can be observed when the polymer is immersed in water at the respective temperature. Furthermore, the response of the polymer in water as well as in humid environment is observed to be very fast; e.g., it responds faster than the commercial sensor used for monitoring the RH in the measurement cell (8 s response time). Together with the biocompatibility reported for pNVCL, the knobs of filament-temperature and cross-linking to tune the described features of the temperature-responsive swelling behavior of these systems make them highly promising for biomedical and/or environmental (sensor) applications.

The Wrinkling Concept Applied to Plasma Polymers—An Innovative Approach for the Fabrication of Flexible Electrodes

Damien Thiry¹, Nathan Vinx¹, Pascal Damman¹, Pierre-Yves Tessier² and Rony Snyders¹; ¹University of Mons, Belgium; ²IMN, France

Following the current development of strategies for the fabrication of structured surfaces, we present in this work an innovative approach for the synthesis of thin films with tunable morphology. Our method is based on the controlled generation of surfaces instabilities in bilayer systems formed by a mechanically responsive plasma polymer films (PPF) synthesized by the Plasma Enhanced Chemical Vapor Deposition (PECVD) method in combination with stiffer coatings.

As a case study, PPF were grown from propanethiol on silicon or flexible polyethylene terephthalate (PET) substrates. AFM data (i.e. peak force quantitative nanomechanical property mapping, scratching experiment) reveals that the nature of the PPF is dramatically affected by the substrate temperature (T_s): from a high viscous liquid (η ~ 10⁶ Pa.s.) to a viscoelastic (E ~ 0.1 GPa) and finally to a stiffer elastic solid (E ~ 0.9 GPa) material when increasing T_s from 10°C to 45°C. This evolution in the mechanical properties is correlated with a pronounced increase in the cross-linking degree of PPF evaluated by ToF-SIMS measurements, combined with a statistical treatment of the data. This trend is ascribed to an increase with T_s in the flux of energy brought to the growing film by positive ions and normalised with respect to the total amount of matter deposited.

In order to inducing a morphological reorganization of the material, we have deposited an Al thin film (50 nm) by the magnetron sputtering technique on the top of a mechanically responsive PPF. The mismatch between the mechanical properties of both layers results in the spontaneous formation of a wrinkled surface. By tuning the thickness as well as the mechanical properties of the PPF layers, the height (i.e. from 0.4 to 5.2 µm) and the width (i.e. from 0.6 µm to 6.5 µm) of the nano/micro wrinkles can be easily tailored in a wide range offering a great
flexibility in terms of surface engineering.

The same methodology was applied on flexible PET substrates. To evaluate the potential of the Al-based wrinkled/PET material as a flexible thin-film electrode, the mechanical stability of the electrode is explored under severe and repeated deformations. For this purpose, applying a strain of 1%, the electrodes are bent up for 10,000 times. The electrical resistance, measured after each bending cycle, shows a relatively stable behavior (the resistance increase only by 15%). In contrast, for a flat Al thin film directly deposited on flexible PET, the electrical resistance dramatically increases by 12,000% after 500 cycles indicating failure of the electrode.

Our results reveal the attractiveness of our method for the fabrication of micro/nano pattern with tuneable dimensions with potential applications in flexible electronics.

3:00 PM BREAK

3:30 PM *FF05.05.06
Controlling the Composition, Hardness and Function of Vapor-Phase Deposited Polymer Films Sung Gap Im; Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of)

iCVD (initiated chemical vapor deposition) is a powerful tool to deposit various kinds of functional polymer films. Especially, the process is capable of exquisite control of its surface composition, elastic modulus, and functions through the introduction of various combinations of functionalities onto target substrates. Compared to conventional liquid phase-based methods, the solvent-free process can generate polymer coatings of extremely high purity, which is essential for various field applications, because such residual impurities produce harmful side effects. In addition, the thin iCVD polymer films remained durable and robust via proper crosslinking, rendering them suitable for the applications in hard environments. Such advantageous characteristics of the iCVD process have been exploited for tissue regeneration, flexible/wearable electronics, biosensors, and functional surface modification for various devices. In this presentation, the controlling of surface properties of functional polymer films and their application to various fields will be reviewed.

4:00 PM FF05.05.07
Scalable, Single-Source, One-Step Synthesis of an Electrocatalyst Sebastian Tigges, Axel Lorke and Nicolas Wöhrl; University Duisburg-Essen and CENIDE, Germany

A novel manufacturing method for the scalable, one-step synthesis of a Pt/C electrocatalyst by inductively coupled plasma-enhanced chemical vapor deposition is presented. The metal-organic precursor platinum acetylacetonate is used to deposit platinum nanoparticles (NPs) and support, carbon nanowalls (CNWs), simultaneously in a single, uncatalyzed process at remarkably low temperatures of 350°C. In general, CNWs exhibit exceptional thermal as well as electrical conductivity and widely adjustable surface area, making them an ideal support for use in energy conversion applications. By adjusting specific process parameters, such as pressure, gas flow rate and temperature, the density, thickness and height of the CNWs, as well as the platinum loading and oxidation state of the resulting catalyst can be tuned according to requirements. Scanning electron microscopy and Raman spectroscopy are used to determine the CNWs’ structural and electronic properties, respectively. Additionally, X-ray photoelectron spectroscopy and Auger electron spectroscopy are used to determine the overall and spatially resolved chemical composition and oxidation state of the catalyst. High-resolution transmission electron microscopy (TEM) reveals the presence of homogeneously distributed platinum particles with a mean particle diameter below 3 nm, resulting in an exceptionally narrow particle distribution with a polydispersity index below 0.1. Furthermore, due to the simultaneous synthesis of both NPs and support, the nanoparticles are expected to be incorporated into the carbon matrix, which is supported by TEM tomography. Such incorporation would greatly improve the immobilization of NPs on the support and thus the long-term stability of the catalyst. Finally, due to the use of a metal-organic precursor, the process can be adjusted to deposit almost any transition metal/CNW-hybrid material, making it a versatile method for a variety of different applications.

4:15 PM FF05.05.08
Chemical Insolubility of Vapor Phase Infiltrated Poly(methyl methacrylate) / AlOx Hybrid Materials Emily K. McGuinness, Collen Z. Leng and Mark D. Losego; Georgia Institute of Technology, United States
Vapor phase infiltration (VPI) is a relatively new processing technique used for transforming polymers into organic-inorganic hybrid materials. VPI has been used to improve polymer mechanical properties, protect fabrics from UV and thermal degradation, dope conducting polymers, and act as a contrasting agent in electron microscopy for imaging phases of polymer blends. Recently, our group has explored a new application for VPI, the protection of thermoplastic polymers from solvent dissolution. In this study, poly(methyl methacrylate) (PMMA) thin films were infiltrated with trimethylaluminum (TMA) and water at different temperatures and to different depths of infiltration. The resultant AlOx / PMMA hybrid films were then exposed to a variety of solvents to explore their stability. Chemical stability was found to vary non-linearly, with infiltration temperature. Films infiltrated at lower temperatures (70°C and 100°C) swelled or partially dissolved in good solvents for neat PMMA, such as toluene or chloroform, and partially dissolved in isopropanol and water, which are not good solvents for PMMA. In comparison, films infiltrated at higher temperatures (130°C) showed enhanced solvent stability in most solvents, even those that dissolved neat PMMA. The increased solvent resistance is likely due to crosslinking between PMMA functional groups and TMA molecules, a reaction that has been reported to vary with temperature. Due to this variability, PMMA films infiltrated at low temperatures are only partially crosslinked while those infiltrated at high temperatures are fully crosslinked, making them more solvent resistant. The increased dissolution of hybrid films in certain alcohols and polar solvents is hypothesized to result from an interaction between the inorganic crosslinker and the solvent. We also found that complete transformation of the polymer into hybrid material was unnecessary for dissolution resistance at higher temperatures. An infiltration depth of 0.5 mm was sufficient for complete resistance to toluene dissolution at room temperature. For proof-of-concept, we applied this treatment to a quarter inch thick laser-etched PMMA sheet and then exposed it to toluene at 60°C for 30 minutes. While the design on the neat PMMA version rapidly dissolved, the sheet with a 0.5 mm AlOx / PMMA subsurface layer showed nearly complete retention of its design. In this talk, we will explore these findings and discuss the differences in solvent stability of AlOx / PMMA hybrid materials as a function of temperature as well as investigate the underlying chemical and structural variations that yielded these results.

4:30 PM *FF05.05.09
Novel Metal-Organic Structures and Engineered Inorganic-Organic Interfaces through ALD/MLD Maarit Karppinen; Aalto University, Finland

The combined ALD/MLD (atomic/molecular layer deposition) technique is strongly emerging as a viable technology for the fabrication of new types of functional metal-organic materials and inorganic-organic interfaces not readily accessible through any other fabrication route. Most excitingly, it is capable of yielding in-situ crystalline thin films of structures similar to those known for so-called coordination polymer or metal-organic framework (MOF) materials synthesized from solutions,[1] or even entirely new compositions/structures.[2] An attractive example is the in-situ lithiated and crystalline thin films of lithium quinone, a promising cathode material for a Li-ion microbattery;[3] the lithium quinone structure contains the Li⁺ cations in a coordinatively unsaturated three-fold coordination, which explains why it can not be synthesized through conventional solution synthesis. Equally exciting are the new metal-organic structures based on photoactive azobenzene,[4] or upconverting lanthanide-ions.[5] Another interesting approach enabled by ALD/MLD is to build artificial superlattices or gradient materials with precisely tailored inorganic-organic interface frequencies,[6] in such layer-engineered hybrid materials the periodically introduced monomolecular organic layers between nm-scale metal oxide layers may efficiently block phonon conduction, enhance mechanical flexibility, control band-gap or magnetic properties, etc.

References
FF05.06.01
Processing and Characterization of Hexagonal Boron Nitride Films of Wide-Area by Chemical Vapor Deposition on Silicon Substrates Ranjan Singhal and Raj N. Singh; Oklahoma State University, United States

Two-dimensional hexagonal boron nitride (2D h-BN) is a single - atom thick layer (monolayer) of alternating boron and nitrogen atoms, which is of great interest and potential due to its excellent electrical, optical, and mechanical properties and isostructural to graphene. To fully utilize the potential of 2D h-BN, wide area processing of high-quality 2D h-BN is of utmost importance. As of now, chemical vapor deposition (CVD) is the most promising method to synthesize 2D h-BN because it provides great control on the thickness of the deposited films (number of layers) and is the best candidate for the industrial scale-up process. In this study, a CVD system was designed for synthesis of two-dimensional hexagonal boron nitride with low and atmospheric pressure capabilities as well as a solid and liquid precursor delivery system. The customized CVD system is also capable of synthesizing other 2D materials like graphene and molybdenum disulfide since it can incorporate different types of precursors and reaction gases. This presentation explores the CVD aspects of h-BN synthesis with a specific focus on the designed CVD reactor system and associated components. h-BN was synthesized directly on non-catalytic silicon substrates via LPCVD, which eliminated the need for a transfer process that can introduce impurities and surface defects (wrinkles, folding). Subsequently, the effect of the precursor flow behavior on the growth of hBN was studied. Scanning electron microscopy (SEM), Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and UV-vis spectroscopy were then used to characterize the deposited h-BN and study the effect of precursor flow kinetics. XPS analysis confirmed the presence of h-BN. Raman spectroscopy further corroborated the formation of h-BN. The approximate crystallite size of the deposited h-BN was also determined by Raman spectroscopy analysis. SEM confirmed the crystallite size estimated from Raman spectroscopy analysis of between 60 – 100 nm.

FF05.06.02
Microplasma-Driven, Area-Selective Atomic Layer Deposition of Aluminum Oxide at 300K Jinhong Kim, Andrey Mironov, Sung-Jin Park and J G. Eden; University of Illinois Urbana Champaign, United States

Area-Selective Atomic Layer Deposition (AS-ALD) of aluminum oxide (Al2O3), driven by arrays of microcavity plasmas (MALD), has been demonstrated. Al2O3 films were grown at 300 K by dissociating oxygen in an array of microcavity plasmas. Metal-oxide-semiconductor capacitors (MOSCAP), fabricated from Al2O3 films deposited on p-Si by MALD with Al top ohmic contacts and Au bottom electrodes, exhibited a breakdown electric field strength of E_{BR} = 6.1 ± 0.2 MV/cm and a hysteresis width of < 1 mV, indicating the presence of negligible traps in the film. The dielectric constant of Al2O3 films, ε_{ox}, was measured from MOSCAP C-V curves to be ε_{ox} = 9.7 ± 0.3. The measured values for E_{BR} and ε_{ox} are higher than conventional values, exhibiting that MALD-grown films are suitable for MOS devices operating under demanding ambient conditions which require extraordinary radiation resistance, thermal conductivity, and chemical stability. The ability to grow Al2O3 films of high quality at 300 K prompted experiments to fabricate Al2O3 arrays of small feature size. AS-MALD of Al2O3 films was accomplished by lift-off lithography. With this process, Al2O3 films having a lateral dimension of 1 - 10 µm and a thickness of ~ 68 nm were deposited. Due to the complete reaction between precursors, the oxygen and aluminum stoichiometric ratio for amorphous Al2O3 films has been measured by EDX and RBS to be ~ 1.5 ± 0.1, demonstrating that negligible levels of impurities and oxygen vacancies exist in the films. All experimental results show that MALD process can be compatible with semiconductor area-selective patterning with narrow lateral dimensions through simple lithography and lift-off.

FF05.06.03
Growth and Characterization of Corundum Structure Oxide Semiconductor on α-Fe2O3 Buffer Layers by The Mist CVD Method Kazuki Shimazoe, Hiroyuki Nishinaka, Daisuke Tahara, Yuta Arata and Masahiro Yoshimoto; Kyoto Institute of Technology, Japan
Corundum structured III-IV oxide materials have been attracted considerable interest from oxide based wide bandgap semiconductor researchers. Typical corundum structured α-Al₂O₃ are widely used as substrates for wide band gap semiconductors, such as GaN, ZnO, and α-Ga₂O₃. The α-Ga₂O₃ in the series of corundum structure exhibits bandgap energy of 5.3 eV and controlling carrier concentration by n-type doping. Further, the α-Ga2O3 produces the possibility to tune a wide range of bandgap by alloying with α-Al₂O₃ (8.8eV) and rh-In₂O₃ (3.7eV) exhibiting the same corundum structure. The epitaxial growth techniques are usually used for the synthesis of these materials. For example, the epitaxial growth supported by α-Fe₂O₃ buffer layers showing the same corundum allowed growing single phase rh-In₂O₃ thin films which have been difficult to synthesis [1].

In this study, the mist CVD method was utilized for the epitaxial corundum oxide thin films and solution mist dissolving precursors was used as CVD precursors. Any precursor can be used as mist CVD precursors that only dissolves the precursor in any solvent. Taking advantages of its feature, we have demonstrated that the phase controlling of corundum oxide thin films were successfully obtained by using various corundum substrates and α-Fe₂O₃ corundum buffer layers.

For the α-Ga₂O₃ epitaxial growth, most researchers have utilized only α-Al₂O₃ substrates with large lattice mismatch for α-Ga₂O₃. However, we featured the LiTaO₃ and LiNbO₃ substrates showing nearly corundum structures with smaller lattice mismatches for α-Ga₂O₃. XRD results revealed α-Ga₂O₃ epitaxial thin films were successfully grown on LiTaO₃ and LiNbO₃ substrates with α-Fe₂O₃ buffer layers. The epitaxial ε-Ga₂O₃ thin films were grown on LiTaO₃ and LiNbO₃ without buffer layer. This is because ε-Ga₂O₃ also has a similar oxygen atom arrangement of the corundum structure and the phase is more stable thermodynamically than that of α-Ga₂O₃. Furthermore, to compare the crystal quality of α-Ga₂O₃ layers on LiNbO₃, LiTaO₃ and α-Al₂O₃, we investigated XRC of asymmetric plane (10-14) α-Ga₂O₃. The FWHMs of XRC for α-Ga₂O₃ on LiTaO₃ and LiNbO₃ were evaluated to be 0.51 degree and that for α-Ga₂O₃ on α-Al₂O₃ is evaluated to be 0.85 degree, indicating that the LiTaO₃ and LiNbO₃ with α-Fe₂O₃ buffer layers are promising materials for α-Ga₂O₃ epitaxial growth.

ITO, which is a typical transparent conductive oxide, possesses two polymorphs; bcc-ITO (bixbyite) and rh-ITO (rhombohedral, corundum). Since the synthesis of rh-ITO requires high-pressure and high-temperature, few reports exist on rh-ITO thin films. Our group previously reported the epitaxial growth of rh-ITO using α-Fe₂O₃ buffer layers on various plane α-Al₂O₃ substrates [2]. However, detailed characterizations, such as dependence on the impurity concentration of rh-ITO thin film is not still investigated. Hence, we report on the characterization of the epitaxial rh-ITO thin films grown on various plane α-Al₂O₃ by mist CVD with α-Fe₂O₃ buffer layers. The rh-ITO thin film prepared on the r-plane α-Al₂O₃ substrate with 5 at.% of Sn ratio in the starting solution possessed the resistivity of 1.73×10⁻⁴ Ωcm, the mobility of 25.8 cm²/Vs, and carrier density of 1.40×10²¹ cm⁻³. Furthermore, the carrier concentration dependence of the mobility of rh-ITO epitaxial thin films was almost similar to that of single crystal bcc-ITO. In this symposium, we will discuss the detailed electrical and optical properties of rh-ITO on various α-Al₂O₃ substrates.


FF05.06.04 Fabrication of Flexible and Epitaxial Oxide Thin Films on Cleaved Synthetic Mica Using Mist Chemical Vapor Deposition
Yuta Arata, Hiroyuki Nishinaka, Daisuke Tahara, Kazuki Shimazoe, Yusuke Ito and Masahiro Yoshimoto; Kyoto Institution of Technology, Japan

Flexible electronic devices leading various wearable applications are expected to revolutionize modern society [1]. For the use of flexible functional materials, it has been mainly reported that the organic materials were formed on flexible substrates by low-temperature processes, such as inkjet printing [2]. However, organic materials generally exhibit low heat resistance and poor stability in a high-temperature environment. Conversely, flexible inorganic materials possess a high heat resistance and high stability in a harsh environment. However, it has been difficult to prepare single crystal thin films allowing to maximize the properties. In this study, we demonstrated the epitaxial growth of oxide thin films on two-dimensional (2D) layered materials by atmospheric chemical vapor deposition (CVD) technique without requiring a vacuum process. The 2D layered materials can be simply peeled off and utilizes as flexible substrates. It has already been reported that oxide thin films were epitaxially grown on 2D layered materials by pulsed laser deposition (PLD) [3]. Moreover, the oxide epitaxially grown on the 2D layered materials maintained its characteristics even in a bent state or after repeated bending. We utilized the mist CVD methods for the epitaxial growth of oxide thin films on 2D layered materials.
The mist CVD can be operated under atmospheric pressure for thin film growth because the stable mist including the CVD precursors is utilized instead of precursors vaporized by bubbling or heating. The mist is ultrasonically atomized from the solution made by dissolving the precursors. Furthermore, any solution precursor can be utilized as CVD precursors if it can be dissolved in solvents. Thus, one apparatus of mist CVD allows growing the various materials, as long as the solution precursors can be prepared. We have demonstrated that the growth of metastable phases gallium oxide (Ga$_2$O$_3$) is controlled by mist CVD using other material buffer layer on 2D layered materials. Ga$_2$O$_3$ has recently attracted attention as an ultra-wide bandgap semiconductor in power devices and deep ultraviolet device applications. Ga$_2$O$_3$ possesses five polymorphs of α-, β-, γ-, δ- and ε-phase [4]. Ga$_2$O$_3$ thin films were grown on cleaved synthetic mica wafers as a 2D layered material substrate. A solution of gallium chloride (GaCl$_3$) in de-ionized water was used as the Ga precursor of mist CVD. X-ray diffraction (XRD) results revealed that ε-Ga$_2$O$_3$ thin films were grown on synthetic mica wafers at the growth temperature of 450-600°C without buffer layers. To obtain α-Ga$_2$O$_3$ thin films, we inserted α-Fe$_2$O$_3$ buffer layers grown by using iron acetylacetonate (Fe(C$_5$H$_7$O$_2$)$_3$) dissolved in de-ionized water as the Fe precursor [5]. As a result, the insertion of the buffer layers allowed growing epitaxially another metastable phase α-Ga$_2$O$_3$ thin films on synthetic mica wafers at the growth temperature of 350-600°C. We succeeded in epitaxial growth of the metastable ε phase and α phase Ga$_2$O$_3$ which are promising as power devices and deep ultraviolet devices on flexible substrates using mist CVD.

In the symposium, we will introduce and discuss the results of epitaxial growth on synthetic mica by mist CVD for not only several Ga$_2$O$_3$ phases but also various oxide thin films.


**FF05.06.05**

**Gaining Insight into Self-Limiting Surface Reactions During Plasma-Assisted Atomic Layer Deposition of III-Nitrides via In Situ Ellipsometry**

Deepa R. Shukla$^1$, Adnan Mohammad$^1$, Saidjafarzoda Ilhom$^1$, Ali Okyay$^2$, Blaine Johns$^3$, Brian Willis$^3$ and Necmi Biyikli$^4$; $^1$University of Connecticut, United States; $^2$Stanford University, United States; $^3$Film Sense LLC, United States

Atomic layer deposition (ALD) is an emerging field in nanoscale materials research featuring atomic-level precision due to its self-limiting growth character. Besides fine thickness control, ALD also provides unmatched three-dimensional conformal and uniform film deposition. Owing to these advantages, ALD already has created a significant impact in aggressively scaled logic and memory device technology based on 3D CMOS transistors, as well as energy storage, solar cells, surface passivation, catalysis, and flexible/wearable devices.

ALD-grown films are vastly characterized via ex-situ measurements to quantify various material properties. However, gaining insight into the saturating surface reactions and growth mechanisms is only possible with real-time in-situ process monitoring of individual ALD cycles. While several in-situ measurement techniques have been employed in ALD research, in-situ ellipsometry stands out as one of the best options for real-time monitoring surface reactions. The promising potential of in-situ spectroscopic ellipsometry has already been demonstrated for a number of materials grown by remote plasma-ALD. Here, we verify that cost-effective multi-wavelength ellipsometer (MWE) can also be used effectively for real-time in-situ analysis of plasma-ALD growth cycles. We demonstrate for the first time that real-time dynamic in-situ MWE measurements convey not only accurate film deposition rate, but as well resolve single chemisorption and ligand exchange reactions with remarkable clarity. Moreover, forcing the limits for fitting the acquired in-situ MWE data, we were able to track the evolution of the optical constants of III-nitride films along the ALD cycles which showed thickness-dependent behavior.

Our main motivation behind this study is to analyze and compare the self-limiting growth characteristics of binary III-nitride (AlN, GaN, and InN) thin films via real-time in-situ ellipsometry and to gain insight into the ALD surface reaction mechanisms including chemical adsorption, ligand removal, and nitrogen incorporation steps.

Despite using the conventional alkyl metal precursors (trimethylaluminum, trimethylgallium, triethylgallium, and trimethylindium) utilized also widely in MOCVD epitaxial growth, their solid-gas surface interactions with nitrogen plasma species shows notable differences, particularly with respect to substrate temperature, plasma power, plasma
exposure time, and plasma gas composition. In terms of substrate temperature, AlN exhibited crystallinity at lower temperatures when compared to GaN and InN. Even at 100 °C, AlN showed crystalline behavior whereas GaN displayed amorphous character up to 200 °C. While Ar/N₂/H₂ composition is optimal for AlN, N₂/H₂ and Ar/N₂ mixtures proved to be optimal for GaN and InN film quality, respectively. Furthermore, we have observed that the inclusion of H₂ gas into the plasma cycles led to substantial deformation of the hexagonal crystal structure and resulted in mixed phase growth with notable c-In₂O₃ and metallic tetragonal In. The possible surface reaction mechanisms that lead to these different growth behaviors will be discussed in detail.

The real-time in-situ data is correlated with film structural, optical, and chemical properties obtained by ex-situ spectroscopic ellipsometer, x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and transmission electron microscopy (TEM) measurements. Our results demonstrate that dynamic in-situ MWE measurements can provide significant insight about the surface reactions taking place during low-temperature plasma-ALD of III-nitride compounds.

FF05.06.06
Fabrication of Ferroelectric Hf₀.₅Zr₀.₅O₂ Thin Film by Atomic Layer Deposition (ALD) Using H₂O₂ Precursor
Hyoungkyu Kim¹, Seokjung Yun¹, Hoon Kim¹, Changdeuck Bae² and Seungbum Hong¹; ¹Korea Advanced Institute of Science and Technology, Korea (the Republic of); ²Sungkyunkwan University, Korea (the Republic of)

Zr doped-hafnium oxides (HZO)-based FeFET/FRAM has recently emerged as the next-generation memory device due to its low power operation, scalability, and Si compatibility. However, it suffers from the limited processing window to secure their ferroelectric properties in terms of thickness, thermal processing effect and high dependence on ozone (O₃) as the oxygen precursor of atomic layer deposition (ALD). Herein, we report on the use of hydrogen peroxide (H₂O₂) precursor as the O₂ source to fabricate HZO thin films via ALD. We optimized the deposition parameters such as purging time, deposition time, and temperature to obtain high and stable ferroelectric properties. Furthermore, we evaluated the thermodynamic reaction energy of hydrogen peroxide and compared the two classes of samples in terms of deposition state, thickness, and chemical composition using X-ray photoelectron spectroscopy (XPS). To analyze the ferroelectric properties of HZO thin films, we characterized the crystalline structure using X-ray diffraction (XRD), and the electrical properties using C-V and P-V measurements. Finally, we investigated the grain size distributions using atomic force microscopy (AFM) and correlated them with their respective crystalline phase. Through this study, we provide a new ALD technique for high-quality HZO thin films for FeFET/FRAM device applications.

FF05.06.07
Use of Refractory-Metal Diffusion Inhibitors in Catalytic Metal Particles for Catalytic CVD Growth of Ultra-Long Carbon Nanotubes (CNTs)
Michael J. Bronikowski and Melissa King; University of Tampa, United States

Recent results are presented from studies of the growth by Chemical Vapor Deposition of Carbon Nanotubes (CNTs), using a novel technique which it is hoped will ultimately lead to the availability of ultra-long CNTs. The method used involves incorporation of refractory, high-melting-point metals into the nano-particles of catalyst metal from which the CNTs nucleate and grow. The refractory metal acts as a diffusion inhibitor, and inclusion of these diffusion inhibitors slows the erosion of the catalyst particles, and thus extends the lifetime of the catalyst particles and hence the length to which CNTs can be grown. This effect has previously been demonstrated for several catalyst/diffusion-inhibitor systems including Mo/Re and Fe/Mo. Here we present new results on the Fe/Re catalyst system: it is shown that inclusion of Re diffusion inhibitor can enhance the lifetime of the iron catalyst particles and give CNT growth to lengths greater than would otherwise result.

FF05.06.08
A Study of Initiated Chemical Vapor Deposition (iCVD) Siloxane Thin-Film Conformality at Different Length Scales
William Livernois, Scott Morrison and William S. O'Shaughnessy; GVD Corporation, United States

Conformal polymer thin films have a wide variety of uses ranging from protective coating applications to surface functionalization and modification. There are a variety of traditional wet methods for depositing polymer films, such as spin coating or drop casting, but substrates with complex features will have issues caused by varying wettability and capillary forces. Initiated chemical vapor deposition (iCVD) is a low-temperature, dry process that deposits conformal polymer thin films from the gas phase. The process uses an initiator compound that is activated by a hot
filament array and polymerizes adsorbed organosilicon precursor on the substrate surface. For this study the reactor parameters have been optimized to maximize conformality of the coating at multiple length scales.

Coating features with irregularities at multiple length scales is a challenge that is commercially relevant both for scaling the process and improving reliability of the coating across a diverse range of substrates. To test conformality and study the effect of geometry on the deposition process high-aspect ratio (>10:1) millimeter and micron scale testing devices were fabricated on silicon. In both length scales, lowering the sticking probability improved conformality of the coating, which could be achieved by varying the temperature of the substrate and reactor pressure. On the millimeter scale, it was clear that the conformality was reaction limited by depletion of the initiator, whereas film growth in the micron-scale features was limited by monomer diffusion and adsorption. Conditions for optimal conformality at both length scales was demonstrated with different sets of reactor conditions which can be combined into a multi-step conformal coating process.

FF05.06.09
Atomic Level Surface Functionalization of a Graphene Oxide Membrane to Break the Permeability-Selectivity Trade-Off in Salt Water Desalination Jihoon Ahn and Kyu-Jung Chae; Korea Maritime & Ocean University, Korea (the Republic of)

Graphene oxide (GO) membranes have shown promising ionic and molecular sieving due to their unique interconnected nanochannels; however, their low salt rejection efficiency caused by an enlarged interlayer spacing between GO flakes limits their wide application in water desalination. For the purpose of enhancing GO membrane performance, this research applies a novel approach to atomic level surface functionalization with precise control, which allowed for the formation of an ultra-thin Al2O3 layer by sequential atomic layer deposition (ALD) to the GO membrane. Due to the strong chemisorption of trimethylaluminum (TMA) to GO, an ultra-thin (1.44 nm) and uniform hydrophilic Al2O3 layer was successfully deposited on the GO membrane under low numbers of ALD cycles. The GO membrane coated with an atomically thin and uniform Al2O3 layer achieved enhanced water permeability (from 40 LMH/bar to 70 LMH/bar) and NaCl rejection up to 67.4 %, successfully overcoming the trade-off between permeability and rejection efficiency. This enhanced water permeability is mainly attributed to the increase in surface hydrophilicity without narrowing the GO membrane pore structure. Dspacing via X-ray diffraction (XRD), surface chemistry via Fouriertransform infrared spectroscopy (FTIR), and water contact angle (WCA) measurements confirmed the effect of ALD on the physico-chemical properties of the GO membrane. The distinctive features of ALD to the GO membrane may contribute towards enhancing its wider application in water desalination.

FF05.06.10
Controlling the Optical and Electronic Properties of Polyaniline (Pani) Using Vapor Phase Infiltration of Titanium Tetrachloride Shawn A. Gregory, Yi Li, Shannon Yee and Mark D. Losego; Georgia Institute of Technology, United States

This talk will discuss our use of vapor phase infiltration (VPI) to alter the optoelectronic properties of poly(aniline) (Pani). VPI is similar to atomic layer deposition (ALD), but instead of cycling viscous flows of co-reactants, VPI doses a single reactant vapor in a static atmosphere followed by a purge-pump cycle. ALD typically provides conformal surface coatings while VPI enables extensive sub-surface diffusion and reactions within organic substrates. In our study, Pani was infiltrated with a single cycle of TiCl4-H2O to yield a hybrid film. This chemistry has not been explored before and was specifically selected because of its reaction products; TiOx has useful optical properties for photovoltaic and photochemical applications while HCl is known to dope Pani and create polaronic charge carriers. We found that Pani films optimally infiltrated with TiCl4 have an electrical conductivity of ca. 0.2 S/cm. To the best of our knowledge, this is the highest electrically conducting Pani film achieved with a single-cycle exposure to a metal-halide vapor. Additionally, as VPI hold time increases, Pani films turn from blue to nearly transparent to green. This color transition is believed to be evidence of the generation of polaronic charge carriers and the concomitant formation of TiOx. The polaronic carriers absorb the red-NIR-MIR spectra (700-5000 nm) while TiOx contributes to unusually high absorbance in the blue-UV region (450 - 350 nm). This combination of optical absorbances in Pani has not been documented before and could be valuable for electrochromic or photovoltaic applications. To better understand processing parameters, we varied the TiCl4 exposure time and measured ex-situ optical signatures. We calculated an effective TiCl4 diffusion coefficient of ca. 10^-15 cm²/s at 80°
C. Additionally, we demonstrated that the relative ratio of UV and IR absorbent species can be controlled by varying reaction temperature. Increasing the reaction temperature likely decreases HCl sorption, ergo decreasing the extent of doping, polaron formation, and IR absorbance. Lastly, we performed XPS measurements to elucidate a reaction mechanism. We found that titanium effectively only binds with oxygen and that nitrogen radical cations (polarons) are present; this further corroborates our hypothesis that TiOx is responsible for the unique blue-UV absorbance and that the electrical conductivity is dominated by polaronic carriers. By better understanding this reaction mechanism and kinetics, VPI precursor chemistry and processing conditions can be optimized for future organic semiconductor doping.

**FF05.06.11**

**Improving the Wet Strength of Nanopaper with Atomic Layer Deposited (ALD) Subnanometer Metal Oxide Coatings**

Yi Li, Mark D. Losego, Rampi Ramprasad and Lihua Chen; Georgia Institute of Technology, United States

Nanocellulosic films (nanopapers) are of interest for packaging, printing, chemical diagnostics, flexible electronics and separation membranes. These nanopaper products often require chemical modification to enhance functionality. Most chemical modification is achieved via wet chemistry methods that can be tedious and energy intensive due to post-processing drying. Here, we discuss the use of atomic layer deposition (ALD), a vapor phase modification technique, to quickly and simply enhance the wet strength and durability of nanopaper. Here, we specifically consider ALD processes that use only a “few” cycles (< 10) to maintain the potential for process scalability and commodity manufacturing. While these “few cycle” ALD treatments do not appear to alter the mechanical properties of the nanopaper in the dry state, wet strength shows a significant enhancement. Here we will report that up to 10 cycles of either aluminum oxide or titanium oxide ALD is sufficient to significantly increase the durability of nanopaper under aggressive aqueous sonication or burst testing (9x increase). In this presentation, we will discuss our investigation into whether this increase in wet strength is the result of enhanced hydrophobic attractions or increase hydrogen bonding attraction. Through a combination of experimental investigations and *ab initio* calculations, we currently believe the M-OH terminations enhance hydrogen bond strength between the neighboring cellulosic nanofibrils.

**FF05.06.12**

**Understanding the Initial Growth During Atomic Layer Deposition of Nickel Sulfide via *In Situ* X-Ray Photoelectron Spectroscopy and Low Energy Ion Scattering**

Ran Zhao, Xinwei Wang and Yuanhong Gao; Peking University, China

Atomic layer deposition (ALD) is a highly useful synthesis method to grow highly-controllable thin-film materials. In a typical ALD process, the initial nucleation and growth is of particular importance, because it not only is crucial for preparing high-quality film–substrate interfaces but also can be engineered to synthesize well-controlled nanoparticles. Therefore, understanding the initial surface chemistry as well as the growth mechanism is of crucial importance for rationally designing functional materials and interfaces by ALD. Over the past several years, ALD of metal sulfides has aroused great attention, especially for their numerous applications in the emerging energy technologies. Many new ALD processes of metal sulfides have been recently developed, and the metal sulfides of which the ALD processes were only recently available include GaS (2014), GeS (2014), MoS2 (2014), LiS (2014), CoOxSx (2015), NiS (2016), MnS (2016), FeS (2017), VSx (2017), Bi2S3 (2017), AlSx (2017), and ReS2 (2018). The investigation of the initial growth on these new metal sulfide ALD processes is certainly valuable and in need.

Our group recently developed a new ALD process of nickel sulfide (NiS) using bis(N,N’-di-tert-butylacetamidinato)nickel(II) (Ni(amd)2) as the nickel precursor and H2S gas as the sulfur source. Herein, we study the initial ALD growth of NiS on SiOx by using the in situ techniques of X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering (LEIS). The reaction scheme during the initial ALD stage is found to be rather different from that in the later steady film growth stage, and therefore a reaction-agglomeration mechanistic scheme is proposed to describe the initial ALD growth. In the scheme, the conversion from Ni–O to NiS in the H2S half-cycles is suggested to be accompanied by the spontaneous agglomeration of the ligand-stripped Ni-containing species to afford NiS clusters, and the agglomeration can re-expose the surface of SiOx and therefore allow the surface to further react with Ni(amd)2 in the subsequent ALD cycles. Using LEIS, the transition from the initial reaction-agglomeration growth to the continuous steady film growth is found to be between 100 and 300 ALD cycles. Ex situ atomic force microscopy (AFM) and transmission electron microscopy (TEM) are further employed to further understand the growth mechanism.
to corroborate the presence of the agglomeration during the initial growth. The results reported herein and the implied growth mechanism should be of great representativeness for the ALD of metal sulfides, and therefore, the findings should be highly valuable for future engineering of functional metal sulfide nanomaterials and interfaces by ALD.

References

FF05.06.13
Epitaxial Growth and Band-Gap Control of Ni$_{1-x}$Mg$_x$O Thin Film by Using Mist CVD Method
Takumi Ikenoue, Masao Miyake and Tetsuji Hirato; Kyoto University, Japan

Development of wide band-gap p-type oxide semiconductors with good properties is essential for various applications that realize resource saving and low power loss. Although oxide semiconductors that show p-type conductivity with wide band-gap are rare, nickel oxide (3.7 eV) has attracted attention. In recent years, p-type oxide semiconductor materials having a larger band gap are required. Therefore, we focused on Ni$_{1-x}$Mg$_x$O, which is a mixed crystal with MgO, which has the same rock salt structure as NiO and has a band gap of 7.8 eV. In addition, in order to improve the properties of these materials, growth was performed using a mist CVD method that enables high-quality film growth even under atmospheric pressure.

In this presentation, Ni$_{1-x}$Mg$_x$O thin films grown by using the mist CVD method will be described in detail. Ni$_{1-x}$Mg$_x$O epitaxial growth was performed on α-Al$_2$O$_3$ or MgO substrates, and carrier concentration control by Li doping was studied. The bandgap of Ni$_{1-x}$Mg$_x$O monotonously increased according to the Mg composition and was controlled in the range of 3.4–4.0 [eV]. It was revealed that the carrier concentration in the Li-doped NiO thin film can be controlled in a wide range only by controlling the Li concentration in the precursor solution.

A wide band-gap p-type oxide semiconductor Ni$_{1-x}$Mg$_x$O was grown by the mist CVD method. These are very high quality despite being grown in a non-vacuum process and are expected to be applied to various devices.

FF05.06.14
Chemical Vapor Deposition Synthesis of a High-Quality MoS$_2$ Layer by H$_2$S/H$_2$ Mixture—A Reactive Molecular Dynamics Study
Sungwook Hong$^{1,2}$, Ken-ichi Nomura$^1$, Rajiv Kalia$^1$, Aiichiro Nakano$^1$ and Priya Vashishta$^1$; $^1$University of Southern California, United States; $^2$California State University, Bakersfield, United States

Layered transition metal dichalcogenides (TMDCs) such as a layered MoS$_2$ are attracting great attentions owing to their outstanding physical, chemical, and mechanical properties, compared with their bulk counterparts. Chemical vapor deposition (CVD) is known to be the most effective way to synthesize the layered MoS$_2$ on the target substrate. While previous studies suggested to use different types of reactants/precursors like sulfur powders, and gaseous H$_2$S and H$_2$ precursors for a higher-quality MoS$_2$ layer, their reaction kinetics and mechanisms have yet to be fully understood. Here, we perform reactive molecular dynamics (RMD) simulations for CVD synthesis of MoS$_2$ layer using three different systems: 1. MoO$_3$ and S$_2$; 2. MoO$_3$ and H$_2$S; 3. MoO$_3$ and H$_2$S/H$_2$ mixture. Our goal is to clarify atomic-level reaction pathways for reduction/sulfidation of the MoO$_3$ slab using different gaseous environments. RMD results reveal that MoO$_3$ slab could be effectively sulfurized by the H$_2$S/H$_2$ mixture. As such, our computational work provides a valuable input for experimental synthesis of TMDCs using the CVD technique.

This work was supported as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC0014607. The simulations were performed at the Argonne Leadership Computing Facility under the DOE INCITE and Aurora Early Science programs, and at the Center for High Performance Computing of the University of Southern California

Finally, this work was supported by a grant from the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC0014607. The simulations were performed at the Argonne Leadership Computing Facility under the DOE INCITE and Aurora Early Science programs, and at the Center for High Performance Computing of the University of Southern California.
Oxidative Chemical Vapor Deposition (oCVD) and Atomic Layer Deposition (ALD) accomplish polymers and oxides synthesis, thickness-defined patterned deposition, and doping in a single process at near-room temperatures (40 - 80 °C) for a broad range of technological applications. Also, both function independent of material solubility and substrate properties to enable insoluble polymers and oxides to be coated in a conformal or uniform manner without any solvent damage to the substrate. This key differentiator from solution-based approaches makes them substrate-independent scalable platform technologies for surface modification and device fabrication.

Based on the commercialization-critical benefits, semiconducting and conducting polymer thin films with suitable properties, patterns, and size can be directly integrated into flexible electronics such as organic photovoltaics on unmodified papers, thereby enhancing the efficiency and lifetime significantly. Meanwhile, H⁺-conducting and O₂ impermeable ultrathin (2 nm) SiO₂ membrane leads to runaway H⁺ flux (3000 nm² s⁻¹) faster than maximum solar photon flux (1500 nm² s⁻¹). As a result, the SiO₂ membrane can act as an enhanced charge-carrier platform, where pushing artificial photosynthesis beyond mass (H⁺) transfer limits, and thus making it scalable to the unprecedented level of several terawatts.

**Fabrication and Characterization of Two-Phase Nanocomposites by Atomic Layer Deposition of Metal Oxides into Mesoporous Thi-Film Oxide Ceramics**

Dominic Boll¹², Erdogan Celik³³, Matthias T. Elm³³ and Torsten Brezesinski¹¹;¹ Karlsruhe Institute of Technology, Germany; ²Technische Universität Darmstadt, Germany; ³Justus-Liebig-Universität Giessen, Germany

Solid electrolytes are one of the key parts in the field of modern energy technology. While zirconia based oxides are used as electrolytes for e.g. solid oxide fuel cells (SOFC) or oxygen sensors, ceria-based solid solutions are promising for applications for electrode materials in SOFCs and heterogeneous catalysts. Great efforts are made to enhance the electrical and / or the ionic conductivity of these solid electrolytes. The transport properties of these oxides can be altered by varying the composition or by nano- and microstructuring the materials. For the later, the primary reason is the increased density of interfaces and/or surfaces. In recent years, enhanced conductivity in nanostructured oxides compared to their bulk counterparts has been observed, but the underlying mechanisms are still not fully understood. This work aims at evaluating the surface effects on the transport properties of nanostructured thin film oxide ceramics. Therefore, a suitable route to produce single-phase mesoporous thin films and two-phase-nanocomposites thereof has to be established.

In this work, we present a method to prepare two-phase nanocomposites made of different types of oxides. The method of Atomic Layer Deposition (ALD) was used to deposit a thin layer of different oxides, e.g. Al₂O₃ or TiO₂, into a mesoporous thin film of yttria-stabilized zirconium oxide (YSZ). Thin porous films were synthesized by an evaporation-induced self-assembly (EISA) process using the dip coating method. Following this route, a mesoporous film of 8mol% YSZ was produced with a pore size diameter of 18 nm and a well-ordered pore structure. This porous film was used as the host material for the Atomic Layer Deposition. The process of ALD is so far the best technique to coat a three-dimensional structure having a high-aspect ratio with a thin, homogeneous and conformal layer along with highly precise thickness control. Up to date, there are only few studies about an ALD process into ordered mesoporous structures. In this context, a new ALD process is established to coat the three-dimensional surface structure of a highly ordered mesoporous thin film. Processing parameters were optimized to enhance the diffusion of the precursor molecules through the entire mesoporous network. The characterization of the coated mesoporous film was done by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray reflectometry (XRR) was used to measure the growth rates of this specific ALD process. To ensure a complete coating on the surface throughout the entire mesoporous film, a cross-section of the film was measured by atom-probe tomography (ATP). Finally, the effect of the surface coating on the transport properties were investigated by impedance spectroscopy. The modification of the pore surface structure was found to affect the conductivity of the mesoporous thin film.

**Zinc Oxide Nanostructure Synthesis on Si(100) by Vapor Phase Transport and the Effect of Antimony Doping on pHotoelectric Properties, Morphology and Structure**

Tarek M. Trad, Parker Blount and Zuleyma Romero; Sam Houston State University, United States

Zinc Oxide (ZnO) has been shown to exhibit semiconducting and piezoelectric dual properties. This has led to a
large commercial demand of ZnO for optoelectronics that operate at the blue-ultraviolet regions. Consequently, varying techniques have been devised to create different nanostructures of ZnO. Here, the single step synthesis of ZnO nanostructures was performed on Si(100) substrates with a thin ZnO seed-layer. A modified chemical vapor deposition (CVD) method was developed to accomplish the structure formation. Sb doping of the structures in the gas phase was performed to study its effects on structure and optoelectronic properties. Different structures were realized including nanofilaments, nanoparticles, microflowers, nanorods, and nanocolumns. Only nanorods/columns are shown in this work. Morphology was examined using scanning electron microscopy (SEM). Energy-dispersive X-ray spectroscopy (EDS) and X-ray powder diffraction (XRD) were used for structural studies. Optoelectronic properties were explored using room-temperature photoluminescence (PL) spectroscopy. PL data show the relative increase in the number of defects and decline in crystal quality upon dopant introduction. Some structural defects might be attributed to the diffusion of Sb ions into the lattices of ZnO, replacement of Zn by Sb, and ionic radii difference. These stacking faults are most likely the reason behind the dominance and broadening of DLE peak.

**FF05.06.19**

**Good Step Coverage of Iridium Metal Films by Spray CVD**

Yoshiyuki Seki¹, Yutaka Sawada¹, Hiroshi Funakubo², Kazuhisa Kawano³ and Noriaki Oshima³; ¹Tokyo Polytechnic University, Japan; ²Tokyo Institute of Technology, Japan; ³TOSOH Corporation, Japan

Metal Ir films have been widely used as electrodes, especially for oxide capacitor including ferroelectric random access memory. For these applications, chemical vapor deposition (CVD) is a most promising process because three dimensional structure capacitor structures are essential to increase the capacitor area on the limited foot print of the substrate. We developed spray chemical vapor deposition, in which CVD source was spray on the heated substrate in air [1-4]. By using this process, three dimensional films of indium tin oxide and Ru with good step coverage were successfully obtained on the trenched substrates. In the present study, we apply this spray CVD to Ir metal films deposition using novel of Ir precursor, (1,3-cyclohexadiene)(ethylcyclopentadienyl)iridium, Ir(EtCp)(CHD). Ir(EtCp)(CHD) is a liquid source at room temperature and exhibited enough vapor pressure (0.1 Torr/75°C), excellent volatility and adequate decomposition temperature. It is already ascertained that Ir metal films grown using Ir(EtCp)(CHD) showed shorter incubation time and higher nucleation density than those of films using Ir(EtCp)(CHD)[5]. Ir(EtCp)(CHD) was dissolved in ethanol and the concentration was fixed at approximately 0.05-0.1 mol/l. The solution was sprayed manually on the substrates in air with an inexpensive atomizer used for cosmetic purposes. The substrates were heated on a hot plate at 200–430 °C. We used non-flat Si substrates (patterning SiO₂/Si, opening depth: 1 μm, opening sizes: less than 1 μm) and plane SiO₂/Si substrates. Film deposition was ascertained on SiO₂/Si substrate at 240–430 °C and deposition rate increased with the deposition temperature, but was saturated above 330 °C. Obtained films consist of Ir metal without any oxide impurity irrespective of the deposition temperature. Films tend to orient to (111) with increasing deposition temperature. Resistivity of these Ir metal films was on the order of 10⁻⁶ Ωcm, which was on the same order with that of bulk Ir metal. Good step coverage was observed for Ir metal films deposited at 270 and 330 °C. This shows that simple spray CVD process deposited in air is a good way to deposit Ir metal films with good conductivity and step coverage.


**FF05.06.20**

**Direct Growth of Single-Layer Terminated Vertical Graphene Nanosheets on Germanium Using Plasma Enhanced Chemical Vapor Deposition**

Abdulrahman S. Al Hagri and ChunYu Lu; Khalifa University, United States

Vertically aligned graphene nanosheet arrays (VAGNAs) exhibit large surface area, excellent electron transport properties, outstanding mechanical strength, high chemical and thermal stability, and enhanced electrochemical activity, which makes them highly promising for application in supercapacitors, batteries, fuel cell catalysts. It is shown that VAGNAs terminated with a high-quality single-layer graphene sheet, can be directly grown on germanium by plasma enhanced chemical vapor deposition without an additional catalyst and at low temperature, which is confirmed by high-resolution transmission electron microscopy and large-scale Raman mapping. The
uniform, centimeter-scale VAGNAs can be used as a surface-enhanced Raman spectroscopy substrate providing evidence of enhanced sensitivity for rhodamine detection down to $1 \times 10^{-6}$ mol L$^{-1}$ due to the existed abundant edges.

**FF05.06.21**

**Growth Yield Variation of Single-Walled Carbon Nanotubes Inside a Horizontal Chemical Vapor Deposition System** Sung-II Jo and Goo-Hwan Jeong; Kangwon National University, Korea (the Republic of)

Single-walled carbon nanotubes (SWNTs) have been expected to be applied to various fields such as nanoelectronic devices, transparent conducting films, energy devices and sensors due to their outstanding physical and chemical properties. A chemical vapor deposition (CVD) is the most popular method for SWNTs synthesis because of its simplicity on SWNTs synthesis process and easy control of process parameters. In general, most of the synthesis experiments have been performed in the central region of the reactor so far where temperature uniformity is guaranteed.

In this study, we report the result of detail investigation of the SWNTs synthesis yield depending on sample position in a horizontal CVD system. Methane and Fe thin films were used as feedstock and catalyst for SWNTs synthesis, respectively. Ultra high resolution scanning electron microscope (UHR-SEM) was used to confirm the synthesis yield variation of SWNTs along the axial distance of the reactor. The morphology and crystallinity of the synthesized SWNTs were evaluated by atomic force microscope and Raman spectroscopy, respectively. Main result of this study shows that the highest synthesis yield of SWNTs was observed at the rare region of the reactor not the central region. The results of this study are expected to be applicable to the synthesis of various nanomaterials using CVD process.

**FF05.06.22**

**Effect of Plasma Ignition on Growth Temperature Decrease of Single-Walled Carbon Nanotubes Using Plasma-Coupled CVD System** Sung-II Jo and Goo-Hwan Jeong; Kangwon National University, Korea (the Republic of)

Single-walled carbon nanotubes (SWNTs) have attracted much attention due to both their outstanding physical properties and their nanoscale dimensions. Although SWNTs can be obtained by several processes, the most prevailing method to control tube structure, growth direction, diameter, and chirality, would be a thermal chemical vapor deposition (TCVD). However, the high temperature operation of this method limits the industrial accessibility. Plasma-enhanced chemical vapor deposition (PECVD) is a well-known for growth temperature reduction although the SWNTs grown by PECVD are generally perpendicular to the substrate in conventional vertical chamber along the electric field line, which limits the further manipulation of SWNTs.

We here demonstrate the low temperature growth of SWNTs using a plasma-assisted TCVD system. The system is made of 1 inch horizontal quartz tube and composed of inductively coupled plasma (ICP) production region for efficient decomposition of feedstock and TCVD region for SWNTs growth region. The growth substrate installed at the center of the TCVD region and varied the distance from the plasma generation region to find avoid probable ion damages. We used iron thin film and ethylene gas as growth catalyst and feedstock, respectively. Optical emission spectroscopy was used to analyze ion and active species in the plasma with respect to the process parameters, such as plasma power, pressure, gas composition, and distance from the plasma formation region. The detail of the results will be discussed at the meeting.

**FF05.06.23**

**Synthesis of Bulk 2D Layered Silver Selenide (Ag$_2$Se) Using Chemical Vapor Deposition as a Potential Candidate for Oxygen Reduction Reaction** Konar Rajashree$^1$, Suparna Das$^1$, Eti Teblum$^1$, Gilbert D. Nessim$^1$ and Alex Schechter$^2$; $^1$Bar Ilan University, Israel; $^2$Ariel University, Israel

Bulk 2D layered materials are promising material platforms to study their properties, surfaces, chemical reactivity, as well as potential applicability in diverse applicative areas. Some of the most commonly researched 2D layered materials under this category are: graphene, boron nitride, black phosphorous, and transition metal chalcogenides (TMCs).

Among the TMCs, silver selenide is of particular interest because this promising Al$_3$B$_2$VI$_2$semiconductor can be used to make solid-state electrochemical sensors, solar cells, magnetic field sensors, optical filters, etc. [1]. Some of the established synthesis methods include the use of micro-emulsion mixing, microwave radiation, sonochemistry, and
Electrochemical potential to drive the decomposition of selenium and/or silver compounds to form Ag₂Se [2]. Although all these synthetic approaches are significant in their respective fields, in our case, we have synthesized Ag₂Se using an atmospheric pressure chemical vapor deposition (AP-CVD). We grew the material on a silver foil in an inert atmosphere, using elemental selenium as the precursor. We characterized the final product using XRD, HR-SEM, TEM, and Elemental Mapping (EDX) to ascertain its stoichiometry and we concluded that we obtained β-Ag₂Se (low-temperature phase). To our knowledge, this is the first report of β-Ag₂Se grown using AP-CVD with this specific morphology to be tested as a prospective candidate for oxygen reduction reaction (ORR). Since any non-platinum catalyst is always considered a viable and cheaper alternative, our idea behind the preparation of this material was to test it for ORR and to find out its applicability towards fuel cells. From the linear sweep voltammograms (LSV), we observed that β-Ag₂Se exhibited -0.2 mA current in 1 M KOH solution at 400 RPM, which is quite higher than that observed for 20 wt.% Pt/C, i.e., -0.2 mA. Again with increasing rotating speed of the rotating disc electrode (RDE), we saw that the current density for both the studied catalysts increased due to the effect of higher mass transfer to the working electrode. Furthermore, our studied catalyst, i.e., β-Ag₂Se exhibited -0.55 mA current in 1 M KOH solution at 2400 rotations per minute (RPM), whereas commercial Pt/C shows -0.2 mA current under the same conditions. These encouraging results point to the unique structural 2D layered morphology of β-Ag₂Se to be responsible for the improved electrocatalytic activity towards ORR in the alkaline medium compared to that of the state-of-the-art cathode catalyst Pt/C.

References:

FF05.06.24
Carbon Nanotubes Growth on TiSiN Barriers via Plasma Enhanced CVD—Analysis of the Physical and Chemical Processes and Modeling Ahmed H. Andalouci1, Ivaylo Hinkov2, Salim Mourad Cherif1 and Samir Farhat1; 1Université Paris 13, France; 2Département de Génie Chimique Université de Technologie Chimique et de Métallurgique, Bulgaria

Aligned multiwall carbon nanotube (CNT) arrays on conductive substrates have been envisaged as interconnects in microelectronics and ultra-high density magnetic information storage material in spintronics. Such applications require the CNTs to be grown vertically aligned, and in direct contact, to conductive substrates [1]. This could be achieved by controlling the physical aspects related to the dewetting of the metal catalyst leading to the formation of a stable assembly of self-organized nanoparticles suitable to catalyse CNT growth. In addition, the use of plasma enhanced chemical vapour deposition (PECVD) allows controlling the gas phase chemistry. In these directions, we propose a simple and reliable fabrication approach to produce controlled cobalt (Co) magnetic nanoparticles by solid state dewetting of ultra-thin Co films deposited on a conductive titanium silicon nitride (TiSiN). TiSiN layers act as barriers to limit diffusion into the bulk of the substrate. Moreover, the low surface energy of TiSiN favours catalyst dewetting, thereby improving CNT forest density and verticality. To control gas phase chemistry, (CH₄/H₂/O₂) mixture gases were decomposed over the catalyst nanoparticles after their dewetting. The addition of oxygen leads to the formation of water H₂O and OH radicals that improves CNT quality.

Experimentally, we achieved the dewetting of cobalt films with thicknesses h=1, 2 and 3 nm by thermal heating at 750°C followed by hydrogen plasma treatment. This resulted in assembly of nanoparticles with quasi spherical shapes and well-controlled size distribution. The mean particle size (D) have been measured from scanning electron microscopy and correlated with the initial film thickness, namely D [endif]--> 6h. Moreover, using the TiSiN barrier allowed obtaining homogeneous nanoparticle distribution with density as high as ~ (4.2 ± 0.1) ×10¹ⁱ cobalt nanoparticles/cm². This value is smaller than the one reported for iron ~ (5.1 ± 0.1) ×10¹² [1]. However, cobalt is more stable regarding oxidation and thus presents a higher magnetization at saturation. After addition of (H₂/CH₄/O₂) (90:10:x) sccm at 10 mbar, PECVD allowed to obtain vertically aligned multi-walled nanotubes. Oxygen flow rate x was varied from 0 to 4 sccm and correlated to the CNT growth rate and surface density. At 2 sccm of oxygen, ultra-dense (10¹¹ nanotubes/cm²) vertically aligned CNTs with well graphitized walls as characterized by high resolution transmission electron microscopy (HRTEM) were obtained. Tow numerical models were proposed to understand the experimental results. As a first approximation, the plasma is described by spatially averaged bulk properties in (0D). This model extends the classical chemistry formulation to nonequilibrium plasma reactors for CNT growth from 134 species in (C,H,O,e-) system involved in 471 gas-phase reactions [2]. The small computational demands of (0D) model, allows kinetics sensitivity analysis and permit the identification of dominant
reactions and key species depicting CNT growth. The reduced chemical scheme was then used within (2D) model including 22 gas species and 100 homogeneous reactions. Both gas and surface chemistries were taken in consideration to calculate CNT growth rate using Surface-Chemkin and Ansys-Fluent softwares. Surface-reaction mechanism specific to cobalt under (H2/CH4/O2) CVD plasma is proposed and considers 16 surface species and 81 surface reactions involving both gaseous species impinging on the surface, adsorbed molecules, atoms and free sites. The bulk material considered is CNT, with mass density of 2.2 g/cm3 and site density ~3.6 ×10^10 moles/cm^2 as estimated from measured nucleation surface density, CNT diameter and number of walls. Optimal CNT rate was found for 2 sccm O2 in good agreement with experimental measurement.


**FF05.06.25**

**Layer Control in Asymmetric CVD Graphene Growth** Haozhe Wang¹, Wei Sun Leong¹, Zhenpeng Yao², GangSeob Jung¹, Qichen Song¹, Marek Hempel¹, Tomas Palacios¹, Gang Chen¹, Markus J. Buehler¹, Alan Aspuru-Guzik²,³ and Jing Kong¹; ¹Massachusetts Institute of Technology, United States; ²Harvard University, United States; ³University of Toronto, Canada

Chemical vapor deposition (CVD) is the most promising approach to obtain high-quality, large-area graphene. Recently, bilayer graphene has attracted massive interests owing to its promising applications as twistronics, superconductors, etc. To obtain graphene layers beyond monolayer, counter-intuitive asymmetric CVD growth is developed to break the original self-limiting nature of growth on copper substrate (Nat Nano 11, 426 (2016)). However, the layer control in graphene remains challenging and lack of study. Researchers fail to obtain pure, high-quality large-scale bilayer graphene and have thus perceived that thicker graphene impurities are inevitable, after more than one decade of research efforts.

Here, we report a technique to control the graphene layer number in asymmetric CVD growth. Owing to counter-intuitive growth principle, we proposed a new physical quantity, named “interface adhesive energy”, that can be used to predict the CVD growth behavior. We show that, through first-principle calculations, this new physical quantity can used to control the resulting graphene layer number. Based on these theoretical understandings, we have devised a new CVD strategy, which results in layer control in asymmetric CVD bilayer graphene growth. Through systematic materials characterization studies (SEM, XPS, Raman, STEM, and AFM), we found that the growth of CVD bilayer graphene on copper catalyst consists of several major steps: (i) dehydrogenation of carbon precursor (i.e. CH₄) at the Cu interior resulting in free carbon atoms, (ii) bulk diffusion of carbon atoms from inner to outer surface of the Cu pocket, (iii) interface diffusion of carbon atoms between the 1stLG and Cu exterior, and (iv) nucleation of graphene adlayers (i.e. 2ndLG, 3rdLG, 4thLG etc.) or growth continuation of the existing graphene layer (i.e. 2ndLG). Through Raman studies, we confirmed that our bilayer graphene is of AB stacking with small twisting angles (θ = 0 - 5°), namely quasi AB-stacked bilayer graphene. Specifically, our samples exhibit 4 Raman characteristic signatures: the positions of G bands ~1580/cm, the positions of 2D bands ~2680/cm, 2D/G intensity ratio ~1, and 2D bands’ full-width-half-maximum ~58/cm. We also proposed an unsupervised learning approach to manage large-volume Raman data. Our artificial-intelligence-assisted Raman analysis approach is very useful for graphene samples in identifying regions of different stacking orders and layer numbers.

In summary, by introducing the concept of interface adhesive energy, we managed to prevent the growths of thicker graphene islands of impurities and realized the long-sought layer control in graphene CVD growth. Confirmed by artificial-intelligence-assisted Raman analysis, the obtained graphene layers were in AB stacking with small twisting angles. Our discoveries on well-controlled growth and coherent characterization of large-area graphene are essential for unlimited innovations based on two-dimensional materials, owing to their electrical, optical, mechanical and chemical properties.

**FF05.06.26**

**Comparative Study of the Effect of Thermal Processes and Rapid Thermal Annealing on the Photoluminescent Emission of Amorphous Silicon Carbide (a-SiC:H)** Maricela Meneses, Mario Moreno, Alfredo Morales, Alfonso Torres, Pedro Rosales and Javier de la Hidalga; National Institute of Astrophysics, Optics and Electronics, Mexico

Nowadays device applications of amorphous silicon carbide (a-SiC:H) include light emitting diodes,
phototransistors, photodetectors, MEMS and solar collectors. The a-SiC:H films have different optical, electrical and structural characteristics depending on the gases mixtures and the deposition technique used. The plasma enhanced chemical vapor deposition (PECVD) technique has several advantages, as its low temperature of deposition (< 200°C), which implies the use of different substrates, as plastics and metal foils, as well this technique produce uniform films.

However also it has been reported that as deposited a-SiC:H films have instability and this could affect the photoluminescent (PL) emission of a-SiC:H films. One way to reduce the instability and defects is by thermal treatments. In conventional thermal treatments the films are exposed to high temperatures for long periods of time in an inert environment, while in the rapid thermal annealing (RTA) the substrates are subjected to very short periods of time (seconds).

In this work we present the effect of thermal processes and rapid thermal annealing on the PL emission of amorphous silicon carbide (a-SiC:H). The a-SiC:H thin films were deposited at a substrate temperature of 150 °C by PECVD, silane (SiH4) and methane (CH4) gases were used. The rapid thermal annealing (RTA) was carried out with a ramp up of 50°C/s at 500 °C for 40 seconds and with a ramp down 120 seconds. The conventional thermal treatment was done with a temperature of 1100 °C for 5400 seconds in forming gas environment.

Our results shows that the a-SiC:H films as deposited, present emission in orange region of the visible spectrum, while the films treated with RTP have an increase in the PL emission intensity, with an emission in the visible region (in the blue color), that increment is attributed to radiative centers related to oxygen. On the other hand with conventional thermal processes the emission is decreased with respect to the deposited films. The above is related to the structural change suffered by the films when are exposed to thermal treatment process. Finally, our results show that RTA is more efficient than conventional thermal treatments in order to increase the PL emission of a-SiC:H films, which is of interest for light emission applications.

FF05.06.27
The Effect of Different Ti Doping Ratios for ZnO Active Layer Thin-Film Transistors Kelsea Yarbrough, Sangram K. Pradhan and Messaoud Bahoura; Norfolk State University, United States

Flexible and transparent electronics have presented a groundbreaking era for the world of display technologies. Zinc oxide (ZnO) amongst the popular transparent conducting oxides are the most commonly used semiconductor for transparent devices, such as liquid crystal displays, solar cells, transparent heaters, and etc. Liquid crystal displays most significant component are thin film transistors (TFT). Modern day TFTs are produced with an active layer of either hydrogenated amorphous silicon(a-Si:H) or indium gallium doped zinc oxide (IGZO). A-Si:H will soon be out shadowed by doped ZnO counterparts due to its minimal channel mobility. IGZO contains indium, which is a toxic, expensive, and whose supply will not be enough for demand by 2020. The indium free oxide-based channel material such as titanium doped zinc oxide (TiZnO) has been immensely studied due to its good electrical and optical properties. High quality TiZnO thins films were grown by atomic layer deposition on n-type silicon, glass, and sapphire substrates. The films were varied with different dopant ratios to properly evaluate and analyze the effect of Ti substitutional atoms in the crystal lattice. The effect of Ti content on microstructures, surface morphology, electrical properties, and optical properties of the films were investigated by Atomic Force Microscopy (AFM), X-Ray Diffraction, Ultra-violet Visible Spectroscopy (UV-VIS), and Hall Effect Measurement System (HMS). AFM provided thin films roughness, grain size, and surface morphology for glass, silicon, and sapphire thin films. XRD provided the effect of how different Ti substitutional atoms doping ratios invaded the crystal lattice. UV-VIS was performed to investigate the high optical transparency for the glass substrates. HMS provided the electrical mobility, conductivity, and resistivity for the active layer of TFT TiZnO thin films. The present work will provide valuable scientific input for TiZnO thin films for the advancement of TFT devices.

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FF05.06.28
Thickness Gradient Film Formation by Spatial Atomic Layer Deposition for High-Throughput Screening of MIM Diodes Abdullah Alshehri1,2, Khaled Ibrahim1, Kissan Mistry1, Jhi Y. Loke1, Mustafa Yavuz1 and Kevin Musselman1; 1University of Waterloo, Canada; 2Prince Sattam Bin Abdulaziz University, Saudi Arabia

Atmospheric pressure spatial atomic layer deposition (AP-SALD) is a fast and scalable thin film deposition
technique that operates in atmospheric pressure. It has the ability to control the film thickness in the atomic scale range and produce uniform and pinhole-free films at modest temperatures (e.g. 80-200°C). AP-SALD is implemented to deposit an insulator film with a thickness gradient as opposed to a film with uniform thickness. To obtain a thickness gradient of metal oxide layers such as Al2O3 or ZnO on Si or glass substrates, we adjusted the distance between the deposition reactor head and the substrate to be 100µm on one side and 150, 190, or 230 µm on the other side. The head-substrate separations used here are sufficiently large that some mixing of the precursors occurs in the gas-phase, resulting in some chemical vapour deposition (CVD). By varying the head-substrate separation across the substrate, the amount of CVD was varied, resulting in different deposition rates across the substrate. To demonstrate the applicability of this technique, combinatorial MIM diodes are fabricated, i.e. diodes with many different thicknesses can be fabricated on a single substrate. The diode performance showed variation with aluminum oxide thickness and the optimal thickness is identified.

FF05.06.30
Vapor-Based Synthesis of Poly(ethylhexyl acrylate-co-acrylic acid) Thin Films as Pressure Sensitive Adhesives Huseyin Sakalak1, Kurtuluş Yılmaz2 and Mustafa Karaman2; 1Selcuk University, Turkey; 2Konya Technical University, Turkey

Pressure sensitive adhesives (PSA) are materials that can bind different surfaces together. They can easily adhere to various surfaces at a light pressure at room temperature. Common acrylate monomers which are used to produce PSA materials are ethylhexyl acrylate (EHA), methyl methacrylate (MMA), and acrylic acid (AA). PSAs based on acrylate polymers are widely used because of their useful properties such as high bonding strength, easiness of application to various surfaces, and low manufacturing cost. Commercially, PSAs are deposited using wet techniques. In this study, P(EHA-co-AA) copolymer thin films were deposited on different surfaces using initiated chemical vapor deposition (iCVD) technique. iCVD is an all-dry, solvent-free vapor deposition strategy for coating of polymers from their corresponding monomers. Use of initiator di-tert butyl peroxide (TBPO) together with the monomer precursors improved the deposition rates substantially while decreasing the activation energy required to carry out the surface polymerization reactions. Acrylic acid was chosen for its suitable polarity and ethyl acrylate was chosen for its hydrophobicity and fluidity. Furthermore, because of its low glass-transition temperature (Tg) EHA acts as a plasticizer in the copolymer film. P(EHA-co-AA) copolymers were synthesized using different ratio of EHA to AA flowrates in the reactor feed to achieve tunable adhesive properties. The adhesive properties of the obtained films were characterized by mechanical tensile tester. XPS, FTIR and SEM analyzies were performed to characterize the chemical structure, composition and surface morphology of the as-deposited nano-adhesive copolymer films. DSC analysis was used to reveal the Tg of the as-deposited copolymer films. It was found that highly homogeneous thin films of P(EHA-co-AA) can be obtained by iCVD with high retention of EHA and AA monomer functionalities. Very high deposition rates up to 400 nm/min were observed. As-deposited materials possessed high adhesive properties, which could be tuned by changing the comonomer ratios in the reactor feed.

FF05.06.31
VACNT/Al2O3 Nanocomposite Fabrication via Novel Water-Assisted Chemical Vapor Deposition Followed by Atomic Layer Deposition Lev Rovinsky1, Barun K. Barick2, Tamar Segal2 and Noa Lachman1; 1Tel Aviv University, Israel; 2Technion–Israel Institute of Technology, Israel

Nanocomposite materials exhibit properties unreachable by conventional materials, as the nanoscale of the fillers allows for size-dependent effects including enhance mechanical and transport properties. However, these exact scales also complicate fabrication making traditional fabrication methods incompatible with ultra-high surface area and the van der Waals forces it creates. By combining chemical vapor deposition (CVD) with atomic layer deposition (ALD), bottom-up approaches, one can circumvent the difficulties plaguing the field of nanocomposites. Alumina (Al2O3) exhibits excellent chemical and thermal stability and very good resistance to wear. However, low thermal and electrical conductance could be both an asset and a liability, sometimes in the same application. These properties can be tailored by incorporating highly thermally and electrically conductive carbon nanotubes (CNT). With that said, in order to conserve the anisotropic properties of CNT in the final form of the material, they must be aligned.

In this work, a vertically aligned carbon nanotubes (VACNT)/alumina nanocomposite material was fabricated. VACNT arrays were grown via water-assisted CVD and then coated with alumina via ALD. Before the ALD step, functionalization in the form of controlled oxidation was done in order to enhance the adhesion between the phases without destroying the anisotropicity. The synergistic effect of alumina and carbon nanotubes allows for improved
thermal stability of the nanocomposite. Properties in the axial and transverse directions of the nanocomposite will be explained.

**FF05.06.32**

**A CsVO3/Quasi-2D Oxide Heterostructure by Chemical Vapor Deposition**  
Saloni Pendse and Jian Shi;  
Rensselaer Polytechnic Institute, United States

As strongly correlated oxides continue to be studied for next generation electronic devices, van der Waals epitaxy is gaining popularity as an effective technique to grow such oxides while ensuring a low-density of misfit and threading dislocations as well as minimum interdiffusion at the interface. In this work, we report an exception to this trend. While attempting to grow VO2 via chemical vapor deposition on CsBiNb2O7, a layered Dion-Jacobson perovskite, we observe the epitaxial growth of CsVO3 instead. This points to an aspect of van der Waals epitaxy not encountered so far - the possibility of an interaction between surface ions of van der Waals epitaxy substrates and the growing material. We confirm the growth of CsVO3 by Raman mapping and reveal the epitaxial relation between CsVO3 and CsBiNb2O7 via electron microscopy diffraction. Since CsVO3 is an excellent broad-band emitting phosphor currently being explored for use in rare-earth free white light-emitting diodes, we also probe photoluminescence properties of the epilayer and model the probable electronic structure. Based on our study, we suggest that the substrate – oxide chemistry may need to be considerably taken into account while designing and implementing van der Waals epitaxy in correlated oxide systems.

**FF05.06.33**

**Role of Gold and Dielectric Spacer in the Manufacture of Electroluminescent Devices Based in Silicon Quantum Dots**  
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With the purpose of increasing the efficiency and control of light emission from silicon quantum dots (SiQDs), several research groups have used different configurations of nanoparticles and nanostructures made by using noble metals (Au, Ag) near the silicon quantum dots [1,2]. A shared feature in the coupled structures reported in those previous works is that all of them have a spacer between the metal and the SiQDs. In turn, the spacer must be a dielectric and must have a well-defined thickness ranging from 10 to 20 nm.

In this work, we use nanolayered structures like those mentioned previously, to manufacture a light emitting device (LED) with a metal-insulator-semiconductor (MIS) configuration. SiQDs embedded in silicon nitride acted as luminescent films and pure silicon nitride serve as a dielectric spacer. Both films were deposited by Remote Plasma Enhanced Chemical Vapor Deposition (RPECVD). Meanwhile, gold nanoparticles (AuNPs) were deposited by sputtering on a p-type silicon substrate.

We evaluate the electroluminescent (EL) spectral enhancement factor which is defined as the ratio of EL intensities of samples with AuNPs and their references without AuNPs. In one of our samples, this ratio at 27.7 mA shows a maximum EL enhancement factor of 7 at about 510 nm and 5.4 at about the maximum EL intensity peak (~600 nm). It is worth to notice that the higher EL enhancement factor in these structures is close to the absorption peak of gold nanoparticles at 538 nm. Therefore, our devices allowed us to prove that there is indeed an electroluminescent enhancement when the appropriate AuNPsSpacer-SiQDs configuration is used.

We have found that EL enhancement may indeed be due to a plasmonic coupling. Nevertheless, we also identify that the presence of gold nanoparticles in the EL device allow a more efficient distribution of charge carriers towards the luminescent centers (SiQDs). Consequently, we conclude that more than one mechanism should be involved in the optimized electroluminescence.

**FF05.06.34**

**Influence of Active Nitrogen Species on InN Growth and Structural Properties in Migration-Enhanced Remote Plasma MOCVD**  
Zaheer Ahmad, Mark Vernon, Garnett B. Cross and Alexander Kozhanov; Georgia State University, United States

We report on the influence of various nitrogen plasma species on the growth and structural properties of indium nitride in migration-enhanced remote-plasma metalorganic chemical vapor deposition. The ion energy and flux have been determined via the atomic emission spectroscopy by the analysis of emission spectra recorded at the growth
surface. The atomic nitrogen ions’ flux has been found to have a significant effect on the growth rate as well as the crystalline quality of indium nitride films. Results of Raman spectroscopy, infrared reflectometry, atomic force microscopy, and charge transport Hall measurement are discussed.

**FF05.06.35**

**Plasma-Enhanced Atomic Layer Deposition of Vanadium Dioxide (VO2) Using TEMA V and Oxygen Plasma**

Adnan Mohammad, Saidjafarzoda Ilhom, Deepa R. Shukla and Necmi Biyikli; University of Connecticut, United States

Vanadium dioxide (VO2) exhibits a unique low-temperature (~70 °C) phase-transition behavior due to a structural change from monoclinic phase (low temperature) to a tetragonal rutile phase structure (high-temperature). Moreover, this phase-transition is ultrafast (< ps) and reversible, which makes VO2 attractive for a wide variety of applications. Also known as metal-insulator transition (MIT), this property can be effectively used in optical and electrical switches, RF-microwave switches, tuneable plasmonic and metamaterial systems, and smart windows. Among the synthesis methods used to deposit VO2 films, chemical vapor deposition, reactive electron-beam evaporation, reactive magnetron sputtering, pulsed-laser deposition, sol-gel methods, and hydrothermal processes have been reported. Atomic layer deposition (ALD) of VO2 films have relatively recently been of interest, mainly due to it’s precision thickness control, large-area uniformity, and low-temperature compatibility. Majority of VO2 ALD research focused on thermal-ALD based growth recipes with either ozone or water vapor are used as the oxygen co-reactant and reported film properties as a function of post-deposition annealing.

In this work, we report on the low-temperature self-limiting growth of VO2 thin films using tetrakis(ethylmethylamino)vanadium(IV) (TEMAV) as metal precursor and oxygen plasma as co-reactant in a plasma enhanced atomic layer deposition system. To the best of our knowledge, this is the first study on the plasma-ALD of VO2 via oxygen plasma. Our main motivation behind using O2 plasma is to reduce the necessary substrate temperature via energetic oxygen radicals and gaining additional degree of freedom in adjusting the film growth conditions through plasma variables such as plasma power, exposure time, O2 partial pressure and plasma gas composition.

VO2 films are deposited on Si(100) samples, which went through a conventional solvent cleaning process just before loading into the reactor chamber for the growth process. Ultratech Fiji G2.0 Plasma-ALD system has been used to carry out the deposition experiments. The substrate temperature has been set to a fixed temperature of 150 °C, mainly due to the narrow temperature window where TEMA V precursor has reasonable vapor pressure and is below the thermal decomposition temperature. The unit ALD cycle used for the VO2 deposition consists of 30-100 ms TEMA V dose which is carried into the reactor via 20 sccm Ar-carrier flow, Ar-purge for 10 s, O2 plasma (50 sccm) at 300W for 10 s, and finally another 10 s of Ar purge. In addition, the TMA V precursor is heated at 115 °C in order to provide sufficient amount of precursor vapor into reactor chamber. The total number of ALD cycles used for film deposition is 300. VO2 film thickness is checked by ex-situ ellipsometry after deposition. The film thicknesses measured for TEMA V pulsing times of 30 and 100 ms are 15.5 and 20.5 nm, respectively. The extracted refractive index ranges within 2.25 - 2.35, while the growth per cycle (GPC) values varied from ~0.5 Å to 0.7 Å. The obtained results agree fairly well with previously published reports in the literature. X-ray diffraction measurements as a function of annealing temperature and ambient will be presented along with the detailed temperature-dependent electrical characteristics of the synthesized VO2 films.

**FF05.06.36**

**Real-Time In Situ Monitoring Atomic Layer Doping Processes for Group-III Doped ZnO Layers—Super-Cycle Versus Co-Dosing Approach**

Adnan Mohammad, Saidjafarzoda Ilhom, Deepa R. Shukla, Md Tashfiq Bin Kashem, ABM Hasan Talukder, Helena Silva, Ali Gokirmak, Brian Willis and Necmi Biyikli; University of Connecticut, United States

We report a comparative study investigating different atomic layer doping (ALDp) strategies to achieve effectively doped ZnO layers. The main motivation of our study is to gain insight into how the surface reactions are affected during the relatively conventional super-cycle approach and less-used co-dosing method. To achieve real-time information, we have carried out in-situ ellipsometric measurements which reveal sub-angstrom film thickness changes as a result of individual chemisorption, ligand exchange, and incorporation reactions. Aluminum-doped ZnO (AZO) has been studied as the material of interest, which finds a wide range of use in solar cells and
transparent/flexible electronics as transparent conducting oxide layers.

Thermal atomic layer deposition (ALD) with diethylzinc (DEZ) and trimethylaluminum (TMA) were used as the metal precursors for ZnO film growth and Al-doping, respectively, while H2O was used as the common co-reactant. We experimented conventional sequential or super-cycle approach and simultaneous or co-dosing methods to form AZO layers with the target of reaching the highest possible conductivity. To the best of our knowledge, the co-dosing approach has not been studied or reported for AZO layers which motivated us for this systematic study. The deposition recipe used for AZO film growth is as the following: DEZ pulse or TMA pulsing for 15 ms; nitrogen purging at a flow of 20 sccm for 10 s; de-ionized water pulse of 15 ms as a co-reactant; nitrogen purging at a flow of 20 sccm for 10 s. The substrate temperature was varied as 100, 150, and 200 °C to understand its impact on doping efficiency. Total number of ALD cycles used is 300 cycles for each film, where the super-cycle ratios were tuned from 1:10 to 1:50 and the priority pulsing of DEZ and TMA is changed for co-dosing experiments.

We have observed that the refractive index of the AZO films changed between 1.95 - 1.87, depending on the Al-doping ratio for super-cycle doped AZO films. However, AZO films doped with the co-dosing approach resulted in films with a refractive index of around 1.6, which very much resembles Al2O3 films. To double-check this result, DEZ is first pulsed shortly before the TMA pulse, however the result did not change, resulting in an Al2O3-like refractive index. This observation indicates that chemisorbed DEZ groups are being replaced by incoming TMA molecules and as a result, ZnO is converted into Al2O3. We have carried out detailed in-situ analysis of the surface reactions for both doping approaches and particularly the co-dosing method where ZnO-to-Al2O3 conversion is observed. The ellipsometric data is supported by x-ray photoelectron spectroscopy (XPS) which reveals the chemical composition and level of atomic doping concentrations. The co-dosing approach is further tested for other group-III element precursors such as triethylgallium (TEG), trimethylindium (TMIn), and triethylboron (TEB), and these experimental results will be presented as well.

**FF05.06.37**
Large-Area, Uniform Growth of Nanoporous Biocompatible Polymer by Pressure- and Flux-Controlled Vapor Deposition
Katelyn Ramsey, H M Azazul Karim and Joonhee Lee; West Virginia University, United States

Nanoporous polymers are emerged as important elements due to their potential applications utilizing controllable optical, mechanical, and microfluidic properties, such as biosensor, which bulk polymer cannot offer. Parylene-C has been used for various micro-electromechanical systems (MEMS) and optoelectrical devices due to its electrical insulation and optical transparency. Moreover, it is commonly used as an encapsulation layer in biomedical devices to take advantages of biocompatibility, low water absorption rate, and pinhole free conformal coating. Several methods were suggested to grow nanostructured parylene-C but still limited to a small area or difficult to control the porosity [1-2]. In this work, to overcome current limitations, we report the novel combinatorial approach of nanoporous parylene growth method by controlling process pressure and vapor flux. Commercial PDS2010 (Specialty Coating System) was modified with custom-designed 3D printed nozzles to provide the directional and localized vapor flux to the substrate, while other parameters are the same. With the elongated tip of nozzle geometry (rectangular) and in increased process pressure, the porous layers were formed due to the enhanced deposition rate. The uniform layers over the 4-inch diameter were successfully grown in the optimized nozzle design. Together with scanning electron microscopy observation, we also characterize the optical properties of the films with the spectroscopic ellipsometry tool for precise porosity measurement. Along with pressure- and flux controlled nanoporous polymer growth, potential applications and an outlook to the future will be discussed.


**FF05.06.38**
Control of Micro-Ring Generation of Fullerene Thin Films Using Mixed Solvent in Mist Vapor Deposition Method
Shigetaka Katori and Risako Taguchi; National Institute of Technology, Tsuyama College, Japan

The mist vapor deposition is one of the film formation technique of organic semiconductor materials that enables printed electronics. The liquid is ultrasonicated into particles of about 20 m in diameter, and sprayed onto the heated...
substrate. The evaporation rate of the solvent is controlled by the substrate temperature. At this time, innumerable micro droplet traces, that is, coffee rings are formed. In the solution process, this undesired structure are affecting the physical and electric properties of formed films. Similarly, in the spray method and the ink jet method, the formation of this coffee ring is one of the causes of deterioration in film quality as compared with vacuum deposition. We examined controlling the generation of micro-coffee ring in the mist deposition method by changing the evaporation rate of the solvent.

A bare fullerene was used as the organic semiconductor material. Two solvents having different boiling points were mixed and used as a solvent. A solvent with a high boiling point is A, a solvent with a low boiling point is B, and the mixing ratio is 20%, 25%, 30%. The difference between the boiling points of these solvents was about 80 degree. The substrate temperature during film formation was changed in the range of 120 to 300 degree. The surface morphology was observed by AFM, and ultraviolet spectroscopy (UPS) and XRD measurements were performed. When the substrate temperature was high a uniform coffee ring with a diameter of about 15-20 microns was formed at 300 degree regardless of the mixing ratio of the solvents. The surface roughness Rq was about 35 nm to 45 nm. On the other hand, when the film formation temperature was changed in the range of 180 to 210 degree, Rq was 7nm to 20 nm. Significant improvement of surface roughness, and no formation of coffee ring was observed in the solvent ratio of 30%

A variation was found in the HOMO level determined by the UPS measurement results due to the difference between the solvent mixing ratio and the film formation temperature. The HOMO level changed in the range of 5.7 eV to 6.26eV. The value of vacuum evaporated fullerene thin film is known to be 6.25 eV. When the mixing ratio of the high boiling point solvent was 25% and 30%, it showed a lower value than the HOM level of vacuum evaporation. On the other hand, when the mixture ratio of the solvent was 20%, the HOMO level equivalent to vacuum evaporation was shown. In particular, the surface roughness was low and the value was at the same level.

We controlled the generation of coffee ring and realized a thin film with the same roughness as vacuum deposition by changing the mixing ratio using high boiling point solvent and low boiling point solvent. Furthermore, by controlling the surface roughness, a thin film with a HOMO level equivalent to that of vacuum deposition was achieved.

**FF05.06.39**

Atomic Layer Deposition of Titanium Sulfide Thin Films and Its Oxidation in Ambient

Hochul Nam, Changdeuck Bae and Hyunjung Shin; Sungkyunkwan University, Korea (the Republic of)

We describe the atomic layer deposition (ALD) of titanium oxysulfide films. A new ALD chemistry of tetrakis(dimethylamido) titanium (IV) and hydrogen sulfide (H2S) is suggested for the synthesis of amorphous titanium sulfide layers. We found that the resulting films subsequently underwent oxidation upon reactions under ambient condition, resulting in titanium oxysulfide (TiO2-xSx). The resultant structures were analyzed by using X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy, indicative of the formation of TiO2-xSx. A combined study of Hall-effect measurements and Mott-Schottky analysis showed n-type semiconductor behaviors possessing a good conductivity. Optical properties testify that the present system has a moderate band gap in between the related binary end compounds such as TiS2 and TiO2

**FF05.06.40**

Conformal Coating of Freestanding Particles by Vapor-Phase Infiltration

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Three dimensional (3D) encapsulation of free-standing particles and powders by atomic layer deposition (ALD) remains a technical challenge. Current solutions, such as fluidized bed reactors, rotary tumblers etc, employ physical agitation to vary the orientation of the particle during the deposition process, thereby exposing all surfaces to the flowing precursors. As a result, these methods require large amounts of the material to be coated, with minimum working quantities typically on the order of 10s to 100s of mg. A technique for encapsulating static particles on substrates would enable the processing of small volumes of material (c.f. bulk powders), down to individual micro- and nano-particles.

Here, we demonstrate the coating on all sides of individual particles resting on an inert polystyrene film. Vapor-phase infiltration [1] is performed on a commercial ALD tool. During this process, organometallic precursors diffuse
through the inert polymer and lead to the growth of a target inorganic film on the particle’s surface, even on the bottom side that is in contact with the polystyrene. We examine the uniformity of the coating by cross-sectional transmission electron microscopy and measure its thickness for different numbers of infiltration cycles.

To demonstrate the usefulness of our technique, we coat III-V semiconductor microdisk particles with a thin layer of aluminum oxide. These microdisks support whispering gallery mode resonances and under optical pumping exhibit single-mode lasing. As free-standing particles, microdisk lasers have applications in biomedical imaging as intracellular probes [2]. We show that a thin (sub-10-nm) coating of aluminum oxide applied by our technique can improve the stability of lasing emission under continuous illumination in an aqueous environment compared with uncoated semiconductor disks.

Our technique is applicable to a range of particles, and generalizable to the growth of different inorganic films. Moreover, sequential vapor infiltration can be performed on a regular ALD tool without needing a special chamber or cleaning procedure.


**FF05.06.41**

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In this work, we have investigated the influence of critical growth parameters on the electrical and optical properties of indium nitride (InN) thin films grown at relatively low-temperatures via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD). InN films were deposited on Si(100) substrates using trimethyl-indium (TMI) and variants of Ar/N2/H2 plasma (N2-only, Ar/N2, and Ar/N2/H2) as the metal precursor and nitrogen co-reactant, respectively. ALD growth experiments have been performed within 50 - 150 W plasma power range and 160 - 240 °C substrate temperature. Dynamic in-situ ellipsometry was employed to observe individual ligand exchange events in real-time during the growth process. Additionally, ex-situ characterizations were done to identify the optical, structural, and chemical properties of the grown InN films. X-ray diffraction (XRD) results showed that only the samples grown at 200 and 240 °C with 100 W rf-power displayed single-phase hexagonal crystalline structure with peak intensity values increasing as a function of substrate temperature. Moreover, varying the plasma chemistry such as addition of H2 to Ar/N2 led to significant microstructural changes resulting in crystal quality degradation and porous films with high carbon content. As such, x-ray photoelectron spectroscopy (XPS) measurements are carried out to further understand the possible reactions taking place in the presence of H2 plasma. The electrical properties (resistivity, carrier density, and Hall mobility) of the polycrystalline InN films are analyzed using I-V and Hall measurements and will be presented in detail. Spectroscopic ellipsometer is utilized to study the spectral absorption characteristics of the optimal InN films to extract the corresponding optical band edge. Finally, with the highest quality InN films, a proof-of-concept visible/near-IR photodetector will be fabricated and tested for performance.

**FF05.06.42**
Growth Behavior and Electrical Properties of Atomic Layer Deposited SrTiO3 on Ge Substrate

Dong Gun Kim; Seoul National University, Korea (the Republic of)

Germanium (Ge) is an impending p-channel substrate to overcome the drain-current saturation problem of MOSFET due to its higher carrier mobility. However, the most critical challenge for adopting Ge as the substrate for the next generation p-MOSFET is the instability at high-k/Ge interfacial region. Strontium titanate, SrTiO3(STO) film was selected as the dielectric because its bulk dielectric constant is as high as 300. In this study, therefore, the growth behaviors and electrical properties of the atomic layer deposited (ALD) SrTiO3 films were studied with the various deposition temperature and annealing temperature. SrTiO3 films were deposited by using Sr(iPr3Cp)2 and Ti(CpMe3)(OMe)2 (Pr, Cp, and Me are propyl, cyclopentadienyl, and methyl groups, respectively) precursor on Ge substrates at 230°C and 370°C. 370°C deposition showed more initial excess deposition of Sr element than 230°C
deposition. Also, a higher growth rate was confirmed at the higher deposition temperature. For ex-situ crystallization, the STO films were annealed at the various annealing temperature ranging from 550-650°C for 5min by rapid thermal annealing. For the electrical analysis, Metal-Insulator-Semiconductor (MIS) capacitors were prepared by depositing TiN/Pt as the metal gate. An extremely high dielectric constant (~285) was confirmed from the slope of the equivalent oxide thickness (EOT) vs. physical oxide thickness (POT) plots. However, the quite high interfacial oxide thickness increased the total EOT values, requiring further interfacial engineering.

**FF05.06.43**
**Characteristics of 2D SnS2 as a Channel Layer in TFT Device**
Hyeongsu Choi, Hyunwoo Park, Namgue Lee and Hyeongtag Jeon; Hanyang University, Korea (the Republic of)

Recently, there were many researches on two-dimensional (2D) materials having semiconducting characteristics like transition metal dichalcogenides (TMDCs). These researches have mainly focused on the realization of original 2D materials characteristics through deposition process. However, representative TMDCs such as MoS2 and WS2 have tried many different disposition methods to overcome the limitations of their high process temperature (≥750°C). Due to their high process temperature, these materials can not be directly applied onto flexible polymer substrates. On the contrary, Tin disulfide (SnS2) is post transition metal sulfide and has low process temperature (<350°C), which is low enough to directly deposit on polymer substrates, and exhibits comparable characteristics with MoS2 and WS2 because of similar hexagonal layered structure. Therefore, we have developed low temperature process of few layer SnS2 thin films with atomic layer deposition method for obtaining 2D material characteristics and investigated the electrical properties by fabricating thin film transistors (TFTs).

In this study, SnS2 thin films were grown by atomic layer deposition with tetrakis(dimethylamino)tin (Sn[N(CH3)2]4, TDMASn) and hydrogen sulfide (H2S, 99.9%) at 150 °C. Subsequently, the post deposition annealing process up to 350°C was performed in 4% H2S gas ambient. We then identified the crystal structure and chemical bonding using X-ray diffractometer (XRD) and X-ray photoelectron spectroscopy (XPS), and the number of SnS2 layers was examined by atomic force microscopy(AFM), Raman analysis and high resolution-transmission electron microscopy (HRTEM). To investigate the switching characteristics of few layer SnS2 thin films, we fabricated bottom gate TFTs using few layer SnS2 thin films as active channel layer. As a result, few layer SnS2 TFTs showed n-type characteristics with on/off current ratio 8.32 x 106, mobility 0.08 cm2/Vs and 830 mV/decade of subthreshold swing.

**FF05.06.44**
**Multiphysics Modeling of Atmospheric Plasma Deposition of Zirconia**
Arash Tourki Samaei and Santanu Chaudhuri; University of Illinois Chicago, United States

The appeal of microwave-assisted atmospheric plasma for surface modification and embedding of chemistry is thwarted by the lack of predictive link between the process parameters, plasma chemistry, surface plasma reactions, and growth of functional layers with control over morphology and phase. The atmospheric plasma deposition of zirconia on a natively grown aluminum oxide layer offers an advanced, robust and cost-effective processing without a vacuum chamber in ambient air. Here, we present a comprehensive multiphysics modeling of the plasma deposition to study the physics of the processing and the metal oxide growth on the substrate. An organometallic evaporation model is adapted for predicting evaporation rate of precursor. This model calculates the growth rates and film thickness of zirconia and demonstrates strong dependency among growth rates and processing parameters including flow rates at different inlets and torch-substrate distance. This optimization study can help to enhance the performance of the experiments and achieve higher growth rate of metal oxide on substrate.

**FF05.06.45**
**Improvement of Reverse Leakage Current Characteristics of Si-Based Homoepitaxial InGaN/GaN Light Emitter for MEMS Applications**
Keun M. Song1, Moonsang Lee2, Hyun Uk Lee2 and Jaekyu Kim3; 1Korea Advanced Nano Fab Center, Korea (the Republic of); 2Korea Basic Science Institute, Korea (the Republic of); 3Hanyang University, Korea (the Republic of)

We report the nature of reverse leakage current characteristics in InGaN/GaN light emitting diodes (LEDs) on freestanding GaN (FS-GaN) crystals detached from a Si substrate for the first time, using temperature-dependent current-voltage (T-I-V) measurement. Based on T-I-V measurement results, carrier transport mechanism of the reverse leakage current is analyzed in the
InGaN/GaN LEDs. Their conduction mechanism can be divided into variable-range hopping and nearest neighbor hopping (NNH) around 360 K, which is enhanced by Poole-Frenkel emission. The analysis of T-I-V curves of the homoepitaxial LEDs yields an activation energy of carriers of 35 meV at -10 V, about 50% higher than that of the conventional ones (Ea = 21 meV at -10 V). This suggests that our homoepitaxial InGaN/GaN LEDs bears the high activation energy as well as low threading dislocation density (about 1 × 106/cm2), effectively suppressing the reverse leakage current. We expect that this study will shed a light on the high reliability and carrier tunneling characteristics of the homoepitaxial InGaN/GaN LEDs produced from a Si substrate and also envision a promising future for their successful adoption by MEMS community.

Significant development of high luminescence efficiency in InGaN/GaN LEDs has offered new futuristic applications such as automotive headlamps, traffic signals, displays, and general lighting. Despite their rapid advances and successful applications in lighting sources, improved efficiency, functionality, and flexibility in LEDs must still be obtained to use LEDs in emerging industries such as the internet of things (IoT), bio-applications, and wearable devices. Furthermore, integration of GaN and Si process enables tremendous new possibilities to Si-based MEMS and system designers.

In this work, we demonstrated homoepitaxial InGaN/GaN LEDs on FS-GaN substrate, which was grown by metal-organic chemical vapor deposition and detached from a Si substrate. To compare the reverse leakage current characteristics in InGaN/GaN LEDs fabricated using FS-GaN grown from a Si substrate, conventional InGaN/GaN LEDs with corresponding structures and the peak emission wavelength were fabricated on sapphire substrate. All the LED structures were fabricated with conventional lateral chip process. We performed temperature-dependent reverse leakage current measurement of InGaN/GaN LEDs. Based on T-I-V measurement results, we will discuss carrier tunneling characteristics of the homoepitaxial InGaN/GaN blue LEDs produced from a Si substrate.
its processability due to increased thermal stability and insolubility. In order to overcome these issues, PEDOT formed with the hydrophilic stabilizing anion Poly(styrenesulfonic acid) (PSS) has been widely used as a solution processable form of PEDOT. However, PSS-stabilizing anions have recently been correlated to anomalous currents in electrolytic capacitors, anisotropic conductivity, and decreased crystallinity. In addition, slurries of pre-polymerized PEDOT limit its infiltration and growth in high aspect ratio structures. Vapor-phase deposition processes are therefore promising methods to increase PEDOT film performance and applications. Until recently, vapor phase synthesis of Poly(3,4-ethylenedioxythiophene) (PEDOT) has relied on solid oxidants which require complex heating and dosing schemes for sequential layer-by-layer processes. Until now, vapor-phase PEDOT deposition has therefore been limited to to vapor phase polymerization (VPP) and oxidative chemical vapor deposition (oCVD) processes.

This work introduces a novel oxidative molecular layer deposition (oMLD) process using the volatile liquid oxidant, antimony(V) chloride (SbCl$_5$), to deposit high performance PEDOT thin films with nanometer precision. Using a home built, hot wall, viscous flow reactor, semi-metallic PEDOT thin films have been deposited with record breaking thin film conductivity of 6700 S cm$^{-1}$ at moderate deposition temperatures (150 °C). In addition to producing high performance PEDOT thin films, the protocol developed in this work has been used to explore the effects of reactor parameters on PEDOT nucleation and growth as well as film characteristics, moving towards greater control over PEDOT performance. Furthermore, this facile oMLD process has enabled the study of substrate dependent nucleation and growth, thereby moving towards an enhanced understanding of PEDOT selective deposition.

8:45 AM FF05.07.03
Device Integration of Ultrathin oCVD PEDOT Films in Perovskite Solar Cell Meysam H. Gharahcheshmeh, Mohammad Mahdi Tavakoli, Edward F. Gleason, Maxwell Robinson, Jing Kong and Karen K. Gleason; Massachusetts Institute of Technology (MIT), United States

Impressive values and systematic tunability of the optoelectronic properties of poly(3,4-ethylenedioxythiophene) (PEDOT) are demonstrated using single-step all-dry process. With the volatile oxidant, vanadium oxytrichloride (VOCl$_3$), pure face-on orientation results from oxidative Chemical Vapor Deposition (oCVD) without any post-deposition rinsing. In contrast, predominately edge-on orientation previously resulted with the solid oxidant FeCl$_3$ at the similar oCVD process conditions and a post-deposition rinsing step is required. At growth temperatures compatible with direct deposition on plastic substrates (140 °C), using the single-step oCVD process with the volatile VOCl$_3$ oxidant, we obtained ~four-fold improvement of direct current conductivity to optical conductivity ratio ) and ten-fold improvement of electrical conductivity as compared to oCVD PEDOT produced using FeCl$_3$. Indeed, the maximum =$50$ for this mechanically flexible polymer exceeds the benchmark for commercial transparent conductors. Varying only the partial pressure of the VOCl$_3$ oxidant induces systematic variation of the b-axis lattice parameter in the oCVD PEDOT crystallites from 6.98 to 7.02 Å and 6.97 to 7.01 Å for films grown at the deposition temperature of 110 °C and 140 °C, respectively. The lowest value correlates with the highest electrical conductivity, largest optical band gap (2.9 eV), and lowest degree of disorder as characterized by the Urbach band edge energy. The utility of the optimized oCVD PEDOT is demonstrated as a hole transport layer (HTL) for the fabrication of an inverted perovskite solar cell (PSC). This device achieves a power conversion efficiency (PCE) of 18.04%, higher than the 16.20% PCE for the control structure having a spun-cast PEDOT:PSS HTL. More significantly, incorporating oCVD PEDOT, rather than PEDOT:PSS, increased device stability approximated two-fold over a 42-day evaluation period.

9:00 AM *FF05.07.04
Development of Devices Based on Stimuli-Responsive Thin Films Deposited by iCVD Anna Maria Coclite; Graz University of Technology, Austria

Stimuli-responsive materials are characterized by dynamic switching of their properties depending on external stimuli (e.g. light, pH, temperature, humidity). In particular, hydrogels change their size and shape when exposed to aqueous environments. Functional and responsive surfaces have been successfully deposited by initiated Chemical Vapor Deposition (iCVD) on a variety of substrates. iCVD allows to obtain stimuli-responsive thin films with high chemical specificity and this is important to obtain a large responsiveness amplitude. In addition, the thin film form allows obtaining fast response.

Fast response and large signal amplitude are fundamental requirements for good sensors. Fast and ultra-fast
humidity sensors based on the optical detection of the change in thickness of the iCVD hydrogels will be shown. The setup was designed without electric components in the vicinity of the active sensor layer and is therefore applicable in harsh environments such as explosive or corrosive ones. The implemented sensor prototype delivered reproducible relative humidity values and the achieved response time for an abrupt change of the humidity was about three times faster compared to one of the fastest commercially available sensors on the market.

Another case of study will be presented in the field of multi-stimuli-responsive materials. A chemical functionalization of the hydrogel surface was performed to add multiple stimuli-responsive functionalities and obtain a smart material that responds to two stimuli at the same time. Modifying the hydrogel surface with solution-based methods is often problematic because of the damages caused by the permeation of solvents in the hydrogel. This issue is completely bypassed by the use of solvent-free techniques, like iCVD. Such polymers were used as drug encapsulants to achieve controlled drug release upon stimuli, with possible application as wound dressings.

9:30 AM FF05.07.05
Functional Polymer Thin Films with Tailored Properties by Initiated Chemical Vapor Deposition Stefan Schröder, Wiebke Reichstein, Maximilian Burk, Adrivit Mukherjee, Cenk Aktas, Thomas Strunskus and Franz Faupel; University of Kiel, Germany

Initiated chemical vapor deposition (iCVD) is a solvent-free, cost efficient synthesis technique to deposit conformal polymeric thin films. The properties of these organic films can be precisely modified by the deposition parameters. The use of different comonomers facilitates copolymerization, which for instance, enables further control over the crosslinking degree and film functionality. This opens a wide field of possible applications, like surface functionalization, functional dielectrics and drug delivery systems. Here, we demonstrate the tailored synthesis of hydrogel-, organosilicon- as well as fluoropolymers and their respective applications for conformal coatings on porous 3D structures, superior functional electret layers, photoswitchable copolymer films, drug delivery systems with barrier layers and adhesion promotion by use of various comonomers within one iCVD process.

9:45 AM BREAK

SESSION FF05.08: Deposition of 2D Materials, Sulphides and Nitrides I
Session Chairs: Elisabeth Blanquet and Steven George
Wednesday Morning, December 4, 2019
Hynes, Level 3, Room 310

10:15 AM FF05.08.01
Molybdenum Disulfides and Diselenides by Atomic Layer Deposition Raul Zazpe1,2, Jaroslav Charvot1, Richard Krumpolec3, Milos Krbal1, Jan Priekyl1, Filip Bures1 and Jan M. Macak1,2; 1University of Pardubice, Czechia; 2Brno University of Technology, Czechia; 3Masaryk University, Czechia

The success of graphene opened a door for a new class of chalcogenide materials with unique properties that can be applied in the semiconductor technology [1]. Monolayers of two-dimensional transition metal dichalcogenides (2D TMDCs) possess a direct band gap [2] that is crucial for optoelectronic applications. Additionally, the direct band gap can be easily tuned by either chemical composition or external stimuli. Next to the optoelectronic applications, where a monolayer planar structure is necessary to employ, a layer of standing flakes, which possesses a large surface area, can be used for hydrogen evolution [3] a photodegradation of organic dyes [4] or as electrodes in Li ion batteries [5].

In principle, TMDCs can be prepared by various top-down (e.g. exfoliation) and bottom-up techniques, such as chemical vapor deposition (CVD) and atomic layer deposition (ALD) growth techniques [1]. MoS2, a typical representative of TMDCs, has been widely studied for many applications. Recently, the possibility to employ ALD as a technique to grow MoS2 has been reported. In these works (CH3)2S2 [6] or H2S [7, 8] were used as the S precursor and Mo(CO)6 [6], MoCl5 [7] or Mo(thd)3 [8] as the Mo precursors. From the practical point of view, MoSe2 is even more interesting than MoS2 since MoSe2 possesses a higher electrical conductivity than MoS2 [9, 10]. Recently, we have shown that ALD deposition of MoSe2 [11] or Mo-O-Se [12] using ((CH3)3Si)2Se as the Se
precursor and the MoCl₅ or Mo(CO)₆, respectively, as the Mo precursors is feasible. The presentation will focus on the synthesis of MoS₂ and MoSe₂ by ALD, their characterization and applications in various fields. Experimental details and some recent photocatalytic and hydrogen evolution results will be presented and discussed.

References:

10:30 AM FF05.08.02
Patterned Growth of Graphene and Hexagonal Boron Nitride Heterostructures Using a “Gettering” CVD Approach Irfan Haider Abidi¹,², Barbaros Oezylmaz¹ and Zhengtang Luo²; ¹National University of Singapore, Singapore; ²The Hong Kong University of Science and Technology, Hong Kong

Two dimensional (2D) materials have reshaped the research interest in the field of electronics and aspired the researchers to develop ultrathin optoelectronic devices. However, in order to steer the progress on a fast track, the synthesis of high-quality 2D materials with desired architect is imperative. In this work we have demonstrated a precursor “gettering” approach for chemical vapor deposition (CVD) to directly grow patterned graphene as well as hexagonal boron nitride (hBN) on Cu substrate using a predesigned mask. Our proposed method is advantageous to the previous reports, which generally involved several post-growth complicated lithographic steps to obtain the desired architect of graphene films. Moreover, the quality of films grown via our method comprises of high quality in terms of layer homogeneity. Interestingly, taking advantage of the same growth substrate (Cu), we have constructed lateral heterostructures of graphene and h-BN through sequential feeding of respective precursors, in one-step CVD process. However, lateral heterostructures growth have been demonstrated previously but those are rather randomly distributed or others require multiple growth steps and complicated lithographic route. Therefore, our method is providing a unique strategy of one-step facile CVD process to build such patterned growth of graphene arrays and their heterostructures that can be integrated with crafting the nanoelectronic circuitry.

10:45 AM FF05.08.03
Wafer Scale MOCVD Grown BN for Encapsulation of 2D Devices Michael Snure¹, Shivashankar Vangala¹ and Gene Siegel²; ¹Air Force Research Laboratory, United States; ²KBR, United States

Due to the amazing and diverse properties of two dimensional (2D) materials, including semiconducting, metallic, insulating, and magnetic, there has been a great interest for more than a decade. A commonality among this class of layered materials is their ability to be thinned and stabilized down to one layer thick. The ability to achieve this thickness with minimal property degradation or even enhancement has generated continued interest for numerous applications. In these atomically thin materials, interactions with the environment, including the substrate and other 3D device elements, greatly degrade properties. Scattering from charged impurities, roughness, and phonons will reduce transport properties affecting device performance. The best solution has been the use of a thin van der Walls (vdW) buffer layers, like hBN. Of the available vdW materials, hBN is one of the only insulators, and due to is dielectric properties, high surface optical phonon energy, and atomically smooth surface, it has been the most successful and widely used material for preserving and protecting the intrinsic properties of 2D materials (graphene, phosphorene, MoS₂, ...). Here, we investigate the application of few-layer sp²-BN as a weakly interacting substrate, passivation layer and dielectric for 2D devices. By metal organic chemical vapor deposition (MOCVD), we grow
few layer wafer scale (2") sp²-BN on sapphire with excellent uniformity. To study this materials application as a weakly interacting encapsulation layer, we use transferred graphene to fabricate arrays of field effect transistors (FET) and investigate impacts on material and device performance compared to conventional dielectric substrates. As a substrate for graphene, MOCVD BN on sapphire results in graphene with a more that 2x increase in mobility and 10x reduction in sheet carrier density compared to on sapphire due to the lower interface doping and SO phonon energy. Through control of MOCVD process conditions, including temperature, pressure and V/III ratio, we can vary BN thickness and surface morphology, which we have used to investigate the role of BN morphology on transport properties. We also explore BN as a passivation layer for protection of conducting 2D layers from the ambient environment and oxidation. Finally, we discuss the use of BN in a 2 layer dielectric stack with atomic layer deposition Al₂O₃ allowing us to form high quality gates without the need for Al seeding.

11:00 AM FF05.08.04
Catalyst Engineering for Scalable 2D Film Control—The Dark Secrets of Bulk Oxygen and Integrated Pathways for Single-Crystal Growth Oliver Burton¹, Vitaly Babenko¹, Vlad-Petru Veigang-Radulescu¹,², Barry Brennan², Andrew Pollard² and Stephan Hofmann¹; ¹University of Cambridge, United Kingdom; ²National Physics Laboratory, United Kingdom

The controllable, reproducible and scalable growth of graphene and related 2D materials remains the foremost challenge for both research and any technologies exploiting their unique properties. While chemical vapour deposition (CVD) has become the most widespread method for 2D material film growth, even basic process parameters remain not well understood due to the manifold, complex parameter space. Here we focus on widely used Cu as process catalyst and reveal the role and control of residual bulk oxygen, as well as showing new integrated process pathways, for achieving uniform Cu(111) epitaxial layers. While oxidation is widely used to remove impurities in metal catalysts and to control the nucleation density of graphene[1], we show that minute concentrations of residual bulk oxygen can significantly deteriorate the quality of as-grown graphene highlighted by an increased Raman D/G ratio, increased propensity to post-growth etching and increased fraction of multi-layer graphene nucleation[2]. Starting from commercial Cu foils, we show that a simple hydrogen annealing step after the initial oxidation allows us to lower the residual oxygen level as measured by time-of-flight secondary ion mass spectrometry to produce graphene of significantly higher quality. This can be effectively combined with a short hydrocarbon exposure time of 10 min to achieve near full mono-layer graphene coverage, suitable for emerging industrial applications. We show that residual oxygen can have an equally significant impact on Fe catalysed h-BN CVD[2,3], and discuss the underlying mechanisms with parallels to well-known processes in metallurgy, catalysis and vacuum science. We further demonstrate the scalable deposition of ultra-low roughness single crystal Cu(111) and 2D material growth within a single synthesis step. The total synthesis from catalyst to 2D film takes less than 2 hours, during which there is no exposure to atmospheric conditions, circumventing the most common source of contaminants. A matching rapid and scalable method of transfer is devised and further improvements for device integration will be discussed[4,5].

References

11:15 AM FF05.08.05
CVD Strategy for Transition Metal Dichalcogenides Monolayers Wei Sun Leong; Massachusetts Institute of Technology (MIT), United States

Since 2011, 2D semiconductor monolayers such as transition metal dichalcogenides (TMD including MoS₂, WS₂, MoSe₂, WSe₂, etc), have attracted tremendous attention owing to their extraordinary properties, setting the stage for new breakthroughs in fundamental nanoscience and applications, from electronics to biosensors. To date, various techniques have been explored to obtain TMD monolayers, and among them, chemical vapor deposition (CVD) synthesis using transition metal oxide and chalcogenide solid precursors is the most commonly adopted approach in many laboratories. In particular, the transition metal oxide precursor was placed at the center of a furnace while the chalcogenide precursor at the upstream of the furnace, with targeted substrate facing down and put above the
crucible containing transition metal oxide precursor. Notably, the amount of precursor used in previous reports is normally surplus, which very often gives rise to chemical reactions between the precursors in each of their containers during synthesis, due to the diffusion of both precursors at the growth temperature. Thus, typically one growth chamber is dedicated to the growth of only one type of TMD to avoid cross-contamination (unless the chamber is used for hetero-TMD structures growth). In another words, the number of TMD that can be synthesized in a lab is limited by the number of CVD setup available in the lab.

We addressed this challenge by redesigning the CVD setup and pruning the amount of precursor used. We have been able to simultaneously synthesize different types of TMD on separate substrates using the same growth chamber. Through computational fluid dynamics modelling, we found that gas species trapped within those slanting substrates in our CVD setup are unable to escape from the trap, and thus avoiding the cross-contamination issue. The synthesized TMD films exhibit high-quality as confirmed by Raman, PL, XPS, AFM, and STEM analyses. Field-effect transistors fabricated on our TMD monolayers exhibit high electron mobility (64 cm²/V·s for MoS₂ and 21 cm²/V·s for WS₂ at room temperature) and large on-off current ratio (10⁷). Remarkably, our devised CVD technique has two advantages: (1) a CVD setup can be used to grow multiple TMD monolayers, which saves a lot of cost and space; (2) Multiple types of TMDs can be synthesized on separate substrates in one CVD cycle.

We also proposed a two-step CVD strategy to construct TMD-only synthetic electronics that can perform logic operations. The backbone of synthetic electronics relies on the possibility to chemically synthesize heterogeneous junctions between conductor and semiconductor, with perfect lattice matching. Interestingly, we found that our one-dimensional, solely TMD made, conductor-semiconductor junctions with large lattice mismatch exhibiting good electrical transport behaviors. We measured contact resistance as low as 500 Ωµm and a Schottky barrier height as small as 30 meV, both among the best values reported to date for contacts to 2D TMDs. Through a combination studies of STEM and second harmonic generation imaging, we confirmed that the semiconductor TMD monolayers nucleate from the vertexes of multi-layered TMD conductor and evolve into monolayer polycrystals. This is an unconventional non-edge epitaxy growth mechanism, and further studies are conducted to understand the interface physics of these lateral TMD junctions. In short, our CVD strategy enables the fabrication of ultrathin, flexible electronics, without the use of complex and costly device fabrication processes.

References:

**Appreciate if this can be indicated as an invited talk. Thank you.**

11:30 AM FF05.08.06
Formation of Micrometer Sized, Hierarchical h-BN Superstructures from Combined PECVD and MOCVD Processes Anja Sutorius¹, Daniel Studler¹, Robert Frohnhoven¹, Yakup Günüllü¹, Yogendra K. Mishra² and Sanjay Mathur¹; ¹University of Cologne, Germany; ²University of Kiel, Germany

Two dimensional materials namely graphene, MoS₂ and borophene went into focus of scientists all over the world due to their interesting properties (e.g. conductivity, flexibility) and possibility of large scale processability. However, the fabrication is bound by the surface chemistry and geometry of the used substrates, as well as the chemical interaction (adsorption and desorption) between substrate and precursor. In this regard, the formation of 2D materials on hierarchical superstructures is very difficult to achieve. Plasma enhanced CVD (PECVD); however, offers a way to overcome the chemical and geometrical restrictions, since the technique is not only able to activate the surface through heavy ion bombardment, but furthermore offers far-from-equilibrium phase formation at room temperature without substrate restrictions.

Here, we report the formation of three-dimensional, hollow h-BN superstructures, as obtained from a combined PE- and MOCVD deposition of B-N bond carrying single-source precursor molecules on ZnO host structures. Through the combination of plasma power, process temperature and time, we were able systematically study h-BN growth on these host materials to clearly demonstrate the suitability of the process for the formation of three-dimensional superstructures from two dimensional materials.
Revisited Thermal and Plasma Enhanced Atomic Layer Deposition Processes of Metal Nitrides—Challenges and Opportunities Elisabeth Blanquet, Arnaud Mantoux, Frederic Mercier, Raphael Boichot, Michel Pons and Carmen Jimenez; University Grenoble Alpes, France

Metal nitrides films stand out as candidates for many strategic industrial applications as they exhibit superior functional properties such as mechanical, electrical and thermal properties. Complementary chemical vapor deposition techniques from High Temperature Chemical Vapor Deposition (HTCVD) to Thermal and Plasma Enhanced Atomic Layer Deposition (T-ALD and PEALD) have been investigated to fabricate metal nitrides thin films. In each case, one of the major challenges is the synthesis of high quality, pure (with no oxygen contamination) material. Among ALD developments, efforts have been focused on the exploration of different precursor molecules, chemical reactions as well as growth processes sequences and conditions.

In this presentation, the examples of aluminum nitride (AlN) and niobium nitride (NbN) deposition process development will be presented. Aluminum nitride (AlN) is a semiconductor material with a wide bandgap, excellent thermal conductivity, high electrical resistance and good behavior towards oxidization and abrasion. AlN films are attractive for many applications in energy, electronic or optoelectronic devices. For instance, thin films are used in piezoelectric transducers and microwave filters applications, in resonators, as passivating coatings, as AlN substrate in high power applications. NbN films are mainly used for single-photon detectors (SSPDs), superconductive radio frequency (SRF) cavities due to their superconducting properties.

We report on the optimizing routes and strategies to obtain the best compromised film properties on these two systems.

Relationship between the Gas-Phase Reactions Occurring within an Electron Cyclotron Resonance- (ECR) Microwave- (MW) CVD Process and the Properties of Hydrocarbon Films Jesús M. García Figueroa and David R. Harding; Laboratory for Laser Energetics and Department of Chemical Engineering, United States

Increasing the energy that is coupled into a plasma by adding a magnetic field of 875G to it to make it ignite at the electron cyclotron resonance- (ECR) frequency (2.45 GHz) changes the gas-phase chemistry that occurs in standard plasma-assisted CVD processes. Films are formed as gas-phase reaction products at significantly higher ion energies (15–30 eV) and, at substrate temperatures that are appreciably lower than those that can be achieved without the electron-cyclotron augmentation. This phenomenon greatly affects the films’ properties.

In this study, the plasma ECR-MW-CVD technique is applied to make different types of hydrocarbon films, of variety of sp\(^3\), sp\(^2\), and sp content, and densities (1.1 to 3.2 g/cm\(^3\)), at substrate temperatures that range from 30 to 200\(^\circ\)C. The role that the composition of the gases (methane, hydrogen, and argon) in conjunction to the plasma power has on the films’ properties is discussed in the context of the enhanced gas-phase chemistry that occurs in the ECR-MW environment. The elemental composition of the films is determined from FTIR and Raman. Their surface morphology, in particular: their smoothness and texture, which are critical for the application that uses these materials as ablators for laser fusion experiments, are observed using SEM and AFM. Other films’ properties that are affected by the energetic species in the ECR-MW environment are determined via gravimetry, nanoindentation, and ellipsometry. The presentation shows the relationship that exists between the chemistry happening near the gas/substrate interface within the ECR-MW environment and the films’ properties.

This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0003856, the University of Rochester, and the New York State Energy Research and Development Authority.

Novel Approach for Conformal Chemical Vapour Phase Deposition of Ultra-Thin Conductive Silver Films
Sabrina M. Wack, Renaud Leturcq, Petru Lunca-Popa and Noureddine Adjeroud; LIST, Luxembourg

The present work demonstrates a novel approach for the conformal deposition of ultra-thin conductive silver (Ag) films on complex substrates. Using an original multi-step plasma-enhanced approach, we demonstrate the deposition of conductive silver films with thickness down to 11 nm. Conductive ultra-thin Ag films are commonly deposited by physical vapour deposition techniques (metal evaporation or sputtering). However, these are line-in-sight methods that do not allow conformal deposition on substrates with complex morphology (e.g. trenches) [1]. Non-line-in-sight methods such as the ones based on chemical vapour phase deposition (Chemical Vapour Deposition-CVD or Atomic Layer Deposition-ALD) usually produce non-electrically-conductive films for thickness below 20-50 nm due to island formation by Volmer-Weber growth mode for metal layers on oxide-based substrate [2]. Moreover, conductive ultra-thin silver films based on ALD (down to 22 nm) [3], require low-temperature deposition (below 120°C), with a very narrow process temperature window (about 10°C).

The deposition is based on Ag(fod)(PEt3) as silver precursor, and H2 plasma as reducing agent. An acceptable process temperature window (> 30°C), and a deposition temperature larger than 120°C for enhanced uniformity and deposition rate have been demonstrated. In these conditions, highly uniform deposition on bent and batched samples have been performed. 20 nm thick films exhibit a resistivity down to 40 μΩ.cm. The resistivity increases up to 1.4 mΩ.cm when reducing the thickness down to 11 nm. The critical thickness below 11 nm is thus very close to the state-of-the-art for sputter-deposited thin films [4], and well below the 22 nm obtained with ALD [3]. The obtained Ag thin films also demonstrate a high reflectance up to 94% and a low absorbance of 3% in the infrared region for a film thickness of 26 nm, showing the high quality of the films. This quality is confirmed by morphological analysis using scanning electron microscopy and atomic force microscopy, as well as by the structural (X-ray diffraction) and chemical (energy dispersive X-ray spectroscopy) properties. This new processing approach opens a very interesting path for the use of ultra-thin silver films for electronic and optoelectronic applications.


2:30 PM BREAK

3:30 PM FF05.09.04
Low-Temperature Self-Limiting Growth of β-Ga2O3 Films on Flexible Substrates via Plasma-Enhanced ALD
Saidjafarzoda Ilhom1, Adnan Mohammad1, Deepa R. Shukla1,2, Brian Willis2 and Necmi Biyikli1; 1The University of Connecticut, United States; 2University of Connecticut, United States

Wide-band gap semiconductors have attracted great research attention due to their unique properties such as operation at much higher voltages and frequencies than conventional semiconductors. Our target is to engineer these materials for device applications in flexible and wearable technologies, which generally require lower deposition temperatures. Towards this goal, we have investigated the low-temperature self-limiting growth of Ga2O3 films on various substrates including glass and Kapton via inductively-coupled plasma-enhanced atomic layer deposition. Extended 300-cycle long runs were carried out to grow thin films on Si(100), glass, and Kapton using triethyl-gallium (TEG) as metal precursor and variants of Ar/O2 plasma (Ar/O2 with different partial pressures and O2-only with different flow rates) as metal precursor and oxygen co-reactant, respectively. Growth experiments have been performed within 150 - 400 °C substrate temperature range at 300 W rf-plasma power. Ex-situ ellipsometry was employed to measure the thickness and optical properties of the films. When O2-only plasma was used, the thickness of the films ranged between 19.32 - 16.88 nm and the as-grown refractive indices stayed fairly close between 1.73 - 1.71 within the scanned temperature range. However, addition of Ar gas to the plasma drastically reduced the refractive index of the films from 1.72 to 1.54, reminding of a possible plasma re-deposition of carbon-rich reaction byproducts or increased incorporation of oxygen. X-ray diffraction (XRD) showed that the as-grown Ga2O3 films exhibit amorphous structure irrespective of substrate temperature in this study. Furthermore, the effect of post-growth thermal annealing is investigated on the enhancement of crystalline quality (which indicates conversion from amorphous to monoclinic β-Ga2O3 crystal phase) and electro-optical properties of the films. Also, X-ray photoelectron spectroscopy (XPS) measurement results of the Ga2O3 samples grown under varying plasma (Ar/O2, O2-only) will be discussed, which provides additional insight into the elemental composition of the films that might
help to understand the changes in the structural, optical, and electrical properties under varying plasma chemistry. A comparative material properties analysis based on the substrate utilized will be carried out which will reveal how the film properties of as-grown Ga2O3 are affected by the substrate material. A future outlook will be provided to overcome the challenges to achieve device quality layers on low-temperature compatible flexible substrates.

3:45 PM FF05.09.05
Synthesis of Hexagonal Boron Nitride Using Microplasma Vianney Mille1, Hiba Kabbara1, Alexandre Tallaire2, Salima Kasri1, Ovidiu Brinza1, Claudia Lazzaroni1 and Guillaume Lombardi1; 1LSPM CNRS UPR3407, France; 2Institut de Recherche de Chimie Paris - IRCP UMR 8247, France

In this presentation, we propose an alternative synthesis method to deposit thin film material hexagonal boron nitride (h-BN) assisted by microplasma source. h-BN thin films are the focus of interest for electronic, optoelectronic applications due to its wide band gap semiconductor. In other hand, microplasmas have attracted growing attention in recent years because of possible applications in other fields such as surface treatment, light sources and nanomaterial synthesis [1]. They can be generated at high pressure which is a favourable condition to better dissociate N2 molecules, a prerequisite to the synthesis of nitride materials at lower temperatures compared to conventional processes. Our deposition reactor is composed of two chambers and the micro-plasma is located at the junction between them. The plasma source consists of an anode-dielectric-cathode sandwich through which one hole of 400 μm in diameter are drilled. The higher pressure chamber (several tens of mbar), favors the production of high density plasma, and consequently high nitrogen dissociation, while the lower pressure chamber (several mbar) limits the nitrogen recombination. The polarizable and heating substrate holder is located in the lower pressure chamber where the boron precursor (BBr3) is injected. The polarization of the substrate holder allows the discharge to be expanded from the hole to the substrate. Suitable conditions can be defined to achieve h-BN thin film synthesis and we report the growth of h-BN on 2 inch-silicon substrates at temperatures below 1000°C. The deposited films are then characterized by XRD and Raman spectroscopy to evaluate the phase purity and quality, and by SEM and TEM to observe the surface morphology and the crystallinity of the material.


4:00 PM *FF05.09.06
Electron Enhanced Atomic Layer Deposition (EE-ALD) Steven M. George; University of Colorado, United States

Electron enhanced atomic layer deposition (EE-ALD) can dramatically reduce the temperatures required for film growth. Temperature reduction is possible because of electron stimulated desorption (ESD) of surface species. The desorption process creates highly reactive surface sites. Precursors can then adsorb efficiently on the reactive surface sites. Our work has demonstrated the EE-ALD of GaN [1], Si [2], BN [3] and Co at room temperature.

Film growth has been performed using alternating exposures of chemical precursors and low energy electrons. In situ ellipsometry measurements have monitored linear film growth versus number of reaction cycles. Additionally, we have observed the dependence of the EE-ALD growth rates on electron energy. Maximum growth rates have varied from 0.3 Å/cycle for Si films at 100-150 eV [2] to 3.2 Å/cycle for BN films at 80-160 eV [3]. Recent measurements have also obtained growth rates of 1.0 Å/cycle for Co films at 140 eV.

Co film growth was performed using sequential cobalt tricarbonyl nitrosyl (CTN, Co(CO)3NO) exposures and low energy electrons. The electrons desorb the CO and NO ligands from CTN on the surface and produce active sites for additional CTN adsorption. A hot filament electron flood gun was initially used as the electron source. One difficulty with the electron flood gun is the long cycle times of > 500 seconds. Much of this cycle time is consumed protecting the flood gun filament from precursor exposures and the long duration of the electron exposure due to the limited current of the electron gun. The cycle time could be reduced significantly using a more robust and higher flux electron source.

A new hollow cathode plasma electron source (HC-PES) has been developed to reduce the cycle time during EE-ALD. The HC-PES has a >600X increase in electron current compared with the electron flood gun. The HC-PES also eliminates the warm-up and cool-down time of the filament of the electron flood gun. The electron current from the HC-PES can be switched from nanoamps to milliamps in < 10 ms. The HC-PES is also chemically insensitive.
and reduces the need for pumping out the chamber following CTN exposures. This presentation will highlight Co EE-ALD performed using this new HC-PES.


4:30 PM FF05.09.07

Deepa R. Shukla1,1, Saidjafarzoda Ilhom1, Adnan Mohammad1, Blaine Johns2 and Necmi Biyikli1,1; 1University of Connecticut, United States; 2Film Sense LLC, United States

GaN is the most significant binary member of the wide bandgap III-nitride material family, with a bandgap energy of 3.4 eV, and is heavily commercialized in applications such as blue light emitters for white-light LEDs, UV photodetectors, high-electron mobility transistor (HEMT)-based transistors for high-speed, high-frequency, and high-power electronics. Molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) are the well-known high-temperature epitaxial growth methods used for GaN deposition, whereas thermionic vacuum arc (TVA), pulsed laser deposition (PVD), reactive magnetron sputtering are among the low-temperature GaN deposition techniques. With the advent in plasma-assisted atomic layer deposition (PA-ALD) within the last decade, an increasing interest has been focused on the low-temperature self-limiting growth of III-nitride films using PA-ALD. While a few number of groups have been active in the film growth and material characterization aspects, reported device applications have been quite limited. In this study, we aim to demonstrate that finely tuned PA-ALD processes can be utilized to synthesize crystalline GaN layers on temperature-sensitive flexible substrates, which can function as electronic device layers for thin-film transistors (TFTs). We have grown GaN thin films at temperatures less than 200°C on Si, glass, and flexible polymeric substrates using PA-ALD featuring capacitively coupled hollow-cathode stainless-steel plasma source. GaN deposition experiments were carried out using two different organometallic gallium precursors: trimethylgallium (TMGa) and triethylgallium (TEGa) to investigate optimal experimental parameters for high crystalline quality for each precursor molecule. The growth process was conducted within an in-situ ellipsometer-integrated compact PA-ALD reactor having a base pressure of 20 mtorr. RF-plasma parameters (power, exposure time, plasma gas composition) and substrate temperature were mainly studied as variable process parameters for each deposition process. For the film thickness and optical constants (refractive index and absorption coefficient), in-situ multi-wavelength and ex-situ spectroscopic ellipsometry measurements and data fitting analysis were carried out. Synthesized GaN films turned out to be transparent non-absorbing within the visible spectrum along with refractive index values approaching 2.2 at 632 nm. The elemental composition was determined using x-ray spectroscopy (XPS). Below detection limit carbon along with relatively low oxygen concentration (< 5 at. %) was observed within the bulk of ALD-grown GaN films. For the structural characterization of the grown films, grazing-incidence x-ray diffraction (GIXRD) analysis was conducted to analyze crystalline quality and crystal grain size. XRD analysis showed single-phase hexagonal wurtzite GaN crystal structure with (002) dominant crystalline orientation. X-ray reflectivity (XRR) was used to comprehend the surface roughness and film density. High-resolution transmission electron microscopy (HR-TEM) analysis confirmed the crystalline structure of GaN films with grain sizes larger than 10 nm. As proof-of-concept device application, we will present our metal-semiconductor-metal (MSM) photodetector characterization results which were fabricated on GaN device layers grown on glass and flexible polymeric substrates. A comparative analysis will be carried out to understand the influence of substrate material as well as the impact of mechanical stress on the flexible device performance. A future outlook will be provided to improve material and device characteristics towards implementing ALD-grown III-nitride layers for flexible/wearable device technology.
**FF05.09.08**

**Magnetic Field-Assisted Chemical Vapor Deposition—New Pathways for Functional Materials**

Daniel Stadler¹, Vanessa Rauch¹, David N. Mueller², Peter Tutacz¹, Thomas Brede³, Michael Frank¹, Tomas Duchon², Thomas Fischer¹, Margret Giesen², Claus M. Schneider³, Cynthia A. Volkert¹ and Sanjay Mathur¹; ¹University of Cologne, Germany; ²Research Center Jülich, Germany; ³Georg-August-University, Germany

Temperature is the key parameter for controlling the phase and film morphology during chemical vapor deposition (CVD), since precursor decomposition, growth rate and obtained phases are depending on the very same. Anyhow, far from equilibrium phases and morphologies are not accessible solely by temperature but also by the application of external electric and magnetic fields. While electric fields often result in additional heating of the specimen, static magnetic (DC) fields do not lead to additional temperature gradients inside the samples and thus offer additional control on phase and morphology of the as-obtained films. In this presentation, magnetic field-assisted CVD (mfCVD) will be presented as novel and selective tool for the phase selective deposition of (magnetic) transition metal oxides and nitrides. The field-matter interplay at various temperatures and field strengths will be highlighted and consequences on physical, morphological and chemical properties of unaltered films will be discussed. Electron microscopy will demonstrate selective influence of the pristine film morphologies, while X-ray diffraction and absorption measurements will reveal changes in the obtained phase evolution and chemical surrounding. Electric, magnetic and catalytic property measurements of oxide films formed in different field environments will finally show the potential of mfCVD as additional manufacturing technique for the synthesis of functional materials.

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**SESSION FF05.10/EN11.10: Joint Session: ALD/CVD for Photovoltaics**

**Session Chairs: Takuya Matsui and Kevin Musselman**

**Thursday Morning, December 5, 2019**

**Hynes, Level 3, Room 310**

**9:00 AM *FF05.10.01/EN11.10.01**

**Atomic Layer Deposited Nanolayers for Silicon Photovoltaics**

Bart Macco, Jimmy Melskens and Erwin Kessels; Eindhoven University of Technology, Netherlands

Thin films are ubiquitous in the preparation of crystalline silicon solar cells. With the introduction of the PERC technology also the method of atomic layer deposition (ALD) has been introduced in high volume manufacturing in photovoltaics. Currently, the technique is quickly gaining market share for the deposition of ultrathin Al₂O₃ nanolayers for rear side surface passivation. The advantages of ALD are that it is scalable, that it is well suited to prepare high quality and uniform nanolayers, and that it is a "soft" deposition technique preventing interface damage. In this presentation the state of the art of ALD for silicon photovoltaics will be discussed as well as some ongoing developments and potential new applications. This includes new materials for surface passivation, nanolayers for passivating contacts, transparent conductive oxides as well as applications of ALD for polysilicon passivating contact solar cells.

**9:30 AM FF05.10.02/EN11.10.02**

**Thermally Stable Passivating Hole-Selective Contacts Using Atomic Layer Deposited Molybdenum Oxide with Thin Aluminum Oxide**

Geoffrey Gregory, Zhengning Gao, Titel Jurca, Parag Banerjee and Kristopher Davis; University of Central Florida, United States

One high efficiency crystalline silicon (c-Si) solar cell that has potential to be cost-competitive with Al-BSF devices while maintaining the passivation quality of PERC structures is the silicon heterojunction. Most notably is the Heterojunction with Intrinsic Thin-layers (HIT) solar cell, which chemically passivates the surface of the c-Si with intrinsic hydrogenated amorphous silicon (a-Si:H) while allowing charge carriers to conduct through the contact. Doped a-Si:H layers then create the potential gradient necessary for carrier diffusion and charge collection to occur.

Even with it's high performance and simplified fabrication process, the HIT solar cell has potential to be improved upon. The a-Si:H layers produce parasitic absorption of high energy light. Many groups have also found the a-Si:H contacts to be sensitive to annealing treatments above 200°C. This limits the processing space for the metallization...
In this work we use Atomic-Layer-Deposited (ALD) MoOx as a hole-selective contact to c-Si in combination with thin SiOx and Al2O3 passivation layers to study the solar cell parameters of carrier selective contacts without the use of a-Si:H. While the optical properties of MoOx present a significant reduction in parasitic absorption compared to a-Si:H, the temperature stability of the material is still in question. Many groups have been unable to anneal MoOx based contacts above 120°C without degrading the electrical properties of the contact. We show that by using a thin Ni capping layer before Al metallization, the contact remains stable up to 300°C with contact resistivities below 10 mΩ-cm². This presents significant improvements on the thermal budget of the MoOx processing sequence and will allow for more appropriate contact formation steps.

Using Ultraviolet Photoelectron Spectroscopy we measure a work function of 6.2 eV in our 5nm MoOx contact. We simulate the band-bending and hole concentration at the c-Si surface as a function of the MoOx contact work function and show that our films exhibit sufficient hole-selective properties. Additionally, High Resolution Transmission Electron Microscopy images show that when a thin Ni capping layer is not used prior to Al metallization, a 2-3 nm Al2O3 layer forms at the Al/MoOx interface. This insulating interlayer contributes to a large barrier to hole transport, making the Al/MoOx contact incompatible with high efficiency heterojunction solar cells. The Al/Ni/MoOx contact, however, exhibits no such interlayer. This suggests that Ni may act as a diffusion barrier to O species during solar cell fabrication.

Finally, we show that by using a thin (~1 nm) Al2O3 passivation layer at the MoOx/c-Si interface, we are able to achieve a minority carrier lifetime of over 1 ms on n-type c-Si.

Recently, Yang et al. have reported 22.1% efficient c-Si solar cell by applying an atomic-layer-deposited (ALD) TiOx thin layer as electron contact to n-type base [1]. The origin of the electron selectivity of TiOx has been ascribed to the asymmetric current flow at the (n) c-Si/TiOx interface where the conduction band offset is much lower than the valence band offset. On the other hand, we recently found that TiOx can be tuned from electron to hole selectivity by controlling the ALD condition etc. [2]. This offers an interesting possibility that TiOx can be used as a hole selective contact alternative to the widely-used p-type a-Si:H and transition-metal oxides such as MoOx, WOx and V2O5. In this contribution, we show for the first time that TiOx thin layers can act as efficient passivating hole selective contacts.

TiOx thin layers were deposited by thermal-ALD on c-Si (FZ, 1 Ωcm, (100), planer, n-type). First, carrier selectivity of the deposited TiOx was studied by measuring Voc of solar cells. To decouple the carrier selectivity from its surface passivation an intrinsic a-Si:H buffer layer was inserted between c-Si and TiOx. A standard SHJ structure of either (i-n) a-Si:H/ITO or (i-p) a-Si:H/ITO stack was formed as a counter electron or hole contact, respectively. It is found that Voc of the solar cell is 200-400 mV higher when using our TiOx as hole contact than using it as electron contact. The SPV measurement showed that the TiOx induces large band bending (~900 mV) with respect to (n) c-Si while almost no band bending is created when deposited on (p) c-Si. This implies the presence of the negative fix charge in the TiOx, which is considered as one of the origins of the observed hole selectivity of the TiOx. Furthermore, we found that the carrier selectivity of TiOx depends significantly on the work function (WF) of the capping metal (or TCO) contact. The Voc is increased monotonically with increasing the WF of the capping layer when using TiOx as hole contacts. This indicates that band bending in (n) c-Si is significantly influenced by the WF of the capping layer, as it is well-known in the MIS contact system. By using an ITO/TiOx/i a-Si:H stack as an emitter layer on (n) c-Si, we obtained a relatively high Voc of 650 mV. Furthermore, the TiOx is also found to act as a good passivation layer with respect to c-Si. An effective lifetime of >1 ms was obtained by depositing TiOx on (n) c-Si without a-Si:H buffer layer. By optimizing both the surface passivation and the hole selectivity of the TiOx layer, we attained solar cell efficiencies of >18%, demonstrating that TiOx has potential of working as an efficient passivating hole selective contact. We discuss the origin of the hole transport in the TiOx which contradicts to the previous transport model based on the band alignment at the TiOx/Si interface.

Hf Doped ZnO Engineering for Various Solar Cells Architectures

Boulos Alfakes1,1, Juan E. Villegas2, ChunYu Lu1,1, Ibraheem Almansouri1 and Matteo Chiesa1,3,1; 1Khalifa University of Science and Technology, United Arab Emirates; 2New York University, United Arab Emirates; 3UiT The Arctic University of Norway, Norway

The excellent electrical, optical and structural tunability of doped zinc oxide (ZnO) makes it a very good candidate for the replacement of indium-based material in the manufacturing of transparent conductive oxides. In this work, we present a comprehensive investigation of ALD grown hafnium doped ZnO within the context of its integration in different solar cells architectures. Specifically, we focus on the low range doping region, where Hf substitution is believed to be the key for band gap tunability without negatively effecting the carrier transport behavior. Scanning and transmission electron microscopy (SEM and TEM), x-ray diffraction, Kelvin probe force microscopy, Hall-effect measurements, spectrophotometry and ellipsometry were utilized to provide conclusive evidence of the suitability of Hf doped ZnO in different solar cells architectures. A band gap increase is being observed, as well as an increase in transmittance with doping. Electrically, doping is causing a decrease in resistivity and in work function. These results are interpreted in light of first-principles density functional theory simulation (DFT) to elucidate the mechanisms responsible for the electronic and electrical properties of Hf doped ZnO. DFT calculations predict a modification in the band structure of ZnO when Hf is substituted and/or embedded in the ZnO matrix as HfO2 phases. The experimentally measured and theoretically calculated modifications in the properties of the ZnO with Hf doping, validates its compatibility with different solar cells architectures.

Fabrication of Sb2S3 Planar Thin-Film Solar Cell with Vapor Transport Deposition (VTD) Method

Yiyu Zeng, Kaiwen Sun, Jialiang Huang, Micheal Nielsen, Martin Green and Xiaojing Hao; University of New South Wales, Australia

Antimony sulphide (Sb2S3) is another attractive photovoltaic material in the chalcogenide group and has drawn a great attention worldwide in the last decade. In contrast to the widely investigated and commercially competitive thin film solar cells such as CuInxGa1-xSe2 and CdTe, Sb2S3 is non-toxic and exists naturally as stibnite minerals, with both while Sb and S are bothas earth abundant elements. Sb2S3 is a binary compound with a single phase, consisting of linked one-dimensional ribbons. Such a ribbon structure provides a preferential pathway for electron transfer if withalong the desired orientation. Antimony sulphide has high absorption coefficient of α>105 and a bandgap of ~1.7eV, making it a suitable top cell candidate for tandem solar cells with silicon to overcome the single-junction Shockley-Queisser efficiency limitation. In the last decade Sb2S3 has been widely utilized as an efficient sensitizer in dye sensitized solar cells fabricated by chemical bath deposition. However, the CBD method is time-consuming with many undesirable oxide by-products, which usually require complex post treatment for the removal of these residuals.Moreover, reported high efficiency Sb2S3 solar cells have utilized unstable and expensive organic hole transport materials such as P3HT Spiro-OMeTAD, and PEDOT:PSS. While inorganic hole transport materials such as NiO and CuSCN have been investigated, the results have not been promising. Recently, Lijian et al. used V2O5 as the hole transport layer (HTL) and obtained a PCE of 4.8%, demonstrating the highest efficiency of a fully inorganic planar Sb2S3 solar cells up to date. However, the open circuit voltage of such the record cell is 550 mV, which indicates a large Voc deficit implying there is still much work to be done to improve the Sb2S3 absorber quality and interface engineering. Recently, a push towards dry vacuum-based methods, such as the thermal evaporation and atom layer deposition, have been employed to grow high quality Sb2S3 and Sb2Se3 in a relatively clean environment. Additionally, the rapid thermal evaporation (RTE) method has been recognized as an effective and reliable method to grow Sb2S3 thin films, achieving an efficiency of 3.5% with a high Voc of 710mV when using CdS as electron transport layer (ETL). However, the reported orientation of the Sb2S3 is not well controlled when deposited by the RTE method. In this work, we report the first fabricated Sb2S3 thin films with vertical orientation by VTD method. To better understand the key factor that enables the vertical growth of Sb2S3, we use the RTE method as a reference, which does not create vertically aligned Sb2S3 crystals on a CdS buffer layer. We achieved the an efficiency of 4.73% with a high Voc of 710 mV by using the iTO/CdS/Sb2S3/Gold configuration via VTD method compared to 370 mV using RTE method. We propose a simple model to describe the growth process.
Atomic-Layer-Deposited ZnO as a Full-Area Passivating, Contacting and Antireflection Layer for c-Si Solar Cells
Bart Macco, Marc Dielen, Bas van de Loo, Jimmy Melskens and Erwin Kessels; Eindhoven University of Technology, Netherlands

The field of c-Si photovoltaics has strongly diversified in recent years with the advent of a wide variety of novel passivation and passivating contact materials. Recently, we have demonstrated excellent surface passivation using stacks of ultrathin (~1.5 nm) RCA SiOₓ capped with ALD ZnO/Al₂O₃, with an implied open-circuit voltage (V_{oc}) of 725 mV on planar c-Si(n) wafers.[1] Within this SiOₓ/ZnO/Al₂O₃ stack, the RCA SiOₓ enables chemical passivation, similar as in poly-Si passivating contacts. The Al₂O₃ layer on top serves as a dense capping layer: It prevents effusion of H from the ZnO upon annealing, which is needed to hydrogenate the SiOₓ.

The unique aspect of the (doped) ZnO is that it is suited as an antireflection coating (simulated J_{sc} of 41.6 mA/cm²) which is also conductive (< 1 mΩcm). Therefore, if a proper tunnel contact between c-Si/SiO₂/ZnO can be made, the ZnO could serve as a full-area passivating, antireflective and lateral transport layer on the front side of a c-Si solar cell. In this work, we demonstrate several crucial steps to enable this application in industrial cells by looking into the influence of texture and doping level, oxide preparation method, metal contacting and thermal stability.

Firstly, we verified that the stack also passivates on textured c-Si(n) wafers (V_{oc} = 728 mV) and that its passivation on n⁺ diffused surfaces (100 Ω/sq) is on par with industrial SiNx. The stack is thermally stable up to ~550 °C, which is not firing-compatible, but allows for a much higher paste curing temperature than for HIT-type cells.

Secondly, we show that the SiOₓ can be prepared in many ways (RCA, LTO, UV/O₃, NAOS) which all yield good passivation. UV/O₃ however yields the best passivation and is a room-temperature, single-sided treatment which allows for accurate control over the oxide thickness (< 1.65 nm).

Thirdly, in order to be able to contact the ZnO by metal, we can selectively remove the insulating Al₂O₃ capping layer from the ZnO after hydrogenation by a wet-etch. Interestingly, no proper tunnel contact (>10 Ωcm²) can be made on 3 Ωcm c-Si(n) wafers, whereas a “first-try” value of ~0.1 Ωcm² was obtained on n⁺ diffused surfaces (100 Ω/sq). This contact resistivity is sufficiently low to use ZnO as a “hybrid” homo/heterojunction contact on n⁺ surfaces: the n⁺ doped Si surface provides electron-selectivity and facilitates tunneling, whereas the ZnO provides full-area passivation and aids in lateral transport, potentially allowing for higher Ohmic FSFs.

Ongoing work focuses on the effect of the doping levels of both the c-Si and ZnO and the integration of the ZnO on the front of a PERC-type cell.


Controllable Fixed Charge Densities of TiO₂–Based Passivation Layer in c-Si Solar Cells
Dohee Kim and Jihun Oh; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Surface passivation of crystalline Si (c-Si) is a key enabler for achieving high efficiency c-Si solar cells. While an Al₂O₃ surface passivation layer grown by atomic layer deposition (ALD) is known for excellent surface passivation for p-type Si from the negative fixed charges in the Al₂O₃ layer, low refractive index of Al₂O₃ demands an additional anti-reflection coating to suppress optical reflection, which leads to extra capital cost in c-Si solar cell manufacturing. Therefore, the multi-functional passivation layer that can provide both the high level of passivation quality and optimum optical property is necessary for high efficiency and cost-effective silicon solar cells.

Here, we designed the multifunctional Al-doped TiO₂ passivation layer using ALD single process for low cost high efficiency silicon solar cells. TiO₂ film grown by ALD is a promising candidate for front multifunctional passivation layer of p⁺-emitter/n-base structure due to negative fixed charge densities and appropriate refractive index for anti-reflection coating of silicon solar cell. ALD process allows to control the composition accurately and provide excellent passivation quality with thin films. In this work, we controlled the Al concentration in TiO₂ film with amorphous phase from 0 to 15.5 % by adjusting the cycle ratio of Al₂O₃ to TiO₂ in ALD process. We then successfully demonstrated that the fixed charge densities of Al-doped TiO₂ passivation layer can be controlled from -8×10¹¹ cm⁻² to -3×10¹² cm⁻² by varying the amount of Al concentration. As a result, we achieved implied V_{oc} up to 709 mV with 15nm thick Al-doped TiO₂ on n-Si by maximizing field-effect passivation. We also investigated the
The growth of oxides by atomic layer deposition (ALD) over lead-halide perovskites in solar cells is attracting increasing attention for improving environmental and mechanical stability. A wide range of materials have now been investigated, including SnO$_2$, TiO$_2$, Al-doped ZnO and zinc tin oxide. These oxide overlayers have led to unencapsulated perovskite solar cells achieving stable performance for 4500 h in ambient air. However, the range of growth temperatures that can be used to grow the oxide overlayers over the perovskite films is restricted to typical values of only 60 - 100 °C due to the low stability of the perovskites. This limits the mobility and density of the oxide films achievable. In this work, we show that we can open up the processing window of oxides grown over lead-halide perovskites by using atmospheric pressure chemical vapor deposition (AP-CVD). This technique yields oxide films with similar uniformity, density and electronic properties as ALD films at similar growth temperatures, but with orders of magnitude higher growth rates [1]. We investigate the growth of TiO$_x$ over thermally-sensitive CH$_3$NH$_3$PbI$_3$ films. We achieve a growth rate of 1.19 ± 0.04 nm s$^{-1}$ at a deposition temperature of 150 °C, which allows 7 nm TiO$_x$ films to be grown in 6 s (compared to >30 min for ALD). We show that this rapid deposition enables TiO$_x$ to be directly grown on CH$_3$NH$_3$PbI$_3$ films without damage to the bulk or surface, as shown by our X-ray diffraction, X-ray photoemission spectroscopy and time-resolved photoluminescence measurements. Indeed, we show that the TiO$_x$ overlayers can be grown at temperatures exceeding 180 °C without a significant drop in efficiency in CH$_3$NH$_3$PbI$_3$ solar cells. These results can be generalised to triple-cation perovskite devices, as well as to AP-CVD SnO$_2$ overlayers. In particular, we show that the conformal nature of the oxide overlayers lead to perovskite devices with improved performance (reaching 19.7% for triple-cation perovskite devices using a 60 nm SnO$_2$ overlayer). Our work demonstrates AP-CVD to be a versatile technique for growing high-quality oxides over a wide range of processing conditions.

Reference
engineering key interfaces within electrochemical cells. This presentation will describe our efforts to address challenges associated with lithium metal and silicon anodes. Thin films are integrated as ultrathin solid electrolytes in Li metal batteries and as protective coatings on Si anodes to limit undesirable side reactions.

Key requirements for electrolytes in solid-state lithium metal batteries are a large electrochemical stability window and low area-specific resistance (ASR). Solid electrolytes must also possess robust mechanical properties to accommodate large-scale production and integration into conventional lithium battery cell designs. To realize these properties, 50 nm-thick films of lithium phosphate oxynitride (Lipon) were deposited onto microporous polymer separators (Celgard) using RF magnetron sputtering. These separators provide a low ASR due to the thin, dense Lipon film; the total resistance of the separator was determined to be 40 Ω cm² in alkyl carbonate electrolytes, which is much lower than traditional ceramic electrolyte membranes, such as those fabricated from Garnet and NASICON-class of solid electrolytes. Furthermore, these composite separators inhibit chemical cross-diffusion and reaction between anode and cathode in both Li-S and Li-LiMn₂O₄ cells. Both the performance of these hybrid separators in practical lithium-metal batteries and fundamental studies of ion transport at the Lipon-liquid electrolyte interface will be presented.

Silicon is also an intriguing next-generation anode offering charge capacities comparable to lithium metal, yet significant challenges arise from the >300% volume expansion of Si during lithiation. To address continual electrochemical reduction of lithium ion battery electrolyte on Si anodes, nanoscale, conformal polymer films were synthesized as artificial solid electrolyte interface (SEI) layers. Initiated chemical vapor deposition (iCVD) was employed to deposit poly(1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane) (pV4D4) onto silicon thin film electrodes. 25 nm-thick pV4D4 films on Si electrodes improved initial coulombic efficiency by 12.9% and capacity retention over 100 cycles by 64.9% relative to untreated electrodes. pV4D4 coatings also improved rate capabilities, enabling higher lithiation capacity at all current densities. Post-cycling FTIR and XPS showed that pV4D4 inhibited electrolyte reduction and altered the SEI composition, with LiF formation being favored. This work will guide further development of polymeric artificial SEIs to mitigate electrolyte reduction and enhance capacity retention in Si electrodes.

2:00 PM FF05.11.02
Atomic Layer Deposition of Alumina on CVD Silicon Nanostructures—Towards the Development of 3D Ultrastable Aqueous Si Microsupercapacitor
Pascal Gentile1, Anthony Valero1,1, Dorian Gaboriau1,1, Adrien Mery1 and Said Sadki2,1; 1CEA Grenoble, France; 2Université Grenoble Alpes, France

In this work Chemical vapor deposition (CVD) and Atomic Layer Deposition (ALD) has been combined to elaborate electrodes for MicroSuperCapacitors (µSCs) devices. A great deal of attention has been focused on µSCs, for which large series of nanostructured active materials have been developed. We have demonstrated through comprehensive investigations the interest of doped silicon nanostructures grown by CVD with Vapor Liquid Solid (VLS) method as electrodes materials for µSCs using ionic liquid electrolytes [2,3]. The fine morphological tuning of the nanostructure allowed by the bottom-up approach enables specific designs of electrode architectures, with a considerable leeway compared to other techniques. Such latitude allows optimizing porosity and ionic and electronic pathways while keeping robust mechanical and thermal performances, depending on the target application. Si Nanostructures (SiNs) such as Si nanowires and Si nanotrees have displayed excellent electrochemical performances being stable over than 1 million cycles of galvanostatic charge/discharge under a 4 V wide electrochemical windows in EMI-TFSI ionic liquid, with large power densities of 10 mW.cm⁻² and good capacitance values of 0.5 mF.cm⁻² at high current density of 0.5 mA.cm⁻² [4].

However a major silicon weakness which was still hindering its use with aqueous electrolytes is the native uncontrolled growth of silica when subjected to ambient atmosphere. Here we have developed a highly conformal passivation coating of a nanometric high-k dielectric layer of Al₂O₃ based on the rising ALD technique. ALD has proven to allow a nanometric thickness control of the deposited layer while being highly conformal and covering. Electrochemical stability performances in ionic liquid, were enhanced allowing symmetric 2 electrodes devices to reach an unprecedented cell voltage of 5.5 V [5], improving energy and maximum power densities compared to pristine nanostructured silicon. The cyclability was also largely enhanced, with only 3% capacitance fade after 10⁶ galvanostatic charge/discharge cycles at 4 V, and no degradation even after several 10⁶ resilience cycles over a 5 V window [5]. Moreover, the protective alumina layer enables the use of aqueous electrolytes for nanostructured Si based µSCs, which significantly increases the specific power of the devices up to 200 mW.cm⁻² at 0.5 mA.cm⁻² while keeping the capacitance performances at 0.5 mF.cm⁻². Furthermore the system is remarkably able to retain
99% of its initial capacitance after 2 billion galvanostatic charge-discharge cycles at high current density of 0.5 mA.cm\(^{-2}\) in an aqueous electrolyte of Na\(_2\)SO\(_4\).

Eventually we have realized a composite SiNs-Alumina-conducting polymer as electrodes for pseudocapacitive device. This device exhibits promising performances with a specific energy of 2 Wh.kg\(^{-1}\) and a power density of 300 W.kg\(^{-1}\) at a current density of 1 A.g\(^{-1}\). The µSCs was able to retain 80% its initial capacitance after 50,000 galvanostatic charge-discharge cycles at 0.5 A.g\(^{-1}\) [6].


2:15 PM FF05.11.03
Atomic Layer Deposition of Hf-Doped ZnO Thin Films with Enhanced Thermoelectric Properties Jenichi Clairvaux Felizco1, Taneli Juntunen2, Jarkko Etula2, Camilla Tossi2, Mutsunori Uenuma1, Yasuaki Ishikawa1, Yukiharu Uraoka1 and Ilkka Tittonen2; 1Nara Institute of Science and Technology, Japan; 2Aalto University, Finland

ZnO has been a well-explored oxide thermoelectric material owing to its low toxicity, high abundance and good chemical stability. Among the deposition techniques used for ZnO thin film fabrication, atomic layer deposition (ALD) is recently gaining attention due to its excellent film uniformity and precise thickness control down to the Angstrom level. It is also an ideal technique for depositing doped ZnO for thermoelectric applications because optimum electrical properties can be achieved by actively controlling the dopant levels. However, reports on the thermoelectric properties of doped ZnO fabricated by ALD have been limited to a few dopants such as Al and Ga [1-2]. Herein, the thermoelectric properties of ALD Hf-doped ZnO (HZO) thin films are reported for the first time. On Si and glass substrates, ALD growth was performed by sequential pulsing of diethylzinc (DeZn) and H\(_2\)O to form the ZnO, and gas pulsing of tetrakis(dimethylamido)hafnium(IV) (TDMAHf) and O\(_2\) to incorporate the dopants. Three supercycles of ZnO and dopant were deposited, wherein one supercycle is composed of varying nominal dopant amounts (0%, 1%, 2%, 3% and 4%). The deposition temperature was 443 K and nitrogen was used as the carrier gas. Thermoelectric properties were measured from 303 to 453 K (heating) and back (cooling) to observe hysteresis. Below 453 K, pure ZnO sample exhibited higher \(\sigma\) compared to all the HZO samples. However, at 453 K, an increase in electrical conductivity of HZO thin films was observed when a minimum of 3% Hf was added. A maximum of 94.9 S/cm was reached for 4% HZO, which was higher than in pure ZnO. In addition, a large hysteresis was observed with the pure ZnO sample during the cooling scan, leading to a sixfold decrease in electrical conductivity. The Seebeck coefficients are almost similar for the ZnO and HZO samples throughout all temperatures during the heating scan, but a large hysteresis was likewise observed during cooling for the pure ZnO and the lightly doped (1% and 2%) HZO. The 3% and 4% HZO samples displayed minimal hysteresis, leading to a highly stable power factor throughout both heating and cooling stages. A maximum power factor of 157 \(\mu\)W/mK\(^2\) was obtained for the 3% HZO sample at 453 K, exceeding that of pure ZnO. Doping with 3% Hf therefore leads to an enhanced thermoelectric power factor as well as improved stability compared to pure ZnO thin films deposited by ALD.


2:30 PM FF05.11.04
ALD Process Control towards Fabrication of Reliable Nano-Sized Memristive Devices Hehe Zhang, Alexander Harddegen, Felix Cüppers, Stephan Aussen and Susanne Hoffmann-Eifert; Forschungszentrum Jülich GmbH, Germany

Redox-based resistive random access memory (ReRAM) devices are intensively investigated as artificial synapses in neuromorphic applications due to their simple fabrication, switching performance and energy efficiency. For the realization of high-density synaptic networks with large connectivity two concepts are pursued. In the stacking of two-dimensional (2D) passive crossbar arrays, the number of stacked layers is limited by patterning issues. Therefore, blocks with even larger numbers of integrated synapses require real 3D stacking of the memory cells. At this end, atomic layer deposition (ALD) becomes the unique deposition method of choice. Due to its surface reaction
controlled characteristic, ALD enables a conformal and pinhole-free coverage of the structured electrodes by ultra-thin metal oxide layers with high structural uniformity. The performance of nanoscale devices from ALD grown oxide thin films is thus a key factor for future 3D ReRAM architectures. Today’s nano-sized ReRAM devices contain resistive switching layers from metal oxide films of a few nanometers in thickness. The precise control of the layer thickness directly affects the electroforming voltage necessary for the onset of the resistive switching, and also the switching reliability. In addition, the layer’s microstructure and the stoichiometry have to be controlled. Therefore, the device performance strongly depends on the precise control of the film growth behavior.

This talk focuses on the comparison of thin film properties obtained for the most studied oxides in ReRAM research, namely, TiOx, Al2O3, TaOx, and HfOx, fabricated from two different ALD processes, this is, thermal ALD using water vapor and plasma-enhanced ALD utilizing a remote oxygen plasma as the oxygen source. Conformal reproducible growth of a few nanometer-thick oxide films onto structured bottom electrodes is the challenge. Characterization combines structural film analysis with electrical device characterization providing feedback for the ALD parameter optimization. By this means reliable 2D micro- and nanoscale ReRAM devices were fabricated. The oxide layer(s) are stacked between a Schottky electrode and an ohmic electrode. Engineering of both interfaces is carried out to further improve the cell reliability. Especially, for the TiOx-based devices it turned out to be advantageous to add a thin Al2O3 tunneling barrier between the Pt Schottky electrode and the oxide layer to gain the control over leakage. Further, it has been shown that the insertion of a thin TiOx layer between the Ti ohmic electrode and the HfOx switching layer reduces the variability in the resistance values and the set voltage. Here, the character of different oxides and the effect of stack order from combination of several oxide films is discussed, aiming at an interface design and a tuning of the switching behavior enabling a more rational design of ReRAM devices.

2:45 PM FF05.11.05
Sequential Infiltration Synthesis of Nano-Porous Alumina for Resistive Switching Memory with Ultra-High On/Off Ratio and Low Voltage Operation
Bhaswar Chakrabarti1,2,3, Khan Alam4,5, Thomas Gage3, Leonidas Ocola1, Ralu Divan1, Daniel Rosenmann1, Abhishek Khanna1, Benjamin Grisafe1, Toby Sanders6, Suman Datta6, Ilke Arsalan6, Supratik Guha1,3 and Abhinav Prakash1; 1The University of Chicago, United States; 2Indian Institute of Technology Madras, India; 3Argonne National Laboratory, United States; 4King Fahd University of Petroleum and Minerals, Saudi Arabia; 5University of Notre Dame, United States; 6Arizona State University, United States

Resistance switching in metal-insulator-metal structures has been extensively studied in recent years due to potential applications in non-volatile memory technology as well as alternative computational frameworks1,2. Despite their scalability (10 nm), device density (4F2), high switching speed and endurance, resistive memories still suffer from considerable performance trade-offs between low voltage operation, high on/off ratio and device variability. In this work we report for the first time sequential infiltration synthesis (SIS) as a pathway to develop ultra nanoporous oxide thin films for high performance conductive-bridge resistive memory. SIS is a recently developed modified atomic layer deposition (ALD) process whereby the inorganic precursor molecules for oxide growth infiltrate a polymer thin film matrix.3,4 In this work we grow nanoporous alumina at 95°C, using Poly (methyl methacrylate) (PMMA) as the polymer phase and trimethyl aluminium (TMA) and water as the ALD precursors. Nanoporous alumina with 5 nm pore size and ~ 70% porosity is obtained after removing the polymer phase by rapid thermal annealing for 20 minutes in a mixture of O2/Ar/N2. Crossbar resistive memory devices of size ranging from 200x200 nm² to 1 µm² are fabricated with Pt as the bottom electrode, nanoporous alumina as the switching layer and Ag as top electrode. The nanoporous alumina devices demonstrate ultra-low operating voltages (~±550 mV) and ultra-high on/off ratio (> 10⁹) in addition to pulse endurance up to 1 million cycles and high temperature (125 °C) retention for up to 10⁴ seconds. The combination of ultra-low operating voltages and extremely high on/off ratio shows the best performance reported so far. In addition, the devices also exhibit low intrinsic variability with standard errors ~2% for the operating voltages, <2% for the on-state resistance and <10% for the off state resistance values. Combining high resolution transmission electron microscopy, 3D tomography and electrical characterizations we argue that the presence of high internal free surface area results in ultra-low power operation.

REFERENCES:

**3:00 PM BREAK**

**3:30 PM FF05.11.06**

Atomic Layer Deposition of Metals and Oxides onto Structured Si to Fabricate Efficient Photoanodes

Maxime Dufond¹, Maimouna Diouf¹, Gabriel Loget², Chiara Cozzi³, Giuseppe Barillaro³, Jean-Manuel Decams⁴, Sandra Haschke⁵, Julien Bachmann⁶, and Lionel Santinacci¹; ¹CNRS, Aix-Marseille Univ., France; ²CNRS, Univ. Rennes 1, France; ³University of Pisa, Italy; ⁴Annealsys SAS, France; ⁵University of Erlangen-Nuremberg, Germany; ⁶Saint Petersburg State University, Russian Federation

Water photosplitting is a promising way to transform the sunlight into a storable and transportable energy source. Among numerous semiconductors, Si can be used as photoanode because it absorbs in the visible range and its electronic structure is suitable to drive water photooxidation [1]. Though, Si suffers from a strong corrosion at high pH and it exhibits a high reflectivity. The present approach consists of depositing oxide and metal thin films to protect the surface and to enhance the Si electroactivity. To further improve the photoelectrode performances, various surface structuring methods are used to enlarge the light absorption, to increase the active area and to improve the charge collection.

Since Atomic Layer Deposition (ALD) is a well-adapted technique to coat both planar and tortuous surfaces, it has been used to grow a thin protective layer of TiO₂ on Si. An exhaustive investigation of the influence of the deposition parameters onto the final photoelectrochemical properties has revealed the crucial impact of the nature of the precursor (titanium isopropoxide, TTIP or tetrakisdimethylamidotitanium, TDMAT) as well as the effect of the process temperature. A perfect stability is reached when the TiO₂ layer is grown using TDMAT at 150°C. This has been ascribed to the easier Ti–N bond breaking during the TDMAT pulse. A detailed electrochemical study has also shown that Si oxidation and etching can proceed through the TiO₂ thin film at open circuit potential (ocp) under low illumination.

To increase the photocurrent and to lower the overvoltage, a co-catalyst must be added. Metallic Ni has been deposited by PVD or electrodeposition [2,3] but the quality of the films is not fully satisfying on tortuous substrates. In the present work, Ni has been deposited onto the TiO₂-covered Si according to a two-step process: (i) conformal ALD of NiO from Ni(CpEt)₂ and O₃ and (ii) the reduction to Ni by annealing under H₂ atmosphere. The efficiency of such multilayered photoelectrodes is drastically improved using significantly less Ni and the photoanodes exhibit a long term stability.

This approach has been extended to structured Si surfaces such as macroporous [4], nanospikes [5] and micropillars [6]. The use of those simple electrochemical structuring methods has led to enhanced water photooxidation on oxide-covered Si. It has been confirmed using another protective layer: Fe₂O₃. Iron oxide is grown by ALD using Fe(CpBu)₂ and O₃. In this later case, the photocurrent is increased by a factor 20 when using Si nanospikes as substrates.

This work shows clearly how various, well-controlled, ALD processes and surface structuring methods can be combined to optimize the photoanode properties. The electrochemical investigations give new insight on the photoelectrochemical phenomena occurring at the solid/liquid junction in both operating conditions and at ocp.

In the past decade, inorganic semiconductor light-emitting diodes (LEDs) based on the gallium nitride (GaN) material system were established in many everyday devices as an integral part of modern communication and consumer electronics. The conventional GaN-based LED technology relies on p-n junctions with embedded indium gallium nitride (InGaN) quantum wells which are used to obtain emission in the blue spectral range. However, the p-doping of GaN involves challenges leading to low conductivity of the p-GaN of several S/cm at high defect densities. Today, the technological difficulties of p-doping have not yet been completely overcome and gain new relevance by the development of three-dimensional (3D) LED structures to further increase the efficiency of LEDs.

In this work, we replaced p-GaN of conventional GaN-LEDs with a p-conductive poly(3,4-ethylenedioxythiophene) (PEDOT) by using oxidative chemical vapor deposition (oCVD) to obtain novel hybrid-LED architectures based on inorganic and organic materials. In comparison to classical wet-deposition techniques, e.g. spin-coating of PEDOT:PSS, we observed conformal, pin-hole free, ultrathin (<100 nm) coatings of oCVD-PEDOT on planar and nano-rod GaN-LED surfaces by using gaseous monomer (EDOT) and oxidant (FeCl₃). We observed stable, blue (~450 nm) electroluminescence (EL) for an applied voltage of > 3 V under ambient conditions for planar hybrid-LED structures which are directly fabricated on full 2"-wafers. We determined the current-voltage profiles of the hybrid-LEDs and obtained diode characteristic behavior. In comparison to conventional p-GaN LEDs the hybrid-LED configuration provides a more intensive, areal light emission which is attributed to the improved lateral conductivity of oCVD-PEDOT with ‘face-on’ orientation of the polymer backbone. Our results demonstrate the feasibility of oCVD for producing and integrating a highly p-conductive transparent polymer thin film into planar LED devices.

Membrane-based organic solvent separations promise a low-energy alternative to traditional thermal separations but require advanced materials that operate reliably in chemically aggressive environments. While inorganic membranes can withstand demanding conditions, they are costly and difficult to scale. Polymeric membranes, such as polymers of intrinsic microporosity, are easily manufactured into form factors consistent with large-scale separations (e.g., hollow fibers), but perform poorly in aggressive solvents. Here, a new post-fabrication membrane modification technique, vapor phase infiltration (VPI) is reported that infuses polymer of intrinsic microporosity 1 (PIM-1) with inorganic constituents to improve stability while generally maintaining the polymer’s macroscale form factor and microporous internal structure. The atomic-scale metal oxide networks within these hybrid membranes protect PIM-1 from swelling or dissolving in organic solvents including: tetrahydrofuran, dichloromethane, and anisole. This atomic-scale metal oxide network further decreases the molecular weight cutoff (MWCO; the smallest molecular weight the membrane “successfully” rejects) in n-heptane and toluene from a MWCO of about 600 g/mol for pristine PIM-1 thin film composite membranes to 204 g/mol for hybrid AlOx/PIM-1 membranes. The hybrid membranes further retain this MWCO and high levels of rejection (>95%) in solvents that traditionally swell or even dissolve pristine PIM-1 (such as ethanol and tetrahydrofuran). The decrease in MWCO and increase in stability of AlOx/PIM-1 hybrid membranes allows them to perform separations not only between solutes and solvents, but also separations of more challenging systems such as those comprising multiple solvents. For example, the hybrid AlOx/PIM-1 membranes are capable of enriching the toluene concentration in a mixture of 90 wt% toluene, 5 wt% 1,3,5-triisopropylbenzene, and 5 wt% 1,3-diisopropylbenzene from 90.0 wt% to 97.8 ± 0.3 wt% toluene. In this talk, we will discuss the chemical mechanisms of the infiltration process that we believe create the hybrid structures necessary to support this enhanced stability and separation performance.

Vapor-Phase Inorganic Infiltration into Hierarchically Self-Assembled Block Copolymer Thin Films Generates Three-Dimensional Electroactive ZnO Nanomesh

Ashwanth Subramanian1, Gregory Doerk2, Kim Kisslinger2, Daniel H. Yi1, Robert B. Grubbs1 and Chang-Yong Nam1,2; 1Stony Brook University, United States; 2Brookhaven National Laboratory, United States
Infiltration synthesis, an emerging material hybridization technique derived from atomic layer deposition (ALD), utilizes the infiltration of vapor-phase organometallic precursors into polymeric templates to generate organic–inorganic hybrids with uniquely enhanced material properties. A subsequent removal of organic matrix from the hybrid further generates functional inorganic nanostructures directly converted from the starting polymeric template, providing a new inorganic nanopatterning methodology. Fundamentally, the infiltration synthesis is mediated by the binding reaction between infiltrating Lewis-acidic organometallic precursors and Lewis-basic functional groups available in the polymer matrix. Hinging on this principle, self-assembled block copolymer (BCP) thin films (e.g., poly(styrene-block-methylmethacrylate) (PS-b-PMMA)) enable an area-selective infiltration of inorganic components owing to the intrinsically available, spatial chemical contrast (i.e., chemically reactive domains being spatially separated from non-reactive domains). While the infiltration synthesis of nanopatterned AlOx is routinely performed by infiltrating trimethylaluminum (TMA) into BCP templates, other more functional metal oxides, such as ZnO, are not readily amenable to the nanopatterning by infiltration synthesis unless a pre-infiltration of insulting AlOx (i.e., “AlOx-priming”) is applied, due to relatively weaker binding affinities between precursors (e.g., diethylzinc (DEZ) for ZnO) and active polymer templates. In this work, we report the infiltration synthesis of optoelectrically active, three-dimensional (3D) pristine ZnO nanomesh architectures by combining a modified infiltration synthesis protocol called micro-dose process with hierarchically stacked self-assembled polystyrene-block-poly(2-vinylpyridine) (PS-b-P2VP) BCP thin films. The combination of new infiltration protocol and more reactive BCP template with 3D hierarchical self-assembly not only obviates the need of AlOx-priming but also generates a new 3D ZnO nanomesh structure, which exhibits optoelectrical functionality, featuring stack-layer-number-dependent electrical conductance resembling the percolative transport originating from the intrinsic morphological network connectivity of the lamellar BCP pattern with symmetric block ratio. The results not only illustrate the first demonstration of electrical functionality based on the ZnO nanoarchitecture directly generated by the infiltration synthesis in self-assembled BCP thin films but also present a new, large-area scalable, metal oxide thin film nanoarchitecture fabrication method utilizing industry-compatible polymer solution coating and ALD. Given the large surface area, 3D porosity, and readily scalable fabrication procedures, the generated ZnO nanomesh promises potential applications as an efficient active medium in chemical and optical sensors.

4:30 PM *FF05.11.10
Atomic Layer Processing—A Toolbox for Fabricating Novel Functional Hybrid Materials Mato Knez1,2; 1CIC nanoGUNE, Spain; 2IKERBASQUE, Spain

Atomic layer processing is an umbrella term for several processing techniques that base on atomic layer deposition (ALD). Those include thin film coatings with inorganic or organic materials, atomic layer etching and polymer infiltration strategies.

The ALD process can be seen from various perspectives. On the one hand, it allows controlled deposition of thin films on a variety of substrates and in this way enables a modification of a given functionality of a surface or even introduction of a new functionality. On the other hand, it may be seen as a chemical reactor that allows precise dosing of a chemical, allowing for chemical interaction and modification of the substrate. Considering both points of view, the process opens large variation possibilities for a design of novel functional materials for emerging applications and devices. Among those functional materials hybrid materials play an increasingly important role. Hybrid materials are in most cases blends of inorganic and organic materials and are considered to be key for the next generation of materials research. The main goal while fabricating such materials is to bridge the worlds of polymers and ceramics, ideally uniting the most desirable properties within a singular material. Furthermore, in a well performing hybrid material the individual components will add value to their counterpart in a synergistic way. In this talk, some approaches will be discussed that show great promise for establishing ALD as the method-of-choice for innovation in technological fields beyond the microelectronics industry. Rather than growing thin conformal films, the ALD process technology is applied to controllably grow nanoparticles on functional substrates adding value to their chemical or electrochemical properties. In an adapted processing mode, the ALD processing technology also allows infusing metals into polymeric substrates, which leads to novel material blends that cannot easily be obtained in other ways. In either of those cases the chemical or physical properties of the initial substrate are improved or new functionalities added. With some showcases, this talk will discuss approaches towards non-traditional application of ALD to fabricate novel materials with great promise in energy storage, catalysis, personal protection or flexible electronics. We will show examples where mechanical and electronic properties of polymeric materials have been significantly improved through nanoscale coatings and infiltration. Those polymers include natural polymers such as spider silk, collagen, etc. as well as technical polymers such as Kevlar, polyaniline and...
polythiophene. The characterization of the resulting material has been done by means of various spectroscopies, microscopies and modelling by density functional theory.

SESSION FF05.12: Devices and Applications Enabled by ALD/CVD II
Session Chairs: Karen Gleason and Sven Van Elshocht
Friday Morning, December 6, 2019
Hynes, Level 3, Room 310

8:30 AM FF05.12.01
On the Origin of the High Conductivity of Intrinsic ALD-ZnO Daniel Hiller¹ and Dirk König²; ¹The Australian National University, Australia; ²University of New South Wales, Australia

ALD-ZnO thin films can achieve conductivities of ≤3 mOhm cm without any intentional doping such as by supercycling ALD-Al2O3 to deposit Al-doped ZnO (AZO). Whereas the latter allows for conductivities down to the 10^-4 Ohm cm range, the mobility of ALD-AZO is significantly reduced by impurity scattering and the free carrier absorption is increased, which induces e.g. optical losses when applied to solar cells. Generally, two different models for the n-type conductivity in ZnO are discussed in the literature: intrinsic ZnO point defects and hydrogen. However, ZnO deposited or grown by methods other than thermal ALD rarely reach the very high conductivity range that is essential for its application as transparent conductive oxide (TCO). Hence, ALD appears to introduce a very efficient intrinsic doping mechanism into the material unlike the other methods. We will show via T-dependent Hall-measurements that the intrinsic doping is so high that it induces a semiconductor-to-metal-transition (Mott transition). By means of isotope studies (deuterium vs. hydrogen) the origin of the ~1 at% H-concentration in the ALD-ZnO thin films is determined. Using a comprehensive range of structural-chemical characterization methods (FTIR, NRA, NMR, c-AFM, XANES at the O and Zn K-edges) the bonding configuration of H in ZnO is studied in detail. Finally, different models for the incorporation of H into the ZnO network and their resulting density of states (DOS) are simulated by density functional theory (DFT) to explain the very high conductivity of ALD-ZnO.

8:45 AM FF05.12.02
Molecular Layer Deposition of Metal-Organic Thin Films with Resistive Switching Properties for Neuromorphic Computing Mikko Nisula and Christophe Detavernier; Ghent University, Belgium

Recently, artificial neural networks (ANN) have revolutionized the field of artificial intelligence with human-like performance in fields such as computer vision and speech recognition. However, the current computers with von Neuman -architecture are ill-suited for the massively parallel operations required for ANNs resulting in high energy consumption. Neuromorphic computing aims to greatly improve the energy efficiency by emulating the functionality and interconnectivity of the biological neural networks on the hardware level. In biological neural networks, communication between neurons is facilitated by synapses that enable combined memory and processing. Development of brain-like computers requires materials and devices that have the same functionalities as the real synapses.

Metal-organic hybrid materials (coordination polymers) present an interesting candidate for this task. Their electronic conductivity can be modulated electrochemically by controlling the oxidation state of the material, and can be used to model the synaptic weight. The interplay of the metal and organic constituents enables the tuning of the electric/electrochemical properties towards low device conductance and low power consumption. Additionally, as the redox reactions are coupled with the motion of an associated counter ion, the difference in the electron and ion mobilities could potentially be harnessed to simulate various time dependent synaptic functionalities such as short- and long-term memory. However, currently the poor processability of coordination polymers limits their applicability for nanotechnology applications.

Here we demonstrate that Molecular Layer Deposition (MLD) is extremely well suited for this application. As an extension to ALD, MLD expands the self-limiting gas-surface reactions to hybrid organic-inorganic materials with the implementation of volatile organic molecules as the co-reactant. As a solvent-free, gas-phase processing technique it is in principle also compatible with the existing CMOS processing methods. As a proof-of-concept, we
developed a novel MLD process for Cu-dithiooxamidate based thin films. The growth and composition of the films is characterized with spectroscopic ellipsometry, XRR, XRD, XPS, AFM and FTIR. The resistive switching properties are explored in simple two-terminal devices arranged in cross-bar arrays of variable node sizes. The deposition process is shown to comply with the principles of ALD with surface saturation limited growth. Excellent thickness uniformity and low surface roughness (RMS < 0.3 nm) can be realized over large area substrates. The solid-state devices demonstrate an oxidation state dependent dynamic conductance range spanning over one order of magnitude. In pulsed operation mode similar to biological neurons, the devices demonstrate many of the basic synaptic functionalities. The rate of change in the device conductance is dependent on the excitation frequency and amplitude, thereby emulating spike-rate and spike timing dependent plasticity (SRDP and STDP). Furthermore, both volatile and non-volatile changes in device conductance can be realized to mimic the short and long-term plasticity (STP and LTP) of the biological synapse.

9:00 AM FF05.12.03
PbI₂ Deposition from Solution-Atomic Layer Deposition for Photovoltaic Application Maïssa Barr¹, Ceyla Asker¹, Soheila Nadiri¹, Karen Forberich², Felix Hoga³, Tobias Stubhan³, Hans Egelhaaf⁵, Christoph J. Brabec² and Julien Bachmann¹; ¹FAU-CTFM, Germany; ²i-MEET, Germany; ³ZAE Bayern - Erneuerbare Energien, Germany

We propose and demonstrate a novel thin film deposition technique by transferring the principles of atomic layer deposition (ALD), known with gaseous precursors, towards precursors dissolved in a liquid. The technique can also be considered as a generalization of already established methods such as the ‘layer by layer’ growth or the ‘successive ion layer adsorption and reaction’ (SILAR). 'Solution ALD' (sALD) shares the fundamental properties of standard ‘gas ALD’ (gALD), specially the self-limiting growth and the ability to coat conformally deep pores. It has been already shown that it is possible to transfer standard reactions from gALD to sALD such as TiO₂ deposition. However, sALD also offers novel opportunities such as overcoming the need for volatile and thermally robust precursors.

In the following the targeted field is photovoltaic. A great deal of interest has appeared on a new generation of material for solar cells application. Among them the perovskites are particularly interesting and the most studied one is CH₃NH₃PbI₃ (MAPI). The existing deposition methods such as spin coating or vapor-deposition techniques do not allow a control at the atomic level. ALD has been used to deposit PbS but it needed a two-step conversion method to obtain a perovskite. Therefore, a new process based on sALD is developed to deposit PbI₂. It allows the use of inexpensive lead salt and it is easy to process. Then, the PbI₂ can be easily converted to MAPI. The PbI₂ deposition was achieved with Pb(NO₃)₂ and LiI via s-ALD on large samples (up to 10 cm*10 cm). The ALD behavior has been shown. The influence of the deposition parameters on the morphology, the crystalline structure and the chemical composition has been investigated by scanning electron microscopy, atomic force microscopy, grazing incidence x-ray diffraction and x-ray photoelectron spectroscopy. The growth of PbI₂ has been studied on different oxides with various chemical pre-treatments. Later, the obtained PbI₂ has been converted to MAPI by vapor annealing. The influence of the temperature, the time and the type of gas on the conversion has been investigated the different substrates. Furthermore, the influence of the ALD parameters on the properties of the perovskite layer has been studied. Thus, the perovskite layer has been integrated into a solar cell.

9:15 AM FF05.12.04
Lithium-Containing Thin Films by Atomic Layer Processing John Hennessy; Jet Propulsion Laboratory, United States

We report on the development of lithium compounds by atomic layer deposition and atomic layer etching for space applications related to far ultraviolet telescope mirrors and energy storage devices. Lithium fluoride is a promising next generation mirror coating material for astrophysics instruments and initial ALD prototype mirrors have exceeded the performance and stability of legacy PVD systems. We have also investigated improvements in stability obtained by the use of nanolaminates with ALD aluminium fluoride. Our HF-based approach to the deposition of these materials has also led to thermal atomic layer etching methods that can be implemented on the same aluminum mirror systems to gently remove native oxide from the aluminum surface. Exploring an interaction between trimethylaluminum and HF has been shown to greatly enhance the etch effect on aluminum oxide as a function of substrate temperature. Planned flight demonstrations of these coatings on NASA sounding rocket and CubeSat missions will be discussed.
The same material system is also a promising battery interface material, and this talk will present initial results on
the passivation of Li-metal anodes using this ALD approach. The use of ALF₃, LiF, and intermediate phases of the
two have been investigated for their ability to improve cycling stability and capacity in test cells. The same
interactions with alkali materials observed in etching experiments is shown to influence the behavior of atomic layer
processing approaches on Li-metal anodes.

9:30 AM FF05.12.05
Atomic Layer Deposition as a Tool to Produce Photonic Materials for High-Temperature Applications Kaline
P. Furlan¹², Robert Zierold², Alexander Y. Petrov³, Robert Blick², Manfred Eich³, Gerold A. Schneider⁴ and Rolf
Janssen¹; ¹TUHH, Germany; ²University of Hamburg, Germany; ³Technische Universität Hamburg-Harburg,
Germany

Highly-porous ceramics are employed in a variety of technological applications, such as filtration, catalysis, heat
insulation and photonics. Photonic materials for high-temperature applications are expected to perform while being
exposed to temperatures higher than at least 800 °C. Nonetheless, this exposure usually causes detrimental
morphological changes with associated impairment of the photonic properties. Such properties are defined during
the fabrication process and are related not only to the material composition but also to the structure present at
different scales. 3D inverse opal photonic crystals (PhCs) are usually produced by the infiltration of a polymeric
template either by sol-gel, colloidal routes, chemical vapor deposition or atomic layer deposition (ALD). Hereby, we
demonstrate the production of ceramic-based photonic materials by combining the controlled self-assembly of
monodisperse particles with ALD. A variety of ceramic PhCs produced via ALD will be presented and their
behavior when exposed to high temperatures depicted. By specifically designing and controlling the ALD process,
materials with tailored composition are obtained which present a photonic stopgap even after exposure at 1400 °C, a
remarkable achievement concerning temperature stability. At last, an example of additive manufacturing combined
with colloidal assembly (AMSA) will be presented as a demonstration of large area templating, which in
combination with ALD creates new possibilities for photonic and highly-porous materials production.

9:45 AM FF05.12.06
ZnO Nanotube-Based Gas Sensors and Metal-Chalcogenide Memristors by Atomic Layer Deposition with an
Oxygen Plasma and Annealing Processes Sungkwon Cho, Kyungsub Lee and Seonghoon Lee; Seoul National
University, Korea (the Republic of)

ZnO nanotubes with a wall thickness on the order of nanometers were produced by atomic layer deposition (ALD)
with an organic template, using diethyl zinc as Zn precursors and water as O precursors. The organic template was
removed by an O₂ plasma process and a thermal annealing process, with the wall structure of the ZnO nanotubes
maintained during the removal of the template. We investigated the response and selectivity of a ZnO nanotube to
ethanol and hydrogen gases as a function of its wall thicknesses. The ZnO nanotubes with a wall thicknesses of 10
nm showed the highest gas response (defined as the ratio of electrical resistances, R_air/R_gas, under air atmosphere to
the mixed air atmosphere with ethanol vapor) of 1184 toward 100 ppm at 450°C. The ZnO nanotube with a wall
thickness of 10 nm was wholly depleted and thus highly responds to the adsorption of chemical species on its
surface. Accurate control of the wall thickness of the ZnO nanotubes is crucial to make ZnO nanotube sensors with
high response. The memristor is considered as the one of the promising candidates for next generation gas sensor,
nanoelectronic computing device. Metal-chalcogenide memristors with small thicknesses and high ionic mobility
were fabricated with ALD, shadow mask patterning technique, and metal electrode deposition.

10:00 AM BREAK

10:30 AM OPEN DISCUSSION

10:45 AM *FF05.12.08
Novel Material and Process Options for Future Technology Nodes in Semiconductor Industry Sven Van
Elshocht; imec, Belgium

As dimensions have been shrunk close to the limits of what is physically possible, novel materials as well as
alternative device concepts and architectures are increasingly required. Examples of such materials can be logic gate
spacers with lower dielectric constants, alternative channel materials with a higher mobility or metals with
decreasing resistivity to name a few. These are being added to the widening list of novel materials with every new
technology node. In addition and independent of the application, there is an ongoing trend of 3D integration: logic
(FinFET), DRAM (trench or pillar capacitors) or NAND Flash (staircase 3D NAND) are examples of the how
devices have been innovated into the third dimension to enable a continued area scaling and related performance
benefit. Such 3D architectures imply the need for conformal deposition techniques such as atomic layer deposition.
In addition, to reduce the level of edge placement error, self-aligned process schemes and the use of selective
deposition is being explored.
In this presentation, we will discuss how the semiconductor landscape is evolving and how material innovation is an
absolute must. We will highlight some of the material options that are being considered and touch upon selective
deposition to facilitate integration schemes.

11:15 AM FF05.12.09
Oxidative Chemical Vapor Deposition Enabled Poly(3-methylthiophene) Coating on Horizontally Aligned
Carbon Nanotubes for Flexible Supercapacitors with Ultrahigh Areal Capacitance Yue Zhou1,2;
1Massachusetts Institute of Technology, United States; 2South Dakota State University, United States

Together with the development of flexible and wearable devices, there is a growing demand of flexible energy
storage devices as power sources. Supercapacitors, bridging the gap between batteries and capacitors, are very
promising among the candidate power solutions. However, one of the key challenges for wide application of such
flexible supercapacitors is that the maximum current density allowed for them is not high enough. The issue is
partially induced by the structure of the electrode materials. Traditionally, randomly aligned carbon nanotubes are
used as electrode material for supercapacitors, hindering the ion transport inside the electrode and therefore limiting
the current density it can achieve. In this work, we demonstrate that horizontally aligned carbon nanotubes (CNTs)
exhibits superior ion transport inside the electrodes, and therefore significantly enhance the maximum current
density. At the same time, conjugated polymers with pseudocapacitive characteristics have drawn much attention for
the application of supercapacitors to enhance their capacitance. We for the first time, demonstrate oxidative
chemical vapor deposition (oCVD) synthesis of a conjugated polymer, poly(3-methylthiophene) (P3MT). With only
one methyl as the side group of the thiophene ring, P3MT demonstrates higher density of effective conjugation
(polythiophene structure) than other modified polythiophene-like polymers, such as PEDOT and poly(3-
hexylthiophene). In this way, the lighter repeating unit increases specific capacitance. With oCVD, we also
demonstrated conformal coating of P3MT on CNTs with an average thickness of ~5 nm. The resulting device
exhibits high areal capacitance of 3.1 F cm-2 at 5 mA cm-2, with areal capacitance shown to remain high at 1.8 F cm-
2 even at a current density of 200 mA cm-2, which is much improved compared to the state-of-the-art devices.
Furthermore, little change in cell performance is observed under high strain, demonstrating the mechanical and
electrochemical stability of the electrodes.
Acknowledgement: This work was supported by Analog Devices, Inc. Some experiments were performed through
use of the core facilities at the Institute for Soldier Nanotechnologies at MIT by the U.S. Army Research Laboratory
and the U.S. Army Research Office under contract number W911NF-13-D-0001. This work was also supported by
SDBOR competitive grant.

11:30 AM FF05.12.10
How Atomic Layer-Deposited Oxides Can Push Artificial Photosynthesis towards Terawatt Scale Won Jun Jo,
Georgios Katsoukis and Heinz Frei; Lawrence Berkeley National Laboratory, United States

Solar-driven CO₂ conversion needs to reach at least a 10 terawatt scale to have impact on the global fuels market. To
realize this unprecedented level of CO₂ fixation using H₂O as electron source, we have adopted a unique method of
leveraging atomic layer deposition (ALD) into the seamless constructions for photocatalytic nanotube arrays, which
are designed for gas-phase CO₂ reduction using sunlight and water. Specifically, such arrays have a large number of
ALD-grown core (Co₃O₄)-shell (SiO₂) nanotubes operating as independent photosynthetic units under ambient
conditions. The SiO₂ nanoshell serves as a H⁺ transmitting and O₂ impermeable membrane to spatially separate H₂O
oxidation catalysis by Co₃O₄ inside of the tube from CO₂ reduction catalysis by Cu nanoparticles outside of the tube.
This inherent product separation geometry allows to address long-standing scientific barriers of optimizing the
combinations of photoactive materials (thermodynamic efficiency) and minimizing charge transfer losses and
unwanted reactions (quantum efficiency) of artificial photosynthetic systems.
Performance evaluation and stepwise improvement of photocatalytic efficiency of the array include the optimization of the nanowall composition for structural stability, as well as quantitative evaluation and mechanistic understanding of charge-carriers (proton and electron) transfer across the core-shell nanotube wall using atomic resolution imaging, infrared spectroscopy, and electrochemical methods. Photocatalytic efficiency of the fully functionalized nanotube array is measured by time-resolved product monitoring through infrared, optical and mass spectroscopy. This measurement is further underpinned by mechanistic framework derived from parallel photocatalytic and photoelectrochemical studies using cm²-scale planar analogs of the core-shell nanotube walls in H-cell configuration.

11:45 AM FF05.12.11
Characterizing the Robustness of β-SiC Coatings for Applications in Magnetic Fusion Energy
Tyler Abrams¹, Stefan Bringuier¹, Sean Gonderman¹, Dmitry Rudakov², Gregory Sinclair³, Ezekial Unterberg⁴, Robert Wilcox⁴ and Leo Holland¹; ¹General Atomics, United States; ²University of California, San Diego, United States; ³Oak Ridge Associated Universities, United States; ⁴Oak Ridge National Laboratory, United States

Spectroscopic measurements of the gross erosion of crystalline silicon carbide (β-SiC) coatings, fabricated via chemical vapor deposition (CVD), have been measured under D and C ion bombardment using the DIII-D National Fusion Facility [1]. These measurements reveal that the physical sputtering of silicon from these SiC coatings is reduced by a factor of ~10 relative to pure Si material in the low ion impact energy range (50-300 eV) relevant to magnetic fusion devices. This result is consistent with TRIM.SP and MD modeling [2] predicting a suppression of Si physical sputtering from β-SiC due to the enhanced surface binding energy imparted by Si-C chemical bonds. A 2-5x reduction in the C chemical erosion rate from SiC is observed relative to ATJ graphite, the standard wall armor material used in DIII-D and many magnetic fusion experiments. The near-elimination of C chemical sputtering from SiC confirms and extends previous studies on high-flux linear plasma devices [3]. No evidence of Si chemical erosion via silane (Si, D) compounds is observed, but some Si II emission persists below the ion impact energy threshold for Si physical sputtering, suggesting that a chemical release mechanism is present.

SiC samples of 100-200 μm thickness were prepared via CVD on ATJ graphite substrates in the General Atomics Nuclear Technologies & Materials Laboratory. These materials were exposed to energetic (50-300 eV) D ion bombardment up to a fluence of 2x10²³ m⁻². Transient plasma pulses with D ion impact energies of 1-2 keV and heat fluxes up to 10 MW m⁻² were also utilized for thermal shock testing. These materials were tested in the DIII-D tokamak using a removable sample exposure probe known as the Divertor Materials Evaluation System (DiMES). In-situ measurements of Si and C gross erosion were conducted using line emission spectroscopy and the S/XB method [4]. No macroscopic damage to the SiC coatings was evident upon post-mortem visual inspection and detailed morphology analysis revealed no detectable change to the surface roughness before and after exposure. Microstructural analysis via SEM indicated features with characteristic size < 5 μm were not preserved, potentially due to evaporation and/or viscous flow processes. Energy Dispersive X-Ray Spectroscopy analysis revealed a slight enrichment of the Si surface concentration, relative to C, after plasma exposure. This result is corroborated by the spectroscopically inferred Si gross erosion measurements, which are quantitatively consistent with TRIM.SP physical sputtering predictions under the ad hoc assumption of a 5% Si enrichment fraction of the SiC surface. These results imply potentially favorable erosion properties for crystalline β-SiC under low impact energy hydrogenic ion bombardment characteristic of magnetic fusion energy devices. In conjunction with the robust neutronic properties of SiC at high temperatures, these results motivate serious consideration of SiC as wall armor material in future high power-density magnetic plasma confinement devices.

Work supported by the US Department of Energy under DE-FC02-04ER54698.

The tutorial will provide the attendees with a short course in advanced experimental and computational techniques as applied to the study of reactive materials. In the experimental section, additive manufacturing techniques, specifically direct ink write (DIW), are discussed in this context. The content will cover the tools, safety considerations for using this technique with reactive materials, challenges associated with material development, and toolpath development. The goal of this section is to provide 3D printing novices with the background to start working in this area, while also providing experienced users with advanced tips and tricks to improve the quality of their prints.

The computational section will focus on the use of molecular and atomistic modeling as they pertain to reactive materials. This content will contain a review of modern tools and state-of-the-art techniques for the modeling of energetic materials and their combination into a multi-scale approach to describe material behavior. The potential of these modeling approaches for the future of energetic materials, from manufacturing issues to advanced modeling of combustion fundamentals and applications, is also presented.

8:30 PM
Practical Aspects of 3D Printing with Reactive Materials
Michael D. Grapes; Lawrence Livermore National Laboratory

Introduction to DIW Printing
A description of DIW in the context of all 3D printing techniques, highlighting ways that it is similar and different.

Materials for DIW Printing (DIW “Inks”)
What are the characteristics of a good DIW ink? How are inks made? How are they tested? Illustrate with specific examples of both inert and reactive inks.

Hardware for DIW Printing
Schematic of a typical DIW printer. Highlight options for materials dispensing and their relative strengths and weaknesses, illustrated with examples.

10:00 AM BREAK
10:30 AM
DIW Print Design

DIW presents unique challenges for print (toolpath) design. Common design decisions are highlighted, including how material properties and the choice of hardware influence the outcome. Introduction to G-code, manual code development, and automated code construction and post-processing.

Mixed and Multimaterial Printing for Reactive Materials

Reactive materials consist of physical mixtures of two or more reactants. Rather than printing a pre-mixed material, these reactants can be mixed on-the-fly or simply deposited in close proximity to each other. This section will review techniques and special considerations for both approaches.

1:30 PM
Atomic-Scale Modeling Tools for Investigating Reactive Materials and Processes Santanu Chaudhuri; Argonne National Laboratory

A review of modern tools for the modelling of energetic materials (including DFT, Molecular Dynamics, force fields and more phenomenological modelling tools) and their combination into a multi-scale approach.

An overview of the state of the art, using atomic scale modelling in the specific context of energetic and reactive materials.

3:00 PM BREAK

3:30 PM

The potential of these modelling approaches for the future of energetic materials, from manufacturing issues to advance modelling of combustion fundamentals and applications.

SYMPOSIUM FF06

Advances in the Fundamental Understanding and Functionalization of Reactive Materials
December 2 - December 5, 2019

Symposium Organizers
Sili Deng, Massachusetts Institute of Technology
Alain Esteve, Laboratoire d'Analyse et d'Architecture des Systems
Lori Groven, South Dakota School of Mines and Technology
Robert Reeves, Lawrence Livermore National Laboratory

* Invited Paper

SESSION FF06.01: Reactive Behavior and Material Properties I
Session Chairs: Lori Groven and Travis Sippel
Monday Morning, December 2, 2019
Hynes, Level 3, Room 308
The Early Stages of Subcritical Reactions in Al/Ni Multilayers Studied by Combined Nanocalorimetry and Sub-Millisecond X-Ray Diffraction

Tobias Neuhauser¹, Gemma Tinti², Harald Leiste¹, Nicola Casati², Michael Stüber¹ and Karsten Woll¹; ¹Karlsruhe Institute of Technology, Germany; ²Paul Scherrer Institut, Switzerland

Subcritical reactions comprise phase transformations in reactive nanolaminates leading to the point of ignition and typically occur under high heating rates above 500 K/s. Harnessing the reaction attributes and the specific metallurgy of subcritical reactions in metallic nanolaminates represents a promising pathway for creating novel types of thin film nanocomposites. Based on this notion we develop so called “Pulsed Metallurgy”. The nanolaminates with their microstructure serve as templates which are transformed into nanocomposites via millisecond short temperature pulses. Thermal pulsing enables us to precisely control the precipitation of hard intermetallic compounds in the soft metallic matrix at the nanoscale. The pulse shape defines the amount as well as morphology of the intermetallic phase. Here, we present first design guidelines for thin film composites based on Al-rich Al/Ni nanolaminates. For the chosen system, we require fundamental knowledge on the thermodynamics and kinetics of the underlying phase transformations during subcritical reactions. Especially, the effect of high heating rates on the phase transformation is explored. We performed chip-based nanocalorimetry and time-resolved X-ray diffraction with synchrotron radiation to in situ explore the phase transformations. In addition to the thermodynamic/kinetic information, this allows us to trace structural changes with a temporal resolution of up to 50 µs. Heating rates from 10 K/s up to 10,000 K/s are chosen to determine the onset and the growth rate of intermetallic phases. Effects of chemical composition are studied. Complementary kinetic studies are performed under isothermal conditions. The analysis of two dimensional X-ray diffraction data gives further insight in the structural evolution during the reaction and their influence on the reaction mechanism. Selected Al/Ni multilayer samples are finally characterized via electron microscopy. Eventually, the calorimetry in combination with the structural data enables us to derive guidelines for microstructure development of Al-based thin film nanocomposites.

Reactive Composites of Boron with Bismuth Fluoride and Bismuth—Preparation, Ignition and Combustion

Siva Kumar Valluri, Karthick Kumarasen Ravi, Mirko Schoenitz and Edward L. Dreizin; New Jersey Institute of Technology, United States

Despite the thermodynamic advantages of boron, its long ignition delay and burn time hinder its widespread application as a practical fuel. The ignition is delayed by the nascent shell of hydrolyzed oxide acting as a diffusion barrier protecting the boron core. The combustion at higher temperatures occurs at the oxide-free boron surface; the rate of this heterogeneous reaction is relatively low. To address these shortcomings, modifying the chemistry of the oxidative process encompassing ignition and combustion, by introducing fluorination was found to be effective. The addition of fluorides like bismuth fluoride (BiF₃) and cobalt fluoride (CoF₂) depressed the ignition temperatures and improved burn times of micron-sized boron-fluoride composites. The focus of this work is to introduce small quantities of bismuth fluoride as an oxidizer to maintain the thermodynamic potential of boron while improving its ignition and combustion rates. Towards this end, different boron-bismuth fluoride composites, (100-x) B-xBiF₃, with 5, 10, 30 and 40 wt. % of bismuth fluoride were prepared. Composites with 10, 30 and 40 wt. % of BiF₃ were prepared by arrested reactive milling. Additionally, composites with 10 and 5 wt. % of BiF₃ were prepared by the solvent based chemical deposition technique. The milled samples were found to have a small quantity of reduced Bi and were contaminated by iron from the milling media and vial walls. Based on recent work, the iron introduced by milling is expected to accelerate combustion of boron. Here, a similar effect of reduced bismuth left behind after fluorination, on boron’s combustion behavior was explored experimentally. Milled boron-bismuth composites were prepared including 92B-8Bi and 69B-31Bi, containing bismuth and iron content comparable to the boron-fluoride composites, 90B-10BiF₃, and 60B-40BiF₃ respectively. A systematic reduction in ignition temperatures with the content of BiF₃ was observed with all milled composites igniting at much lower temperatures than boron. At a heating rate of 2500 K/s, milled composites 90B-10BiF₃, 70B-30BiF₃, and 60B-40BiF₃ ignited at 650, 600 and 580 °C respectively. The coated sample 90B-10BiF₃ ignited in a range of temperatures, with an average of 650 °C, while 95B-5BiF₃ did not ignite at temperatures under 1200 °C. The thermogravimetric analysis in aerobic conditions shows an oxidation step around 500 °C for all composites. The reference boron sample had an oxidative weight gain at a higher temperature, 710 °C. All the composite particles were heated and ignited by a CO₂ laser beam in air. They exhibited shorter burn times compared to similar-sized
boron particles. A reduction in burn-times with an increase in bismuth fluoride content was observed. For a particle of 1-micron size, boron had a burn-time of 2.1 ms. The milled composites 90B-10BiF₃, 70B-30BiF₃, and 60B-40BiF₃ exhibited burn-times of 0.38, 0.33, and 0.28 ms respectively, almost an order of magnitude faster than boron. The boron-bismuth composites were found to burn slightly faster than boron. Analysis of partially reacted products shows bismuth retained in particle till boron melting point. The combustion mechanism and reaction pathways involving the species will be discussed.

11:00 AM *FF06.01.03
Reactive Materials for Ceramics Fabrication Alex Mukasyan; Notre Dame University, United States

Phenomenon of self-sustained chemical reactions that sub-sonically propagate along the high-energy density material is widely used for fabrication of different ceramics [1,2]. The specifics of synthesis condition in such combustion front are as follows: short (0.1-10 ms) reaction time, high temperatures (2000-4000 K) and extremely high rate for temperature change (10⁴-10⁶ K/s). These features allow fabrication of materials with unique microstructures and properties. In this work, we report recent results on combustion synthesis (CS) of different materials including ultra-high temperature ceramics, high entropy ceramics, metastable phases, as well as cubic boron nitride. Special attention is paid to such novel synthetic routes as reactive spark plasma sintering (SPS), CS with mechanical stimulation, as well as solution combustion synthesis.

Specifically it is shown that SPS of reactive materials [3] allows one-step rapid fabrication of dense bulk nanostructured ceramics (e.g. SiC, B₄C, HfCN) with high mechanical properties. Application of similar approach in combination with high-energy ball milling permits production of high entropy carbides and nitrides. It is also demonstrated that CS in B-TiN reactive system under shock-wave conditions leads to formation of c-BN phase [4]. Finally, using self-sustained waves in reactive solutions of metal nitrates and different fuels (e.g. hexamethylenetetramine and glycine) allows synthesis of metastable metal nitrides phases [5].


11:30 AM FF06.01.04
Glassy Amorphous Organic Energetics Rajen Patel¹, Victor Stepanov¹ and Hongwei Qiu²; ¹U.S. Army Research Laboratory, United States; ²Leidos, United States

Glassy amorphous organic energetics is a new field offering several novel areas for study. While practical application might be limited due to low density and propensity to crystallization of amorphous energetics, the scientific opportunities are fertile. For example, they allow an in depth view of crystallization in real time, even of novel systems such as cocrystals, and the in situ characterization of pores, cracks and other gross defects as they form. The ability to quantify and characterize the crystallization of an organic material would not only be an important step in the science of crystallization, but could have broader application to the pharmaceutical, biological science, and energetic materials communities. Amorphous energetic formulations with relatively low excipient (i.e. polymer used to inhibit crystallization) loadings were studied as they crystallized. This allowed several key determinations to be made that linked porosity and crystallinity of the material during this dynamic process. This is especially critical, as porosity is a critical parameter in the sensitivity and mechanical properties of an explosive, two key drivers for future munitions applications. Furthermore, the results will have an impact on the study of crystallization from both a practical and theoretical standpoint.

11:45 AM FF06.01.05
**Shape and Size Effects on the Oxidation of Aluminum Powders** Pierre-Henry Esposito¹, Thomas Neisius², Renaud Denoyel¹ and Marie-Vanessa Coulet¹; ¹CNRS-Aix Marseille Univ, France; ²CNRS, Aix-Marseille Univ., France

Aluminum powders are commonly used in the formulation of reactive materials [1]. In those materials, there is a definitive interest in improving the reactivity of aluminum powders and the actual trend is to produce powders with a high specific surface areas (higher than 10m²/g) i.e. aluminium nanopowders. Without any consideration of the scale, aluminium particles are covered by a thin alumina layer whose thickness does not vary much with the particle size [2]. The enhanced reactivity due to the use of nanosized powders is proposed to be linked to size reduction effects of the particles and to the structural and microstructural characteristics of both the metallic core and this alumina layer.

The standard synthesis routes for nanopowders are atomization and wire electro-explosion techniques. Such techniques produce powders with spherical morphology. High-energy ball milling has been recently proposed as an alternative procedure to produce micro- or nano- aluminum powders. They possess a flake like morphology and have different reactivity compared to the spherical ones [3]. This technique has also been shown to be able to produce reactive composite materials [4].

In this contribution, we propose a comparative study of the oxidation mechanisms of aluminum powders as a function of their shape (spheres versus flakes) and size (micro versus nano). Thermogravimetric and differential thermal analysis performed under dry Air up to 1500°C are used to evaluate the oxidation behaviour of the powders. The morphology of the various powders is followed for different oxidation temperatures using gas adsorption, transmission electron microscopy (TEM) and energy filtered transmission electron microscopy (EFTEM) [5]. Finally, the oxidation mechanisms are studied using kinetically controlled thermal analysis [6]. In this mode, keeping the oxidation rate constant, the kinetics equations are simplified which facilitates the modeling of the experimental data. The observed differences between the oxidation mechanisms are discussed as a function of the shape and the size of the particles.

*The Direction Générale des Armées (DGA) and the University of Aix-Marseille (AMU) are acknowledged for funding the PhD of P.H. ESPOSITO.*

catalytic effect. Moreover, the graphene foam-based structures provide an additional benefit of increased thermal transport. It is well-known that heat transport also plays an important role in the combustion of solid fuels; higher thermal conductivity or diffusivity usually results in higher burn rates. Most solid fuels have a thermal conductivity in the range of 0.1-1 W/m-K, which is much lower than that of these graphene-based materials (up to a few thousand W/m-K). Indeed, carbon nanomaterials such as carbon nanotubes and graphene, because of their high thermal conductivity and large surface-to-volume ratio, have been used as nano-fillers to enhance the thermal conductivity of various composites and as heat exchangers in nano-electronic devices.

Motivated by the above, we explored the potential of GF structures, which were functionalized with a transition metal oxide manganese dioxide such as MnO$_2$ or CuO using a hydrothermal approach. The propellants we chose were Nitrocellulose (NC) and hybrid Ammonium Perchlorate-Nitrocellulose (AP-NC). For nitrocellulose with GF supported MnO$_2$, burn rate enhancements up to 9 times were obtained with the activation energies being lowered by 17%. However, without the use of GF as the supporting structure, using only MnO$_2$ oxide nanoparticles, burn rate enhancements only up to 2 times were obtained with the activation energies being lowered by 3.6%. Although, the presence of GF in itself does not have any catalytic effect on the propellant decomposition, the GF supported metal-oxide particles provided a more efficient contact between the propellant and the metal-oxide. This was in contrast to the traditional solid-fuel/metal-oxide mixture prepared in which a continuous contact between the propellant and the catalyst was not achieved because of the random mixing of metal oxide particles into the fuel matrix. For AP-NC, the CuO-functionalized GF micro-structures significantly enhanced the burn rates, up to 7 times the bulk value, which was attributed to the combined physical (increased thermal transport) and chemical (enhanced thermal decomposition) effects. TG (thermogravimetric) and DSC (differential scanning calorimetry) analysis showed the activation energy of AP-NC was lowered by 22% with the use of the CuO-functionalized GF structures.

2:15 PM FF06.02.02
Flexoelectricity in Al/Fluoropolymer Reactives Mikel J. Zaitzeff and Lori J. Groven; South Dakota School of Mines & Technology, United States

In the past few years there has been increased interest in the development of smart reactives. Towards that, the reactive system Al/THV, and Al/PVDF have been explored for their piezoelectricity and ability to be switched to a more sensitive state. Early work indicates that even non-piezoelectric composites could exhibit sensitization behavior, but it was not well explained. A possible explanation is the flexoelectric effect. Flexoelectricity in induced by an inhomogeneous strain gradient capable of switching, poling, and spontaneous polarization. This allows for the flexoelectric effect to produce similar effects as the piezoelectric effect without the need for a true piezoelectric. For example, unpoled PVDF has been found to exhibit the flexoelectric effect and in fabricated composites has been shown to have apparent $d_{33}$ coefficients on par with poled PVDF. In this effort THV and PVDF with various loadings of micron scale aluminum are considered and the flexoelectric coefficients measured. It is shown that THV exhibits a higher flexoelectric coefficient than PVDF and with inclusion of aluminum increases. PVDF exhibits a flexoelectric coefficient of 3.9, 5.2, and 6.1 nC/m at 0, 33, and 50 weight percent aluminum respectively. THV exhibits a flexoelectric coefficient of 5.1 and 7.0 nC/m at 0 and 33 weight percent aluminum respectively.

2:30 PM FF06.02.03
Development of Multimodal Antibacterial Surfaces Using Porous Amine-Reactive Films Incorporating Lubricant and Silver Nanoparticles Jieun Lee$^1$, Jin Yoo$^1$, Sanghyuk Wooh$^2$ and Kookheon Char$^1$; $^1$Seoul National University, Korea (the Republic of); $^2$Chung-Ang University, Korea (the Republic of)

Surface functionalization provides efficient strategy to significantly improve material surfaces to overcome the infectious problems from microbial fouling in many medical devices and food processing equipment. Anti-biofouling has been improved by passive or active ways. Passive antifouling strategies aim to prevent the initial adsorption of foulants, while active strategies aim to eliminate proliferative fouling by destruction of the chemical structure and inactivation of the cells. However, neither passive antifouling strategies nor active antifouling strategies can solely resist biofouling due to their inherent limitations. To achieve highly effective anti-biofouling surfaces, integration of bactericidal and bacteria-repellency is highly in demand. Herein, we successfully developed multimodal antibacterial surfaces for waterborne and airborne bacteria with the benefit of combination of anti-adhesion (passive) and bactericidal (active) properties of the surfaces. We elaborated multi-functionalizable porous amine-reactive (PAR) polymer films from poly(pentafluorophenyl acrylate) (PPFPA).
Pentafluorophenyl ester groups in the PAR films facilitate to create multiple functionalities through a simple post-modification under mild condition, based on their high reactivity towards various primary amines. To retain lubricant in films, porous structures of PPFPA films were developed by vapor-induced phase separation (VIPS) of polystyrene (PS)/PPFPA mixture and selective removal of PS. Attributing to excellent amine-reactive property of PPFPA, porous amine-reactive (PAR) films enable imparting versatile physiochemical functionalities on surfaces via sequential post-polymerization modification. Amine-containing molecules (i.e., amine-polydimethylsiloxane (amine-PDMS) and dopamine) and silver nanoparticles (AgNPs) were introduced on PAR films in serial order, followed by silicone oil infusion into PAR films.

Antibacterial efficiency of the developed surfaces was assessed for both Gram-negative bacteria (*Escherichia coli*, *E. coli*) and Gram-positive (*B. cereus and S. aureus*). We confirmed that lubricant-infused PAR films inhibit adhesion of not only waterborne bacteria but also airborne bacteria. To the best of our knowledge, this is the first study to utilize slippery surfaces as antibacterial surfaces for airborne bacteria. According to previous studies, contact-killing strategy is necessary to minimize airborne bacterial adhesion, the lubricant infused surfaces were insufficient to prevent airborne bacteria adhesion thoroughly. On the contrary, the AgNPs incorporated lubricant infused surface showed nearly perfect antibacterial efficiency for airborne bacteria owing to bacterial resistance of AgNPs. Furthermore, the L-infused Ag@DP-PAR possessing contact-killing activity has potential to be sustained longer than biocide-leaching system and to have lower toxicity. The aim of this work is to develop efficient and multimodal antibacterial surfaces toward both waterborne and airborne bacteria as the first proof of concept for application of PAR films with multi-functionalities by post-modification. Thus, the platform presented in this study suggests a new door to develop an effective multimodal anti-biofouling surface.

2:45 PM BREAK

SESSION FF06.03: Effects of Process on Reactive Materials Behavior I
Session Chairs: Sili Deng and Kyle Sullivan
Monday Afternoon, December 2, 2019
Hynes, Level 3, Room 308

3:15 PM FF06.03.01
Preparation of Ti-Al-B Reactive Metal Powders from Titanium Borohydride Matthew Finn and Albert Epshteyn; U.S. Naval Research Laboratory, United States

Reactive materials aim to release large amounts of energy in a rapid yet controlled fashion. These materials include but are not limited to; thermites, intermetallics, or metal polymers which can be prepared from a variety of different metals and metal precursors. Titanium borides have drawn a great deal of interest as reactive materials; however, the high temperatures often required for their preparation results in materials with high hardness but low energy. Our group has previously reported a low temperature method for preparing hydrogen containing Ti-B materials from the decomposition titanium borohydride (Ti(BH₄)). This presentation details our work to optimize and expand upon this concept. Isolating and stabilizing the borohydride precursor affords greater control of the final materials. This allows for improved purity, more facile processing, and ultimately higher energy content. We can also control the inclusion of other metal additives such as aluminum. The resulting in Ti/Al/B materials have distinct properties compared to reactives prepared via other methods. The synthesis, processing, and characterization of these materials will be discussed.

3:30 PM FF06.03.02
Resodyn Acoustic Processing of Ni-Al for Cold-Spray Applications Ryan D. Macy, Michael J. Carter, Grant A. Crawford and Lori J. Groven; South Dakota School of Mines & Technology, United States

Metal-based reactive composites are a leading contender for use as structural energetic materials, but their utility is limited by low reactivity and relatively high ignition temperatures. Recent studies of the Ni-Al reactive system have shown that with the use of high-energy ball milling and subsequent wet grinding the ignition temperature can be tailored and be as low as 500 K. Therefore, we have extended this technique and demonstrate a processing technique using the Resodyn LabRam that allows bulk manufacture of reactive-composite powders suitable for cold spray use.
Following this, cold spray technology is demonstrated as a potential additive manufacturing technique to produce structural energetic materials. A baseline physical mixture of Ni-Al powder, milled Ni-Al nano-laminated composite particles, and other reactive composite particles are reported. Using a VRC high pressure spray system, nitrogen as the carrier gas and a deposit temperature of 100 °C, it is shown that the nanolaminate structure is retained and no pre-reaction occurs during deposition. The microstructure, mechanical properties, and combustion behavior of the as-deposited materials are also detailed.

3:45 PM FF06.03.03
Nanoporous Metals from Thermal Decomposition of Transition Metal Dichalcogenides Swarnendu Chatterjee, Yawei Li, Saad Intikhab and Joshua Snyder; Drexel University, United States

Development of nanoporosity on metals and alloys is a well-known pathway for making three dimensional high surface area structures especially useful for catalysis. Majority of the techniques are based on selective removal of a sacrificial metal from an alloy, a method known as dealloying. The driving force for the traditional electrochemical/chemical dealloying is difference of redox potentials and dissolution tendencies amongst the constituent metals. This limits the process to few noble metals e.g. Pt, Pd, Au etc. that can make homogeneous alloys with less noble metals. More recently liquid metal dealloying and vapor phase dealloying have been also identified to mimic the process of traditional dealloying based on difference of affinities of thermal dissolution in a liquid metal, and vapor pressures of the constituent metals, respectively. However, these are still restricted to few metals and the primary challenges lie with obtaining homogeneity in precursor alloy and limiting the pore size within 100 nm upon spinodal decomposition. Here, we present gas phase thermal decomposition of transition metal dichalcogenides (TMDs) as an alternative to dealloying that generates nanopores for a broader class of metals including refractory metals like W, Mo, Re etc. The chalcogen is removed from the surface by both reductive reaction with hydrogen and evaporation at elevated temperatures, which leads to the rearrangement and surface diffusion of the remaining metal atoms that evolve into an interconnected bicontinuous nanoporous network. Based on varying dynamics of pore formation and residual chalcogen contents for different TMDs, we have proposed a mechanism that emulates the decomposition process. The availability of vast library of TMDs having inherent atomistic homogeneity makes it a universal technique that can be utilized to make nanoporous metals.

References.

4:00 PM *FF06.03.04
How Synthesis and Processing Parameters Affect Reactivity of Sonochemically-Generated Ti-Al-B Reactive Metal Powders Albert Epshteyn, Matthew Finn, Rohit Jacob and Brian Fisher; U.S. Naval Research Laboratory, United States

Previously we demonstrated that the sonochemically-mediated decomposition of in-situ generated complex metal hydrides is a versatile methodology for the synthesis of unique metastable reactive mixed-metal nanopowders (RMNPs) that can be tuned for high energy content while also possessing other highly desirable solid fuel characteristics. In this latest iteration of our efforts to further improve the Ti-Al-B RMNP fuels, we made the effort to eliminate any parasitic impurities and focused on the sonochemically-mediated reaction process to evaluate the effects of the various synthetic and processing parameters on the final fuel properties. To that end we took the time to better purify the LiAlH₄, and then the syntheses were carried out using both the original approach of adding etheral solutions of LiAlH₄ and LiBH₄ to TiCl₄, as well as the reverse. We also employed a different approach of synthesizing the ether adduct of Ti(BH₄)₂, which was then reacted with LiAlH₄. The product powders were characterized for particle sizing and slow oxidation via thermogravimetric analysis, and subjected to careful elemental analysis via both ICP-OES of digests for metals content and combustion analysis for C, H, and N. New approaches were also explored in the compatibilization of the powders with HTPB cross-linking chemistry to produce RMNP-HTPB composites, the combustion behavior of which was then characterized in oxygen bomb
calorimetry, as well as heterogeneous strand-burn experiments. While the powders produced by different methods had similar elemental compositions, each of the newly produced materials reproducibly exhibited surprisingly unique combustion behavior.

4:30 PM FF06.03.05
Spherical Composite Powders Prepared by Mechanical Milling
Mehnaz Mursalat, Daniel Hastings, Mirko Schoenitz and Edward L. Dreizin; New Jersey Institute of Technology, United States

In energetic, pharmaceutical and other industries, dealing with spherical powders is attractive because of the ease of their handling and high flowability. Spherical powders are also of interest as feedstock materials for additive manufacturing. For metals, it is common to prepare spherical powders by atomization of melts, which is not suitable for most reactive materials. For non-metals, extrusion, spheronization, and emulsion polymerization are used, which are not compatible with many reactive materials sensitive to heating or having limited solubility in polymers. This work describes preparation of spherical composite powders of reactive materials by high-energy mechanical milling. Powders are ball milled in presence of two immiscible fluids (hexane and acetonitrile). It is observed that spherical composite powders are formed at a specific solid/liquid ratio, when the volume of solid is matched to that of acetonitrile. It is also found that the total volume of liquid must be at least twice as big as the volume of the solid powder. Reactive spherical powders were prepared with compositions of aluminum-rich thermites with copper and iron oxides as oxidizers, with an aluminum-boron composite as well as pure with aluminum, titanium, and boron. Additionally, spherical powders were prepared using fumed silica and iron oxide. Some of the formed spheres, such as those of fumed silica were not mechanically stable and easily fell apart, while others, such as those of aluminum or thermites were stable and could be easily handled. The powders were observed using optical and scanning electron microscopy. For selected powders, particle size distributions were measured. For both aluminum and boron the particle sizes became smaller at longer milling times. It is hypothesized that the spherical powders are formed from Pickering emulsions generated in the milling vial when the loaded liquid/solid mixture is mechanically agitated. Droplets of acetonitrile are expected to form in the continuous hexane phase and be stabilized by solid particles adsorbed to the hexane/acetonitrile interfaces. It is further hypothesized that because of the large amount of the loaded solid powder, the Pickering emulsion in this case coexists with a dense suspension of powder in hexane, the continuous phase. The presence of suspended powder makes it difficult to destabilize the emulsion droplets mechanically: when the surface is stretched and becomes unstable it rapidly adsorbs a suspended particle to become stabilized. The interaction of a dense suspension with Pickering emulsion droplets is proposed to lead to accumulation of the solid phase inside droplets, which causes formation of the spherical powders as observed here. Preparation, characterization, and reactivity of the prepared powders will be discussed.

SESSION FF06.04: Atomistic Modeling of Reactive Materials
Session Chairs: Albert Epshteyn and Alain Esteve
Tuesday Morning, December 3, 2019
Hynes, Level 3, Room 308

9:00 AM FF06.04.01
Growth of Polycyclic Aromatic Hydrocarbons During Carbon-Fiber Processing from Density Functional Theory
Taishan Zhu1,1, Yanming Wang1,1, Jeramie J. Adams2, Jeffrey C. Grossman1 and Nicola Ferralis1;
1Massachusetts Institute of Technology, United States; 2Western Research Institute, United States

The growth of polycyclic aromatic hydrocarbons (PAH) is the chemistry dominating the formation of interstellar organic substances, various biogeochemical cycles and modern industry processes, but their mechanisms remain unclear. In this work, we study various cycloaddition mechanisms at intermediate temperatures (300-800 °C), including hydrogen abstract acetylene addition and polynuclear oligomerization, using first-principles approaches. Based on gas chromatography mass spectrometry measurements, we identify proxy molecules for heavy hydrocarbons such as coal tar pitch that is often used as a precursor for carbon-fiber processing. For a given molecular component and byproduct, rather than using the conventional bottom-up approach that hypothesizes growth from reactants, we develop a top-down framework to automatically enumerate all possible pathways through
splitting products to possible reactants, with molecular symmetry considered. These individual pathways are evaluated in a high-throughput manner, based on which a Bayesian description of cycloaddition mechanism is constructed. Moreover, the construction of such Bayesian mechanism at varying temperature reveals different mechanisms at different temperatures, suggesting different dominant pathways in the formation of large aromatic clusters in coal tar pitch processing leading to further insights towards the optimization of the synthesis of pitch-based carbon fibers. Moreover, the growth mechanisms could also give insights to other PAH chemical reactions, such as soot formation.

9:15 AM  FF06.04.02
Modelling Energetics across Interfaces—Atomistic Molecular Dynamics Simulations of the Shock Loading of Reactive Nanolaminates Leah Granger¹, Jon-Paul Maria², Sergey Matveev³, Dana D. Diott¹ and Donald Brenner¹;
¹North Carolina State University, United States; ²The Pennsylvania State University, United States; ³University of Illinois at Urbana-Champaign, United States

Reactive inorganic nanolaminates containing metastable interfaces, such as those between metals and metal oxides, can undergo exothermic reactions when disturbed by heat or shock. While the chemical thermodynamics associated with reactivity in these systems is relatively straightforward, the mechanisms by which this chemistry is initiated are unknown. This is due in large part to the potential complexity of the dynamics and the challenges associated with experimental probes of dynamics at buried interfaces.

Using molecular dynamics simulations, we investigated the mechanisms by which the energy of a shock pulse delivered by a simulated flyer plate can initiate chemical mixing at a buried metal-metal interface. The simulations show plastic damage in the form of dislocations that are initiated at the edges of the flyer plate due to shear forces. This damage at the plate edges is consistent with recent experiments by Diott and co-workers in which the initiation of buried exothermic reactivity in a reactive nanolaminate is observed in a ring pattern that matches the flyer plate shape. Depending on the crystal orientation and the energy delivered by the flyer plate, the simulated dislocations can reach a buried interface. In the case of a Cu-Zr nanolaminate containing two buried layers with thicknesses of about 35Å, the dislocations were observed in the simulations to be terminated at the first interface, but with an elastic energy pulse that is transferred into subsequent layers. Hence the mechanisms by which energy is delivered across a series of buried interfaces may be different depending on the interface location with respect to the shock pulse. In these initial simulations little interfacial mixing was observed on a picosecond timescale. We will also discuss related simulations in which a simulated shock pulse is delivered across a buried metal-metal-oxide interface, where charge transfer and significantly exothermic chemistry play a large role that is missing from the dynamics of the buried metal interfaces.

This work was supported by the U.S. Department of Defense, Multidisciplinary University Research Initiative through the Army Research Office, Grant No. W911NF-16-1-0406.

9:30 AM  **FF06.04.03**
Reactivity of Ni/Al and Ti/Al Nano-Composites—An Atomic-Scale Description Florence S. Baras and Olivier Politano; ICB, CNRS-Université Bourgogne Franche-Comté, France

Reactive materials based on metallic elements are produced by various methods. The basic method for the production of multilayer reactive nano-foils is the layer-by-layer magnetron deposition. The thickness of each layer may vary from several nanometers to microns, while the number of the layers "stacked" in one foil may vary from ten to thousands. An alternative and less expensive method for the production of reactive nano-foils is a mechanical method combining high-energy ball mill and cold rolling. The ball milled and cold rolled foils possess relatively high non-uniformity, intermittence, and tortuosity, as compared to the magnetron deposited films. However, nanometer-scale Ni and Al layers are present in the material. A very peculiar property of reactive multilayer nano-foils is that a reaction between pure metals initiated at one edge of the sample will propagate throughout the system in a self-sustained way. The heat released locally allows the reaction to proceed without any further supply of energy. During this talk, we will review the mean features of ignition and reaction in nano-layered metallic systems Me/Al, with Me=Ni or Ti. We will also give some insight into the effect of production by a mechanical method.

The understanding of the reaction mechanisms in reactive nano-composites relies on the study of reaction kinetics,
heat and mass transfer, as well as the dynamics of structural transformations. Besides the usual multi-physics description, the atomistic approach provided by Molecular Dynamics (MD) simulations becomes a useful tool in describing the behavior of reactive materials. MD simulations indeed give the basic atomistic steps leading to observed microstructure beyond any thermodynamic or kinetic modeling. MD simulations can be considered as a model that offers a counterpart to in-situ experiments to explore elemental mechanisms. In the case of nanometric metallic multilayers, MD proves to be a very appropriate method for numerical studies, as the accessible time and length scales are in the same range of magnitude as in “real” experiments. During this talk, we will review the main features of combustion synthesis in nanofoils considering Ni/Al as a model system [1]. The reactivity of Ti/Al nanofoils will also be analyzed. We will show how modeling and experiments are complementary approaches in order to detect intrinsic behaviors and reactive mechanisms.

In the second part of the talk, we will focus on the mechanical method of production. The idea here is to develop molecular dynamics simulations in order to study the possible elemental mechanisms (compaction, shear, plastic deformation, welding, fracturing,…) that can be observed during high energy ball milling. We will present our calculations to mimic the first impact due to grinding balls. A set of spherical Al and Ni (Ti) particles were submitted to a rapid compression. The compression produces compaction of the powder by removing empty spaces between the particles. Once the particles are compacted, they start to undergo plastic deformation. Indeed, the ductile Al mostly deforms whereas Ni remains more spherical. An increase in the number of atoms in mixing zones was observed. The detailed atomistic analysis allows us to follow the progressive amorphization, the formation of defects, the induced chemical mixing and the possibility of recrystallization due to this first hit. The ignition of such a system will be characterized.

Finally, we will show how large-scale MD simulations can handle more and more complex systems. We were able to consider complex nanostructures in order to understand the role of defects or intricate microstructure in nanostructured samples. As an example, we will show self-sustained propagation in a system made of disordered nanostructured grains.


10:00 AM BREAK

SESSION FF06.05: Effects of Process on Reactive Materials Behavior II
Session Chairs: Albert Epshteyn and Alain Esteve
Tuesday Morning, December 3, 2019
Hynes, Level 3, Room 308

10:30 AM FF06.05.01
The Role of Octylamine Ligands in the Stabilization of CuO Nanoparticles as a Determinant of the Al/CuO Redox Reaction Ségolène Palussière1,2, Jeremy Cure1, Pierre Fau2, Katia Fajerweg2, Myrtil L. Kahn2, Alain Esteve1 and Carole Rossi; 1University of Toulouse, LAAS-CNRS, France; 2University of Toulouse, LCC-CNRS, France

Among energetic materials, nanothermites are known for their high volumetric energy densities (up to 16 kJ/cm3), adiabatic flame temperature (> 2600 °C) and high reaction (burn) rates. One of the promising materials for integration into micro devices is Al/CuO nanocomposite because of its high enthalpy of oxidation-reduction reaction [1]. Increasing the contact surface between both components of the thermite composite should lead to improved properties. The control of the particles size, the morphology and the distribution of the nanoparticles inside the composite is therefore of paramount importance.

Recently, an original synthesis approach has been proposed to produce ultra-small CuO nanoparticles (ca. 5 nm) functionalized with octylamine ligands. This approach consists in the formation of the CuO nanoparticles by the
controlled hydrolysis and/or oxidation of an organometallic precursor (i.e. copper amidinate), in the presence of octylamine. [2] These usual ligands stabilize the CuO nanoparticles which can be beneficial to enhance the coating of Al particles with smaller CuO ones during the physical mixing. Thermally characterized by Differential Scanning Calorimetry (DSC), Al/CuO nanothermites thus produced react differently compared to those produced following the same mixing process but from commercial CuO nanoparticles.

Using a variety of characterization techniques, including microscopy, spectroscopy, mass spectrometry and calorimetry (ATG/DSC), the structural and chemical evolution of CuO nanoparticles stabilized with octylamine ligands are characterized upon heating. This enables us to depict the main decomposition processes taking place at the CuO surface at low temperature (< 500 °C) [3]: the ligands fragment into organic species accompanied with CO2 release, which promotes the CuO reduction into Cu2O and further Cu. Then an optimization process to overcome the ligands-induced CuO degradation at low temperature is proposed. Al/CuO nanothermite reaction is analysed, in terms of onset temperature and energy released.

References:

10:45 AM FF06.05.02
Plasma-Based Synthesis of an Air Stable Polymer/Mg Nanocomposites for Hydrogen Storage Applications
Hui Liang1,2, Xi Geng2, Wenjiang Li2, Adriano Panepinto1, Minfang Chen2, Rony Snyders1 and Damien Thiry1;
1University of Mons, Belgium; 2Tianjin University of Technology, China

Hydrogen is considered as a promising alternative energy carrier due to its high energy density, great variety of potential sources, light weight and low environmental impact. Though the storage of hydrogen via Mg-based nanomaterials is very promising, the high reactivity of Mg towards oxygen leads to the easy formation of MgO, which blocks the penetration of hydrogen in the material, limiting the performance of the device.

In this work, in order to overcome this limitation, we propose to synthesize bilayer nanostructured Mg/polymer thin films using cold plasma-based processes. The process consists of two steps: (i) the synthesis of Mg nanostructured films by magnetron sputtering at grazing incidence and (ii) the coverage of the metallic nanostructured film by plasma polymerization from ethylene precursor. This method should allow (i) to control the porosity of Mg films by simply modifying depositions parameters such as temperature, incidence angle of the depositing particles (α) or pressure, and (ii) to avoid oxidation of the Mg-based nano-objects by protecting them with a highly cross-linked plasma polymer.

SEM characterization of the samples has revealed the presence of isolated Mg-based nanocolumns. Both the intercolumnar space (i.e. from 20 to 100 nm) and the diameter of the nano-objects (i.e. from 100 to 300 nm) depend on the incidence angle of the depositing particles. This evolution is directly related to the competition between surface diffusion and shadowing effect as confirmed by kinetic Monte Carlo methods. Mg-based nanostructures were homogeneously covered by a carbon/hydrogen-based plasma polymer which protects the films against oxidation. The obtained material reveals a high potential for efficient hydrogen storage.

11:00 AM *FF06.05.03
Improving Boron for Combustion Applications
Kerrilee A. Chintersingh-Dinnall, Mirko Schoenitz and Edward L. Dreizin; New Jersey Institute of Technology, United States

Beyond their most common use for structural and catalytic purposes, metals are also great fuels due to their higher heats of combustion compared to traditional hydrocarbons. In particular, boron has been of interest as a high-energy density fuel additive in explosives and propellants. Some of the challenges are that boron particles tend to agglomerate, have lengthy ignition delays and very low combustion rates. Researchers have attributed the ignition delays to boron’s naturally occurring inhibiting oxide layer impeding further oxidation at low temperatures. For full-fledged combustion occurring at high temperatures when boron oxide is gasified, current studies report that boron particles burn in two consecutive stages; however, the actual reaction mechanism is poorly understood.

Despite many years of relevant research, quantitative combustion data on practically interesting, micron-sized boron particles are limited. Most proposed modifications to boron were designed to reduce its ignition delays by adding new chemical components and thus substantially diminished the energy density of the resulting composite material. Research aimed to accelerate boron combustion at high temperatures is generally lacking.

The motivation of this work was to achieve higher burn rates for boron powders without jeopardizing their
thermochemical performance, safety and stability and to develop an experimentally validated model adequately
describing oxidation kinetics for boron that can be used in practical simulations for a broad range of temperatures.
This study also was aimed to close the gap in data for combustion of fine boron particles in varying oxidizing
environments. Commercial boron powders were modified, and both as received and modified powders were used in
oxidation, ignition, and combustion experiments. Materials were prepared by mechanical milling or wet synthesis
techniques and burned in air, in hydrocarbon combustion products, and in steam/nitrogen environments. Combustion
and ignition characteristics were determined from optical measurements and images and described as trends of burn
times or ignition delays versus particle size. Strategies to modify boron’s heterogeneous reactions by functionalizing
its surface by organic solvents and using transition metals as “shuttle catalysts” have been explored. It was found
washing powders with acetonitrile removes hydrated surface oxide and reduces their ignition delays while not
leading to rapid aging and re-oxidation at ambient conditions. Doping boron with as low as 5 wt% of transition
metals (Fe or Hf) accelerates surface reaction rates leading to shorter particle burn times compared to the starting
commercial powder. A kinetic model was derived from low-temperature thermo-analytical measurements to
describe the oxidation of complex aggregated boron particles accounting for their surface morphology. Comparison
with particle combustion experiments showed that the same model can describe reactions at high temperatures
typical of full-fledged boron combustion, suggesting that the same heterogeneous reactions govern both ignition and
combustion of boron. Further, results suggest that the morphology of as received boron powders comprising micron-
sized agglomerates of finer primary particles does not always change to spherical droplets even at temperatures
exceeding the boron melting point. This leads to variation in burn rates and temperatures for various particles.

11:30 AM FF06.05.04
Tuning Reactivity of Al-CuO Thermites Prepared by Arrested Reactive Milling Using Liquid Process
Control Agents Mehnaz Mursalat, Mirko Schoenitz and Edward L. Dreizin; New Jersey Institute of Technology,
United States

Reactions in nanocomposite thermitites prepared by Arrested Reactive Milling (ARM) occur at the interfaces between
fuel and oxidizer and are affected by structure and properties of the interfacial layers formed during milling. For
many materials prepared by ARM, an organic process control agent (PCA) is used to limit cold welding which serve
as heat sink for the mechanically initiated exothermic reactions. While PCA directly controls shapes and sizes of the
powders being milled, the presence of an organic substance can also modify and functionalize the forming
interfaces, e.g., by forming carbide, oxycarbide, or nitride inclusions or even sublayers. Such possible effects are
explored here for Al-CuO thermitite. Previously, such thermitites were prepared by ARM using hexane as PCA. Here,
samples of Al-CuO thermitites were prepared using staged milling. In the first stage, Al and CuO powders were
individually pre-milled in acetonitrile, a polar PCA. The products were recovered, dried, and used in the second
stage milling, for which hexane served as PCA. In the second stage, pre-milled Al and CuO powders were combined
together or with respective as-received powders. The products were characterized by scanning electron microscopy,
thermal analysis and heated filament ignition experiments. Pre-milling CuO in acetonitrile did not affect properties
of the obtained thermitites. The samples including aluminum powder subjected to the first stage milling in acetonitrile
were found to ignite at a lower temperature and have stronger low-temperature exothermic reactions. When as
received aluminum was processed using hexane only, the ignition temperature did not depend on heating rate,
suggesting that the ignition was governed by a phase change occurring at the Al-CuO interface. Conversely, for
thermitites prepared using aluminum pre-milled in acetonitrile, the ignition temperature increased with heating rate,
suggesting that a reaction with thermally activated kinetics lead to ignition.

11:45 AM FF06.05.05
Functionally Grading Density in Thin Films of Energetic Materials for Detonation Wave Shaping Eric C.
Forrest, Robert Knepper, Michael P. Marquez and Alexander S. Tappan; Sandia National Laboratories, United
States

Physical vapor deposition (PVD) of energetic materials, including high explosives such as pentaerythritol
tetranitrate (PETN), has enabled an unprecedented level of control over energetic material morphology and
microstructure compared to traditional powder processing techniques. Previous research demonstrated the ability to
control the crystal orientation, grain size, and subsequent density and porosity of PETN films, through manipulation
of substrate surface energy alone. This has profound implications for initiation sensitivity and detonation wave
velocity in crystalline high explosives, which are strongly dependent on grain size, porosity, and unreacted explosive
material density, respectively.
In this study, we investigate novel methods to create functionally graded density in thin films of PETN for the purpose of detonation wave shaping. Specifically, we alter local substrate surface energy to attain desired morphology of PETN, with low surface energy areas used to create porous regions in the PETN film, and high surface energy areas to create denser regions. The technique is demonstrated with both simple linear geometries as well as more complex shapes using different masking and deposition techniques. Energetic film thicknesses range from approximately 10 µm to 100 µm, with relative, controlled density variations of 10-20% achieved in a single deposition. Characterization results for the energetic films, including scanning electron microscopy, surface profilometry, and X-ray diffraction, are presented. Scanning electron microscopy of surfaces and of fracture cross sections portrays the variation in microstructure and density achieved across PETN films. Pole figures taken at different locations on the energetic films demonstrate differences in crystalline orientation that contribute to observed density changes.

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SESSION FF06.06: Applications of Reactive Materials II
Session Chairs: Michael Abere and Michael Zachariah
Tuesday Afternoon, December 3, 2019
Hynes, Level 3, Room 308

1:30 PM FF06.06.01
Neutralization of Chemical Warfare Agent Simulants DIMP and TEP Using Al/Mg/Zr Composite Metal Powders Preetom Borah¹, Rylie Lodes², Adam Sims², Nick Glumac² and Timothy P. Weihs¹; ¹John's Hopkins University, United States; ²University of Illinois at Urbana-Champaign, United States

Reactive composite metal fuels synthesized from varying amounts of Al, Mg, and Zr have previously shown promise in bio-agent defeat applications due to their high combustion efficiency, low ignition thresholds, and tunable combustion processes. Here, we report preliminary results on the efficacy of these powders for the related application of chemical agent defeat. Composite metal powders synthesized using high energy ball milling were ignited using PETN explosive charges in a combustion chamber containing chemical agent simulants Diisopropyl methylphosphonate (DIMP) and Triethyl phosphate (TEP), separately. Once the powders are ignited, the heat from combustion vaporizes the liquid simulant and then continues to burn. Burn times and reactive metal particle temperatures were evaluated using two-color pyrometry in conjunction with high speed videography. The concentration of DIMP and TEP were monitored over time, utilizing quantum cascade lasers (QCLs) for infrared spectroscopy, and we observe a reduction in the concentration of both species over the time period of microseconds. The composition of the powders was varied to monitor the effect of Al/Mg/Zr ratios on the rate of decomposition and the overall surrogate neutralization capability. Comparisons were also made between the synthesized composite powders and similarly sized Al powder. Lastly, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were utilized to observe the microstructure of post-reaction oxide materials. Taken together, the collective data set demonstrates the ability of composite metal powders to neutralize these chemical agent surrogates.

1:45 PM FF06.06.02
Environmentally Friendly Time Delays Based on Reactive Nanolaminates Shane Q. Arlington, Joey Chen and Timothy P. Weihs; Johns Hopkins University, United States

Both commercial and military explosives frequently rely on time delays, devices which are triggered from some external event and, after a precisely controlled time, initiate detonation of the explosive charge. The design of these...
devices typically includes a delay column which controls the time between the external trigger and the propagated signal by means of a controlled exothermic reaction. Typically, these reactions involve hazardous materials such as lead oxides, chromates, and azides. While there has been a push to remove or mitigate the hazardous materials used in these delays, no comparable low-cost environmentally friendly alternatives have yet been widely adopted. Nanolaminates such as Ni/Al are known to react in a controllable and consistent self-propagating manner and can be fabricated with environmentally friendly materials. However, their reaction velocities are typically too high for chemical time delays manufactured into small and simple geometries. Here we present a method to dramatically reduce the reaction propagation velocity of nanolaminate films through architectural control of the sample substrates. By depositing reactive nanolaminates on woven polymeric meshes, we can reduce the velocity by orders of magnitude while maintaining the desirable levels of sensitivity, shelf-stability, and scalability of production of typical multilayer films. In this work, we explore the reaction behavior of these on-mesh delays as a function of the reactive thin film properties, as well as the properties of the underlying substrate. We will present a model for the underlying mechanisms of the interrupted propagation which slows the net velocity, and we propose designs for integrated delays based on these materials.

2:00 PM *FF06.06.03
Electromagnetic Control of Energetic Materials—A Prelude to Smart Energetics Travis Sippel; Iowa State University, United States

The future of energetic systems may require on-command tuning of energy output: In-mission control of solid rocket motor thrust to meet revised trajectories, dynamic control of countermeasure light emission to overwhelm advanced ordnance guidance systems, and in-flight sensitization/tuning of ordnance energy release. This talk presents recent materials fabrication strategies through which electromagnetic control can be designed into energetic materials. Materials strategies enabling localization of microwave energy deposition to the gas phase flame, the condensed phase, or the burning surface are discussed with application to solid propellant burning rate control, ignition, and extinguishment; dynamic control of pyrotechnic luminosity and color chroma; and thermites and propellants with thermally switchable microwave ignitability. Functional grading of the condensed phase as well as models of condensed phase absorption are also discussed. Finally, future directions and applications of dynamically controllable energetics are proposed, including synergies with other recent advances.

2:30 PM BREAK

3:00 PM FF06.07.01
Role of Grain Boundaries and Columnar Microstructures on Atomic Diffusion and Combustion in Ni/Al Nanolaminates Brandon Witbeck1,2 and Douglas E. Spearot1; 1University of Florida, United States; 2Air Force Research Laboratory, United States

Ni/Al nanolaminates are reactive composite materials with highly customizable combustion characteristics. These characteristics can be modified by altering system nanostructure through high precision synthesis techniques like physical vapor deposition (PVD). PVD has also been shown to form grains with diameters on the order of a single layer thickness and grain boundaries (GB) that may extend through the Ni/Al interface across multiple layers. The current work uses molecular dynamics simulations to investigate the effects of grain size and specific GB structures on Ni/Al nanolaminate combustion. Reaction rates are shown to increase with decreasing grain size on the same order of magnitude as increases caused by reductions in bilayer thickness, the fundamental attribute typically used to characterize nanolaminate combustion. Reaction peak temperatures are also shown to increase with decreasing grain size. To assess the role of specific GB structures, minimum energy GB structures are constructed and simulated in Ni/Al nanolaminate combustion. Effective diffusion coefficients are computed for each GB. Arrhenius descriptions of diffusion are constructed and shown to be a function of both GB structure and concentration, revealing stronger...
GB effects at temperatures below the Al melting point. Finally, GB effects on diffusion are shown to affect published continuum-scale calculations of both Ni/Al nanolaminate ignition temperature and combustion wave velocity.

**3:15 PM FF06.07.02**  
**Effect of Bilayers Arrangement on Self-Propagating Reactions of Thermite Reactive Nanolaminate Films**  
Petra Hanusova and Jon-Paul Maria; The Pennsylvania State University, United States

Reactive nanolaminate (RNL) multilayer thin films, as a family of energetic materials, attract large attention recently due to the large storing capacity over a long term and its capability of tuning energy and power output. Despite the termite reaction has been known for decades, the fundamental transport mechanisms during oxygen exchange between reactants needs to be examined more carefully to understand how the released energy can be tuned and controlled. This work studies the phase transformations and properties of ZnO/Zr RNL films grown by physical vapor deposition (PVD) as the main synthesis method in producing well-defined interfacial areas and excellent control of reactant layer spacing and stoichiometry. Thermal annealing was performed to ignite the exothermic reaction between individual layers, and the resulting phase transformations and reaction products were analyzed by means of X-ray diffraction (XRD) analysis. We found that the RNLs reacted to completion, as seen by the presence of the terminal metal Zn and the terminal oxide ZrO₂, measured by XRD. Furthermore, XRD reveals that in the RNL films, adjacent layers react and form an intermetallic intermediate, which provides additional energy to the system and assists the thermite reaction to completion. In addition, differential scanning calorimetry (DSC) and ultrafast shock spectroscopy were used to study how numbers of layers and interface density influence the reactive and thermal behavior of RNLs. The DSC results showed the activation energy decreases with increasing numbers of bilayers. In other words, larger interfacial area, increases the RNL reactivity.

**3:30 PM *FF06.07.03**  
**Microstructural and Mechanical Property Characterization of Reaction Synthesis-Produced Aluminum Metal Matrix Composites**  
Ethan Sullivan¹, Jacob Nuechterlain², A. Polizzi², Jeremy Iten², Stephen Liu¹ and Marcia Domack³; ¹Colorado School of Mines, United States; ²Elementum 3D, United States; ³NASA, United States

Wrought aluminum alloys, particularly those exhibiting high strength, are already seeing extensive use in aerospace and automotive applications given their high strength-to-weight ratio. Additive manufacturing (AM) of these alloys has grown more commonplace in an effort to meet the demands of these industries while overcoming the limitations of conventional manufacturing processes. However, many alloys of this class possess a propensity for solidification cracking, resulting in reduced ductility and tensile strength, which tends to make them unsuitable for welding and AM processes. Also, especially for aerospace applications, higher stiffness and more robust high-temperature properties are desired of these alloys. Addition of ceramic particulates to an aluminum alloy matrix to form a metal matrix composite (MMC) has been shown to both mitigate solidification cracking and achieve these desired properties. For ideal minimization of solidification cracking and to ensure uniform mechanical properties, the reinforcement phase must be uniformly distributed and possess a small mean diameter. Reaction synthesis refers to the reaction between precursor materials to form nanoscale particles that act as grain refiners or material reinforcement. Particles are formed in-situ during welding and AM processing through an exothermic reaction. Reaction synthesis can be used to form ceramic or intermetallic products that serve as the reinforcing phase in a MMC. Reaction synthesis is also able to address the poor wettability of the ceramic phase with the aluminum matrix through the presence of much higher temperatures during the reaction.

In this work, aluminum-based reactive additive manufacturing (RAM) powder blend feedstocks are employed in welding, laser powder-bed fusion (PBF), and electron beam freeform fabrication (EBF³) processes to examine the effect of feedstock composition and morphology on microstructure and mechanical properties. Blended powder was the feedstock for the laser PBF process and powder core filled wire was the feedstock for welding and the EBF³ process. The RAM feedstocks were characterized using scanning electron microscopy and particle size analysis. X-ray diffraction confirmed the presence of ceramic and intermetallic secondary phases in material fabricated using the RAM feedstocks. Light optical microscopy and electron back-scatter diffraction were used to examine texturing and the extent of grain refinement among the various feedstock compositions and the different fabrication processes. ASTM subsize tensile and Charpy specimens were used to measure the tensile strength and impact energy of materials produced by each process. Finally, differential thermal analysis was used to compare the heat evolution
during solidification of the RAM powder feedstocks compared to inert aluminum powders.

4:00 PM FF06.07.04  
**Tailoring Reaction Temperature and Propagation Velocity in Ni/Al Multilayers—Understanding and Preventing Substrate Quenching**  
Stefano Danzi, Maxence Menetrey, Jelena Wohlwend and Ralph Spolenak; ETH Zurich, Laboratory for Nanometallurgy, Switzerland

Ni/Al multilayers are reactive nanostructures consisting of alternating Ni and Al layers that can release heat through a self-sustained propagating exothermic reaction. Sparked by advances in physical vapor deposition, the renewed interest towards these materials propelled over the past two decades the development of applications where the multilayers’ heat release is targeted towards a specific functionality. Prominent examples include the development of miniaturized heat sources for micro-propulsion and on-demand healing of metal thin films. In many cases, however, Ni/Al multilayers are designed to work in intimate thermal contact with other components, or on a specific substrate, which act as heat sinks by extracting heat from the propagating reaction front. These conductive losses may reduce both the maximum temperature and the propagation velocity of the reaction until a point where the propagation is ultimately quenched, a process that so far has only been qualitatively observed. In this work, we study the influence of thin film heat sinks such as gold, copper and silicon, on the propagation velocity and temperature of the self-sustained heat wave produced by the NiAl intermetallic-forming reaction. Both the reaction temperature and propagation speed are shown to be linearly decreasing functions of the heat sink thickness up to a critical thickness for which the reaction propagation is completely quenched (~350nm for gold and copper, ~1.3µm for silicon). Further, we demonstrate that a multilayer Al₂O₃/Zr/Al₂O₃ thermal barrier between the heat source and the heat sink prevents reaction quenching and enables stable propagation in otherwise quenched conditions. The results of this study provide a detailed overview of the propagation behavior of Ni/Al multilayers on thin heat sinks and demonstrate that the reaction propagation can be critically controlled and eventually stopped by varying the thickness of a thin heat sink. Together with the introduction of a nanoscale thermal barrier, these results will facilitate the integration of Ni/Al multilayers as intrinsic heat sources on different substrates for applications in micro/nano-devices.

4:15 PM FF06.07.05  
**In Situ High-Speed Simultaneous X-Ray Phase Contrast Imaging and Diffraction for Dynamic Temperature and Morphology Measurements**  
Ibrahim E. Gunduz; Naval Postgraduate School, United States

High-strain mechanical loading of polymer-bonded explosives can produce significant localized heating due to microstructural heterogeneities. Detailed in-situ observations of the processes governing the generation of heat in these materials are challenging, yet they are important for improving predictive modeling tools for safety and performance. Here we report on a novel high-speed, high-resolution in-situ synchrotron x-ray diagnostic, combining phase contrast imaging with diffraction during heating of an explosive particle in a binder. We demonstrate that the morphology changes can help identify heating mechanisms, whereas the measured diffraction spot shifts from the single crystal can be used to track in-situ temperatures, verified by thermal modeling based on infrared camera measurements on the outside surface of the samples.

4:30 PM FF06.07.06  
**Effects of Post-Processing on Sol-Gel Synthesized Hard Magnetic Nanoparticles**  
Keri A. Ledford, Jason H. Nadler and David Reid; Georgia Tech Research Institute, United States

Hard magnetic nanoparticles have been synthesized by a solution-based combustion method. Strontium hexaferrite (SrFe₁₂O₁₉) was prepared by a sol-gel approach that allowed stoichiometric control of the nitrate-citrate gel by complexing specific ratios of metal nitrates with citric acid, and the subsequent auto-combustion reaction resulted in nanometer range particles. Material structure was analyzed by x-ray diffraction (XRD), and the nanometer-range particle size and shape were characterized by scanning transmission electron microscopy (STEM) and dynamic light scattering (DLS). The effects of calcining on the crystal structure and particle coarsening were investigated and characterized by XRD, STEM, and DLS. The electromagnetic permeability of toroids, pressed from pre- and post-calcined nanopowders, were measured with a 7mm coaxial airline.
8:45 AM FF06.08.01
Microstructure and Mechanical Properties of Swaged High-Density Reactive Materials for Use in High-Velocity Impact Testing
Jesse P. Grant1, Kevin McNesby2 and Timothy P. Weihs3; 1Johns Hopkins University, United States; 2US Army Research Laboratory, United States

The need to counter weapons of mass destruction with reduced collateral damage in urban environments has necessitated the development of countermeasures containing pre-formed, dense reactive materials. A crucial first step in understanding the impact and combustion performance of high-density reactive materials compacts is to characterize the effect that processing has on the microstructure and mechanical properties of the compacts. Here, we discuss the fabrication and characterization of high-density, reactive metallic composites formed through radial forging (swaging). The composites are formed by mixing dense, elemental powders of tantalum or tungsten with ball-milled reactive composite powders comprised of aluminum, magnesium, and zirconium; these powder mixtures are then compacted to near theoretical density through room temperature mechanical swaging. We manipulate process parameters such as the size of the elemental and composite powders and the degree of swaging, and we characterize the impact on the resulting microstructures and mechanical properties of the dense composites. These properties will, in turn, be used to understand the fragmentation of the composites on impact, as well as their reaction products and energy release.

9:00 AM FF06.08.02
Shock-Induced Reaction Synthesis of Boron Nitride from Mechanically Activated GaN and B Nano-Composite
Wesley W. Chapman1, Josh Pauls2, Metin Örnek1, Alex Mukasyan2 and Steve Son1; 1Purdue University, United States; 2University of Notre Dame, United States

It has been shown recently that cubic boron nitride (c-BN) can be formed through the ultra-fast (0.1-5 µs) shock-initiated reaction of TiN and B, leading to the synthesis of TiB2 and BN. In this study, we have further investigated the synthesis of boron nitride using different precursor nitrogen sources, ZrN, GaN, Cr2N. The shock-induced reaction of a ZrN+3B system will be reported herein. The composite ZrN+3B nano-powders were produced through high-energy ball milling to provide intimate, homogenous, mixing and were subsequently shocked to ~20 GPa using a copper recovery capsule, copper flyer, and a PETN based explosive. X-Ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) has been used to identify the phases and chemical bonding characteristics of the shocked powder. XRD results confirm that the precursor powder system has successfully reacted and formed hexagonal BN (h-BN). FTIR spectra corroborated the formation of h-BN and revealed a band near 1100 cm⁻¹, which suggests the existence of c-BN or wurtzitic BN, or both. These results could pave the way for in-situ creation of impact resistant ceramics.

9:15 AM *FF06.08.03
Tuning the Breakup of Reactive Fragment Materials
Joseph Hooper; Naval Postgraduate School, United States

The reactive-fragment concept involves explosive or gun launch of a reactive material, which then travels some distance before impact on a target. Upon impact, the fragment should shatter into a fine debris cloud and begin combusting, creating either thermal or overpressure damage. These competing requirements create a challenge for material design, as the fragment must be sufficiently tough to survive energetic launch without failure but still brittle enough to break up catastrophically when impacting a target. The majority of materials that work well in this role are pure metal compositions that rely on aerobic combustion for energy release. Traditional powder metallurgy techniques like hot isostatic pressing have been the most widely employed for fabrication of reactive fragments.

In this talk I review several years of research (especially within the Navy) on the material properties, energy release,
and fragmentation of this subclass of reactive materials. The degree to which the material shatters on impact is critical for aerobic combustion, but efforts to rationally tune the energy release of reactive frags has been hindered by the lack of experimental fragmentation data. I will discuss our efforts to directly recover and analyze brittle debris from high-velocity reactive frag impact or explosive launch using soft catch media. This data has allowed the development of analytic fragmentation models which provide a first step towards more advanced continuum and mesoscale modeling efforts.

9:45 AM BREAK

SESSION FF06.09: Advanced Manufacturing of Reactive Materials
Session Chairs: Michael Grapes and Timothy Weihs
Wednesday Morning, December 4, 2019
Hynes, Level 3, Room 308

10:15 AM *FF06.09.01

The mixing process of multimaterial systems can impart microstructure that can affect the overall material properties such as mechanical response and reactivity. In-line mixing has been implemented with a variety of feedstocks including siloxanes, sol-gel formulations, and reactive materials where the chemistry has been optimized for extrusion-based 3D printing. The behavior of the feedstocks requires additional characterization due to the complex fluid behavior present when introducing additional shear energy through mixing. This is especially true when mixing materials with vastly different densities, rheological behavior, and mechanical properties. The use of an active mixing printhead in 3D printing processes requires an understanding of how the processing dictates the microstructure and correlates to the resulting material properties. Characterization techniques such as mechanical testing and reactivity measurements are used to determine the connection between the microstructure due to the printing parameters, and the macro-scale behavior of printed structures. While in-line mixing has been utilized for a diverse set of materials, reactive materials are of special interest. Reactive materials benefit immensely from in-line mixing since the reaction kinetics can be controlled by printing parameters such as flow rate, mixing volume, and mixing speed. Additionally, the reaction is initiated in the mixing volume, reducing safety concerns when working with hazardous materials. An overview of multimaterial printing processes with an emphasis on reactive materials is presented.

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10:45 AM FF06.09.02
Aqueous Dispersion of Hydrophobic Pigments at High Solids Concentrations Manish K. Mishra1,2, Alexander Katz1, Yijun Guo1, Antony V. Dyk3, James Bohling1, Ahmet Kusoglu2, Adam Z. Weber2, Kebede Beshah3, John Roper III1, Clayton J. Radke1 and Futiyani Wang1; 1University of California Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3The Dow Chemical Company, United States

Controlling the surface chemistry of inorganic-oxide nanoparticles and their dispersion in water is an essential requirement for many technologies including ink and paint formulations. Competing requirements are typically encountered, when considering the necessity of water wettability of the nanoparticle surface in order to render low-viscosity aqueous dispersion on the one hand, and the need for water-barrier properties in the dried film on the other hand. Building on nearly a decade of advances in the surface modification and tailoring of surface chemistry of inorganic-oxide nanoparticles, which include poly(1→4)-β-glucan, alkylsilane-hexamethyldisilazane, and polysiloxane surface modification strategies, here we describe the synthesis of nanoparticles that exhibit a
combination of hydrophilic and hydrophobic character. These nanoparticles are hydrophilic in the wet state, and hydrophobic in the dry state, as characterized by capillary rise, contact angle, and water-uptake measurements. We describe the synthesis of such nanoparticles, and the importance of both electrostatic effects as well as steric effects of stabilization in aqueous dispersion, the latter characterized by $^{29}\text{Si}$ CP/MAS NMR spectroscopy and thermogravimetric analysis. We also study the flow behavior of the concentrated aqueous dispersion of modified-nanoparticles by rheometry, which reveals a low viscosity of the dispersions, thus making them ideal for applications.

References:

11:00 AM FF06.09.03
**Development of a Dual Nozzle Vibration Assisted 3D Printer with Applications to Reactive Materials** Aaron Afriat, Monique S. McClain, Jeffrey F. Rhoads, Ibrahim E. Gunduz, Steve Son and John C. McCaw; Purdue University, United States

Vibration Assisted 3D Printing (VAP) is a new direct-write manufacturing approach in which a nozzle resonates to enable dynamic flow control with constant driving pressure. Recent work suggests that VAP is capable to print highly viscous composite materials and propellants with applications to variable geometry solid rocket propellant, gun propellant, biological materials, ceramics and more. Developing a dual-nozzle VAP printer integrates two materials in a variety of configurations to explore topics such as combined energetic materials. An open-source Fused Deposition Modeling (FDM) 3D printer is modified to incorporate two VAP printing heads, each including a transducer and a 5cc syringe in contact with an ultrasonic transducer tip. The transducers are connected to a function generator and linear amplifier to generate the vibration frequency and amplitude needed for extrusion. A dual output compressor generates back pressure to keep a constant flow of material. A UV light is also incorporated to cure UV-curable propellants. Either of the VAP heads can be swapped with a FDM head to incorporate hybrid VAP/FDM prints. Such application includes printing various geometries of a support structure for a reactive material. Developing a dual nozzle VAP is a desirable step to investigate a wider range of energetics applications as well as implementations outside of the field. Here we present initial results of a dual nozzle VAP printer with examples of potential applications.

11:15 AM FF06.09.04
**Using Architecture to Control Burn Properties of 3D Printed Al/CuO Thermite Structures** Elliot R. Wainwright$^{1,2}$, Kyle T. Sullivan$^1$ and Michael Grapes$^1$; $^1$Lawrence Livermore National Laboratory, United States; $^2$Johns Hopkins University, United States

Breakthroughs in additive manufacturing of energetic materials, particularly direct ink write 3D printing, have allowed for greater control of performance by manipulation of architecture and/or composition. Here, we demonstrate control over the self-propagating reaction properties of 3D printed Al/CuO thermite by generating lattice structures with various void contents and filament sizes. The thermite is produced via on-the-fly static mixing of constituent Al and CuO inks, decreasing the risk associated with handling such materials. By reducing the fundamental print width (i.e. filament size) and introducing even small amounts of engineered porosity, we show that energy release rates can be increased by more than 100x over full-density burn strips. We also report on unique channel structures, which display propagation velocities of over 100 m/s due to confinement of the hot gas and molten particles released by the thermite reaction. We present Ashby plots which demonstrate the design space for...
3D printed thermites and discuss the wide level of control we achieve over the energy release rate using architecture with a single thermite formulation.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-776741.

11:30 AM FF06.09.05
A Comprehensive Study to Investigate the Supramolecular Interaction of Low-Molecular-Weight Gelators and Ultraviolet-Curable Monomers Zuoxin Zhou, Lea Santu, Christopher Tuck, Derek Irvine, David Amabilino and Ricky Wildman; University of Nottingham, United Kingdom

Monomers containing acrylate/methacrylate functional groups have attracted intensive interest due to the ability to polymerize readily under ultraviolet exposure. However, it would have great benefits for many applications if a network could be pre-established to support the monomers. A promising approach is to use low-molecular-weight gelators, which are capable of forming a physical 3D network to entrap and immobilize liquids. This might potentially form a dual network, modifying physical properties (rheology, morphology and others) of composites. The aim of this study is to obtain comprehensive results via investigating the interaction between gelators and monomers.

Methodology: Nine thermo-responsive gelators (A-I) with different structures were investigated. Each gelator was mixed with 29 monomers at 10 mg/ml. Gel tests were performed using a Crystallisation Systems Crystal16. Samples were heated gradually from 20°C to 120°C and cooling back to 25°C. Light transmission was recorded for each sample to determine gelation temperatures. Gel stiffness was characterized using an oscillatory rheometer and xerogels morphology were characterised via SEM.

Statistical analysis has been performed to build the relationship between gelation and 10 monomer parameters including: molecular weight, atom account, partition coefficient, hydrophilic-lipophilic balance (HLB), polar surface area, refractivity, Reichardt’s polarity (E<sub>T</sub>(30)), Kamlet-Taft polarizability, hydrogen bonding donor, and hydrogen bonding acceptor. Hansen’s HSPiP software was also used to understand the gelation.

Results and Discussion: There were three bis-urea gelators that formed gels with a significant amount of monomers: A (20 monomers), B (18 monomers), C (12 monomers), and a cyclohexanone derivative (D) formed gels with 19 monomers. The bis-urea molecules provided strong hydrogen bonding as the driving force for molecules to self-assemble into fibrous network. However, the acrylate/methacrylate monomers may mediate the process of hydrogen bonding molecular recognition pathways. The cyclohexanone derivative was of particular interests because its supramolecular mechanism was primarily relying on π-π stacking and London dispersion force contributed by the alkyl chains. Linear symmetrical bis-ureas demonstrated their interaction with monomers was most influential by E<sub>T</sub>(30) (p value = 0.004, F value = 5.72). As for the remaining gelators, partition coefficient and HLB were the solvent properties that had the most significant impact on correlating gelator-monomer interaction.

The asymmetrical bis-urea exhibited morphologies of self-assembly into thick fiber bundles whereas the cyclohexanone derivative formed plate-shaped morphologies. However, the linear symmetrical bis-ureas formed intertwining flexible networks with primarily single-strand fibrils. The results indicated that hydrogen bonding tended to favor self-assembly into single-strand fibers whereas self-assembly via aromatic interaction lead to non-fibrous arrangement. The gels formed from bis-ureas and cyclohexanone derivative were in the same range of storage modulus with the highest achieved above 4000 Pa at 1 Hz and the lowest below 50 Pa. However, none of the gels formed from gelator C was above 800 Pa. Linear symmetrical bis-urea gelator with longer alkyl chain resulting in higher gelation temperature and lower stiffness due to partially forming crystalline precipitation. Extensive precipitation has been observed on the surfaces of the gels formed from L-cysteine-derived double hydrocarbon chain.

11:45 AM FF06.09.06
Model Materials to Develop Particle Chemistries for Reaction Assisted Additive Manufacturing Shane Q. Arlington, Shashank Vummidi Lakshman, Sara C. Barron, Jeffery B. DeLisio, Juan C. Rodriguez, Sharada Narayanan, Gregory Fritz and Timothy P. Weihs; 1Johns Hopkins University, United States; 2Charles Stark Draper Laboratory, United States

Recent developments in additive manufacturing have drastically improved the ability to rapidly prototype and assess product design and viability. However, for products with integrated electronics, the ability to 3D print devices incorporating electronic components is limited by the small number of conductive inks, such as nanosilver. As the
most common conductive ink, nanosilver's high surface diffusivity allows it to sinter at low temperatures, resulting in electric interconnects with low resistivity. However, that same surface diffusivity causes poor durability as the printed lines can fail due to electromigration even at moderate current densities. Here, we demonstrate a new pathway to creating stable, electrically conductive printer interconnects, wherein the powders used to formulate the ink have stored chemical energy which assists in the sintering process and produces a low-resistivity product phase. The particles contain pairs of elements, such as Zr-C, Ti-C, and V-C, that have high heats of reaction, embedded in a soft, low melting temperature and low resistivity matrix, such as Al or a Cu-Ag alloy. This technology allows for the use of stable conductive materials, such as carbides, which would otherwise necessitate very high processing temperatures. To investigate the selection of chemistries suitable for these reaction-assisted inks, samples with highly controlled composition and microstructure were generated via physical vapor deposition (PVD) and the effects of chemistry and ignition method on the product phases, resistivity, and microstructure were assessed. These PVD materials serve as model materials and provide a toolbox for tuning stoichiometry when developing commercially viable powders for reaction assisted additive manufacturing applications.

SESSION FF06.10: Reactive Behavior and Material Properties III
Session Chairs: Joseph Hooper and David Kittell
Thursday Morning, December 5, 2019
Hynes, Level 3, Room 308

9:00 AM FF06.10.01
Interface Engineering with Metal Nanoparticles to Tune Ignition of Al/CuO Nanothermite Baptiste Julien, Jeremy Cure, Andrea Nicollet, Severine Vivies, Alain Esteve and Carole Rossi; LAAS CNRS, France

As typical energy storage materials, nanothermites which contain Al and oxide, have attracted much more attention for their broad potential applications in both civilian and military fields. They exhibit not only better combustion efficiencies and better ignitability compared to traditional monomolecular explosives but also the reaction outputs can be tuned thanks to the selections of fuels, oxidizers, architectures and reactant size allowing multiple actions. The performance and sensitivity of these materials are critically dependent on the properties of both active materials, Al and oxide, and their interfaces which control the reactants diffusion and thus reaction kinetics. Among nanothermites, sputter-deposited Al/CuO multilayers represent the state-of-the-art of energetic nanomaterials for tunable ignition to replace old hot-wire ignitor. To apply these 2D layered materials into products, it is now important to modulate the layers features in a controllable manner to fit the application requirements which are often contradictory in terms of ignition threshold, expected high for safety reasons, and reactivity. For example, decreasing the bilayer thickness below 150 nm permits to reach self-propagation velocities ~100 m/s but also led to instabilities and potential non-desired ignition, so that the materials can not be handled in a reliable manner. In this paper, we propose a new strategy based on utilizing uniformly distributed gold nanoparticles at the first interface to - upon thermal stimulation - generate reactive hot spots serving as ignition precursors. We first report a fast, low-cost and scalable approach to produce uniformly distributed gold nanoparticles onto the first sputtered CuO nanolayer using a photo-deposition method before sputtering the Al/CuO nanothermite on top. Then, we discuss the thermal-mechanical energy-transfer mechanisms that govern the initiation of redox reaction. Under thermal stimulation, Gold nanoparticles serve as localized-heat absorbers triggering locally the redox reaction and thus producing reactive micro-sized hot-spots. These hot-spots generate stress-induced mechanical rupture of the structure. The following disintegration of the layered material project Al droplets that burns into the environment. The ignition and flame characterization including emission spectra analyses as well as electronic microscopy observation completed in this work have allowed the construction of the following fundamental description of the ignition and reaction scenario in Al/CuO nanolaminates being ignited upon ultra-fast ramping. Upon heating the redox reaction begins between the Al and CuO reactant layers in the bulk material. In the reaction zone, the temperature quickly increases and produces localized highly stressed zones (hot-spots) leading to the disintegration of the nanolaminate before the entire Al reservoir has reacted. This explains why the observed flame temperature is above the Al vaporization point and, even, in some particular conditions, above the Al2O3 vaporization point. When the multilayer structure breaks apart, it disperses in the ambient unreacted, melted Al and CuO. Both continue to react, now with the additional possibility for unreacted Al to burn with environmental oxidizers such as those found in air.
Finally, we provide a perspective on the advantages of using gold nanoparticles as ignition triggers and suggest design strategies for highly efficient, stable while tunable Al/CuO nanothermites for commercial applications.

9:15 AM FF06.10.02
The Transition between Oxidation Mechanisms for Aluminum Clusters and Nanoparticles Kyle R. Overdeep, Claron J. Ridge, Yan Xin, Tonya N. Jensen, Scott L. Anderson and C. Michael Lindsay;
1University of Dayton Research Institute, United States; 2Air Force Research Laboratory, United States; 3Florida State University, United States; 4The University of Utah, United States

Micron-scale and nanometer-scale aluminum (nAl) particles are often considered attractive choices for fuels in energetic materials. In general, reaction rates increase as particle size decreases, owing to the increased surface area and reduced diffusion lengths between reactants. The oxidation behavior for aluminum nanoparticles >10 nm has been widely studied, and so has the oxidation behavior of clusters <1 nm (primarily for catalysis applications). These two regimes exhibit vastly different reaction mechanisms, but there is no experimental work observing oxidation behavior for intermediate size particles from 1-10 nm. The present study investigates this transition regime by producing unpassivated aluminum particles of this size range using Superfluid Helium Droplet Assembly (SHeDA), and then oxidizing the particles by rapidly transferring them from ultra-high vacuum (UHV) to ambient air. Scanning Transmission Electron Microscopy with EDS (STEM/EDS) and X-ray Photoelectron Spectroscopy (XPS) showed that particles < 4 nm vaporize upon oxidation while particles > 4 nm do not. We have hypothesized that this is a critical diameter, based on a rapid decrease in cohesive energy at this size, and is the threshold between the oxygen-etching mechanism of clusters and the heterogeneous oxidation of nanoparticles.

9:30 AM *FF06.10.03
From Synthesis to Application—Al/Zr-Based Reactive Composite Metal Fuels Elliot R. Wainwright and Timothy P. Weihs; Johns Hopkins University, United States

The introduction of novel reactive metal fuels into various explosive, pyrotechnic, and agent defeat applications requires an understanding of how ignition, combustion, and large-scale performance properties are coupled and how they depend on powder properties. Here, we will discuss the last five years of research on Al and Zr-based composite metal fuel powders that are synthesized via the scalable method of high energy ball milling. We will describe the entire lifecycle of these materials, including their synthesis, initiation, and combustion at both the individual particle and macroscopic fireball scales. These composite fuels are unique in that they have independently tunable ignition and combustion properties that includes a two-stage burn process (vapor then condensed phase). The composite metal powders demonstrate a significant decrease in ignition thresholds and substantial increases in combustion efficiency and burn time relative to pure Al powders of similar or smaller sizes. Through collaborations with a variety of research groups at ARL, NSWC-IHEODTD, Argonne National Lab, and several universities, we have explored the fundamental ignition and combustion mechanisms of these composites using multiple methods such as laser-induced plasmas, heated filaments, and explosive launch tests. In this presentation, we will summarize the results of these collaborations, as well as our own work, characterizing the dependence of ignition and burn mechanisms on powder parameters that include microstructure, size, chemistry, and environment.

10:00 AM BREAK

SESSION FF06.11: Reactive Material Experimental Techniques I
Session Chairs: Joseph Hooper and David Kittell
Thursday Morning, December 5, 2019
Hynes, Level 3, Room 308

10:30 AM FF06.11.01
Algorithm-Improved High Speed and Non-Invasive Confocal Raman Imaging of Two-Dimensional Materials
Sachin Nair, Jun Gao, Qirong Yao, Michael H. Duits, Cees Otto and Frieder Mugele; University of Twente, Netherlands
Confocal Raman microscopy is an important tool to characterize two dimensional (2D) materials, but the low flux of generated Raman scattered photons significantly hinders its expanding applications. For metastable materials such as graphene oxide (GO), the low signal flux is aggravated by the requirement of an extremely low laser dose to avoid or minimize laser-induced sample damage. In this work, we introduce algorithm-improved Confocal Raman Microscopy (ai-CRM), a fast and non-invasive confocal Raman microscopy (CRM) method based on a combination of an electron multiplying charge-coupled device (EMCCD), and principal component analysis (PCA) guided data de-noising. Using graphene and GO as a proof-of-concept, we demonstrate that ai-CRM can increase the Raman scanning rate by at least one order of magnitude with respect to state-of-the-art works. Meanwhile, GO can be imaged at a laser dose that is 2 to 3 orders of magnitude lower than previously reported, to the extent that the influence of laser illumination on the properties of the material can be avoided. We show that ai-CRM enables fast and spatially resolved quantitative analysis, such as mapping the defect density of graphene sheets. It is also demonstrated that the method can be extended to fast imaging of other 2D materials including Molybdenum Sulfide (MoS$_2$), Tungsten Sulfide (WS$_2$) and Boron Nitride (BN), and the three-dimensional distributions of nano-composite materials. Since ai-CRM is based on general mathematical principles, it is cost-effective, facile-to-implement and universally applicable to many other materials as well as other hyperspectral imaging methods such as surface-enhanced Raman scattering, hyperspectral infrared microscopy, and photo-luminescent microscopy.

**10:45 AM FF06.11.02**  
**Non-Contact Density and Thermal Conductivity Measurements of Encased Organic Thin Films and Thin-Film Explosives** Elbara O. Ziade$^1$, Christopher Perez$^2$ and Eric C. Forrest$^1$; $^1$Sandia National Laboratories, United States; $^2$Stanford University, United States

Vapor-deposited thin-film explosives provided a pathway to fundamentally understand the physics of explosives initiation and detonation. However, the physical properties of vapor-deposited thin-films deviate from their bulk counterparts and must be carefully characterized. Specifically, density, which is a primary physical parameter in detonation performance, varies depending on the substrate and across the thickness of a vapor-deposited thin-films. A gravimetric measurement of density can be obtained by dividing the measured mass of the thin-film by its measured volume. Unfortunately, variations in film thickness and limitations in balance resolution result in large uncertainty in these calculations and limit our ability to reliably measure density.

In this work, we present a novel method for non-contact technique for density and thermal conductivity measurements of encased organic thin-films and thin-film explosives. Four films of indomethacin and an array of varying thickness pentaerythritol tetranitrate (PETN) thin-films were vapor-deposited on silicon and fused silica substrates. The samples with encased with aluminum and gold thin-films and the density of the samples was measured with Frequency Domain Thermoreflectance (FDTR). Our results are compared to those obtained through gravimetric measurements and are in good agreement and prove to be a more reliable method for local density measurements of thin-film explosives and demonstrate the applicability of our technique for future microenergetics research.

**11:00 AM *FF06.11.03**  
**Direct Observation of Shock-Induced Energetic Material Decomposition** Keith A. Nelson; Massachusetts Institute of Technology, United States

We have developed methods for laser-driven shock loading of energetic materials and direct observation of shock-induced energetic material decomposition [1-3]. Small RDX crystallites embedded in polymer hosts are subjected to focusing quasi-2D shocks, and shock propagation and material responses are observed with a multi-frame camera that can record up to 16 frames in a single event with as little as 3 ns between frames. The results from many shocked crystals consistently show decomposition occurring initially along a single well-defined crystalline plane, with additional decomposition following depending on the shock pressure that is reached. Chemical and physical decomposition are apparent from the images and from photoemission that is also measured in real time. Post-mortem SEM and ultra-small-angle x-ray scattering reveal shock-induced voids whose sizes and shapes depend on the extent of chemical as well as physical decomposition.

Increases in RDX sensitivity also are observed under some conditions. When multiple crystallites are in contact, decomposition occurs preferentially at the regions of contact where stress localization is likely. Multiple shocks also have profound effects on sensitivity, with the extent of decomposition induced by a first weak shock far less than the decomposition induced by a second weak shock delivered to the same crystal as the first. The method is well suited...
11:30 AM FF06.11.04
Mass Spectrometric Study of the Formation of Key Intermediates in Iron Oxide Synthesis Flames Yasin Karakaya and Tina Kasper; University of Duisburg-Essen, Germany

Synthesis of functional materials in flame reactors is a reliable method to produce pure nanoparticles or coatings with unique physical and chemical properties, which are of great interest to a wide field of applications as additives, e.g. in edibles and medicine. The properties of flame-synthesized nanoparticles strongly depend on the particle size. The size can be influenced, for example, by the temperature of the synthesis and precursor concentration. The network of chemical reactions of the precursor decomposition interacts with the flame chemistry and forms key intermediates that are involved in particle growth. Consequently, the fundamental understanding of the decomposition of the iron based precursor to key intermediate species and stable products and the inception of particles during flame synthesis is of major importance for planned synthesis processes. Time-of-flight mass spectrometric in-situ measurements of iron pentacarbonyl doped model flames can identify which species occur in the synthesis flames. This information is the first step in generating a reaction model of the chemical processes in flame synthesis.

In this study, the decomposition of iron pentacarbonyl (Fe(CO)5) and the reaction pathways in laminar H2/C2H4/O2/Ar synthesis flames at low pressure are investigated. For a chemically controllable synthesis and functionalization of tailored iron oxide particles in flames, gaseous intermediates that act as building units during particle formation have to be identified. The analysis of the neutral intermediates is performed with aid of electron ionization molecular beam mass spectrometry (EI-MBMS). The extraction of a representative sample from the particle-laden flow of a synthesis flame by using an intrusive sampling technique for the mass spectrometric analysis is an ongoing challenge, because easily condensing iron containing species can obstruct the sampling probe. As a result, species with the structure Fe-O-H are still difficult to detect. Naturally occurring cationic iron containing species can be extracted from the flame with a novel sampling technique, which reveals cationic reaction pathways in the flame. The sampling of naturally occurring cations from flames allows measurements with high sampling efficiency for iron containing intermediates, thus overcoming one of the major difficulties in the EI-MBMS work. Here, cations with the structure Fe(OH)2+/Fe(OH)2H+ revealing the presence of neutral Fe(OH)2 and the cations Fe(OH)3+/Fe(OH)3H+ allude to the presence of Fe(OH)2 and hydroxide clusters with the structure Fe2O3H+. This study sheds some light on the gap between precursor decomposition and formation of nascent particles in iron oxide synthesis flames. Data sets with concentration profiles of neutrals and cations are provided for the validation of kinetic reaction mechanisms in combustion synthesis processes.

11:45 AM FF06.11.05
Laser Ablation of Natural Carbonaceous Materials—Chemistry, Tunability and Applications Xining Zang, Cuiying Jian, Nicola Ferralis and Jeffrey C. Grossman; Massachusetts Institute of Technology, United States

Polyaromatic carbonaceous materials (such as coal, tar, and pitch) are a family of materials with extremely rich chemistry and complex structures, representing a massive opportunity for their use in a range of potential applications. However, a deeper understanding of their electronic and structural properties at the microscopic scale is essential before they can be utilized in applications that require targeted properties and performance as well as large-scale manufacturing. In this talk, we present our recent work using laser ablation as a processing tool to induce extremely high local temperatures in thin films of natural carbon materials. Our results reveal the laser thermal
effect can control the H:C ratio, sp2 concentration, and graphitic stacking which are key structural fingerprint
determining the electrical properties of processed carbon materials. The laser ablation of carbonaceous materials
involves two key steps dehydrogenation and restacking behavior of polyaromatic hydrocarbons (PAHs). The broad
tunability of the two factors result in a wide distribution of carbon materials crystallinity from amorphous to highly
graphitic, with a sequential broad distribution of conductivity up to $10^5$ S/m. Semiconducting carbonaceous
materials require relative high H:C, while highly graphitized carbon is desired for conductivity electrodes. Both
experimental and simulation results indicate a graphitic cluster formation mechanism of NPAHs involving aromatic
corea, alkane “glue” molecules, and additive aromatic agents. These results shed light on the potential of natural
carbon to be utilized in active components, and can be used to guide the tuning of their electrical, structural and
chemical properties, paving the way towards their use far beyond simply disposal or burning.

SESSION FF06.12: Reactive Material Experimental Techniques II
Session Chairs: Edward Dreizin and Carole Rossi
Thursday Afternoon, December 5, 2019
Hynes, Level 3, Room 308

1:30 PM FF06.12.01
Characterization of Frontally Polymerizable Adhesives Daniel S. Camarda1, Matthew J. Lampe1, Alan J. Lesser1,
Dennis Volleberg2, Mark D. Minnichelli3 and Anna M. Mueller-Cristadoro3; 1University of Massachusetts Amherst,
United States; 2Eindhoven University of Technology, Netherlands; 3BASF, Germany

Frontal Polymerization is a reaction that, following initiation, releases sufficient energy to further polymerize,
creating a spatially propagating wave front. The present work utilizes this process in epoxy formulations where
frontal polymerization is driven by the exotherm released from cationic ring opening of the epoxide monomers.
Accordingly, this technology is advantageous in creating high-T_g, high-performing thermosets in that curing takes
place without the use of costly energy sources or VOCs. Frontally polymerizable epoxies are envisioned to have
relevance in a variety of applications where mechanical strength and chemical resistance is required. More
specifically, the use of frontally polymerizable epoxies as adhesives is investigated herein.

In this paper, the adhesion performance of a frontally polymerized formulation to a wide range of substrates is
investigated. Results discussing the influence of substrate properties, adhesive morphology, and boundary conditions
on adhesion will be presented in this work. Adhesion testing utilized a lap shear configuration and the shear stress
distribution was calculated using a shear lag model. This model was formulated to enable the calculation of the
stress distribution when adhering two substrates with different material properties. Consequently, an adhesion
investigation was facilitated where adhesion to one substrate was exceptional thereby promoting failure at another
material interface. Further, in all cases at least one interface was selected to be transparent, allowing for in-situ
measurements of the polymerization propagation rates and resulting morphology. Herein, the mechanisms of
adhesion to the various substrates will also be discussed.

1:45 PM FF06.12.02
A Reaction Violence Test for Safety Screening of Thermites Kyle T. Sullivan and Eric Avalos; Lawrence
Livermore National Lab, United States

The reaction mechanisms in thermite powders is a highly complex process, and involves various non-equilibrium
and equilibrium processes as fuel and oxide particles react to form mixed-phase products on a rapid time scale.
Understanding this process involves understanding of the various length and time scales and how they contribute to
the reaction processes. Fundamental studies can help better our understanding of the reaction mechanisms,
specifically as they pertain to safety and performance. In this work, we present a small scale test designed to
evaluate the reaction violence of thermites at the formulation scale. A small charge is placed at the sealed end of a
clear, acrylic tube, and ignited. This results in rapid entrainment and flow of the powder. The velocity of this flow
can give a relative ranking of the pressurization, as intermediate gases are released and drive this flow. The burn
time of the dispersed powder can yield information about the thermal profile, which is important to know when
evaluating heating effects such as damage to a target or safety shielding requirements. The test can easily be
modified as-needed, but is an important first step in evaluating the safety characteristics of new materials, and towards developing a better fundamental understanding of how the material attributes can control this behavior. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-760652.

2:00 PM *FF06.12.03

In Operando High-Speed Microscopy and Thermometry to Track Reaction Propagation

Dylan Kline1,2, Haiyang Wang2 and Michael R. Zachariah2; 1University of Maryland, United States; 2University of California, United States

Understanding structure-function relationships is exceedingly difficult because the characteristic length scale of the microphysics (composition and thermal gradients) is usually much smaller than the characteristic length scale of the measurement. To address this mismatch we employ a new high-speed microscopy/thermometry capability that enables ~ μs time and ~ μm spatial resolution as applied to highly exothermic reaction propagation. This enabled us to directly observe reactive sintering and the reaction front at high spatial and temporal resolution.

We show the usefulness of this approach for three specific examples. An important proposed mechanism in nanothermites reactions – reactive sintering – plays a significant role on the combustion performance of nanothermites. Experiments on the Al + CuO nanocomposite system reveals a reaction front thickness to be ~30 μm and temperatures in excess of 3000 K, resulting in a thermal gradient in excess of 10⁷ K m⁻¹. The local microscopic reactive sintering velocity is found to be an order of magnitude higher than macroscale flame velocity. In this observed mechanism, propagation is very similar to the general concept of laminar gas reaction theory in which reaction front velocity ~ (thermal diffusivity x reaction rate)¹²⁻¹

In a second example, recent studies have demonstrated a counterintuitive result in that additives with thermally insulating properties – notably SiO₂ particles – can enhance the propagation rate in solid propellants. Using high-speed microscopy and thermometry on 3D printed solid propellant films containing both thermally conducting (graphite) and insulating (SiO₂) to investigate the role of these additives on film propagation rate. It was found that addition of SiO₂ particles increased the effective surface area of the reaction front through inhomogeneous heat transfer in the films, and that such corrugation of the reaction front area on the micron scale manifests itself as a global increase in the propagation rate on the macro scale. Graphite additive was observed to have a substantially lower burning surface area and propagation rate, suggesting that the effect of reaction front surface area is larger than the effect of thermal diffusivity for low-weight percent additives in solid propellants. In the last example we will demonstrate how the use of microwaves can be used to initiate and moderate burn rate using metal coated nanoparticles that optimize absorption.

2:30 PM BREAK

3:00 PM FF06.12.04

In-Depth Understanding of Reactive Aluminum/Aluminum Iodate Hexahydrate Nanoparticles via Advanced Material Characterizations

Chi-Chin Wu1, Jianguo Wen2, Scott D. Walck3, Jennifer L. Gottfried1 and Rose A. Pesce-Rodriguez4; 1U.S. Army Research Laboratory, United States; 2Argonne National Laboratory, United States; 3Service Engineering Inc., United States

Metallic nanoparticles, such as nano-aluminum (nAl), are promising candidates as the next generation energetic additives for improved combustion and detonation effects in explosive/propellant formulations. Their high theoretical energy content and potentially rapid burning of nAl, enabled by the high surface area to volume ratio, are very desirable characteristics for energetics. This work aims to enhance fundamental understanding of the chemical and structural properties for reactive aluminum-aluminum iodate hexahydrate (AIH) composite nanoparticles. The composites were produced by treating commercial nAl particles (60-100 nm average particle diameter) with helium and argon inert plasmas using custom-designed atmospheric dielectric barrier discharge reactors followed by subsequent mixing with acidic iodic solution (HIO₃) to form the energetic oxidizing salt, aluminum iodate hexahydrate (AIH) on the nAl surface. High resolution transmission electron microscopy (HRTEM) micrographs revealed unique miniature crystalline structures within the amorphous alumina (Al₂O₃) shell surrounding the crystalline Al core and at the outermost particle surface with only one to two monolayer thickness. Elemental maps obtained from scanning TEM (STEM) experiments demonstrated distinctly different distributions of AIH crystallites on the nAl surface for the nAl-AIH composites produced by different gases during the plasma treatment. X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy were used to study surface functional
groups of the nAl-AIH nanoparticles. This paper emphasizes the significance of exploiting advanced materials characterizations to enhance in-depth understanding of reactive nAl-AIH composites by revealing the plasma-dependent altered surface chemical and structural properties.

SESSION FF06.13: Continuum and Mesoscale Modeling of Reactive Materials
Session Chairs: Edward Dreizin and Carole Rossi
Thursday Afternoon, December 5, 2019
Hynes, Level 3, Room 308

3:15 PM FF06.13.01
Analytical Prediction of Spin Band Widths in Co/Al Nanolaminates Michael J. Abere1, Catherine Sobczak2 and David P. Adams2; 1Lawrence Livermore National Laboratory, United States; 2Sandia National Laboratories, United States

The propagation of sputter deposited Co/Al nanolaminates is known to have a bilayer thickness dependent instability. The specific 2D instability observed involves the transverse propagation of a band in front of a stalled front commonly referred to as a “spin band.” Previous laser ignition studies have revealed that preheating to the point of pre-reaction removes enough stored chemical energy to slow propagation. Here, a single step diffusion limited reaction model is implemented into a time dependent heat spreading model to calculate the magnitude of pre-reaction ahead of a propagating front. To determine the amount of stored chemical energy lost as a function of pre-reaction thickness, films with product phase diffusion barriers were grown and characterized. This pre-reaction model is combined with an analytical calculation of propagation velocity, which allows for a prediction of quench length. The energy-depletion based model for spin band width is then tested on normally stable bilayer designs where instabilities have been induced through the addition of diluent product phase layers within the reactant layers.

This work was supported by the Sandia National Laboratory Directed Research and Development (LDRD) program. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under Contract No. DE-NA0003525. This work describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the U.S. Government.

3:30 PM *FF06.13.02
3D Simulations of Reaction Front Dynamics in a 1:1 Co/Al Reactive Multilayer System David Kittell, Michael J. Abere and David P. Adams; Sandia National Laboratories, United States

Reactive multilayers are uniformly structured materials that may be ignited to produce rapid and localized heating. While this class of material is well-known, and has long been studied for a variety of applications (e.g. joining, brazing, or near-net shape forming of intermetallic parts), only recently have the related thermochemical reactions been implemented in large 3D computer simulations. Original modeling efforts through the early 2000s considered flame propagation in one dimension; this approach is useful to compare with the measured reaction front velocities and flame front thicknesses. Such 1D models provide physical insights into the material behavior, as velocity and front thickness are varied experimentally by controlling the multilayer periodicity and total film thickness. However, high speed videography has shown that the reaction fronts can be non-planar [1], for certain periodic spacings (i.e. bilayer), ambient temperatures, gaseous environments, as well as other design conditions. In particular, various instability modes have been observed, including auto-oscillation of the reaction front (1D instability), spinning reaction fronts (2D or 3D instability), and chaotic reaction propagation (3D instability). Such behavior may only be explored in large finite element analysis (FEA) codes (e.g. [2]), where the current state-of-the-art is thought to be on the order of 10 to 100 million elements for a reactive thermal analysis on modern high-performance computing resources.
In this work, an empirically-driven reduced order model for 1:1 Co/Al multilayers is implemented in Aria, a Galerkin FEA code developed by Sandia National Laboratories, and part of the SIERRA computational framework. The reduced model is a diffusion-limited reaction model based on the one by Hardt and Phung [3]; this model has been previously used to predict the ignition delay, propagation velocity, and quench limits for different Co/Al and Al/Pt multilayer designs [4]. Now, the reaction model is coupled to empirical thermophysical property data obtained from years of testing at Sandia. This includes: an anisotropic thermal conductivity model, mixture heat capacity, melting and phase change with formation enthalpies, piecewise continuous diffusivity with an Arrhenius dependence on temperature, and bilayer-dependent species concentration profiles. To summarize this implementation, we present the most up-to-date model fits for 1:1 Co/Al and the associated equations which are assumed to govern the reaction front dynamics. Next, large 3D simulation results show that the fully detailed model is able to predict planar as well as non-planar fronts, which are then examined for their heating rates and thermal gradients. From these simulations, it is hypothesized that real instabilities originate from nucleation sites. In order to artificially induce this nucleation, we show numerical initiation schemes that break the symmetry of the calculation, with different boundary conditions and multilayer edge geometries. Finally, one case of a spinlike reaction front is discussed in greater detail to compare and contrast with the mechanism originally proposed in [5].


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**Modelling the Thermal Aging of Al/CuO Thermites in the Form of Nanolaminate Thin Films and Its Effect on Performances**

Guillaume Lahiner¹, Mehdi Djafari Rouhani¹, Nicolas Richard², Carole Rossi¹ and Alain Esteve¹;

¹LAAS-CNRS, France; ²CEA-DAM, France

Nanoenergetic materials deposited in the form of nanolaminates have been developed for welding purposes or as micro-initiators. One major advantage lies in their ability to be integrated on a chip via conventional MEMs fabrication techniques such as sputter deposition. Their integration and miniaturization in circuits open a number of new functional perspectives in miniaturized systems (security, actuation, local heat source...). One of the main obstacles to use these materials and deploy them at a large-scale is to guarantee and preserve their performance and safety under long term storage. To this end, predicting and quantifying the impact of thermal aging on nanolaminate structures and their energetic performance is of crucial importance.

Recently, an experimental investigation dedicated to the identification of a reaction scenario of Al/CuO nanolaminate at very low heating rate, typically used in Differential Scanning Calorimetry (a few tens of degree per sec.) has been proposed, establishing a number of basic mechanisms [1]. From low to medium range temperatures (<500°C), we evidenced that degradation of the nanolaminate is governed by the transport of oxygen across the growing layer of Al2O3 separating Al and CuO, exhibiting multiple steps with corresponding structural variants in the interface. On this basis, we developed a heterogeneous reaction model [2] integrating an ensemble of basic reaction mechanisms (oxygen diffusion, structural transformations, polymorphic phase changes) as the simulation core of a modelling platform, NICAM (for Nanolaminates Ignition Combustion and Aging Model) to: (i) simulate accelerated thermal aging, (ii) predict the effect of aging on nanolaminate performance in terms of combustion, flame propagation and initiation delay. We discuss “in silico” experiments with varying parameters such as layer thicknesses, stoichiometric ratio, initiation power, substrate thermal conductivity, or the size of the heating zone. For each case studied, we provide the nominal conditions of aging and how performance is altered, in terms of initiation delay, flame propagation and heat release.

[1] Structure and chemical characterization at the atomic level of reactions in Al/CuO multilayers, Iman Abdallah, James Zapata, Guillaume Lahiner, Benedicte Warot-Fonrose, Jeremy Cure, Yves Chabal, Alain Esteve, Carole
Interest in reactive nanocomposites has experienced massive growth due to the proclivity of these energetic materials to provide highly adaptable, attractive solutions to pyrotechnical problems requiring large amounts of energy in the form of heat or pressure. These nanothermites, constructed of a fuel-oxidizer pairing, produce extremely exothermic reduction-oxidation reactions with highly tunable properties including the gas production, flame temperature, burn rate, or visual effect. By adapting the thermite couple materials to produce the desired reactions, these nanoenergetic materials have applications in MEMS as heat sources or micro-initiators, the aerospace industry as solid propellant, propulsion systems, or space vehicle separation, mining time delay elements, among others. The study and characterization of different nanothermites and their reactions by experiment can be costly, difficult to standardize or quantify, and even dangerous to manufacture. Up to this point, many experimental studies and most numerical simulation of nanothermites have been based on the Al/CuO nanothermite due to the abundance of the materials and elevated base of understanding in the community, but it is not applicable for all possible domains. Computational modelization provides an economical, relatively quick, and safe method to characterize the different options available for these applications.

This work presents a novel phenomenological model based on the Deal-Grove diffusion/reaction scheme for mixed powder-based nanothermites. It is based purely on the condensed phase reaction, including diffusion of oxygen atoms across interfaces in addition to reactive sintering. These cause the initial agglomeration and melting of the mixed nanoparticles due to an external heating source that begins the self-sustaining reaction due to the exothermic reduction and oxidation of the metal oxide and metal fuel, respectively. With inputs such as the initial particle materials, size and nature, and associated properties, such as diffusion coefficient, the wetting contact angle of coalescence, the stoichiometric ratio, the compaction rate (as a percentage of the Theoretical Max Density), and the initiation method, results like the initiation delay, total burn time, and speed of steady-state propagation are produced. We first discuss the role of condensed phase mechanisms and sintering on the initiation of an Al/CuO mixture as a function of the heating ramp or initiation mode (resistive versus laser heating). This leads to a comparative study of the driving force in initiation between condensed or gas phase mechanisms. [1] A benchmark study is then completed on commonly used thermite couples, their initiation and propagation, with an emphasis on low-gas or gasless thermites for specific applications in mining or space domains. These simulated results are validated with available experiment where possible, with the hope that this information can provide a framework reference for new or existing applications looking for a certain range of pyrotechnical effects.

Quantum spintronics is an emerging field of spin coherence and spin correlations at or near room temperature, and their effects on a wide range of properties, including spin dynamics and light emission from color centers in solids, spin and charge transport in organic materials, spin-dependent transport in tunnel junctions, dynamic nuclear polarization, and animal sensing of magnetic fields. Room-temperature quantum spintronic systems can be much more sensitive to external perturbations than sensors that must be very near thermal equilibrium. Applications include sensing of magnetic fields in biological systems (e.g. color centers in diamond and other wide-band-gap semiconductors and insulators), control of light emission intensity from organic light emitting diodes (e.g. thermally-activated delayed fluorescence), spin injection, spin dynamics, and coherent optical interactions with single spins (color-center photonics). Highly sensitive room-temperature spin systems also feature prominently in proposals for very low power electronic logic.

This tutorial will provide an introduction to the materials and operating regimes that tend to exhibit room-temperature spin coherence and spin correlations, methods of calculating and measuring these properties, areas of initial application and critical open questions.

1:30 PM
**Theory of Quantum Spintronics** Michael Flatté, The University of Iowa

The theoretical criteria for a stable, room-temperature quantum coherent system will be described, and several examples will be presented. Methods of calculating the response of a quantum coherent system to external fields and perturbations will be presented, including density matrices, stochastic Liouville equations, and master equations. Recent progress in predicting specific quantum coherent systems, such as density functional theory for new color centers in wide-gap semiconductors, will be surveyed. The ideal performance of quantum spintronic devices will be compared with other sensors or information processing approaches.

2:15 PM
**Quantum Magnonics and Magnonic Materials** Ezekiel Johnston-Haperin, The Ohio State University

Magnon excitations of magnetic materials are of increasing interest for quantum applications due to their broad spatial extent and their potential to efficient coupling to systems ranging from isolated single spins to microwave and optical photons. One of the central challenges in this field is the identification of materials with sufficiently low loss to support these emerging applications. Critical materials constraints and the current state of materials development will be presented.

3:00 PM BREAK

3:30 PM
**Optical Coupling to Quantum-Coherent Spins** David Awschalom, The University of Chicago

Coherent coupling of light to spin coherent systems, especially for color centers in diamond and silicon carbide, will be described in detail. Nonequilibrium polarization/pumping, manipulation of the spin state, and efficient detection will be presented, along with criteria for pulse shaping that can be used for low-error manipulation of the spin state of a quantum coherent system.
The design, fabrication, and measurement of photonic devices that efficiently integrate a quantum coherent spin with a cavity will be described. Methods of manipulating the quantum spin to bring it into resonance with the cavity, such as through acoustic oscillations or electrical gates, will be presented. The figures of merit for spin-photon coupling will be derived and compared with state-of-the-art coupling of other quantum coherent systems.

**SYMPOSIUM MQ01**

Coherent and Correlated Magnetic Materials for Hybrid Quantum Interfaces  
December 2 - December 6, 2019

Symposium Organizers  
Andrew Fisher, Imperial College London  
Shunsuki Fukami, Tohoku University  
Evelyn Hu, Harvard University  
Ezekiel Johnston-Halperin, The Ohio State University

* Invited Paper

SESSION MQ01.01: Single Spins and Single Photons  
Session Chairs: Ezekiel Johnston-Halperin and Patrick Maletinsky  
Monday Afternoon, December 2, 2019  
Hynes, Level 2, Room 202

1:30 PM MQ01.01.01  
**Electronic, Spin and Structural Properties of Er³⁺ Doped Yttria: Y₂O₃**  
Cuneyt Sahin¹,², Tian Zhong² and Michael E. Flatté¹,²,³; ¹University of Iowa, United States; ²The University of Chicago, United States; ³Eindhoven University of Technology, Netherlands

Rare earth ions in oxide materials have been extensively studied due to narrow transitions with long coherence times and high quantum efficiency between electronic levels of partially filled f-shells. This results in the fabrication of optical amplifiers with high quantum efficiency and optimal wavelength in telecommunication applications, high power solid-state lasers, and usage in optical storage, data, and quantum information processing [1]. Furthermore, yttrium oxide (Y₂O₃) as one of these oxide materials with a high dielectric constant has gained attraction for being an alternative for replacing silicon dioxide in metal-oxide-semiconductor devices [2].

Here we study electronic, structural, and spin properties of trivalent rare-earth element erbium (Er³⁺) impurities in the cubic bulk Y₂O₃ with a wide band gap of 5.8 eV. The primitive cell of the yttria has 40 atoms, however, a conventional bixbyite supercell with 80 atoms is used for impurity calculations. As one of the most promising dopants, Er³⁺ substitutes an yttrium atom at two symmetrically inequivalent and octahedrally coordinated cation sites (C₂ and C₃) with an equal probability. First, we compute structural parameters such as lattice constant and elastic properties within the density functional theory using a Monkhorst-Pack k-point grid of 2x2x2 for Brillouin zone integration, the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation potential and the pseudopotential method in a plane wave basis. We also calculate the electronic band structure and the density of states of the bulk and doped yttria. The results of the electronic and structural calculations are in a good agreement with experimental measurements. Then we proceed to calculate the formation energies of Er³⁺ impurities as point defects at two different sites using the defect formation energy formula [3]. We
also investigate the formation energies of different charged states as a function of the Fermi level.

We also calculate individual defect properties such as level splittings and g-tensors using an effective crystal field Hamiltonian with Wybourne normalization and treat the Zeeman and hyperfine interactions as a perturbation. Group theoretical studies [4] show that the low crystal symmetry of Er\(^{3+}\) sites requires only a small number of crystal-field parameters to model energy levels of the dopants sufficiently. We show that g-tensor of the ground state that is calculated from this Hamiltonian is highly anisotropic with a large component along one direction. Presence of an abundant isotope of the \(^{167}\)Er with a non-zero nuclear spin and anisotropic g-tensor suggest that an experimental control of the spin dynamics of this system is possible through the Zeeman and hyperfine interaction.

We acknowledge funding from the Center for Emergent Materials, an NSF MRSEC under Award No. DMR-1420451 and by NSF EAGER Award No. 1843044.


1:45 PM MQ01.01.02
Nanoscale Structure of the Orbital Magnetic Moment of a Single Dopant Spin in a Semiconductor

Adonai R. Cruz\(^1\) and Michael E. Flatté\(^2,1\); \(^1\)Eindhoven University of Technology, Netherlands; \(^2\)University of Iowa, United States

The localized electron spin of a single impurity in a semiconductor is a promising system to realize quantum information schemes [1]. Coherent control of this spin depends on understanding the structure of the magnetic moment that couples the system with external fields. In this work we investigate the orbital contribution to the magnetic moment originated from the spin-orbit induced circulating current associated with the ground state of a single magnetic impurity in zincblende III-V semiconductor. This circulating current is dissipationless and represents an electron moving in a closed trajectory [2]. The orbital moment associated with the circulating current could be directly measured by the dc-magnetic field it produces through nanoscale magnetometry techniques provided by NV-centers in diamond [3].

In this project we developed a formalism employing Green's functions obtained by the Koster-Slater technique [4] with a sp\(^3\)d\(^5\)s\(^*\) empirical tight-binding Hamiltonian [5,6] to describe the host material. We calculated the circulating current and orbital moments of a single Mn dopant in GaAs. The spin-correlated orbital moments originates from the hybridization between the Mn(d\(^3\)) spin-polarized electrons and the As dangling bonds leading to t\(_2\)-symmetric triplet acceptor states in the band-gap above the valence band edge.


* This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 721394

2:00 PM *MQ01.01.03
Electrical Manipulation of Isolated Quantum Spins Using Classical SiC Devices

Christopher P. Anderson\(^1\), Alexandre Bourassa\(^1\), K.C. Miao\(^1\) and David D. Awschalom\(^2,1\); \(^1\)The University of Chicago, United States; \(^2\)Argonne National Laboratory, United States

The neutral divacancy (VV0) in silicon carbide (SiC) exhibits robust spin coherence and a high-quality near-infrared spin-photon interface in a material compatible with mature fabrication techniques. Here, we make use of this
scalable semiconductor host and design electronic devices to manipulate embedded isolated quantum systems. Specifically, we create and isolate single VV0 defects in a commercial p-i-n diode [1]. This simple integration enables engineering of the defect’s charge environment and drastically reduces electric field noise. Surprisingly, the use of electrical gating results in mitigating spectral diffusion and achieving near-lifetime limited optical lines. Furthermore, by exploiting field confinement of the junction, we show that the optical transitions can be gate-tuned by nearly a terahertz. This geometry also provides a method for using electric fields combined with optical excitation to enable deterministic charge state control.

Applying gigahertz ac electric fields to SiC devices produces coherent interference in the form of Landau-Zener-Stückelberg fringes, arising from interactions between microwave and optical photons [2], even in the absence of a microwave resonator. We demonstrate lifetime-limited optical coherence and clock-like spin transitions that result in increased robustness against magnetic noise. Electrical driving of optical transitions offers advantages over spin-based coupling and points towards new types of hybrid quantum systems. These results reveal new opportunities for electrical manipulation of spin-based quantum systems in scalable SiC electronic devices.

This work was done in collaboration with S. L. Bayliss, A. L. Crook, P. J. Mintun, S. J. Whiteley, G. Wolfowicz, H. Abe, A. Gali, V. Ivady, T. Ohshima, G. Thiering, P. Udvarhelyi.


2:30 PM MQ01.01.04
Spin-Photon Interfaces Based on Tin-Vacancy Quantum Emitters in Diamond Matthew Trusheim, Lorenzo De Santis, Kevin C. Chen and Dirk Englund; Massachusetts Institute of Technology, United States

Inversion-symmetric quantum emitters in diamond, such as the silicon-vacancy, germanium-vacancy, and the recently-discovered tin-vacancy complexes, are promising candidates for quantum networking as their optical coherence is protected from electric field noise. Emitters containing a heavier element, such as Sn or Pb, are of particular interest as their large spin-orbit coupling reduces phonon scattering at easily achievable (non-3He dilution) temperatures, offering the possibility of long spin coherence – a key requirement for scalable quantum networks. Here we report on the development of coherent spin-photon interfaces based on Sn-vacancy emitters, including optical and spin coherence measurements and integration into nanophotonic devices. The narrow optical linewidths and long spin coherence times observed, combined with robustness to fabrication-induced damage, place the SnV among the best-known solid-state spin-photon interfaces.

2:45 PM MQ01.01.05
Quantum Emitters with Tailored Optical and Spin Physics Christopher J. Ciccarino1, Johannes Flick1, Isaac Harris1,2, Dirk R. Englund2 and Prineha Narang1; 1Harvard University, United States; 2Massachusetts Institute of Technology, United States

Color centers have emerged as leading solid-state “artificial atoms” for a range of technologies from quantum sensing to quantum networks. Concerted research efforts are now underway to identify new color centers that combine the favorable spin properties of the nitrogen vacancy (NV−) with the spectral stability of the silicon vacancy (SiV−) centers of diamond. Using a first principles approach, we investigate quantum defects in both 3D (diamond) and 2D (hexagonal boron nitride) hosts with the aim of unlocking and understanding the optical and spin physics. In diamond, we will discuss insights into Jahn-Teller interactions, including the product and dynamic Jahn-Teller distortions related to both group III and group IV color centers. Further, we show the instabilities and charge-states associated with each of these group III/IV defects and the implications in quantum information science related to both spin and spectral stability. In hBN, we discuss the origin of defect emission, in particular the importance of the level of theory invoked to describe charge states and defect-defect interactions.

3:00 PM MQ01.01.06
Vanadium Spin Qubits as Telecom Quantum Emitters in Silicon Carbide Gary Wolfowicz1,2, Christopher P. Anderson1, Berk Diler1, Oleg G. Poluektov2, Joseph F. Heremans2,3 and David D. Awschalom1,2; 1The University of Chicago, United States; 2Argonne National Laboratory, United States
Quantum emitters in the solid state with addressable spin registers are promising platforms for quantum communication, yet few emit in the narrow telecom band necessary for low-loss fiber networks. This scarcity is compounded by the low brightness and hard-to-engineer host materials of erbium ions, the prototypical telecom emitter, motivating the search for alternative systems.

Here we create and isolate single vanadium dopants in silicon carbide (SiC) with emission in the O-band (1278-1388 nm) and with brightness allowing cavity-free detection, in a commercial, wafer scale and CMOS-compatible material [1]. We demonstrate that their emission is stable and relatively narrow even near surfaces, showing strong promise for integration with nanoscale devices.

In ensembles, we characterize the complex physics provided by the $d^1$ orbital of these transition metals, including a systematic study of the five different sites available in the 4H and 6H polytypes of SiC. The optical transitions are observed to be sensitive to mass shifts from the distribution of nearest neighbor silicon and carbon isotopes, potentially enabling optically-resolved nuclear spin registers.

Optically detected magnetic resonance of ground state and excited spin transitions reveal a variety of hyperfine interactions with the vanadium nuclear spin and their related clock transitions for use as quantum memories. Finally, we demonstrate coherent quantum control of the spin state at 3.3 K, limited by thermal relaxation effects. These results provide a path for telecom emitters in the solid-state for quantum applications.


3:15 PM BREAK

SESSION MQ01.02: Single Spins and Electron Transport

Session Chairs: Christian Degen and Ezekiel Johnston-Halperin

Monday Afternoon, December 2, 2019

Hynes, Level 2, Room 202

3:30 PM MQ01.02.01
Spin Filtering through Chiral Molecule Monolayers on Semiconductors Tianhan Liu¹, Longqian Hu¹, Eric Lochner³, Peng Xiong¹, Xiaolei Wang², Hailong Wang², Jianhua Zhao², Gang Shi², Fan Gao³, Honglei Feng³ and Yongqing Li³; ¹Florida State University, United States; ²Institute of Semiconductors, China; ³Institute of Physics, China

The effect of structural chirality-induced spin selectivity (CISS) has been observed in a host of nanostructures involving chiral molecule monolayers on noble metals.¹ Realizing CISS on semiconductors could open new pathways of spin injection and detection on semiconductors without using any magnetic materials. However, there has been no report of such experiments on planar semiconductor surfaces. Here, we report on the self-assembly of thiolated dsDNA and polyalanine monolayers on GaAs and its magnetic variant, (Ga,Mn)As, which is used as a spin analyzer to ascertain CISS through the chiral molecules. The monolayer assemblies on GaAs are studied by AFM and ellipsometry and compared with those on Au. On Au, "blocking" by hydrophobic alkanethiol self-assembled monolayers is necessary to achieve assembly of dsDNA oriented away from the substrate. The assembly on GaAs is made possible by an ammonium sulfide treatment for oxide removal and surface passivation,² on which the polyalanines form oriented SAM without any "blocking".

We further study the spin-selective electron transport across vertical junctions of (Ga,Mn)As/polyalanine/Au. The bottom (Ga,Mn)As electrode is epitaxially strained, resulting in perpendicular magnetic anisotropy. The micrometer scale junctions are formed in openings in a hardened PMMA layer on the (Ga,Mn)As defined by electron beam lithography. The native oxide on the exposed (Ga,Mn)As is removed by ion milling, followed immediately by
polyalanine monolayer self-assembly in a solution. The top Cr/Au electrodes are thermally evaporated under liquid nitrogen cooling. The CISS effect is evidenced by measuring the magnetoresistance of the junctions: Sweeping the perpendicular magnetic field at low temperatures, sharp changes in the junction resistance are observed at the coercive fields of the (Ga,Mn)As, indicating spin filtering of electrons from the Au electrode by the polyalanine monolayer. The spin polarization of the electrons from GaAs filtered by polyalanines may be determined quantitatively by spin-resolved superconducting tunneling with a thin Al counter-electrode.


3:45 PM MQ01.02.02
Imaging Spin Dependent Properties of Individual Dopants through DC Magnetoresistance of Spin-Polarized Scanning Tunneling Microscopy Current
Stephen R. McMillan1,2, Nicholas J. Harmon3 and Michael E. Flatté1,2,4;
1University of Iowa, United States; 2The University of Chicago, United States; 3University of Evansville, United States; 4Eindhoven University of Technology, Netherlands

A detailed understanding of two-level quantum systems in complex environments is necessary for the development of quantum information and sensing applications [1,2]. Individual or small clusters of dopants with remarkably long coherence times are addressable via scanning tunneling microscopy (STM) and the exchange interaction between dopants can be measured [3-6]. Through the use of localized magnetic contacts, for instance a spin-polarized STM, the correlations between the dopant spin state and the magnetization of the tip yields insight into the coherent dynamics at the addressed site. We propose a method to dynamically probe the spin-dependent properties of a spin-1/2 dopant exchange coupled to a charge-stable spin-1/2 state in the presence of a milliTesla dc transverse magnetic field embedded in a weakly conducting host. Calculations of the magnetoresistance through the mediating dopant rely on a stochastic Liouville approach where the density matrix of the two-dopant system is tracked and a steady state solution is found. The MR in these systems provides signatures of the exchange interaction, hyperfine coupling, spin decoherence, and g-factor. An extension of the spin-1/2 case to a system with spin-1 is applicable to systems like the divacancy defect in silicon carbide.

We acknowledge support from DOE BES through Grant No. DE-SC0016447.


4:00 PM *MQ01.02.03
Quantum Coherent Single-Spin Dynamical Effects in DC Electrical Transport
Michael E. Flatté; University of Iowa, United States

A broad range of quantum-coherent spin centers have been identified in optically-accessible materials, especially including nitrogen-vacancy, silicon-vacancy, and germanium-vacancy centers in diamond, divacancies and transition-metal dopants in several polytypes of silicon carbide, and even spin centers in two-dimensional materials such as hexagonal boron nitride. Some of these materials, however, allow good electrical transport (such as silicon carbide), and other spin centers have been found in materials that cannot be easily probed optically. Some of these, such as dopants in silicon, have been probed using electron spin resonance techniques that require an rf field. Recently, however, it has become clear that dc techniques can electrically manipulate and measure the spin orientations of spin centers through the establishment and release of electrical transport bottlenecks. The key requirements of these approaches are a spin-polarized electrical contact and a small transverse magnetic field, however no ac field of any type is required. Some examples of the potential for this approach will be described, including the proposal to measure, at room temperature, the micro-eV-scale exchange and hyperfine fields between spins in a semiconductor using dc magnetoresistance, and the room-temperature observation of hyperfine interactions in a trap at the Si-SiOx interface in a MOSFET.

Aspects of this work were supported by DOE DE-SC0016447 and HDTRA1-18-1-0012.
Electrically Detected Electron Nuclear Double Resonance in a Transistor

Brian R. Manning¹, Ryan J. Waskiewicz¹, Duane J. McCrory² and Patrick M. Lenahan¹; ¹The Pennsylvania State University, United States; ²Keysight Technologies, United States

Electron paramagnetic resonance (EPR) techniques offer unrivaled analytical power in the identification of the physical and chemical nature of point defects in semiconductors and insulators. However, the sensitivity of conventional EPR is about 10 billion defects. This number greatly exceeds the number of performance-limiting defects in technologically relevant solid-state devices. Electrically detected magnetic resonance (EDMR) is at least 7 orders of magnitude more sensitive than its parent technique, EPR [1,2]. This enormous enhancement in sensitivity makes EDMR a powerful tool in the investigation of point defects in nano-scale electronic device. This sensitivity also makes EDMR potentially useful in various spintronic applications. Although EDMR is a powerful tool, its analytical power could be greatly enhanced with the addition of a nuclear magnetic resonance (NMR) component. The conventional double resonance technique known as electron nuclear double resonance (ENDOR) combines EPR and NMR and has the analytical power to provide detailed atomic scale information about paramagnetic defects in semiconductors and insulators [3]. The absolute sensitivity of conventional ENDOR is grossly inferior that of classical EPR, making the technique essentially impossible for studies of nano-scale electronic devices. This also makes the exploitation of long nuclear spin decoherence times quite difficult via classical ENDOR. We show that, by utilizing EDMR detection, ENDOR sensitivity may be enhanced by many orders of magnitude, opening possibilities for electrically detected ENDOR (EDENDOR) to contribute substantially to solid-state device physics, possibly including some spintronic applications. We have developed a sensitive EDENDOR spectrometer and demonstrate that it can provide reasonably high signal to noise spectra involving ^14N nuclear spins interacting with deep level defects in the base-emitter junction of a fully processed 4H-SiC bipolar junction transistor at room temperature. The EDENDOR spectrometer utilizes a single loop non-resonant antenna that is placed within a TE102 microwave cavity adjacent to the transistor to generate the NMR oscillating magnetic field. A frequency sweep is supplied to the NMR coil loop via an arbitrary waveform generator (AWG). To maintain constant power to the loop, a proportional-integral-derivative (PID) controller has been used to feedback a real time measurement of the power through the loop and adjust the output. This suppresses the non-resonant background which could otherwise obscure the EDENDOR response. To the best of our knowledge this is the first time ENDOR measurements have ever been made within a fully processed transistor.


Charge State Control of Single Spins in Semiconductor Devices

Christopher P. Anderson, Alexandre Bourassa and David D. Awschalom; University of Chicago, United States

Silicon Carbide (SiC) has recently established itself as a viable host for defect-based spin qubits, providing a diamond-like host for spins with silicon-like fabrication and doping control. In particular, neutral divacancies (VV⁰) in SiC have shown exceptional spin coherence and a viable telecom spin-photon interface for entanglement schemes. Here, we isolate for the first time single VV⁰ in functioning, doped, commercial semiconductor p-i-n devices and use the diode to control and tune these defects. In this talk, we focus in particular on the control of the charge state of the single spins in the device.

Controlling charge dynamics has allowed for key demonstrations in quantum sensing and communications. Additionally, the charge states of single spins can be utilized in spin-to-charge conversion, enabling single-shot optical readout and even electrical readout of single spins. However, the understanding and control of charge for single spins in SiC remains unexplored.

In this work, integration of single spins into the p-i-n device enables a demonstration of deterministic charge state
control of single VV$^0$ spin defects, and a careful study the defect’s photo-dynamics. These results allow for the stabilization of the desired charge state of the defect and reduce ionization and spectral hopping of the orbital structure. Furthermore, integration into the device allows for electrically gating of the single photon emission, and control of formation of these defects using fermi-level engineering.

Leveraging of the mature SiC semiconductor device technology creates exciting opportunities for electrical control, manipulation and readout of both the spin and charge degrees of freedom in these quantum emitters.

Related publication:

SESSION MQ01.03/EL05.07: Joint Session: Quantum Effects
Session Chairs: James Haigh and Patrick Maletinsky
Tuesday Afternoon, December 3, 2019
Hynes, Level 1, Room 107

1:30 PM *MQ01.03.01/EL05.07.01
The Tin Vacancy Center in Diamond—An Interesting New Qubit Candidate? Christoph Becher; Saarland University, Germany

Quantum bits based on soli-state spins are promising and potentially scalable systems for the implementation of quantum technologies ranging from quantum information processing to quantum-enhanced sensing and metrology. Ideally, they combine individually addressable spins with very long coherence times, optical emission spectra with narrow homogeneous and inhomogeneous broadenings and bright single-photon emission. In this respect, impurity-vacancy color centers in diamond based on group-IV elements (SiV, GeV, SnV, PbV) have emerged as interesting systems promising to combine all desired favorable properties.

Both the SiV and the GeV center feature superior spectral properties, i.e. at liquid helium temperatures (4K), they exhibit a narrow zero phonon line (ZPL) with a four-line fine structure and close to lifetime-limited linewidths [1,2]. Furthermore, both allow for fast all-optical addressing and control of their spin states [3,4]. However, at temperatures around 4K both color centers exhibit spin coherence times (T2$^*$) of only a few ten nanoseconds due to phonon-induced decoherence processes [3,4] and the SiV reaches millisecond spin coherence times only at millikelvin temperatures and in pure samples [3,5]. A potential resort are vacancy defects with a heavier group-IV impurity atom, such as SnV and PbV centers, featuring a larger ground state splitting and thus less susceptibility to phonon-induced decoherence.

Here, we report on spectroscopy of SnV centers [6,7,8] where we find two charge states, i.e. SnV(-) and SnV(0), which both show promising optical properties. The SnV(-) features a ground and excited state splitting considerably larger (850 GHz and 3000 GHz, respectively) as compared to the SiV center, potentially enabling long spin coherence times even at liquid He temperatures. This defect is a bright single photon emitter, showing a narrow inhomogeneous distribution of zero phonon lines in a high-temperature annealed sample [6] and truly lifetime-limited transition linewidths down to 20 MHz. Furthermore, we determine the charge transition from the negative to the neutral charge state as a function of the excitation wavelength and find it to coincide well with theoretical predictions [9]. For the SnV(0) center we find emission lines that again agree well with theoretical calculations [10]. The neutral charge state is particularly interesting due to its potentially long electron spin coherence times.

Development of Scalable Technology for NV-Magnetometry and Photonics on Single Crystalline Diamond

Christian Giese¹, Patricia Quellmalz¹, Helge Gehring², Wolfram Pernice² and Christoph E. Nebel¹; ¹Fraunhofer IAF, Germany; ²University Muenster, Germany

The unique properties of the negatively charged nitrogen vacancy color center (NV⁻) in single crystalline diamond have been explored for developing new types of devices for photonics and scanning probe magnetometers with high sensitivity and spatial resolution over more than a decade. This growing field is in need of thin, free-standing ultraclean diamond devices with complex geometries. The fabrication of such structures in large numbers will be the topic of this presentation.

Free-standing diamond devices as photonic crystals or NV-scanning-probe heads are typically manufactured from diamond membranes of below 30µm thickness. The latter are expensive and available only in small numbers which makes a scaling of the production very challenging. In addition to this, the homogeneity in thickness below micron level is crucial for many applications and remains practically unachievable via polishing on large surfaces.

An alternative method based on so-called faraday-cage-angled-etch (FCAE) pioneered at the group of prof. Loncar at Harvard university is based on the capability to create free-standing diamond devices via dry chemical underetching. We have employed FCAE to create mechanical and optical components and will report on the characteristics of the devices investigated via SEM as well as optical and mechanical metrology.

References


Rapid, High-Resolution Magnetic Microscopy of Single Magnetic Microbeads

Julia M. McCoey, Robert W. de Gille, Babak Nasr, Jean-Philippe Tetienne, Liam T. Hall, David A. Simpson and Lloyd Hollenberg; University of Melbourne, Australia

Magnetic microparticles are used in a variety of research applications including cell sorting, targeted drug delivery and optical force traction microscopy. The magnetic properties of such particles can be customized for specific applications with the uniformity of individual magnetic microparticles having a significant bearing on their function. Prior to the study discussed here, most magnetic characterization techniques have quantified the magnetic properties from large bead ensembles. As such, there is a significant demand for magnetic imaging techniques to evaluate and visualize the magnetic fields from single beads. New insights into the magnetic uniformity, anisotropy, and alignment of magnetic domains can be found through measurements of the magnetic properties of single beads. Here, magnetic microscopy based on the nitrogen-vacancy centre in diamond is applied to image and characterize individual magnetic beads with varying magnetic and structural properties: ferromagnetic and superparamagnetic/paramagnetic, shell (coated with magnetic material), and solid (magnetic material dispersed in matrix). The magnetic microscopy described here probes both the fluctuating moments of the beads studied as well as their static magnetic moments. The single-bead magnetic images identify irregularities in the magnetic profiles from individual bead populations. Magnetic simulations account for the varying magnetic profiles and allow to infer the magnetization of individual beads. Additionally, this work shows that the imaging technique can be adapted to achieve illumination-free tracking of magnetic beads, opening the possibility of tracking cell movements and mechanics in photosensitive contexts.

2. Veiseh, O., Gunn, J. W. & Zhang, M. Design and fabrication of magnetic nanoparticles for targeted drug delivery

2:30 PM *MQ01.03.04/EL05.07.04
Quantum Sensing of Atomically Thin Magnets Patrick Maletinsky; Basel University, Switzerland

The recent discovery of long-range magnetic order in atomically thin `van der Waals’ (vdW) crystals has attracted significant attention due to their fundamental and technological interest, including predictions of exotic magnetic phases and unique opportunities to control magnetism at the atomic scale. I will present recent experiments, where we employ a single-spin-based quantum sensing technology for quantitative, nanoscale probing of atomically thin vdW magnets. Specifically, I will describe experiments, where we employ a diamond-based, scanning probe quantum sensor to address magnetism in the prototypical vdW magnet CrI3, down to the level of atomic monolayers. Our approach enabled nanoscale imaging of magnetic domains, quantitative determination of CrI3’s layer-dependent magnetization, and revealed a delicate interplay between magnetic and crystalline order in CrI3. Next to addressing fundamental open questions in the nanomagnetism of atomically thin CrI3, our results yield attractive perspectives for future probing of dynamical properties of two-dimensional spin systems using single spin quantum sensors. Amongst other things, these could yield experimental evidence for the still elusive quantum spin liquid, which is believed to occur in monolayers of certain vdW compounds.

3:00 PM BREAK

3:30 PM *MQ01.03.05/EL05.07.05
Imaging the Domain Pattern of In-Plane Layered Antiferromagnets using Diamond Magnetometry Martin S. Wornle, Pol Welter and Christian Degen; ETH Zurich, Switzerland

Antiferromagnetic materials are promising candidates for new memory devices with fast electrical writing and readout capabilities. Imaging the magnetic state of antiferromagnets on the sub-micrometer scale, however, is challenging because these materials do not exhibit a macroscopic magnetization.

In this talk, we will discuss the application of scanning diamond magnetometry for investigating the microscopic domain structure of in-plane layered antiferromagnets, like tetragonal CuMnAs. After introducing the basics of the technique, we will discuss models and concepts for analyzing the magnetic stray field emanating from the antiferromagnetic domains. We will further show that current pulses lead to changes in the domain pattern and analyze these changes as a function of the current amplitude and direction.

4:00 PM MQ01.03.06/EL05.07.06
Metrology Driven Development of Point Defect Synthesis and Localization Nazar Delegan1, Samuel J. Whiteley2,3, Edward Bielejec1, David D. Awschalom2,3 and Joseph F. Heremans1,2; 1Argonne National Laboratory, United States; 2The University of Chicago, United States; 3Sandia National Laboratories, United States

The negative nitrogen-vacancy (NV-) defect in diamond has quantum spin properties observable from cryogenic temperatures to ~1000 K. Parallel to this, SiC based divacancy (VV) complexes photoluminesce in the telecom infrared range, extending their technological applicability. Both of these spin-based quantum sensors are known to be responsive to changes in local strain, electric, magnetic, and thermal fields. Building on this foundation, we discuss recent advances of defect 3D localization in the context of improving and controlling their spatial resolution and crystalline environment. This progress is fueled by nanoimplantation and nanoscale strain-sensitive X-ray imaging techniques. The insights provided serve to better understand the defect’s lattice surroundings, guide future synthesis efforts, improve the creation efficiency, and advance the goal maintaining coherence times of the spin states.

4:15 PM MQ01.03.07/EL05.07.07
First Principles Discovery and Understanding of Color Centers in Diamond for Quantum Information Science Isaac Harris1,2, Christopher J. Ciccarino2, Johannes Flick2, Dirk R. Englund1 and Prineha Narang2; 1Massachusetts Institute of Technology, United States; 2Harvard University, United States

Defect centers in diamond are promising candidates for applications such as quantum sensing, networking and computation. Previous work has experimentally identified several defects such as the NV– and group IV related defects. However none of these color centers have shown the ideal combination of optical transitions, coherence times, and ease of fabrication and integration, motivating an ab initio search of new color centers in diamond.

Towards this goal, we present first principles calculations of a new class of emitters, the group III-vacancies, which are theoretically shown to have a promising ground state structure for quantum applications, a noise insensitive optical transition, and are thermodynamically favored in intrinsic diamond. The ground state fine structure, as well as the excited electronic structure will be discussed in this talk. Further, we will show the electron-phonon coupling parameter calculations to determine the Jahn-Teller distortion, as well as the phonon sideband of the optical emission. Finally, we will discuss how the ab initio results compare with experimental quantities such as the ground state spin structure and optical emission properties.

4:30 PM *MQ01.03.08/EL05.07.08
Understanding and Mitigating Quantum Decoherence of Nitrogen-Vacancy Center Spins for High-Spatial Resolution Quantum Sensing Ania Bleszynski Jayich1 and Dolev Bluvstein2; 1University of California, Santa Barbara, United States; 2Harvard University, United States

The nitrogen vacancy (NV) center defect in diamond is emerging as a powerful quantum-enabled technology, in particular in the realm of sensing and imaging with ultra-high spatial resolution. The performance of these solid-state quantum sensors is highly dependent on their quantum coherence and charge-state stability, which are sensitive to their local environment. Surfaces are an important part of the defect's environment, in particular when targeting high spatial resolution sensing, which necessitates close proximity between the sensor and target. To identify and mitigate the deleterious environmental effects, I discuss several materials-based and quantum-control approaches. Specifically, I discuss the formation of highly-coherent NV centers via a gentle, bottom-up method of nitrogen delta-doping during chemical vapor deposition growth of diamond thin films followed by low energy (~ 150 keV) electron irradiation. I present measurements of the density and coherence properties of the NV centers formed in this way as a function of growth and irradiation parameters [1]. In the second part of the talk, I discuss the spin and charge state properties of shallow NV centers, and introduce techniques to mitigate decoherence due to paramagnetic surface spins [2] as well as charge state instabilities near surfaces [3]. These approaches to improved sensors will ultimately enable truly nanoscale spatial resolution imaging of magnetic, electric, and thermal fields in a variety of condensed matter and biological systems.


Ultrastrong Magnon-Magnon Coupling in YFeO$_3$ in Magnetic Fields up to 30 T
Takuma Makihara$^1$, Gary T. Noe$^1$, Xinwei Li$^1$, Kenji Hayashida$^1$, Nicolas Marquez$^1$, Xiaoxuan Ma$^2$, Zuanming Jin$^2$, Wei Ren$^2$, Guohong Ma$^2$, Shixun Cao$^2$, Motoaki Bamba$^{3,4}$ and Junichiro Kono$^{1,1}$; $^1$Rice University, United States; $^2$Shanghai University, China; $^3$Kyoto University, Japan; $^4$Japan Science and Technology Agency, Japan

There is currently much interest in studying quantum optical phenomena in solid state systems to realize large-scale quantum information processing applications. In addition to scalability, solid state systems can be intrinsically advantageous to atomic systems due to the vastly larger number of electrons and many-body interactions that lead to cooperative enhancement of quantum optical phenomena. One example is Dicke cooperativity, where a system of $N$ dipoles coupled to an optical field experience an enhancement of light-matter coupling strength by a factor of $N^{1/2}$ [1]. Thus, solid state systems are particularly well-suited for studying exotic quantum optical phenomena that occur in regimes of light-matter coupling that are inaccessible to atomic systems, such as the ultrastrong coupling regime [2].

We recently demonstrated the extension of ultrastrong coupling to matter-matter coupling. Namely, we observed Dicke cooperativity between Er$^{3+}$ electron paramagnetic resonance and a vacuum magnon field of Fe$^{3+}$ spins in Y$^{3+}$ doped ErFeO$_3$ samples, and the collectively enhanced coupling strength was in the ultrastrong coupling regime [3]. In this work, we further demonstrate matter-matter ultrastrong coupling between two magnon modes in YFeO$_3$. This rare earth orthoferrite is a canted antiferromagnet due to its two antiparallel spin sublattices slightly tilting towards each other, yielding a weak ferromagnetic moment. There are two distinct magnon modes in YFeO$_3$, referred to as the quasi-ferromagnetic (qFM) mode and the quasi-antiferromagnetic (qAFM) mode, corresponding to coherent spin precessions with terahertz (THz) frequencies. These magnons can be excited by magnetic dipolar interactions between the Fe$^{3+}$ spins and a THz pulse, after which they precess at their Larmor frequency [4]. We studied the magnon frequency as a function of applied magnetic field strength and the direction of the magnetic field, i.e., the angle with respect to the weak ferromagnetic moment. When the applied magnetic field strength was tuned between 0 T and 30 T and the direction was not aligned with one of the crystallographic axes, anticrossing between the qFM and qAFM magnon frequencies was observed, demonstrating ultrastrong magnon-magnon coupling.

THz time-domain spectroscopy studies of YFeO$_3$ up to 30 T were performed using our tabletop pulsed magnet that uniquely marries strong magnetic fields and diverse optical spectroscopies [5]. We characterized magnons in YFeO$_3$ at different angles between the applied magnetic field and the weak ferromagnetic moment, which points along the $c$-axis. Specifically, we measured transmitted THz waveforms for five different samples of YFeO$_3$ cut such that the magnetic field was directed in the $b$-$c$ plane and at an angle of 0, 20, 40, 60, and 90 degrees with respect to the $c$-axis. We observed clear anticrossing between the qFM and qAFM magnon frequencies as we tuned the magnetic field between 0 T and 30 T in samples with relative angles of 20, 40, and 60 degrees.

Using the Herrmann model, we calculated the qFM and qAFM magnon frequencies for our experimental geometry [6]. The applied magnetic field breaks the symmetries of the two modes, and the mixing of these modes causes anticrossing. We found excellent agreement between experimentally measured and calculated frequencies. Most importantly, the vacuum Rabi splitting was found to be a sizeable fraction of the resonance frequency, showing that the qFM and qAFM magnon-magnon coupling strength is in the ultrastrong coupling regime.


8:30 AM *MQ01.04.02
Enhancing the Interaction of Magnons and Optical Photons
James A. Haigh; Hitachi Cambridge Laboratory, United Kingdom

To build hybrid quantum interfaces based on magnons, it will be important to optimise the coupling strength to both optical and microwave fields. While magnons can be routinely coupled to microwave photons in a coherent way, there is still a long way to go to achieve similarly strong coupling in the optical domain. This is because the strength
of magneto-optical interactions through the Faraday effect are typically very weak. In order to strengthen the magneto-optical interaction, the magnetic material can be embedded in a high quality-factor optical cavity. Such devices have been used to demonstrate that the scattering of optical photons with magnons can be significantly enhanced [1]. I will present our measurements on resonant magnon scattering in yttrium iron garnet, and discuss whether the limit of strong coupling can be achieved. In addition, optimizing the optical coupling requires reducing the volume of magnetic material. Although this is in conflict with the requirements for strong microwave coupling, we have shown the coupling strength can be maintained through the use of low-impedance microwave resonators [2].


9:00 AM MQ01.04.03
Phono-Magnetic Analogs to Opto-Magnetic Effects Dominik M. Juraschek1,2, Sebastian Stepanow2, Prineha Narang1 and Nicola Spaldin2; 1Harvard University, United States; 2ETH Zürich, Switzerland

Over the past few years, it has become possible to control the magnetic order of materials on timescales smaller than a picosecond, promising application in advanced data storage and data processing in spintronic devices. One ingredient is the coherent excitation of spin waves, which can be achieved by driving the spins with the magnetic or electric field components of an ultrashort light pulse. The basic interaction of light with a magnetic material is described by the opto-magnetic effects, of which the most prominent examples are the inverse Faraday and inverse Cotton-Mouton effects. There, the irradiated light acts as an effective magnetic field on the spins of the magnetic ions in the material, and coherent collective precession of the spins is induced via an impulsive stimulated Raman scattering mechanism [1,2].

Here, we present an alternative route of exciting coherent spin waves by coupling the magnetic degrees of freedom to the crystal lattice. We introduce the phenomenology of the analog magneto-phononic and phono-magnetic effects, in which coherently excited vibrational quanta take the place of the light quanta. Here, the coherent lattice vibrations couple to the magnetic order through the spin-phonon coupling, and the underlying mechanism is ionic Raman scattering, which had been proposed already half a century ago, and has only been demonstrated within this decade in the context of nonlinear phononics. The mechanism is less dissipative and reduces parasitic electronic effects compared to impulsive stimulated Raman scattering due to the lower energy of the excitation at mid-infrared wavelengths compared to visible light. Using density functional theory calculations in combination with phenomenological modeling for the paradigm antiferromagnet nickel oxide (NiO), we show that the phono-magnetic effects can potentially overcome the efficiency of the established opto-magnetic effects [3].


9:15 AM MQ01.04.04
Solid-State Room-Temperature Masers—A Platform for Macroscopic Dicke States Jonathan Breeze1, Enrico Salvadori2, Juna Sathian3, Neil Alford1 and Christopher W. Kay3,4; 1Imperial College London, United Kingdom; 2University of Turin, Italy; 3University of Saarland, Germany; 4University College London, United Kingdom

The solid-state maser, invented in the 1950s, had a much less impressive career than its younger sibling the laser, mainly due to its dependence on cryogenic refrigeration and high-vacuum systems. Despite this, masers found niche application in deep-space communications and radio astronomy due to their unparalleled performance as low-noise amplifiers and oscillators.

In 2012, the first room-temperature solid-state maser was demonstrated, employing an high-Q cavity coupled ensemble of inverted triplet states in photo-excited pentacene molecules doped into a p-terphenyl host [1].

Since then, this new class of maser has been dramatically miniaturized [2], characterized on nanosecond timescales
and shown to exhibit Rabi oscillations and normal-mode splitting, hallmarks of the strong-coupling regime of cavity quantum electrodynamics [4]. Unfortunately, the $p$-terphenyl host is volatile, has very poor thermal properties and unfavourable triplet sublevel decay rates – so that only pulsed operation lasting less than a millisecond has been observed to date. Alternative inorganic materials containing spin-polarizable defects such as diamond nitrogen-vacancy (NV) centres and [5,6] and vacancies in silicon carbide [7] have been proposed due to their slow spin-lattice relaxation and spin dephasing rates. These materials have the additional advantage of excellent thermal and mechanical properties.

In this talk I will discuss the development of the organic pentacene solid-state room-temperature maser and how the quest for continuous operation naturally led towards diamond and nitrogen-vacancy centres. I will report on the recently reported continuous-wave room-temperature maser based on optically pumped charged nitrogen-vacancy (NV) defect centres in diamond [8]. I will also discuss prospects for the macroscopic quantum (Dicke) states and multipartite entanglement supported by masers [4,9] and the immediate challenges.

magnon density of states, magnon spin diffusion length, and magnon-phonon coupling. These properties are central to the design and fabrication of future generations of quantum coherent devices, and will help to guide the development of this emerging class of highly coherent magnetic materials.

10:30 AM *MQ01.05.02
Quantum-Enhanced Sensing in Magnonics with a Superconducting Qubit Dany Lachance-Quirion1, Samuel P. Wolski1, Yutaka Tabuchi1, Shingo Kono2, Koji Usami1 and Yasunobu Nakamura1,2; 1The University of Tokyo, Japan; 2RIKEN, Japan

The quantum regime of magnonics has been recently explored thanks to the strong and coherent interaction engineered between a superconducting qubit and the uniform magnetostatic mode, or Kittel mode, of a spherical ferrimagnetic crystal of yttrium iron garnet (YIG) [1-4]. With this architecture of quantum magnonics, single quanta of collective spin excitations, called magnons, have been resolved by using the qubit as a quantum sensor when the hybrid system reaches the strong dispersive regime [3, 4]. Here, we use this strong dispersive interaction to demonstrate novel protocols for quantum-enhanced sensing of magnons in a ferromagnetic crystal. First, we demonstrate a magnon detection sensitivity of about $10^{-3}$ magnons/$\sqrt{\text{Hz}}$ by using a simple quantum sensing protocol that relies on the dephasing of the qubit from the presence of magnons in the ferromagnetic crystal. In a second experiment, we entangle the Kittel mode with the qubit through a conditional excitation of the qubit, which we use to demonstrate the single shot detection of a single magnon with a detection efficiency of about 69%. This demonstration brings the equivalent of the single photon detector to the field of magnonics. Furthermore, using this conditional qubit excitation, we can perform tomography measurements of the vacuum and coherent states of the Kittel mode and thereby study the dynamics of magnons in the quantum regime. These measurements have enabled us to confirm the absence of a significant pure dephasing mechanism for the Kittel mode of YIG in the quantum regime. Finally, we discuss our progress towards preparing and characterizing quantum states of magnons, as well as our investigation regarding the origin of losses of the Kittel mode in the quantum regime [2, 5].


11:00 AM MQ01.05.03
Fringe Fields and Spin Waves in V[TCNE]$_{x}$ Cylindrical Disks Denis Candido1,2 and Michael E. Flatté1,2,3; 1University of Iowa, United States; 2University of Chicago, United States; 3Eindhoven University of Technology, Netherlands

Through the application of a rf magnetic field in ferrimagnetic materials it becomes possible to create magnetostatic spin waves [1,2]. These collective excitations have been recently getting attention due to their applicability in both devices and fundamental research, which stems from the their long spin lifetimes and absence of ohmic losses. In this work we obtain the magnetostatic resonant modes of a ferrimagnetic V[TCNE]$_{x}$ disk [3] on top of a diamond substrate. Most importantly, we calculate analytically the spectrum, the fringe field and the magnetization obtained through the pinning condition at both top and bottom disk surfaces. In addition, we also perform the relaxation of the pinning condition and analyze its consequences in the spectrum, fringe fields and magnetization. We present our results for two different magnetic field directions: in plane and out of plane of the disk. The material is based on work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Award Number DE-SC0019250.


11:15 AM MQ01.05.04
Dispersion Relations and Linewidths of 1D and 2D Magnonic Crystals of V[TCNE]$_{x=2}$ Kwangyul Hu$^1$ and Michael E. Flatté$^{1,2,3}$; $^1$University of Iowa, United States; $^2$University of Chicago, United States; $^3$Eindhoven University of Technology, Netherlands

The ferromagnet yttrium iron garnet (YIG) has attracted considerable attention for studying quantum magnonics for the advantages such as long spin lifetime [1], narrow ferromagnetic linewidth (FMR), low Gilbert damping constant [2] and high Q factor [3]. However, a specific superlattice substrate gadolinium gallium garnet (GGG) is required to fabricate high quality YIG thin films [4], preventing the broad application of YIG such as with silicon. Recent studies have revealed that an organic based ferrimagnet, V[TCNE]$_{x=2}$ is an excellent alternative to YIG. High quality V[TCNE]$_{x=2}$ can be grown on various flexible substrates such as glass, quartz and Si wafer using low temperature CVD [5]. This suggests that V[TCNE]$_{x=2}$ is an attractive magnonic media with the same advantages as YIG [6-8].

Here, we present the dispersion relations and linewidths of quasi one-dimensional and two-dimensional periodic magnonic crystals of V[TCNE]$_{x=2}$ calculated by using Landau-Lifshitz-Gilbert (LLG) formalism [9]. For the one-dimensional magnonic crystals, periodic layers of two alternating materials is studied. For the two-dimensional magnonic crystals, we considered infinitely long cylinders embedded in a host material forming a square lattice periodic structure. In both cases, V[TCNE]$_{x=2}$ combined with well known ferromagnets such as YIG and cobalt are considered. We focus on unit cells with a lattice constant of a=100nm in an external dipolar field of $H_0\mu_0=0.1T$. Our results can be extended to investigate other properties of V[TCNE]$_{x=2}$ such as spin wave propagation and their applications.

We acknowledge support from NSF EFRI NewLAW under Award No. EFMA-1741666.


11:30 AM MQ01.05.05
Photodriven Quantum Teleportation of an Electron Spin State in a Covalent Donor-Acceptor-Radical System
Michael R. Wasielewski, Brandon Rugg, Matthew D. Krzyaniak, Brian T. Phelan, Mark Ratner and Ryan Young; Northwestern University, United States

Quantum teleportation is essential to the development of many aspects of quantum information science (QIS). Toward this goal, we demonstrate electron spin state teleportation in an ensemble of covalent organic donor-acceptor-stable radical (D-A-R) molecules. Following preparation of a specific electron spin state on R in a magnetic field using a microwave pulse, photoexcitation of A results in the formation of an entangled electron spin pair D\textsuperscript{+}-A\textsuperscript{-}. The spontaneous ultrafast chemical reaction D\textsuperscript{+}-A\textsuperscript{-} \rightarrow D\textsuperscript{+}-A\textsuperscript{-}R constitutes the Bell state measurement step necessary to carry out spin state teleportation. Quantum state tomography of the R and D\textsuperscript{+} spin states using pulse electron paramagnetic resonance spectroscopy shows that the spin state of R is teleported to D\textsuperscript{+} with high fidelity. This result affords the possibility that chemical synthesis can create complex nanostructures for QIS applications.

11:45 AM MQ01.05.06
Low Damping Ferromagnetic Resonance in Electron-Beam Patterned, High-Q Vanadium Tetracyanoethylene Magnon Cavities
Andrew J. Franson\textsuperscript{1}, Na Zhu\textsuperscript{2}, Seth Kurfman\textsuperscript{1}, Michael Chilcote\textsuperscript{1}, Denis Candido\textsuperscript{1}, Kristen Buchanan\textsuperscript{4}, Michael E. Flatté\textsuperscript{3}, Hong Tang\textsuperscript{2} and Ezekiel Johnston-Halperin\textsuperscript{1}; \textsuperscript{1}The Ohio State
On-chip integration of patterned, low-loss magnetic materials and magnon cavities into microwave devices and circuits presents many challenges due to the specific conditions that are required to grow ferrite materials, driving the need for flip-chip and other indirect fabrication techniques. The low-loss ($\alpha = (3.98 \pm 0.22) \times 10^{-5}$), room-temperature ferrimagnetic coordination compound vanadium tetracyanoethylene ($V[TCNE]_x$) is a promising new material for these applications that is potentially compatible with semiconductor processing. Here we present the deposition, patterning, and characterization of $V[TCNE]_x$ thin films with lateral dimensions ranging from 1 micron to several millimeters. We employ electron-beam lithography and liftoff using an aluminum encapsulated poly(methyl methacrylate), poly(methyl methacrylate-methacrylic acid) copolymer bilayer (PMMA/P(MMA-MAA)) on sapphire and silicon. This process can be trivially extended to other common semiconductor substrates. Films patterned via this method maintain low-loss characteristics down to 25 microns with only a factor of 2 increase down to 5 microns. A rich structure of thickness and radial confined spin wave modes reveals the quality of the patterned films. Further fitting, simulation, and analytic analysis providing an exchange constant, $A_{ex} = (2.2 \pm 0.5) \times 10^{-15} \text{ J/m}$, as well as insights into the mode character and surface spin pinning. Below a micron, the deposition is non-conformal which leads to interesting and potentially useful changes in morphology. This work establishes the versatility of $V[TCNE]_x$ for applications requiring highly coherent magnetic excitations ranging from microwave communication to quantum information.

SESSION MQ01.06/MQ02.06/MQ03.06: Panel Discussion: Quantum Materials
Session Chairs: Jeffrey McCallum and Christopher Richardson
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 202

3:30 PM PANEL DISCUSSION: QUANTUM MATERIALS

SESSION MQ01.07: Magnetic Materials
Session Chair: Evelyn Hu
Thursday Afternoon, December 5, 2019
Hynes, Level 2, Room 202

1:30 PM *MQ01.07.01
Noncollinear Magnetism in Complex Oxide Superlattices Jennifer E. Hoffman and Jason D. Hoffman: Harvard University, United States

Noncollinear magnetic textures give rise to interesting charge and spin transport properties, and allow for control of magnetism using small electric currents. While these textures have been observed in a number of bulk materials and in thin films, realizing non-collinear magnetism in heterostructures presents new avenues to control their properties using tailored interfaces and gate electric fields. We have discovered noncollinear magnetism in superlattices comprised of two metallic perovskites, La$_2$/3Sr$_1$/3MnO$_3$ (LSMO) and LaNiO$_3$ (LNO). The superlattices are synthesized using oxide molecular beam epitaxy and characterized with a variety of means, including x-ray and neutron scattering. We find that the angle between the magnetization of the LSMO layers varies in an oscillatory manner with the thickness of the intervening LNO. We demonstrate a memory device in one such superlattice, where the magnetic state of the noncollinear magnetism is reversibly switched between different orientations using a small magnetic field and read out in real time using a combination of the anomalous Nernst effect and anisotropic magnetoresistance measurements. Finally, we discuss the growth and characterization of additional complex-oxide-based systems and devices, such as LaVO$_3$.

2:00 PM MQ01.07.02
Electric Field Control of the Magnetic and Associated Metal-Insulator Transitions in Iridates
Juan Ignacio Beltrán1,2, Andrea Peralta2, Javier Tornos2, Fernando Gallego1, Carlos León2, Jacobo Santamaría2 and Carmen Muñoz2; 1Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, ICMM (CSIC), Spain; 2Universidad Complutense de Madrid, Spain

Iridates are of great importance to investigate the realization of exotic quantum phenomena generated by non-negligible spin-orbit coupling. The strontium-based iridates, with the perovskite structure and a valence band derived from the 5d orbitals of Ir, exhibit electronic and magnetic ground states resulting from the subtle interplay of spin-orbit coupling, electron-electron correlation and dimensionality. Therefore, they are highly susceptible to small changes in the relative strength of the different interactions. In the Ruddlesden-Popper series Srm+1Ir2O3m+1 (m=1,2, … ∞), the two-dimensional compounds, m = 1 and 2, present an antiferromagnetic (AF) Mott insulating ground state, with canted planar and out of plane AF orderings, respectively. Conversely, the three-dimensional SrIrO3 is semi-metallic, non-magnetic and shows non-trivial topological features. Here, based on a multi-fold approach relying on magneto-transport measurements and first-principles calculations, we demonstrate the reversible tuning of the magnetic and electric ground state of thin SrIrO3 films by external electric fields. Ultra-thin epitaxial SrIrO3 films grown on SrTiO3 exhibit thickness dependent metal-insulator and associated magnetic transitions. Its ground state evolves from a magnetic insulator, for 1 or 2 unit cell (u.c.), to a paramagnetic semi-metal, for n > 3 u.c. thicknesses. Moreover, for the thicker metal films, an electric field perpendicular to the film drives a metal-insulator and a simultaneous paramagnetic to weak ferromagnetic transition. We explore the transitions in ultra-thin layers of SrIrO3, 3 < n < 8 u.c., by electric double layer techniques, which employ ionic liquid as gate dielectric, and prove that the metal-insulator and magnetic transitions are reversible. In addition, we show that the weak ferromagnetic behavior induced by the electric field arises from an underlying canted AF order within the basal plane. The orbital and spin moment canting rigidly tracks the staggered rotations of the IrO6 octahedra, which results in out-of-plane ferromagnetic spin components induced by the Dzyaloshinskii–Moriya interaction. We discuss the role of the orbital magnetism and Rashba spin-orbit interaction -due to the breaking of inversion symmetry- in the stabilization of the magnetic insulator state. The electric field, via the Rashba interaction, promotes a moment reorientation of the disordered paramagnetic state, which is at the root of the metal-insulator transition. This novel behavior is a consequence of the unique character of the semi-metallic SrIrO3 ground state, it illustrates the exotic spin interactions in iridates and points to a new paradigm for device structures in which magnetic states are reversibly manipulated by electric fields.

This work was supported by the Spanish Ministerio de Ciencia e Innovación through MINECO/FEDER Grants MAT2015-66888-C3-1R and RTI2018-097895-B-C41.

Mechanistic Insights into the Superexchange-Interaction-Driven Negative Thermal Expansion in CuO
Yuanpeng Zhang1,2, Marshall McDonnell2, Stuart Calder2 and Matt Tucker2; 1National Institute of Standards and Technology, United States; 2Oak Ridge National Laboratory, United States

Thermal expansion is an important consideration in many applied fields ranging from large-scale infrastructure building to high-precision instrumentation. Starting from the discovery of isotropic negative thermal expansion (NTE) in ZrW2O8 by Sleight, et al. in 1996 [1], NTE has been an intensely studied material phenomenon. For NTE, one, two, or all three dimensions of the material shrink with increasing temperature, which is counter to both our intuition and experience. NTE is believed to be connected with various origins, such as geometrical flexibility, ferroelectricity and magnetism [2]. Such connections then provide potential routes for controlling the thermal expansion utilizing NTE materials. Specifically concerning the superexchange driven NTE, increasing of atomic distances is beneficial for reducing the on-site Coulomb repulsion (through reducing, e.g. the p-d orbital overlapping) and therefore is potentially accounting for the expanding of lattice as T decreases (i.e. NTE). However, the lattice expansion in turn tends to reduce the magnetic coupling. Therefore, it brings in an outstanding question – how the interplay between superexchange interaction and lattice expansion proceeds as T decreases. Concerning the implication for tuning NTE of superexchange systems in general sense, it is important to resolve such a question. To this aim, we revisit the superexchange involved anisotropic NTE of CuO [3].

The negative thermal expansion (NTE) in CuO is explained via electron-transfer-driven superexchange interaction. The elusive connection between the spin-lattice coupling and NTE of CuO is investigated by neutron scattering and principal strain axes analysis. The density functional theory calculations show as the temperature decreases, the
continuously increasing electron transfer accounts for enhancing the superexchange interaction along – the principal NTE direction. It is further rationalized that only when the interaction along is preferably enhanced to a certain level compared to the other competing antiferromagnetically exchange pathways can the corresponding NTE occur. Outcomes from this work have implications for controlling the thermal expansion through superexchange interaction, via, for example, optical manipulation, electrons or holes doping, etc.

References

2:30 PM *MQ01.07.04*

**Growth and Properties of Magnetic Heusler Epitaxial Thin Films**

Chris J. Palmstrom; University of California, Santa Barbara, United States

Heusler compounds have been predicted and experimentally shown to exhibit novel electronic and magnetic properties, such as half-metallic ferromagnetism, semiconducting and superconducting. The spin dependent transport across ferromagnet/semiconductor or ferromagnet/insulator interfaces depends critically on their structure and electronic properties, which include the semiconductor doping beneath the ferromagnetic contact, as well as the contact metallization. Interfacial reactions, the formation of non-magnetic interlayers, and conductivity mismatch have been attributed to low spin injection efficiency. In the case of epitaxial Fe3Ga/GaAs(001) interfaces, the interface reconstruction was found to depend on the GaAs(001) surface reconstruction and the Fe3Ga growth conditions. Co2MnSi is predicted to be half-metallic and we have demonstrated record high spin accumulation at Co2MnSi/GaAs(001) interfaces in lateral spin transport device structures and also investigated electronic structure tuning with Co2(Mn,Fe)Si/GaAs(001) heterostructures. The variation in the spin polarization in the GaAs is consistent with the Fermi level increasing in the Co2(Mn,Fe)Si films with the increase in the number of valence electrons per formula unit with the addition of Fe. This results in a sign change in the spin polarization between Co2MnSi and Co2FeSi contacts.

The magnetic damping and magnetoresistance were found to depend on the composition of Co2-xMn1+xSi films grown on MgO(001). Current-induced spin-orbit torque in Co2FeAl/Pt ultrathin bilayers have been investigated as a function of temperature. By substituting Fe for Ti, the half-Heusler CoTiSb can be controllably tuned from a semiconductor to ferromagnetic metal. We have also demonstrated, by both angle-resolved photoemission and magnetotransport measurements, Fermi level tuning of topological PtLuSb by substituting Au for Pt, which results in control of the dominant carrier type and density.

Using a combination of molecular beam epitaxy and in-situ scanning tunneling microscopy and x-ray photoelectron spectroscopy, we have investigated the surface atomic structure, the interface formation and growth mechanisms. Ab-initio theory and ex-situ transmission electron microscopy studies corroborate the Heusler/semiconductor interfacial atomic structure.

In this presentation, I will discuss the molecular beam epitaxial growth and tuning of properties of Heusler compounds with emphasis for spintronic and hybrid quantum interfaces.

3:00 PM BREAK

SESSION MQ01.08: Spin, Orbit and Topology
Session Chairs: Evelyn Hu and Ezekiel Johnston-Halperin
Thursday Afternoon, December 5, 2019
Hynes, Level 2, Room 202

3:30 PM *MQ01.08.01*

**Spin-Orbit Torque Switching of Antiferromagnet and Ferrimagnet**

Feng Pan, Cheng Song, Xianzhe Chen and Xiaofeng Zhou; Tsinghua University, China
Antiferromagnets with zero net magnetic moment, strong anti-interference and ultrafast switching speed have potential competitiveness in high-density data storage. Electrical switching of antiferromagnets is at the heart of their device application \[1,2\]. The antiferromagnetic insulator NiO and metal Mn\(_2\)Au, which is manifested electrically via spin Hall magnetoresistance in NiO/Pt bilayers \[3\] as well as a combination of anisotropic magnetoresistance and spin Hall magnetoresistance in Mn\(_2\)Au/Pt bilayers \[4\]. The antiferromagnetic moments are switched towards the current direction, different from the vertical configuration in the fieldlike torque scenario in a Mn\(_2\)Au single layer \[5\]. Electric field is used to switch the magnetic moment of Mn\(_2\)Au films grown on piezoelectric Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))\(_{0.7}\)Ti\(_{0.3}\)O\(_3\) (PMN-PT) (011) substrates. When the electric field is swept, the easy axis of Mn\(_2\)Au is switched between [100] and [0 1] directions of PMN-PT (011) at room temperature, exhibiting a butterfly-like switching feature. This feature indicates that the underlying mechanism is the electric field-induced ferroelastic strain. Such a transition of the easy axis leads to the change of threshold current for the field-like torque switching of Mn\(_2\)Au \[6\]. Recently, we also realize a bulk spin-orbit torque in ferrimagnetic CoTb, and provides a possible mechanism to explain this unusual phenomenon. Electrical switching of antiferromagnetic and ferrimagnetic moments pave the way for all-electrical writing and readout in antiferromagnetic spintronics.

I am grateful to the contribution by Prof. Yaroslav Tserkovnyak, Dr. Jia Zhang, Dr. Ran Cheng, Prof. Yonggang Zhao, and Dr. Wanjun Jiang.


4:00 PM MQ01.08.02
**Spin-Orbit Torques in Mn\(_2\)Au/Permalloy Bilayers** Cheng Song\(^1\), Xiaolong Fan\(^2\), Wenwen Kong\(^2\), Xiaofeng Zhou\(^1\) and Feng Pan\(^1\); \(^1\)Tsinghua University, China; \(^2\)Lanzhou University, China

The global centrosymmetry plus broken sublattice inversion symmetry crystal structure of antiferromagnetic (AFM) Mn\(_2\)Au result in the Néel spin-orbit torque (NSOT) switching of its Néel vector direction. In this talk, I will present our recent progress on the spin-charge conversion and spin-orbit torques generated by Mn\(_2\)Au films, where its special crystal structure is strongly involved. Current-induced spin-orbit torques generated by Mn\(_2\)Au was measured in Mn\(_2\)Au/Permalloy bilayers with the spin-torque ferromagnetic resonance (ST-FMR). Unlike the spin-charge conversion in generally used heavy metal/ferromagnetic metal and AFM/ferromagnetic metal bilayers, we find that besides a spin polarization along transverse direction (y-axis), in Mn\(_2\)Au films there is a spin polarization along the film normal direction (z-axis), which is perpendicular to the charge current (x-axis). The AFM Mn\(_2\)Au broken sublattice inversion symmetry crystal structure induced unusual spin polarization along the film normal direction and subsequent in-plane field-like torque. The film thickness and angular dependence of the spin polarization along z-axis are thoroughly investigated. Our observation adds a different dimension to spin-orbit torque.

4:15 PM MQ01.08.03
**Microscopic Dynamics and Optoelectronic Response of Type-I Weyl Semimetals from First Principles**
Christina Garcia, Jennifer Coulter and Prineha Narang; Harvard University, United States

The transition metal monopnictides TaAs, NbAs, TaP, and NbP have been well-studied in the past few years since they were first predicted and experimentally confirmed to be Weyl semimetals. Much work has been done in further characterization of these materials and probing of additional Weyl physics signatures, including studies of both linear and nonlinear optics. However, some of the microscopics of these systems relevant to designing complex device architectures utilizing the Weyl nodes’ linear dispersion in the bulk of the crystal are still not fully understood. In this talk, we address the temperature dependence of the linear optical responses in TaAs and NbAs. We present the real and imaginary parts of an experimentally relevant complex dielectric function for these materials as functions of frequency, temperature, and polarization direction, incorporating scattering rates calculated from first principles. From these we also present linear optical conductivity predictions which agree well with experiment where experiment exists for TaAs. Finally, we examine the effect of chemical potential on the optical...
conductivity, which can be used to understand the role of the Weyl nodes in these optical responses.


4:30 PM *MQ01.08.04
Topological Materials for Quantum Devices and Beyond Claudia Felser, Johannes Gooth and Kaustuv Manna; Max Planck Institute, Germany

Topological insulators, Weyl and Dirac semimetals and new Fermions are new quantum states of matter, which have attracted considerable interest from the condensed matter community. Heusler compounds are a remarkable class of materials which exhibit a wide range of extraordinary multi-functionalities including tunable topological insulators, half metallic ferromagnets and non collinear topological spin structures [1]. The required band inversion has already been unambiguously identified by angle-resolved photoemission (ARPES) and transport [2, 3]. Weyl and Dirac semimetals open up new research directions and applications that result from the large Berry phases that they exhibit: these lead to giant anomalous Hall effect (AHE), giant anomalous Nernst and spin Hall effects (SHE) and topological spin structures [4]. Examples discussed in the talk are Mn3Sn, Co3Sn2S2 and Co2MnGa. In the 2D limited we propose a Quantum anomalous Hall effect for Co3Sn2S2 [5, 6]. However the number of correlated materials with topological properties is limited. With Ta2Se8I a material with a competition between a Weyl semimetal and a charge density wave might open a new field “axion insulators” [7]


1:30 PM *MQ01.09.01
Tuning Optical and Spin-Valley Properties in van der Waals Heterostructures Bernhard Urbaszek1, Mikhail Glazov2, Marina Semina2, Xavier Marie1, Cedric Robert1, Scott Crooker3, Mateusz Goryca3, Shivangi Shree3, Bo Han1 and Honghua Fang1; 1Institut National des Sciences Appliquées de Toulouse, France; 2Ioffe Institute, Russian Federation; 3Los Alamos National Laboratory, United States

The optical properties of transition metal dichalcogenide (TMD) monolayers (MLs) are dominated by excitons, electron and hole pairs bound by Coulomb attraction [1]. In this talk we report recent results on linear and non-linear optical spectroscopy of these atomically thin semiconductors for applications in optoelectronics and spintronics. We discuss fundamental parameters such as the optical bandgap and the photoluminescence emission time and yield that can be tuned by changing the dielectric environment of the monolayers and using different substrate materials and heterostructure fabrication techniques [2,3]. We discuss the polarization dynamics of excitons and resident carriers in different TMD materials giving access to spin and valley physics, governed by very different physical processes in the case of excitons as compared to resident carriers [4].

2:00 PM *MQ01.09.02  
**Optical Measurements of Electron and Nuclear Spin Polarization in Semiconductors**  
Vanessa Sih; University of Michigan, United States

Greater control of nuclear spin polarization could provide breakthroughs in both classical and quantum information storage and processing. In this talk, I will describe optical pump-probe techniques that generate and measure an electron spin polarization that persists over several laser pulse repetition periods in a gallium arsenide epilayer. Spins excited from successive laser pulses interfere, either constructively or destructively, depending on the Larmor spin precession frequency, which is determined by both the applied magnetic field and nuclear Overhauser field, and we demonstrate a dynamic nuclear polarization that actively responds to the external magnetic field sweep direction, sweep rate, and magnitude of transverse electron spin polarization [1]. We show that the electron-nuclear spin system retains memory of the external field history, including interruptions and reversals in magnetic field sweeps. [1] “Observation of magnetic field sweep direction dependent dynamic nuclear polarization under periodic optical electron spin pumping,” M. Macmahon, J. R. Iafrate, M. J. Dominguez, and V. Sih, Phys. Rev. B 99, 075201 (2019).

2:30 PM MQ01.09.03  
**Exciton-Polaritons as a Tool to Control the Emission Characteristics of Exciton and Trions Bound to Te$_2$ in ZnSe**  
Anne-Laurence Phaneuf-L’Heureux, Mathias Pont and Sebastien Francoeur; Polytechnique, Genie physique, Canada

Te$_2$ molecules in ZnSe form a quantum defect that offers advantageous characteristics, including a high optical uniformity due to its atomic nature and a strong optical dipole moment matching those from semiconductor nanostructures, for the development of efficient spin-photon interfaces for applications in quantum optics, communications and networks. In this work, we demonstrate that excitons-polaritons generated in the ZnSe host material can be used to deterministically control the emission characteristics of excitons and trions bound to a single Te$_2$ molecule. In particular, the emission efficiency is increased by two orders of magnitude, indicating a very efficient coupling between free excitons and Te$_2$ bound states. Scanning the free-exciton band with a narrow-frequency tunable laser over the free exciton spectral region reveals strong in-phase oscillations with a period of about 1 meV in the bound exciton emission intensity, emission energy, and emission linewidth. These modulations are explained by the strong coupling naturally occurring in ZnSe between photons and free-excitons, or exciton-polaritons. This type of cooperative process whereby a host excitation is used to control the behavior of a single emitter has never been reported before. It allows deterministically controlling the emission properties and enables the development of new coherent control scheme, such as the rotation of spins without the need for an external magnetic field.

2:45 PM MQ01.09.04  
**Resonant Excitation of Excitons and Trions Bound to Te$_2$ Molecules in ZnSe**  
Mathias Pont, Anne-Laurence Phaneuf-L’Heureux and Sebastien Francoeur; Polytechnique, Genie physique, Canada

Te$_2$ molecules in ZnSe form an isoelectronic center capable of binding a single hole, an exciton, a positively charged exciton, or a biexciton. This defect offers two advantageous characteristics for the development of spin-photon interfaces for applications in quantum optics, communications and networks. It provides the optical uniformity of atomic defects composed of a few atoms, like NV or other color centers in diamond, and the remarkable optical dipole moments found in semiconductor nanostructure.

In this work, we perform resonant excitation on a single Te$_2$ molecule in ZnSe. Resonant excitation reveals the intrinsic absorption linewidth of exciton and trion states. It is found that the addition of ultra weak non-resonant above band gap excitation can be used to stabilize the environment by reducing charge fluctuations, thereby allowing the measurement of much narrower absorption linewidths. Resonant excitation also reveals the participation of several bulk phonons along with phonons that have been reported in ZnSe. They are associated with localized phonons bound to the Te$_2$ molecule. In addition, resonant excitation on single Te$_2$ molecules reveals exciton tunneling to a nearby Te$_2$ molecule. Tunneling efficiency depends sensitively of the energetic separation, the respective orientation of the two molecules and the angular nature of the optical excited and detected exciton.
wavefunctions. These results pave the way towards resonant fluorescence and quantum optics with atomic-sized defects in semiconductor materials.

3:00 PM MQ01.09.05
Gate-Controllable Spin Splitting and Giant Proximity Magnetoresistance in InAs Induced by a Magnetic Proximity Effect Anh Le Duc1,1, Kosuke Takiguchi1, Takahiro Chiba2, Tomohiro Koyama3,3, Daichi Chiba3,3 and Masaaki Tanaka1,1; 1The University of Tokyo, Japan; 2National Institute of Technology, Fukushima College, Japan; 3Osaka University, Japan

The magnetic proximity effect (MPE)[1], which occurs due to the magnetic coupling within a few monolayers at the interface of two magnetically dissimilar layers, is effective in incorporating magnetic effects into nonmagnetic (NM) materials. In particular, the MPE at ferromagnetic (FM)/NM interfaces, where the NM layer is a material with strong spin-orbit coupling—typically a heavy metal, topological insulator, or two-dimensional electron gas (2DEG) with a strong Rashba effect—, has attracted much attention as promisingly open routes toward realizing Majorana fermions without using a strong magnetic field. However, the magnetic coupling at the FM/NM interface is typically a short range (~1 nm), which limits the strength of the MPE and hinders the ability of electrical gating of the effect.

Here, we show that the magnetic coupling range of MPE in a NM/FM bilayer can be dramatically enhanced, at least by two orders of magnitude, to several tens of nm on the NM side by using a semiconductor quantum well (QW) as the NM layer. The bilayers under study consist of InAs (thickness \( t = 15 - 40 \) nm)/(Ga,Fe)Sb (15 nm, 20% Fe) grown on AlSb buffer/semi-insulating GaAs (100) substrates by molecular beam epitaxy. This bilayer system has several unique properties that are particularly suitable for demonstrating MPE: i) (Ga,Fe)Sb is a p-type ferromagnetic semiconductor (FMS) with a high Curie temperature \( T_C (> 300 \) K)[2,3], while InAs QW is a typical Rashba 2DEG system with high electron mobility. ii) The lattice mismatch between InAs and (Ga,Fe)Sb is only \( \sim 0.1\% \); thus, high-quality heterostructures can be epitaxially grown. iii) InAs/(Ga,Fe)Sb is a type-III heterostructure, i.e., the conduction band bottom of InAs is lower than the valence band top of (Ga,Fe)Sb at the NM/FM interface, which enables large penetration of the electron wavefunction into the (Ga,Fe)Sb side. iv) The resistivity of the (Ga,Fe)Sb layer is two orders of magnitude higher than that of the InAs 2DEG, particularly at low temperature. Therefore, the electrical transport in these bilayers is dominated (> 99%) by the InAs 2DEG. We fabricate field-effect transistor structures on these InAs/(Ga,Fe)Sb bilayers, and measure magnetotransport properties using a standard four-terminal method.

We demonstrate that a new giant magnetoresistance (~80% at 14 T), which we call proximity magnetoresistance (PMR), is induced in the InAs 2DEG due to the MPE from the neighbouring (Ga,Fe)Sb layer. This PMR is two orders of magnitude larger, and its dependence on the magnetic field direction has a unique symmetry, which is different from the MR observed in other NM/FM bilayers reported to date. The PMR magnitude can be controlled over one order of magnitude by a gate voltage \( V_g \). These results are explained by the penetration of the InAs 2DEG wavefunction into (Ga,Fe)Sb, which is effectively modulated by \( V_g \). By fitting our modified Khosla-Fischer model to these PMR data, we find that a spontaneous spin splitting \( \Delta E \) is induced in the InAs channel by the MPE from (Ga,Fe)Sb. The magnitude of \( \Delta E \) is largely modulated from 0.17 to 3.8 meV when applying \( V_g \) between \( \pm 3\) V. In principle, this gate-controlled spin splitting and the new PMR provide a mechanism to locally access Majorana fermions in InAs-based Josephson junctions[4], and introduce a new concept of magnetic-gating spin transistors in which the NM channel current is modulated by both electrical and magnetic means[5].

This work was partly supported by Grants-in-Aid for Scientific Research (Nos. 16H02095, 17H04922, 18H05345), the CREST Program (JPMJCR1777) of JST, Yazaki Foundation for Science & Technology, and Spin-RNJ.


3:15 PM BREAK
3:30 PM MQ01.10.01
Spin Pumping into Superconducting Materials through Cr/Fe Interfaces  
Murat Cubukcu¹, Alex Chan², Alexander Vanstone², Sachio Komori³, Juliet Thompson³, Kun-Rok Jeon³, Chiara Ciccarelli³, Mark Blamire³, Jason Robinson³, Lesley F. Cohen² and Hidekazu Kurebayashi¹; ¹London Centre for Nanotechnology, United Kingdom; ²Imperial College London, United Kingdom; ³University of Cambridge, United Kingdom

There is currently a great deal of interest in the research field of superconducting spintronics [1]. In particular, the generation of spin-polarised (triplet) Cooper-pairs is a central topic. Long-range transportation of triplet Cooper-pairs, compared to singlet Cooper-pairs within a neighbouring ferromagnet, has been measured in a number of magnetic Josephson junctions with spatially inhomogeneous magnetisation [1,2]. We have demonstrated generation of the triplet Cooper-pairs spin currents and detection by spin pumping experiments in Pt/Nb/NiFe samples [3]. The observed enhancement of spin relaxation (or Gilbert damping) in this case implies that when Nb turns superconducting, a spin channel opens allowing spin-pumped magnons in NiFe to be dissipated at the Pt sink layer. This is in stark contrast to the picture of singlet Cooper-pairs which are unable to carry away any angular momentum, leading to the reduction of Gilbert damping below $T_c$. A proposed driving mechanism is the interaction of the spin-orbit coupling in Pt and the magnetic exchange interaction through the Nb layer. In this presentation, we will show our study of applying the same measurement techniques to other material systems. Of particular interest is an Fe/Cr interface where spin-glass states are formed to generate spin misalignments [4]. We will describe how the Gilbert damping parameter behaves below and above $T_c$ and the implications for spin transport through the Fe/Cr/Nb interfaces, in terms of the triplet Cooper-pair generation.


3:45 PM MQ01.10.02
Spin-Filtering of Triplet Cooper Pairs and Suppression in an S-Wave Superconductor  
Lesley F. Cohen¹, Sachio Komori², James Devine-Stoneman², Mark Blamire² and Jason Robinson²; ¹Imperial College, United Kingdom; ²University of Cambridge, United Kingdom

Spin selectivity in a ferromagnet results from a difference in the density of up- and down-spin electrons at the Fermi energy as a consequence of which the scattering rates depend on the spin-orientation of electrons. This property is utilized in spintronics to control the flow of electrons by ferromagnets in a ferromagnet/normal metal/ferromagnet pseudo spin-valve.

The feasibility of superconducting spintronics depends on a spin-sensitivity of ferromagnets to the spin of equal-spin triplet Cooper pairs generated at superconductor(S)/ferromagnet(F) heterostructures with magnetic inhomogeneity at the S/F interface (1). In this talk we report Nb/Cr/Fe/Cu/Fe/Cr/Nb triplet Josephson junctions in which Cr/Fe interfaces act as triplet generators (2) and where the magnetization-alignment between the Fe layers controls the critical current ($I_c$). Furthermore, we will discuss equivalent junctions in which the central layer of Cu is substituted for a 10-40 nm thick layer of superconducting Nb; in these junctions we observe a suppression of $I_c$ below the critical temperature of the central Nb layer indicating a blocking of triplet pairs by the Nb singlet density of states.


4:00 PM MQ01.10.03
Nodal Superconducting Exchange Coupling  
Jason Robinson and Sachio Komori; University of Cambridge, United Kingdom

The superconducting equivalent of giant magnetoresistance involves placing a thin-film superconductor between two ferromagnetic layers. A change of magnetization-alignment in such a superconducting spin-valve from parallel (P) to antiparallel (AP) creates a positive shift in the superconducting transition temperature [$\Delta T_c=T_c(P)-T_c(AP)$] due to
an interplay of the magnetic exchange energy and the superconducting condensate. The magnitude of $\Delta T_c$ scales inversely with the superconductor thickness ($d_s$) and is zero when $d_s$ exceeds the superconducting coherence length ($\xi$). In this talk I will discuss a superconducting spin-valve effect involving a different underlying mechanism in which magnetization-alignment and $\Delta T_c$ are determined by the nodal quasiparticle-excitation states on the Fermi surface of the $d$-wave superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO) grown between the insulating ferromagnet $Pr_{0.8}Ca_{0.2}MnO_3$. We observe $\Delta T_c$ values of 2 K with $\Delta T_c$ oscillating with $d_s$ over a length scale exceeding 100 $\xi$ and, for particular values of $d_s$, we find that the superconducting state reinforces an antiparallel magnetization-alignment. The results pave the way for all-oxide superconducting memory$^2$ in which superconductivity modulates the magnetic state.


4:15 PM MQ01.10.04
**Spin-Dependent Phenomena across the Crystalline BaTiO$_3$-Germanium Interface** Yichen Jia, Cristina Visani, Charles H. Ahn and Frederick J. Walker; Yale University, United States

The epitaxial integration of functional oxides on conventional semiconductors using advanced molecular beam epitaxy opens new opportunities for coupling their unique properties with semiconductors for post-CMOS computing paradigms. Here we explore spin-dependent phenomena in Permalloy-BaTiO$_3$-Germanium heterostructures and demonstrate an interesting correlation between charge transport and magneto-resistive response across the crystalline BaTiO$_3$-Germanium interface. In the quantum tunneling charge transport region, we observe Hanle and inverted Hanle effect with a full width at half maximum of ~100 mT. The single Hanle peak evolves into a superposition of two peaks with opposite polarity and distinct linewidth when impurity-assisted charge transport becomes dominant. Our result serves as a step towards understanding the origin of the magnetoresistance in oxide tunnel junctions.

4:30 PM MQ01.10.05
**Transport Spin Polarization of Pt/ferromagnetic Insulator Bilayers** Michael S. Osofsky$^1$, Joseph Prestigiacomo$^2$, Peng Li$^2$ and Yuri Suzuki$^2$; $^1$Naval Research Laboratory, United States; $^2$Stanford University, United States

It has been shown that the anomalous Hall effect can be observed in platinum films deposited on a ferromagnetic insulator which implies the existence of a magnetic proximity effect [1]. One of the key features of ferromagnetic metals is a net spin polarization of the carriers at the Fermi energy which enable the functionality of spintronic devices. In this presentation we show that spin polarized carriers are indeed present in Pt films of various thicknesses that were deposited on magnesium aluminum ferrite (MAFO) using point contact Andreev scattering [2]. The results were obtained by extracting conductance vs. voltage data from I-V curves taken through contacts formed by driving a sharpened superconducting Nb tip into the Pt/MAFO samples. The resulting spectra were then analysed using a modified BTK theory of supercurrent conversion at a normal/superconductor interface to obtain the values of the transport spin polarization.

The authors acknowledge the support of the Basic Research Office of the Assistant Secretary of Defense for Research and Engineering under the Laboratory University Collaboration Initiative (LUCI) and Vannevar Bush Faculty Fellowship (funded by the Office of Naval Research through grant N00014-15-1-0045).

References

4:45 PM MQ01.10.06
**An Electronically-Controlled High Mobility Spin-Polarized Electron Gas at Engineered Oxide Interfaces** Yunzhong Chen; Technical University of Denmark, Denmark
The emergent two-dimensional electron gas (2DEG) and magnetism at the SrTiO$_3$-based oxide interfaces open new avenues for spintronics. However, to date, the “marriage” between the ferromagnetism and the high mobility 2DEG remains elusive. The recent introduction of a magnetic buffer layer of EuTiO$_3$ at the conducting interface gives rise to spin polarization but lowers the electron mobility significantly. Based on our former finding of charge transfer induced modulation doping at oxide interfaces, herein, we inserted a ferromagnetic insulating BaFeO$_3$ (BFO) buffer layer at the epitaxial LaAlO$_3$/SrTiO$_3$ (LAO/STO) interface and achieved a high mobility spin polarized 2DEG when the BFO is as thin as 1 unit cell (uc). Element-specific X-ray magnetic circular dichroism (XMCD) measurements reveal a paramagnetic nature of both the 1uc-BFO buffer layer and the 2DEG. Nevertheless, the spin polarization of the single band 2DEG is found to be enhanced strongly as electrons are depleted from the interface which is dramatically different from the multiple band spin polarized 2DEGs. The unique high mobility spin polarized 2DEG provides an intriguing material platform to design all-oxide spintronic devices.

References:

**SYMPOSIUM MQ02**

TUTORIAL: Introduction to Ion Trap and Superconducting Qubits and Their Material Challenges
December 1 - December 1, 2019

* Invited Paper

**TUTORIAL**

Introduction to Ion Trap and Superconducting Qubits and Their Material Challenges

Sunday Morning, December 1, 2019
Hynes, Level 2, Room 202

Ion trap and superconducting qubits are two of the most popular quantum computing platforms in academia and industry but the performance of the qubits can be severely limited by their surrounding material quality. Surface defects, dielectric loss, anomalous heating in surface traps, unwanted coupling to spins and defects - all these material properties influence coherence times, the time qubits retain their quantum properties, which put the ultimate limit on the ability to run algorithms in quantum computing processors.

The tutorial will overview the basics of ion trap and superconducting qubits and the history of material development for these two quantum computing platforms. The tutorial will provide good opportunities for material scientists, who wants to engage in quantum information science, to learn about quantum computing devices and the ongoing challenges in the material research for quantum computation.

8:30 AM
Frederick Wellstood, Joint Quantum Institute, University of Maryland
In this tutorial, we will overview the basics of superconducting qubits and their material structures. Key concepts related to their material properties such as coherence times will be introduced as well as the characterization methods. The history of the superconducting qubit material research will be reviewed as well as the current challenges with future directions.

10:00 AM BREAK

10:30 AM
Materials Considerations for Trapped-Ion Quantum Information Processing
John Chiaverini, Lincoln Laboratory, Massachusetts Institute of Technology

This tutorial will cover the basics of ion trap qubits, why material choices matter with surface traps and how the material properties can affect the scaling of the ion trap qubits. The current challenges and future directions will be reviewed.

SYMPOSIUM MQ02

Materials for Quantum Computing Applications
December 2 - December 6, 2019

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* Invited Paper

SESSION MQ02.01: Atomic and Epitaxial Materials for Quantum Computing Devices
Session Chairs: Dohun Kim and Hanhee Paik
Monday Morning, December 2, 2019
Hynes, Level 2, Room 202

8:30 AM *MQ02.01.01
Selective Area Epitaxy of a Materials Platform for Scalable Quantum Computing
Leo Kouwenhoven;
Microsoft/Delft University of Technology, Netherlands

Nanoscale hybrid III-V semiconductor/superconductor heterostructures have demonstrated potential to advanced quantum transport physics, in particular to host the elusive Majorana quasiparticles. Virtually all progress on the materials side in the last 6 years has relied on high quality vapor liquid solid growth of III-V free-standing nanowires functionalized at a later stage by ex-situ deposited Al. Despite these early successes a more robust,
scalable materials platform is still missing to enable the future topological quantum computer. Here I will report on our progress in using molecular beam epitaxy (MBE) to grow both III-V semiconductor nanowire networks and a high quality epitaxial s-wave metal superconductor, using selective area epitaxy. I will first introduce the current state of the art, advantages and challenges of the selective area approach and MBE with respect to other growth techniques and geometries. Fundamental knowledge gained by growth studies will be applied to obtain reproducible, high yield advanced high spin-orbit III-V nanowire/superconductor networks. I will present low temperature transport experiments that characterize the quality of the materials.

9:00 AM MQ02.01.02
Lattice-Matching Strategy for Coherent Interface Design of Josephson Junction—Al/AlOx/Al vs Re/Al2O3/Re Chang-Eun Kim, Keith Ray and Vincenzo Lordi; Lawrence Livermore National Laboratory, United States

Amorphous aluminum oxide-based tunnel junctions have been widely adopted for fabricating superconducting qubit devices, but further improvement is hindered by potentially fundamental limits of uniformity and interactions with intrinsic tunneling two-level-systems (tTLS) originating from amorphous AlOx and disordered interfaces. The amorphization and disordering are inevitable due to large lattice mismatch between crystalline aluminum oxide and the aluminum substrate. The Re/Al2O3/Re material stack has well-matched lattice parameters, and prior work has demonstrated reduced TLS density. We aim to understand the materials property of these interfaces, detailing their thermodynamic property such as interfacial energy and work of adhesion; and structure-related electronic properties such as fundamental energy gap, ionic charge transfer, and local dipole formation. The results show how the lattice-matching strategy improved several microscopic properties of the tunnel barrier junction, laying out a strategy to develop more coherent superconducting quantum computing components. (Prepared by LLNL under Contract DE-AC52-07NA27344.)

9:15 AM MQ02.01.03
Atomic-Scale Fabrication of Donor-Based Quantum Devices in Silicon Xiqiao Wang1,2, Ranjit Kashid1, Jonathan Wyrick1, Pradeep Namboodiri1 and Richard Silver1; 1National Institute of Standards and Technology, United States; 2University of Maryland-College Park, United States

Donor-based qubits in silicon have attracted broad interest as a promising candidate for scalable solid-state quantum computing. Central to the scalability and performance of this quantum system is atomically precise control of dopant confinement and single dopant placement in silicon. Atomically precise fabrication in silicon has enabled atom-by-atom control and characterization of quantum materials properties for quantum information processing and quantum simulation applications, such as high-fidelity spin readout/initialization and tunable exchange coupling in multi-qubit gate operations.

Success in atomically precise fabrication is a direct consequence of controlling materials properties at the atomic scale. This presentation will present our recent advances to address critical challenges in atomically precise fabrication and characterization of donor-based quantum devices in silicon by using enhanced STM-based hydrogen lithography to define atomically precise dopant-based devices, and by suppressing atomic-scale dopant movement during device encapsulation overgrowth. We will report on STM-defined single electron transistors that can be used as charge sensors, where the source/island/drain tunnel coupling can be controlled with atomic-precision for the optimization of charge sensing performance. We will present resonant tunneling spectroscopy analysis of STM-defined single and few donor quantum dots with atomically defined tunnel gaps. Finally, we combine single/few donor quantum dots with atomically defined single electron transistors as charge sensors and report our recent results in atomic-scale control of tunnel coupling between few-donor quantum dots and single electron charge sensors to illustrate the impact of atomically defined tunnel coupling on single electron charge sensing and spin selective-readout.

9:30 AM *MQ02.01.04
Towards PAMBE Grown Nitride Superconductors for Epitaxial Josephson Junctions and Quantum Circuits Christopher Richardson; University of Maryland, United States

Low microwave loss superconducting circuit components are a necessity of fabricating high-fidelity
superconducting qubits. Accordingly, significant research has focused on making high-quality planar resonators from elemental and nitride superconductors. Josephson junctions are the nonlinear component of superconducting qubits, that also need to be high performance. Interestingly, superconducting qubits all use Josephson junctions fabricated from aluminum and aluminum oxide using the double angle evaporation process. Details of this alternative design will be presented.

Plasma assisted Molecular beam epitaxy (PAMBE) is used to grow niobium titanium nitride alloys (Nb,Ti₁₋ₓN) and wide bandgap nitride (AlN) superconductors directly on sapphire wafers. This combination of nitride materials provides sufficient degrees of freedom that synthesis of an epitaxial Josephson junction may be possible. Growth results of Nb,Ti₁₋ₓN films on c-plane sapphire substrates, and initial trilayer NbTiN/AlN/NbTiN (superconductor-insulator-superconductor) Josephson junction structures on sapphire will be presented along with structural analysis and results from superconducting IV and microwave-loss measurements.

10:00 AM BREAK

SESSION MQ02.02: Fabrication and Materials for Qubits
Session Chairs: Tracy Northup and Ben Palmer
Monday Morning, December 2, 2019
Hynes, Level 2, Room 202

10:30 AM MQ02.02 01
Protecting Superconducting Qubits from Phonon Mediated Decay Yaniv J. Rosen, Matthew Horsley, Sara Harrison, Eric Holland, Allan Chang, Tiziana Bond and Jonathan DuBois; Lawrence Livermore National Laboratory, United States

For quantum computing to become fault tolerant, the underlying quantum bits must be effectively isolated from the noisy environment. It is well known that including an electromagnetic bandgap around the qubit operating frequency improves coherence for superconducting circuits. However, investigations of bandgaps to other environmental coupling mechanisms remain largely unexplored. We present a method to enhance the coherence of superconducting circuits by introducing a phononic bandgap around the device operating frequency. The phononic bandgap blocks resonant decay of defect states within the gapped frequency range, removing the electromagnetic coupling to phonons at the gap frequencies. We constructed a multi-scale model that derives the decrease in the density of states due to the bandgap and the resulting increase in defect state T₁ times. We demonstrated that emission rates from in-plane defect states can be suppressed by up to two orders of magnitude. We combine these simulations with full master equation simulations to demonstrate the suppression of qubit energy relaxation even when interacting with 200 defects states.

10:45 AM *MQ02.02.02
3D Integration to Enable High Coherence and Connectivity for Superconducting Qubits Danna Rosenberg¹, J. Mallek², D. Yost¹, M. Schwartz¹, R. Das¹, J.L. Yoder¹, G. Calusine¹, E. Golden¹, B. Huffman¹, Alexander Melville¹, A. Sevi¹, W. Woods¹ and W.D. Oliver¹,²; ¹Lincoln Laboratory, Massachusetts Institute of Technology, United States; ²Massachusetts Institute of Technology, United States

As the field of superconducting qubits progresses, it will become increasingly important to use 3D integration to address large arrays of qubits. Traditional 3D integration methods pose challenges for superconducting qubits, because these qubits are vulnerable to losses introduced by bulk dielectrics and at interfaces. To overcome these challenges, we are developing a novel three-tier stack where an interposer with superconducting through-silicon vias (TSVs) isolates sensitive qubits from a potentially-lossy readout and interconnect chip. This isolation prevents degradation of the qubit coherence time, and the high-aspect ratio superconducting TSVs enable dense circuitry to control and read out the qubits. The components of the three-tier stack are bonded using indium bump bonds, providing both structural support and a galvanic connection between the three chips. I will present our work developing and characterizing 3D integration components including indium bumps and TSVs, and I will discuss recent demonstrations incorporating superconducting TSVs in qubit control and readout circuitry.

Final Program 1/13/2020 1774
This research was funded by the Office of the Director of National Intelligence (ODNI), Intelligence Advanced Research Projects Activity (IARPA) and by the Assistant Secretary of Defense for Research & Engineering under Air Force Contract No. FA8721-05-C-0002. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of ODNI, IARPA, or the US Government.

11:15 AM *MQ02.02.03
Microfabricated Ion Traps for Quantum Information Science  
Susan Clark, Matthew Blain, Raymond Haltli, Craig Hogle, Daniel Lobser, Melissa Revelle, Christopher Yale and Peter Maunz; Sandia National Laboratory, United States

Trapped ion systems have many advantages that make them promising quantum computing platforms. They are well isolated from the environment, feature high-fidelity quantum operations, and exhibit basically no idle errors. Microfabrication enables the realization of complex traps that allow one to precisely control large ion chains, move qubits through the trap, and reconfigure the trapped ion quantum processor, which are necessary features for building large scale systems capable of performing complex algorithms. However, microfabricated surface traps bring unique challenges. Proximity of ions to trap structures can lead to electric field noise which induces anomalous heating of ions in the trap. Routing through traps to make complex electrode patterns leads to higher capacitances and thus higher thermal dissipation on the device. Also, complex RF geometry can lead to excessive micromotion and AC Stark shifts, which can vary or broaden the energy levels used to perform gates. Reducing these sources of error is essential to further improve the fidelity of trapped ion quantum processors.

We will present Sandia’s ion-trap microfabrication capabilities and introduce ion trap designs that are being used in the leading trapped-ion groups, as well as our characterization and mitigations for these sources of error. We show exquisite classical control of ions as well as high-fidelity quantum operations, demonstrating the viability of microfabricated surface electrode ion traps for quantum information processors.

SNL is managed and operated by NTI under DOE NNSA contract DE-NA0003525. SAND2019-6322 A

8:00 AM MQ02.03.01
Quantum Spin System in a Semiconducting Diode  
Alexandre Bourassa¹, Christopher P. Anderson¹ and David D. Awschalom¹²; ¹The University of Chicago, United States; ²Argonne National Laboratory, United States

The neutral divacancy (VV⁰) in silicon carbide (SiC) is a candidate solid state qubit which promises a combination of long spin coherence and near-infrared emission in a material which is already optimized for state-of-the-art scalable semiconductor manufacturing. Here, we use this mature host material to integrate quantum states into classical electronic devices.

First, we show that we can create and isolate single divacancy in p-i-n diodes. We then perform spin manipulation and readout of these single defects inside the junction and demonstrate high fidelity Rabi oscillations (with >98% contrast). This allows us to measure a long spin coherence time (T₂) which persist inside the device.

Second, we use the diode to confine the electric field in the i-layer which allows us to Stark tune the single photon emission frequency by almost a terahertz. Furthermore, since this field is applied along the defect axis, the tuning does not change the symmetry of the orbitals which minimizes unwanted spin flip rate.

Finally, we show how we can use charge depletion in the junction to drastically reduce electric field noise at the defect. This allows us to effectively eliminate spectral diffusion and obtain an optical linewidth approaching the
lifetime limit of the emitter (a 50x enhancement). Moreover, we show that this optical line is very stable and fluctuates by less than a linewidth over many hours.

Overall, these results demonstrate the power in integrating quantum states into engineered classical electronics devices.

Related publication:

8:15 AM MQ02.03.02
Er Doped Y₂O₃ on Silicon—Development and Characterization of a Scalable Quantum Memory Platform
Manish Kumar K. Singh¹, Abhinav Prakash¹,², Tijana Rajh², Gary Wolfowicz¹,², Yizhong Huang¹,², Christina Wicker¹, Alan Dibos², Jianguo Wen², David D. Awschalom¹,², Tian Zhong¹,² and Supratik Guha¹,²; ¹University of Chicago, United States; ²Argonne National Laboratory, United States

Rare earth ions (REI) have a spin-optical interface that enables storage of optical quantum information in the long-lived nuclear spin levels. Further, a microwave resonator can couple to the spin transitions inductively, making REI suitable for quantum memory and transduction applications. In the case of Er³⁺, the optical excitation matches the telecom transmission wavelength (~1.55 um), making it technologically attractive. When embedded in a crystalline host, the full 5s and 5p orbitals of the REI shield the intra 4f electrons from the crystal field effects from the host. This results in very narrow transition linewidths and high spectral stability, making it an ideal candidate for solid state quantum memory. Long coherence times of 1.3s in Er:YSO [1] bulk single crystals have been demonstrated. However, very little has been done in this regard when it comes to demonstrating thin films that could be integrated into scalable devices.

Using molecular beam epitaxy (MBE), we demonstrate the growth and characterization of high quality single crystal thin films of Er:Y₂O₃ on Si 111. Using optical and electron paramagnetic resonance spectroscopy, we confirm that Er substitutes for Y at both C2 and C3 sites in the bixbyite structure of Y₂O₃. We obtain a photoluminescence linewidth of 7.9 GHz and 5.1 GHz for the 1536 nm transition (4I13/2 → 4I15/2) at 4 K and 7 mK, respectively. We will discuss the role of the microstructure (carried out using extensive electron microscopy), the use of buffer layers, the Y₂O₃/Si and the Y₂O₃/air interface, and the optimization of these parameters that led to the demonstration of narrow optical linewidth of Er³⁺. We also discuss the gains resulting from using enriched ¹⁶⁷Er (91.5%) as the dopant.

In order to transfer the growth processes for compatibility with compact, optically modulated solid state devices, it is necessary to develop these heterostructures on silicon-on-Insulator (SOI) wafers—preferably (but not necessarily) oriented along <100>—so that they may be integrated with silicon photonics based optical waveguides. We demonstrate the growth of Y₂O₃ on Si 100 with a Y₂O₃/Si(110)//Si(100) epitaxial relationship. We will also report on the demonstration of full SOI/Er:Y₂O₃/Si overlayer heterostructures and the quality of optical waveguides fabricated using this platform.


8:30 AM *MQ02.03.03
Integrated Photonic Devices and Materials for Scalable Trapped-Ion Quantum Logic
Karan Mehta, Chi Zhang, Maciej Malinowski, Thanh-Long Nguyen and Jonathan Home; ETH Zürich, Switzerland

Trapped-ion quantum systems are a promising platform for large-scale quantum information processing, with all relevant operations having been demonstrated with the highest fidelities in any qubits to date [1,2], and fully connected systems with of order 10 qubits [3]. Given this established set of basic operations, methods to allow their robust implementation at a large scale, while also significantly reducing error rates, will play an increasingly central role in work towards realizing useful quantum processors.

A major element of this in the context of trapped-ion qubits will be the integration of optics used to control many
ions in parallel into the ion traps themselves [4]. This enables stable beam delivery, tight focusing to µm-scale spots for individual ion-addressing and efficient power usage, and straightforward parallelization. I will describe our recent work at ETH developing on these ideas [5], in devices with efficient fiber coupling on multiple channels directly to waveguides on trap die (2 dB coupling loss measured at 729 nm wavelengths), and low-loss routing and emission to ions trapped 50 µm above the surface of the chip. I will present our work towards realizing multi-qubit quantum logic in these devices, a few novel beam arrangements utilizing such optics, and observations on relevant noise sources present owing to the various materials near the ions.

Our current experiments are based on integrated devices for light at red and near-IR wavelengths, and use modulators off-chip. In longer-term systems there will be considerable interest in compact integrated modulators, including for blue and near-UV wavelengths, able to be implemented within the trap chip. This will motivate research on thin-film material systems suitable for integrated electro- and acousto-optic devices at short wavelengths; these would additionally have broad applicability beyond quantum information.


9:00 AM MQ02.03.04
Aluminum Gallium Arsenide Photonic Waveguides for 780 nm Optical Delivery for Quantum Sensors Based on Ultra-Cold Atoms of Rubidium Jessica O. Maclean1, Mark Greenaway2, Richard Campion1, Mark Fromhold1 and Chris Mellor1; 1University of Nottingham, United Kingdom; 2Loughborough University, United Kingdom

An on-chip approach to optical delivery for portable quantum sensors is described. The optical design, epitaxy, nanofabrication and measurement of polarisation-maintaining, deep-etched aluminium gallium arsenide (AlxGa1-xAs) waveguides for near-infra-red 780 nm light was achieved, in an analogous approach to earlier work at (1300-1550) nm wavelengths [1]. Material characterisation techniques were developed to infer improved optical quality and reduced optical loss intrinsic to the material, grown by Molecular Beam Epitaxy (MBE). High, continuous-wave optical power densities were guided with low polarisation noise and photonic waveguide performance was stable over time. The optical loss was measured to be below 4.3(±0.4) dB cm⁻¹ corresponding to an attenuation coefficient, α, of 1.0 (±0.08) cm⁻¹ for single mode waveguides and demonstrating improved performance data [2]. The polarisation extinction ratio was better than −19 (±1) dB for orthogonal polarisations. These novel components illustrate the feasibility of passive photonic integrated circuits for the 780 nm wavelength. Future work will investigate the optical switching properties of these structures. The ultimate aim of the work is the creation of waveguide-based photonic circuits for compact cold atom sensors based on the D2 hyperfine transition of 87Rb at 780.24 nm [3]. Further applications include free-space short-wave communications, hybrid quantum systems [4] and epitaxial structures transparent to shorter wavelengths for other cold atom species and trapped ions. To this end, recent experiments examined device functionality as a function of wavelength.

Acknowledgements: We should like to thank Dr M.C. Rosamond and Prof. E.H. Linfield for expertise in Electron Beam Lithography at the School of Electronic and Electrical Engineering, University of Leeds, UK. This work was supported by the Engineering and Physical Sciences Research Council [grant number SM-30535 EP/M013294/1] through the EPSRC UK Quantum Technologies Hub for Sensors and Metrology.

9:15 AM MQ02.03.05
Thermodynamic Performance Limits for Optical Microcavities Christopher L. Panuski, Ryan Hamerly and Dirk R. Englund; Massachusetts Institute of Technology, United States

High quality factor ($Q$), small mode volume ($V$) optical microcavities are coveted for a variety of applications, including low-energy nonlinear optics and precision sensing. Recent theory and fabrication advances have led to the experimental realization of resonators featuring subwavelength mode confinement and quality factors exceeding 10 million. These continued improvements lend a natural question – is there any limit to the highly sought-after $Q/V$ ratio? Here, we show that the presence of thermo-refractive noise (TRN) – stochastic perturbations of the cavity material’s index of refraction due to fundamental temperature fluctuations – imposes a fundamental bound of the achievable cavity performance. Specifically, our results reveal a mode volume-dependent limit to an “effective quality factor,” which accounts for both intrinsic decay and resonant frequency noise. We compare this performance bound in various common integrated photonics materials systems, and explore the implications for proposed all-optical quantum information schemes. These results thus illustrate the importance of considering thermal noise in state-of-the-art microcavities, but also inform the choice of materials and processes which minimize its performance impact.

9:30 AM MQ02.03.06
Design and Fabrication of Large-Scale Defect-Free Arrays of Artificial Atoms Coupled to Photonic Waveguides Tsung-Ju Lu1, Noel Wan1, Kevin C. Chen1, Michael Walsh1, Matthew Trusheim1, Lorenzo De Santis1, Eric Bersin1, Isaac Harris1, Sara Mouradian1, Edward Bielejec2 and Dirk Englund1; 1Massachusetts Institute of Technology, United States; 2Sandia National Laboratories, United States

Atom-like emitters in diamond are among the promising qubits for quantum computing and information processing. In particular, the silicon vacancy (SiV) and germanium vacancy (GeV) centers are outstanding emitters due to their long spin coherence times and narrow optical transitions. Here, we describe the design and fabrication of diamond waveguide arrays containing single SiV and GeV centers coupled to aluminum nitride photonic circuits. A high-yield qubit creation process along with deterministic photonic nanofabrication produces unity coupling of emitters to single-mode diamond waveguide arrays. These arrays are subsequently assembled on aluminum nitride photonic waveguide arrays for on-chip routing and manipulation of photons. The combination of these advances allows the initial demonstration of a 72-channel solid-state spin qubit microphotonic chip for large-scale manipulation of quantum information.

9:45 AM MQ02.03.07
Narrow Optical Linewidths in Implanted Erbium Ions Paul Stevenson, Christopher M. Phenicie, Sacha Welinski, Brendon C. Rose, Stephen A. Lyon, Robert J. Cava, Nathalie P. de Leon and Jeffrey Thompson; Princeton University, United States

Erbium ions are a promising resource for long-range quantum communication applications. Optical transitions operating at 1.5μm minimize propagation loss in optical fibers, enabling communication on the 100 km scale, while electron and nuclear spin degrees of freedom can be used as a local quantum memory. However, currently known hosts for Er$^{3+}$ ions contain atoms with nonzero nuclear spin, which leads to magnetic noise that dephases the Er$^{3+}$ electron spin.

We present a new approach to incorporating Er$^{3+}$ into nuclear spin free materials via ion implantation while achieving narrow (~4GHz) inhomogeneous optical linewidths. By implanting Er$^3$ into crystalline hosts of appropriate symmetry, we are able to significantly reduce the effect of inhomogeneous broadening on the optical linewidths, observing few GHz linewidths prior to thermal processing. We use a hybrid optical-ESR technique to unambiguously relate optical and spin degrees of freedom in the system. These results present a general route forward for incorporating Er$^{3+}$ and other ions into non-standard crystalline hosts.
10:00 AM BREAK

10:30 AM *MQ02.03.08
Long Distance Quantum Networks Based on Color Centers in Diamond  Nathalie P. de Leon; Princeton University, United States

Color centers in diamond are promising candidates for quantum networks, as they can serve as solid state quantum memories with efficient optical transitions. Prior work has focused on the NV- center in diamond, which exhibits long spin coherence times and has narrow, spin-conserving optical transitions. However, the NV- center is prone to spectral diffusion, and over 97% of emission is in an incoherent phonon side band, severely limiting scalability. Alternatively, SiV- exhibits excellent optical properties, with 70% of its emission in the zero phonon line and a narrow inhomogeneous linewidth. However, SiV- suffers from significant interaction with phonons, with spin coherence times limited by an orbital relaxation time (T1) of around 40 ns at 5 K.

Informed by the limitations of NV- and SiV-, we have developed new methods to control the diamond Fermi level to stabilize the neutral charge state of SiV, thus accessing a new spin configuration. SiV0 exhibits a spin T1 of around 1 minute at 4 K, coherence time (T2) approaching 1 second, over 90% of emission in the zero phonon line, and near-transform limited optical linewidths, making it a promising candidate for applications in quantum networks.

11:00 AM MQ02.03.09
Magneto-Optical Properties of Neutral Group-IV Vacancy Color Centers in Diamond from First Principles  Adam Gali1,2 and Gergo Thiering1; 1Hungarian Academy of Sciences, Hungary; 2Budapest University of Technology and Economics, Hungary

The neutral silicon-vacancy color center has S=1 spin with long longitudinal spin relaxation time, close-to-unity Debye-Waller factor, and its optical transition is intrinsically resistant against stray electric fields. These properties are attractive in quantum communication applications. Unlike the negatively charged silicon-vacancy color centers, the magneto-optical properties of the neutral silicon-vacancy center is not well understood. Furthermore, the other neutral XV split-vacancy complexes in diamond, where X and V labels a group-IV impurity atom of X = Si, Ge, Sn, Pb and the vacancy, are practically unknown, although the negatively charged counterparts can be fabricated in diamond.

Our first principles calculations reveal the charge state stability of the neutral XV split-vacancy complexes in diamond which may guide the experiments to create these centers. In addition, we develop and apply ab initio theory to quantify the strength of electron–phonon coupling for neutral XV complexes in diamond, and find a significant impact on the corresponding optical properties of these centers. Our results show good agreement with recent experimental data on the prospective neutral SiV quantum bit, and reveals the complex nature of the excited states of neutral XV color centers in diamond. We predict the zero-phonon-line of neutral XV color centers in diamond and other magneto-optical properties.

Support from UNKP-17-3-III New National Excellence Program of the Ministry of Human Capacities of Hungary, the National Research Development and Innovation Office of Hungary within the Quantum Technology National Excellence Program (Project Contract No. 2017-1.2.1-NKP-2017-00001), and the European Commission of H2020 ASTERIQS project (Grant No. 820394) is acknowledged. We thank the National Information Infrastructure Development Program for the high-performance computing resources in Hungary.

11:15 AM MQ02.03.10
A 72-Channel Diamond Quantum Memory Array Integrated in a Microphotonic Chip  Noel Wan1, Tsung-Ju Lu1, Kevin C. Chen1, Michael Walsh1, Matthew Trusheim1, Lorenzo De Santis1, Eric Biersin1, Isaac Harris1, Sara Mouradian1, Edward Bielejec2 and Dirk R. Englund3; 1Massachusetts Institute of Technology, United States; 2Sandia National Laboratories, United States

Optically active spins coupled to single-mode diamond optical waveguides are efficient spin-photon interfaces for quantum networks. In a previous abstract, we described the unity creation, coupling and integration of single silicon vacancy (SiV) and germanium vacancy (GeV) in diamond waveguide arrays with a large-scale photonic integrated
circuit (PIC) in aluminum nitride. Here, we present the detailed characterization of our 72-qubit quantum memory chip. Single-photon emission from 72 distinct optical channels are routed in the PIC and coupled to optical fibers. We performed low-temperature laser spectroscopy of the emitters, confirming that lifetime-limited optical transitions from both SiV and GeV centers are preserved following nanofabrication, micromanipulation and heterogeneous integration. With qubit energy and spin control, this fiber-coupled quantum photonic circuit establishes the prospects for high-efficiency, multiplexed quantum repeaters on a chip.

11:30 AM MQ02.03.11
Noise Resilient Entanglement Creation of Remote Quantum Memories Hyeongrak Choi and Dirk Englund; Massachusetts Institute of Technology, United States

Entanglement is a core component in quantum information science including quantum computing and quantum repeater. Indistinguishability of two sub-systems is a prerequisite for measurement-based entanglement, and thus, its creation process is very susceptible to any kinds of local noise. In this work, we propose a noise resilient entanglement protocol based on detuned Rayleigh scattering of photons from atomic memories. In principle, near unity fidelity is possible in the presence of noise, and only limited by the energy splitting of state selective transitions. The protocol make use of a cyclic transition and is compatible with ancillary memory spins such as nuclear spins. The combination of these properties enables fault-tolerant quantum repeater with quantum error correcting nodes.

11:45 AM MQ02.03.12
Ab Initio Radiative Lifetime of Point Defects in Hexagonal Boron Nitride Shiyuan Gao, Hsiao-Yi Chen and Marco Bernardi; California Institute of Technology, United States

Point defects in hexagonal boron nitride (hBN) have recently emerged as potential single-photon emitters due to their high brightness, strong zero-phonon line and room temperature stability. However, the atomic structures of the point defects to which light emission in hBN has been attributed are still unknown. Several candidate defect structures have been proposed using density-functional theory (DFT) calculations, which have so far focused on the defect formation energy, structure, symmetry, and electronic energy levels; yet, direct comparisons with experiments remain inconclusive. In this talk, we present first-principles calculations of the optical excitation energy and radiative lifetimes of various defects in monolayer hBN; our results are obtained from DFT plus the GW-Bethe-Salpeter Equation (BSE) method, which properly accounts for dielectric screening and excitonic effects, and can provide accurate radiative lifetimes. We find that the radiative lifetimes of various defect structures can differ by an order of magnitude due to microscopic details such as the defect optical transition dipoles and spin polarization. We identify several defects with optical transitions close to the 2 eV value found in experiments, including an NV-like defect with a two-level structure with 2.4 eV optical transition and a 72 ns radiative lifetime, as well as defects with ~20 ns radiative lifetimes. Our results provide a new approach for identifying promising defect structures for single photon emitters and quantum technology applications.
materials and epitaxial synthesis techniques that can yield quantum engineered hybrid materials platforms of interest in this context. Examples include magnetically-doped topological insulators that host robust quantum anomalous Hall insulator or axion insulator phases [2] and oxide-topological insulator interfaces that allow erasable spatial patterning of magnetic and chemical potential landscapes at the mesoscale [3]. Finally, we provide a perspective on the potential opportunities and the daunting challenges for experimentally realizing topological quantum computing platforms using these hybrid quantum materials [4].

Supported by the Penn State 2DCC-MIP under NSF grant (DMR-1539916).


2:00 PM MQ02.04.02
Quantized Superconductor-Semiconductor Nanowire Junctions Sabbir A. Khan1, Ajuan Cui1, Charalampos Lampadaris1, Martin E. Cachaza1, Jung-H. Kang1, Lukas Stampfer2, Joachim E. Sestoft2, Filip Krizek2, Yu Liu1, Thomas S. Jespersen2 and Peter Krogstrup1; 1University of Copenhagen, Denmark; 2Niels Bohr Institute, University of Copenhagen, Denmark

One-dimensional hybrid superconductor/semiconductor (SU/SE) nanowires are promising material platforms for gatable superconducting device measurements.1,2 In this research we grow stacking-faults-free InAs, InSb and InAs0.3Sb0.7 nanowire networks with epitaxial Al shadowed junctions in single-step growth process using molecular beam epitaxy (MBE). We compare different material systems and discuss associated pros and cons. We also study the formation of superconductor/semiconductor junctions and characterize the structural and electrical properties of the junctions. We show optimized junctions provide enhanced transport properties exhibiting repeatable quantized conductance for all three type of wires and potential host for Majorana bound states. Furthermore, we characterize both in-situ and post-growth processed junctions in a single nanowire and demonstrate in-situ SU-SE junctions exhibit clean surface morphology and enhanced electrical transport.

References

The project was supported by the European Union Horizon 2020 research and innovation program under the Marie-Curie grant agreement No 722176, Microsoft Station Q, the European Research Council (ERC) under the grant agreement No.716655 (HEMs-DAM), and the Microsoft Quantum project.

2:15 PM OPEN DISCUSSION

2:30 PM MQ02.04.04
Evidence for Helical Hinge Zero Modes in an Fe-Based Superconductor Mason Gray1, Josef Freudenstein1, Shu Yan F. Zhao2, Ryan O’Connor1, Samuel Jenkins1, Narendra Kumar1, Marcel Hoek1, Abigail Kopec1, Takashi Taniguchi3, Kenji Watanabe3, Ruidan Zhong4, Genda Gu4 and Kenneth Burch1; 1Boston College, United States; 2Harvard University, United States; 3National Institute for Materials Science, Japan; 4Brookhaven National Laboratory, United States

Combining topology and superconductivity provides a powerful tool for investigating fundamental physics as well as a route to fault-tolerant quantum computing. There is mounting evidence that the Fe-Based Superconductor FeTe0.55Se0.45 (FTS) may also be topologically non-trivial. Should the superconducting order be s±, then FTS could be a higher order topological superconductor with Helical Hinge Zero Modes (HHZM). To test the presence of these modes we’ve fabricated normal-metal/superconductor junctions on different surfaces via 2D atomic crystal
heterostructures. As expected, junctions in contact with the hinge reveal a sharp zero-bias anomaly that is absent when tunneling purely into the c-axis. Additionally, the shape and suppression with temperature are consistent with highly coherent modes along the hinge, and are incongruous with other origins of zero bias anomalies. Furthermore, additional measurements with soft-point contacts in bulk samples with various Fe interstitial contents demonstrate the intrinsic nature of the observed mode. Thus we provide evidence that FTS is indeed a higher order topological superconductor.

2:45 PM MQ02.04.05
Computational Database of Topologically Non-Trivial Materials Using Spin-Orbit Spillage Kamal Choudhary; National Institute of Standards and Technology, United States

The Majorana fermion based topological quantum computing (QC) has immense potential for decreasing decoherence, which is one of greatest challenges for conventional QC. However, very few topological materials are known to date. To accelerate the identification of topological materials, we present a novel methodology to identify topologically non-trivial materials based on band inversion induced by spin-orbit coupling (SOC) effect. Specifically, we compare the density functional theory (DFT) based wavefunctions with and without spin-orbit coupling and compute the ‘spin-orbit-spillage’ as a measure of band inversion. Due to its ease of calculation, without any need for symmetry analysis or dense k-point interpolation, the spillage is an excellent tool for identifying topologically non-trivial materials. Out of 30000 materials available in the JARVIS-DFT database, we applied this methodology to more than 4835 non-magnetic materials consisting of heavy atoms and low bandgaps. We found 1868 candidate materials with high-spillage (using 0.5 as a threshold). We validated our methodology by carrying out conventional Wannier-interpolation calculations for 289 candidate materials. We demonstrate that in addition to $Z_2$ topological insulators, this screening method successfully identified many semimetals and topological crystalline insulators. Importantly, our approach is applicable to the investigation of disordered or distorted as well as magnetic materials, because it is not based on symmetry considerations. We discuss some individual example materials, as well as trends throughout our dataset, which is available at the websites: https://www.ctcms.nist.gov/~knc6/JVASP.html and https://jarvis.nist.gov/.

3:00 PM BREAK

SESSION MQ02.05: Superconducting Quantum Devices
Session Chairs: Hanhee Paik and Ben Palmer
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 202

1:30 PM *MQ02.05.01
Low Loss Superconducting Circuits for Quantum Computing Vivekananda Parampalli Adiga; IBM T.J. Watson Research Center, United States

Low loss microwave circuits are an essential ingredient that enables superconducting quantum processors. Most of the present day superconducting quantum computers rely on qubits and resonators with long life times to demonstrate basic quantum computing applications. To reach the goal of a fault tolerant universal quantum computer with superconducting circuits, coherence times still need to improve several orders of magnitude. Some improvements will likely come from better designs, fabrication processes, and materials used to build quantum processors. In this talk I will discuss the history of coherence improvements in qubits and current challenges in achieving low loss quantum circuits.

2:00 PM *MQ02.05.02
Materials Developments for Superconducting Quantum Circuits David Pappas; National Institute of Standards and Technology, United States

Rapid progress in being made towards optimizing materials to increase coherence superconducting quantum circuits. In particular, both intrinsic and extrinsic materials and effects have been studied. In the former, new techniques to
study the effects of dielectric loss and the role of defects in and around junctions have been devised as well as new ideas for mitigating these effects and designing new types of qubits. For the latter, extrinsic causes of decoherence including the effects of radiation, quasiparticles, piezoelectricity, trapped flux, and excess photons. In this talk a general review of coherence and fabrication techniques for this circuits will be given with a few examples from the general literature. So of our work on intrinsic effects will be discussed, including studies of long-term measurements of highly coherent, non-tunable superconducting transmon qubits. Measurements of relaxation and dephasing are used to understand the low-frequency burst noise in coherence times and qubit transition frequency, leading to information about the microscopic origin of the intrinsic decoherence mechanisms in Josephson qubits. Progress towards a test-bed for studying loss in superconducting resonators and the associated analysis and interpretations will be presented. Interlaboratory comparisons of these analysis will be presented.

2:30 PM BREAK

SESSION MQ02.06/MQ01.06/MQ03.06: Panel Discussion: Quantum Materials
Session Chairs: Jeffrey McCallum and Christopher Richardson
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 202

3:30 PM PANEL DISCUSSION: QUANTUM MATERIALS

SESSION MQ02.07: Silicon and Germanium Materials for Qubits
Session Chairs: Dohun Kim and Hanhee Paik
Thursday Morning, December 5, 2019
Hynes, Level 2, Room 202

8:30 AM MQ02.07.01
Growth and Characterization of a Novel Si/SiGe Heterostructure for Quantum Dot Qubits Thomas W. McJunkin1, Evan R. MacQuarrie1, Samuel F. Neyens1, Brandur Thorgrimsson1, Joelle Corrigan1, John P. Dodson1, Leah Tom1, Donald E. Savage1, Max G. Lagally1, Robert Joynt1, Mark Friesen1, Susan N. Coppersmith1,2 and Mark A. Eriksson1; 1University of Wisconsin–Madison, United States; 2University of New South Wales, Australia

In recent years, silicon-based quantum dots have been shown to be a promising avenue for quantum computing. However, the near-degeneracy of the two low-lying valley states in silicon quantum wells can inhibit the formation of distinct quantum states. Motivated by the desire to increase the magnitude and tunability of this valley splitting, a Si/SiGe heterostructure is grown with a thin layer of SiGe embedded within the silicon quantum well. The Si/SiGe heterostructure is grown via UHV-CVD on a linearly graded SiGe alloy with a final germanium concentration of 29%. STEM measurements reveal the quantum well structure to consist of a ~10 nm silicon layer, followed by a thin ~1 nm SiGe layer, and subsequent ~2 nm layer of pure silicon. Above this quantum well, a ~35 nm layer of SiGe with 29% germanium is grown to separate the quantum well from the surface. The intent of this ~1 nm layer of SiGe, positioned just below the upper interface of the quantum well, is to modify the valley splitting of electrons in a 2-dimensional electron gas (2DEG) that reside near this interface. By varying an external vertical electric field, the electron wavefunction can be moved on and off this spike in germanium concentration, modifying the magnitude of the valley splitting.

We report electronic measurements of both Hall bars and electrically gated quantum dot devices that are fabricated on this heterostructure. Shubnikov-de Haas (SdH) and quantum Hall (QH) measurements reveal a peak transport mobility in excess of 100,000 cm²/(V s) at 6 x 10¹¹ cm⁻² carrier density. We report SdH and QH measurements over a wide range of carrier density and magnetic field in the form of a fan diagram. Valley splitting values are measured in the quantum dot device by magneto-spectroscopy, in which a few-electron dot transition is measured while an in-plane magnetic field is swept. Measuring at the second, third, and fourth electron transition in the quantum dot, we find valley splittings of 29, 48, and 65 μeV, respectively. To measure tunability of valley splitting, nearby gate
voltages are changed to vary the vertical electric field at constant charge occupation. We find that both the lowest lying valley splitting and the valley splitting in the first excited orbital can be tuned over a factor of 2 by means of such changes in gate voltage. Additionally, we report modeling of the applied electric field at the dot in support of experimental results.

8:45 AM *MQ02.07.02
Isotope Materials Engineering for Silicon Quantum Computing Kohei M. Itoh; Keio University, Japan

A series of recent high-impact researches on silicon-based quantum computers [1] has proven that it is crucial to prepare high quality silicon matrixes that are free of background nuclear spins. For example, electron spin qubits placed in a natural silicon substrate decoher quickly due to their interaction with background $^{29}$Si nuclear spins that exist with the natural abundance of 4.7%. On the other hand, electron spin qubits placed in zero-nuclear-spin $^{28}$Si stable isotope matrixes show much extended coherence time leading to increase in the possible quantum gate operation number and gate fidelity [1].

This talk will review the state-of-the-art in silicon isotope materials engineering [2] followed by in-depth discussions on how not only the background $^{29}$Si nuclear spins but also the mass fluctuation caused by co-existence of $^{28}$Si, $^{29}$Si, and $^{30}$Si isotopes can affect the properties of both electron and nuclear spin qubits placed in silicon. While majority of the results that will be presented are obtained in the present author’s group, some significant and relevant results achieved under the projects supported by the MEXT - Quantum Leap Flagship Program in Japan are also introduced.

This work has been supported by the Center for Spintronics Research Network, Keio University. The author acknowledges fruitful collaborations with Satoru Miyamoto, Noritaka Usami, Yusuke Hoshi, Seigo Tarucha’s group, Mark Eriksson’s group, Andrew Dzurak’s group and Andrea Morello’s group.


9:15 AM *MQ02.07.03
Quantum Computing with Silicon and Germanium Menno Veldhorst and Luca Petit; Delft University of Technology, Netherlands

Semiconductor quantum dots constitute a promising platform for quantum computation. More than two decades of intensive research has led to impressive demonstrations of single-shot initialization and readout, coherent control, and coupling of single electron spins. Group IV materials have emerged as leading platforms, since they can be isotopically enriched to remove nuclear spin decoherence to provide excellent quantum coherence.

I will present our efforts on silicon and germanium quantum devices and discuss the opportunities in these systems. In silicon, these include operation at elevated temperatures for hot-qubit operation, enabling to integrate classical electronics on the same chip for scalability and superior control. In germanium, I will show fast single and two qubit logic, and semiconductor-superconductor devices for novel hybrid quantum hardware. Moving forward, I will discuss our vision to increase the number of qubits toward practical quantum information.

9:45 AM MQ02.07.04
Transport in Ultra-Scaled Ge Quantum Dots Masiar Sistani1, Jovian Delaforce2, Cecile Naud2, Roman Kramer2, Olivier Buisson2, Minh Anh Loung2, Martien Hertog2 and Alois Lugstein1; 1Technische Universität Wien, Austria; 2Université Grenoble Alpes, France

Metal-semiconductor-metal heterostructures are attractive for both fundamental studies of low-dimensional nanostructures as well as future high-performance low power dissipating nanoelectronic and quantum devices. Most notably, they bear enormous potential for a vast array of key components for quantum computing such as SQUIDs, oscillators, mixers and amplifiers. In this context, combining high carrier mobilities and leveraging strong quantum
confinement effects due to a more than five times larger exciton Bohr radius compared to Si, Ge occupies an exceptional position for the development of novel quantum devices in the post Si era. Here, we demonstrate that utilizing a thermally induced exchange reaction between single-crystalline Ge nanowires and Al pads, monolithic Al-Ge-Al nanowire heterostructures with ultra-small Ge segments contacted by self-aligned, quasi-1D, crystalline Al leads can be fabricated without lithographic constraints. High-resolution transmission electron microscopy and energy dispersive X-ray spectroscopy proved the composition and perfect crystallinity of these metal–semiconductor nanowire heterostructures. Integrating such nanowire heterostructures as active channels in electrostatically gated field-effect transistor devices, provides a platform for the systematic investigation of electrical transport mechanisms in ultra-scaled Ge nanowires. In contrast to common short channel devices, the 1D monolithic metal-semiconductor-metal architecture effectively prevents screening of the gate electric field by lithographically defined contacts and thus enables perfect electrostatic control of field effect devices. We will demonstrate ballistic transport as well as quantum ballistic transport phenomena, which were systematically investigated depending on the Ge channel length and nanowire diameter. Temperature depending measurements in the range between 5 K and 300 K of the resistivity and gate-dependent conductance measurements including a detailed bias spectroscopy study revealed transport through spin-degenerate 1D sub-bands in ultra-scaled Ge channels up to room temperature. Finally, we will present low temperature (400 mK) DC spectroscopy measurements, revealing the high gate-tunability of hole transport in ultra-scaled Ge channels monolithically integrated in Al-Ge-Al nanowire heterostructures. In particular, we will show the ability to tune the Ge segment from a completely insulating regime, through a low conductive regime, that exhibits properties of a single-hole transistor, to a superconducting regime, resembling a Josephson field effect transistor with a maximum critical current of 15 nA. The experimental proof of exchanging Cooper-pairs between superconducting Al leads through a gate-tunable Ge channel, mediated by the superconducting proximity effect is the first demonstration of superconductivity induced in a pure Ge channel.

10:00 AM BREAK

10:30 AM MQ02.07.05
Measurement of the Strain Induced Modulation of Tunnel Barriers in Nanoscale Silicon Quantum Devices
Ryan Stein1,2, Joshua Pomeroy3, Neil M. Zimmerman3 and M. D. Stewart4; 1University of Maryland, United States; 2Joint Quantum Institute, United States; 3National Institute of Standards and Technology, United States

For quantum dots (QD) in the silicon MOS system, the local potential is a defining factor in device performance. Silicon-based devices experience a local potential modulation at the edge of lithographically defined gates due to mechanical strain. The strain originates in the mismatch of the coefficient of thermal expansion (CTE) between silicon and the gate material as well as the intrinsic strain from the deposition process. The resulting potential modulation is large enough to alter the tunnel coupling or induce unintentional QDs at low temperatures. Here, we present measurements of the barrier height in tunnel junction devices defined by aluminum and titanium gates. These measurements reveal the difference in barrier height between the two materials due to strain. Our results agree with COMSOL simulations which use the CTE value achieved in the deposition and strongly disagree with simulations which use the bulk CTE value. These results show that using simulations alone as a guide towards improving devices performance is inadequate thus highlighting the need for more experimental work.

10:45 AM MQ02.07.06
Atomically Sharp, Tensile Strained Ge Light-Hole Quantum Well on Si
Simone Assali, Aashish Kumar, Samik Mukherjee, Jérôme Nicolas, Patrick Del Vecchio, Anis Attiaoui and Oussama Moutanabbir; Ecole Polytechnique de Montreal, Canada

Highly tensile strained Ge quantum well (QW) is a long-sought-for low-dimensional system to investigate and develop hole spin-based qubits and high hole mobility electronics. Under tensile in-plane biaxial strain, light-hole (LH) occupies the top of the valence band and the LH-HH splitting can exceed 100s meV. Moreover, when the tensile in-plane biaxial strain exceeds 1.5% only LH is confined in the QW thus minimizing LH-HH interactions. With this perspective, this work provides the first experimental demonstration of the epitaxial growth of tensile strained Ge QW on Si substrates. Sn-rich GeSn layers are used as barriers to achieve high tensile in-plane biaxial strain and engineering the band structure for LH confinement. We will discuss the epitaxial growth of this tensile-strained GeSn/Ge/GeSn heterostructure exhibiting atomically-sharp interfaces and in-plane biaxial strain above 1.5
% grown on a lattice-mismatched Ge$_{0.86}$Sn$_{0.14}$ substrate. The sharpness of the interfaces across the Ge/GeSn heterostructure will be addressed using EELS and atom probe tomography (APT) measurements. A tunable s-Ge layer thickness ranging from ~13 nm down to ~1.2 nm is achieved. The pseudomorphic nature of the s-Ge layer will be discussed based on TEM/STEM and XRD-RSM measurements, while dislocations are mainly observed in the low Sn content buffer layers.[1,2] Ongoing work focuses on band structure calculations and low-temperature magneto-electric transport measurements to probe the confined LH states in the grown s-Ge QWs.[3]

References

11:00 AM *MQ02.07.07
Single and Two Spin Qubits with High Fidelity Limited by Environment Noise in Si Quantum Dots
Seigo Tarucha; RIKEN, Center for Emergent Matter Science, Japan

To date various materials have been used to fabricate spin qubit devices for quantum computation. Some devices are advantageous for fast qubit operations and others for low noise operations or weak decoherence. Among them isotopically purified silicon is one of the appropriate choices to achieve high-fidelity in single and two-qubit gates. So far we have used quantum dots (QDs) made in GaAs, natural Si/SiGe, and isotopically purified 28Si/SiGe materials to implement high-fidelity spin qubits and study the decoherence mechanisms. Decoherene generally arises from coupling of spin to the environment, which is a source of magnetic and charge noise. In this talk I will first discuss the noise source to the electron spin in the GaAs, natural Si, and 28Si QDs equipped with a micro-magnet. We measure the noise dynamics of the environment to fluctuate the Zeeman field or Larmor precession on the spin, and assign the fidelity limiting factor to nuclear spin noise in GaAs and natural Si, while 1/f-like charge noise in 28Si. For the 28Si/SiGe the highest fidelity of 99.93% has been achieved, and to further raise the fidelity it is crucial to eliminate the charge noise. We have developed a feedback technique to suppress the low frequency magnetic noise in GaAs QDs, and then observed enhancement of the decoherence time but limited by the 1/f-like charge noise same as in 28Si/SiGe QDs. Secondly I will discuss cross-correlated noise in Si QD spin qubits. We used the Ramsey interference protocol to evaluate the power spectral densities of correlated and anti-correlated noise between two Rabi frequencies. We observed positively cross-correlated noise in the low-frequency range. Such noise correlation between qubits may influence two-spin entanglement control and quantum error correction performance.

11:30 AM MQ02.07.08
A Group IV Platform for Light-Hole Qubits
Patrick Del Vecchio, Anis Attiaoui, Simone Assali and Oussama Moutanabbir; École Polytechnique de Montréal, Canada

For decades, Si-compatible low-dimensional systems and quantum devices have been exploiting either tensile strained Si or compressively strained Germanium (Ge) quantum wells (QWs), which are the only group IV systems that can currently be routinely obtained using SiGe as growth template and barrier layers. For quantum information, the former has been used as the building block for electron spin qubits, whereas the latter has been explored in new schemes for hole spin qubits. Herein, we present a third low-dimension system consisting of highly tensile strained Ge QW integrated on an optically active platform and discuss its basic properties experimentally and theoretically. The growth of tensile strained Ge QW is achieved using direct bandgap GeSn as barrier layers grown on silicon wafers. This heterostructure yields high tensile strain in Ge QW and band structure corresponding to a sizable light hole-heavy hole (LH-HH) splitting exceeding 100 meV. Unlike compressively strained Ge, the top of the valence band is occupied by LH in tensile strained Ge. Interestingly, by tuning the tensile strain above 1.5%, only LH can be confined in the QW and LH-HH mixing can be strongly reduced. We also found a high LH g-factor anisotropy in the GeSn/Ge/GeSn QW, with $g = 21.8$ for in-plane B-field and $g = 0.69$ for perpendicular-to-plane field.

These properties lay the groundwork to implement LH spin qubits with potentially easier manipulation due to the combined effects of the large Rashba-type spin-orbit interaction (SOI), the absence of Dresselhaus SOI, and the spin $\frac{1}{2}$ of LH. Indeed, for quantum computing, tensile strained Ge QW combines all the sought-for advantages of Ge in...
qubits including: (i) high hole mobility; (ii) holes have much stronger spin-orbit coupling, which can be exploited to achieve much faster spin manipulations; (iii) the fourfold degeneracy of the valence band, which is not compatible with the two-level system at the core of quantum system, is eliminated by introducing strain and quantum confinement in the QW. This leads to a reduced hole effective mass and a large intrinsic splitting between LH and HH bands, which can enable high mobilities and tunnel rates in addition to eliminating the need for smaller quantum dot size; and (iv) a reduced hyperfine interaction with surrounding nuclear spins for improved quantum coherence as Ge can be purified to remove nuclear spin-full $^{73}$Ge impurities.

Ongoing work includes transport measurements of the fabricated QWs, which will give a clear description of the hole mobility within the structure. Additionally, a detailed discussion of the mechanisms of spin manipulation within such heterostructures will be presented, including various spin manipulation schemes such as EDSR and g-tensor modulation resonance.

11:45 AM MQ02.07.09
InAs-EuS-Al Hybrid Nanowires Yu Liu and Peter Krogstrup; University of Copenhagen, Denmark

Material development holds promise as the basis of topological quantum computing with Majorana fermions. These quasiparticles have been predicted to be formed in semiconductor nanowires coupled to conventional superconductors. This prediction was followed by a series of experiments providing strong evidence. However, in the current system, an external magnetic field along the NW axis is always needed to realize Majorana states.

Therefore, in order to integrate and scale up qubit devices, it is aimed to induce a self-sustaining parallel magnetic field on semiconductor–superconductor hybrid NWs. Composite materials using ferromagnetic insulators (FMIs) in close proximity to a semiconductor – superconductor structure have been proposed as a solution to reach a zero-field topological state, where the effective Zeeman splitting is induced by an magnetic exchange coupling by the FMI. In this work, we grow epitaxial semiconductor – ferromagnetic insulator – superconductor InAs-EuS-Al hybrid nanowires in-situ in the molecular beam epitaxy system. The results show the superconducting hard gap, the hysteretic evolution of density of states as a function of magnetic field and the shape-defined magnetic single domain structures based on well-controlled epitaxy, which suggests that this highly ordered material system is a promising platform for scalable topological quantum computing.

References
of 600 mK. We compare the measured $Q$ data to a model based on loss from the interaction of the superconducting resonator with lossy two-level systems and separately to a model we have developed based on non-equilibrium quasiparticles accumulating in regions of the TiNx film with a lower superconducting gap (D). To distinguish between these competing models, we will also discuss results where we apply superconducting pair-breaking infrared light directly to the resonator device and measure the loss.

8:30 AM MQ02.08.02
(S)TEM Characterization of Josephson Junctions in Qubits Xiaotao Liu1, John M. Kreikebaum2, Stefano Cabrini1, Frank Ogletree1, Virginia P. Altoe1, Irfan Siddiqi2 and Andrew M. Minor2,1; 1Lawrence Berkeley National Laboratory, United States; 2University of California, Berkeley, United States

The development of predictable superconducting circuits incorporating Josephson Junctions (J-Junctions) is essential for developing scalable quantum computing devices. Here we report on atomic resolution analysis of J-Junctions consisting of two polycrystalline Al layers separated by a barrier layer of amorphous AlOx. Samples were also probed with analytical (S)TEM techniques such as EDS and EELS, and correlated with the performance of the device. Our results demonstrate that both the top-Al and the bottom-Al layers comprise columnar grains of around 30 nm with a AlOx barrier layer approximately 3-5 nm thick. Our analysis will discuss how the e-beam evaporation process effects the microstructure of the resulting layers. For instance, the roughness of the Al/AlOx interface seems to be related to grain boundaries in the Al layers. The effect of residual strain will also be discussed, correlated with device performance and analysis of the local strain field with scanning nanobeam diffraction (4D-STEM).

8:45 AM MQ02.08.03
Evidence for Majorana Bound States in an Iron-Based Superconductor Shivu Zhu1, Dongfei Wang1, Lingyuan Kong1, Peng Fan1, Hui Chen1, Wenyao Liu1, Lu Cao1, Yujie Sun1, Yuyang Zhang1, Shixuan Du1, John Schneeloch2, Ruidan Zhong2, Genda Gu2, Liang Fu3, Hong Ding1 and Hong-Jun Gao1; 1Institute of Physics and University of Chinese Academy of Sciences, Chinese Academy of Sciences (CAS), China; 2Brookhaven National Laboratory, United States; 3Massachusetts Institute of Technology, United States

Majorana bound states (MBSs) are spatially-localized zero-energy fractional quasiparticles with non-Abelian braiding statistics that hold great promise for topological quantum computing. By using scanning tunneling microscopy/spectroscopy (STM/STS), here we report the observation of MBSs in a single material platform of high-$T_c$ iron-based superconductors, FeTe$_{0.55}$Se$_{0.45}$, which combined advantages of simple material, high-$T_c$, and large ratio of $\Delta/\Delta_F$. We observed a sharp zero-bias peak inside a vortex core that does not split when moving away from the vortex center. The evolution of the peak under varying magnetic field, temperature, and tunneling barrier is consistent with the tunneling to a nearly pure MBS, separated from nontopological bound states [1]. We further investigated the MBS and observed a conductance plateau feature, which is protected by the Majorana particle-hole symmetry [2]. The observations not only prove a strong evidence of MBSs in this iron-based superconductor, but also offer a single-material platform for Majorana braiding at relatively high temperature.


9:00 AM *MQ02.08.04
Anomalous Charge Noise in Superconducting Qubits Robert McDermott; University of Wisconsin-Madison, United States

We have used Ramsey tomography to characterize charge noise in a weakly charge-sensitive superconducting qubit. We find a charge noise that scales with frequency as $1/f^\alpha$ over 5 decades with $\alpha = 1.93$ and a magnitude $S_q(1 \text{ Hz}) = 2.9 \times 10^4 \text{ e}^2/\text{Hz}$. The noise exponent and magnitude of the low-frequency noise are much larger than those seen in prior work on single electron transistors, yet are consistent with reports of frequency noise in other superconducting qubits. Moreover, we observe frequent large-amplitude jumps in offset charge exceeding $0.1e$; these large discrete charge jumps are incompatible with a picture of localized dipole-like two-level fluctuators. The data reveal an unexpected dependence of charge noise on device scale and suggest models involving either charge drift or fluctuating patch potentials. We describe follow-on experiments to systematically explore the dependence of charge noise on device geometry.
9:30 AM MQ02.08.05
Demonstrating Ultra-Stable Aluminum Oxide SETs as Potential Charge Sensors for Quantum Computing
Yanxue Hong1,2, Ryan Stein1,2, Neil M. Zimmerman2, M. D. Stewart2 and Joshua Pomeroy2; 1University of Maryland, United States; 2National Institute of Standards and Technology, United States

In spin-based quantum computing, the spin readout is achieved through spin-to-charge conversion and single-electron charge detection. Often, single-electron transistors (SETs) capacitively coupled to the qubit are used for sensing the charge transition. Since the SET control curve is sensitive to the electrostatic environment, the local charge stability is of great importance. Although metallic SETs are simple to fabricate, historically they were found to be very unstable, preventing use as charge sensors. We revisit this challenge by using plasma oxidized aluminum oxide (AlOx) tunnel barrier based SETs. We have successfully overcome the charge offset drift issue previously seen in metallic Al/AlOx/Al SETs. The long-term charge stability presented here are better than any other reported metallic SETs, with standard deviation of ≪ 0.01 e over 7.5 days. To evaluate the charge sensing ability, we plan to couple the plasma oxidized Al/AlOx/Al SET to a quantum dot and sense the charge of the quantum dot. By modeling in FastCap and using the data, a 1 e charge change on the quantum dot will cause a measurable current shift in the SET control curve. This charge sensing measurement will be a significant step for the application of ultra-stable Al/AlOx/Al SETs in a quantum computing architecture.

9:45 AM BREAK

10:15 AM MQ02.08.06

Phosphorus dopants placed with atomic precision using scanning tunneling microscopy-based hydrogen depassivation lithography on silicon (Si:P) have long been considered a leading pathway to both high-performance conventional and quantum electronic devices. However, the realization of practical Si:P device architectures requires low processing temperatures to keep the carefully placed dopants from diffusing.

Among recent developments in the field are advanced molecular beam epitaxy (MBE) techniques and integration of microfabrication processes like ion implantation and surface gates. Much of this effort has focused on preserving the atomic fidelity of Si:P devices by minimizing P dopant diffusion and segregation. However, the incorporation of vacancies and contaminants into both the P dopant layer and Si capping layer also significantly impacts the performance of resulting devices and must often be balanced with the need for low process temperatures. An improved understanding of the whole material system is necessary for optimization of devices and systems, particularly for integration with conventional CMOS technology.

Here, we report on the presence and influence of atomic defects in both the dopant layer and Si overgrowth, the techniques available for characterization of these defects, and the influence of defects on the properties of the resulting Si:P devices. Using a combination of optical spectroscopy, transport measurements, and transmission electron microscopy, we relate the appearance of defects in the Si:P and Si films to parameters of the fabrication process and the electronic characteristics of the resulting devices. This is directly applicable to the next generation of digital electronics at the atomic limits of precision and has implications for quantum applications.

This work was supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories, and was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. DOE, Office of Basic Energy Sciences user facility. Sandia National Laboratories is managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy under contract DE-NA-0003525. The views expressed in this abstract do not necessary represent the views of the U.S. DOE or the United States Government.

10:30 AM MQ02.08.07
Direct Probing of the Electronic Structure of Hybrid InAs/Al Interfaces Sergei Schuwalow1,2, Niels B
Hybrid epitaxial semiconductor-superconductor materials have recently shown promise as a platform for topological quantum computing applications. Targeted engineering of their key ingredient, the electronic hybridization, requires detailed understanding of the electrostatic properties, in particular the alignment between the band edges of the semiconductor and the Fermi level, in the vicinity of the interface. In this work we use a combination of angle-resolved photoelectron spectroscopy (ARPES) measurements, Schroedinger-Poisson (SP) calculations and a core level fitting procedure to obtain the band offset and other fundamental electronic structure parameters of a promising materials platform for topological Majorana devices, the buried InAs(100)/Al interface. Furthermore, we demonstrate how starting from the investigation of the pristine InAs(100) surface, this combined approach makes it possible to access the electrostatic properties of any heterostructure with the same substrate on which a sequence of core level spectra can be obtained. To verify the validity of our approach we compare the result with the first direct observation of a buried InAs/Al electron accumulation layer.

10:45 AM *MQ02.08.08
Materials and Surface Considerations for High-Fidelity Trapped-Ion Quantum Information Processing John Chiaverini; MIT Lincoln Laboratory, United States

Atomic ions arrayed and manipulated via electromagnetic fields form the basis for one of the leading candidate systems for quantum computing, with potential applications in quantum sensing and communications as well. While ion traps based on a combination of radio-frequency and static electric fields applied to microfabricated electrode structures have emerged as a powerful platform for this technology, electric-field noise originating from the electrode surfaces of small traps can limit quantum operation fidelity. Though the mechanisms behind this noise are not completely understood, recent experiments have uncovered evidence that is helping to constrain possible theories. I will describe our experimental work utilizing temperature variation and ion-milling treatment of microfabricated traps made from multiple materials in order to better understand and potentially mitigate ion heating due to electric-field noise.

11:15 AM MQ02.08.09
Supercurrent in All-Van-der-Waals Josephson Tunnel Junctions Qing Li1,1, I-Jan Wang1, Megan Yamoah1, Kenji Watanabe2, Takashi Taniguchi2, Simon Gustavsson1, Terry P. Orlando1,1, Pablo Jarillo-Herrero1 and William D. Oliver1,1,3; 1Massachusetts Institute of Technology, United States; 2National Institute for Materials Science, Japan; 3Massachusetts Institute of Technology (MIT) Lincoln Laboratory, United States

Van der Waals (vdW) materials and their heterostructures have been extensively studied and broadly applied, owing to their extraordinary and versatile electronic properties in combination with epitaxially-precise interfaces. While vdW heterostructures have been well investigated via DC transport and optical techniques, experimental exploration in the microwave regime has heretofore been relatively limited. This has left an unexplored potential for incorporating the advantages of vdW materials into the circuit quantum electrodynamics (cQED) platform of relevance to advancing quantum technologies.

Two-level-systems (TLS) are identified as a major coherence-limiting factor that exist both within and at the interface of amorphous oxide found in current qubit devices. To investigate the concentration of TLSs in vdW dielectric materials, we recently studied the microwave loss of hexagonal boron nitride (hBN), a dielectric that can be used to both encapsulate qubits and to serve as the tunneling barrier of Josephson junctions. We were able to extract a lower bound for the hBN quality factor of ~3x10^8, at least two orders of magnitude higher than that of amorphous dielectric materials such as AlOx or SiOx commonly used in current quantum devices.

Motivated by these promising results, in this work, we fabricate and characterize high-quality, all-vdW Josephson junctions, a key component in superconducting quantum circuits. VdW heterostructures consisting of 2D transition metal dichalcogenide (TMD) superconductors and thin layers of hBN are assembled together in an inert (argon-filled) environment, which promotes pristine materials with atomically flat interfaces. These procedures may significantly reduce the number of two-level-systems. We measure the vdW tunnel junction in temperature well
below the superconducting gap and characterize its DC and AC Josephson response. We expect these efforts will lead to high-coherence qubit devices with small form factors.

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SYMPOSIUM MQ03

Predictive Synthesis and Advanced Characterization of Emerging Quantum Materials
December 2 - December 5, 2019

Symposium Organizers
Alex Frano, University of California, San Diego
Mingda Li, Massachusetts Institute of Technology
Suchitra Sebastian, Cambridge University
Hua Zhou, Argonne National Laboratory

* Invited Paper

SESSION MQ03.01: Advanced in Topological Quantum Materials
Session Chairs: Mingda Li and Hua Zhou
Monday Morning, December 2, 2019
Hynes, Level 2, Room 203

8:00 AM *MQ03.01.01
Topological Physics in HgTe-Based Quantum Devices Laurens Molenkamp, Julius-Maximilians-Universität Würzburg, Germany

Suitably structured HgTe is a topological insulator in both 2- (a quantum well wider than some 6.3 nm) and 3 (an epilayer grown under tensile strain) dimensions. The material has favorable properties for quantum transport studies, i.e. a good mobility and a complete absence of bulk carriers, which allowed us to demonstrate variety of novel transport effects.

A novel development is the use of wet etching technologies to fabricate HgTe based nanostructures. This approach allows a much higher transport quality in nanodevices. We have fabricated quantum point contacts, which show remarkable spin selective transport behavior. Additionally, we have developed a gate-training technique, which pushes the scattering length for the quantum spin Hall effect well above 100 mum. A further recent development is the realization that van Hove singularities in the valence band may give rise to remarkable transport effect, such as e.g. the realization of a n=-1 quantum Hall plateau at fields as low as 20 mT.

Another regime we can study is topological superconductivity, which can be achieved by inducing superconductivity in the topological surface states of these materials. Special emphasis will be given to recent results on the ac Josephson effect. We will present data on Shapiro step behavior that is a very strong indication for the presence of a gapless Andreev mode in our Josephson junctions, both in 2- and in 3-dimensional structure. An additional and very direct evidence for the presence of a zero mode is our observation of Josephson radiation at an energy equal to half the superconducting gap.

Controlling the strain of the HgTe layers strain opens up yet another line a research. We have recently optimized MBE growth of so-called virtual substrates ((Cd,Zn)Te superlattices as a buffer on a GaAs substrate), that allow us
to vary the strain from 0.4% tensile to 1.5% compressive. While tensile strain turns 3-dimensional HgTe into a narrow gap insulator, compressive strain turns the material into a topological (Weyl) semimetal, exhibiting clear signs of the Adler-Bell-Jackiw anomaly in its magnetoresistance. In quantum wells, compressive strain allows inverted energy gaps up to 60 meV.

8:30 AM *MQ03.01.02
New Progress in Quantum Anomalous Hall Effect Qi-Kun Xue1,2; 1Tsinghua University, China; 2Beijing Academy of Quantum Information Sciences, China

The quantum anomalous Hall (QAH) effect is a quantum Hall effect induced by spontaneous magnetization, and occurs in two-dimensional insulators with topologically nontrivial electronic band structure which is characterized by a non-zero Chern number. It was first experimentally observed in the thin films of magnetically doped (Bi,Sb)2Te3 topological insulators (TIs) in 2013, more than thirty years after the discovery of the first quantum Hall effect by Klaus von Klitzing. In this talk, I will report on some recent experimental progresses in this direction. By co-doping of Cr and V into (Bi,Sb)2Te3 TI films and developing intrinsic magnetic topological insulator, we are able to significantly increase the observation temperature of QAH effect. More interestingly, we can construct other topological states of matter such as axion insulator, quantum spin Hall insulator and QAH insulator of high Chern number by growing QAH insulator-based heterostructures.

9:00 AM MQ03.01.03
Experimental Verification of Magnetic-Field-Induced Topological Phase Transition in Fe-Doped Topological Insulator (Bi,Sb)nSe3 Thin Films Junichi Shiogai1, Yosuke Satake1, Grzegorz P. Mazur2, Shojiro Kimura1, Satoshi Awaji1, Kohei Fujiwara1, Tsutomu Nojima1, Kentaro Nomura1, Seigo Souma1,2, Takaomi Sato3,4, Tomasz Dietl2,4, Qi-Kun Xue1,2; 1Tsinghua University, China; 2Beijing Academy of Quantum Information Sciences, China

Thin film synthesis of the emergent quantum materials is a prerequisite technique to observe novel topological phases such as quantum Hall [1] or quantum anomalous Hall (QAH) state [2-5] and exotic proximity effects at hetero-junction with magnets and superconductors [6]. The QAH phase accompanying a dissipation-less chiral edge channel has been achieved in one example of three-dimensional topological insulator (3D-TI), (Bi,Sb)2Te3 with a magnetic dopant Cr or V, which fulfills two requirements: (i) inducing an exchange gap by magnetic impurity doping and (ii) tuning Fermi level (EF) into the gap by electrostatic gating in a thin film form [2]. A representative 3D-TI Bi1-xSbxTe3 is another candidate platform to study such an exotic topological phase because of an inherently large bulk insulating gap [7]. However, by comparing with a well-investigated (Bi,Sb)2Te3 3D-TI compound, there has been little progress on EF tuning technique in (Bi1-xSbx)2Se3 probably owing to a low solubility limit of Sb below x ~ 0.5 [8], making it difficult to study the Dirac feature of this system by electrical transport measurements. To date, we have developed a buffer layer technique to stabilize rich Sb-doped (Bi1-xSbx)2Se3 in molecular beam epitaxy. With precise tuning of Bi/Sb composition ratio and thickness in a field-effect transistor (FET), we materialized the EF tuning across the charge neutral point (CNP) [9,10].

In this study, based on these established EF tuning techniques, we investigate magneto-transport properties of Fe-doped (Bi1-xSbx)2Se3 heterostructures. The Fe-doped sample with EF tuned around CNP behaves like an insulator at zero magnetic field. By sweeping a perpendicular magnetic field, topological phase transition emerges from Anderson insulator to QAH state [11]. A clear insulator-to-metal transition was observed in magnetoresistance with a large Hall resistance by application of a high magnetic field up to 24 T. Furthermore, a (Bi1-xSbx)2Se3-based FET exhibits the large Hall resistance approaching the quantized value (h/e2) at around 14 T. With these set of the data, we concluded that a magnetic-field-induced QAH state was verified in Fe-doped (Bi1-xSbx)2Se3 thin films. Combining well-regulated growth technique for precise tuning of EF and high-field transport measurements sheds light on the hidden topological phases in a wide variety of emerging quantum materials.

Experimental Realization of Thin-Film LaAlGe—A Type II Weyl Semimetal

Niraj Bhattarai1,2, Rajendra P. Dulal3, Andrew Forbes1,2, Christopher Gassen1,2, Ian Pegg1,2 and John Philip1,2; 1The Catholic University of America, United States; 2The Vitreous State Laboratory, United States; 3Chapman University, United States

The rare-earth based ternary compounds RAlGe (R=La, Ce, Pr) are Weyl semimetals, in which LaAlGe exhibits type II Weyl semimetal behavior with space-inversion symmetry breaking. In this article, we report the growth, characterization, and transport measurements of LaAlGe thin films grown by molecular beam epitaxy. Extensive analysis of the longitudinal resistivity shows that the system displays semimetallic behavior. An upturn at a temperature below 35 K is observed in the resistivity curve due to weak localization. Observed resistivity behavior and a leap in activation energy gap from 1.67 meV to 103 meV suggest a near room temperature semimetal-to-semiconductor transition. We also observed a positive longitudinal magnetoresistance at and below 30 K and an ordinary Hall effect with nearly temperature independent Hall coefficient between 10 and 200 K. Furthermore, electrons are the majority of the charge carriers in our thin film samples.

Single-Layer Mott Insulator 1T-TaSe2—Exotic Orbital Texture and Spin Liquid Behavior

Yi Chen1, Wei Ruan1, Shujie Tang2, Meng Wu1, Amy Y. Liu1, Joel E. Moore1, Zhi-Xun Shen2, Steven G. Louie1, Patrick A. Lee4, Sung-Kwan Mo3 and Michael Crommie1; 1University of California, Berkeley, United States; 2Stanford University, United States; 3Lawrence Berkeley National Laboratory, United States; 4Massachusetts Institute of Technology, United States

Mott insulating behavior is induced by strong electron correlation and can lead to exotic states of matter such as unconventional superconductivity and quantum spin liquids. Recent advances in van der Waals material synthesis enable the exploration of novel Mott systems in the two-dimensional (2D) limit. Here we report characterization of the local electronic properties of the single-layer Mott insulator 1T-TaSe2 via spatial- and momentum-resolved spectroscopy involving scanning tunneling microscopy (STM) and angle-resolved photoemission. Our combined experimental and theoretical study indicates that electron correlation induces a robust Mott insulator state in single-layer 1T-TaSe2 that is accompanied by novel real-space orbital texture. By placing single-layer 1T-TaSe2 onto a metal, we observe a strong Kondo resonance peak at the Fermi level, verifying the existence of local moments in this 2D Mott insulator. Finally, STM dI/dV imaging at the Hubbard band edges reveals a new incommensurate superstructure with a wavevector close to 2k_F of a half-filled spinon band, indicating a possible formation of a spinon-related density wave.

Challenges in Synthesis and Characterization of Topological and Quantum Materials

David A. Tennant; Oak Ridge National Laboratory, United States

Quantum materials are rapidly advancing but still present great challenges. Topological quantum materials in particular are receiving great attention as they provide potentially robust routes to quantum information processing that are protected against decoherence processes. Among key challenges are the prediction and realization of magnetic materials in the form of magnetic Weyl semimetals and quantum spin liquids as ways of realizing exotic quasiparticles such as Majorana fermions that can be used for application. These materials present new experimental challenges in terms of identifying their quasiparticles and demonstrating quantum coherence in their ground states states. Here I will show how we are using the integrated application of machine learning along with experiment and synthesis to advance the discovery and understanding of these materials.

Polarized Raman Spectroscopy of Single Nanoflakes of the Type-II Weyl Semimetal NbIrTe4

Iraj A. Shojaei1, Congcong Le2, Brenden Ortiz2, Giriraj Jnawali1, Seyyedesadaf Pournia1, Samuel Linser1, Howard E. Jackson1, Leigh M. Smith1, Fuchun Zhang2 and Stephen Wilson3; 1University of Cincinnati, United States; 2University of the Chinese Academy of Sciences, China; 3UC Santa Barbara, United States
We make detailed polarized micro-Raman spectroscopy measurements of single nanoflake of the layered ternary compound NbIrTe$_4$. Thin 10 to 100 nm thick layers were exfoliated from single crystals and dispersed onto a silicon substrate. The a and b crystalline axes lay in the plane of the nanoflake with the c-axis perpendicular to the layer. Micro-Raman spectra were taken in the backscattered geometry using both 633 nm and 514 nm laser light with the incoming and outgoing light parallel to the c-axis with the scattered light polarization selected to be both parallel and perpendicular to the incoming laser polarization. Our results indicate strongly anisotropic Raman peaks which are consistent with the broken inversion symmetry of the crystal, which is an essential enabling condition for a Weyl semimetal. The large orthorhombic unit cell of this material has 24 atoms and belongs to the space group Pmn2$_1$ (point group c$_{2v}$) which predicts 69 active Raman modes with A$_{1,2}$ and B$_{1,2}$ irreducible representations. Since our excitation is parallel to the c-axis we can only detect the A$_{1,2}$ modes. Density Functional Theory (DFT) calculations for the A$_{1,2}$ modes show close correspondence with both the frequency and symmetries of the modes detected in our measurement. The normal mode vibrations for each mode are also determined. All A$_1$ modes have vibrations in the bc-plane of the crystal structure, so they include out-of-plane vibrations, while the A$_2$ modes show atoms which vibrate only along the a-axis of the lattice structure, with in-plane vibrations. Fits to the rotational symmetry of each mode allow us to extract the relative electron-phonon constants for each mode. Some evidence is seen that the electron-phonon interaction is modified for the different energy excitation conditions.

We acknowledge the financial support of the NSF through grants DMR 1507844, DMR 1531373, DMR 1505549 and ECCS 1509706.

11:00 AM MQ03.01.08
Circularly Polarized Transient Reflectivity in the Type II Weyl Semimetal NbIrTe$_4$ Samuel Linser¹, Giriraj Jnawali¹, Seyyedesadaf Pournia¹, Iraj A. Shojaei¹, Howard E. Jackson¹, Leigh M. Smith¹, Congcong Le², Fuchun Zhang², Brenden Ortiz² and Stephen Wilson³; ¹University of Cincinnati, United States; ²UC Santa Barbara, United States; ³University of the Chinese Academy of Sciences, China

Weyl semimetals have recently attracted intense research interest for exhibiting chiral Weyl nodes which are displaced in momentum space because of band crossings. When photoexcited with circularly polarized light transport measurements have been shown to be consistent with a chiral anomaly where the number of particles with a given chirality are not conserved. Though such photogalvanic measurements have confirmed the presence of chiral nodes in Weyl semimetals, little is presently understood about the dynamic behavior of the chiral particles. We exfoliate single thin flakes from a bulk crystal of NbIrTe$_4$ which is a ternary variant of WTe$_2$ with broken inversion symmetry. DFT calculations have shown that there are 16 Weyl nodes in the Brillouin zone, eight lying in the k$_z$ = 0 plane and eight lying in the k$_z$ = ±0.2 plane. We excite the flake with laser pulses incident along the c crystal axis, which is normal to plane of the flake defined by the a and b axes. The thin flake is excited by a near-infrared (NIR) 1.5 eV 140 fs pump laser pulse, and probed by a delayed circularly polarized mid-infrared (MIR) pulse with an energy which can be tuned from 0.3 to 1.2 eV. We show that the transient reflectivity response of the NbIrTe$_4$ exhibits distinct dynamics depending on the circular polarization of the MIR probe pulse. The peak response at zero time has opposite phase for probe pulses of opposite handedness. This initial strong polarized response decays rapidly within 1 ps, but the weaker remaining signal decays slowly within 500 to 1000 ps before reaching equilibrium. The dynamics of the polarized transient reflectivity do not respond to the circular polarization of the NIR pump pulse. We suggest that the distribution of the chiral particles is perturbed by the modulation of the Fermi level caused by the strong NIR pump pulse.

We acknowledge the financial support of the NSF through grants DMR 1507844, DMR 1531373, and ECCS 1509706. S.D.W. acknowledges the support of NSF DMR 1505549.

11:15 AM MQ03.01.09
Detection of the Photogalvanic Effect in NbIrTe$_4$—A Type II Weyl Semimetal Seyyedesadaf Pournia¹, Giriraj Jnawali¹, Iraj A. Shojaei¹, Samuel Linser¹, Howard E. Jackson¹, Leigh M. Smith¹, Brenden Ortiz², Stephen Wilson³, Congcong Le² and Fuchun Zhang³; ¹University of Cincinnati, United States; ²UC Santa Barbara, United States; ³University of the Chinese Academy of Sciences, China

We investigate the optically driven transport properties of NbIrTe$_4$, which is a candidate type II Weyl semimetal.
which lacks spatial inversion symmetry. DFT calculations show that this ternary analog to WTe$_2$ exhibits 16 Weyl nodes, eight in the $k_z = 0$ plane and eight in the $k_z = \pm 0.2$ plane. A 100 nm flake of this material was exfoliated from a bulk crystal and dispersed on a Si++/SiO$_2$ substrate. 300 nm thick Ti/Al metal pads were deposited on two sides of the nanoflake by photolithography, metal deposition and liftoff. The device was mounted on a gold chip carrier, and after wire bonding, it was placed on the cold finger of an optical cryostat. A tunable polarized infrared laser was used to excite the device parallel to the c-axis normal to the flake. The I-V measurement shows that the resistivity of the device is about 2 mm.$\Omega$W at 300K and 0.2 mm.$\Omega$W at 10K. The photocurrent measurement with light linearly polarized along the “a” and “b” crystal directions shows photoresponse with different magnitudes in these two directions. Using a quarter wave plate for excitation between 1000 and 3000 nm (0.4 to 1.2 eV), the photoresponse was measured for a full rotation, with different amplitudes seen for right hand and left hand circular polarizations, revealing the circular photogalvanic effect which is consistent with the chiral nature of the Weyl nodes in this material.

We acknowledge the financial support of NSF through grants DMR 1507844, DMR 1531373, DMR 1505549 and ECCS 1509706.

11:30 AM MQ03.01.10
Electron-Phonon Coupling and the Decay of Chirality in Weyl Semimetals
Gavin Osterhoudt$^1$, Jennifer Coulter$^2$, Christina Garcia$^2$, Yiping Wang$^1$, Vincent Plisson$^1$, Bing Shen$^1$, Ni Ni$^3$, Prineha Narang$^2$ and Kenneth Burch$^1$; 1Boston College, United States; 2Harvard University, United States; 3University of California, Los Angeles, United States

Weyl semimetals are a class of recently realized topological semimetals characterized by three-dimensional linear dispersions known as Weyl nodes. A key feature of these materials is the low energy excitations in the vicinity of the Weyl nodes possess a chirality – their spins and momentum are locked either parallel or anti-parallel to one another. As such, considerable research attention has been focused on investigating these novel electronic properties. Despite this, little effort has been directed towards an understanding of their vibrational properties or the coupling between the two systems. In this talk we present experimental and computational results which reveal the interplay between the vibrational and electronic systems for the prototypical type-I Weyl semimetals NbAs and TaAs. In temperature dependent Raman measurements of phonon linewidths we observe an unusual dominance of electron-phonon based scattering of optical phonons into electron-hole pairs. Computational calculations of the mode resolved electron-phonon coupling strength not only confirm the presence of this scattering channel, but reveal other phonon mediated scattering channels which connect the disparate Fermi surfaces in the vicinity of the Weyl nodes.

11:45 AM MQ03.01.11
Synthesis of Cd$_3$As$_2$ Epilayers on II-VI Semiconductor Platforms via Molecular Beam Epitaxy
Anthony Rice and Kirstin M. Alberi; National Renewable Energy Lab, United States

The three-dimensional Dirac semimetal Cd$_3$As$_2$ has exhibited a number of interesting properties, including linear dispersion in the bulk electronic structure, Fermi arc surface states and giant magnetoresistance [1-3]. Many of these discoveries were made in bulk single crystal material due to the relative ease of synthesis. Epitaxial thin films have also been instrumental in detecting the quantum Hall effect and studying the influence of confinement on its properties [4]. Future investigation of Cd$_3$As$_2$ properties and devices will increasingly benefit from synthesis in thin film form and will critically depend on our ability to control defects, dopants, surfaces and interfaces during the growth process.

Here, we present a framework for imparting control during the growth of high quality Cd$_3$As$_2$ epilayers by molecular beam epitaxy. Our approach consists of three tactics to improve the electron mobility. The use of lattice-engineered II-VI Cd$_{1-x}$Zn$_x$Te buffer layers grown on GaAs substrates with a small degree of miscut reduces extended twin and dislocation defects. Growth from elemental Cd and As$_2$ sources rather than a Cd$_3$As$_2$ compound source allows for careful control of the chemical potential during growth and the resulting point defect populations. Illumination of the growth surfaces of both the II-VI buffer layer and Cd$_3$As$_2$ epilayer with a broadband source is further found to improve surface smoothness. Together, these methods have produced electron mobilities as high as
18,000 cm²/Vs in bulk epilayers even though growth is carried out at substrate temperatures no higher than 120 C. We will discuss the underlying mechanisms as well as prospects for using them to probe various aspects of defect physics in Cd₃As₂.


SESSION MQ03.02: Advanced Characterizations for Emerging Quantum Materials
Session Chairs: Alex Frano and Zhan Zhang
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 203

1:30 PM *MQ03.02.01
Scattering Studies of Lattice Dynamics Coupled to Charge and Spin Degrees-of-Freedom Olivier Delaire:
Duke University, United States

A detailed understanding of lattice vibrations is needed to build microscopic theories of transport and thermodynamics in emerging quantum materials. The interplay between phonons and other degrees-of-freedom of charge and spin has long been known to be critical in ferroelectrics/multiferroics, metal insulator transitions, as well as some aspects of superconductivity, including at high pressures or in nematic phases. Large deviations from harmonic potential energy surfaces, as in the Landau double-well picture, also give rise to interesting anharmonic phonon properties characterized by extensive interactions between phonon quasiparticles and pronounced renormalization effects, which can be tuned to zero temperature at ferroelectric quantum critical points. Further, phonons directly modulate the potential seen by electrons and offer a means to control the electronic structure and its topology, either thermally or via coherent excitations. I will highlight recent developments and achievements in studies of phonons in emergent quantum materials. In particular, I will discuss scattering techniques such as inelastic neutron / x-ray scattering, which can map phonon dispersions and linewidths throughout the Brillouin zone, and time-domain spectroscopies that can probe coupling mechanisms and far-from-equilibrium regimes. In addition, first-principles simulations of phonons can often be directly compared to these experiments and provide further insights into phonon couplings to charge, spin and orbital degrees of freedom.

2:00 PM *MQ03.02.02
Probing Broken Symmetries of Quantum Materials by Resonant Ultrasound Spectroscopy Paula Giraldo-Gallo¹, Jose A. Galvis³, Albert Migliori³, Fedor F. Balakirev³, Jon B. Betts³, Shimpei Ono⁴, Stephen Hayden⁵, Ross D. McDonald³, Brad J. Ramshaw⁶, Arkady Shekhter¹ and Gregory S. Boebinger¹; ¹Universidad de Los Andes, Colombia; ²Universidad Central, Colombia; ³Los Alamos National Laboratory, United States; ⁴Central Research Institute of Electric Power Industry, Japan; ⁵University of Bristol, United Kingdom; ⁶Cornell University, United States; ⁷Florida State University, United States

Determining the broken symmetries at a thermodynamic phase transition is an essential tool for understanding, or at least constraining, the microscopic mechanisms that lead to novel ground states in quantum materials. Resonant Ultrasound Spectroscopy (RUS) is a characterization technique that measures the spectrum of mechanical resonances of a solid, which allows the determination of its elastic tensor, a thermodynamic quantity that contains symmetry specific information of the ground state. Tracking the evolution of the elastic tensor through a phase transition allows determining which symmetries are broken in the transition, and to propose better suited order parameters.

In this talk I will present RUS measurements of unconventional superconductors and charge density wave compounds. I will focus on the La₂-xSrₓCuO₄ cuprate superconductor, for which we observe a strong softening of the C₆₆ elastic shear moduli, associated with the B₂₃ symmetry channel, as temperature is decreased and an
orthorhombic to tetragonal structural phase transition is approached. The temperature dependence of this softening is consistent with a Curie-like temperature dependence. This softening persists even for Sr compositions for which the tetragonal to orthorhombic structural transition is not seen. The B2g softening is truncated by the opening of the superconducting gap, evidenced by the stiffening of C66 below Tc. These observations suggest an electronic nematic origin for this softening, similar to what has been observed in Ba-pnictide superconductors.

2:30 PM MQ03.02.03
Ultrasensitive Nanoscale Calorimetry for the Characterization of Emerging Quantum Materials Charles T. Harris, Peter Sharma, Lisa A. Tracy, Rupert Lewis and Tzu-Ming Lu; Sandia National Labs, United States

Properties relevant to quantum materials are characterized by the material’s ground states and excitations. Complementary to electrical and optical measurements, heat capacity measurements performed on quantum materials can reveal information about the material’s density of states. Many emergent materials that are synthesized in the laboratory exist at nanometer length scales, and performing heat capacity measurements on these materials in the monolayer limit presents a formidable challenge. Typical commercial calorimeters require bulk samples and operate between 300K to 2K. Microfabricated calorimeters, compared to commercial systems, possess a significantly smaller thermal mass, and because of this drastically reduced size, they inherently have greater sensitivity to thermal signals. Here we present a method of performing ultrasensitive calorimetry on nanoscale quantum materials. Our microfabricated calorimeter possesses an intrinsic heat capacity that is 1000 times lower than state-of-the-art thin-film calorimeters and has been designed to operate over a wide temperature range, permitting measurements of low-energy excitations that occur at sub-Kelvin temperatures. Our calorimeter design also facilitates transmission electron microscopy measurements, allowing structure-property correlations on the same material of interest. In this presentation, I will explain the design and operation of this ultrasensitive calorimeter, present heat capacity measurements, and discuss various nanoscale material loading techniques, including the opportunities and the challenges inherent to these measurements.

2:45 PM MQ03.02.04
Correlative Total Tomography of III-As Nanowire Quantum Wells—Deconvolving Structure-Property Relationships at the Nanoscale Megan O. Hill1, Jonas Lähnemann2, Jesús Herranz2, Oliver Marquardt2, Guanhui Gao2, Ali Al Hassan3, Arman Davtyan1, Stephan O. Hruszkewycz1, Martin V. Holt2, Chunyi Huang1, Irene Calvo-Almazán1, Uwe Jahn2, Ullrich Pietsch2, Lutz Geelhaar2 and Lincoln J. Lauhon1; 1Northwestern University, United States; 2Leibniz-Institut im Forschungsverbund Berlin e.V., Germany; 3Naturwissenschaftlich-Technische Fakultät der Universität Siegen, Germany; 4Argonne National Laboratory, United States

Ternary III-As nanowire (NW) heterostructures provide a path to quantum confined structures of zero, one, and two dimensions integrated on Si, making them candidates for quantum-enabled applications including single photon emission and manipulation of Majorana Fermions [1,2]. Tomographic imaging of nanoscale composition is necessary to determine the confinement potentials of charge carriers and to understand and optimize growth. Furthermore, correlated analysis of nanoscale properties is needed to develop quantitative understanding of the influence that composition, strain, phase, and defect structure has on band structure. We have used a novel combination of characterization methods to correlate the 3-D structure of (In,Ga)As quantum wells (QWs) on GaAs NWs with their spatially varying optical properties at the nanoscale. While these classes of heterostructures are being developed both as quantum wires and emitter structures, we focus here on emission due to the significant interest in efficient compact and near-IR lasers for on-chip optical interconnects. Towards that end, spatially resolved cathodoluminescence (CL) was used to investigate the emission of InGaAs QWs grown on GaAs NWs that switched from the zincblende (ZB) to wurtzite (WZ) phase along their length, leading to brighter and blue-shifted emission in the WZ region. Electron backscatter diffraction and nano-probe based x-ray diffraction (nanoXRD), directly correlated with CL, established this correlation. Synchrotron-based nanoXRD was also used to probe position-dependent strain along multiple crystallographic directions with 25-50 nm spatial resolution. Atom probe tomography (APT) was then used in direct correlation with CL to image the composition and morphology of the embedded (In,Ga)As QWs. APT revealed that the In mole fraction is significantly reduced in WZ compared to ZB QWs, while the QW thickness is unchanged. Correlated measurements of composition, morphology, strain, and structure were combined as input for band structure calculations, leading to a predicted emission shift of 95 meV between the WZ and ZB region that is in reasonable agreement with the CL results (70-80 meV shift). This correlative analysis, using an array of advanced characterization tools, ultimately enabled deconvolution of complex spatial variations in electronic structure in a way not previously possible, and can be extended to a range of buried
quantum heterostructures. To explore the limits of the methodology, we will also discuss the application of coherent x-ray diffraction imaging to non-destructively image strain in embedded radial QWs as small as 8 nm in diameter.


2. Lähnemann, J., Hill, M.O., ..., Lauhon, L.J., & Geelhaar, L. "Correlated nanoscale analysis of the emission from wurtzite versus zincblende (In, Ga) As/GaAs nanowire core-shell quantum wells." Nano Letters 19 (2019) ASAP. DOI: 10.1021/acs.nanolett.9b01241

3:00 PM BREAK

3:30 PM *MQ03.02.05
Imaging Effects of Electronic Correlations in Twisted Bilayer Graphene Stevan Nadj-Perge; California Institute of Technology, United States

Twisted bilayer graphene with a twist angle close to 1° features isolated flat electronic bands that form a strongly correlated electronic system. Here we investigate properties of this system by probing local tunneling density of states using scanning tunneling microscopy and spectroscopy. We show that the flat bands get highly deformed when they are aligned with the Fermi level using electrostatic gating. At half filling of the bands, we observe the development of gaps originating from correlated insulating states. Near charge neutrality, we find a previously unidentified correlated regime featuring a substantially enhanced flat band splitting that we describe within a microscopic model predicting a strong tendency towards nematic ordering. Our results provide basis for microscopic understanding of correlated quantum phases in small angle twisted bilayer graphene.

4:00 PM MQ03.02.06
Experimental Determination of the Ionization Energies of MoSe2, WS2 and MoS2 Using Photoemission Electron Microscopy Taisuke Ohta1, Morgann Berg1, Thomas Beechem1, Calvin Chan1, Kunital Keyshar2, Xiang Zhang2, Robert Vajtai2, Gautam Gupta2, Pulickel Ajayan2 and Aditya D. Mohite2; 1Sandia National Laboratories, United States; 2Rice University, United States; 3Los Alamos National Laboratory, United States

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals would line up with respect to each other. Defined as an energy separation between the vacuum level and the highest occupied electronic states, the ionization energy is of particular importance for atomically-thin transition metal dichalcogenides (TMD) to predict the performance of their heterostructures as well as their interfaces with metal contacts. Ionization energies have been investigated based on theoretical calculations, but to the best of our knowledge, no systematic experimental confirmation is reported for the wide range of TMDs and other emerging quantum materials, despite their importance.

Here we present a new approach to study the electronic properties of prototypical TMDs, MoSe2, WS2, and MoS2 monolayer and multilayer flakes, supported on thick silicon oxide (SiO2) film, using a photoemission electron microscopy combined with a deep ultraviolet (DUV) illumination. We determine the band alignments of monolayer to multilayer junctions in these four materials, and show that the ionization energy decreases from MoS2, WS2, to MoSe2 as predicted by density functional calculations. We further extend this experimental approach to quantify Schottky barriers at the TMDs-metal contacts. This work reveals a new metrology approach to conduct systematic studies of electronic properties of TMDs.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). T. O. is supported by the CINT user program and Sandia LDRD. The work performed by M. B. is supported by the CINT postdoc program. K. K. was supported by the Army Research Office MURI grant W911NF-11-1-0362. A. D. M. is supported by LANL LDRD program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

4:15 PM MQ03.02.07
Scanning Tunneling Microscopy of Nanomaterials, New Yang-Mills Observe-on Regge Beta Decay and Relativistic Dark Matter Stephen Sharma1,2; 1University of California, Berkeley, United States; 2University of
Motivating experimental and theoretical physics is a desire for grand unification and practical solutions to real world problems. The highest resolution visualization of nanomaterials comes from the scanning tunneling electron microscope (STM). It probes quantum states through a conducting stylus. Further investigation into the collapse of the wavefunction necessitates the creation of a new particle that solves a problem in Yang-Mills symplectic rotations. From Clebsch-Gordon coefficients and the resultant Green’s functions fields, a single source particle is uncovered, the observe-on. This unification means that the neutrino does not exist. Regge theory and angular momentum at the quantum scale imply funny SU(2) particle states that carry the Fermi-Curie deconvolution. When applying this rotational correction to galactic cores, the perturbation to the mass density length contraction generates a pseudo-energy and pseudo-central force from a frame dragging effect. This is dark matter. This work is a theoretical exploration into ideas central to hyperspace Aharonov-Bohm dimensions, dark matter, Yang-Mills theory, quantum STM experiments, fusion, and the connections that make emergent properties like the scientific endeavor a conscious entity. New s-matrix theory and string geodesic landscapes discard quantum loop theories. Really, though, this is an experimental thrust into tunneling and how quantum probes unify with relativity to allow scientists to predict the properties of particles and surfaces with unique electronic and nuclear states beyond the standard model.

4:30 PM MQ03.02.08
Direct Imaging Revealing Halved Ferromagnetism in Tensile-Strained LaCoO₃ Thin Films Dechao Meng¹, Qiyuan Feng², Jinghua Guo³, Chao Ma⁴, Xiaofang Zhai⁵, Qingyou Lu² and Yalin Lu²; ¹China Academy of Engineering Physics, China; ²University of Science and Technology of China, China; ³Lawrence Berkeley National Laboratory, United States; ⁴Hunan University, China

The enigma of the emergent ferromagnetic state in tensile-strained LaCoO₃ thin films remains to be explored because of the lack of a well agreed explanation. The direct magnetic imaging technique using a low-temperature magnetic force microscope (MFM) is critical to reveal new aspects of the ferromagnetism by investigating the lateral magnetic phase distribution. Here we show the experimental demonstration of the rare halved occupation of the ferromagnetic state in tensile-strained LaCoO₃ thin films on SrTiO₃ substrates using the MFM. The films have uniformly strained lattice structure and minimal oxygen vacancies beyond the measurement limit. It is found that percolated ferromagnetic regions with typical sizes between 100 nm and 200 nm occupy about 50% of the entire film, even down to the lowest achievable temperature of 4.5 K and up to the largest magnetic field of 13.4 T. Preformed ferromagnetic droplets were still observed when the temperature is 20 K above the Curie temperature indicating the existence of possible Griffiths phase. Our study demonstrated a sub-micron level phase separation in high quality LaCoO₃ thin films, which has substantial implications in revealing the intrinsic nature of the emergent ferromagnetism.


SESSION MQ03.03: Quantum Phenomena in Epitaxial Thin Films, Heterostructures and Interfaces
Session Chairs: Olivier Delaire and Julia Mundy
Tuesday Morning, December 3, 2019
Hynes, Level 2, Room 203

8:00 AM *MQ03.03.01
Probing Topological Magnetic Interfaces with Next-Generation Neutron Reflectometry Alexander Grutter; National Institute of Standards and Technology, United States

Whether it originates in crystallinity, magnetism, or electronic structure, interfacial symmetry breaking represents one of the most powerful tools for the realization of new quantum materials with advanced functionality. Mismatches in band topology and time reversal symmetry across interfaces have been harnessed to open gaps in the surface states of topological insulators or to induce topological transitions. Heterostructures interfacing
superconductors with a quantum anomalous hall insulator (QAHI) have been reported to exhibit signatures of Majorana fermions, while two-dimensional systems with strong spin-orbit interactions have long been suspected of harboring skyrmions at interfaces with perpendicular magnetic materials. In all of these cases, our understanding of the underlying physics has hinged critically on the ability to precisely understand and isolate the properties of the interface from the bulk of the system. By decomposing the magnetic and electronic properties on a layer-by-layer and element-resolved basis, new quantum material systems may be robustly understood and designed. In this talk, I will discuss our recent progress in combining depth-resolved information from polarized neutron reflectometry with element-specific information from soft X-ray spectroscopy to design and control magnetic interfaces in topologically nontrivial systems such as (Bi,Sb)2Te3/antiferromagnet and Bi2Se3/oxide heterostructures. I will focus in particular on the new capabilities enabled by CANDOR, the new polychromatic neutron reflectometer at the NIST Center for Neutron Research. A highly intensity-limited technique, the application of neutron reflectometry has been critically hampered by the long measurement times necessary to probe the trace magnetic signal in systems such as superconductors and QAHIs. By implementing a polychromatic beam with multiplexed energy analyzing detectors, CANDOR allows for multiple orders of magnitude intensity gains, allowing even more sensitive measurements to be performed in hours instead of days.

8:30 AM MQ03.03.02

Resolving Interfacial Charge Transfer in Buried Monolayers with Resonant X-Ray Reflectometry Ryan Need1, Patrick Marshall2, Susanne Stemmer2 and Stephen Wilson2; 1University of Florida, United States; 2University of California Santa Barbara, United States

More and more frequently, the interfaces between electronic thin films are playing critical roles in the operations and functions of our electronic devices. As we move towards new computing paradigms, it’s the interfaces of quantum materials with strongly coupled degrees of freedom and complex phase behavior that show the greatest potential to revolutionize the ways we store, process, and transfer information. Yet, the same coupled degrees of freedom that give quantum materials their unique and desirable properties place stringent requirements on the local structure and composition at the interfaces, where the presence of unintended defects can diminish spin polarized currents and destroy coherent quantum states. However, characterizing the physics at these interfaces, which are often buried deep below the sample surface, remains difficult. Addressing this challenge requires a technique capable of measuring the local electronic structure with high-resolution depth dependence.

In this talk, we show how linearly polarized resonant X-ray reflectometry (RXR) can be used to visualize charge transfer in complex oxide superlattices with atomic layer resolution. From our RXR measurements, we extract valence depth profiles of SmTiO3(SmTO)/SrTiO3 (STO) heterostructures with STO quantum wells varying in thickness from five SrO planes to a single SrO plane. At the polar-nonpolar SmTO/STO interface, an electrostatic discontinuity leads to approximately half an electron per area unit cell transferred from the interfacial SmO layer into the neighboring STO quantum well. We observe this charge transfer as a suppression of the t2g absorption peaks that minimizes contrast with the neighboring SmTO layers at those energies and leads to a pronounced absence of superlattice peaks in the reflectivity data. Our results demonstrate the sensitivity of RXR to electronic reconstruction in the monolayer limit and establish RXR as a powerful means of characterizing charge transfer at the buried interfaces of quantum materials.

8:45 AM MQ03.03.03

Heterogeneity in the Epitaxial Thin Film with Full Field X-Ray Diffraction Microscopy Zhan Zhang1, Nouamane Laanait2, Seohyoung Chang3, Hua Zhou1, Han Xu4, Zhenlin Luo4, Dillon Fong1 and John Freeland1; 1Argonne National Laboratory, United States; 2Oak Ridge National Laboratory, United States; 3Chung-Ang University, Korea (the Republic of); 4University of Science and Technology of China, China

Epitaxial thin films, especially the oxide thin films, have been studied extensively due to their emerging properties and potentials in various applications, such as energy storage and data storage. Many factors, such as the chemical state, the strain state, and presence of the external field, can affects the thin film structure, which in turn influences the properties. While the unit cell level atomic structures of such thin film materials are fairly well known/defined, the recent interests are steered towards how the unit cells and nano-sized domains are organized into the macroscopic functional materials. This so-called meso-scale structure turns out to be not that simple due to the spatial inhomogeneity in the thin film as it minimizes the total energy in response to the internal and external
stimulant. Availability of spatial-resolved and/or time-resolved structures of such systems would be critical to a better understanding and eventually designing function-oriented new materials. A diffraction based, full field X-ray microscopy method, the X-ray reflection interface microscopy (XRIM), has been adopted to study the surfaces, buried interfaces, and thin film material systems at meso-scale, with sub-nanometer + sensitivity in the surface normal direction and <80 nm lateral resolution.

With the penetrating power of hard X-rays, XRIM can emphasize the features at different depth from the top surface by choosing proper scattering conditions, making it an excellent candidate to study the films in-operando in real time. Combined with the reciprocal space mapping (RSM), the spatially resolved structure evolution can be identified. A few examples will be discussed to demonstrate the capability of XRIM method and its potential applications in a broader field.

9:00 AM MQ03.03.04
Exploring Buried Layers and Interfaces Using Angle-Resolved Hard X-Ray Photoelectron Spectroscopy Anna Regoutz; University College London, United Kingdom

Modern materials science often concerns not isolated, bulk materials, but materials as part of larger, complex thinfilm-based heterostructures. The final behaviour of such systems is in many cases dominated by the interfaces between materials and cannot usually be inferred from the bulk characteristics of the individual components.

One of the main challenges complicating a full understanding of such complex systems is the availability of direct characterisation methods for buried layers and in particular the interfaces between them. We greatly lack direct probes for chemical states and electronic structure at interfaces, which present a special challenge for physical characterisation techniques due to their spatial confinement, the fact that by their nature interfaces are buried beneath a variety of overlayers, and the starkly different behaviour of chemical species at interfaces compared to surfaces and the bulk. Advanced X-ray spectroscopy methods can tackle some of these issues, and X-ray Photoelectron Spectroscopy (XPS) in particular can deliver great insight as it combines both qualitative and quantitative information on elemental distributions, chemical environments, and valence states.

Here, we present a systematic study using angle-resolved hard X-ray photoelectron spectroscopy (AR-HAXPES) to study buried layers and interfaces. Hard X-rays provide increased depth information and using an angle-resolved approach, highly depth-resolved information monitoring elemental and electronic structure changes across thin films stacks and interfaces is possible. Well defined 4H-SiC/SiO₂ heterostructures are used as a test system representing a complex, defect rich system, in which knowledge of the precise nature of defects is limited. The samples were treated in a variety of nitrogen-containing atmospheres (N₂, NO, NH₃ and NO+NH₃) after the initial fabrication procedure, which leads to different distributions and chemical states of nitrogen across the heterostructures, which can compensate defects in particular at the interface. SiC is a wide band gap semiconductor, that is widely used for power electronic applications and therefore of great interest in itself.

Clear differences are observed in HAXPES spectra after high temperature treatments and across the heterostructures. Angle-resolved Si 2s and 1s, C 1s, O 1s, and N 1s core level spectra are analysed to give a complete picture of chemical environments present in the oxide and carbide layers and particularly at and around the interface. In addition, valence band spectra are used to provide an insight into changes in the electronic structure of the materials. Ultimately, we show that AR-HAXPES can be applied to the investigation of buried features and interfaces and related phenomena.

9:15 AM MQ03.03.05
Tuning the Electronic Properties of the 4D Transition Metal Oxide LaRhO₃ Juan Jiang, TaeKyung Lee, Sangjae Lee, Sohrab Ismail-Beigi, Frederick J. Walker and Charles H. Ahn; Yale University, United States

Perovskite transition metal oxides exhibit various novel properties due to the interactions of strongly correlated electrons. These interactions are well known in the 3d transition metal oxides, such as LaCoO₃, where multiple spin states can be observed. Electronic correlations are expected to change as the transition metal is changed from Co to Rh in the same column of the periodic table. To explore these changes, we grow high quality La₁₋ₓSrₓRhO₃ thin films with Sr concentrations as high as 50% on both LaAlO₃ and SrTiO₃ substrates by molecular beam epitaxy. Systematic changes in both structure and electronic transport have been observed that can be directly tied to the
This work is supported by a grant from the Department of Energy, Basic Energy Sciences under grant number DE-SC0019211.

9:30 AM BREAK

10:00 AM  MQ03.03.06
Couplings at Oxide Interfaces in Perovskites and Double-Perovskites Marta Gibert; University of Zurich, Switzerland

Complex-oxide heterostructures have garnered much attention as a path to couple the rich variety of properties of these materials, but also for the many routes they offer for the stabilization of novel behaviors. Understanding the electronic and structural reconstructions occurring at interfaces is therefore key for the success of interface engineering. In the last years, control of the structural couplings of the oxygen sublattices during epitaxy synthesis is arising as a very powerful route to manipulate the states of matter in complex oxides. Whereas this strategy is starting to settle as one of the main mechanisms governing interfacial couplings in oxide heterostructures, we show here a system where, despite first glance prognosis, the dominant coupling is instead electronic in nature. The chosen heterostructures are high quality epitaxial NdNiO3/SmNiO3 superlattices and the occurring of the metal-insulating transition (single or double depending on the layer period) is the interesting functionality investigated. I will also focus on the family of double-perovskite compounds A2NiMnO6 (A being a rare earth cation), which is characterized by an insulating ferromagnetic behavior, with the end member La2NiMnO6 displaying a Curie temperature approaching room temperature (≈ 280K). The magnetism of these double-perovskite thin films will be investigated down to few unit cells. All thin films and superlattices are grown by off-axis magnetron sputtering.

10:30 AM MQ03.03.07
Order Parameter Control in Perovskite Nickelates via Oxygen Vacancies Zhen Zhang and Shriram Ramanathan; Purdue University, United States

The electronic structure and electromagnetic properties of perovskite nickelate quantum materials are highly sensitive to orbital occupancy and strain. In this work, we will discuss how oxygen vacancies can be injected into perovskite nickelates such as NdNiO3 in a reversible and controlled manner and can cause massive electronic phase changes by which the charge carriers are localized within unit cell dimensions. The distribution of oxygen vacancies can further be controlled spatially by bias voltage in a solid-state device creating functionally graded quantum systems. We will present experimental results combining variable temperature electronic transport and X-ray spectroscopic data to illustrate how the Ni-site orbital filling influences multiple order parameters such as electronic band gap, optical gap and spin ordering. These studies suggest the potential of nickelates as model systems for fundamental understanding of strong electron interactions by controlling concentration of oxygen vacancies and further their potential use in electronic switches.

10:45 AM MQ03.03.08
Tunable Resistivity Exponents in the Metallic Phase of Epitaxial Nickelates Qikai Guo1, César Magèn2, Saeedeh Farokhipoor1 and Beatriz Noheda1,3; 1Zernike Institute for Advanced Materials, University of Groningen, Netherlands; 2Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Universidad de Zaragoza, Spain; 3Groningen Center for Cognitive Systems and Materials, Netherlands

The tunable resistivity of materials undergoing metal-insulator transitions (MIT) holds great promise for resistive switching applications, such as adaptable electronics and cognitive computing. Among the materials with MIT, rare-earth nickelates (RENiO3 with RE denoting a trivalent rare earth element) present a very interesting case because their MIT can be controlled by using different RE elements or by epitaxial strain [1-3]. Moreover, it has been reported that eliminating the MIT in nickelates by orbital engineering would give rise to a superconducting state, which could be more robust than that of the cuprates [4]. Thus, it becomes important to have an accurate picture of the relevant electron interactions in the intermediate temperature regimes, just before the MIT takes place. However, despite the vast amount of recent works, transport in nickelates is not yet fully understood. Based on different scaling exponents of the resistivity as a function of temperature reported in this material, various hypotheses, such as bad metal, Fermi-liquid (FL), non-fermi liquid (NFL), or even the crossover between FL and
NFL, had been proposed to describe the intriguing behavior of nickelates. However, the issue of matching these different hypotheses in one material rises the question on how to interpret the experimentally obtained apparent exponents.

Here, by investigating a series of NNO films grown on different substrates, we reveal an evolution of the resistivity-temperature apparent power law exponent of the metallic phase as a function of epitaxial strain and the associated induced disorder. Our experimental results support recent theoretical predictions by Patel et al. [5], which propose that the combined effect of electron interactions and disorder can give rise to a continuous variation of the exponents. These results demonstrate that the assessment of FL or NFL behavior based on the measurement of exponent of the power law temperature dependence of resistivity should be preceded by a detail analysis of the disorder.


11:00 AM MQ03.03.09
Complex Oxides at Weakly Coupled Interface—Epitaxy and Electrical Property Jian Shi; Rensselaer Polytechnic Institute, United States

Among various efforts to integrate quantum technology-associated complex oxides materials (e.g. nonlinear and strongly correlated oxides) on electronic substrates, thin film epitaxy has been regarded as one promising solution due to its feasibility for mass production, controllability over film dimension and high-density device integrability. However, most epitaxial oxides grown on Si are populated with defects such as grain boundaries and dislocations. The fundamental challenge lies in the fact that Si and most oxides have large lattice mismatch, which brings significant strain energy when film is below critical thickness but leads to populated misfit dislocations and threading dislocations when film is above its critical thickness. In this talk, to tackle these issues, I will show how we design and develop unconventional epitaxy approaches featured by weakly-coupled film-substrate interface. The model materials in this talk include correlated oxides and nonlinear electro-optic oxides. I will also show how the weakly-coupled complex oxides behave differently from films produced by conventional epitaxy under external stimuli.

11:30 AM MQ03.03.10
Accessing Novel Correlated Materials with Entropy Stabilization Synthesis Alessandro R. Mazza, Yogesh Sharma, Elizabeth M. Skoropata and T. Zac Ward; Oak Ridge National Laboratory, United States

Disorder is an important aspect of correlated quantum systems. As examples, it can be used to manipulate superconductivity, stabilize quantum spin liquid states, and enable scaling of non-fermi liquid responses. While synthesis of new quantum materials is generally focused on creating perfect crystals comprised of only a few elemental building blocks, we will present our recent efforts to create high quality crystals with a high degree of configurational elemental disorder on sublattice sites. The intent is to gain knowledge of how maximizing local microstates might enable the emergence of new and unexpected macrostates. Complex crystal structures comprising two or more sublattices, such as those in the perovskite family, are particularly promising. This is due to the nearest neighbor cations on one configurationally disordered sublattice being tied together by an intermediate common and uniform anion sublattice.

As an example, we present our recent stabilization of single crystal epitaxial films of the ABO3 perovskite La(Cr0.2Mn0.2Fe0.2Co0.2Ni0.2)O3. XRD and STEM-EELS studies confirm crystallinity, epitaxy, and full site mixing of the 5 B-site elements (no single element clustering). Experimental results from neutron studies, XMCD, and SQUID magnetometry demonstrate unexpected long-range magnetic ordering which is highly tunable through lattice symmetry modification.

11:45 AM MQ03.03.11
Regaining a Dimension—Mechanically-Transferrable 2D InAs Nanofins Grown by Selective-Area-Epitaxy Jakob M. Seidl1, Jan G. Gluschke1, Xiaoming Yuan2,3, S Naureen2,4, Naeem Shahid2,5, Hoe Tan2, Chennupati Jagadish2, Adam Micolich1 and Philippe Caroff6; 1University of New South Wales, Australia; 2The Australian
Semiconductor nanowires have seen great success for the last two decades and have opened the doors to a multitude of device applications [1]. However, emerging quantum devices often require more elaborate geometries that go beyond single one-dimensional wires. Selective-area-epitaxy (SAE) can overcome this limitation because it offers an approach to growing nearly arbitrary shapes, as demonstrated recently [2-4]. Most SAE-grown nanostructures are bound to their growth substrate which, while attractive for large scale processing, makes few-sample fabrication costly and challenging. We report on growth and electrical characterization of free standing InAs nanofins grown by selective-area-epitaxy [5]. Their rectangular footprint can be deliberately tuned to give structures ranging from 1D nanorods to thin 2D nanosheets with good height control. The high aspect ratio allows us to mechanically transfer them to device substrates where they lie flat and can be fabricated into devices with multiple contacts, top- and back-gates. Our devices show excellent prospects for fabrication into more sophisticated devices, e.g., by adding functional elements like superconducting contacts or by top-down patterning them into desired shapes after growth. InAs nanofin growth proceeded via metal-organic vapor phase epitaxy (MOVPE) on an InP (111B) substrate covered with a SiOx mask. During growth, nucleation occurs in lithographically pre-patterned rectangular openings in the SiOx. As with SAE growth of nanowires, the crystal retains the shape given by the rectangular openings if their long axis is aligned correctly relative to underlying crystallographic axes. Rectangular nanofins with typical width 1-4 μm, height ~ 4 μm and thickness < 85 nm were grown. After mechanical transfer to a prepatterned substrate these nanofins were fabricated into field-effect transistor devices with multiple ohmic contacts, a global back-gate and local top-gates. Low-temperature (T = 300 mK) electrical characterisation shows reliable contact performance with resistances below 10 kΩ. Hall measurements give electron densities of $1.5 - 7 \times 10^{17}/\text{cm}^3$ with good density control via the back-gate. We obtain field-effect mobilities of up 4400 cm²/Vs, systematically higher than transport mobilities extracted from Hall effect data, yet similar to what is found in InAs nanowires [6]. Reproducible quantum interference is visible in the magnetoconductance at large and small magnetic field scales. A robust weak anti-localisation (WAL) peak is visible around B = 0 T, which evolves with back-gate voltage. Fitting to this peak gives phase-coherence lengths $L_\phi = 200-600$ nm and spin-relaxation lengths $L_{SO} = 150-350$ nm. We see no signs of quantum-Hall effect in our accessible field range ($B \leq 2$ T).


Observation and Manipulation of Coupled Order Parameters and Domains in Magnetoelectric Multiferroics
Tsuyoshi Kimura; The University of Tokyo, Japan

In multiferroics having two or more ferroic orders simultaneously, multiple order parameters coexist in a system, sometimes couple with each other, and exhibit nontrivial crossed phenomena such as magnetoelectric effect. To date, various mechanisms have been proposed for the origin of multiferroicity. For example, in multiferroics which exhibit a certain conical spiral spin order, both ferromagnetic and ferroelectric order parameters can develop due to the magnetic order and their domains can be coupled with each other. In this presentation, we show selective observations, control, and understanding of coupled order parameters and domains which coexist in magnetoelectric multiferroics breaking both space inversion and time reversal symmetries. Examples of such multiferroic oxides are hexaferrites (e.g., Ba$_{1.3}$Sr$_{0.7}$CoZnFe$_{11}$AlO$_{22}$) showing the so-called alternating longitudinal conical structure and olivine-type manganese germanate Mn$_2$GeO$_4$ showing canted antiferromagnetic conical spin chains. For the observations, we adopted single-crystal measurements of scanning resonant x-ray microdiffraction for the hexaferrites or (un)polarized neutron scattering for the manganese germanate. These techniques clarify multiple magnetic order parameters and domain structures and their manipulations by external stimuli such as magnetic and electric fields in these peculiar multiferroics. This work has been done in collaboration with H. Ueda, R. Misawa, J. K. H. Fischer, K. Kimura, Y. Tanaka, Y. Wakabayashi, T. Honda, J. S. White, M. Kenzelmann, and A. B. Harris.

2:00 PM *MQ03.04.02
Stabilizing Emergent Ground States in Multifunctional BiFeO$_3$ Using Interfacial Electrostatic Engineering
Julia Mundy$^1$, Colin Heikes$^2$, Bastien F. Grosso$^3$, Dan Ferenc Segedin$^1$, William D. Ratcliffe$^2$, Nicola Spaldin$^3$, Ramamoorthy Ramesh$^4$ and Darrell G. Schlom$^5$; $^1$Harvard University, United States; $^2$National Institute of Standards and Technology, United States; $^3$ETH Zürich, Switzerland; $^4$University of California, Berkeley, United States; $^5$Cornell University, United States

Dielectric capacitors hold a tremendous advantage for energy storage due to their fast charge/discharge times and stability in comparison to batteries and supercapacitors. A key limitation to today's dielectric capacitors, however, is the low storage capacity of conventional dielectric materials. To mitigate this issue, antiferroelectric materials have been proposed, but relatively few families of antiferroelectric materials have been identified to date. Here, we propose a new design strategy for the construction of lead-free antiferroelectric materials using interfacial electrostatic engineering. We begin with a ferroelectric material with one of the highest known bulk polarizations, BiFeO$_3$. We show that by confining atomically-precise thin layers of BiFeO$_3$ in a dielectric matrix that we can induce a metastable antiferroelectric structure. Application of an electric field reversibly switches between this new phase and a ferroelectric state, in addition, tuning of the dielectric layer causes coexistence of the ferroelectric and antiferroelectric states. Precise engineering of the structure generates an antiferroelectric phase with energy storage comparable to that of the best lead-based materials. The use of electrostatic confinement provides a new pathway for the design of engineered antiferroelectric materials with large and potentially coupled responses.

2:30 PM MQ03.04.03
Electrically Switchable Magnetism and Topological Hall Effect in SrRuO$_3$ Thin Films Jinxing Zhang; Beijing Normal University, China

Reversibly controlling topological orders is fundamentally important but challenging. Strongly correlated oxides with coexistence and competition of multiple d electron order parameters may provide a platform for robust and controllable topological phases. Here, high-spin state and topological Hall effect are achieved in ultrathin SrRuO$_3$thin filmson SrTiO$_3$substrates. Oxygen vacancies transferred from SrTiO$_3$to the ultrathin SrRuO$_3$reconstructs Ru-4d electronic structure and orbital occupancy, leading to an enhancement of magnetic moment and an ~370 meV energy gap opening. Therefore, symmetry broken and Dzyaloshinskii–Moriya interaction in this ultrathin oxide structure give rise to a topological order in spin state, where the topological Hall effect can be reversibly switched by an electric-field-rectifying oxygen ionic diode.

2:45 PM MQ03.04.04
A Correlated Material by Hydrogenation—HCsBiNb$_2$O$_7$ Lifu Zhang and Jian Shi; Rensselaer Polytechnic Institute, United States

Correlated compounds serve as model systems to study interactions among lattice, spin, charge and orbital degree of
freedom. Understanding the correlation and phase transition mechanisms in these compounds is paramount for the innovation of next-generation ultrafast and high-efficiency electronic/photonic devices. However, the number of discovered correlated oxides by now is still quite limited. Here we apply hydrogenation to create a new phase of correlated material HCsBiNb2O7 (HCBNO). We first synthesize CsBiNb2O7 (CBNO), a layered in-plane ferroelectric perovskite, by molten salt method and then dope it via hydrogenation in 5% H2 of Ar/H2 gas. This doping process is reversible and can induce pronounced changes in its optical properties, accompanying with electronic modulations. To achieve sufficient hydrogenation of the CBNO, atomically dispersed Pt catalyst was used to promote hydrogen spillover under a temperature of 475 °C. Raman and XRD characterization indicate the hydrogen is reversibly absorbed into, and released from CBNO without destroying its lattice structure. Ultraviolet-visible spectrum shows a significant increase (~ 3 times) in absorption after hydrogenation and transport measurement shows a nearly 10 times increase in electric conductivity, comparing to the pure CBNO at room temperature. Resistance-temperature measurement and ultraviolet photoelectron spectrum further confirm the transition of electronic orbital configurations. Our finding suggests the possibility of reversible modulation in CBNO via hydrogenation and may give some enlightenment in exploring novel electronic and photonic devices with complex correlated oxides.

3:00 PM BREAK

3:30 PM *MQ03.04.05
Antiferromagnetic Spin Engineering in LaFeO3—A Route towards Uniaxial Néel Vector Control
Kristoffer Kjærness1, Tianxian Nan2, Ingrid G. Hallsteinsen1,3, Ruofan Li2, Alireza Qaiumzadeh1, Jonathan Schad4, Magnus Moreau1,2, Sverre Magnus Selbach1, Alexander Grutter6, Elke Arenholz3, Arne Brataas1, Daniel C. Ralph2, Chang-Beom Eom7 and Thomas Tybell1; 1Norwegian University of Science and Technology, Norway; 2Cornell University, United States; 3Lawrence Berkeley National Laboratory, United States; 4University of Wisconsin—Madison, United States; 5Silicon Labs Norway, Norway; 6National Institute of Standards and Technology, United States

Spintronics based on antiferromagnetic (AF) materials are attractive for energy efficient device technology, offering robustness against magnetic perturbations and ultra-high frequency spin dynamics allowing for THz device technology. Currently, there is focus on developing methodologies to tailor the AF spin texture. Transition metal oxide-based systems are in this regard promising candidates, and here, we present how anisotropic strain engineering permits tailoring of the AF Neel vector in epitaxial single crystalline LaFeO3 thin films synthesized by pulsed laser deposition. LaFeO3 is a prototypical G-type antiferromagnet with high Néel temperature. To impose anisotropic strain, we rely on the (111) pseudocubic facet of orthorhombic scandate- and gallate-based oxide substrates. X-ray studies confirm a lowering of LaFeO3 symmetry, from orthorhombic in bulk to monoclinic or triclinic, depending on the choice of substrate and the magnitude of anisotropic strain, in thin films. This is in accordance with DFT calculations. Epitaxial engineering allows us to efficiently tune the magnetic anisotropy from bi-axial in bulk to uniaxial in our thin films, as inferred from soft x-ray spectroscopy. By increasing the LaFeO3 thickness transition of the uniaxial spin direction takes place, a change from an out-of-plane to an in-plane AF spin axis above 16 d111-layers. We will discuss the possibilities that anisotropic strain engineering offers to tune the interface AF spin texture between LaFeO3 and a ferromagnet in a deterministic fashion, as confirmed by soft x-ray spectroscopy and spin-polarized neutron reflectivity. Furthermore, we will present non-local spin transport studies to exemplify that the uniaxial Néel vector control allows engineering of anisotropic spin transport. The experimental data will be correlated to spin transport theory.

4:00 PM MQ03.04.06
Coherent Imaging of Antiferromagnetic Domain Dynamics
Sangiae Lee1, Juan Jiang1, Gilberto Fabbris2, Claudio Mazzoli2, Mark Dean2, Frederick J. Walker1 and Charles H. Ahn1; 1Yale University, United States; 2Brookhaven National Laboratory, United States

Understanding the dynamics and energetics of the antiferromagnetic (AF) domains is of general and timely interest for the application of these magnetic materials in spin-based electronics for computing and communications. A fundamental requirement to understand and control AF domains involves the ability to image them. X-ray photon correlation spectroscopy (XPCS) measurements via coherent x-ray scattering can be employed to image the AF order parameter in thin films and to access the information about their dynamics. Recent studies on NdNiO3 (NNO) have shown that its electronic and magnetic phase transitions can be tuned by confining the nickelate layers to reduced dimensions in heterostructures. We study the AF ground state for atomically layered (NdNiO3)m/(NdAlO3)n heterostructures.
heterostructures to demonstrate that dimensional confinement enhances the phase fluctuations at AF domain boundaries. We analyze the speckle patterns arising from coherent x-ray scattering to access the information on long- and short- ranged correlations for varying thickness of nickelate layers, m. We find that the dynamics of the AF domain boundaries are dramatically enhanced as the reduced dimensionality of the NNO layers approach the 2D limit. Our study demonstrates a path to characterize dimensional effects on long-range order and the ability to control AF domain configurations in oxide heterostructures.

4:15 PM *MQ03.04.07
Neutron Investigation of the Phase Transitions and Domain Dynamics of Multiferroic GaV₄S₈
Jeffrey W.
Lynn¹, William D. Ratcliff¹, Marcus Bleuel¹,², Rebecca L. Dally¹, Heung-Sik Kim³,⁴, Kristjan Haule¹, David
Vanderbilt¹, Lunyong Zhang¹ and Sang Wook Cheong⁵; ¹National Institute of Standards and Technology, United
States; ²University of Maryland, United States; ³Rutgers University, United States; ⁴Kangwon National University, Korea (the Republic of); ⁵Pohang University of Science and Technology, Korea (the Republic of); ⁶Rutgers, The State University of New Jersey, United States

We have carried out neutron diffraction and small angle neutron scattering measurements on a high quality single crystal of the cubic lacunar spinel GaV₄S₈ multiferroic as a function of magnetic field and temperature. The system undergoes a structural transition at 44 K to a non-centrosymmetric rhombohedral symmetry and becomes ferroelectric. The system then orders magnetically below ~13 K into an incommensurate cycloidal phase. Further reduction of temperature transforms the system below 7 K into a ferromagnetic ground state. The ferromagnetic order parameter appears to be continuous with an ordered moment of 0.9 μB at the lowest temperature. Measurements of the magnetic intensities using both polarized neutron diffraction measurements and unpolarized field-induced moment measurements in the temperature range between the magnetic and ferroelectric transitions demonstrate that the single electron spin is distributed across all four V ions of the V₄ molecular unit, and does not just reside on the single apical V ion. This is in reasonable agreement with DFT calculations which show a moment on all four V but with an enhanced occupancy on the apical V in the ferroelectric phase. In the vicinity and below the transition to long range magnetic order there is a clear coupling of the ferroelectric and magnetic order parameters, necessitating polarized neutron measurements to determine the magnetic form factor. Field-dependent SANS data exhibit the cycloidal and skyrmion phases, which have been investigated in detail as a function of temperature and applied magnetic field. The intensities depend strongly on both temperature and field, while the incommensurate wave vector is strongly temperature dependent but exhibits a very weak field dependence. Finally, the skyrmion dynamics have been investigated at long time scales using the neutron time-tagging technique with a periodic perturbative magnetic field complementing the steady-state applied field. Varying the amplitude and frequency of the perturbation has been used to reveal important details of the time dependence of the Néel-type skyrmions as well as other aspects of the magnetic order.

4:45 PM MQ03.04.08
Raman Spectroscopy as a Probe of Magnetic Phenomena in Layered Quantum Materials
Amber McCready¹, Jeffrey Simpson¹,², Thuc Mai¹,³, Rolando Valdes Aguilar¹ and Angela Hight Walker¹; ¹National Institute of Standards and Technology, United States; ²Towson University, United States; ³The Ohio State University, United States

Recent observations of long-ranged magnetic ordering in van der Waals bonded, layered magnetic materials down to the single layer limit has led to a plethora of research dedicated to the study of two-dimensional (2D) magnets, with plenty of opportunities to investigate fundamental physics and potential quantum applications. With these materials, the properties are typically strongly correlated to the number of layers, with new physics occurring in the few-layer (~few nm) regime. In this sense, common techniques used to measure magnetic behavior such as neutron scattering and SQUID are at a disadvantage due to sample size requirements. On the other hand, Raman spectroscopy, which has diffraction-limited spatial resolution, is a powerful, non-destructive optical method to probe magnetism in 2D layered materials through inelastic scattering. An amazing amount of information is quantified from the Raman spectra such as layer thickness, disorder, edge and grain boundaries, strain, etc. Raman also efficiently probes the evolution of the spin-phonon interactions and magnetic excitations, such as magnons, as a function of temperature, laser energy, polarization, and magnetic field. I will discuss how we used our unique magneto-Raman capabilities to study the magnetic properties of the metal phosphorus trisulfide family (MPS₃, where M = Fe, Mn, and Ni) which are layered antiferromagnetic semiconductors. While the three materials have the same crystal structure, their varying spin structures result in distinct behavior as a function of temperature and magnetic field, which will be
presented herein. In FePS$_3$, we investigated spin-phonon coupling as well as the emergence of new modes in the magnetically ordered state that were not present in MnPS$_3$. Through magneto-Raman spectroscopy, we will show that one of these modes is actually a Raman-active magnon, where the symmetry behavior of the magnon can be explained using the magnetic point group of FePS$_3$.

SESSION MQ03.05: Charge, Spin and Topological Orders in Unconventional Superconductivity
Session Chairs: Alex Frano and Mingda Li
Wednesday Morning, December 4, 2019
Hynes, Level 2, Room 203

8:00 AM *MQ03.05.01
Superconductivity in an Infinite-Layer Nickelate Danfeng Li$^{1,2}$, Kyo Hoon Lee$^{1,2}$, Baiyang Wang$^{1,2}$, Motoki Osada$^{1,2}$, Samuel Crossley$^{1,2}$, Hyo Young Lee$^{1,2}$, Ye Cui$^{1,2}$, Yasuyuki Hikita$^1$ and Harold Y. Hwang$^{1,2}$; $^1$SLAC National Accelerator Laboratory, United States; $^2$Stanford University, United States

Since the discovery of high-$T_c$ superconductivity in (La,Ba)$_2$CuO$_4$, superconductivity in nickel oxide compounds has been a target of interest for many years. We report the observation of superconductivity in an infinite-layer nickelate that is isostructural to the infinite-layer cuprates [1]. Using soft chemistry topotactic reduction, single crystal infinite-layer nickelate thin films are synthesized by reducing the perovskite precursor phase. Experiments on these films indicate a $T_c$ of ~9-15 K. This compound can be considered one member of a series of reduced layered nickelate crystal structures, suggesting the possibility of a family of nickelate superconductors. In this talk, I will describe the film synthesis, discuss the superconductivity measurements, and present the latest developments in this emerging field.


8:30 AM *MQ03.05.02
Recent Developments from X-Ray Scattering Studies on Charge Order in High-$T_c$ Superconducting Cuprates
Matteo Minola; Max Planck Institute for Solid State Research, Germany

Incommensurate charge order (CO) has been identified as the leading competitor of high-temperature superconductivity in all major families of layered copper oxides, but the perplexing variety of CO states in different cuprates has confounded investigations of its impact on the transport and thermodynamic properties. The three-dimensional (3D) CO observed in YBa$_2$Cu$_3$O$_{6+x}$ (YBCO) in high magnetic fields is of particular interest, because quantum transport measurements have revealed detailed information about the corresponding Fermi surface. Here, we report a high-resolution inelastic hard x-ray scattering study of the high-temperature superconductor YBa$_2$Cu$_3$O$_{6.67}$ under uniaxial stress and show that a 3D long-range-ordered charge density wave (CDW) state akin to that observed in field along the $b$-axis can be induced by pressure applied along the $a$-axis, in the absence of magnetic fields and after enhancing the planar 2D CDW [1]. The amplitude of the 3D CDW is strongly suppressed below the superconducting transition temperature, indicating strong thermodynamic competition with superconductivity. We also show that a strong softening of an optical phonon mode is associated with the transition. We also used resonant soft X-ray scattering (RXS) at the Cu $L_3$ edge to investigate the planar symmetry of the strain-induced enhancement of the 2D CDW as well as the energy- and temperature-dependence of the 3D CDW scattering peak in single crystals of YBCO [2] and we compare the results with RXS data on the 3D charge order discovered in YBCO films grown epitaxially on SrTiO$_3$ (STO) [3]. The findings offer fresh perspectives for experiments elucidating the influence of 3D CDW on the electronic properties of cuprates without the need to apply high magnetic fields.

References

9:00 AM *MQ03.05.03
Coupling between Dynamic Magnetic and Charge-Order Correlations in the Cuprates Measured by RIXS
Eduardo H. da Silva Neto; University of California Davis, United States

Charge order has now been observed in several cuprate high-temperature superconductors. We report a resonant inelastic x-ray scattering experiment on the electron-doped cuprate NCCO that demonstrates the existence of dynamic correlations at the charge-order wave vector. Upon cooling we observe a softening in the electronic response, which has been predicted to occur for a d-wave charge order in electron-doped cuprates. At low temperatures, the energy range of these excitations coincides with that of the dispersive magnetic modes known as paramagnons. Furthermore, measurements where the polarization of the scattered photon is resolved indicate that the dynamic response at the charge-order wave vector primarily involves spin-flip excitations. Overall, our findings indicate a coupling between dynamic magnetic and charge-order correlations in the cuprates.

9:30 AM MQ03.05.04
Light Induced Non-Volatile Switching of Superconductivity in Single Layer FeSe on SrTiO$_3$ Heterostructures
Ming Yang, Chenhui Yan, Yanjun Ma, Lian Li and Cheng Cen; West Virginia University, United States

The capability of controlling superconductivity by light is highly desirable for active quantum device applications. Since superconductors rarely exhibit strong photoresponses, and optically sensitive materials are often not superconducting, the efficient coupling of these two characters in a single material can be very challenging. Here we show that, in FeSe/SrTiO$_3$ heterostructures, the superconducting transition temperature in FeSe monolayer can be effectively raised by the interband photoexcitations in the SrTiO$_3$ substrate. Attributed to a light induced metastable polar distortion uniquely enabled by the FeSe/SrTiO$_3$ interface, this effect only requires a less than 50 µW cm$^{-2}$ continuous-wave light field. The fast optical generation of superconducting zero resistance state is non-volatile but can be rapidly reversed by applying voltage pulses to the back of SrTiO$_3$ substrate. The capability of switching FeSe repeatedly and reliably between normal and superconducting states demonstrate the great potential of making energy-efficient quantum optoelectronics at designed correlated interfaces.

9:45 AM MQ03.05.05
In Situ Micromechanical Characterization of Iron-Based High Temperature Superconductors
Seok-Woo Lee, Gyuho Song, John T. Sypek and Shuyang Xiao; University of Connecticut, United States

High temperature Fe-based superconductors have recently drawn a strong attention due to their superconducting capability even in the presence of magnetic Fe, which has been regarded as a harmful element for superconductivity. Particularly, ThCr$_2$Si$_2$-structured Fe-based superconductors have been extensively studied due to their strong pressure sensitivity of structure and electronic/magnetic properties. Under hydrostatic pressure, they undergo the collapsed tetragonal (cT) phase transition through the formation of Si-Si type bonds. During this process, a magnetic state changes and superconductivity often disappears. Therefore, it is interesting to understand how mechanical deformation influences electronic structure, magnetism, and superconductivity.

For the last decade, nanomechanics community has reported numerous papers regarding the size-dependent strengthening and toughening at the nanometer scale; as the sample dimension decreases, a material can withstand the larger elastic deformation under uniaxial mechanical loading. For instance, silicon nanowire can be uniaxially stretched up to a strain above 15% before failure. This giant elastic deformability at the nano-scale can certainly open a new opportunity of “Strain-Engineering of Superconductors”. In this presentation, we will introduce our custom-built in-situ cryogenic micromechanical testing system that allows us to characterize mechanical behaviors of micron-sized iron-based high temperature superconductor under uniaxial mechanical loading. Micropillars of various ThCr$_2$Si$_2$-type iron-based superconductors were fabricated using focused ion beam milling, and uniaxial mechanical tests were performed along a [0 0 1] direction. Contrast to the conventional belief of easy brittle fracture under uniaxial loading, our results show the giant elastic strain over 10%, which is high enough to see the cT phase transition. This large elastic deformation is reversible, implying that it is possible to induce the forward and backward transitions continuously under the application of cyclic force. Thus, the giant elastic deformability at the
nano-scale is still hold for iron-based superconductors. Compared to hydrostatic pressure, uniaxial mechanical loading has a great advantage to apply a mechanical force along a chosen crystallographic orientation. In addition, our on-going development of liquid helium cooling capability will allow us to explore the effects of uniaxial deformation on superconductivity. We will share some of our preliminary results of in-situ cryogenic mechanical testing on high temperature superconductor, CaKFe4As4 at T=40~298 K. We strongly believe that the combination of nanomechanics and superconductivity will create a unique opportunity to explore the effects of unconventionally large elastic strain on the critical temperature of superconductivity, magnetism, and electronic structures of superconductors.

10:00 AM BREAK

10:30 AM *MQ03.05.06

Pair-Density Waves and Gapless Spin Fluctuations in Cuprate Superconductors John M. Tranquada; Brookhaven National Laboratory, United States

An unusual form of two-dimensional (2D) superconductivity has been observed in bulk crystals of La2-xBaxCuO4 (LBCO) with x ~ 1/8. To explain the apparent frustration of interlayer Josephson coupling, the occurrence of pair-density-wave superconductivity has been proposed [1], which is compatible with the known existence of spin and charge stripe orders. To test this possibility further, we recently performed transport measurements in a c-axis magnetic field of up to 35 T. At a temperature of less than 1 K, evidence was found for a progression, with increasing field, from 3D order to reentrant 2D superconductivity to an unusual metallic state with very large resistance per plane but negligible Hall effect. To see whether such behavior is unique to LBCO, crystals of La2-xCa1+xCu2O6 have been grown. Annealing in high-pressure oxygen results in dilute intergrowths of La2CuO4 and La8Cu8O20; however, the apparent Ca-enrichment of the main phase results in a superconducting transition temperature $T_c$ as high as 55 K [3]. Transport measurements demonstrate a decoupling of the superconducting bilayers in modest magnetic field [4]. Time-of-flight neutron scattering measurements reveal low-energy spin fluctuations that do not develop a gap below $T_c$ [5]. This behavior is similar to that in LBCO, suggesting the importance of intertwined order.

Work at Brookhaven is supported by the Office of Basic Energy Sciences, Materials Sciences and Engineering Division, U.S. Department of Energy, through Contract No. DE-SC0012704.


11:00 AM MQ03.05.07

Growth of Single Crystals of Ni,ZrTe2 and Investigation of Superconducting Properties Lucas F. Correa, Frederico Santos and Antonio Machado; University of São Paulo, Brazil

This work is about the growth of high quality single crystals by the CVD method of dicalcogens that crystallize in the CdI2 prototype. Preliminary results shown in this plan strongly suggest that it is possible to grow high quality single crystals by this method represented by a member of the family which is Ni0.02ZrTe2. Band structure calculations, as well as some results reported in the literature, show that this type of prototype presents a non-trivial topology and, in this sense, the superconductivity that coming from this prototype can be a clear example of non-artificial topological superconductors. In addition to these aspects relevant to Condensed Matter Physics, the following plan intends to complement the formation of this candidate, in this effervescent area of the new Condensed Matter Physics

11:15 AM MQ03.05.08

Polyanions as Spacers to Create 2D Iron Materials Yohann Bréard; Crismat Laboratory, France

The properties of materials are determined by their dimensionality but also by the interatomic chemical bonding. It is then of interest to combine effort to control both aspects: chemical and dimensional. The low dimensional
transition metal oxides showing 2D magnetic sheets, are of great interest due to their strong magnetic and electronic anisotropies which usually lead to complex phenomena (as spin density waves, superconducting, or step magnetization reversibility to name a few). In addition to the fundamental interest, spintronic applications are also of great interest: 2D spin-valve compounds, or magnetic tunnel junction are currently heavily exploited for magnetic random access memory (MRAM) memories. The latter two-dimensional structure compounds consist mainly of alternately ferromagnetic and non-magnetic layers that are generally obtained by the thin-film deposition technique. It is of interest to obtain new solid 2D materials with an angstrom-scale alternation of magnetic / non-magnetic layers inherent to their atomic structure, through which analysing the spin-dependent transport. On the other hand, this would avoid the current synthesis by thin film deposition more complicated to implement.

The use of voluminous polyanions can leads to original 2D atomic structures - This has been amply demonstrated in cuprates superconductors (Sr2CuO2(CO3), La1.85Sr0.15Cu1-x(SO4)xO4)). Paradoxically, few studies have been conducted in mixed polyanion iron oxide systems. We can nevertheless quote the oxyphosphate compound SrFe3(PO4)O or the oxycarbonate Sr4Fe2O6(CO3), described by Yamaura and Bréard. The latter is an intergrowth between SrFeO3 perovskite layers and "rock-salt" SrO layers where FeO6 octahedra of the middle perovskite layer has been replaced by carbonate groups showing the possibility to create intergrowths between carbonates and a transition metal which is not a Jahn-Teller element. This substitution strategy has been recently extended to sulfate anions which are also divalent but even larger than carbonates and more electronegative than oxygen and carbonates; They have also a radically different geometry. All these differences lead to different magneto electric behaviors that will be highlighted in the presentation.

11:30 AM MQ03.05.09
Kauzmann Entropy Paradox, and the "Ideal Glass Transition" Viewed as a Self-Dual Critical Point at the Four-Dimensional Crystal/Glass Quantum Phase Transition Caroline S. Gorham and David E. Laughlin; Carnegie Mellon University, United States

Notwithstanding decades of work, the realization of a fundamental understanding of amorphous structures and their transport properties has remained a great challenge. In this research, we approach a description of amorphous structures by considering thermodynamic descriptions of the solidification of undercooled fluids upon the adoption of a quaternion orientational order parameter. Unlike the first-order transition of a liquid into a crystal, the glass transition is an entirely different phenomenon. In particular, as the temperature of an undercooled liquid decreases the difference in entropy between the liquid and solid phase decreases. At a certain point, known as the Kauzmann point that may be achieved in the limit of an infinitely slow cooling rate, the entropies of the liquid and crystal phase are equal. At the Kauzmann point, which occurs at a finite Kauzmann temperature, the liquid adopts a unique state of lowest energy such that its entropy approaches zero as temperature approaches zero. Herein, the "ideal glass transition" that occurs at the Kauzmann point is identified as a first order quantum phase transition between crystalline and non-crystalline solid states that are characterized by a four-dimensional quaternion orientational order parameter. In particular, there is a discrete change in the topology of the orientational order parameter manifold of the solid state at this critical point from a three-dimensional torus ($T^3$) to a three-dimensional sphere ($S^3$). Similarities between the finite temperature first-order crystal-to-glass transition and the superfluid-to-Mott insulator quantum phase transition are identified herein.

SESSION MQ03.06/MQ01.06/MQ02.06: Panel Discussion: Quantum Materials
Session Chairs: Jeffrey McCallum and Christopher Richardson
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 202

3:30 PM PANEL DISCUSSION: QUANTUM MATERIALS

SESSION MQ03.07: Spin-Orbital Coupling in Quantum Materials
Session Chairs: Thomas Tybell and Hua Zhou
8:30 AM  *MQ03.07.01

**Strain-Induced Enhanced Berry Curvature in Pyrochlore Iridate Thin Film**  
Tae Won Noh\(^1,2\), 1Center for Correlated Electron Systems, Institute for Basic Science, Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

Pyrochlore iridates have been predicted to exhibit many fascinating topologically non-trivial states due to strong spin-orbit coupling (SOC) and electron correlations [1]. Importantly, they have the all-in-all-out (AIAO) antiferromagnetic ordering that breaks time reversal symmetry (TRS). With broken TRS, it was predicted that a magnetic Weyl semimetal (WSM) phase could emerge in pyrochlore iridates. In addition, theoretical studies revealed the emergence of a new topological phase of which are hidden in the bulk and manifest only in thin films [3-5]. In spite of these exotic phenomena, most of the works were focused on the bulk single crystals or ex-situ grown relaxed films. The multi-phase boundary of iridium presents an extreme difficulty in the in-situ epitaxial growth of such thin film samples.

Here, we report a high quality Nd\(_2\)Ir\(_2\)O\(_7\) thin film grown on Yttrium stabilized ZrO\(_2\) (YSZ) substrates by pulsed laser deposition, using a special in-situ growth technique called “repeated rapid pulse annealing epitaxy”. A large anomalous Hall effect (AHE) signal was observed in Nd\(_2\)Ir\(_2\)O\(_7\) thin film where the size is ~ 10\(^6\) times larger than that of Nd\(_2\)Ir\(_2\)O\(_7\) bulk. The tight binding calculation provided that strain effect can produce large Berry curvatures in the system and responsible to give large anomalous Hall effect. Moreover, we have observed chiral anomaly from the transport measurement which considered to be related to its possible magnetic WSM states. Our finding highlights that strain effect in pyrochlore iridates can be the way to engineer Berry curvature. Moreover, it may open a door to investigate the Berry curvature engineered correlated topological states in the oxides.

References:

9:00 AM  MQ03.07.02

**Synthesis of Barium Iridates with Unconventional Magnetic Ground States**  
Xiang Chen\(^1,2\), Dongsheng Yuan\(^1\), Siqi Wang\(^2\) and Robert Birgeneau\(^2,1\); 1Lawrence Berkeley National Laboratory, United States; 2University of California, Berkeley, United States

Realization of new states of quantum matter is persistently desired in condensed matter physics and material science engineering. Some outstanding example systems include high transition temperature superconductors (high Tc SC), topological insulators (TI), quantum spin liquids (QSL), etc… A recently reported spin trimer chain compound Ba\(_4\)Ir\(_3\)O\(_10\), which crystallizes in a different lattice than conventional geometrically frustrated motifs such as in pyrochlore and Kagome lattice, might offer a new platform for engineering unusual quantum spin liquid states. The similar chain compound BaIrO\(_3\), however, exhibits magnetic order at much elevated temperature 183 K, concomitant with the onset of charge density order. Here we report the powder and single crystal growth of a plethora of Barium Iridium Oxides with contrasting unconventional magnetic ground states which share a great deal of structural similarities. Our current explorations indicate a potential playground for emerging quantum materials in Barium Iridates.

9:15 AM  *MQ03.07.04

**Towards Building and Testing Quantum Structures Atom-by-Atom with Electron Beams**  
Stephen Jesse, Ondrej Dyck, Andrew Lupini and Sergei Kalinin; Oak Ridge National Laboratory, United States

Fabricating atomic scale structures remains as an ultimate goal of nanotechnology. Scanning Probe Microscopes and molecular self-assembly have demonstrated important successes towards achieving this goal. In this presentation, I discuss research activity towards the use of the atomically focused beam of a scanning transmission electron microscope (STEM) to control and direct matter on the atomic scale. Traditionally, STEM’s are perceived only as
imaging tools and the material modifications induced by their highly energetic (on the order of 100 kV) and highly focused (sub-angstrom) beams considered as undesirable beam damage. However, if these material changes can be directed through precise control over beam trajectory, the use of active feed-back, and control over temperature and environment, it is possible to use the STEM as a platform for not just imaging, but manufacturing at the atomic scale. We have demonstrated single defect formation, controlled individual dopant placement and migration, and drilling and milling in single layer 2D materials with the goal of building materials and devices for quantum application. I will introduce several examples of beam-induced fabrication on the atomic level, and demonstrate how beam control, rapid image analytics based on traditional and artificial intelligence techniques, better insight through modelling, and image- and spectroscopy-based feedback allows for controlling matter on atomic level and investigating emergent properties.

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Division of Materials Science and Engineering, Basic Energy Sciences and was performed at the Oak Ridge National Laboratory’s Center for Nanophase Materials Sciences (CNMS), a U.S. Department of Energy, Office of Science User Facility.

9:45 AM BREAK

10:15 AM *MQ03.07.05
The Many Faces of Spin—Orbit Coupling in Quantum Materials Alessandra Lanzara1,2; 1University of California Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

Just when we thought the spin-orbit interaction in solids was finally explained, a plethora of new discoveries have appeared, challenging our understanding and imagination of what the implications and manifestation of this relativistic effect might be. Today the field of spin-orbit coupling is a vibrant one, ranging from the construction of revolutionary experimental tools for imaging spins of electrons in both momentum, energy and time domain, to the development of new theories and models aimed at predicting and explaining unexpected behaviors. In this talk I will present an overview on the state of the art experimental techniques to study such interaction in condensed matter physics, and I will discuss a couple of examples of how such interaction evolves from 2D transition metal dichalcogenides, to topological insulators and finally unconventional superconductors where such interaction gets coupled with strong correlation leading to novel behavior.

10:45 AM MQ03.07.06
A New Magnetic Topological Quantum Material Candidate by Design Xin Gui1, Ivo Pletikosic2,3, Huibo Cao4, Hung-Ju Tien1, Xitong Xu4, Ruidan Zhong4, Guangqiang Wang5, Tay-Rong Chang5, Shuang Jia6, Tonica Valla2, Weiwei Xie1 and Robert J. Cava1; 1Louisiana State University, United States; 2Brookhaven National Laboratory, United States; 3Princeton University, United States; 4Oak Ridge National Laboratory, United States; 5National Cheng Kung University, Taiwan; 6Peking University, China

Magnetism, when combined with an unconventional electronic band structure, can give rise to forefront electronic properties such as the quantum anomalous Hall effect, axion electrodynamics and Majorana fermions. Here we report the characterization of high-quality crystals of EuSn2P2, a new quantum material specifically designed to engender unconventional electronic states plus magnetism. EuSn2P2 has a layered, Bi2Te3-type structure. Ferromagnetic interactions dominate the Curie-Weiss susceptibility, but a transition to antiferromagnetic ordering occurs near 30 K. Neutron diffraction reveals that this is due to two-dimensional ferromagnetic spin alignment within individual Eu layers and antiferromagnetic alignment between layers - this magnetic state surrounds the Sn-P layers at low temperatures. The bulk electrical resistivity is sensitive to the magnetism. Electronic structure calculations reveal that EuSn2P2 might be a strong topological insulator, which can be a new magnetic topological quantum material (MTQM) candidate. The calculations show that surface states should be present, and they are indeed observed by ARPES measurements.

11:00 AM MQ03.07.07
Fermi Level Tuning and Quantum Coherent Transport in Bi-Doped Pb1-xSnxSe Jiashu Wang1, Xinyu Liu1, Seul-Ki Bac2, Sanghoon Lee2, Jacek K. Furdyna4 and Badih A. Assaf3; 1University of Notre Dame, United States; 2Korea University, Korea (the Republic of)
Pb$_{1-x}$Sn$_x$Se (x<0.4) is a narrow gap semiconductor and it can have topological phase transition to topological crystalline insulator (TCI) when the concentration of Sn increases. Its electronic properties are sensitive to electric and magnetic fields. It is thus worth considering in the fabrication of electronic devices. Here we investigated the MBE growth of Pb$_{1-x}$Sn$_x$Se (x=0.2-0.3) doped with Bi and characterized the sample using X-ray diffraction (XRD), and magneto-transport measurement. We showed that doping Bismuth into the sample can significantly lower the carrier density, even change its type from p=2.9×10$^{18}$ cm$^{-3}$ to n=1.1×10$^{19}$ cm$^{-3}$. We studied how quantum coherent transport depends on this tuning process. This tunability can be useful in the fabrication of quantum devices.

11:15 AM MQ03.07.08
Single Crystal Growth and Low-Temperature Characterization of Nonsymmorphic Ca$_2$Pt$_2$Ga Frederico Santos$^{1,2}$, Priscila Rosa$^1$, Joe Thompson$^1$, Eric Bauer$^1$, Filip Ronning$^1$ and Sean Thomas$^1$; $^1$Los Alamos National Laboratory, United States; $^2$Universidade de Sao Paulo, Brazil

Recently, about 25% of all known uncorrelated compounds have been predicted to host topological properties. According to these theoretical predictions, Ca$_2$Pt$_2$Ga is a filling-enforced topological semimetal candidate. Here we present a route for the synthesis of Ca$_2$Pt$_2$Ga single crystals, which are characterized by single crystal x-ray diffraction, energy dispersive spectroscopy, magnetic susceptibility, electrical resistivity, Hall effect and heat capacity at low temperatures. We will compare our experimental data with theoretical expectations.

11:30 AM MQ03.07.09
Electronic and Mechanical Property Characterization of Pure β-Tungsten Films Heun Tae Lee$^1$, Akira Nagakubo$^1$, Hitoshi Yamaoka$^2$, Hitoshi Sato$^1$, Yoshio Ueda$^1$ and Hirotsugu Ogi$^1$; $^1$Osaka University, Japan; $^2$RIKEN SPring-8 Center, Japan; $^3$Hiroshima Synchrotron Radiation Center, Hiroshima University, Japan

Thin film β-tungsten (β-W) is attracting extensive attention due to its giant spin Hall effect and promising application in spintronics as memory devices. Large spin currents have been used to set the magnetization of adjacent magnetic layers using the spin torque effect [1], and utilization of the large spin-Hall angle of β-W (0.3) [2] appears promising. However, the reason for the large magnitude of the spin Hall angle in β-W is presently not known. Clarifying whether the giant spin Hall effect arises from extrinsic or intrinsic properties is the first step towards engineering β-W based spin torque devices. Extrinsic effects arise from spin-dependent scattering with impurities or band structure peculiarities. To date, no work has experimentally examined the electronic density of states in pure β-W thin films. In this work, we present high-resolution valence band spectra near the Fermi level of pure β-W thin films measured by photoelectron spectroscopy using synchrotron radiation. Only fine difference in the double peak structure between -2 and -4 eV is observed between β-W and α-W. Such effects are qualitatively reproduced in calculations. However, the experimental spectra are complicated by the presence of oxygen surface contamination, and its presence is never reduced completely even after successive in-vacuo sputtering. Large spin Hall angles reported in other thin film materials generally arise due to spin-orbit interaction of impurities [3], or resonant/surface skew scattering effects with impurity sites [4]. Our results indicate that the role of oxygen impurities on β-W surfaces should be clarified in the reported large spin Hall angles of β-W layered systems. The mechanical and structural properties of thin films were characterized using a combination of novel picosecond ultrasonic measurements and standard X-ray diffraction. The calculated elastic constants using density functional theory agreed within 10% of the experimental values for both β-W and α-W.

SESSION MT01.01: Electronic Structure I
Session Chairs: Enrique Martinez and William Witt
Monday Morning, December 2, 2019
Hynes, Level 2, Room 206

8:00 AM *MT01.01.01
Recent Work Involving Orbital-Free Density Functional Theory William C. Witt¹, Beatriz Gonzalez del Rio¹, Florian Libisch², Kaili Jiang¹ and Emily A. Carter¹; ¹Princeton University, United States; ²Vienna University of Technology, Austria

Simulations based on modern orbital-free density (OF) functional theory (DFT) can be orders of magnitude faster than those performed with conventional Kohn-Sham DFT, largely because OF-DFT does not require any wavefunction operations. However, while OF-DFT is sufficiently accurate for many materials of practical relevance, it cannot yet replace wavefunction-based KS-DFT entirely, a longstanding goal. We report recent progress towards this goal, beginning with advances in the construction of the local pseudopotentials (LPSs) that are commonly employed to account for the electron-ion (screened nucleus) interaction. In particular, we highlight a method for constructing LPSs appropriate for both solid and liquid phases, commenting on OF-DFT simulations that recently confirmed the existence of a second excitation mode in the collective dynamics of liquid Sn. We also discuss efforts to overcome the main obstacle to universally accurate OF-DFT, which is determining the (noninteracting) electron kinetic energy without recourse to wavefunctions. These efforts range from careful study of the local, gradient-based kinetic energy density of nearly free electrons, including the derivation of new response functions for this purpose, to hybrid techniques that incorporate localized atom-centered density matrices within the usual OF formalism. We conclude by outlining recent updates to our widely used OF-DFT code, PROFESS.

8:30 AM MT01.01.02
Has the Ubiquitous Use of Plane Wave DFT Codes Distorted the Perception of Functional Behavior and of the Need for +U? Daniel Koch¹ and Sergei Manzhos²; ¹National University of Singapore, Singapore; ²Institut National de la Recherche Scientifique, Canada

DFT-based computational materials science literature is dominated by the use of plane wave codes, with a single such code being most widely used. In the modeling of bulk materials and interfaces, GGA functionals remain most widely used. There is a well-established narrative according to which such functionals (e.g. the popular PBE functional) cannot reproduce localized states, resulting from e.g. doping of oxides with alkali and alkaline earth atoms, and cannot correctly reproduce the qualitative nature of the bandstructure, e.g. ordering of p and d bands in some oxides. This is typically remedied by the use of the Hubbard correction (DFT+U). Such correction, however, often distorts the geometry and worsens the issue of local minima in density optimization. The perceived need to employ the Hubbard correction for semiconductor but not for metallic phases is also an issue, as it may be impossible to correctly model different phases with a single computational setup; this in turn makes more difficult the modeling of phenomena involving phase transitions.
We show that it is possible to obtain qualitatively correct bandstructures and localization of states with the PBE functional without the Hubbard correction when using localized basis sets in cases where +U is necessary with plane waves. This was observed in different codes, using pseudopotentials or all-electron calculations. Correct band ordering can be obtained (such as O(p) dominated valence band maximum in NiO) and localized states and spin ladders due to interstitial n-doping can be obtained in oxides (titania and vanadia). Moreover, without +U, qualitatively correct bandstructures can be obtained with PBE for metallic and semiconductor phases of VO2 simultaneously, which we could not obtain in VASP without or with +U with commonly used U values. Formation energies computed in such systems without +U are in good agreement with experiments (as probed by insertion voltages with oxide cathodes in metal ion batteries).

We highlight the fact that with plane wave basis sets, expansion errors are higher for localized than for delocalized states, which could be contributing to artificial delocalization. To fully nivellate this issue, unrealistically high plane wave cutoffs could be required.

8:45 AM *MT01.01.03
Fast, Accurate and Scalable Large-Scale DFT Calculations Using DFT-FE Phani Motamarri, Sambit Das and Vikram Gavini; University of Michigan, United States

Large-scale DFT calculations are very crucial to improve the predictive capabilities of computation based design of new materials in a variety of application areas. For example, accurate determination of dislocation core properties in metals and semiconductors, understanding ion conduction mechanisms and computing diffusivities in solid-state electrolytes, and large-scale bio-molecular simulations, all require the ability to conduct accurate and computationally efficient DFT calculations involving many thousands of atoms on both metallic and insulating systems. However, the solution to governing equations in DFT demands significant computational resources, and accurate DFT calculations are routinely limited to materials systems with at most a few thousands of electrons restricting the system sizes to a few hundred atoms. This computational complexity is of even bigger concern in the context of ab-initio molecular dynamics with long time-scales, and geometry relaxation of large-scale systems needing large number of relaxation steps.

To overcome the above limitations, an open-source code DFT-FE [1] based on adaptive finite-element discretization of DFT has recently been developed. This talk will present the methodological and algorithmic advances incorporated into DFT-FE, which has enabled systematically convergent and computationally efficient large-scale DFT calculations on materials systems with tens of thousands of electrons for both metallic and insulating systems, on massively parallel computing architectures, while allowing for arbitrary boundary conditions and complex geometries. Key computational ideas involved in the development of DFT-FE will be discussed, which include: (i) a unified real-space formulation for DFT treating both pseudopotential and all-electron calculations in the same framework [2]; (ii) mesh adaption for efficient finite-element discretization [2]; (iii) adaptive higher-order spectral finite-element framework in conjunction with Chebyshev acceleration [3], spectrum splitting based Rayleigh procedure combined with mixed precision arithmetic; (iv) configurational force approach for geometry optimization [4]. The numerical investigations conducted with DFT-FE on representative benchmark examples will be presented alongside performance comparisons with other widely used DFT codes like Quantum Espresso and ABINIT.

References


9:15 AM *MT01.01.04
Unraveling Exciton Dynamics in 2D van der Waals Heterostructures Junyi Liu, Xu Zhang and Gang Lu; California State University Northridge, United States
Two-dimensional (2D) van der Waals (vdW) heterostructures offer a fascinating platform to pursue fundamental science and novel device applications. Owing to quantum size confinement and reduced dielectric screening, electron-electron interaction and excitonic effect are prominent in 2D materials, which could dominate their electron and exciton dynamics. Recent experiments have revealed ultrafast charge (~100 fs) and energy (~1 ps) transfer dynamics in transition metal dichalcogenides (TMDs) heterostructures, which is surprising giving the strong electron-hole binding of the interlayer excitons. Most theoretical calculations to understand the experiments were performed based on local and semi-local exchange-correlation functionals, thus cannot capture the excitonic effect accurately. In this talk, I will introduce a first-principles method that combines non-adiabatic molecular dynamics (with the fewest switch surface hopping algorithm) and linear-response time-dependent density functional theory. Importantly, the method is formulated in the planewave bases and PAW pseudopotentials with range-separated hybrid functionals. As a result, the method can capture the excitonic effect accurately in extended 2D heterostructures. Using this method, we can shed light on the ultrafast charge transfer dynamics in TMD vdW heterostructures and elucidate the role of “hot” excitons in promoting ultrafast charge transfer despite the momentum mismatch in twisted heterostructures. We can also examine the properties of interlayer and intralayer excitons trapped by the moiré superlattices in the twisted heterostructures, and tune their properties and lifetimes by changing the twist angle, pressure and electric field.

9:45 AM MT01.01.05
Computational Raman Spectroscopy Based on Time-Dependent Density Functional Perturbation Theory Xu Zhang; California State University, Northridge, United States

Vibrational Raman spectroscopy is a widely used analytical tool in gas-phase and condensed-matter materials. Interpretation of the Raman spectra and detailed deduction of structures and/or conformations require theoretical simulations. However, the application of the present established computational Raman approaches to large-scale systems remains challenging, in a large part owing to their high computational demand. Here we propose a method that combine plane-wave pseudopotential method, time-dependent density functional perturbation theory and an elegant Lagrangian approach to circumvent key bottlenecks of Raman spectra simulations for large-scale systems. The method is validated for several molecular and solid systems, and exhibits excellent agreements with the experimental Raman spectra. We show that the method has a quadratic computational scaling with the number of electrons which can treat systems with more than 4000 electrons, opening doors for many large-scale Raman computations that are beyond the reach of previous approaches.

10:00 AM BREAK

10:30 AM *MT01.01.06
High-Throughput Materials Discovery and Development—Breakthroughs and Challenges in the Mapping of the Materials Genome Marco Buongiorno Nardelli; University of North Texas, United States

High-Throughput Quantum-Mechanics computation of materials properties by ab initio methods has become the foundation of an effective approach to materials design, discovery and characterization. This data driven approach to materials science currently presents the most promising path to the development of advanced technological materials that could solve or mitigate important social and economic challenges of the 21st century. In particular, the rapid proliferation of computational data on materials properties presents the possibility to complement and extend materials property databases where the experimental data is lacking and difficult to obtain. The practical realization of these opportunities depends almost exclusively on the design of efficient algorithms for electronic structure simulations of realistic material systems beyond the limitations of the current standard theories. In this talk, I will review recent progress in theoretical and computational tools for data generation and advanced characterization, and in particular, discuss the development and validation of novel functionals within Density Functional Theory and of local basis representations for effective ab-initio tight-binding schemes.

Applications of these methods to a variety of systems (anomalous transport properties of 2D materials, topological insulators, minerals as novel thermoelectrics, etc.) will be showcased.

11:00 AM MT01.01.07
Accurate Ab Initio Tight Binding for Magnesium Richard Fogarty, Jana Smutna and Andrew P. Horsfield; Imperial College London, United Kingdom
Magnesium alloys are promising as lightweight structural materials, electrodes in Mg batteries, and for use in medical implants.\textsuperscript{1-3} As use of Mg is limited largely due to poor corrosion resistance a better understanding of these processes is required. Corrosion is an electrochemical process, involving transfer of electrons, thus a quantum mechanical theory is needed to model it. Density functional theory (DFT) has been used to study aspects of Mg corrosion, but its high cost limits the length and time scales which can be probed.\textsuperscript{4,5} Density functional tight binding (DFTB) represents a cheaper, though approximate, alternative to full DFT that maintains a fully quantum mechanical description. In this work we present a DFTB model for Mg which can describe the many properties of the metallic system at a level similar to DFT.

Compared to plane-wave DFT, our model introduces three approximations: we use the Harris-Foulkes functional up to first order (no self-consistency); we use a small (single-zeta) \textit{spd} basis set; we treat electron exchange and correlation in an approximate way using the McWeda method.\textsuperscript{6}

The validity of our DFTB model is demonstrated by comparison to plane-wave results for structural properties (e.g. volumes and bulk-moduli), electronic properties (density of states) and defect energies (self-interstitials and vacancies). Future work will focus on adding the necessary elements to investigate aqueous magnesium corrosion.

References
protocols, which often couple several specialised codes, make a quantitative description of error propagation and uncertainty quantification a critical issue.

To handle this high level of complexity we have developed the integrated development environment (IDE) pyiron – http://pyiron.org. The pyiron IDE combines a web based source code editor, a job management system for build automation, and a hierarchical data management solution. The core components of the pyiron IDE are pyiron objects based on an abstract class, which links application structures such as atomistic structures, projects, jobs, simulation protocols and computing resources with persistent storage and an interactive user environment. The simulation protocols within the pyiron IDE are constructed using the Python programming language.

In order to analyse the delicate interplay of uncertainties in our complex protocols, we introduce the concept of uncertainty phase diagrams. Based on this concept we model the convergence gradients of the contributing errors. It also provides a firm basis to automate the convergence process. Employing this approach we find that already the determination of the equilibrium lattice constant and bulk modulus require a careful analysis of the fitting of energy-volume curves, going beyond the consideration of standard convergence parameters like energy cutoff and k-points. Our investigations revealed that commonly used rules of the thumb for fitting ground state materials properties become invalid for high precision calculations, as the dominating sources of error change.

SESSION MT01.02: Electronic Structure II
Session Chairs: Marc Cawkwell and Gideon Simpson
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 206

1:30 PM MT01.02.01
The Limits of Two-Center Tight Binding for Close-Packed Metals Jana Smutna, Richard Fogarty, Mark R. Wenman and Andrew P. Horsfield; Department of Materials, Imperial College London, United Kingdom

Tight binding models offer a compromise between the accuracy and transferability of DFT and the speed of empirical force field models. By explicitly computing the electronic structure of a given system, they can improve the understanding of the bonding in a given material. The use of a limited basis set of atom-centric orbitals and further approximations allow computationally expensive numerical integration to be replaced by a fast interpolation between pre-calculated values.

These models are promising when it comes to modeling corrosion or large scale defects (e.g. dislocation cores), where a good description of bonding plays a major role, but the system sizes needed are beyond the reach of conventional DFT. In particular, we would like to gain mechanistic insights about the effect of irradiation on the corrosion of zirconium alloy nuclear fuel cladding. To model the interaction of alloying and impurity elements with the damage resulting from neutron irradiation, a tight binding model capable of representing a range of impurity and alloying elements and atomic environments with good accuracy and transferability is needed. Here, we concentrate on the case of zirconium, however, the results can be generalised to most close-packed metals.

The majority of current methods for building tight binding models are heavily dependent on optimisation, making the addition of new elements challenging and the transferability limited [1,2].

In this work, we have followed a systematic, parameter-free method, starting from an appropriate choice of basis set and evaluating the effect of further approximations on the model. We have explored the two-centre approximation for both the pair potential and the components of the Hamiltonian matrix: crystal field terms and hopping integrals. While transferable and reasonably accurate corrections to the first two components are relatively straightforward, an equivalent correction for the hopping integrals is both theoretically and computationally challenging. We show that keeping the hopping integrals two-centre but adjusting their distance dependence causes significant transferability problems not only when describing other crystal structures, point defects or interstitial impurities, but also when simply considering one crystal structure in tension or compression.

The inclusion of three-centre integrals significantly improves the transferability of the model.

References
1. Schnell I, Jones MD, Rudin SP, Albers RC. Tight-binding calculations of the elastic constants and phonons of hcp
Understanding phonon-mediated heat transfer at the nanoscale remains an open and technologically-important challenge, with diverse applications across thermoelectrics, nanoelectronics, catalytic cells, and nanotheranostics. Such systems are often spatially inhomogeneous, necessitating theoretical descriptions with spatial resolution, and consist of non-crystalline disordered solids. Ab initio mathematical treatments developed for studies of lattice vibrations in perfectly ordered crystals, however, offer limited utility in investigations of disordered solids. These limitations include: (i) inseparability of diagonal (substitutional), off-diagonal, and ‘environmental’ disorder, and (ii) inconsistency in using perfect lattice states (i.e. phonons) as basis functions for the momentum representation of collective excitations. Numerical calculations, using lattice and molecular dynamics, on simulated disordered solids have corroborated the breakdown of phonons as well-defined excitations (i.e. with mean free paths much larger than their wavelength), and have suggested an alternate classification of ‘propagons’, ‘diffusons’, and ‘locons’.

While these advances have provided insight in spatially homogeneous (bulk) thermal transport in disordered solids, they depart from the intuitive ‘kinetic theory’ picture and as such offer limited use in atomistic-to-continuum modeling of spatially-resolved transport. We treat the medium as a continuum capable of supporting approximate plane-wave excitations, experiencing scattering due to the atomistic disorder, in much the same way external plane waves (e.g. x-rays) would. We compute these scattering rates, first proposed by Ziman and Morgan, from first principles using Fermi’s golden rule. In particular, the formalism requires access to the real-space harmonic and anharmonic interatomic force constants which, we will show in this talk, are extracted at finite temperature by sampling the canonical phase-space using Born-Oppenheimer ab initio molecular dynamics (BO AIMD). We demonstrate this formalism by computing the spatially-resolved thermal transport across crystalline/amorphous silicon (Si/α-Si) heterostructures with micron dimensions, length scales typically not accessible to (classical) molecular dynamics.


2:00 PM MT01.02.03
Polynomial Expansion and Purification Methods for Large Scale Electronic Structure Calculations Purnima Ghale and Harley T. Johnson; University of Illinois at Urbana-Champaign, United States

Computing the density matrix for a large Hamiltonian is the most expensive part of many electronic structure calculations. At zero temperature, the density matrix is a projection matrix constructed from the outer product of the lowest occupied eigenstates, satisfying idempotency and trace conditions. In this talk, we present a method combining two well-known algorithms – the Kernel Polynomial Expansion (KPE) method and Spectral Projection Purification – which allows us to obtain idempotent density matrices of large systems while relying only on sparse matrix-vector multiplication kernels. An implicit representation of the density matrix is obtained by combining the two aforementioned algorithms, which is then sampled using random vectors. This scheme allows us to compute the density matrix at linear computational cost in terms of floating-point operations. Additionally, the method is independent of the underlying basis set, and does not require the density matrix to be sparse. Within the context of density-functional based tight-binding (DFTB), we present results of self-consistent density matrix calculations of systems containing $10^7$ atoms. As an application of the method, we present results on time-dependent electron emission from dielectric surfaces under AC voltages in the kHz frequency range. The added challenge here is that...
while oscillations of the electronic system are in the THz or higher range, added perturbations due to AC voltage are in the kHz frequency range. As such, direct integration of the evolution of the electronic system requires long time-scales. We solve this challenge first using a semi-classical approximation in order to avoid temporal integration. Additionally, we show that a kernel polynomial expansion of the time-evolution operator can be used to allow direct integration of the quantum-mechanical evolution under an external AC voltage. This demonstration of KPE for both the electronic structure and the time integration of the system provides a computationally efficient framework for an inherently multiscale electronic structure problem, with implications for a variety of challenging problems.

2:15 PM MT01.02.04
Extreme Electric Fields in DFT Michael Ashton, Arpit Mishra, Christoph Freysoldt and Jörg Neugebauer; Max Planck Institute for Iron Research, Germany

Strong ($10^{10}$ V/m) electric fields can be used to trigger chemical processes with extreme precision by selectively stabilizing or weakening bonds to initiate reactions which are otherwise slow or do not proceed at all. The ability to manipulate electric fields to tailor and stimulate bond-breaking events is therefore a powerful experimental control knob, but one whose effects are difficult to predict due to a lack of suitable tools to probe its associated atomic-scale mechanisms. Atom Probe Tomography (APT) directly probes field-induced bond-breaking mechanisms, but its results must be interpreted through theoretical models, which are currently overly simplistic. Here we introduce a novel approach, which we term the Generalized Dipole Correction (GDC), that enables the direct study of ultra-high fields effecting bond-breaking and desorption at the level of single atoms using Density Functional Theory (DFT). As a prototype application, we consider field evaporation from a kinked W (110) surface. We reveal two qualitatively different competing mechanisms that can be switched by the applied field.

2:30 PM MT01.02.05
Atomic Scale Einstein-de Haas Effect Tomos Wells¹, Andrew P. Horsfield¹, Matthew Foulkes¹,² and Sergei Dudarev¹; ¹Imperial College London, United Kingdom; ²University of Illinois at Urbana-Champaign, United States

The Einstein-de Haas (EdH) effect, where the spin angular momentum of electrons is transferred to the mechanical angular momentum of atoms, was established experimentally in 1915. While a semi-classical explanation of the effect exists, modern electronic structure methods have not yet been applied to study this phenomenon. In this talk we investigate its microscopic origins by means of a non-collinear tight-binding model of an O₂ dimer as implemented in Ref. [1]. This includes the effects of spin-orbit coupling, coupling to an external magnetic field, and non-collinear Stoner exchange. By varying an external magnetic field in the presence of spin-orbit coupling, a torque can be generated on the dimer, validating the presence of the EdH effect. Avoided energy level crossings and the rate of change of magnetic field determine the evolution of the spin. We find also that the torque exerted on the nuclei by the electrons in a time-varying $B$ field is not only due to the EdH effect: other contributions arise from field-induced changes in the electronic orbital angular momentum and from the direct action of the Faraday electric field associated with the time-varying magnetic field.


2:45 PM MT01.02.06
Algorithms for the Generation of Generalized Monkhorst-Pack Grids Yunzhe Wang, Adarsh Balasubramanian, Pandu Wisesa and Tim Mueller; Johns Hopkins University, United States

Computational materials research has become increasingly vital in probing the properties of crystalline materials, especially in screening materials at a large scale to accelerate material discoveries for a wide range of applications.¹,² A routine operation for calculating the properties of crystalline materials is the evaluation of integrations over the Brillouin zone, which can be approximated by sampling the Brillouin zone at a set of points known as $k$-points. Many popular computational materials software packages generate $k$-points using the traditional Monkhorst-Pack (MP) scheme,³ which creates $k$-point grids that are regular and aligned with the reciprocal lattice vectors. We have previously demonstrated that much more efficient lattices can be generated if the Monkhorst Pack approach is generalized by relaxing the requirement that the grids be aligned with the reciprocal lattice vectors,⁴ which has since been confirmed by other researchers.⁵ This approach can roughly double the speed of well-converged calculations on crystalline materials, providing strong incentives to find an efficient algorithm for fast generation of
generalised Monkhorst-Pack grids.

Here, we present algorithms for rapidly generating generalized Monkhorst-Pack grids. To better serve the computational materials community, we provide three implementations of these algorithms in various languages and formats:
1. **K-Point Grid Server**: a ready-to-use online application with a pre-generated database for fast search.
2. **K-Point Grid Generator**: an open-source, stand-alone application for runtime environments that might not have an internet connection.
3. **kplib**: a lightweight open-source C++ library that does not make use of databases, for integration with computational materials software packages.

Benchmark results are provided to demonstrate the speed of these algorithms and the quality of generated grids.

**References**

**3:00 PM BREAK**

**3:30 PM MT01.02.07**
**Simulating Material Dynamics on Near-Term Quantum Computers**
Lindsay Bassman¹, Aravind Krishnamoorthy¹, Kuang Liu¹, Yifan Geng¹, Daniel Shebib¹, Shogo Fukushima², Fuyuki Shimojo², Rajiv Kalia¹, Aiichiro Nakano¹ and Priya Vashishta¹; ¹University of Southern California, United States; ²Kumamoto University, Japan

High-accuracy quantum simulations of materials is becoming increasingly important for the development of new devices for electronic, thermoelectric, and energy applications. While these simulations tend to scale exponentially with the size of the system on classical computers, it has been shown that they can be made to scale polynomially on quantum computers. Performing dynamic simulations on quantum computers, therefore, can open new doors by allowing systems of larger (and more relevant) sizes to be simulated. In this work, we simulate photonic control of emergent magnetism in a two-dimensional material on Rigetti’s Aspen quantum processor. Results from the quantum computer are found to be in good qualitative agreement with theoretical ground-truth results, and in even better agreement with results from classically simulated noisy qubits. Furthermore, we map out the feasibility bounds of such dynamical simulations on state-of-the-art, near-term and near-future quantum computers.

This work was supported as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC0014607.

**3:45 PM MT01.02.08**
**Determining Nanoscale Structures from Experimental Data Using FANTASTX**
Eric Schwenker¹,², Venkata S Chaitanya Kolluru¹, Arun Kumar Mannodi Kanakkithodi¹, Spener Hills¹ and Maria K. Chan¹; ¹Argonne National Laboratory, United States; ²Northwestern University, United States

Determining the atomistic details of nanoscale structures is a fundamental problem. Although there are both experimental and computational methods to determine these nanoscale structures, they both possess limitations. We develop the FANTASTX code (Fully Automated Nanoscale To Atomistic Structure from Theory and eXperiment) to overcome the limitations of either by combining both experimental and computational data. We demonstrate the effectiveness of FANTASTX by determining the structures of nanoparticles and solid interfaces from x-ray and electron microscopy data combined with atomistic and first principles energies, using multi-objective optimization and a variety of canonical and grand canonical sampling algorithms.
The properties of molecules and materials are ultimately determined at the atomistic level. On the other side, their behavior at macroscopic scales is far more relevant to model for example chemical reactor processes and to determine promising changes to optimize catalysts, additives, and operating conditions in industrial processing plants. The multi-scale simulation platform ReaxPro aims to provide a customer-ready solution by combining several well-established tools and simulation programs such as the Amsterdam Modeling Suite, kinetic Monte Carlo methods, and computational fluid dynamics to bridge the many orders of magnitude in scale between atomistic quantum chemistry models and macroscopic chemical reactor design.

Such multi-scale simulations will not only significantly reduce experimentation costs but also allow for an in-silico high-throughput screening and predictions to guide experiments. In addition, valuable insights into the mechanisms at each scale can be gained in order to help researchers to improve reactor designs at different levels. The multi-scale material and process optimization of ReaxPro can also be applied in other fields of chemical industries such as the application-specific design of new polymers, photovoltaics, and batteries.

We have developed a module for calculating the mobility and conductivity of semiconducting materials based on the iterative method as proposed by Rode [1]. Various physical properties calculated through the density function theory (DFT) are used as inputs. We show the use of this module for Cadmium Sulfide (CdS) and Zinc Selenide (ZnSe). Since this strategy can take into consideration the inelastic scattering of the carriers due to the phonons, this module should serve a better objective than those based on the relaxation time approximation.

References

We introduce an orbital free electron density functional approximation based on alchemical perturbation theory[1]. Given convergent perturbations of a suitable reference system, the accuracy of popular self-consistent Kohn-Sham density functional estimates of properties of new molecules can be systematically surpassed - at negligible cost.

For example, using the CCSD solution for N₂, APDFT calculated properties of CO are more accurate than PBE already at 1st order (energies and dipole moments) and 2nd order (quadrupole-moments and forces).

The associated energy functional is an approximation to the integrated energy derivative, requiring only perturbed reference electron densities: No self-consistent field equations are necessary to estimate energies and electron densities. Instead, our approach relies on the electron density response w.r.t nuclear charges and treats changes of nuclear charges at any sites as perturbations to the system. We show that the resulting expansion in perturbation orders converges quickly by analytical proof for the hydrogenic atom and for any free atom. Numerical convergence is shown for alchemical perturbations of H₂, N₂, and benzene[1, 2].

APDFT based estimates of the electron density of a target molecule are obtained for the same perturbations. Estimated electronic ground state properties considered include covalent bonding potentials, atomic forces, as well as dipole and quadrupole moments.

We demonstrate the applicability of APDFT to scan a large chemical space by using 13 CCSD single point calculations to predict changes in energy and forces by BN-doping a C_{20} fullerene. This allows us to give total energy estimates for all 3.1 million uniquely BN-doped fullerenes.
APDFT is widely applicable to any level of theory that makes electron densities available and allows to assess a combinatorial number of molecules with one fixed set of calculations rather than calculating molecules one-by-one.

If the perturbation series converges and if the reference level of theory is of sufficient quality, APDFT represents a systematically improving DFT approximation of hierarchies of accuracy.


8:30 AM MT01.03.02
Machine Learning Exchange Correlation Functionals for Density Functional Theory David Clark¹, Blake Duschakto¹, Simon Batzner¹,², Jonathan Vandermause¹ and Boris Kozinsky¹; ¹Harvard University, United States; ²Massachusetts Institute of Technology, United States

Density Functional Theory (DFT) has become a ubiquitous and vital tool in a wide range of materials physics problems. It occupies an important space in the tradeoff between accuracy and computational cost - able to achieve high levels of accuracy and maintain computational feasibility. Within the DFT formulation this tradeoff is adjusted through the exchange-correlation energy functional. Advanced functionals can be substantially more accurate but can also be far more expensive computationally. Recent work has attempted to push back the optimal performance tradeoff curve through machine learned functionals trained on high level exchange-correlation energies, such as those from hybrid functionals or CCSD(T) [1,2]. A common theme among these is to assume a local model, where the exchange-correlation energy is a sum of local contributions.

While recent efforts have been primarily driven by neural network models to predict these contributions, we consider an alternative procedure wherein the electronic densities are projected onto a Gaussian basis to drastically reduce their dimensionality. An ordinary least squares problem is then solved to regress the exchange-correlation energy. In this context, we examine the limitations of a local model: we demonstrate that our model can accurately reproduce LDA functional data and explore effects on accuracy when trained on hybrid functionals. We further consider the implications of this model in its capacity to accurately and efficiently predict material properties.


8:45 AM MT01.03.03
Machine-Learning-Aided Development of Empirical Force-Fields Mathieu Bauchy; University of California, Los Angeles, United States

The development of reliable, yet computationally-efficient interatomic forcefields is key to ensure the accuracy of classical molecular dynamics simulations. However, parameterizing new forcefields is notoriously challenging, since the high number of parameters renders traditional optimization methods inefficient or subject to bias. Here, we present a new parametrization method based on machine learning, which combines ab initio molecular dynamics
simulations and Bayesian optimization. By taking the examples of silicate and chalcogenide glass, we show that our method yields new some empirical interatomic forcefields that offer an unprecedented level of agreement with ab initio simulations. This method offers a new route to efficiently parametrize new interatomic forcefields for disordered solids in a non-biased fashion.

9:00 AM *MT01.03.04
Toward Efficient Methods for Generating Transferable Neural-Network Interatomic Potentials Talat S. Rahman; University of Central Florida, United States

Recent developments in neural network interatomic potentials have provided a pathway for reliable large-length and long-time scales atomistic simulations. However, their transferability is questionable because of incompleteness of the training dataset that relies on structure-energy (and/or forces) calculated using density functional theory (DFT), leading to inaccurate extrapolations or interpolations of the neural network. In this talk, we present two efficient methods for generating configurational spaces for training dataset: (1) molecular dynamics simulations with large time steps and (2) random walks on uniform grids. Both methods create chaotic displacements of atoms that move them far from equilibrium positions or trajectories, effectively enlarging the configurational space. We will demonstrate the effectiveness of the methods using examples of transferable neural network interatomic potential for: 1) the Si(001) surface and 2) defect-laden, two dimensional, hexagonal boron nitride (dh-BN). Both potentials are able to predict total energy within few meV of that obtained from DFT. Molecular dynamics simulations of the Si(001) surface for a wide range of temperature that show that the asymmetric, buckled structure of the surface dimer exists at all temperatures, but their increased flipping rate leads to a larger occurrence of the symmetric configuration, shedding light on the semiconducting-conducting transition of the surface. In the case of dh-BN the method allows simulations of grain-boundary structures consisting of thousands of atoms whose local configuration is not included in the training set. We compare our results with available data and discuss the pros and cons of the approach.

* Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354.

9:30 AM MT01.03.05
Neural Network Force Model for Large Scale Molecular Dynamics Simulation of Phase Change Materials Pankaj Rajak¹, Ken-ichi Nomura², Subodh C. Tiwari², Ye Luo¹, Aiichiro Nakano², Rajiv Kalia² and Priya Vashishta²; ¹Argonne National Laboratory, United States; ²University of Southern California, United States

High quality force field models are not available for many phase change materials such as Ge₂Sb₂Te₅, which has diverse applications in neuromorphic computing devices and non-volatile memory. Designing semi-empirical force fields for these systems is nontrivial and also doing ab-initio molecular dynamics (MD) simulations is not scalable for large systems, which is important to amorphization and recrystallization in these systems. We have developed a neural network (NN) based force field model for Ge₂Sb₂Te₅ which is trained using ab-initio MD simulations data to directly produce atomic forces at density functional theory (DFT) level accuracy. The neural-network architecture and input parameters of the feature vector for each atom type are optimized for training using Bayesian optimization so as to design a model with higher accuracy but with minimum complexity. Special care is taken to design radial and angular feature vectors that obey translational and permutational invariance and rotational covariance for forces. The accuracy of the NN force field model is validated by doing a MD simulation using NN force field model for up to 100,000 atoms and by computing various structural and dynamical properties such as radial distribution function, bond angle distribution, neutron structure factor and phonon density-of-states.

Acknowledgment
This work was supported as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under award number DE-SC0014607. The simulations were performed at the Argonne Leadership Computing Facility under the DOE INCITE and Aurora ESP programs and at the Center for High Performance Computing of the University of Southern California.

9:45 AM MT01.03.06
Learning Direct, Symmetry-Preserving and Efficient Force-Fields with Tensor-Field Neural Networks Simon L. Batzner¹,², Tess E. Smidt³ and Boris Kozinsky¹; ¹Harvard University, United States; ²Massachusetts Institute of
Deep Learning has emerged as a powerful tool for accelerating simulations of molecular and condensed matter by learning complex representations of the potential energy directly from atomic positions without the need for handcrafted descriptors. We present a deep learning approach aimed at molecular dynamics that directly predicts atomic forces instead of total energy. The proposed force-field is rotationally covariant, handles multiple species naturally, and bypasses the need for computing expensive derivatives of an energy-based model by predicting atomic forces directly from atomic position coordinates. The proposed algorithm achieves very high accuracy on a data set of organic molecules while outperforming energy-based models with respect to computational efficiency, both at time of training and inference. We show that our proposed method can accurately reproduce thermodynamic and kinetic materials properties from Molecular Dynamics simulations and benchmark the efficiency of the direct force prediction against energy-based models.

10:00 AM BREAK

10:30 AM MT01.03.07
An Extendable Framework to Design Empirical Potential with Tuneable Accuracy Artur Tamm and Amit Samanta; Lawrence Livermore National Laboratory, United States

We present a general framework to generate machine learned interatomic potentials from ab initio density functional theory (DFT) databases. In our framework, atomic structure information residing in the configuration space is projected on to a space of descriptors that can systematically capture local many-body correlations. Specifically, we have included two-body, and a variety of three and four-body correlations. These correlations are realised using Chebyshev basis functions, but the framework is general and other basis functions can be used. To generate the inter-atomic potential, we have explored linear as well as non-linear regression techniques with different regularisations. The different correlation terms were grouped according to the number of atoms, and according to the bonds present in them. These variables control the dimensionality of the parameter set of the interatomic potential. We applied this framework to generate an interatomic potential for germanium using DFT (hybrid functional) database consisting of about 1.5 million atoms environments. This database includes structures with different crystal symmetries as well as liquid and amorphous structures. Different potential models were generated by using different types of correlation descriptors and the effect of different correlations were compared by analysing root mean square error as well as with histogram of errors between the model and DFT. In summary, we have developed a framework for building potentials with tuneable accuracy and shown its application to the case of germanium. The model is implemented as an extension to LAMMPS molecular dynamics code and can be used in large-scale simulations.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

10:45 AM *MT01.03.08
Molecular Dynamics Simulation Using Neural-Network Force Field Trained from Ab Initio Calculations Lin-Wang Wang; Lawrence Berkeley National Laboratory, United States

Neural-network force field (NN-FF) has become an intensly studied topic in recent years. In this talk, I will present our recent work in developing NN-FF and using it in molecular dynamics simulations. In our approach to train the NN-FF, not only we use the atomic forces from ab initio calculations, we also use decomposed atomic energies from density functional theory (DFT) calculations. This increases the number of data set, also makes the training process easier. We have developed Si and Na NN-FF in this approach. We also developed multiple element force fields like Al-H and Fe-H. We have used the NN-FF to study the crystal Si growth from melt Si. This NN-FF shows similar behavior as that of the direct DFT calculations, but it allows us to study much larger systems. I will also present our approaches to deal with long range Coulomb interactions for systems with ionic charges.
11:15 AM MT01.03.09  
**Simultaneous Structure Exploration and Machine-Learned Potential Fitting**  
Noam Bernstein¹, Gabor Csanyi² and Volker Deringer²; ¹U S Naval Research Lab, United States; ²University of Cambridge, United Kingdom

Defining interatomic potentials as a high-dimensional fit of the reference (usually density functional theory) potential energy surface by taking advantage of regression methods from machine learning has recently become a powerful approach. However, because of their variational freedom, such potentials require large fitting datasets, which are typically developed using large amounts of manual selection and tuning of configurations by the researcher. To simplify this process, we present a highly automated iterative method where a preliminary Gaussian approximation potential (GAP) is used to carry out random-structure searches, and selected configurations from the searches are used to fit the next iteration's GAP. The resulting set of configurations constitutes an effective fitting database, spanning a wide range of geometries with a minimal number of reference energy evaluations. We test the method on several elemental and multi-component materials with different bonding types, from insulators to metals, including boron with its complex icosahedral $\alpha$-B$_{12}$ structure and the phase-change material GeTe. We show how the process converges in a few iterations, and how the resulting potentials reproduce the reference DFT values on a number of bulk and defect properties.

11:30 AM MT01.03.10  
**Effect of Particle Geometry on T$_1$- and T$_2$-weighted Relaxivities for MRI Applications**  
Alexis G. Lavin and Bibek Thapa; Universidad de Puerto Rico, United States

MRI contrast agents based on iron oxide nanoparticles are advantageous alternatives to Gadolinium-based contrast agents in terms of toxicity, safety, and biocompatibility. However, it remains necessary to develop novel iron oxide nanoparticles able induce better T$_1$- and T$_2$-weighted relaxivities. Specifically, the manipulation of the iron oxide particle geometry should help increase the effective surface while provoking larger local disturbances in the magnetic field with a concomitant enhancement in relaxivities. Thereby, we synthesized spherical, cubic, hexagonal, and star-shaped iron oxide nanoparticles, characterized their structural and magnetic properties, and measured their T$_1$- and T$_2$-weighted relaxivities. The results show a significant relaxivity enhancement for the non-spherical particles, thus confirming the hypothesis that geometry has a large impact on the nanoparticles ability to locally disturb the random arrangement of the spins. We will discuss the nanoparticles property-function relationships and their potential as MRI dual T$_1$-T$_2$ contrast agents.

11:45 AM MT01.03.11  
**Lattice Dynamics and Thermodynamics of Strongly Anharmonic Solids via Bayesian Learning and Convolutional Neural Networks**  
Taishan Zhu, Sheng Gong and Jeffrey C. Grossman; Massachusetts Institute of Technology, United States

Strongly anharmonic solids have been widely sought, ranging from thermoelectrics to multiferroics and to shape-memory materials, but the effects of strong anharmonicity to their thermodynamic and transport properties are less understood. In this work, we extend our earlier crystal graph convolutional neural network framework, and explore an alternative Bayesian description for the vibrational modes and their transport in strongly anharmonic solids exhibiting soft modes. We demonstrate our theory on a one-dimensional toy lattice, including a probabilistic extension to the conventional phononic dispersion relationship, as well as its consequences to lattice conductivity, other thermal properties, and phase transition. This Bayesian framework also provides naturally an uncertainty quantifying scheme for these physical quantities, including those uncertainties inherent for meta-stable and partial-crystal-partial-glass solids. Our theory is then extended to two halide perovskites: all inorganic CsPbI$_3$, and hybrid inorganic-organic MAPbI$_3$, and our Bayesian predictions are compared with existing experiments of heat capacity and lattice conductivity. More interestingly, some anomalous phononics observed from experiments could be explained within this framework.
SESSION MT01.04: Empirical Methods I
Session Chairs: Anders Niklasson and Talat Rahman
Tuesday Afternoon, December 3, 2019
Hynes, Level 2, Room 206

1:30 PM MT01.04.01
Machine Learning for the Construction of Lattice Based Models Mattias Ångqvist1, Fredrik Eriksson1, William Armando Muñoz1, Magnus Rahm1, Erik Fransson1, Céline Durniak2, Piotr Rozyczko2, Thomas Holm Rod2 and Paul Erhart1; 1Chalmers University of Technology, Sweden; 2European Spallation Source, Denmark

Modeling the thermodynamic and kinetic properties of materials commonly requires taking into account both vibrational and compositional degrees of freedom. While electronic structure calculations strictly speaking can provide the necessary information, they are computationally too demanding for many practical purposes. One therefore requires models that can reproduce the relevant parts of the potential energy landscape at a much smaller computational cost.

Here, we will present a set of software packages that we developed over the course of the last years that allow one to rapidly construct and sample models that map vibrational (hiPhive [1]) and/or compositional degrees of freedom (icet [2]).

These tools can be integrated in a homogeneous Python based workflow, which combines structure generation, electronic structure calculations, model construction, thermodynamic sampling, and subsequent analysis. Example applications include the prediction of alloy phase diagrams, temperature driven phase transitions, thermal conductivities, and ordering phenomena.


1:45 PM MT01.04.02
AGNI—A Machine Learning Platform for the Rapid Prediction of Atomistic Properties James E. Chapman, Rohit Batra, Huan D. Tran, Chiho Kim, Anand Chandrasekaran, Deepak Kamal, Christopher B. Kuenneth and Rampi Ramprasad; Georgia Institute of Technology, United States

Propelled partly by the Materials Genome Initiative, and partly by the algorithmic developments and the resounding successes of data-driven efforts in other domains, machine learning (ML) strategies are beginning to take shape within several subfields of materials science[1-4]. One area of enormous importance is atomic-level materials phenomena, which spans numerous fields from electronic structure theory to mechanical failure, and has been dominated by either quantum mechanics (QM) based methods [4-7]—which are time-intensive, but accurate and versatile—or semi-empirical/ classical methods[8,9]—which are fast but are significantly limited in veracity, versatility and transferability. ML methods have the potential to bridge the chasm between the two extremes and can combine the best of both worlds. We have created a platform for the rapid prediction of properties such as potential energy, atomic forces, stresses, charge density, and the electronic density of states. Our ML-models are trained on accurate QM reference data, and can reproduce the QM results with the same level of accuracy but several orders of magnitude faster [10-15]. The ML models can also be progressively improved in quality by periodically (or on-demand) exposing them to fresh QM data in regions of poor performance, a feature that currently is either impossible or daunting with modern empirical/classical methods. Our ML models may thus be used to perform large-scale and/or long-time simulations of important materials phenomena previously beyond the reaches of QM based methods. Here, we demonstrate the power and versatility of this new platform in correctly capturing electronic, thermodynamic, mechanical, and diffusive properties for a variety of systems, with the hope of ushering in a new era of atomic-level understanding of materials.

References:
Dislocations, which are line defects in solid, are a dominant factor of plastic deformation of solid. For advanced material design, it is very important to clarify the details of dislocation mechanics and dynamics. The energetics of dislocation mainly consists of the following two-part: atomic dislocation core and long-range elastic field. The dislocation core structure and behavior determine the mobility of individual dislocations and the condition of reactions between them. The elastic interaction determines the structure of mesoscopic aggregate of dislocations, such as dislocation cell walls. This structure is directly connected macroscopic mechanical behavior of crystals, such as work hardening.

To investigate the long-range elastic interaction, discrete dislocation dynamics (DD) modeling is a powerful tool, because it can treat micrometer scale in a realistic time scale. DD modeling is based on dislocation elastic theory. So, DD modeling requires the mobility and condition of the reaction of dislocations as input parameters. To investigate the dislocation core structure, the atomistic modeling is very suitable, because dislocation core structure and behavior are severely affected by the discreteness of atomic spacing. High accuracy density functional theory (DFT) calculations have established a leading position in atomistic modeling in decades. Due to the high-cost calculation of DFT, the number of atoms in DFT calculation is limited to a few hundreds, practically.

One solution to link the DD modeling and DFT atomic modeling is an atomic potential based on artificial neural network (ANN) framework [1]. By the universal approximation theorem, the ANN potential can compute any function. Therefore, with enough DFT training data, ANN potential becomes sophisticated replica potential of DFT calculation. In this work, we construct the atomic ANN potential for iron (Fe).

For DFT training data, we prepare the 5173 atomic structure of Fe calculated by Quantum ESPRESSO package [4]. For crystal structure data, we select the FCC, HCP, BCC and simple cubic structure. For defect data, we select the vacancy, divacancy, self-interstitial (T-site, O-site, [100], [110], [111]-dumbbell) and (100), (110), (111) and (112) surfaces model. To predict the exact dislocation core structure, we also prepare generalized stacking fault energy (GSF) surface on (110) and (112). The Chebyshev descriptor developed by Artrith et el. is used for the input descriptor of the atomic environment [2,3]. For neural network training, we use the aenet package by Artrith et el [3].

By using ANN potential, We investigate the a/2<111> screw dislocation core structure in BCC iron, where a is lattice constant. The screw dislocation core predicted by constructed ANN potential has nondegenerate compact structure. We also evaluate the Peierls barrier of a/2<111> screw dislocation by using the nudged elastic band (NEB) method. The Peierls barrier is estimated as 36.6 meV in units of length of Burgers vector. These results are a good agreement with previous DFT calculation [5].

2:15 PM *MT01.04.04
Modeling Light Interstitials in Materials Ju Li; Massachusetts Institute of Technology, United States

Light interstitial atoms such as hydrogen, helium, oxygen, carbon and nitrogen are known to have profound effects on the material properties experimentally. Ab initio and atomistic methods are employed to address their equilibrium segregation, effect on thermally activated processes, as well as non-equilibrium effects. A conceptual framework based on Gibbs adsorption isotherm, but generalized to the saddle state, with activation strain-volume/entropy/excess, is developed to interpret the simulation and experimental results.

2:45 PM MT01.04.05
Improving the Accuracy of Coupled Spin and Lattice Simulations Julien Tranchida; Sandia National Laboratories (NM), United States

The approach consisting in coupling spin and molecular dynamics is an increasingly popular numerical method allowing to investigate the reciprocal influence of lattice vibrations and magnetization dynamics. Through the recently added SPIN package, LAMMPS now allows to perform such simulations at unprecedented accuracy and scale. A brief overview of this implementation and of some of its recent improvements will be first presented.

Although this implementation greatly improved the available algorithms for this methodology, the lack of magneto-elastic potentials remains a strong limitation to its development. Indeed, the most commonly used approach consists in overlaying the magnetic interactions on top of a purely mechanical potential (typically, a magnetic exchange interaction on top of an EAM potential), all those interactions being parametrized separately. As the magnetic interactions generates rather small forces compared to the mechanical potential, this approach proved to be sufficient to obtain numerous first order results.

However, it remains a rather crude approximation and cannot be used to recover fine experimental results. In this presentation, a new methodology based on high-fidelity machine-learned inter-atomic potential approaches and enabling to circumvent this difficulty will be presented.

3:00 PM BREAK

3:30 PM MT01.04.06
Advancing Atomistic Capabilities for Heterogenous Systems Difan Zhang¹, Yuxiang Wang², Alexandre Fonseca³ and Susan B. Sinnott²; ¹Pacific Northwest National Laboratory, United States; ²The Pennsylvania State University, United States; ³Universidade Estadual de Campinas (UNICAMP), Brazil

Interactions between heterogeneous systems are challenging to model with high fidelity at the atomic scale across significant length scales. This presentation describes recent developments of third-generation charge optimized many-body (COMB3) potentials to enable metal-carbon interactions in classical molecular dynamics simulations. The potentials are applied to investigate the interaction of carbon materials, including metal-carbide-derived-carbons (CDCs) with titanium and aluminum, and the interactions of graphene and buckyballs with copper and aluminum surfaces. The results provide new insights into the bonding character at these interfaces and the role of defects, bond-angle, and temperature on interatomic interactions.

3:45 PM MT01.04.07
Absolute Free Energy Calculation for Liquid Metals and Alloys Michael Widom; Carnegie Mellon University, United States

First principles molecular dynamics efficiently calculates the internal energy of metals, both in liquid and solid form. We show that the liquid state correlation functions that are a byproduct of the simulation allow a similarly efficient calculation of absolute entropy based on a simple variant of the classical "S2" method. The method is quite accurate for nearly free electron metals, as demonstrated by comparison with experimental data for elemental liquid metals. For liquid alloys, hybrid Monte Carlo/molecular dynamics is utilized to enhance ensemble sampling. We combine the energy and entropy to calculate absolute free energies in liquid metals in order to explain the occurrence
of phase separation in liquid Li-Na compared with the eutectic in Na-K.

4:00 PM MT01.04.08
Fast and Accurate Machine Learning Models for Exhaustive Microstructure Sampling of Chemically Complex Materials
Hsin-An Chen¹, Ping-Han Tang¹, Guan-Jie Chen², Yen-Ching Wu², Sheng-Han Teng¹ and Chun-Wei Pao¹; ¹Academia Sinica, Taiwan; ²National Taiwan University, Taiwan

Chemically complex materials, namely materials comprised of multiple chemical components, are playing an increasingly important role in material applications including high entropy alloys (HEAs) for structural materials and complex mixed ion perovskite materials for solar cells as well as optoelectronic devices. The microstructures of these materials, for example, chemical short-range orders or phase segregations are critical for the material performance; however, characterization of microstructures of these chemically complex materials poses grand challenges to both experimentalists and theorists. From computer simulation perspective, exhaustive sampling of microstructures is computationally prohibitive for density functional theory (DFT) calculations owing to both system size and computation time limitations. Herein, we demonstrate that by utilizing neural network energy predictors trained from numerous images from DFT calculations, a 10⁵ computational speedup can be obtained by implementing the neural network predictor into the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), while retaining high fidelity to DFT calculations. Hence, the neural network energy predictor allows us to perform exhaustive sampling of systems of thousands of atoms of CoCrFeNi HEAs and FAₓMA₁₋ₓPb₁Br₃₋y perovskite materials using Monte Carlo in combination with molecular dynamics simulations, thereby providing atomistic insights into microstructures and chemical short-range orders of these chemically complex materials with DFT accuracy.

4:15 PM MT01.04.09
Framework for Amorphous Polymer Synthesis to Study Dielectric Properties Using Polarizable Reactive Molecular Dynamics
Ankit Mishra¹, Ken-ichi Nomura¹, Subodh C. Tiwari¹, Aiichiro Nakano¹, Rajiv Kalia¹, Priya Vashishta¹, Rampi Ramprasad², Gregory A. Sotzing³ and Yang Cao³; ¹University of Southern California, United States; ²Georgia Institute of Technology, United States; ³University of Connecticut, United States

New dielectric polymer materials with high energy density while maintaining low loss at high applied electric fields are needed for increased energy and power density required in modern electronics. We propose a polarizable reactive molecular dynamics-based framework that offers near-quantum accuracy for estimating dielectric properties of various polymer systems within a small fraction of quantum-calculation time. We use this framework to demonstrate the essential role of morphological complexity that governs dielectric constant of industrially relevant model polymer systems. Our framework supports high dielectric performance of PDTC-HK511 and TDI-EDR148 polymer systems, which have been identified through rational co-design strategy based on advanced computational screening procedures. The proposed framework can augment screening procedures for identifying polymer dielectrics that are significantly better than the current state of the art.

4:30 PM MT01.04.10
Bayesian Active Learning of Gaussian Process Weight Force Fields—Application to Stability of 2D Materials
Yu Xie, Jonathan Vandermause, Lixin Sun, Andrea Cepellotti and Boris Kozinsky; Harvard University, United States

Gaussian process regression was previously demonstrated to provide quantitative Bayesian estimates of prediction uncertainty, enabling on-the-fly active learning of force fields in molecular dynamics of rare events¹. However, the time complexity in this method of prediction grows linearly with the training data size. We build on earlier attempt to exploit the structure of the N-body kernel function, to decompose the prediction expression into contributions that can be interpolated in order to approximate atomic forces, without loss of accuracy compared to the full regression². Crucially, this approach no longer depends on training size and accelerates the Gaussian process prediction by several order of magnitudes. We present a method of mapping (1) force fields from the underlying kernel, and (2) predictive variance (uncertainty), combined with dimension reduction approaches. This method can be combined into an end-to-end on-the-fly Bayesian active learning workflow, accelerating prediction of both the force values and variances, with ab-initio accuracy and rigorous Bayesian uncertainty quantification. We demonstrate this workflow on large-scale molecular dynamics simulations of properties of 2D stanene and related structures, including adatom migration and melting transition.
Ability to compute reaction rates from free energy is the key to understand many chemical and physical biology problems, for example, surface catalytic reactions and protein folding. Enhanced sampling methods, such as metadynamics and umbrella sampling, can accelerate slow transitions and improve their statistical estimates by biasing molecular dynamics in a low-dimensional reaction coordinate / collective variable (CV) space. The choice of these CVs coordinates determines the efficiency and accuracy of sampling. However, choosing good CVs can be challenging, requiring chemical intuition, experience and many trial-and-error tests. Here, we proposed to use a machine learning dimensionality reduction approach to automate the design of collective variables. A multi-task machine learning algorithm is employed to learn collective variables from transition path ensembles. In this algorithm, one neural network is trained to map atomic configurations to a lower dimensional latent space, and two additional neural networks are trained to map the latent space to potential energies and metastable state labels. A specific training procedure optimizes the latent space to preserve the information of potential energies and the progression of reaction pathways. The resulting latent space can be used as CVs for metadynamics and umbrella sampling in a wide variety of reactive systems. This approach has been tested on model systems that have two metastable states with one reaction pathway, including a Muller-Brown potential model and alanine dipeptide.
Free Energy Minimization for the Prediction of Molecular Crystal Structures at Finite Temperatures
Hiroyuki Matsui1, Seiji Tsuzuki2, Yukihiro Shimoi2 and Tatsuo Hasegawa3; 1Yamagata University, Japan; 2National Institute of Advanced Industrial Science and Technology (AIST), Japan; 3The University of Tokyo, Japan

Most of the previous works on the prediction of molecular crystal structures have been based on the (static) lattice energy minimization (LEM), which neglects thermal and zero-point molecular vibrations. This leads to the neglection of thermal effects such as thermal expansion and phase transition. Another more serious drawback of LEM is that it results in too many polymorphs, which can be considered as a kind of artifacts, compared to experiments. Here we propose a new approach for the prediction of molecular crystal structures at finite temperatures by taking into account thermal and zero-point phonons. Our approach, free energy minimization (FEM), minimizes the Gibbs free energy which contains static lattice energy, phonon energy, and entropy-related term. Since the Gibbs free energy can be defined in equilibrium states only, the search space of FEM is not the whole set of the Cartesian product of lattice parameters and atom positions as in LEM but is its subset with constraints that all atoms are at equilibrium positions. In other words, only lattice parameters are regarded as independent variables, and atom positions are dependent variables determined by the constraints. As a proof of concept, we demonstrate the FEM simulation of crystal structures of solid argon. The lattice constants by LEM was found 1.6% smaller than the experimental value at 10 K. On the other hand, the lattice constants by FEM exhibited smaller mismatch, 0.5%, with experiments and also reproduced the thermal expansion quite well. In addition, FEM showed that the minimum point of the Gibbs free energy disappears above 87 K, which is consistent with the experimental boiling point of argon, 87.30 K. The reproduction of the unstability of argon crystal above the boiling point implies that FEM can properly eliminate polymorphs which are unstable at specified temperatures.

MT01.05.03
Determining the Structure of Rosette Nanotubes Using Multi-Scale Molecular Modeling—Ring Stack vs Helical Tube
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Rosette Nanotubes (RNTs) are tubular soft materials self-assembled from guanine-cytosine (GAC) hybrid molecules, which can be covalently functionalized for use in various applications. They have been shown to be effective assemblies in regenerative medicine, drug display and delivery, and catalysis.

Previous spectroscopic studies suggest they have a structure which is formed by hexameric rings, maintained by self-complementary hydrogen bonds, that are further stacked and supported by π-π interactions, which form the ring-stacked RNTs. While this mode of association maximizes the hydrogen bonding interactions and results in efficient π-π stacking, it is also possible to envision that the GAC modules assume a helical organization defining a tubular core. Imaging the nanotube using scanning tunneling microscopy (STM) proved inconclusive in differentiating the two configurations. Furthermore, comparing the calculated chemical shifts of the nitrogen atoms of the GAC monomers of both the stacked-tube (ST) and helical tube (HT) configurations showed no significant difference between them.

We further investigated this possibility by using the lysine-functionalized RNT (K1-RNT) and applying multi-scale molecular modeling methods, which include Monte-Carlo conformational search, molecular dynamics, and the statistical mechanical theory of molecular liquids, 3D-RISM theory. We considered three structures of the K1-RNT: ST, left-handed HT (LHT), and right-handed HT (RHT). Our results suggest that the formation of ST, LHT, and RHT K1-RNTs in water are favorable and are enthalpically driven. Moreover, 3D-RISM analysis suggests that the RHT conformation is more probable than the ST and LHT RNTs and this is due to a more favorable solute-solvent interaction energy. Using the 3D distribution of solvent sites around the RNTs (from 3D-RISM calculations), we were also able to determine the solvation structure and estimate the free energy of binding of each water molecule in the RNT channel. The results also corroborate the higher probability of the RHT conformation occurring. Studies are being done to verify these findings.

MT01.05.04
Comparison of Classical Molecular Dynamics and Ab Initio Molecular Dynamics Methods for Modeling Solvent - Lithium Salt Systems in Lithium Air Batteries
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Lithium-air batteries are an active area of research because of their potential to have a much higher energy density than traditional lithium-ion batteries. However, they are not yet commercially viable due to poor efficiency, high charging voltages, and low cycle lifetimes. Experimental studies of Li-air batteries with aprotic solvents have shown that the O\textsubscript{2} reduction starts when superoxide (O\textsubscript{2}⁻) forms in solvent and reacts with Li⁺ to form lithium superoxide (Li⁺-O\textsubscript{2}⁻). Solid Li\textsubscript{2}O\textsubscript{2} then forms as the final discharge product on the cathode. Recent experimental work has suggested that the choice of solvent and the presence of any lithium salts in the system may have a large impact on how the discharge product forms at the cathode. We therefore modelled the clustering of lithium salt molecules in solvent systems without LiO\textsubscript{2} present by performing explicit solvent calculations using both classical molecular dynamics and \textit{ab initio} molecular dynamics simulations. Properties such as the vibrational density of states, coordination number, and structure factor were calculated for these simulations, and the results from the classical and \textit{ab initio} simulations were compared both with each other and with experimental data. Large differences in properties such as coordination number were observed for classical versus \textit{ab initio} simulations, which was not expected based on the widespread use of classical molecular dynamics for modeling solvent behavior. A summary of our results comparing and benchmarking computational approaches for properties such as vibrational density of states and coordination numbers for pure solvent and solvent-salt systems will be presented.

MT01.05.05

Uncovering Molecular Scale Driving Forces in Aggregation of Peptides for Silica Precipitation

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Biomimeralization is a widespread process in living organisms through which hierarchical mineral assemblies are formed under moderate conditions of temperature and pH. To this end Silaffin, a naturally occurring protein known to mediate the silica biomimeralization process in diatoms, has been widely studied. In particular, R5 - the 19-residue segment of Silaffin, was found to precipitate silica in vitro, and has been extensively employed as a model peptide in many experiments and simulations to elucidate the driving forces of biomimeralization. For R5 to facilitate silica or titania precipitation in solution, there must be sufficient negative charge in the system to compensate for the relatively high positive charge on the peptide. In vitro, this has been accomplished with phosphate buffer to mimic post translational modification in the form of serine phosphorylation known to occur in vivo. Sprenger et al. used molecular dynamics (MD) to study the atomic mechanism underlying the phenomenon of protein-mediated biomimeralization, focusing on the role of pH and phosphorylation. The interaction of wild type R5, along with two mutants (local phosphorylation and global phosphorylation) to silica was investigated, and it was found that phosphorylation decreased the binding free energy at acidic and neutral pH. While the trends match experimental results of R5 binding on silica, peptide-surface binding is not the primary indicator of biomimeralization efficiency. The key role of phosphate suggests peptide-peptide interactions play an important role in the nascent phase of biomimeralization and in this work, we study R5 peptide dimerization, to shed light on inter-peptide interactions that enable the uniform templating of silica. To match closely to experimental systems, we study R5 dimers under five distinct conditions. These are (1) wild type R5 (2) R5 with phosphate ions (3) R5 with phosphorylation on Ser1 (4) R5 with phosphorylation on Ser14 (5) globally phosphorylated R5. Enhanced sampling using Parallel Bias Metadynamics with Partitioned Families (PBMetaD-PF) was employed to ensure convergence of the free energy profiles. Results indicate that R5 dimerizes in the presence of phosphorylated serine, or with phosphate ion in solution; and impacts of the number/location of phosphoserine in peptide is also observed. Dimer conformations are analyzed using K-means clustering algorithm. This work provides molecular insight on peptide aggregation in biomimeralization, and could potentially inform rational design of protein and nanomaterials.

MT01.05.06

Fracture in Nanoporous Gold—A Combined Simulation and Experimental Study

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We present an experimental/simulation integrated study examining crack propagation in nanoporous gold. We utilized a simulation technique that combines continuum fracture mechanics with molecular dynamics. We applied this to a large atomistic digital sample of nanoporous gold to implement mode I crack propagation. Crack propagation tests were also conducted on an experimental sample, prepared via chemical dealloying and observed via in-situ TEM microscopy. We observed cracks in both samples propagating by the same mechanisms of sequential individual ligament failure. A series of nanowire computational deformation tests were also conducted to understand individual ligament behavior, and how this influences the overall sample fracture. This iterative direct
experiment/simulation comparison provides new insight into the failure response of nanoporous gold.

**MT01.05.07**  
**Atomistic Studies of the Diffusion of H-Vacancy Complex in Cu**  
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Vacancy diffusion under hydrogen (H) environments is important to the mechanical performance of structural  
materials, such as in hydrogen embrittlement and hydrogen blistering. The vacancy diffusion is believed to  
be retarded by trapping H-atoms forming H-vacancy complexes. The diffusivity of the H-vacancy complex can be  
estimated using long-time molecular dynamics simulations or static energetics calculations provided that the  
thermodynamic equilibrium distribution of H-atoms around the vacancy has been achieved. From the static  
ergetics calculations based on the harmonic transition state theory, we found that the vacancy diffusion coefficient  
in Cu-H system decreases exponentially as the H-concentration increases by considering the apparent probabilities  
of various H-vacancy complexes at its ground state and the energy barrier of vacancy diffusion calculated from an  
embedded-atom-method potential. However, this H-concentration dependency of vacancy diffusivity is denied by  
the direct molecular dynamics simulations, which shows that H-atoms strongly enhance the diffusion of the vacancy  
with increasing H-concentration. It should be noted that the number of trapped H-atoms along the diffusion pathway  
was kept constant in the static energetics calculations. From the viewpoints of statistical sense, the varied number of  
trapped H-atoms along the diffusion pathway should be allowed. Therefore, we used the potential-of-mean-force  
method to study the vacancy diffusion under H-environments so that the thermodynamic equilibrium distribution of  
H around the vacancy can be achieved along the diffusion pathway. We found that the vacancy can trap more  
number of H-atoms at its saddle-point than that at its ground state, which can be characterized by an activation  
excess. According to the generalized Gibbs isotherm, the higher chemical potential of H-atoms significantly  
decreases the energy barrier of the vacancy diffusion. Thus, the vacancy diffusivity is enhanced by H-atoms, which  
is in consistent with the results of the direct molecular dynamics simulations. This effect of H is believed to be  
general in other thermal activation processes that can attract more H-atoms at its saddle-point.

**MT01.05.08**  
**A Computational Study of Cubic Thin Films in WC-Co Cemented Carbides**  
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WC-Co cemented carbides combine superb hardness with high toughness making them ideal for usage in cutting  
applications and in wear resistance tools. Thin films of cubic stacking have been observed experimentally at the  
phase boundary between WC and Co when doping with Ti and V. These films could potentially inhibit grain growth  
and are thus important to understand as grain size play a crucial role for the mechanical properties of the material.  
Experimental results have also shown that these types of films are present in undoped WC-Co.

Here we construct, using ab-initio calculations and modeling, an interface phase diagram for thin films in undoped  
and Ti doped WC-Co. We employ cluster-expansions to model mixed metal layers and carbon vacancies. Monte  
Carlo simulations are used to sample the configurational entropy. We include vibrational contribution to the free  
energy by using force-constant regression in order to extract the harmonic free energy. Configurational and  
vibrational entropy are all shown to be important factors in order to understand this stabilization of cubic thin films  
in WC-Co. The calculated thermodynamic properties of the cubic thin films are compared to experimental studies  
and show good agreement.

**MT01.05.09**  
**icet—A Python Library for Constructing and Sampling Alloy Cluster Expansions**  
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Alloy cluster expansions (CEs) provide an accurate and computationally efficient mapping of the potential energy  
surface of multi-component systems that enables comprehensive sampling of the many-dimensional configuration  
space. Here, the integrated cluster expansion toolkit (icet), a flexible, extensible, and computationally efficient software  
package, is introduced for the construction and sampling of CEs.
icet is largely written in Python for easy integration in comprehensive workflows, including first-principles calculations for the generation of reference data and machine learning libraries for training and validation. The package enables training using a variety of linear regression algorithms with and without regularization, Bayesian regression, feature selection, and cross-validation. It also provides complementary functionality for structure enumeration and mapping as well as data management and analysis. Potential applications are illustrated by several examples, including (1) studying chemical ordering and associated properties in a series of intermetallic clathrates as a function of composition and temperature and (2) by predicting the phase diagrams of bulk and surface alloys.


MT01.05.10
A Koopman's Compliant Exchange Correlation Potential for Semiconductors Michael Lorke, Thomas Frauenheim and Peter Deak; University of Bremen, Germany

Density functional theory is the workhorse of theoretical materials investigations. Due to the shortcoming of (semi-)local exchange correlation potentials, hybrid functionals have been established for practical calculations to describe surfaces, molecular adsorption, and defects. These functionals operate by mixing between semi-local and Hartree-Fock exchange semi-empirically. However, their parameters have to be optimized for every material separately. To treat materials with a more physics driven approach and without the need of parameter optimization is possible with many-body approaches like GW, but at an immense increase in computational costs and without the access to total energies and hence geometry optimization.

We propose a novel exchange correlation potential for semiconductor materials, that is based on physical properties of the underlying microscopic screening. We demonstrate that it reproduces the low temperature band gap of several materials. Moreover, on the example of defects in semicon-ductors, it respects the required linearity condition of the total energy with the fractional occupation number, as expressed by the generalized Koopman’s theorem. It is shown, that all technologically relevant Gallium-based semiconductors can be treated with a common choice of the functional. We also can treat the infamous case of ZnO with the same functional. As the parameters of the calculation can in principle be determined from ab initio calculations, our approach can be seen as a non-empirical approximation.

MT01.05.11
A Non-Empirical Method for Eliminating Delocalization and Static Correlation Errors within Density Functional Theory for Studying Correlated Materials Akash Bajaj, Fang Liu and Heather J. Kulik; Massachusetts Institute of Technology, United States

Presently available exchange-correlation functionals in density functional theory (DFT) suffer from a number of errors, including many electron self-interaction error or delocalization error. Eliminating delocalization error (i.e., deviation from piecewise linearity) has been shown to improve property estimation, including relative energies and especially properties directly tied to the improved orbital energies such as the band gap. However, all common approaches to mediating this delocalization error (e.g., global or range separated hybrid functionals or DFT+U) do so at the cost of increasing fractional spin error i.e. the static correlation error, which worsens other essential properties (e.g., bond dissociation energies and activation energies), thereby presenting a challenge for studying correlated materials where both these errors are simultaneously prevalent. We develop a general approach to avoid this trade-off by returning to the exact flat-plane constraint that arises from the union of the fractional spin and piecewise linearity constraints. We examine the shapes of semi-local DFT errors with respect to the flat plane condition and use these deviations to construct new, approximate, functional forms that can recover the flat-plane condition. Our judiciously-modified DFT (jmDFT) approach for constructing few-parameter, low-order corrections to conventional xc-functionals adds no computational overhead to semi-local DFT while recovering the flat-plane constraint. We describe how our approach relates to commonly used Hubbard corrections (i.e., DFT+U and DFT+U+J), thereby emphasizing their relation to improving DFT+U. Using this observation, we outline expressions that can be used to extract jmDFT parameters in a first-principles manner and study how such expressions compare with those employed in the ab initio computation of Hubbard parameters. Finally, we show how to employ this low-
cost, non-empirical framework to the study of transition-metal based correlated materials.

MT01.05.12
Modelling and Simulation of Mesenchymal Stem Cells Differentiation and Proliferation on PCL-Graphene Scaffold at Molecular and Cellular Level
Qi Wu¹, Pegi Haliti¹, Bhushan Dharmadhikari¹, Tolga Kaya² and Prabir Patra¹,¹; ¹University of Bridgeport, United States; ²Sacred Heart University, United States

The fast-growing field of regenerative medicine is closely related to the advances in tissue engineering and material sciences. Biomaterials have a prominent role as an architectural framework, similar to the innate Extracellular Matrix (ECM), which can re-establish normal functions of deteriorated tissues. In this research, computational methods were used to study the relationship in both molecular and cellular levels of mesenchymal stem cells (MSCs) differentiated into neuronal lineage in electrospun polycaprolactone-graphene (PCL-GRA) scaffold. Specifically, we used molecular dynamics (MD) simulation to investigate the interactions of the scaffold with actin protein and Cellular Potts Model (CPM) to study cellular behaviors such as cell attachment, differentiation, and proliferation. For a better understanding of neuron cell mobility on PCL-GRA scaffold, we investigated the interactions of F-actin protein, which controls the mobility and influences the dendritic spines for neuronal cells. For computational simplicity, we used the actin monomer; globular actin (G-actin). For the entire duration of 100 ns MD simulation, the Van der Waals (VDW) energy between F-actin and PCL-GRA scaffold shows negative values, which represent strong attractive forces between our scaffold and G-actin. We considered G-actin residues within 5 Å from PCL-GRA surface as “interacted residues.” Hydrogen bonds established between LYS 326 residue of G-actin and polycaprolactone chains, which also suggest non-bonding electrostatic interaction between two molecules. For the cellular level interaction, we are using CPM, a computational lattice-based model which uses the stochastic Monte Carlo’s probabilistic model by minimizing the system’s total energy. MSCs extend filopodia and spread along the strain orientation, where PCL fibers are stiffest. The mobility and adhesion of MSCs are controlled by cell-to-cell forces and cell-to-scaffold forces which are incorporated in our CPM model. Our CPM simulation results show that in randomly aligned PCL fibers, cells tend to travel up gradients toward the areas where the graphene concentration is higher. Addition of graphene to PCL scaffold improves cell attachment and viability as compared to only PCL scaffold. Our results indicate that besides the intrinsic factors assigned to the stem cells, the extrinsic parameters of the PCL-GRA interaction have a significant role in the creation of focal adhesion points, cell motility, and cellular attachment.

MT01.05.13
Running Collective Variable-Driven Hyper Dynamics in Parallel to Accelerate Molecular Dynamics Simulation of Initial Stage of Carbon Nanotube Growth
Satoru Fukuhara and Yasushi Shibuta; The University of Tokyo, Japan

Catalytic chemical vapor deposition (CCVD) is a widely used method to synthesize carbon nanotubes (CNTs). To control the property (e.g. length, diameter and chirality) of CNT, it is essential to understand the formation mechanism of CNT. Molecular dynamics (MD) simulation is a useful method to observe the formation process. However, MD simulation can only reach the time scale of nanoseconds and is not enough to directly observe the growth of CNTs at low temperature where catalysts remain solid. Therefore, we adopt a recently proposed acceleration method called collective variable-driven hyperdynamics (CVHD) method [1]. In CVHD method, firstly a collective variable (CV) is set and the CV is biased gradually in the same way as metadynamics [2]. Unlike metadynamics, CVHD reset the CV and the bias on it once the system undergo a transition. In this way, CVHD method can reproduce correct dynamics of the system. However, CVHD has a problem that the magnitude of acceleration decreases as the number of target reaction increases. This problem will be fatal in the simulation of CNT because CNT formation process contains migrations of multiple carbon atoms. In this study, we solve this problem by executing CVHD method in parallel (parallel CVHD hereinafter). Specifically, multiple CVs are set according to the number of carbons present in the system, and bias potentials are gradually added to each CVs. When a carbon atoms undergo a transition, the bias potential of the corresponding carbon is reset based on the CVHD method.

In order to confirm the correctness of parallel CVHD, activation energy of carbon atom migration is compared with not accelerated MD. The activation energies are derived from the Arrhenius plot of migration frequency of two carbon atoms in bulk iron. The activation energy gained with parallel CVHD was consistent with not accelerated MD. Subsequently, in order to observe the migration and segregation process of carbon atoms, which is important in the formation of CNT, 20 carbon atoms are randomly put in a slab iron of 1100 atoms and parallel CVHD is
performed at 600K. In the 1 ns calculations of not accelerated MD, almost no migration of carbon was observed. Whereas in the parallel CVHD, an acceleration rate of about 700 times is realized, and it was possible to observe atom migration to the surface.


MT01.05.15
Capturing Electron-Phonon Coupling and Electronic Stopping in Molecular Dynamics Simulations with a Unified Model
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We present a Langevin based stochastic model with spatial correlations and local environment dependence capable of capturing both the electron-phonon interaction as well as electronic stopping in classical molecular dynamics (MD). The model is parametrised by fitting to data from smaller scale first principles simulations, such as real-time time-dependent density functional theory (TDDFT), resulting with a solution that does not have tunable additional parameters. The framework is readily extendable to multicomponent systems and is implemented as an extension to widely used LAMMPS code. We show the application of our model in the case of Ni crystal, where we illustrate the non-equilibrium dynamics of phonon modes and a NiFeCr solid solution. In the latter case the electronic stopping regime as well as thermal equilibration is illustrated by collision cascade MD simulations at different initial conditions (PKA energies). Our model is able to excite and damp phonon modes with different wavevectors with rates in good agreement with quantum theory, which has been lacking so far in classical simulations studying non-equilibrium dynamics. Also, in collision damage simulations the model transitions smoothly from electronic stopping mode, where the coupling is strong, to the electron-phonon regime, weak coupling, as the projectile slows down and does not explore high electronic-density regions. In summary, the developed model is able to describe the non-equilibrium as well as equilibrium dynamics of a system due to electron-ion interaction and could be further applied to various phenomena such as, laser-matter interaction, compression shockwave dynamics, and radiation damage.

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MT01.05.16
First Passage Algorithms for Sink Strength Calculations—Application to Vacancy Emission and Absorption
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Kinetic Monte Carlo techniques are extensively used to simulate the evolution of defects in materials and to study irradiation effects in particular. All these methods are based on a master equation involving a transition rate matrix. Transition rates are derived from an energetic model in which defects and atoms may either occupy substitute and interstitial sites of a crystalline lattice or exhibit off-lattice in a continuous space. Unfortunately, Kinetic Monte Carlo methods become inefficient when the transition rate matrix associated with the master equation exhibits a broad spectrum of frequencies. Vacancies perform a huge number of transitions between a few atomic configurations connected to each other by small energy barriers. These connected configurations form trapping basins from which the typical escape time for a particle is much higher than the typical time to cross the small barriers inside the basins. The system remains stuck in metastable thermodynamic states. Acceleration techniques based on the theory of absorbing Markov chains are currently being used in Kinetic Monte Carlo simulations to overcome kinetic trapping in low energy basins. This is achieved by drawing escaping events to distant locations.
from the exact first-passage and no-passage distributions. These two distributions can be formally expressed through the eigenvalue decomposition of the transition rate matrix. Assuming reversible diffusion processes, a property usually satisfied by defects in metals and alloys in and out of equilibrium, we show that the involved linear and eigenvalue problems to be solved can be symmetrized. Furthermore, the slowest modes, those associated with the smallest eigenvalues, are observed to contribute the most to the first-passage and no-passage distributions. As a result, Krylov subspace projection techniques implementing reverse iterations provide us with an efficient tool for accurately approximating the two desired distributions at a relatively low cost. We discuss the convergence, scalability and range of applicability of the approach. We demonstrate its efficiency by computing sink strengths and transition currents for the emission and absorption of vacancies from and to cavities in Aluminium at low defect concentrations.

MT01.05.17
Phase Field Modeling of Rapid Solidification of Ti-Ni Alloy Parameterized Using Interfacial Properties Calculated from Atomistic Simulations Sepideh Kavousi, Brian R. Novak and Dorel Moldovan; Louisiana State University, United States

We present a molecular-dynamics (MD) informed phase field simulation approach to study the microstructure evolution during solidification of Ni-Ti alloys. In the conventional phase-field model developed by Echebarria et al. (EFKP) [1] the kinetic coefficient for solidification of dilute binary alloys is assumed to be zero. However, in the newly-developed phase-field model by Pinomaa and Provatas [2], based on the Crystal Growth Model (CGM), it has been shown that consideration of the kinetic coefficient may play an important role for capturing the effect of solute trapping. Using MD simulations, we calculate the anisotropic kinetic coefficient and crystal-melt interfacial free energy by employing the free solidification and capillary fluctuation method, respectively. Then, using the MD-calculated crystal-melt interfacial properties, we parameterize both the EFKP and Pinomaa-Provatas phase field models and investigate how the partition coefficient changes with the solidification velocity. Work supported by the U.S. National Science Foundation (NSF OIA-1541079).


MT01.05.18
General Correlation between Electronic Factors and Solute-Defect Interactions in bcc Refractory Metals Yong-Jie Hu¹, Ge Zhao², Baiyu Zhang³, Zi-Kui Liu¹, Xiaofeng Qian³ and Liang Qi¹; ¹University of Michigan, United States; ²The Pennsylvania State University, United States; ³Texas A&M University, United States

The interactions between solute atoms and crystalline defects such as vacancies, dislocations, and grain boundaries are essential in determining physical, chemical and mechanical properties of alloys. Here we present a general correlation between two electronic factors and the solute-defect interaction energies in binary alloys of body-centered-cubic (bcc) refractory metals (such as W and Ta) with transition-metal substitutional solutes. One electronic factor is the bimodality of the $d$-orbital local density of states for a matrix atom at the substitutional site, and the other is related to the hybridization strength between the valence $sp$- and $d$-bands for the same matrix atom. Remarkably, the correlation is independent of the types of defects and the locations of substitutional sites, following a linear relation for a particular pair of solute-matrix elements. The correlation plus a residual-correction model can provide a novel and quantitative guidance to predict the solute-defect interactions in alloys based on electronic structures.

MT01.05.19
Study of Water Diffusion across Nanocomposite Reverse Osmosis Membranes—A Combined Molecular Dynamics and Kinetic Monte Carlo Approach Rodolfo Cruz-Silva¹, Syogo Tejima¹,², Aaron Morelos¹, Josue Ortiz-Medina¹,³, Takuya Hayashi¹, Kenji Takeuchi¹, Mauricio Terrones¹,³ and Morinobu Endo¹; ¹Shinshu University, Japan; ²Research Organization for Information Science and Technology, Japan; ³Universidad Panamericana, Mexico; ⁴The Pennsylvania State University, United States

Reverse osmosis membranes are increasingly being used for water desalination and purification. These membranes
consist of a very thin (100-200 nm thick) selective layer, often made of crosslinked aromatic polyamide (PA), on top of a porous support. Understanding the mechanism of diffusion across the selective layer is key to improve the performance of current membranes. So far, classical molecular dynamics has been very useful to explain the hydration, water diffusion, and salt rejection mechanisms in plain PA membranes. Recently, nanocomposite membranes containing carbon nanotubes (CNTs) mixed with PA have shown high permeation and salt rejection and good chlorine resistance. However, the mechanism of diffusion is still not completely understood and in fact, there is no agreement on how CNTs increase the permeability of these membranes. While some researchers suggest that water flows within the embedded nanotubes, other researchers suggest they are impermeable. Unfortunately, the characteristic dimensions of CNTs (diameter around 10-12 nm, and several hundred nm length) requires using large simulation boxes that forbids the use of molecular dynamics. In this work, we used a multiscale approach by combining classical molecular dynamics and a simplified kinetic Monte Carlo approach to study the water diffusion across CNT-PA nanocomposite membranes. Briefly, we built a relatively small cell of PA and PA containing a single CNT. By using classical molecular dynamics, we calculated the free-energy-potential field in both cells. We implemented later a simplified kinetic Monte Carlo algorithm to simulate the diffusion of water molecules across 200 nm thick CNT-PA nanocomposite membranes and we were able to study the effect of CNT's concentrations on water permeation across the membranes.

MT01.05.20
Cluster Dynamics Modelling of Materials—A New Hybrid Deterministic/Stochastic Coupling Approach
Manuel Athenes¹, Thomas Jourdan¹, Gilles Adjanor¹,² and Pierre Terrier¹,²; ¹CEA, France; ²CERMICS, France

Deterministic simulations of the rate equations governing cluster dynamics in materials are limited by the number of equations to integrate. Stochastic simulations are limited by the high frequency of certain events. We propose a coupling method combining deterministic and stochastic approaches. It allows handling different time scale phenomena for cluster dynamics. This method, based on a splitting of the dynamics, is generic and we highlight two different hybrid deterministic/stochastic methods. These coupling schemes are highly parallelizable and specifically designed to treat large size cluster problems. The proof of concept is made on a simple model of vacancy clustering under thermal ageing.

MT01.05.21
Graphene Surface Chemistry and Oxidation in High Temperature Applications
José Graña-Otero, Simon Schmitt, Siamak Mahmoudi, Evan Sullivan and Gangotri Dey; University of Kentucky, United States

The chemistry of graphene is relatively well-known at relatively low temperatures, when the ambient gas is artificially limited to atomic or molecular oxygen in ultra-low pressure conditions for Electron Microscopy studies and epoxy is typically the only adsorbed surface species. The same applies at regular ambient conditions when air consists only of molecular species such as oxygen, nitrogen or water vapor, which have negligible small degrees of dissociation. Chemisorption of these molecular species is effectively prevented by fairly large activation energies, which severely limits their chemisorption concentrations and therefore play no role in the graphene surface chemistry.

However, carbon materials are extensively used in high-temperature conditions such as Thermal Protection Systems for Hypersonic flight applications. Carbon oxidation plays in these applications a critical role because it actually gasifies carbon in the form of gaseous CO and CO₂ therefore removing the protective layer. However, the chemistry of the graphene surface is not well known in these high temperature environments, which are characterized by large concentrations of highly reactive radicals such as hydroxyl or atomic oxygen, nitrogen and hydrogen. These species chemisorb on the graphene surface with very low or even no energy barrier at all, so they can reach high surface concentrations, competing with oxygen for carbon sites and therefore effectively reducing the oxygen coverage. However, the energetics and kinetics of these species on the graphene surface is almost completely unexplored.

Using DFT calculations, we have systematically studied the kinetics and dynamics of surface processes such as chemisorption, desorption and surface hopping on the graphene surface of atomic hydrogen, nitrogen, oxygen and hydroxyl, which typically populate the graphene surface in these high-temperature environments. We have also studied the interaction and reactions among them. Our ultimate goal is to develop a detailed kinetic mechanism including surface species and reactions among them in much the same way as those already available in combustion of hydrocarbon fuels. We have found for instance that oxygen can chemisorb in an on-top-of-carbon configuration,
in addition to the well-known epoxy form. We have studied as well interaction effects among near neighbors, showing actually that clustering is energetically favored, an effect already observed in the case of atomic chemisorbed hydrogen.

On the other hand, we have studied the oxidation dynamics. Compared to the dynamics of these surface species, oxidation occurs in times scales several orders of magnitude slower, which make oxidation events very infrequent. In order to overcome this rare-event limitation, we have used kinetic Monte-Carlo simulations to study the gasification dynamics. In particular, we have been able to simulate and explain the well-known pitting, so characteristic of graphene and graphite oxidation. We show in particular how, in the more relevant conditions for applications high-temperature environments, the presence of all those other surface species modifies the oxidation and pit growth rates with respect to the corresponding values found in the highly controlled conditions of Electronic Microscopy studies.

MT01.05.22
The Hiphive Package for the Extraction of High-Order Force Constants by Machine Learning Fredrik Eriksson, Erik Fransson and Paul Erhart; Chalmers University of Technology, Sweden

The efficient extraction of force constants (FCs) is crucial for the analysis of many thermodynamic materials properties. Approaches based on the systematic enumeration of finite differences scale poorly with system size and can rarely extend beyond third order when input data is obtained from first-principles calculations. Methods based on parameter fitting in the spirit of interatomic potentials, on the other hand, can extract FC parameters from semi-random configurations of high information density and advanced regularized regression methods can recover physical solutions from a limited amount of data. Here, the hiphive Python package, that enables the construction of force constant models up to arbitrary order is presented. hiphive exploits crystal symmetries to reduce the number of free parameters and then employs advanced machine learning algorithms to extract the force constants. Depending on the problem at hand, both over and underdetermined systems are handled efficiently. The FCs can be subsequently analyzed directly and or be used to carry out, for example, molecular dynamics simulations. The utility of this approach is demonstrated via several examples including ideal and defective monolayers of MoS2 as well as bulk nickel.


MT01.05.23
Light Absorption and Refractive Index During Agglomeration and Surface Growth of Carbonaceous Nanoparticles Georgios A. Kelesidis and Sotiris E. Pratsinis; ETH Zürich, Switzerland

Optical characterization of carbonaceous materials (e.g., Laser Induced Incandescence, LII) is important in fire detection and manufacturing of various grades of carbon black and even their impact on climate largely depends on light absorption. For example, the contribution of carbonaceous materials to global warming (~25 % of the total anthropogenic contribution) has currently the highest uncertainty among all contributions (CO2, CH4, etc.), as their optical properties depend on their precise composition quantified by C/H and morphology. Understanding the light absorption of carbonaceous particles is essential to their characterization and selective sensing by fire detectors and can improve the accuracy of climate models.

Here, the impact of composition on the light absorption from carbonaceous particles is investigated by coupling mesoscale Discrete Element Modeling (DEM) [1] with Discrete Dipole Approximation (DDA) during their surface growth and agglomeration [2]. The Mass Absorption Cross-section, MAC, of these agglomerates is estimated by DDA and validated against atomistic point dipole interactions and mesoscale DDA simulations [2]. Using a refractive index, RI, for mature soot with large C/H > 4.5 [3] yields constant MAC and absorption function E overestimating the light absorption up to 75 % of nascent soot with C/H < 4.5. The RI is interpolated between those of nascent and mature soot for wavelength, $\lambda = 1064$ nm to account for quantum confinement and evolving number of clustered sp2-bonded rings. This affects the optical band gap, $E_g$, resulting in excellent agreement of the DEM-derived evolutions of MAC and E with the corresponding LII measurements in methane [4] and ethylene premixed flames [5]. The $E_g$ of nascent soot decreases during agglomeration, increasing MAC and E by 65 %. The good agreement between DEM and LII data confirms that carbonaceous particle dynamics by surface growth and agglomeration strongly correlate with particle composition and RI that are essential for quantifying carbonaceous particle light absorption.
Mesoporous materials have attracted considerable attention in the past for their applications in catalysis, sorption, separation, hydrogen storage, oil & gas extraction, etc. and as host matrices for optically and electronically active components. In the recent past, mesoporous siliceous materials (MSM’s) have also shown tremendous potential in drug delivery technologies. Their superior thermophysical, mechanical, and chemical properties such as variable pore size, pore morphology, and surface functionalizability create avenues for optimized interactions between drug molecules and carriers. A widely adopted method of synthesis of these structures is evaporation-induced self-assembly (EISA). In EISA, control of pore morphology and liquid crystalline mesophases is accomplished by controlling the environmental conditions such as temperature, orientation of micelles, pH, and also the solvent evaporation rate and the block copolymer used as precursor. An important concern is that the packing of individual mesoporous solids in to a container can result in internal pores between individual mesoporous structures of larger sizes (>50 nm). Hence a monolithic solid is desired and has to be synthesized directly from the precursors. Synthesis of monoliths is highly challenging as it results in the formation of cracks. Prior studies have shown that cracks can be partially alleviated by controlling solvent evaporation rates, supercritical CO2 drying, or by using liquid paraffin in the synthesis mixture.

While the usual practice is to experiment with the block copolymers, surfactants, rate of evaporation, and the time involved in polymerization, proper guidelines for the rational synthesis of mesoporous siliceous monoliths is not available yet. Hence, as the first stride to address this issue, here, we present a molecular dynamics (MD) simulation routine that can serve as a guideline to the synthesis of mesoporous structures. Combining non-reactive and reactive MD, we simulate the non-reactive self-assembly process followed by chemical events leading to the evolution of porous structures. We implement a 3-step process using a water-solvated pluronic-based tri-block copolymer having both hydrophilic and hydrophobic groups in it. In the first step, we equilibrate the system with concentration > critical micelle concentration and temperature higher than the critical micelle temperature allowing for the non-reactive self-assembly of the surfactant molecules. OPLSAA force field [1] is used to drive this co-operative assembly. Secondly, we introduce silicic acid as the silica precursor for the micelle system and equilibrate using ReaxFF reactive force field [2] to enable chemical reactions leading to the formation of skeletal Si-O-Si bonds. To condense the silica precursor to the organic template, we use the accelerated bond-boosting scheme [3] within the ReaxFF molecular dynamics framework, which essentially bypasses the transition state complexes with high activation energy requirements, thereby achieving laboratory timescales in MD simulations. Following this, as the final step, by preferentially evaporating water solvent, MSM structures are obtained. We study the structural and mechanical properties of MSM’s to gain insights on molecular structure, localized heterogeneities, crack formation, etc., thereby elucidating the process of synthesis of mesoporous siliceous materials.

References
Hydrogen is a promising clean fuel. A key bottleneck to its widespread utilization is the susceptibility of materials used in hydrogen distribution infrastructure (typically steels) to embrittlement and failure. This necessitates the use of permeation barriers to prevent hydrogen ingress into the steel. Al₂O₃ is a popular hydrogen barrier, due to its low hydrogen permeability. Our recent study on bulk Al₂O₃ [1] using an ab initio thermodynamics approach has shown that the hydrogen solubility and diffusivity in Al₂O₃ can be further reduced by dopant engineering. Specifically, doping with Si, Ti, Fe and Cr reduces the solubility of free protons to negligible amounts, and traps protons at aluminum vacancy sites with high binding energy (~3 eV), in turn, reducing diffusivity.

While the intrinsic hydrogen permeation resistance of bulk Al₂O₃ is attractive, it is more lucrative to use a multilayer structure of alternating Al₂O₃ and Al layers as the coating. Such a structure is advantageous on multiple fronts: (a) it has high toughness and fatigue resistance, preventing cracking of Al₂O₃, thus avoiding fast diffusion pathways for hydrogen ingress to the steel, (b) it is self-healing, and (c) space charge engineering of the high interfacial area can help reduce hydrogen permeation further. The latter is the aim of this study.

Density functional theory was used to obtain the formation energies of various native, hydrogen and dopant (Mg, Si, Ti, Fe, Cr, B, C, N) defects in the bulk and defect segregation energies to the Al₂O₃|Al interface core. Using these energies as input, a continuum model was developed, which self-consistently solved Poisson’s equation to obtain the defect concentrations at the interface. Results show that in the undoped case, free hydrogen interstitials are depleted in the space charge region and accumulate at the core. This hydrogen buildup can lead to blistering of the interface, thus, deteriorating coating performance. Dopants were then utilized to prevent hydrogen accumulation at the core and ensure trapping of hydrogen in the space-charge region. To identify the impact of the interface on hydrogen diffusivity, effect of dopants on hydrogen migration barriers across the interface was studied using nudged elastic band method. The work of adhesion of doped interfaces was also calculated, which has implications for the effect of dopants on the spall tendency of the interface.

The robust coupling of ab initio methods and continuum modeling in this study helps take advantage of the accuracy of first principles calculations while overcoming the spatial limitation of such methods. It is emphasized that the fundamental results of this study can be extended to other systems where the metal/oxide interface affects device efficiency, such as the electrode/electrolyte interface in resistive switching devices and the metal/dielectric interface in metal-oxide-semiconductor devices.


MT01.05.26
Exploration of Mechanical Control Over Chiral Magnetic Phases from Atomistic to Mesoscopic Length Scales
Daniil A. Kitchaev and Anton Van der Ven; University of California Santa Barbara, United States

Chiral (Dzyaloshinskii-Moriya) magnetic interactions give rise to a wide range of complex magnetic phases, from helical and cycloidal spin textures to topological phases such as skyrmions. Due to the sensitivity of these interactions to precise atomistic environments and their symmetry, even mild strain can profoundly change the character and relative stability of the resulting magnetic phases. We first use phenomenological arguments to chart out how strain may alter chiral magnetic interactions, identifying the strain fields necessary to stabilize various types of magnetic phases in materials of any symmetry. In order to test these predictions, we construct strain-coupled magnetic phase diagrams from first-principles, by relying on density functional theory, cluster expansions, Hamiltonian Monte Carlo, and phase field techniques. This scale-bridging model reveals that strain fields readily accessible by a wide range of experimental techniques can be used to precisely control magnetic phase behavior and the emergence of topological phases in common high-symmetry ferromagnetic materials.

MT01.05.27
Optical and Electrical Properties of Point Defects in Cubic Zirconia
Elizabeth Chavira1, Mourad Boujnah1, A. El Kenz2, M. Loulidi2, H. Ez-Zahraouy2 and A. Benyoussef3; 1Universidad Nacional Autónoma de México, Mexico; 2Mohammed V. University, Morocco; 3Hassan II Academy of Science and Technology, Morocco

Electronic, optical and electrical properties of the point defects in cubic unit cell ZrO₂ were calculated by using the density functional theory (DFT) calculation based on full potential linear augmented plane wave (FP-LAPW). The exchange-correlation potential is treated by the Gradient Generalization Approximation (GGA) and the recently proposed by Tran and Blaha the modified Becke-Johnson potential (TB-mBJ) which successfully corrects the band-gap problem found with GGA for a wide range of materials. The energetics of point defects is studied after
optimization of positions. Our results indicate that the ZrO antisite has the lowest formation energy and could thus be the acceptor defect responsible for the p-type conductivity of undoped cubic ZrO$_2$. However, based on our electronic structure obtained using the TB-mBJ method we have calculated various optical properties, including the complex index of refraction, absorption and transmittance coefficients. Furthermore, the electrical properties of each point defects have been investigated using the Boltzmann transport theory.

MT01.05.28
First-Principles Study of H$_x$WO$_3$ for Neuromorphic Computing Applications Konstantin Klyukin and Bilge Yildiz; Massachusetts Institute of Technology, United States

Neuromorphic computing paradigm holds much promise for applications that require big data analysis and artificial intelligence. The key components in neuromorphic circuits are devices that exhibit a history-dependent conductivity modulation, which could efficiently represent synaptic weights in artificial neural networks. However, an accurate and fast modulation of the conductance over a wide dynamic range is proved to be challenging. Recent experimental studies showed that a gradual change in electronic conductivity of WO$_3$ can be achieved by hydrogen doping, giving rise to the ability to have a large number of conduction states. However, the relationship between hydrogen concentration and electric conductance is not linear and WO$_3$ could undergo phase transitions upon hydrogenation. In this work, atomistic density functional theory calculation are used to establish the correlation between H content and H$_x$WO$_3$ conductivity and determine the rate-limiting steps of hydrogen intercalation process. This allows us to determine the most relevant hydrogen concentration range and guide experimental studies.

MT01.05.29
Real Space Renormalization Method for Atomic Scale Modeling of Thermoelectric Transport in Macroscopic Devices Chumin Wang and Vicenta Sanchez; Universidad Nacional Autonoma de Mexico, Mexico

Electronic transport has been traditionally studied by means of the reciprocal lattice method, which has successfully explained many physical properties of crystalline solids through the electronic band theory, such as the optical absorption and the thirty-orders-of-magnitude difference in the electrical resistivity between a good conductor and a typical insulator [1]. However, current electronic devices frequently contain multiple non-periodic structural interfaces and their presence avoids the use of reciprocal space. An alternative way to investigate the electron and phonon transport at atomic scale in macroscopic thermoelectric devices, which allow a direct conversion between thermal and electrical energies without harmful pollution, could be by using the real space renormalization method [2]. This method combined with the convolution theorem has the advantage of being numerically accurate and computationally efficient, i.e., able to address 10$^{24}$ non-periodically located atoms without introducing additional approximations [3]. It is well known that the metals are poor thermoelectric materials. In contrast, segmented metallic nanowires have a band structure by design, which combines with a properly placed chemical potential by applying a gate voltage could archive a good thermoelectric power [4,5]. In this work, we study thermoelectric properties of periodic and quasiperiodically segmented macroscopic-length nanowires with and without branches by means of the Kubo-Greenwood formula, in which tight-binding and Born models are respectively used for the calculation of electric and lattice thermal conductivities [6-8]. The results show a substantial growth of the thermoelectric figure of merit (ZT) induced by the long-range quasiperiodic disorder, because it diminishes the thermal conduction of long wavelength acoustic phonons being such phonons usually not altered by local defects neither impurities [9].

This work has been partially supported by UNAM-IN106317, UNAM-IN115519 and CONACyT-252943. Computations were performed at Miztli of DGTIC, UNAM.

Improved understanding of aqueous solutions at charged graphitic interfaces is critical for designing new carbon-based materials for energy storage and water desalination. However, many mechanistic details of the interfacial interactions remain unclear, including how interfacial structure and response are dictated by intrinsic properties of solvated ions under applied voltage. This knowledge gap is partly related to the challenge in simulating aqueous interfaces in the presence of a bias potential. Here, we combine a newly developed hybrid first-principles/continuum simulations with electrochemical measurements to investigate adsorption of several alkali-metal cations at the interface with charged graphene and within graphene slit-pores. We confirm that adsorption energy increases with ionic radius, while being highly dependent on pore size under confinement conditions. In addition, in contrast with conventional electrochemical models, we find that interfacial charge transfer contributes non-negligibly to this interaction and can be further enhanced by confinement. Overall, the measured interfacial capacitance trends result from a complex interplay between voltage, confinement, and specific ion effects—including ion hydration and degree of charge transfer. The results provide broad implications for optimizing electrochemical interfaces for energy storage and water desalination.

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

Effect of Surface Defects on Field-Induced Hot-Carrier Chemistry in Dielectric Polymers

Subodh C. Tiwari1, Hiroyuki Kumazoe2, Thomas Linker1, Rampi Ramprasad1, Rajiv Kalia1, Aiichiro Nakano1, Fuyuki Shimojo2 and Priya Vashishta1; 1University of Southern California, United States; 2Kumamoto University, Japan

Performance of dielectric polymers under high electric field is limited by the electrical breakdown, which is commonly understood as an avalanche of processes such as carrier multiplication and defect generation, triggered by field-accelerated hot electrons and holes. We model the hot-carriers transport in dielectric polymer, Polyethylene, with excited-state quantum molecular dynamics simulations in presence of electric field, which reveal multiple microscopic processes induced by hot electrons and holes under an electric field ranging between 100 and 1200 MV/m. We found that electronic-excitation energy is rapidly dissipated due to strong electron-phonon scattering. This, in turn, creates other electron-hole pairs to cause carrier multiplication. The key chemical damage occurs due to localization of holes of the surface of slabm which weaken carbon-carbon bonds on the surface. We will also discuss the effects of field strength and pre-existing surface defects (e.g., –COOH and –OH) on the field-induced hot-carrier dynamics and chemistry. Such quantitative information can be incorporated into first principles-informed, predictive modeling of dielectric breakdown.

This work was supported by the Office of Naval Research through a Multi-University Research Initiative (MURI) grant N00014-17-1-2656. The computations were carried out at the Center for High Performance Computing of the University of Southern California.

Towards Predictive Design of Bio/Nano Interfaces of Self-Assembled Peptides on Single Atomic Layer Materials

Siddharth S. Rath, Tatum G. Hennig, Pedro Fisher-Marques, Nitya K. Kumar, Tyler D. Jorgenson, David Starkebaum, Rene Overney and Mehmet Sarikaya; University of Washington, United States

Spontaneous self-organization of solid binding peptides on single layer atomic materials (SAP/SLAM) offers a great potential in exploiting these systems for bioelectronic and biosensing applications. The molecular interaction at the...
bio/nano soft interface between the peptide and the solid material is dependent on the conformations of the peptides and the surrounding conditions such as pH and temperature that affect the molecular structures, conformations, binding, and self-assembly in a myriad of ways. Although molecular dynamics has been used to study protein folding problems, here we demonstrate a closed-loop data pipeline molecular-dynamics implementation in SAP/SLAM systems. We perform molecular dynamics simulation on a wild type peptide, obtained from directed evolution experiments, that self-assembles on graphene at neutral pH and room temperature. Several mutants of the WT peptide are used to investigate whether they display spontaneous self-assembly under different pH and temperatures. Principal components analysis is paired with gaussian mixture model clustering to obtain full-peptide conformation propensities and automated analysis is done to obtain information about the conformations at different processing conditions on graphene and in aqueous solution. We show that while the WT peptide assembles on graphene at neutral pH and room temperature, the charge-neutral mutant assemblies under a wide range of pH (3.0 < pH < 9.0) and has a highly similar conformations over the range of pH conditions. Similarly, the tyrosine to tryptophan mutant assemblies at higher temperatures with a clear change in conformations from that of low temperature conditions. Knowing conformations of peptides and how the mutants affect conformation at different conditions is crucial in understanding the molecular footprint of the peptide on the surface. The knowledge of soft bio/nano interface structure will facilitate DFT calculations downstream to understand effect of self-assembly on the band structure changes happening in the SAP/SLAM systems. These studies eventually will lead to the predictive atomistic algorithms design of unique bio/nano systems defined by genetically selected peptides and single atomic layers materials towards biosensors, bioelectronics and biomolecular fuel cells. As part of the Materials Genome Initiative, the research is supported by NSF-DMREF program through the grant DMR-1629071.

MT01.05.34
Oxidation State and Coordination of Cu-Dimers in Cu-ssz-13—A First-Principles Study Unni Engedahl, Henrik Grönbeck and Anders Hellman; Chalmers University of Technology, Sweden

Direct methane-to-methanol conversion, which enables transformation of gas-phase methane to liquid methanol under mild conditions, is considered a dream reaction. At present the reaction is often realised via a three-step cycle; an activation phase, a reaction phase, and finally an extraction phase. Copper ion-exchanged zeolites have been suggested as promising catalysts for this reaction, although the nature of the actives sites is still under debate. Here we examine, using ab-initio molecular dynamics and first-principles thermodynamics, oxidation state and coordination of Cu-dimers inside the chabazite structure Cu-SSZ-13 under relevant experimental conditions. At room temperature, the formation energy of the Cu-dimers shows a multitude of Cu2(HxOy) clusters being exergonic. However, at the higher temperatures of the relevant reaction conditions only Cu2O and Cu2(OH) remain as thermodynamically stable structures. In the three step cycle, these are thus identified as the relevant structures for the activation and extraction phase, respectively.

MT01.05.35
There’s Room in the Middle—Nanocluster Coordination as an Approach to Mesoscale Modeling Forrest Kaatz1 and Adhemar Bultheel2; 1Mesalands Community College, United States; 2KU Leuven, Belgium

The mesoscale connects the molecular and atomic to the bulk. This size regime has posed a conundrum for modeling, as it is outside the realm of density functional theory (DFT) and molecular dynamics (MD) may not be appropriate. We use a chemical graph theory approach and compute the adjacency matrix for the clusters. This leads to identification of the coordination of each site. We demonstrate mesoscale relationships for the magic formulas of clusters, the radial distribution function (RDF) and nanocalysis. The number of bonds, atoms, and coordination numbers exhibit magic number character versus the number of shells, n, as the size of the clusters increases. Next, we use gold nanoclusters as model systems to generate their corresponding RDFs. The integrated intensity of the first peak in the RDF is related to magic formulas for the number of bonds (neighbors) and the number of atoms, as a function of n. Each unique cluster type and size has a structural fingerprint in its corresponding RDF. Lastly, the coordination style method is key to studying nanocalysis and creating a mesoscale model free of arbitrary parameters for sizes ~ 3 nm < D < 100 nm. We apply DFT, informational statistical mechanics, and thermodynamics to complete the model. This provides a theoretical scheme to determine the size and shape dependence of the entropy and enthalpy of nanocluster-adsorbate systems. We present examples from the literature, where others model cluster properties such as melting temperatures, cohesive energy, magnetic moments, Curie temperature, and the melting entropy and enthalpy using coordination numbers. We summarize the potential of these techniques to reach any mesoscale size, using magic formulas.
MT01.05.36
Vibrationally Accurate Interatomic Potentials Andrew D. Rohskopf and Asegun Henry; Massachusetts Institute of Technology, United States

Molecular dynamics (MD) simulations provide a general technique to study thermal vibrations/phonons and their contributions to thermal transport. However, despite the widespread usage of MD to study phonons, direct comparisons between experiments and simulations are often associated with low fidelity, due to a lack of accurate interatomic potentials (IPs). This issue therefore imposes a major barrier to utilizing MD for studying thermal transport and deriving new physically meaningful insights. Towards solving this problem, we present a new approach to making EIPs specifically optimized for accurately describing phonons and thermal vibrations. The approach enables nearly exact reproduction of ab initio phonon dispersion relations (i.e., < 1%) error), along with accurate forces and thermal conductivity (i.e., < 10% error), with low computational expense like that of traditional EIPs.

SESSION MT01.06: Empirical Methods II
Session Chairs: Manuel Athenes and Tony Lelièvre
Wednesday Morning, December 4, 2019
Hynes, Level 2, Room 206

8:00 AM *MT01.06.01
Structures and Transformations of Metal Nanocrystals Kristen A. Fichthorn; The Pennsylvania State University, United States

A significant challenge in the development of functional nanomaterials is understanding the growth of colloidal metal nanocrystals. One bottleneck is understanding the evolution of nanocrystal seeds from nuclei. Seeds play a critical role in nanostructure formation, as the shape of the seed often determines the final nanocrystal shape. The interplay between structural transitions, deposition, and etching as seeds grow from nuclei leads to a myriad of metastable nanocrystal morphologies. To understand this interplay and its ramifications for seed structure, we conducted replica-exchange molecular dynamics simulations to quantify how the structures Ag and Cu seeds evolve in vacuum, as well as in a solution environment, with increasing size and as a function of temperature. Using common-neighbor analysis, we create barcodes to describe the distribution of nanocrystal structures as a function of size and temperature. We obtain energy barriers for the transformations of selected seeds from one shape to another. Several critical branching sizes emerge, at which intervention by solution processing may influence the final nanocrystal shape. Knowledge from these studies will enable the development of strategic synthesis protocols to achieve selective nanostructure yields.

8:30 AM MT01.06.02
Multiscale Modeling of Phase Transformation Microstructures Ananya Renuka Balakrishna; University of Minnesota, United States

Phase transformation microstructures have an abrupt change in lattice geometry that significantly affects material properties. For example, a cubic to tetragonal lattice transformation induces polarization in ferroelectric materials, and a similar lattice transformation during charging/discharging of battery materials induces large volume changes. Current material models describe phase transformation phenomena at different length and time scales. On the one hand, continuum methods such as phase-field models describe microstructural evolution by typically homogenizing the crystallographic texture of the material, and do not model individual lattice transformations. On the other hand, atomistic models such as the first principle methods and molecular dynamics models provide atomistic insights into lattice transformation, but are not applicable to the length scale and time scales for microstructural evolution. In my talk, I will introduce a novel theoretical framework that couples a Cahn-Hilliard model (continuum scale) with a phase-field crystal model (atomistic scale) to describe phase transformation microstructures in crystalline materials. I will show how this modeling technique can be applied to engineer crystallographic features of phase transformation materials (such as battery materials, ferroelectrics, ferromagnets) to enhance their material properties.
and lifespans.

8:45 AM *MT01.06.03
**Atomistic Analysis of Grain Boundary Segregation in Polycrystals** Malik Wagih and Christopher A. Schuh; Massachusetts Institute of Technology, United States

Nanocrystalline alloys can be designed to be stable by *intentional grain boundary segregation*: by using alloying elements that will segregate to the boundaries and lower the grain boundary energy, the driving force for grain growth can be attenuated or even eliminated. The main thermodynamic data necessary for predicting stability in nanocrystalline alloys is the segregation strength of the alloying element, quantified by the segregation energy. Segregation energy is usually calculated precisely only for specific high-symmetry boundaries that are not representative of the spectrum of states in a true polycrystal, or estimated in a semi-empirical manner for some “average” grain boundary assumed typical of a polycrystal. In this work, we outline the thermodynamic and computational framework to address equilibrium grain boundary segregation in full polycrystalline grain boundary networks, by developing a variety of atomistic tools. Specifically, we aim to understand the full spectrum of segregation energies, as well as the role of solute-solute interactions at the boundary. Our efforts to apply these methods across many alloy systems will also be addressed.

9:15 AM MT01.06.04
**Investigating Complex Grain Boundary with Solute Segregation via a Combination of Genetic Algorithm and Grand Carnonical Ensemble** Mingfei Zhang, Yong-Jie Hu, Chaoming Yang and Liang Qi; University of Michigan, United States

The interactions between solute atoms and crystalline defects such as dislocations and grain boundaries play an essential role in determining physical, chemical and mechanical properties of solid-solution alloys. In recent years, the ability to predict solute segregation at high symmetry grain boundaries from first principles have been widely studied. However, previous algorithms have mainly focused on the simple grain boundary structures for dilute solute cases due to the costly computation power needed by density functional theory (DFT). Here, we present a general atomistic approach to optimize the structures and simulate solute segregation trends of grain boundaries in multiple component systems by the combination of a highly efficient genetic algorithm and the grand canonical ensemble, in which components are not restricted to dilute or stoichiometric cases. Different chemical potential can be used as input for creating different reservoirs for the grain boundary phases. In our study, thousands-atom grain boundary systems will be investigated by well-established empirical potentials (MEAM or EAM potentials) for Mg-based alloy systems, like Mg-Y or Mg-Zn, which are potential candidates for lightweight structural components as a result of their low density and high specific strength. Because of the complicated potential energy landscapes (PEL) coming from both geometric and occupational freedom, we will either average a good amount of small configurations by Boltzmann statistics based on their energy distributions for patterned segregation systems or use a large supercell to study cluster segregation systems across the grain boundaries. Final structures will then be used to investigate the effect of solute on mechanical behaviors of grain boundary systems.

9:30 AM *MT01.06.05
**Three Stages of Work Hardening in Full Atomistic Details—No Kidding** Luis Zepeda-Ruiz1, Alexander Stukowski2, Nicolas Bertin1, Tomas Oppelstrup1, Nathan Barton1, Rodrigo Freitas3,4 and Vasily V. Bulatov1; 1Lawrence Livermore National Laboratory, United States; 2Darmstadt University, Germany; 3Stanford University, United States; 4University of California, Berkeley, United States

We will present ultra-large scale Molecular Dynamics simulations of aluminum single crystals subjected to uniaxial tension. We observe that appearance (or not) of three-stage hardening depends on the initial crystallographic orientation of the straining axis and results from crystal rotation. In its turn, crystal rotation is a direct consequence of co-axiality forced on the specimen by the testing machine, the view widely accepted in the phenomenological Crystal Plasticity community since the classical studies of Schmid predating dislocations. Remarkably, stress-strain behaviors, slip system activity and crystal rotations observed in our high-rate MD simulations are in an exact qualitative agreement with quasistatic experiments suggesting that physics of crystal plasticity scales, i.e. dislocation mechanisms defining crystal plasticity response remain the same over twelve decades of straining rates.
10:00 AM BREAK

10:30 AM MT01.06.06
Uncertainty-Driven Construction of Markov Models—Finding and Evaluating Transition Rates Thomas D. Swinburne1, Danny Perez2 and Mihai-Cosmin Marinica3; 1CNRS / CINAM, France; 2Los Alamos National Laboratory, United States; 3CEA Saclay, France

When the dynamics of a high dimensional system is characterized by long periods in metastable energy basins with rare interbasin transition, a rigorous coarse grained representation is a Markov chain with suitable transition rates. If well constructed, such models can provide a valuable, robust connection between atomistic and mesoscale material models. However, with finite resources sampling is always incomplete, which if uncontrolled can have catastrophic consequences on the model validity. Furthermore, commonly used harmonic rate theories can fail at surprisingly low homologous temperatures. I will talk about recent work that uses a robust Poisson-Bayes estimator of sampling completeness to autonomously manage and optimize massively parallel sampling of defective crystal energy landscapes[1] and a novel path-based scheme to evaluate anharmonic contributions to transition state theory predictions of reaction rates[2].

[1] TD Swinburne and D Perez, Self-optimized construction of transition rate matrices from accelerated atomistic simulations with Bayesian uncertainty quantification, Physical Review Materials 2018

10:45 AM *MT01.06.08
Morphological Transitions in Cu Islands Grown on Strained Cu(100) Jacques G. Amar, Ehsan H. Sabbar, Indiras Khatri and Yunsic Shim; University of Toledo, United States

A variety of experiments on submonolayer metal heteroepitaxial growth have demonstrated that the combined effects of strain and bonding can lead to interesting shape transitions and/or defect formation, although the corresponding mechanisms and/or defect structure are not well understood. In order to better understand the underlying mechanisms as well as separate out the effects of strain from “chemical” effects, we have carried out temperature-accelerated dynamics simulations [1] of a simple model system corresponding to the submonolayer growth of Cu on a biaxially strained Cu(100) substrate at 200 K. In the case of 2% compressive strain we find - as was previously found for Cu/Ni(100) growth [2] – that multi-atom “pop-out” events which create open step-edges are enhanced, leading to the formation of blobby islands with a mixture of open and closed step-edges. In contrast, for larger (4%) compressive strain, the presence of submonolayer islands is found to promote the formation of substrate vacancies which eventually (once they come close to each other near an island) leads to the formation of stacking faults in both the substrate and island. The kinetics of this transition is characterized by a large activation barrier along with a prefactor which is tens of orders of magnitude larger than is typical of atomic processes in fcc metals. A theoretical estimate for the prefactor based on an estimate of the change in entropy in going from the initial state to the transition state is found to be in good agreement with our simulation results. In contrast, the prefactor for the reverse transition is much smaller, leading to a negligible rate at 200 K. Finally, we consider the case of 8% tensile strain for which the dominant monomer diffusion mechanism corresponds to exchange with the underlying substrate. In this case a shape transition is observed with increasing island size from isotropic to strongly anisotropic islands. A theoretical estimate of the critical size for the shape transition based on recent theoretical results [3] will be presented which is in good agreement with our simulations.


11:15 AM MT01.06.09
A Simple Local Expression for the Prefactor in Transition State Theory Sara Kadkhodaei1 and Axel van de Walle2; 1University of Illinois at Chicago, United States; 2Brown University, United States

We present a simple and accurate computational technique to determine the frequency prefactor in harmonic transition state theory without necessitating full phonon density of states (DOS) calculations. The atoms in the system are partitioned into an “active region,” where the kinetic process takes place, and an “environment”
surrounding the active region. It is shown that the prefactor can be obtained by a partial phonon DOS calculation of the active region with a simple correction term accounting for the environment, under reasonable assumptions regarding atomic interactions. This model enables the use of plane wave density function theory calculations for diffusion description in large systems where the full Hessian calculation becomes intractable. Convergence with respect to the size of the active region is investigated for different systems and different diffusion processes, as well as the reduction in computational costs when compared to full phonon DOS calculation. Additionally, we introduce an open source implementation of the algorithm that can be added as an extension to Large-scale Atomic/Molecular Massively Parallel Simulator software.

SESSION MT01.07: Coarse Graining Methods
Session Chairs: Javier Llorca and Thomas Swinburne
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 206

1:30 PM *MT01.07.00
Next Generation Extended Lagrangian First Principles Molecular Dynamics Anders M. Niklasson; Los Alamos National Laboratory, United States

Extended Lagrangian Born-Oppenheimer molecular dynamics enables stable simulations without relying on an expensive self-consistent field optimization prior to the force evaluations. The formulation is different from extended Lagrangian Car-Parrinello molecular dynamics and samples the potential energy surface with an accuracy that is of 4th-order in the integration time step instead of 2nd-order. No fictitious mass parameters need to be tuned and the integration time steps is limited only by the integration time step of regular Born-Oppenheimer molecular dynamics. However, the formalism includes a particular metric kernel that needs to be approximated. For most systems a simple scaled delta function is sufficient, but for more challenging materials a more accurate approximation is needed. I will present some recently developed low-rank kernel approximations using Krylov subspace expansions in combination with preconditioners that allow stable (SCF-free) simulations even of highly challenging systems including chemical reactions.

2:00 PM *MT01.07.01
Phase Field Crystal Modeling of Electromigration in Metals Nikolas Provatas and Nan Wang; McGill University, Canada

This talk will present the results of a recent phase field crystal modelling study of electromigration. The newly formulated model successfully captures some well-known electromigration induced phenomenologies like the Blech effect and mean time to failure, as well as the failure mechanisms in interconnects at atomic scale through formation of voids at triple junctions and surface steps motion. We also discuss extensions and future directions of coupling this approach with first principles calculations.

SESSION MT01.08: Rough Energy Landscapes
Session Chairs: David Aristoff and Thomas Swinburne
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 206

2:30 PM BREAK

3:30 PM MT01.08.01
Sampling on Rough Energy Landscapes Gideon Simpson¹ and Petr Plechac²; ¹Drexel University, United States; ²University of Delaware, United States
Rough energy landscapes appear in a variety of applications including disordered media and soft matter. In this work, we examine challenges to sampling from Boltzmann distributions associated with rough energy landscapes. Here, the roughness will correspond to highly oscillatory, but bounded, perturbations of a fundamentally smooth landscape. Through a combination of numerical experiments and asymptotic analysis, we demonstrate that the performance of Metropolis Adjusted Langevin Algorithm can be severely attenuated as the roughness increases. In contrast, we prove, rigorously, that Random Walk Metropolis is insensitive to such roughness. We also formulate two alternative sampling strategies that incorporate large scale features of the energy landscape, while resisting the impact of roughness; these also outperform Random Walk Metropolis. Numerical experiments on these landscapes are presented that confirm our predictions. Open analysis questions and numerical challenges are also highlighted.

3:45 PM MT01.08.02
**Strengthening of Al-Cu Alloys by Guinier-Preston Zones—Predictions from Atomistic Simulations**
Gustavo Esteban-Manzanares¹, Bárbara Bellón¹, Ioannis Papadimitriou¹, Enrique Martínez² and Javier Llorca¹,³; ¹IMDEA Materials Institute, Spain; ²Los Alamos National Laboratory, United States; ³Technical University of Madrid, Spain

A multiscale modelling strategy based on molecular statics and molecular dynamics simulations in combination with transition state theory has been developed to determine the flow stress of Al-Cu alloy containing Guinier-Preston zones as a function of temperature. The flow stress is assumed to depend on two contributions. The athermal contribution is given by the Taylor model and only depends on the elastic constants of the Al alloy, the dislocation density and the Burgers vector. The thermal contribution can be calculated following transition state theory from the obstacle strength and the free energy barrier.

Molecular statics simulations in combination with thermal annealing was used to determine the obstacle strength (the stress necessary to overcome the obstacle in the absence of thermal energy) for edge dislocations interacting with Guinier-Preston zones in two different orientations (0 and 60 degrees). It was found that the introduction of thermal annealing after each strain increment was critical to avoid the locking of the simulations in local minima which leads to an overestimation of the obstacle strength and to unrealistic interaction mechanisms between the dislocation and the Guinier-Preston zone in both orientations. The rate at which dislocations overcome the Guinier-Preston zone was determined as a function of the applied strain and temperature from molecular dynamics simulations. This information was used to determine the thermodynamic quantities that control this process, namely the activation energy, the activation entropy and the activation volume for both dislocation/Guinier-Preston zone orientations.

The predictions of the model were compared with experimental data in the literature as well as new data obtained by means of micropillar compression tests in an Al - 4 wt. % Cu alloy naturally aged at ambient temperature to obtain a homogenous distribution of Guinier-Preston zones. They were in good agreement at ambient temperature although modelling results overestimated the flow stress at low temperature. Overall, this talk presents a coherent multiscale methodology to determine the effect of Guinier-Preston zones in the flow stress of Al alloys by means of atomistic simulations.

4:00 PM *MT01.08.03
**Modelling the Solidification of Glasses**
Steven D. Kenny, Jamieson K. Christie and Ying Zhou; Loughborough University, United Kingdom

Glass is used in a wide variety of fields, from nuclear waste encapsulation to biomedicine. Computer simulation is often used to understand the connection between glass composition, structure and properties. Existing modelling typically uses Molecular Dynamics approaches to simulate the cooling of glass and these simulations can only simulate cooling rates down to about $10^{9}$K/s. This is several orders of magnitude faster than experimental cooling rates even for the most rapidly quenched glasses.

The cooling rate of the glass is known to affect the structure of the glass including the connectivity of the 3D structure and how ions are incorporated into the glass. The gap between experimental and modelling cooling rates thus make it difficult to compare results and to gain insight into the role of glass composition on its properties.

In this work we will discuss using a parSplice approach to model the cooling of glasses. We will discuss the
differences observed in the glass structure when lower cooling rates are explored through this approach and the potential for the application of this methodology to other systems. The efficiency of the methodology and the limits this places on its applicability will also be discussed.

4:30 PM *MT01.08.04
Configuration-Based Energy Minimization of 2D Incommensurate Heterostructures Mitchell Luskin; University of Minnesota, United States

We derive and analyze a novel approach for modeling and computing the mechanical relaxation of incommensurate 2D heterostructures. Our approach parametrizes the relaxation pattern by the compact local configuration space rather than real space, thus bypassing the need for the standard supercell approximation and giving a true aperiodic atomistic configuration. Our model extends the computationally accessible regime of weakly coupled bilayers with similar orientations or lattice spacing, for example materials with a small relative twist where the widely studied large-scale moire patterns arise. Our model uses a generalized stacking fault energy for interlayer interactions and makes possible the simulation of the relaxation of multi-layer heterostructures for which a planar moire pattern does not exist.

SESSION MT01.09: Accelerated Molecular Dynamics
Session Chairs: Kristen Fichthorn and Enrique Martinez
Thursday Morning, December 5, 2019
Hynes, Level 2, Room 206

8:30 AM *MT01.09.01
Mathematical Foundations of Accelerated Molecular Dynamics Methods Tony Lelièvre1,2; 1Ecole des Ponts, France; 2Imperial College London, United Kingdom

We will present recent works which aim at understanding the mathematical foundations of first order kinetics and the harmonic transition state theory. The cornerstone of the analysis is the notion of quasi stationary distribution. This analysis sheds a new light on the accelerated molecular dynamics algorithms which have been proposed by Arthur Voter and co-workers in the late nineties. It also opens the route to generalizations of the original algorithms, in particular of the Parallel Replica algorithm.

References:

9:00 AM *MT01.09.02
Long-Time Dynamics Without Predefined States—A Data-Driven Parallel Replica Dynamics Approach Danny Perez; Los Alamos National Laboratory, United States

One of the most stringent limitation of conventional molecular dynamics is the extremely short timescales that are amenable to direct simulation, even when massively-parallel resources are invested in the calculation. The Parallel Replica Dynamics (ParRep) method, introduced by A. Voter, unlocks the potential of parallel architectures by allowing for an effective parallelization of the problem in the time-domain. However, in order to benefit from this extension of timescales, practitioners of ParRep need first address two issues: i) the identification of metastable sets on the energy landscape of the system, and ii) the accurate estimation of the time required to relax to the quasi-stationary distribution in each set. Both these problems can be readily addressed on smooth energy landscapes, but become extremely difficult for complex systems, where considerable prior knowledge often needs to be injected in the construction of the metastable states; a process which, even then, remains error prone.
We show how both these problems can be tackled simultaneously using data analysis techniques derived from the stochastic Koopman operator formalism. In this new method, states are locally defined and characterized on-the-fly by analyzing the trajectories produced as part of the ParRep simulation itself. To do so, the algorithm requires only the specification of a (potentially large) number of atomistic descriptors in terms of which the states will be implicitly defined. We demonstrate the new approach through long-time simulations of biomolecules and of soft defects in metals.

9:30 AM MT01.09.03  
Shape Fluctuation of Metallic Nanoclusters—Observations from Long-Timescale Simulations  
Rao Huang¹ and Danny Perez²; ¹Xiamen University, China; ²Los Alamos National Laboratory, United States

Metallic nanoclusters are functional materials with many applications owing to their unique physical and chemical properties, which are sensitively controlled by their shapes and structures. An in-depth understanding of their morphology stability is therefore of crucial importance. It has been well documented by transmission electron microscopy (TEM) studies that metallic nanoclusters can interconvert between different isomers. However, the relevant mechanisms remain elusive because the timescales of such shape fluctuations are too short to be resolved experimentally and yet too long for conventional atomistic simulations. By employing a recently introduced Accelerated Molecular Dynamics method, Parallel Trajectory Splicing, we present simulations that reached timescales of milliseconds and thus provide a clear description of the dynamic process of the experimentally observed shape fluctuation in metallic nanoclusters. We observe transformations back and forth between face-centered-cubic (fcc) and structures with five-fold symmetry (decahedron or icosahedron). These transitions occur following either by a partial-dislocation-mediated twinning mechanism or by a surface-reconstruction driven process. The identified pathway is in remarkable agreement with the existing microscopy results and serves as further evidence that shape fluctuation can occur directly through thermal activation, without involving melting or other external factors.

9:45 AM MT01.09.04  
Parallel Trajectory Splicing for the Exascale  
Andrew Garmon¹,² and Danny Perez²; ¹Clemson University, United States; ²Los Alamos National Laboratory, United States

A range of specialized Molecular Dynamics (MD) methods have been developed in order to overcome the challenge of reaching longer timescales in systems that evolve through sequences of rare events. In this talk, we consider Parallel Trajectory Splicing (ParSplice) which works by generating large number of trajectory segments in parallel in such a way that they can later be assembled into a single statistically correct state-to-state trajectory, enabling parallel speedups up to the number of parallel workers. In practice, the ability for ParSplice to scale significantly improves when it is possible to predict where the trajectory will be found in the future. With this insight in mind, we develop a maximum likelihood transition model that is updated on the fly and make use of an uncertainty-driven estimator to approximate the optimal distribution of trajectory segments to be generated next.

This work was supported by the U.S. Department of Energy Office of Science Graduate Student Research (SCGSR) program, administered by the Oak Ridge Institute for Science and Education under DE SC0014664 and by the Exascale Computing Project (17-SC-20-SC).

10:00 AM BREAK

10:30 AM MT01.09.05  
Accelerated Molecular Dynamics Simulations of Dislocation Climb in Nickel  
Lauren T. Smith¹,², Anne Marie Z. Tan³,², Thomas D. Swinburne⁴,³, Danny Perez² and Dallas R. Trinkle²; ¹University of California, Santa Barbara, United States; ²University of Illinois at Urbana-Champaign, United States; ³University of Florida, United States; ⁴CNRS, CINAM, France; ²Los Alamos National Laboratory, United States

The mechanical behavior of materials operating under high temperatures is strongly influenced by creep mechanisms such as dislocation climb which are controlled by the diffusion of vacancies. However, atomistic simulations of these mechanisms have traditionally been impractical due to the long time scales required. To
overcome these time scale challenges, we use Parallel Trajectory Splicing (ParSplice), an accelerated molecular
dynamics method, to simulate dislocation climb in nickel. We focus on modeling the activity of a vacancy near a jog
on an edge dislocation in order to observe vacancy pipe diffusion and vacancy absorption at the jog. Using
ParSplice, we are able to achieve a total simulation time of over 4 μs for a system containing approximately 16,000
atoms, during which over 2000 vacancy diffusion and absorption events occurred. Based on these results, we
estimate average rates for pipe diffusion and vacancy absorption into the jog; results are in good agreement with
molecular static calculations.

10:45 AM *MT01.09.06
Atomistic/Discrete-Dislocations/Continuum Coupling in 3D William A. Curtin¹, Max Hodapp² and Guillaume
Anciaux¹; ¹Ecole Polytechnique Federale Lausanne, Switzerland, Switzerland; ²Skolkovo Institute of Science and
Technology, Russian Federation

Capturing plasticity at realistic dislocation densities with high configurational complexity requires a continuum-
level discrete dislocation dynamics (DDD) description. However, many features controlling dislocation motion are
inherently atomistic, such as the interaction of dislocations with solutes, precipitates, cracks, and interfaces. Here,
we review a recent multiscale concurrent coupled atomistic/discrete-dislocation model in 3d that couples the DDD
code Paradis and the MD code LAMMPS [1]. The need for precise matching of continuum dislocation properties to
atomistic dislocation properties is demonstrated, and issues in making this connection are also discussed. A full
coupling of atomistic and continuum domains requires solution of an elasticity problem in the continuum domain.
Standard methods such as FE are computationally infeasible. We thus present a Greens function implementation
where H-matrices and a Newton-Krylov solution scheme are employed to achieve computational efficiency with
controllable accuracy [2].


11:15 AM *MT01.09.07
Multi-Scale Modeling of Structural and Heat Transport Properties of 2D Materials Tapio Ala-Nissila¹,²; ¹Aalto
University, Finland; ²Loughborough University, United Kingdom

Novel 2D materials have unusual properties, many of which are coupled to their large scale structural properties.
Microscopic modeling of structure and transport is a formidable challenge due to a wide span of length and time
scales involved. I will review recent progress in structural multiscale modeling of 2D materials and thin
heteroepitaxial overlayers [1], and graphene and h-BN [2,3] in particular, based on the Phase Field Crystal (PFC)
model combined with Molecular Dynamics and Quantum Density Functional Theory. The PFC model allows one to
reach diffusive time scales at the atomic scale, which facilitates quantitative characterisation of domain walls,
dislocations, grain boundaries, and strain-driven self-organisation up to micron length scales. I will discuss how PFC
generated multigrain systems can be further used for Molecular Dynamics simulations of thermal conduction in
selected 2D materials [3,4].

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312298).
Modelling Native Defects in Transparent Conducting Oxides Using the hybrid QM/MM Embedded Cluster Technique

Qing Hou, John Buckeridge, Alexey A. Sokol, Jingcheng Guan and Richard Catlow; University College London, United Kingdom

For n-type transparent conducting oxide (TCO) materials such as SnO₂, In₂O₃ and ZnO, native defects play a key role in electronic conductivity. Depending on their electronic structure, energetics and geometries, defects can act as donors, resulting in intrinsic n-type conductivity, or can compensate extrinsic donors such as Sn in In₂O₃. Predictive modelling of the properties of defects in such systems requires a detailed description of the dielectric response of the host material, which can be difficult to obtain using standard supercell techniques. Here, we employ the hybrid quantum mechanical/molecular mechanical (QM/MM) embedded cluster method, a multi-region approach that allows us to model defects at the true dilute limit, with polarisation effects described in an accurate and consistent manner. Moreover, we develop techniques to analyse the energetic balance between electrons bound to donors in diffuse and compact states, a difficult problem regardless of the model employed. We benchmark our results where possible and find good agreement with experiment for a variety of defect-related properties.

SESSION MT01.10: Energy Landscape
Session Chairs: William Curtin and Danny Perez
Thursday Afternoon, December 5, 2019
Hynes, Level 2, Room 206

Systematic Saddle Point Searches from a Given Initial State Minimum

Hannes Jonsson; University of Iceland, Iceland

In long time scale simulations based on the adaptive kinetic Monte Carlo (AKMC) method (sometimes referred to as on-the-fly KMC, or self-learning KMC) the essential task is to find all relevant, low lying first order saddle points on the energy ridge surrounding a given initial state minimum without preconceived notion of the possible final states. In current implementations of the method, several random initial displacements from the minimum are used as starting points for climbs up the energy surface to sample the saddle points. While schemes have been developed to improve the sampling and reduce the occurrence of reconvergence on known saddle points [1], a significant concern are saddle points that are hard to reach for example when the basin of attraction does not reach the boundary of the convex region around the local minimum, and the waisted computational effort when the same saddle point is found repeatedly. A systematic approach where a scalar quantity based on semi-local information about the energy surface is used to move from a local minimum along a linear path with bifurcation points so as to map out all first order saddle points will be presented [2]. Also, the use of Gaussian process regression in this context to reduce the number of energy and atomic force evaluations will be discussed, analogous to what has already been reported for nudged elastic band calculations [3].


Identification and Comparison of Interstitial Defect Configurations in Alumina

Alina Kononov, Ethan Shapera and Andre Schleife; University of Illinois at Urbana-Champ, United States

Aluminum is well-known for its exceptional resistance to high-temperature corrosion via oxidation. This is attributed to the formation of a scale, i.e. a thin oxide film on the surface. This protective layer acts as a barrier to diffusion and prevents further deterioration. However, despite tremendous efforts, the mechanisms that underlie the slow diffusion through the scale are poorly understood. Unfortunately, this limits the development of highly
corrosion resistant materials that are required, for instance, in the high-temperature environments encountered in the petrol industry.

In this work, we lay the foundation for further computational research on diffusivity of defects by computing formation energies of point defects in aluminum oxide from first-principles. We specifically explore the influence of exchange and correlation by comparing standard density functional theory to hybrid-functional results and we also study the influence of spin polarization. This allows us to confirm previous studies showing that a peroxide split interstitial defect is energetically favorable to the traditionally considered, quasi-atomic oxygen interstitial defect at the octahedral site. Interestingly, we also find such a displaced ground-state configuration for aluminum interstitials. In order to efficiently sample possible starting atomic geometries for these as well as extrinsic interstitials, we explore using Bayesian analysis. In our work, we also investigate the viability of octahedral configurations for extrinsic interstitials and we examine the impact of defect charge state on the ground-state geometry. These so far overlooked lower-energy geometries possibly point at the possibility of a more general mechanism in this material for interstitial formation and can, hence, influence defect migration paths and predictions for diffusion properties.

2:15 PM *MT01.10.03
Fast First-Passage Algorithms for Reversible Markov Processes on a Lattice—Application to Cluster Diffusion and Aggregation in α-Iron Manuel Athenes1, Savneet Kaur1, Gilles Adjanor2 and Thomas Jourdan1;
1CEA, France; 2EDF, France

Transport properties of point defects are crucial physical quantities governing the microstructural evolution of metals and alloys. Characterizing the kinetics of defects in presence of energetic and entropic traps is notoriously difficult due to the emergence of well separated time scales in the simulations. We herein describe fast first-passage algorithms based on the theory of absorbing Markov chains assuming that defects undergo reversible diffusion. We show that the absorbing transition rate matrix can be transformed into a symmetric definite-positive matrix and that this similarity transformations considerably simplifies the computational tasks. The efficiency of the approach is demonstrated in simulations of diffusion and aggregation of Copper and Manganese clusters in α-iron. Substantial accelerations are achieved by directly sampling the important rare events contributing to atomic transport.

2:45 PM MT01.10.04
Generalized Numerical Solutions for Stochastic Dynamics of First-Order Phase Transformations Nicholas Julian1,2, Enrique Martinez2 and Jaime Marian1; 1University of California, Los Angeles, United States; 2Los Alamos National Laboratory, United States

Modeling physical systems as stochastic processes helps capture natural fluctuations and improves long-time accuracy. Yet, the physical processes which may be confidently formulated in terms of an easily computable stochastic process are limited to those which are driven exclusively by either rare events or Gaussian white noise. Additionally, the stochastic integration schemes used in the development and implementation of these algorithms have been traditionally based on solving the Itô and Stratonovich integrals, which do not preserve the chain rule for differentiation or the Newton-Leibniz integration rule when applied to Lévy processes driven by combined rare events and continuous-in-time Brownian motion, e.g. liquid-solid phase transformations. In this presentation we explore the consequences of solving the Marcus canonical integral, which preserves the aforementioned rules when applied to Lévy processes, to stochastic simulations of material phase transformations.

3:00 PM BREAK

SESSION MT01.11: Reactive Force Field
Session Chairs: Hannes Jonsson and Gideon Simpson
Thursday Afternoon, December 5, 2019
Hynes, Level 2, Room 206

3:30 PM *MT01.11.01
Systematic Development of Reliable Machine Learning Interatomic Models
Ellad B. Tadmor; University of Minnesota, United States

The recent development of machine learning interatomic models (IMs) provides a promising avenue to extend the scope of first principles methods to materials problems on larger length and time scales. Machine learning IMs interpolate a training set of density functional theory (DFT) calculations and can provide close to DFT accuracy at a fraction of the computational cost. A challenge is the inherent lack of transferability of machine learning IMs; their predictions "far" from the training set are suspect. Using 2D materials as a test system, we address this limitation in two ways: (1) we develop a hybrid IM that combines the known physics of long-range dispersion with a neural network (NN) to model short-range interactions for multilayer graphene systems; (2) we apply an NN dropout technique to assess the uncertainty in predictions of the IM to prevent its use outside its range of validity. These techniques along with tools for automated training have been implemented within a general-purpose fitting framework called KLFF (KIM-Based Learning-Integrated Fitting Framework). KLFF is an open source Python package compatible with the Knowledgebase of Interatomic Models (KIM) application programming interface (API) standard, allowing IMs fit with it and distributed through https://openkim.org to be used by a wide variety of simulation codes compatible with the KIM API.

4:00 PM MT01.11.02
An Initial Design-Based Deep Learning Framework for ReaxFF Force Field Training
Mert Y. Sengul1, Ying Hung2, Tirthankar Dasgupta2 and Adri van Duin1; 1The Pennsylvania State University, United States; 2Rutgers, The State University of New Jersey, United States

Atomistic level investigations are required for the discovery of novel material properties which, in turn, results in advancements in technology such as batteries, capacitors, etc. Most of the atomistic-scale modeling methods that have been developed to conduct these investigations are restricted to small systems due to associated computational costs. On the other hand, it is possible to simulate large atomistic systems using ReaxFF, which is a very reliable and transferable reactive force field concept used by a broad academic and industrial user community. In ReaxFF, inter and intra-atomic interactions are calculated by functionals that involve system-specific parameters. These parameters must be optimized for each materials system, a task requiring exploration of multi-dimensional parameter landscape to obtain a high level of accuracy. However, the current ReaxFF optimization method is a sequential search algorithm which is limited in terms of exploring a wider parameter space. Moreover, due to the consecutive nature of the method, the optimization algorithm is non-parallelizable. In this respect, this study develops an initial design-based machine learning (ML) framework to enable a fast and high-quality force field development to improve the ReaxFF optimization algorithm.

Initially, a Latin Hypercube Design (LHD) algorithm is used to explore the parameter landscape extensively. The LHD passes the information about explored regions to the ML method for model training. The ML method is composed of regression and classification models. A deep learning model finds the minimum discrepancy regions, while a classification model classifies the physically-feasible/unfeasible regions in parameter landscape. This ML method eliminates unfeasible regions, which originate from the unphysical atomistic interactions, and constructs a more comprehensive understanding of a physically meaningful parameter landscape. In addition, the developed framework is easily parallelizable; thus, it will significantly reduce the force field optimization time while increasing the quality by benefitting from ML. The performance of the framework will be evaluated by its application to systems with available force field parameter sets including 2D materials and alloys.

4:15 PM MT01.11.03
Estimating Machine Learning Uncertainty for Kinetic Monte Carlo Migration Barrier Regression
Jyri Kimari, Jussi Määttä, Viacheslav Bazaliy, Teemu Roos, Kai H. Nordlund and Flyura Djurabekova; University of Helsinki, Finland

Kinetic Monte Carlo (KMC) is the method of choice for studying diffusion in solid materials. The method is often limited in accuracy by the quality of the migration energy barriers used to describe the system of interest. Here is KMC's tradeoff between precision and computational cost - a more detailed description of the energy barriers will typically require either heavier precalculations, or resolving barriers on-the-fly.

Like in the realm of potential energy functions, machine learning (ML) offers a way to bridge the computational gap
in this problem also. We have expanded a KMC model for the Cu surface, earlier developed in our group, by employing ML for the purpose of avoiding some of the barrier calculations. Our most recent pursuit is for an active learning scheme, which as a first stepping stone requires the ability to estimate uncertainties of the predicted barrier values. For some ML methods, such as Gaussian process regression, this property comes out-of-the-box, while for others, like artificial neural networks, we have had to resort to more specialized tricks. In this talk, we present the progress we have made in estimating the uncertainty of various regression models, as well as the developing framework around the active learning scheme — when to trust the regressor during the KMC simulation, and when should the oracle be queried for more precise data.

4:30 PM MT01.11.04
Computational Study on the Dielectric Strength of the Crosslinked Polyethylene Using e-ReaxFF Reactive Force Field Dooman Akbarian, Dundar Yilmaz, Hunter Woodward, Jonathan Moore and Adri van Duin; 1The Pennsylvania State University, United States; 2The Dow Chemical Company, United States

Cross-linked Polyethylene (XLPE) has been recognized as an outstanding insulator for high-voltage power cables due to its favorable structural integrity at high temperature, lower moisture sensitivity, chemical resistance, and lower rates of failure due to aging. Dicumyl Peroxide (DCP) is the main PE crosslinking agent, however, DCP-initiated crosslinking leads to the formation of different byproducts such as cumyl alcohol, acetonitrile, methylvinylnitrene, water and methane that remain in the final product and may have adverse effects on cable function and its long-term properties. Previous studies stated that the byproducts such as cumyl alcohol (CA), acetonitrile (AN), α-methylstyrene and antioxidant additives can cause a space charge formation in the final product and affect electrical properties of the XLPE. Currently, our knowledge is limited about the effects of the byproducts on the properties of the final XLPE product. By understanding on how the crosslinking byproducts change the XLPE properties, improvements may be formulated relative to the conventional XLPE cable. In order to design and optimize the XLPE cables, it is crucial to obtain detailed, atomistic-scale insight of the XLPE chemistry since each and every byproduct in the XLPE affect differently to the polymer’s electrical properties, thus the effects of each of the byproducts should be investigated. Quantum Mechanic (QM) methods are considered the most accurate technique among atomistic simulation methods, however, due to high computational costs, these first-principles techniques can only be viable for relatively small length and short time scales events. The ReaxFF reactive force field method can model chemical reactions based on the bond order concept without the full expense of QM methods, and it has been successfully applied to a wide range of systems such as polymeric fibers, covalent, metallic, and metal oxide/hydride/carbide materials. e-ReaxFF method is an extension of the ReaxFF method with description of an explicit electron-like or hole-like particle. In this study, we used e-ReaxFF technique to investigate the role of XLPE byproducts, and processing variables on the dielectric strength of the PE. To achieve this, we developed an e-ReaxFF reactive force field verified against DFT data obtained for XLPE chemistry. Then, using this force field, we performed MD simulations to find the effects of different byproducts, temperature, density, the ratio of byproducts to PE on the dielectric strength of the PE.

4:45 PM MT01.11.05
Machine Learning Assisted Hybrid Reactive Molecular Dynamics Simulations Dundar E. Yilmaz, Karthik Ganesan, Muraleedharan Gopal, Chen Chen, Dooman Akbarian and Adri van Duin; The Pennsylvania State University, United States

Molecular dynamics (MD) simulations with Reactive force field (ReaxFF) provide valuable insight due to accurate description of chemistry of the material. This comes with a computational cost which limits size and time scale of the simulation. Non-reactive models, such as OPLS, may provide accurate description of the dynamics of the system without chemical reactions. Typically OPLS runs fifty times faster compared to ReaxFF. We developed a hybrid framework which utilize ReaxFF for chemical reactions while using non-reactive force field to accelerate MD simulation. In this framework, chemically active regions such as surfaces, radical sites, described with ReaxFF and rest of the system described with OPLS. A tracking tool utilized to define reactive and non-reactive regions during the simulation. ReaxFF uses a unique parameter set for each atom, bond, angle and dihedral types, however OPLS parameters depends on local bond topology. Since ReaxFF allows chemical reactions, bond topology of the system changes during the simulation. We used a Machine Learning based model to predict OPLS parameters in order to dynamically transfer atoms from reactive to non-reactive regions. As a test case, we consider cross-linking of poly ethylene with dicumyl peroxide with large scale hybrid simulations. We achieved significant improve in the computational efficiency and were able to simulate realistic size systems.
TUTORIAL: Applied Machine Learning for Materials Research and Development
December 1 - December 1, 2019

This will be a hands-on tutorial. We will begin with an overview of applied machine-learning fundamentals. Then will showcase successful applications of machine learning to solve materials R&D challenges including diagnosis, process optimization and discovery/design. We will also review some of the hardware developments that have emerged in parallel with machine-learning tools. In closing, a perspective on future challenges in this field will be offered.

8:30 AM
Hands-On Deep Learning for Materials Edward Kim, Citrine Informatics

A brief conceptual overview of basic deep learning concepts will be provided, and these concepts will be introduced alongside more familiar (e.g., linear) machine learning methods. Attendees will then have the opportunity to build and train their own neural network models in Jupyter + Python.

10:00 AM BREAK

10:30 AM
Success Cases Edward Kim, Citrine Informatics; Joshua Schrier, Fordham University; Tonio Buonassisi, Massachusetts Institute of Technology

Citrine will highlight recent success cases in sequential (active) learning and related methods.

1:30 PM
Taking ML into the Lab: Hardware Developments Joshua Schrier, Fordham University

ML and AI are "brains" making sense of data, but we also need "hands" to conduct new experiments and collect the results. This section of the tutorial will provide an overview of the general classes of automated and high-throughput synthesis and characterization methods, highlight efforts at a variety of scales, discuss shared challenges, and provide resources for further learning. The intended audience includes both non-experimentalists who want to learn more about where their data comes and "traditional" experimentalist interested in learning about possibilities for automating the performance and data collection of their experiments to facilitate interactions with machine-learning.
Where does your data come from and how did it get there?

- A brief history of lab automation and experiments-for-data's-sake.
- Survey of current initiatives, efforts and challenges

Small, Medium, or Large? Experimentation scale in space and time.

- Highlights of national-scale through lab-scale instrumentation capabilities.
- Survey of current initiatives, efforts, and challenges

Closing the loop: Autonomy and the need for Software and Data Management

- Software environments for managing experiment requests and data export.
- Survey of current initiatives, efforts, and challenges

3:00 PM BREAK

3:30 PM
What's the Best Experiment to do Next? An Introduction to Gaussian Processes and Active Learning
A. Gilad Kusne, National Institute of Standards and Technology

A common challenge is identifying the best (most informative) experiment to perform next in the lab or in silico. Active learning provides a framework for doing just that. This tutorial will use open source tools (Anaconda, Jupyter, scikit learn, etc.) and hands on exercises in Jupyter to introduce attendees to Gaussian Processes and Active Learning. Attendees will first learn about the Bayesian method of Gaussian process regression, a regression method that provides uncertainty for its predictions. We will then investigate a variety of Active Learning and Bayesian Optimization schemes that exploit these predictions (and their uncertainties) for selecting the next experiment to perform. Attendees who want to follow along on their own laptops should come with Anaconda Python 3.7 already installed.

Gaussian Processes

- Introduction to Gaussian Process theory
- Hands on Exercises

Active Learning and Bayesian Optimization

- Introduction to a variety of Active Learning schemes
- Hands on Exercises

TUTORIAL
Applied Machine Learning for Materials Research and Development
Sunday Morning, December 1, 2019
Hynes, Level 2, Room 210

This will be a hands-on tutorial. We will begin with an overview of applied machine-learning fundamentals. Then will showcase successful applications of machine learning to solve materials R&D challenges including diagnosis,
process optimization and discovery/design. We will also review some of the hardware developments that have emerged in parallel with machine-learning tools. In closing, a perspective on future challenges in this field will be offered.

8:30 AM  
**Hands-On Deep Learning for Materials** Edward Kim, Citrine Informatics

A brief conceptual overview of basic deep learning concepts will be provided, and these concepts will be introduced alongside more familiar (e.g., linear) machine learning methods. Attendees will then have the opportunity to build and train their own neural network models in Jupyter + Python.

10:00 AM BREAK

10:30 AM  
**Success Cases** Edward Kim, Citrine Informatics; Joshua Schrier, Fordham University; Tonio Buonassisi, Massachusetts Institute of Technology

Citrine will highlight recent success cases in sequential (active) learning and related methods.

1:30 PM  
**Taking ML into the Lab: Hardware Developments** Joshua Schrier, Fordham University

ML and AI are "brains" making sense of data, but we also need "hands" to conduct new experiments and collect the results. This section of the tutorial will provide an overview of the general classes of automated and high-throughput synthesis and characterization methods, highlight efforts at a variety of scales, discuss shared challenges, and provide resources for further learning. The intended audience includes both non-experimentalists who want to learn more about where their data comes and "traditional" experimentalist interested in learning about possibilities for automating the performance and data collection of their experiments to facilitate interactions with machine-learning.

Where does your data come from and how did it get there?

- A brief history of lab automation and experiments-for-data's-sake.
- Survey of current initiatives, efforts and challenges

Small, Medium, or Large? Experimentation scale in space and time.

- Highlights of national-scale through lab-scale instrumentation capabilities.
- Survey of current initiatives, efforts, and challenges

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Gaussian Processes

- Introduction to Gaussian Process theory
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- Introduction to a variety of Active Learning schemes
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SYMPOSIUM MT02

Closing the Loop—Using Machine Learning in High-Throughput Discovery of New Materials
December 2 - December 6, 2019

Symposium Organizers
Jason Hattrick-Simpers, National Institute of Standards and Technology
Barnabas Poczos, Carnegie Mellon University
Markus Reiher, ETH Zurich
Aleksandra Vojvodic, University of Pennsylvania

Symposium Support
Bronze
Machine Learning: Science and Technology | IOP Publishing
Matter & Patterns | Cell Press

* Invited Paper

SESSION MT02.01/MT03.01: Joint Session: Autonomous Science I
Session Chairs: Tonio Buonassisi, Jason Hattrick-Simpers, Kedar Hippalgaonkar and Benji Maruyama
Monday Morning, December 2, 2019
Hynes, Level 2, Room 210

8:00 AM *MT02.01.01/MT03.01.01
Autonomous Research Systems for Materials Development—2019 Workshop Summary Benji Maruyama¹, Eric A. Stach², Gilad Kusne³, Jason R. Hattrick-Simpers³ and Brian L. DeCost³; ¹Air Force Research Laboratory, United States; ²University of Pennsylvania, United States; ³National Institute of Standards and Technology, United States

This presentation will summarize the results of our “Autonomous Research for Materials Development Workshop,” where a multidisciplinary group of materials researchers, computer scientists and AI/ML experts explored the
opportunities, barriers and future investments. Closed-loop autonomous research systems are disrupting the research process. The current materials research process is slow and expensive; taking decades from invention to commercialization. Researchers are now exploiting advances in artificial intelligence (AI), autonomy & robotics, along with modeling and simulation to create research robots capable of doing iterative experimentation orders of magnitude faster than today.

We propose a “Moore’s Law for the Speed of Research,” where the rate of advancement increases exponentially, and the cost of research drops exponentially. We consider a renaissance in “Citizen Science” where access to online research robots makes science widely available. This presentation will highlight advances in autonomous research and consider the implications of AI-driven experimentation on the materials landscape.

8:30 AM *MT02.01.02/MT03.01.02
Self-Driving Laboratories for Accelerating Discovery of Thin-Film Materials Curtis P. Berlinguette1,1, Jason E. Hein1, Alan Aspuru-Guzik2,3, Benjamin P. MacLeod1, Fraser G. Parlane1 and Brian Lam1; 1The University of British Columbia, Canada; 2Canadian Institute for Advanced Research (CIFAR), Canada; 3The University of Toronto, Canada

This presentation will focus on our self-driving laboratory for thin film materials discovery and optimization. Discovering high-performance, low-cost materials is an integral component of technology innovation cycles, particularly in the clean energy sector. The linear methodology currently used to develop optimal materials can take decades, which impedes the translation of innovative technologies from conception to market. Our interdisciplinary team is utilizing advanced robotics and machine learning to overcome this challenge. We are closing the feedback loop in thin film materials research by enabling our self-driving robotics platform named “Ada” to design, perform, and learn from its own experiments efficiently and in real time. As a proof-of-principle set of experiments, we will show how Ada discovers and optimizes high-performance, low-cost hole transport materials for use in advanced solar cells. I will also showcase how Ada’s modular design can enable the automated and autonomous discovery of materials for other clean energy technologies.

9:00 AM MT02.01.03/MT03.01.03
An Inter-Laboratory High Throughput Experimental and Open Materials Data Study of Sn-Zn-Ti-O Jason R. Hattrick-Simpers1, Andriy Zakutayev2, Sara Barron1, Zachary Trautt1, Nam Nguyen1, Kamal Choudhary1, John D. Perkins2, Caleb Phillips2, Gilad Kusne1, Feng Yi1, Apurva Mehta3 and Martin Green1; 1National Institute of Standards and Technology, United States; 2National Renewable Energy Laboratory, United States; 3SLAC National Accelerator Laboratory, United States

We present the results of an inter-laboratory high-throughput experimental (HTE) study which focused on measurement reproducibility and data exchange. Over the past 20 years, a great number of HTE techniques for synthesizing and characterizing thin-film oxides have been developed and reported. To date, however, there has not been a comprehensive study of how values measured for a series of properties (e.g. conductivity or optical band gap) on the same library compare across labs. Nor has there been a study that has attempted to normalize the hand-off of HTE samples and data. Here we report on the first such study using the Sn-Zn-Ti-O transparent conducting oxide system.

A series of Sn-Zn-Ti-O samples were deposited via Pulsed Laser Deposition and magnetron co-sputtering. At each institution a set of HTE measurements were made for typical properties including structure, thickness, conductivity, and optical bandgap. The samples were then exchanged between the two labs and the same set of properties were measured at the other lab and the data exchanged via an agreed upon uniform format. A few lessons learned and several scientific observations regarding the reproducibility of HTE results gathered during this process will be discussed. An important lesson was the importance of deciding upon, and using, consistent measurement grids within a lab (and during exchanges) for all measurements, as this will impact future data archiving and retrieval. It was observed that qualitative trends are well reproduced even when two labs use very different methods for measuring a property, for instance ellipsometry versus transmission-reflection UV-VIS spectroscopy. However, quantitative comparisons were found to be measurement specific and spanned from excellent (bandgaps measured within a mean absolute error < 0.1 eV) to relatively poor (log resistivity measurements within a mean absolute error of 2). In the latter case, we believe that differences in sample probe geometries coupled to large changes in the properties of small composition regions were the most likely source of the poor correlation. The lessons learned and best practices obtained will be discussed.
Automated Microcrack Inspection in Photovoltaics Silicon Wafers by Unsupervised Anomaly Detection via Variational Auto-Encoder

Zhe Liu, Felipe Oviedo, Emanuel M. Sachs and Tonio Buonassisi; Massachusetts Institute of Technology, United States

The presence of microcracks in silicon wafers significantly reduces wafer strength, yielding wafer breakage during the manufacturing process, transportation and field operation. With the trend of decreasing wafer thickness for cost reduction purposes, thinner wafers are more prone to breakage in the presence of microcracks [1]. To enable a smooth transition to thin wafers for even cheaper photovoltaic modules, we recently developed a high-throughput prototype for in-line crack detection for silicon wafers [2]. This tool scans silicon wafer in the near-edge regions for micro-cracks and outputs linescan signals from a linescan camera, where no crack shows a smooth, undisrupted profile. As an in-line detection tool, it also requires a rapid and reliable algorithm that automatically identifies the presence of a micro-crack within a second after wafer scanning. In this work, we adopted an unsupervised machine learning method for anomaly detection, because the presence of microcracks above the critical length is typically a statistically rare event in the current PV production line (typically less than 5%). Specifically, a generative machine learning algorithm variational auto-encoder (VAE) is used to identify scans with microcracks [3]. The working principle of this algorithm is that: (1) VAE encodes the linescan profiles into lower-dimension vectors of latent variables, and then the latent variables are reconstructed back to linescan profile with the goal of minimized error; (2) because of most linescan profiles are very similar smooth curves without any cracks, the VAE model is trained to be biased toward linescan without cracks; (3) whenever a linescan profile for a crack appears, the trained VAE model generates a vastly different profile with a significant reconstruction error; (4) the crack is then detected by monitoring anomalous reconstruction error. The advantage of this unsupervised VAE method over the previous neural network method [4] is that it does not require a large amount of labelled crack data with different crack shapes (which can be very difficult to obtain). We demonstrate successful crack detections with several different wafer types (e.g., multi, mono, as-cut, and textured) and crack shapes (e.g., line-shape, cross-star, L-shape). We show that, with statistical analysis, this VAE-based anomaly detection could be a reliable and versatile method to enable the rapid detection of microcracks in silicon wafers.

Reference:
machine regression model was trained for the prediction of the OSC at each measured temperature. This model uses descriptors in which physical properties are considered to represent the features of the OSC. These features were automatically extracted using grid search to achieve each model with the highest accuracy. It is found that the features related to the stability of the oxygen atoms in the crystal and the crystal structure itself such as cohesive energy, which is obtained from the first-principles calculation, are highly correlated with the OSC. The present model predicts the OSC of 1,300 existing oxides registered in the in-house electronic structure calculation database. Several dozen materials with promising high OSC were proposed through this virtual screening. We synthesized one of the screened materials and experimentally confirmed that it indicates higher OSC than the conventional OSM, p-CZ.

9:45 AM BREAK

10:15 AM *MT02.01.06/MT03.01.06
The Metaphysics of Chemical Reactivity and Materials Discovery Lee Cronin; University of Glasgow, United Kingdom

Discovery in chemistry falls mainly into one of four types of areas with the discovery of new molecules, new reactions, new reactivity, and finally new physical properties of the resulting compounds or materials. Establishing new reactivity leads to new reactions which also leads to new molecules. This is therefore the order of impact for discoveries in terms of the amount of chemical knowledge that they contribute. Such findings must, by definition, belong outside the known or predictable; and they are outliers and as such can oppose conventions, assumptions and biases. By developing the meta-physics of chemistry and chemical reactivity we should be able to establish a new set of ontologies in chemistry that relate back to the practical core operations, but also can be translated into molecular structures and the discovery of function. The truth of chemistry lies with finding the intrinsic reactivity of the input chemicals, and then encouraging or enabling reactivity by process control. Whilst the new discovery and reaction should be translatable to chemical bonding theory, chemists need to grapple with the fact that the application of the current rules will not allow discovery, instead they will act to restrict it to the known rules. So chemical discovery requires that the current rules are updated, broken, or new ones are made where before there were none. The discovery of Diels-Alder or cross-coupling reactions are excellent examples of new rules that were just discovered without any prior warning.

Without a deeper development of a meta-physics of chemistry the use of big data and artificial intelligence will just tell us what we already know we know, and maybe predictable extensions, rather than enabling discovery. The challenge for the chemist is not the use of artificial intelligence, but the intelligent use of algorithms and automation for novel discoveries. In this talk I will explain how this might be possible.

References

10:45 AM MT02.01.07/MT03.01.07
Robot-Accelerated Perovskite Investigation and Discovery (RAPID)—A High-throughput Approach Towards Metal Halide Perovskite Single Crystal Discovery Zhi Li1, Mansoor Ani N. Nellikkal2, Liana Alves2, Peter Parrilla2, Ian M. Pendleton2, Matthias Zeller3, Joshua Schrier4, Alexander Norquist5 and Emory Chan1;
1Lawrence Berkeley National Lab, United States; 2Haverford College, United States; 3Purdue University, United States; 4Fordham University, United States

Metal halide perovskites have emerged as promising materials for next-generation photovoltaic and optoelectronic devices. The discovery and full characterization of new metal halide perovskite-derived materials have been limited by the difficulty of growing high quality single crystals needed for single crystal X-ray diffraction studies. The formation of large single crystals is non-trivial, owing to the vastness of the chemical search space with enormous compositional degrees of freedom. We present the first automated, high-throughput approach for metal halide
perovskite single crystal discovery based on inverse temperature crystallization (ITC) as a means to rapidly identify and optimize synthesis conditions for the formation of high quality single crystals. Using our automated approach, we have carried out a total of over 5000 metal halide perovskite synthesis reactions spanning six chemical systems. Through this unbiased search of the experimental space, we have more than doubled the number of metal halide perovskite materials accessible by ITC method and discovered a new perovskite structure. Combining machine learning and other statistical methods, we quantify the total experimental space and the likelihood of large single crystal formation. Moreover, machine learning models have been constructed for each chemical system, in which single crystal formation is modeled. This work is a proof of concept that a combined approach of high throughput experimentation and machine learning can be effective in the study of metal halide perovskite crystallization. The approach presented here is designed to be generalizable to different synthetic routes for the acceleration of materials discovery.

11:00 AM MT02.01.08/MT03.01.08
Optimizing Hole Transport Materials with a Self-Driving Thin-Film Laboratory Benjamin P. MacLeod1,1, Fraser G. Parlane1,1, Thomas D. Morrissey1,1, Florian Häse2,3,4, Loïc M. Roch2,3,4, Kevan Dettelbach1, Raphael Moreira1, Lars Yunker1, Michael Rooney1, Joseph Deeth1, Veronica Lai1, Gordon Ng, Henry Situ1, Ray Zhang1, Alán Aspuru-Guzik2,3,4, Jason E. Hein1 and Curtis P. Berlinguette1,1,1; 1The University of British Columbia, Canada; 2Harvard University, United States; 3University of Toronto, Canada; 4Vector Institute for Artificial Intelligence, Canada

Self-driving laboratories combine algorithmic data analysis and experiment planning with robotic workflows to autonomously optimize one or more experimental figures of merit. This approach is applicable to challenging multi-parameter and multi-objective optimization problems such as the optimization of thin film materials within the vast design space of composition, deposition, and processing conditions. Here we describe a self-driving laboratory capable of formulating inks, depositing films via spin-coating, characterizing the resulting thin films using multiple techniques, and planning new experiments based on previous experimental data using the ChemOS experiment orchestration software. The utility of this self-driving laboratory is demonstrated by autonomously optimizing optical and electronic properties of hole transport materials, which are crucial to the operation of a variety of thin-film-based optoelectronic devices. The autonomous optimization manipulates the film composition and annealing protocol to maximize a hole-mobility surrogate obtained by fusing data from transmission-reflection UV-Vis-NIR spectroscopy and 4-point probe conductivity measurements.


11:15 AM MT02.01.09/MT03.01.09

In the development of next-generation photovoltaics and light-emitting diodes, colloidal inorganic perovskite quantum dots (PQDs) have drawn notable attention for their highly tunable bandgap properties, high-charge carrier mobility and defect tolerance, and adaptability towards solution phase processing. However, studies of this material group and other colloidal semiconductor nanocrystals requires extensive exploration of their massive reaction parameter space within highly controlled reaction environments. Conventional flask-based, trial-and-error approaches are, therefore, highly unlikely to effectively capture the full potential and optimal synthesis conditions of these high-priority materials. Further complicating this process, across the accessible bandgap range, optimal synthesis parameters will vary significantly. Flow synthesis platforms have recently been demonstrated as a time- and material-efficient reaction monitoring strategy for synthesis, screening, and optimization of colloidal nanomaterials. The high sampling rate, low chemical consumption, and precise process control (automation) of flow reactors greatly reduces the challenges in exploring complex reaction spaces; however, high-throughput reaction screening technologies alone are likely not able to make significant breakthroughs, due to the massive scope of relevant colloidal synthesis conditions.

In this work, we present a modular microfluidic platform integrated with a machine learning (ML)-enhanced reaction optimization algorithm for on-demand synthesis of high-quality inorganic perovskite QDs with desired optical properties using a homogeneous anion exchange reaction. The intelligent QD synthesis platform consists of
multiple computer-controlled pumps for on-demand reagent delivery/dosing, a flow path selector valve for automated selection of the halide salt source, and an in-line flow cell for automatic UV-Vis absorption and photoluminescence spectroscopy. Utilizing a utility function, an array of trained neural networks, and a global optimization algorithm, the intelligent QD manufacturing platform, approaches a target emission bandgap, while minimizing emission linewidth and maximizing quantum yield by tuning the concentrations of the precursors. Halide salt precursors are mixed within a highly efficient inline micromixer before combining with the perovskite QDs and gas-liquid segmentation. Monitoring each halide exchange condition requires less than 180 uL of total halide salt precursor and 170 uL of starting perovskite QDs per sample. Integration with a ML-enhanced optimization algorithm enables the system to reach optimized synthesis conditions, across all six variables, for a target emission energy of 2.2 eV in 238 samples and 83 mL of chemicals without any prior training. More advanced optimization methods and pre-training with archived experimental data will further reduce this optimization time and cost. The versatility and modularity of the developed intelligent QD synthesis platform make it readily adaptable for on-demand synthesis of other colloidal nanomaterials.

11:30 AM MT02.01.10/MT03.01.10
Autonomously Optimizing Thin Film Morphologies Using Machine Vision Fraser G. Parlane, Benjamin P. MacLeod, Nina Taherimakhsousi, Alan Aspuru-Guzik, Jason E. Hein and Curtis P. Berlinguette; University of British Columbia, Canada; University of Toronto, Canada

The morphologies of solution-deposited thin films are frequently governed by complex combinations of processes from domains including multi-phase fluid flow, heat transfer, nucleation, solid mechanics, and interfacial phenomena. This complexity can frustrate both theoretical and empirical attempts to understand and control the morphologies of such films. Here we report an autonomous robotic system that uses machine vision feedback to determine optimal experimental parameters to achieve homogeneous, high-quality films via spin coating. An ink-formulating and spin-coating robot equipped with an imaging system provides images of thin films to a computer vision algorithm which grades the quality of the thin films. This grading assessment provides input to an optimization algorithm that chooses the next ink formulation with the goal of identifying regions in the parameter space of ink formulation and spin-coating conditions that result in high-quality films.


SESSION MT02.02/MT03.02: Joint Session: Autonomous Science II
Session Chairs: Gilad Kusne, Markus Reiher and Aleksandra Vojvodic
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 210

1:30 PM *MT02.02.01/MT03.02.01
Quantum Machine Learning in Chemical Space Anatole von Lilienfeld and Guido Falk von Rudorff; University of Basel, Switzerland

Many of the most relevant chemical properties of matter depend explicitly on atomistic and electronic details, rendering a first principles approach to chemistry mandatory. Alas, even when using high-performance computers, brute force high-throughput screening of compounds is beyond any capacity for all but the simplest systems and properties due to the combinatorial nature of chemical space, i.e. all compositional, constitutional, and conformational isomers. Consequently, efficient exploration algorithms need to exploit all implicit redundancies present in chemical space. I will discuss recently developed alchemical perturbation theory and quantum machine learning based approaches for interpolating quantum mechanical observables in compositional and constitutional space. Numerical results of our models indicate controlled accuracy and favourable computational efficiency.

2:00 PM *MT02.02.02/MT03.02.02
AI for Automating Materials Discovery Carla Gomes and Bruce van Dover; Cornell University, United States
Artificial Intelligence (AI) is a rapidly advancing field. Novel machine learning methods combined with reasoning and search techniques have led us to reach new milestones with increasing frequency, from self-driving cars to computer vision, machine translation, computer Go trained on human play, to Go and Chess world-champion level play using pure self-training strategies. These ever-expanding AI capabilities open up exciting new avenues for automating scientific discovery. I will discuss our work on using AI for accelerating and automating materials discovery. In particular, we have focused on high-throughput structure determination for combinatorial materials discovery and on solving the phase map diagram problem for composition libraries. While standard statistical and machine learning methods are important to address this challenge, they fail to incorporate relationships arising from the physics of the underlying materials. I will introduce an effective approach based on a tight integration of machine learning methods, to deal with noise and uncertainty in the measurement data, with optimization and inference techniques, to incorporate the rich set of constraints arising from the underlying physics. Finally, I will describe our vision and progress concerning Scientific Autonomous Reasoning Agent (SARA), a multi-Agent system to accelerate materials discovery integrating in a synergistic and complementary way, first principles quantum physics, experimental materials synthesis, processing, and characterization, and AI based algorithms for reasoning and scientific discovery, including the representation, planning, optimization, and learning of materials knowledge.

2:30 PM MT02.02.03/MT03.02.03
Machine Learning Methodologies to Enhance Automated Synthesis of New Materials Jonathan Fine, Armen Beck and Gaurav Chopra; Purdue University, United States

Functional groups link analytical, physical, organic, and materials chemistry and are therefore central to the chemical sciences. In both analytical and organic chemistry functional groups are used to predict the reactivity of molecules, select a solvent for a given reaction, and validate a reaction using measurable changes in the properties of a molecule. Current approaches to incorporate functional groups in the prediction, planning and verification of reaction conditions rely on human intervention and input. For example, the solvent used for a given transformation is chosen by a skilled organic chemist using intuition gained from the study of how the functional groups in a molecule dictate its solubility in a solvent. To verify if the reaction took place resulting in an unknown chemical entity, the state-of-the-art method is to accurately identify all functional groups of the reactants and products. This process is time-consuming, involves manual or database dependent analysis and interpretation of a Fourier Transform Infra-Red (FTIR) spectrum or Mass Spectroscopy (MS) data using previously established rules and experience of a skilled spectroscopist. These processes are subject to trial and error for compounds with multiple functional groups and for compounds that not well characterized in the literature. Such issues hinder the automated development and characterization of truly new materials with minimal human intervention. We present fast deep learning methods to select the optimal solvent for a given reaction in a transformation-free manner and identify all the functional groups for both the products and reactants for any given reaction. Our methods do not use any database, pre-established rules or procedures to perform either task and use the general definition of functional groups as a ‘collection of atoms’ instead of simple chemical groups traditionally assigned by chemists. We use Artificial Neural Networks (ANNs) to derive patterns and correlations between these collections of atoms and the solvents used to carryout a given chemical reaction using 2.3 million patented reactions available from the United States Patent and Trademark Office. Our methodology is the first to differentiate solvents by their precise chemical structure instead of simply choosing a solvent class and yields a 5-fold cross-validated average F1-score greater than 0.9. Solvent predictions obtained from this model have been validated both in silico using Density Functional Theory and using experimental in situ techniques. To verify that a reaction has occurred, we trained separate ANNs on 7393 publicly available FTIR and MS combined spectra obtained from the NIST Webbook. Instead of using multiple binary classifiers used in previous works to assign functional groups, our approach treats the classification problem in a multi-class, multi-label fashion. The model has a cross-validated F1 score higher than 0.82 for 14 out of 17 defined functional groups. To showcase the practical utility of our method, we introduce two new metrics (Molecular F1 score and Molecular Perfection rate) to measure the performance of identifying all functional groups on molecules. The optimized model has a Molecular F1 score of 0.92 and a Molecular Perfection rate of 72%. Additionally, backpropagation of our model reveals IR patterns typically used by human chemists to identify standard groups, suggesting a convergence of the model on known spectral features that are diagnostic of particular functional groups. We further show that the introduction of additional functional groups does not decrease the performance of our model. Finally, we show redundancy in FTIR and MS data by encoding all our features in a latent space that retains the accuracy of the original model. These results reveal the importance of using machine learning for automated identification of new reaction conditions and functional groups to achieve autonomous
processes in the future.

2:45 PM MT02.02.04/MT03.02.04
Autonomous Research Systems—Phase Mapping & Materials Optimization Gilad Kusne; National Institute of Standards and Technology, United States

The last few decades have seen significant advancements in materials research tools, allowing researchers to rapidly synthesize and characterize large numbers of samples - a major step toward high-throughput materials discovery. Machine learning has been tasked to aid in converting the collected materials property data into actionable knowledge, and more recently it has been used to assist in experiment design. In this talk we present the next step in machine learning for materials research - autonomous materials research systems. We first demonstrate autonomous measurement systems for phase mapping, followed by a discussion of ongoing work in building fully autonomous systems. For the autonomous measurement systems, machine learning controls X-ray diffraction measurement equipment both in the lab and at the beamline to identify phase maps from composition spreads with a minimum number of measurements. The algorithm also capitalizes on prior knowledge in the form of physics theory and external databases, both theory-based and experiment-based, to more rapidly hone in on the optimal phase map. The phase map is then exploited for functional material optimization.

3:00 PM BREAK

3:30 PM *MT02.02.05/MT03.02.05
Information Extraction and Learning by Large-Scale Text-Mining of the Scientific Literature Gerbrand Ceder; University of California, Berkeley, United States

The overwhelming majority of scientific knowledge is published as text, which is difficult to analyze by either traditional statistical analysis or modern machine learning methods. In contrast, the main source of machine-interpretable data for the materials research community has come from structured property databases which encompass only a small fraction of the knowledge present in the research literature. Beyond property values, publications contain valuable knowledge regarding the connections and relationships between the data items as interpreted by the authors. I will show multiple ways to extract useful information from scientific text in both supervised and unsupervised ways. I will show that materials science knowledge present in the published literature can be efficiently encoded as information-dense word embeddings (vector representations of words) without human labelling or supervision. These embeddings capture complex materials science concepts such as the underlying structure of the periodic table and structure-property relationships in materials. Furthermore, we demonstrate that an unsupervised method can recommend materials for functional applications several years before their discovery. This suggests that latent knowledge regarding future discoveries is to a large extent embedded in past publications. In a more supervised way, we have also demonstrated the extraction of codified synthesis recipes from text. Extraction the details of synthesis, including precursor compounds, synthesis operations and their numerical details, requires a very high precision of information extraction, and a tolerance to deal with imprecise and non-standard language. I will show how a large data set of codified solid-state synthesis reactions has been obtained and be queried to obtain interesting information on choice of synthesis operations and precursors is related to the target material.

4:00 PM *MT02.02.06/MT03.02.06
Autonomous Scanning Droplet Cell for On-Demand Alloy Electrodeposition and Characterization Brian L. DeCost, Howie Joress, Trevor Braun, Zachary Trautt, Gilad Kusne and Jason R. Hattrick-Simpers; National Institute of Standards and Technology, United States

We are developing an autonomous scanning droplet cell (ASDC) capable of on-demand electrodeposition and real-time electrochemical characterization for investigating multicomponent alloy systems for favorable corrosion-resistance properties. The ASDC consists of a millimeter-scale electrochemical cell and an array of programmable pumps that can be used to electrodeposit an alloy film and immediately acquire polarization curves to obtain electrochemical quantities of interest, such as the passive current density and oxide breakdown potential. We model these quantities using Gaussian Process regression to select the most informative series of alloys to synthesize and characterize, continuously updating the model as new electrochemical data is acquired. Our initial studies focus on systems that are likely to form corrosion-resistant metallic glasses (MGs) and single-phase multi-principle element
alloys (MPEAs).

The ASDC is an open exemplar autonomous system that provides insight into both technical and methodological aspects of building and deploying robust closed-loop synthesis and characterization platforms. Our approach is to build loosely-coupled modular experimental, automation, and communications systems to 1. support rapid prototyping, debugging, and verification while producing meaningful scientific output and 2. enable integration into future large-scale multi-user and multi-instrument distributed laboratory systems. We address both of the main challenges that autonomous science systems face: learning to reliably synthesize materials and mapping material specification and processing to structure and properties. We will discuss the incorporation of prior knowledge in the form of theoretical and data-driven predictive models, as well as the integration of online and offline multi-modal experimental data streams. Ultimately, closed-loop automated materials synthesis and characterization platforms offer much more than a means of engineering materials properties and performance through black-box optimization algorithms: they offer the potential to develop and deploy new algorithms for generating and testing scientific hypotheses.

4:30 PM MT02.02.07/MT03.02.07
Autonomous Electrolyte Discovery for Batteries with Experimentally Informed Bayesian Optimization
Adarsh Dave, Sven Burke, Jared Mitchell, Kirthevasan Kandasamy, Biswajit Paria, Barnabas Poczos, Venkatasubramanian Viswanathan and Jay F. Whitaacre; Carnegie Mellon University, United States

An autonomous battery electrolyte experimental platform capable of mixing multi-component electrolyte systems and characterizing the transport and electrochemical properties in a high-throughput manner is disclosed. A Bayesian optimization software package found novel electrolyte compositions through optimization of the high-dimensional electrolyte design space over key design objectives like electrochemical stability and conductivity. Electrolyte optimization is difficult because 1) electrolyte evaluation is expensive and takes time, and 2) the space of possible electrolytes is expansive, formed by many possible choices for solvents (often in ternary blends), salts (often in binary mixtures), and trace additives. Bayesian optimization methods are well suited for the optimization of high-dimensional functions with costly evaluations, often producing an efficient design-of-experiments to converge on multi-objective optimal formulations in few experiments. To expedite the optimization over the expansive design space, theoretical predictions of electrolyte properties via the Advanced Electrolyte Model were utilized as “priors” in the statistical model.

Implementation of the novel experimental platform was carried out by two novel test stands developed to automate the mixing and characterization of electrolytes: Otto (for aqueous systems) and Clio (for aprotic/organic systems). The test stands characterized the ionic conductivity and electrochemical stability of electrolyte systems, featuring a four-electrode conductivity probe, pH meter, and a flow-through three-electrode cell and potentiostat. Clio also integrated electrochemically active electrodes for optimization of electrolyte/electrode systems. The active electrode systems used were common functional ceramic metal oxides.

A software orchestration and data layer linked the test-stands to human experimenters and machine-learning packages through a web-services architecture; all experiment data and meta-data is saved in a database. Additional out-of-the-loop characterization was conducted on cathodic systems to validate composition, structure, and oxidation state.

The aqueous design space consisted of aqueous blends of lithium and sodium salts, including nitrates, sulfates, and other commonly-used battery salts. High-concentration aqueous electrolyte candidates were discovered by optimizing of electrochemical voltage stability and conductivity, including low-cost, high-performing alternatives to known but costly aqueous electrolytes (e.g. LiTFSI). Clio’s design space includes blends of both aprotic organic solvents and solutes in addition to various compositions of electrochemically active electrodes. The test-stands are demonstrated to be significantly faster than common human experimentation techniques, converging on novel, optimized electrolyte mixtures in mere hours or days of experimentation.
MT02.03.01
Autonomous Experimental Phase Analysis of Oxide Systems Demonstrated via Optical Imaging and Spectroscopy  
Aine Connolly, Duncan Sutherland, Max Amsler, Sebastian Ament, Michael O. Thompson, Bruce van Dover and Carla Gomes; Cornell University, United States

Efficient autonomous exploration of phase behavior requires real-time dynamically coupled experiments and characterization that can lead to intelligent search trajectories through high-dimensional system parameter space. Employing lateral gradient Laser Spike Annealing (lg-LSA) with a combination of optical microscopy and optical spectroscopy, we demonstrate such a closed loop experimental protocol that enables efficient and rapid mapping of transition boundaries across a wide range of thin film oxide stoichiometry and synthesis conditions. Laser Spike Annealing (lg-LSA) rapidly heats thin oxide films which quench to various metastable phases depending on the peak temperature and cooling rate. With a lateral annealing temperature gradient of 2 – 3 K/μm, spatially localized probes (e.g. microbeam X-ray diffraction or optical spectroscopy) can readily characterize the resulting structures. However, only a few temperatures near transitions are necessary to establish the phase behavior, and an autonomous search must efficiently probe those neighborhoods. Coupling immediate post-exposure imaging and spectroscopy of critical temperature bands after each individual lgLSA exposure, subsequent experiments can be optimized to guide the search with loop-times of one to two minutes. This autonomous closed-loop experimental process thus enables rapid identification of synthesis condition boundaries at phase transitions. Results are shown for a variety of oxide thin films including Bi$_2$O$_3$ and MnTiO$_3$.

MT02.03.02
Accelerating Materials Discovery with Autonomous Job Control Systems Aided by Machine Learning  
Chenru Duan, Jon Paul Janet, Aditya Nandy, Fang Liu and Heather J. Kulik; Massachusetts Institute of Technology, United States

Computational high throughput data generation is essential in materials discovery. Although automation of first-principles simulation has enabled rapid data generation, challenges remain in the most compelling materials spaces (e.g., open-shell transition metal chemistry) to ensure that the data is of sufficient quality, either for automated determination of design rules or in training of machine learning property prediction models. For inorganic chemistry, two key challenges remain at the stage of first-principles data generation: i) chosen ligands and metals may not form a stable complex and ii) calculations may fall outside the domain of applicability of the first-principles method. When such challenges are encountered, they can erode the value of data points in a data set, and such points may need to be removed. Typically, one detects these failures only after a calculation is completed, wasting computational resources. To address this problem, we incorporated machine learning (ML) models into our high-throughput discovery tools for inorganic chemistry. These ML models are capable of predicting the outcomes of a calculation. We built a calculation outcome classifier directly from topological, heuristic features prior to simulation to prescreen a large pool of candidate materials without requiring any first-principles calculations. Inspired by the data distribution in the latent space, we designed an uncertainty quantification metric specifically for classification tasks, lowering the risk of terminating jobs that are likely to be fruitful. To achieve higher transferability in inorganic complex discovery, an ML model that utilizes the information generated during simulation is also developed, which directs the on-the-fly decision of whether to abandon an in-progress calculation. Upon implementing this “dynamic” classifier in current high-throughput screening workflows, we achieve around two-fold acceleration in data generation with no loss of feasible lead compounds. We expect our meta-decision approach to be broadly useful in data set generation with first-principles calculations for the accelerated design of materials.

MT02.03.03
Autonomous Experimentation for Mechanical Design  
Aldair E. Gongora$^1$, Bowen Xu$^1$, Wyatt C. Perry$^1$, Chika S. Okoye$^1$, Patrick F. Riley$^2$, Kristofer Reyes$^3$, Elise F. Morgan$^1$ and Keith A. Brown$^1$; $^1$Boston University, United States; $^2$Google Research, United States; $^3$University at Buffalo, The State University of New York, United States

The high level of control afforded by additive manufacturing presents innumerable possibilities for design with each design choice potentially influencing mechanical performance. While tools exist for optimizing many facets of mechanical performance, improving failure properties, however, poses a challenge due to the stochastic nature of failure and the difficulty in reliably predicting the role of the microstructure introduced during manufacturing. As a
result, design for failure performance typically occurs manually through iterative manufacture and testing. In this work, we present the realization and use of an autonomous research system (ARS) for designing and optimizing a model family of additively manufactured structures for mechanical performance. This novel approach to mechanical design combines high-throughput automated experimentation with active learning-guided experimentation to enhance the speed of experimental campaigns and the knowledge gained from each experiment. In order to evaluate this approach, the ARS was tasked with exploring and optimizing a parametric model family of structures for energy absorption. Not only was the ARS able to identify higher performing structures with an order of magnitude fewer experiments than a grid-based design of experiments approach, but it was able to do so in 36 hours. Additionally, evaluating the performance of different learning approaches on the ARS showed fascinating deviations from purely computational studies, highlighting the importance of experimental validation in the active learning community. The use of autonomous research systems for the design of structures for properties that cannot be effectively simulated represents a shift in the conventional design process and could have an impact in materials development and mechanical design in a manner that facilities the convergence of machine learning, physical experimentation, and design.

**MT02.03.04**

**Efficient Selection of Categorical Process Variables for Autonomous Experimentation**

Florian Häse¹,²,³, Loïc M. Roch¹,²,³ and Alan Aspuru-Guzik³,²;¹;¹Harvard University, United States;²Vector Institute for Artificial Intelligence, Canada;³University of Toronto, Canada

Self-driving laboratories provide promising opportunities to enable autonomous experimentation for a substantial acceleration of scientific discovery. By combining automated experimentation platforms with algorithmic experiment planning strategies based on machine learning, self-driving laboratories implement a closed-loop approach to experimentation. The performance and acceleration of a self-driving laboratory critically depend on the efficiency of its experiment planning strategies to operate in low-data regimes while executing only the most informative experiments. Experimentation procedures can be governed by gradually changeable parameters such as temperature or residence time, but can also involve distinct choices, for example the selection of a catalyst or a solvent. Although a plethora of algorithms have been developed to determine the optimal values of continuous variables, the efficient selection of categorical variables still remains challenging under the constraints posed by typical experimentation settings. Here, we introduce Gryffin, a framework developed to facilitate autonomous experimentation for processes involving categorical variables. Gryffin is built upon concepts from Bayesian optimization and Bayesian kernel density estimation, which have previously been shown promising performance for continuous parameter selection. Contrary to existing methods, Gryffin can accelerate the optimization process by leveraging domain knowledge in the form of user-provided descriptors for the categorical choices. Balancing the provided domain knowledge with the collected experimental feedback on-the-fly, Gryffin is capable of learning more informative representations of the categorical experimentation parameters. These learned representations can evidence relevant properties of the categorical parameters to enable the derivation of design choices. We highlight the applicability and performance of Gryffin on three different problems bridging materials science and chemistry: (i) the design of hybrid organic-inorganic perovskites, (ii) the discovery of non-fullerene acceptor candidates for organic photovoltaics, and (iii) the optimization of Suzuki-Miyaura cross-coupling reactions. Gryffin outperforms existing methods in all three applications, and identifies the best performing material compositions or experimental conditions by probing only a fraction of the search space. Finally, we outline our recent results with Gryffin as an experiment planning strategy in self-driving laboratories for thin-film materials and reaction optimization.
Dynamics Tian Xie, Arthur France-Lanord, Yanning Wang, Yang Shao-Horn and Jeffrey C. Grossman; Massachusetts Institute of Technology, United States

Understanding the dynamical processes that govern the performance of functional materials is essential for the design of next generation materials to tackle global energy and environmental challenges. Many of these processes involve the dynamics of individual atoms or small molecules in condensed phases, e.g. lithium ions in electrolytes, water molecules in membranes, molten atoms at interfaces, etc., which are difficult to understand due to the complexity of local environments.

In this talk, we will present Graph Dynamical Networks (G DyNets) [1], an unsupervised learning approach to learn atomic scale dynamics from molecular dynamics trajectories for arbitrary phases and environments. We demonstrate that learning local dynamics is exponentially easier than global dynamics in material systems. Then, we apply this approach to two complex systems -- silicon atoms at liquid-solid interfaces, and lithium ions in amorphous polymer electrolytes. We show that our approach gains important dynamical information for both materials that is otherwise difficult to obtain, and provides atomic scale explanations to some experimental observed phenomena. With the large amounts of molecular dynamics data generated every day in nearly every aspect of materials design, this approach has the potential to provide a broadly applicable, automated tool to understand atomic scale dynamics in material systems.


9:15 AM MT02.04.03
Fast and Accurate Interatomic Potentials by Genetic Programming Alberto Hernandez, Adarsh Balasubramanian, Fenglin Yuan, Simon Mason and Tim Mueller; Johns Hopkins University, United States

In recent years there has been great progress in the use of machine learning algorithms to develop interatomic potential models. Machine-learned potential models are typically orders of magnitude faster than density functional theory but also orders of magnitude slower than physics-derived models such as the embedded atom method. We demonstrate that machine learning, in the form of genetic programming, can be used to develop accurate and transferable many-body potential models that are as fast as the embedded atom method, making them suitable to model materials on extreme time and length scales. The key to our approach is to explore a hypothesis space of models based on fundamental physical principles and to select models from this hypothesis space based on their accuracy, speed, and simplicity. We demonstrate our approach by developing fast and accurate interatomic potential models for copper that generalize well to properties they were not trained on. Our approach requires relatively small sets of training data, making it possible to generate training data using highly accurate methods at a reasonable computational cost. We discuss the open-source implementation of our algorithm and additional features including extensions to systems with multiple elements.

9:30 AM MT02.04.04
On-the-Fly Bayesian Active Learning of Interpretable Force Fields for Atomistic Rare Events Jonathan Vandermause¹, Steven B. Torrisi¹, Simon L. Batzner¹, Yu Xie¹, Lixin Sun¹, Alexie Kolpak² and Boris Kozinsky¹; ¹Harvard University, United States; ²Massachusetts Institute of Technology, United States

Recent machine learning (ML) approaches to modeling the Born-Oppenheimer potential energy surface have been shown to approach first principles accuracy for a number of molecular and solid-state systems. However, most ML potentials return point estimates of the quantities of interest (typically energies, forces, and stresses) rather than a predictive distribution that reflects model uncertainty. Without uncertainty estimates, a laborious fitting procedure is required, which usually involves selecting thousands of reference structures from a database of first principles calculations. Here, we show that active learning based on Gaussian process (GP) regression can accelerate the training of high-quality force fields by making use of accurate Bayesian estimates of model error.

Through a series of tests on randomly generated bulk aluminum structures, we demonstrate that the Bayesian error of our GP potentials correlates strongly with the true error of the model on out-of-sample structures. We then use the Bayesian error to implement an active learning molecular dynamics method, in which DFT is called only when the Bayesian error of the GP model rises above an adaptive threshold based on the optimized noise hyperparameter of
the GP. All model hyperparameters are optimized whenever an atomic environment and its force components are added to the training set, allowing the error threshold to adapt to novel environments encountered during the simulation.

We discuss applications of this on-the-fly learning method to crystal melts, vacancy diffusion, and adatom diffusion for a range of single- and multi-component systems. By combining DFT with GP regression in a single molecular dynamics simulation, an accurate multi-phase force field for bulk aluminum is obtained with fewer than 100 DFT calls. Moreover, we demonstrate that our Bayesian potentials can be flexibly and automatically updated when the system deviates from previous training data. Because of the low-dimensional structure of our kernel function, we show that our potentials can be mapped to a much cheaper regression model approaching the efficiency of classical potentials. Such a reduction in the computational cost of training, updating, and applying machine-learned potentials promises to extend ML modeling to a wider class of materials than has been possible to date.

9:45 AM MT02.04.05
Predicting Potential Energy Surfaces with Machine Learning Matti Hellström; Software for Chemistry & Materials BV, Netherlands

Atomistic simulations of molecules and materials require a reliable way to evaluate the underlying potential energy surface. Furthermore, realistic simulations of materials with complexities such as grain boundaries, vacancies, impurities, and interfaces, often imply large scale models comprising many thousands or even millions of atoms and thus, the use of very efficient computational chemistry methods. Machine learning (ML) methods can bridge the gap between often prohibitively expensive electronic structure calculations and efficient but often not sufficiently accurate force fields. In this contribution, we describe how an ML method based on artificial neural networks can be applied to describe chemical reactions in several complex systems, such as electrolyte solutions [1] and at solid/liquid interfaces [2]. These simulations provide unprecedented detail and insight into the working and degradation mechanisms of batteries, fuel cells, and other electrochemical systems.

Although neural networks are ideally suited for describing complex non-linear functions like potential energy surfaces, they are still not routinely employed for this purpose [3]. Here, we will present our work for overcoming the main obstacles for widespread adoption, relating to (i) construction of suitable training and validation sets, (ii) automation of the featurization of different molecules and materials, and (iii) the choice of loss function for the neural network optimization.

The neural network method is implemented as part of the Amsterdam Modeling Suite, a software package containing a sophisticated molecular dynamics engine and first-principles, semi-empirical, and atomistic potential methods. This software environment allows for seamless transitions between the different levels of theory and greatly simplifies the construction of the neural network potential. Our ultimate goal is to provide the chemistry, biochemistry, and materials science communities with an all-purpose computationally inexpensive method that can be used in simulations related to solving challenging problems in energy, renewables, climate change reduction, and health care.


10:00 AM BREAK

10:30 AM *MT02.04.06
Data-Driven Materials Design and Machine Learning Using the Materials Project Kristin A. Persson1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

The powerful combination of supercomputing resources, robust algorithms for solving the laws of physics and state-of-the-art software infrastructure are enabling rapid, systematic calculations of real materials properties from
quantum mechanics across chemistry and structure. A result of this paradigm change are databases like the *Materials Project* (www.materialsproject.org) which is charting the properties of all known inorganic materials and beyond, designing novel materials and offering the data free of charge to the community together with online analysis and design algorithms. The growing body of available, reliable data has reached the stage where automated learning algorithms can be effectively trained and utilized to accelerate all aspects of the materials design cycle: from property prediction, to materials synthesis and characterization. To exemplify the approach of data-driven materials design, we will survey a few in-house case studies and the application of accelerated learning – from prediction, to synthesis and characterization - showcasing rapid iteration between ideas, computations, insight and new materials development.

11:00 AM MT02.04.07
**Constructing Reliable Machine-Learning Potential for Solid-State Reaction: Example of Ni Silicidation**  
Wonseok Jeong, Dongsun Yoo, Kyuhyun Lee and Seungwu Han; Seoul National University, Korea (the Republic of)

Molecular dynamics (MD) using classical interatomic potentials can provide valuable information at the atomistic scale. However, when the simulation involves chemical reactions of bond breaking and forming along with mixed bonding characters, it is challenging to develop an accurate force field for the system and sometimes practically impossible. In this respect, the machine-learning potentials (MLPs) are highly anticipated since they are based on flexible mathematical structures with no pre-fixed form. The parameters in the machine-learning model are automatically optimized on the reference data, often from the density functional theory. Nevertheless, MLP has a critical drawback; it can produce unphysical results when MLP is applied on configurations that are not included in the training set. This is particularly problematic in the solid state reaction that involves constant bonding breaking and formation. In this presentation, we discuss the process of developing a reliable neural network potential (NNP) for a challenging solid-state reaction - thermal silicidation of nickel at the Ni-Si interface. We present a systematic way to build up the training set that can describe the interface reaction. In order to obtain the prediction uncertainty for certain local configurations, we utilize replica NNPs that are trained directly on the atomic energy of the reference NNP. We find that the temporal variation of compositions across the interface agrees well with the experiment.

11:15 AM MT02.04.08
**Gaussian Process-Based Refinement of Dispersion Corrections**  
Stefan Gugler¹, Markus Reiher¹ and Jonny Proppe²; ¹ETH Zürich, Switzerland; ²University of Goettingen, Germany

We employ Gaussian process (GP) regression to account for systematic errors in D3-type dispersion corrections.[1] We refer to the associated, statistically improved model as D3-GP. It is trained on differences between interaction energies obtained from PBE-D3(BJ)/ma-def2-QZVPP and DLPNO-CCSD(T)/CBS calculations of 1,248 molecular dimers, which resemble the dispersion-dominated systems contained in the S66 data set. To train our D3-GP model, we used features derived from the matrix of atom-pairwise D3(BJ) interaction terms: (a) a distance-resolved interaction energy histogram, histD3(BJ), and (b) eigenvalues of the interaction matrix ordered according to their decreasing absolute value, eigD3(BJ).

We demonstrate that the posterior variance can be approximately updated from only the input variables (features) of the new training system, which are obtained efficiently from D3(BJ) calculations. In this way, we can collect a batch of new training systems before the corresponding electronic-structure calculations are carried out at the same time. We refer to this selection approach as batchwise variance-based sampling (BVS).

BVS-guided active learning is an essential component of our D3-GP workflow, which is implemented in a black-box fashion.

Once provided with reference data for new molecular systems, the underlying GP model automatically learns to adapt to these and similar systems.

This approach leads overall to a self-improving model (D3-GP) that predicts system-focused and GP-refined D3-type dispersion corrections for any given system of reference data.

Doing Less for More—Multi-Information Bayesian Optimization and the Computational Sciences
Henry C. Herbol, Matthias Poloczek and Paulette Clancy; 1Johns Hopkins University, United States; 2The University of Arizona, United States

For half a century, computational methods such as Density Functional Theory (DFT) and Molecular Dynamics (MD) have allowed scientists to study atomic-scale systems. These methods and approaches have consistently been characterized as either “slow, small, and accurate” or “fast, large, and inaccurate” and virtually any combination in-between (with the exception of the most desirable combination: “fast, large, and accurate”). For instance, DFT is well established in modeling electronic properties of materials; however, due to scaling issues, DFT is typically limited to smaller atomic systems, or fully periodic crystals. For phenomena, such as nanoparticle nucleation, which demand large system sizes, MD is typically the method of choice. Adding to the complexity, within each method the user has to select a choice of functional or force field, which possess different degrees of computational complexity.

In recent years, Machine Learning (ML) methods have begun to be used to ameliorate these computational costs, while maintaining acceptable levels of accuracy. From Neural Nets, to Random Forests, to Gaussian Process Regressions, machine learning approaches are increasingly being used to replace DFT and MD as objective functions. Methods such as Bayesian Optimization are of particular interest in situations where data is scarce and expensive, which covers a number of important materials processes. As a result, ML is becoming an attractive tool in the computational sciences as a means to minimize the number of required expensive calculations.

In this work, we discuss the merging of these fields, ML and computational sciences, with a primary focus on showing how to utilize multiple information sources in the context of computational science problems. Multi Information Source Optimization using a Knowledge Gradient (misoKG) as an acquisition function was developed in 2017 by Poloczek and Frazier for a Gaussian Process Bayesian Optimization approach. Their initial design, tested against the well-known Rosenbrock benchmark, used a noisy alternative with a presumed lower cost to minimize the Rosenbrock at a smaller total cost than that of standard (“workhorse”) Expected Improvement and Knowledge Gradient methods. The statistical model in the original paper involved replicating the kernel for each information source, potentially scaling the number of hyperparameters to unreasonable high levels. Here, we extend their original statistical model to produce a more scalable approach, as well as applying misoKG to several computational problems, showcasing the benefits of using cheap, but at times inaccurate, calculations to model atomic systems.

Our new method employs an Intrinsic Coregionalization Model that avoids the addition of hyperparameters, and is shown to minimize the Rosenbrock benchmark in considerably less cost than the alternatives. We test the base method against the interatomic DFT binding energy of metal halide perovskite salts and solvents, using different solvents and different levels of theory as alternative information sources. A more direct study of functionals and their uses as alternative information sources is then made with the study of carbon monoxide.

Machine Learning-Assisted Acceleration of DFT without Machine-Learning Errors
Alexander Shapeev; Skolkovo Institute of Science and Technology, Russian Federation

Machine-learning potentials are a promising alternative combining both, efficiency of the empirical interatomic potentials and accuracy of quantum-mechanical interatomic interaction models. Unlike empirical potentials that are reused for solving a new problem with the old materials, machine-learning potentials are usually re-parametrized for a new problem at hand. Hence a major bottleneck of such potentials: it takes large amounts manual work to construct a database and fit a new potential.

I will present an approach based on moment tensor potentials [Shapeev (2016)] active learning of automatically constructing machine-learning potentials [Gubaev (2019)]. For example, in the problem of computing the vibrational free energy of a compound, an actively learning potential will select those configurations for which predicting energy and forces results in extrapolation during molecular dynamics. These configurations will be evaluated with DFT and added to the training set. This procedure will run until the potential can run molecular dynamics completely without extrapolation. Special care it taken to make sure that changing the potential on-the-fly would not hinder the accuracy of statistical averaging. Active learning, thus, closes the loop and makes the algorithm of computing free energy fully automatic.

The resulting automatic algorithm would still contain small systematic and often uncontrollable errors due to approximation of quantum mechanics with a surrogate model. However, in some applications, this error can be corrected for at the last stage of the algorithm. For instance, the last step of computation of the free energy can be a...
thermodynamic integration computing the difference between the free energy as given by the machine-learning potential and the DFT free energy. This results into an automatic algorithm without the systematic error in the final answer. Only the statistical error remains which is still much smaller compared to using DFT alone.

The proposed approach of accelerating DFT calculations by automatically constructing machine-learning potentials and correcting for their systematic errors will also be illustrated on the problems of constructing of convex hulls of stable alloy structures and computing high-temperature elastic constants of crystals.

References


dimensionality reduction techniques applied to stress-strain curves. Results show that CNN is able to effectively predict latent space representations of stress-strain curves, with a training set orders of magnitude smaller than the design space. These results demonstrate the potential to use machine learning to accelerate composite design characterization and optimization.

2:00 PM *MT02.05.03  
**Accelerating Discovery in Inorganic Chemistry with Machine Learning** Heather J. Kulik, Jon Paul Janet, Chenru Duan, Aditya Nandy, Naveen Arunachalam and Daniel Harper; Massachusetts Institute of Technology, United States

Although the discovery and synthesis of new materials, catalysts, and functional molecules represents the foremost effort that unifies thousands of researchers in the chemical science community, presently characterized compounds represent a minute fraction of chemical space. The highly tunable electronic structure properties of inorganic complexes (i.e., variable spin, oxidation state, and coordination number) make them attractive targets for applications in energy storage, functional materials, and catalysis but present a daunting combinatorial challenge. This vast transition metal compound space cannot be fully enumerated by any traditional Edisonian approach. In order to advance quantitative structure-activity relationships, reveal emergent phenomena, and accelerate design of materials and catalysts, smarter and faster computational approaches are needed. I will outline our efforts to accelerate first-principles (i.e., with density functional theory, or DFT) screening of inorganic complexes for catalysis and materials science applications. We develop machine learning (ML) models (e.g., artificial neural networks) that predict both properties and simulation outcomes. We integrate these tools into an automated design workflow that can make essential decisions on which simulations are best to carry out and why, with awareness of ML model and DFT model uncertainty. I will describe applications of these tools for advancing understanding in catalysis and functional spin crossover materials.

2:30 PM *MT02.05.04  
**Advances in Interatomic Potentials for Materials** Gabor Csanyi; University of Cambridge, United Kingdom

Modelling the deformation of metals is one of the success stories of atomic scale modelling over the past four decades. Increasingly complex functional forms, from pair potentials to embedded atom models and bond order potentials, allowed the quantitative description of different crystal structures, point and line defects, shedding light on many elementary processes governing failure, phase stability, surface phenomena etc. Interestingly, the accuracy with which these models describe the potential energy surface corresponding to the electronic ground state has not changed over the decades and is rather limited. The success is thus largely empirical in nature - and follows from the sophistication of the modeller and the judicious compromises made in order to solve specific problems. The parallel developments in electronic structure theory on the other hand provided exquisite quantitative agreement with experiments e.g. for thermomechanical properties, phase stability, and defect energetics. I will report on recent work of a growing community, who have managed to bring these two worlds together, and construct extremely accurate functional representations of the interatomic potential. These developments rely on a very large amount of highly accurate electronic structure data, on non-parametric function fitting, and on sophisticated representation theory that brings with it guarantees of completeness and convergence.

3:00 PM BREAK

3:30 PM *MT02.05.05  
**Polymer Informatics—Current Status and Critical Next Steps** Ramamurthy Ramprasad; Georgia Institute of Technology, United States

The Materials Genome Initiative (MGI) has heralded a sea change in the philosophy of materials design. In an increasing number of applications, the successful deployment of novel materials has benefited from the use of computational, experimental and informatics methodologies. Here, we describe the role played by computational and experimental data generation and capture, polymer fingerprinting, machine-learning based property prediction models, and algorithms for designing polymers meeting target property requirements. These efforts have culminated in the creation of an online Polymer Informatics platform (https://www.polymergenome.org) to guide ongoing and future polymer discovery and design [1-3]. Challenges that remain will be examined, and systematic steps that may be taken to extend the applicability of such informatics efforts to a wide range of technological domains will be
Present polymer synthesis techniques excessively strain research resources properties as they are largely Edisonian in approach.[1] Coupled with largely manual experimentation, the timeline for new polymer innovation are prohibitively slow.

While the global materials science community has recognized that machine learning could be a viable technique to accelerate materials discovery, it’s application towards experimental polymer design has been lacking. One of the reasons could be the inherent difficulty of modelling polymer systems due to their complexity multiple length scales. There have been efforts in fingerprinting,[2] which have shown success to DFT generated data. However, these are gross over-simplifications which do not generalize well towards experimental data.

Through a case study, we demonstrate the critical steps that are needed when building machine learning algorithms in polymer property prediction and polymer design. Building on this, we present the future of polymer design via a combination of intelligent data management, high throughput experimentation, high speed diagnostics and machine learning towards closed-loop autonomous experimentation.

Chemical design of SiO$_2$-based glasses with high elastic moduli and low weight is of great interest. However, it is difficult to find a universal expression to predict the elastic moduli according to the glass composition before synthesis since the elastic moduli are a complex function of interatomic bonds and their ordering at different length scales. Here we show that the densities and elastic moduli of SiO$_2$-based glasses can be efficiently predicted by machine learning (ML) techniques across a complex compositional space with multiple (>10) types of additive oxides besides SiO$_2$. Our machine learning approach relies on a training set generated by high-throughput molecular dynamic (MD) simulations, a set of elaborately constructed descriptors that bridges the empirical statistical modeling with the fundamental physics of interatomic bonding, and a statistical learning/predicting model developed by implementing least absolute shrinkage and selection operator with a gradient boost machine (GBM-LASSO). By just training with a dataset that only composed of binary and ternary glass samples, our model shows remarkable learning accuracy and outstanding extrapolation ability to predict the density and elastic moduli for k-nary glasses that beyond the training set. Finally, as an example to illustrate the potential applications of our ML model, we perform a rapid screening ~100,000 compositions of a quinary glass system to construct a compositional-property database that allows for a fruitful overview on the glass density and elastic properties.

SESSION MT02.06: Poster Session II: Machine Learning for Potentials and from Theory
Session Chairs: Jason Hattrick-Simpers, Barnabas Poczos, Markus Reiher and Aleksandra Vojvodic
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

MT02.06.01
Combining Polymorphism and Machine Learning for Materials Discovery Fadwa El Mellouhi; QEERI-HBKU, Qatar
The computer-aided design of materials has witnessed important progress over the past few years. This being said, it depends crucially on the crystal structure and the polymorphs considered. I will show how we considered various polymorphism to obtain new stable and undiscovered compounds based on the assessment of the relative stability of various phases with respect to a reference structure. These calculations rely on the calculation of the thermodynamic stability by computing the convex hull energy aided by open-source computational databases.
I will also summarize some of our recent findings using DFT combined with machine learning to perform a systematic analysis of the structure-to-property relations exploring fully inorganic ABC$_3$ chalcogenide (I-V-VI$_3$), halide (I-II-VII$_3$) and some hybrid perovskites. The analysis focused on the role of BC$_6$ octahedral deformations, rotations and tilts over the thermodynamic stability and optical properties of the compounds. Machine learning algorithms helped to estimate the relations between the octahedral deformation and the bandgap, and established a similarity map among all the calculated compounds. We propose that compositions grouped together on the similarity map are amenable to form mix-ion compounds, offering interesting guidelines on how to engineer mix-phase perovskites.

This work have been supported by the Qatar National Research Fund (QNRF) through the National Priorities Research Program (NPRP8-090-2-047).

MT02.06.02
Data-Driven Accurate Positioning of the Band Edges of MXenes Avanish Mishra$^{1,2}$, Arunkumar C. Rajan$^2$, Rinkle Juneja$^2$ and Abhishek K. Singh$^2$; $^1$University of Connecticut, United States; $^2$Indian Institute of Science, Bangalore, India
MXenes are a vast class of two-dimensional (2D) materials exfoliated from corresponding MAX phases, which get functionalized due to the availability of unsaturated surface charges. A total of 25,000 MXenes has already been generated and are stored in a functional materials database named, aNANt, which are metallic or semiconducting in nature depending upon the surface termination. MXenes possess variability in their properties and are considered...
promising for electronic, photovoltaic, and photocatalytic applications. However, other than the band gap, these properties rely on the accurate position of the band edges. Hence, to synthesize MXenes for various applications, a prior knowledge of the accurate position of their band edges at an absolute scale is essential; computing these with conventional methods would take years for all the MXenes. A local or semilocal functional-based approach within density functional theory always underestimates the band gap. Furthermore, it fails to predict the accurate position of the band edges. We develop a machine learning model for positioning the band edges with GW level of accuracy having a minimum error of 0.12 eV. An intuitive model is proposed based on the combination of Perdew–Burke–Ernzerhof band edge and vacuum potential having a correlation of 0.93 with GW band edges, which is able to capture the physical origin behind the shift of reference level and unravel the role of surface functionalization in controlling it. These models can be utilized to identify MXenes for the desired application in an accelerated manner.

MT02.06.03
Predicting Nanoscale Static Friction of 2D Materials via Machine Learning Techniques Behnoosh Sattari Baboukani1, Kristofer Reyes1, Zhijiang Ye2 and Prathima Nalam1; 1University at Buffalo, United States; 2Miami university, United States

Shear properties of two-dimensional (2D) materials such as graphene, molybdenum disulfide (MoS2) or boron nitride exhibit significant dependence on interlayer interactions and lattice orientations. The static friction of 2D materials originates from the stick-slip pattern generated during shearing of the layers. Within the framework of Prandtl-Tomlinson model, the corrugated potential Energy Surface (PES) barrier of the shearing interface results in stick-slip instabilities and tuning the interlayer interactions such as van der Waals, electrostatic forces and identifying the appropriate lattice orientations between two similar 2D materials can enable the identification of promising ‘candidates’ with super lubricating properties. Currently, over few dozen 2D materials have been successfully synthesized and other thousand 3D materials have been identified with potential exfoliation properties, and hence to identify the 2D material with highest lubricity machine learning tools are highly valuable.

In this study, 15 different 2D materials from two different families i.e. the graphene family (includes graphene, hydrogenated graphene, fluorographene and hexagonal boron nitride) and transition metal dichalcogenide family (TMDs includes MX2, M: Mo, Nb, W, Ti - S: S, Se, Te) were selected. PES for five 2D materials, estimated via molecular dynamics (MD) simulations or density function theory (DFT) approximations, were extracted from the literature and employed as the training data. We use a combination of geometric, electronic, mechanical, phonon vibration-related and physical descriptors of 2D material in Bayesian modeling and transfer learning techniques to predict maximum PES for 10 different 2D materials. Strong pairwise correlations were observed among the 2D materials within the same family. Posterior predictions showed hydrogenated graphene presented the lowest corrugation barrier i.e. ~45 % smaller than graphene. To validate the model, potentials for hydrogenated graphene were established and molecular dynamics simulations was performed to estimate a PES value of 1.8 meV/A°2, which was found to be 10% smaller and within the range of the uncertainty as estimated by the Bayesian modeling. Further, the band gap energies for 3 TMDs were predicted using same descriptor set and the predicted values were found to be similar with the DFT-calculated band gap values. Descriptor sensitivity analysis indicates that the maximum energy barrier values were controlled mostly by structural, mechanical and phonon vibrational properties of the system, not by the electronic properties. Finally, the PES for TMDs were found to be highly correlated to the polarizability and the size of the chalcogen atom. The robust model generated in our current study creates a platform for predicting and estimating the lubrication of properties for other novel and unexplored 2D materials and as well for 2D-based heterostructures.

MT02.06.04
Linking Predictions of Protein Structure and Disorder through Molecular Simulation Claire Hsu1, Anna Tarakanova2 and Markus J. Buehler1; 1Massachusetts Institute of Technology, United States; 2University of Connecticut, United States

Intrinsically disordered proteins (IDPs) and intrinsically disordered regions within proteins (IDRs) have been shown to serve an increasingly expansive list of biological functions, including regulation of transcription and translation, protein phosphorylation, cellular signal transduction, regulation of self-assembly of large protein complexes, as well as mechanical roles. The link between function and protein disorder has motivated several recent advances in experimental techniques for identifying disordered regions. Common current techniques include X-ray crystallography, NMR spectroscopy, mass spectrometry, electron microscopy, and small-angle X-ray scattering;
recent advances have extended the length and time-scales of such methods, often combining multiple techniques together to better capture dynamic regions that signal disorder. However, experimental methods for disorder classification still do not scale to the level of experimentally curated structural information in folded protein structure databases. In addition, disorder predictors rely on several different definitions of disorder and fail to account for the continuous order-disorder spectrum. To better capture disorder in protein structure, we link disorder predictions to the performance of secondary structure predictor algorithms developed for folded proteins and conduct molecular dynamics simulations on representative proteins from the Protein Data Bank to determine regions of high motion. We find that secondary structure predictor performance can be leveraged to confirm regions of disorder identified by disorder predictors. In addition, low accuracy secondary structure predictions coupled with high dynamics as suggested by molecular simulations suggest a lack of static structure and, thus, a presence of disorder in regions that may not have a consensus disorder prediction. While disorder databases scale to size and experimental techniques continue to develop, secondary structure predictors and molecular simulations can improve disorder predictor performance, which can lead to the discovery of novel functions of IDPs and IDRs.

**MT02.06.05**  
**Metadynamics Sampling for Training Machine-Learning Interatomic Potential** Dongsun Yoo, Wonseok Jeong, Kyuhyun Lee and Seungwu Han; Seoul National University, Korea (the Republic of)

Machine-learning interatomic potential (MLIP) is getting much attention as a promising computational tool that can give the accuracy of quantum mechanical calculations with the cost of classical force-fields. Among many forms of MLIP suggested to date, neural network potential and Gaussian approximation potential are the two most popular models.

The construction of reliable MLIP requires a careful selection of training set. The training set is usually selected by intuition and experience; practitioners select a set of structures that are expected to appear during the simulations. However, unexpected structures can emerge during the simulation, giving unreliable results or even catastrophic failures. This is a major obstacle against wide use of MLIP. Several methods were proposed to remedy this problem: the detection of out-of-training-set structures, e.g. query-by-committee method, and on-the-fly training. Still, the selection of training set is the major bottleneck to the construction of MLIP.

In this presentation, we suggest a new form of metadynamics to efficiently sample a wide range of local environments, enabling easier construction of MLIP. We use a descriptor vector, which is a direct input to machine-learning model, as collective variables. That is to say, collective variables represent atomistic local environment rather than the state of the entire system. Metadynamics simulations starting from certain structures can sample a wide range of local environments so that it is easier to construct general-purpose potential. Metadynamics sampling also increases the stability of trained potential. We will demonstrate its performance with neural network potential.

**MT02.06.07**  
**Computational Exploration of Near-Infrared Absorbing Polymethine Dyes** Daniele Padula¹, Roland Hany¹, Frank Nuesch¹ and Mark P. Waller²; ¹Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; ²Pending.ai, Australia

In this contribution, we present a Machine Learning/Quantum Chemical approach aimed at identifying new organic molecules able to absorb in the NIR region of the spectrum. We obtain a pool of potential candidates exploiting Machine Learning models able to generate text representations of molecules. The molecules obtained through this generative model are biased towards classes of compounds that are well known to absorb in the NIR region, such as squaraines, cyanines, croconates and other organic semiconductors. The generated molecules are then clustered with Cheminformatics approaches, and their synthetic accessibility assessed through Monte Carlo Tree Search approaches to retrosynthesis. Finally, their electronic properties are screened through quantum chemical methods of increasing complexity to progressively reduce the pool of candidate materials. Additionally, to reduce the computational cost of future quantum chemical screenings, we will assess whether it is possible to formulate new descriptors that are good predictors of the electronic properties of a molecule.

**MT02.06.09**  
**A General Machine Learning Framework for Impurity Level Prediction in Semiconductors** Arun Kumar Mannodi Kanakkithodi and Maria K. Chan; Argonne National Laboratory, United States
Electronic levels introduced by impurities and defects in the middle of the band gap are critically important in semiconductors for optoelectronic, photovoltaic (PV) and quantum sensing applications. While "deep" defect levels can prove catastrophic for PV performance by causing non-radiative carrier recombination, impurity levels in the band gap could also be entangled for quantum sensing or lead to increased absorption of sub-gap photons which can enhance efficiencies. Predicting formation energies and charge transition levels for defects in semiconductors is thus paramount; density functional theory (DFT) calculations have been widely applied for such studies to overcome experimental bottlenecks. However, the requirement of large supercells, advanced levels of theory, and inclusion of charge corrections make these computations very expensive, and trends and knowledge from previous calculations are not exploited in subsequent ones.

In this work, we combine high-throughput DFT and machine learning (ML) to develop general predictive models for the formation enthalpy and charge transition levels of impurities in two broad semiconductor classes: (a) ABX3 halide perovskites, and (b) group IV, III-V and II-VI semiconductors. DFT data is generated for impurity atoms selected from across the periodic table and simulated in various possible cation, anion or interstitial sites. Any "semiconductor + impurity" combination is converted into a unique feature vector based on the identity and electronic properties of the semiconductor, the tabulated elemental properties of the impurity atom, information about the defect site coordination environment, as well as some electronic and energetic properties computed using low cost unit cell defect calculations. State-of-the-art neural networks, random forest and ridge regression methods are applied to train models for (a) impurity formation enthalpy, and (b) impurity charge transition levels, based on the input feature vector. Model performance is evaluated for different ML techniques, sets of features, and size and nature of training dataset; the best predictive models thus obtained are deployed for comprehensive prediction and design purposes. It is seen that models trained on defects and impurities in end point compositions are applicable to intermediate compositions as well: for instance, by training on data from pure canonical AB semiconductors like CdTe, ZnO, GaAs and SiC, the ML models can make accurate predictions for impurities in alloyed compositions of the same compounds, such as CdTe₁₋ₓSeₓ, Cd₁₋ₓZnₓO, Al₁₋ₓGaₓAs₁₋ₓSbx, etc. This versatility of the machine learned-models provides an avenue to access the energetic and optoelectronic impact of any atomic impurity in any possible pure or mixed composition semiconductor belonging to the same chemical space. We use the predictive models to quickly screen for dominating impurities, that is impurities that shift the equilibrium Fermi level in the semiconductor as determined by dominant native defects, in hundreds of possible compositions in the halide perovskite and groups IV, III-V and II-VI semiconductor spaces. The quick and accurate estimation of interesting dopants/impurities in semiconductors would not be possible without machine learned models, and the strategy applied in this work is applicable to any class of semiconductors.

MT02.06.10
Machine Learning Study of Magnetic Two-Dimensional Materials Trevor David Rhone, Shaan Desai, Wei Chen, Amir Yacoby and Efthimios Kaxiras; Harvard University, United States

The discovery of intrinsic magnetism in monolayer CrI3 and bilayer Cr2Ge2Te6 created great interest in two-dimensional (2D) materials with intrinsic magnetic order. How many of these materials exist? What are their properties? We present a study of 2D materials with intrinsic magnetic order, materials at the forefront of physics research. We use materials informatics (machine learning applied to materials science) to study the magnetic and thermodynamic properties of 2D materials. Crystal structures based on monolayer Cr2Ge2Te6, of the form A₂B₂X₆, are studied using density functional theory (DFT) calculations and machine learning tools. Magnetic properties, such as the magnetic moment are determined. The formation energies are also calculated and used to estimate the chemical stability. We show that machine learning, combined with DFT, provides a computationally efficient means to predict properties of two-dimensional (2D) magnets. In addition, data analytics provides insights into the microscopic origins of magnetic ordering in 2D. This novel approach to materials research paves the way for the rapid discovery of chemically stable 2D magnetic materials.

MT02.06.11
Machine-Learning-Based Band Gap Predictions of Functionalized MXenes Arunkumar C. Rajan, Avanish Mishra, Swanti Satsangi and Abhishek K. Singh; Indian Institute of Science Bangalore, India

MXene is a recent addition to the ever-growing family of two-dimensional (2D)-materials, promising for optical, electronic, energy storage and photocatalytic applications. Utilizing a statistical learning-based approach, we electronically characterize this vast class of materials by predicting their band gaps with GW level accuracy. Using a
classification model, MXene having finite band gaps are filtered out and few of them are selected to build a machine learning model. The model is built by correlating the easily available elemental and computed properties as features with respect to calculated GW band gaps of selected MXene. Depending upon feature combinations, Gaussian process regression method resulted in an optimized model yielding low root-mean-squared-error of 0.14 eV, which can be employed to estimate the accurate GW band gaps of tens of thousands of MXenes [1] within minutes. Our results demonstrate that machine learning model can bypass band gap underestimation problem of local and semi-local functionals used in DFT calculations, without subsequent correction using time-consuming GW approach [2].


MT02.06.12
Machine Learning the Fundamental Tradeoffs between Conductivity and Voltage Stability in Solid State Electrolytes Karun Kumar Rao, Michael Nikolaou, Yan Yao and Lars Grabow; University of Houston, United States

All solid state batteries provide many safety advantages over traditional lithium-ion batteries by replacing the combustible organic liquid electrolyte with a ceramic solid-state electrolyte. However, reported superionic conductors with conductivities approaching that of liquid electrolytes are unstable in contact with a lithium anode leading to increased internal cell resistance and poor cyclability. Conversely, compounds stable at the anode or cathode interfaces often do not exhibit useful bulk ionic conductivities. Although \textit{ab initio} methods exist to study each ionic conductivity and voltage stability range independently, there is no established theory to connect these two properties. Here, we leverage machine learning (ML) to investigate the role of crystal structure in the tradeoff between voltage stability and ionic conductivity. To this end, we trained a partial least squares (PLS) machine learning algorithm using the valence electronic density as a descriptor of 60 known solid-state electrolytes along with their corresponding ionic conductivity, anodic voltage limit, and cathodic voltage limit. In addition to exploring electron density, we also evaluate translationally invariant Fourier-based descriptors. The trained model has an 80% prediction accuracy and suggests that within the search space of crystal structures, the voltage stability and ionic conductivity are inherently inversely correlated. A multi-objective optimization also suggests that materials with positively correlated ionic conductivity and voltage stability may be highly anisotropic. Our PLS machine learning model, compared to the more conventional neural networks and other such models, has the benefit of being able to predict and explore the relationship between multiple properties and retains a high level of interpretability versus other ‘black box’ machine learning models. Moreover, we successfully quantify the uncertainty and confidence intervals in our model predictions which are often overlooked in other methods. The PLS model successfully identifies and quantifies the BCC anion substructure and channels as effective descriptors, which is in good agreement with prior work.\cite{Wang:2015} Using this model, we screened through a database of ca. 14,000 materials and identified five new promising solid state electrolyte candidates to have conductivities greater than 16 mS/cm. The model predictions were subsequently verified with \textit{ab initio} molecular dynamics simulations. The proposed ML model and electron density based descriptors may be used in future studies to elucidate other complicated structure-property relationships for other applications with high accuracy and without sacrificing interpretability.

References:

MT02.06.13
Spectral Optimization and Temperature Control for Electronic and Optoelectronic Devices Using Machine Learning Po-Ying Chen\textsuperscript{1}, Quang-Tuyen Le\textsuperscript{1}, Nan-Yow Chen\textsuperscript{2}, An-Cheng Yang\textsuperscript{2} and Yu-Chieh Lo\textsuperscript{1}; \textsuperscript{1}National Chiao Tung University, Taiwan; \textsuperscript{2}National Center for High-Performance Computing, Taiwan

The temperature and the cooling power of electronic components are important to many kinds of commercial electronic devices. There are lots of factors that could raise the temperature, and sunlight is one of them. However, when using solar cell as the power resource of devices, we can’t prevent it from sun exposure. Therefore, finding a proper material which has the best ability to reduce the temperature becomes inevitable. Recently, applying machine learning on material design has been significantly promoted, so we introduced machine learning to help us find out the better cooling materials. TensorFlow is the machine learning module in this work, and an optical simulation
software called DiffractMOD is used to produce training data. At first, besides the refractive index and extinction coefficient of different materials, a variety of geometric structures were also set as input. Next, DiffractMOD would output the transmittance, reflectance, and absorptance of corresponding wavelength. Furthermore, to calculate the equilibrium temperature and cooling power, we performed Fourier-transform infrared spectroscopy. By feeding those data into an autoencoder which is based on convolutional neural network, we could train the model and predict the optical coefficients and geometries for optimal performance. In this case, it can cool down the devices most effectively.

**MT02.06.14**

**Deep Learning for Multiscale Atomistic Modeling of Multicomponent Crystal Chemistries Coupled with Hirshfeld Surface Analyses**

Arpan Mukherjee, Aparajita Dasgupta, Tianmu Zhang, Scott Broderick and Krishna Rajan; University at Buffalo, United States

Hirshfeld Surfaces are coupled to machine learning to map information on the impact of each pair-wise interaction between bond chemistry and bond geometry in multicomponent systems. The Hirshfeld Surfaces encode both chemical bonding and molecular geometry information and are extremely effective in providing a multiscale electronic structure signature for accelerated materials selection and design, while providing an electronic fingerprint which captures both bond geometry and bond chemistry. Based on their geometric and chemical bonding interactions, we have developed libraries of fingerprints which are computationally ready to be analyzed with various machine learning methods. From the new library of Hirshfeld Surface calculations, when coupled with new analysis approach, we rapidly define similarity in compounds computationally. We show the application of machine learning approaches, such as convolutional neural networks, to quantitatively find and extract characteristics in the material fingerprints to develop rapid classifications across multiple material classes, chemistries and properties.

**MT02.06.15**

**Phase-Field Modeling and Machine Learning of Electric-Thermal-Mechanical Breakdown of Polymer-Based Dielectrics**

Jianjun Wang¹, Zhonghui Shen², Yang Shen² and Long-Qing Chen²; ¹The Pennsylvania State University, United States; ²Tsinghua University, China

Polymer nanocomposites are attracting rapidly increasing attention due to their many of advantages and promising potentials, arising from the designable and optimizable synergetic interaction between the polymer matrix and the functional filler nanoparticles. For example, they can be used in capacitors which are crucial components in energy storage for advanced electrical and power systems, such as electric hybrid vehicles and solar power generators. To achieve a high-energy-density storage in a dielectric capacitor, a combination of high dielectric constant and high breakdown strength is required. However, normal dielectrics with high dielectric constants tend to have low breakdown strength while those with high breakdown strength tend to have low dielectric constant. Therefore, optimizing a combination of dielectric constant and breakdown strength has been a grand challenge. A common approach to overcoming this dilemma is making polymer-ceramic nanocomposites which own the high breakdown strength of the polymer and the high dielectric constant of ceramics, so as to give rise to a high energy density which is proportional to the product of the dielectric constant and the square of the breakdown strength. In my presentation, I will show a computational approach by combining high-throughput phase-field simulations and machine learning to understand the breakdown mechanisms of polymer nanocomposite dielectrics under different operating conditions, as well as to design novel microstructures to achieve optimized breakdown strength, maximized energy storage and operating temperature. An analytical expression of the breakdown strength as function of the dielectric constant, electrical conductivity, and Young’s modulus was obtained from machine learning, which can be used to semiquantitatively predict the breakdown strength of the P(VDF-HFP)-based nanocomposites. I will also take about some targeted experiments which were designed to verify the high-throughput phase-field simulations and machine learning results.

**References:** (* and # represent corresponding author and co-first author, respectively)


Using Data Driven Models to Gain Insight on Spin- and Oxidation-State Dependent Behavior of Reaction Energetics for Light Alkane Oxidation

Aditya Nandy, Jon Paul Janet, Chenru Duan and Heather J. Kulik;
Massachusetts Institute of Technology, United States

Biological systems readily catalyze difficult chemical transformations such as direct methane to methanol conversion with high selectivity using earth abundant transition metals (e.g. Fe and Cu). Computational high-throughput virtual screening (HTVS) with first-principles density functional theory (DFT) can play a valuable role in unearthing design rules for scalable, industrially viable synthetic analogues that preserve this selectivity and activity. Single-site catalysts represent the most promising analogues to these enzymes, often enabling atom-economy and selectivity not possible with bulk heterogeneous catalysts. Simultaneously, a wide chemical space must be explored to uncover potential single-site catalysts to simultaneously address other constraints, such as high turnover number or robustness, earth abundance, and synthesizability. Single-site catalysts have the added dimensionality of spin- and oxidation-state—which can drastically impact the structure-property relationships of molecular complexes—and remain unexplored for catalyst reaction energetics. The large dimensionality of the single-site catalyst chemical space becomes quickly intractable with DFT. Thus, we demonstrate our developments on data-driven models for key steps in single-site light alkane oxidation catalysts, which enable the prediction of reaction energetics in a spin- and oxidation-state dependent manner close to the accuracy of DFT. We first compare prediction of reaction energetics to other quantum mechanical properties that we have predicted, such as spin-splitting energetics, ionization potential, and frontier orbital energetics. We then discuss insights on representative catalytic reaction steps such as oxo formation and hydrogen atom transfer, including their dependence on spin- and oxidation-state. Lastly, we demonstrate the power of artificial neural-network and kernel ridge regression models for purposes of screening, enabling screens of large design spaces that would be infeasible to screen by DFT, even with the reduction in number of calculations through the use of descriptor energies. We uncover cases of molecules that would be overlooked by quantum mechanical descriptors, or would be missed by chemical intuition. Having separate data driven models for different reaction energy steps allows predictions of reaction energies that contain weak or nonexistent linear free energy relationships (LFERs), commonly employed in heterogeneous catalysis, but less prevalent in homogeneous catalysis.

Self-Evolving Neural Network Potentials for Supramolecular Interactions

Wujie Wang, William Harris and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

Neural networks based on atomic embeddings have demonstrated accurate force and energy evaluations to simulate physical systems [1-5]. However, training neural potentials requires expensive sampling of configurational space and one needs to perform ab initio MD simulations to generate training data [6]. For the purpose of high throughput discovery, such brute force sampling is computationally infeasible to screen thousands of molecules. To this end, we propose a self-consistent strategy that accelerates the sampling and training of transferable neural networks over molecular space of interests, particularly to capture supramolecular interactions that are critical for applications like designing chelating agents and electrolytes. The proposed method combines deep neural network training and active sampling of both chemical and configurational space in an end-to-end fashion to 1) bypass expensive ab initio MD sampling and 2) leverage the transferable configurational information across species. We show that this active learning [7] method can improve neural network potentials in a self-consistent way and demonstrate its use in performing high throughput screening of lithium binding molecules.

References:
MT02.06.18
Artificial Intelligence Design of Tunable Nanocomposites for Crack Resistance  
Chi-Hua Yu, Zhao Qin and Markus J. Buehler; Massachusetts Institute of Technology, United States

Here we report a new design approach for nanocomposite materials using artificial intelligence (AI). The algorithm consists of a machine learning predictor conjoined with an AI improved genetic algorithm, applied to discover materials designs in a vast space of possible solutions. Facilitated by a generative neural network that is trained with a dataset of thousands of combinations of soft and brittle materials to generate high resolution tessellate geometries, we design the material properties of novel graphene nanocomposites without running conventional simulations. Through the algorithm, we extend the capability of physical simulations beyond property predictions to optimize the fracture toughness by altering the material distribution. The solutions are generated by our AI model at a dramatically lower computational cost compared to brute-force searching methods. We further investigate the physical mechanism for improving the performance behind the AI approach and demonstrate the ability of AI to search for optimal designs with very limited sampling. Molecular dynamics simulations of the nanocomposite designs show that our AI design improves the performance by effectively decreasing the stress concentration at crack tips.

The AI approach reported here can be easily applied to other nanocomposites, biomaterials, and other material classes, and provides a transferrable, efficient and reliable design approach.

SESSION MT02.07/MT03.08: Joint Session: Machine Learning Augmented High-Throughput Experimentation I
Session Chairs: Jason Hattrick-Simpers and Bruce van Dover
Wednesday Morning, December 4, 2019
Hynes, Level 2, Room 210

8:00 AM *MT02.07.01/MT03.08.01
Automating Experiments and Data Interpretation in Solar Fuels and Catalysis Research  
John M. Gregoire; California Institute of Technology, United States

Automating critical steps of synthesis and screening experiments enables a variety of modes of materials exploration. High throughput experimentation comprises a family of techniques wherein materials systems can be comprehensively explored, and the resulting data relationships, e.g. composition-property and composition-structure-property relationships, are emblematic of the knowledge obtained from the experiments. Application of high throughput experimentation for solar fuels technology, in particular (photo)electrocatalysis of the oxygen evolution reaction, has led to a breadth of discoveries, many of which are based on high throughput computational screening. The resulting database of experiments, which is publicly released as the JCAP Materials Experiment and Analysis Database (MEAD) containing 6.5 million measurement files collected on 1.5 million materials samples, is a key resource for developing and evaluating algorithms that automate data interpretation. Successes to date include application of machine learning techniques to learn, identify, and communicate hidden data relationships. At a high level, these algorithms automatically generate answers to human-identified research questions, moving the frontier of artificial intelligence in materials discovery to the automatic identification of the interesting research questions.
8:30 AM MT02.07.02/MT03.08.02
Cooperative Learning for Materials Systems Valentin Stanev; University of Maryland, College Park, United States

Recently, materials scientists have started to utilize machine learning to accelerate experimental research. Active learning – an AI field dedicated to optimal experimental design – is a particularly promising tool; it provides systematic means to identify the shortest path toward a material with some desired properties or the experiments that maximize knowledge of the explored space. In many materials science tasks, however, the goal is to obtain a mapping between two or more experimentally measured quantities. Standard active learning algorithms may not be optimal for such complex scientific problems. Reducing the experimental effort to obtain such mappings can be optimized not by independently running several active learning tasks but rather by a strategy coordinating different experiments performed simultaneously. In this talk I will present the idea of cooperative learning, and illustrate it with examples from several different high-throughput studies.

8:45 AM MT02.07.03/MT03.08.03
Exploring Catalyst Chemistries beyond Scaling Laws using Statistical Learning Scott Broderick, Aparajita Dasgupta, Thaicia Stona and Krishna Rajan; University at Buffalo, United States

We have significantly expanded the knowledge-base of metal catalysts through a unique combination of manifold learning, Gaussian process regression and clustering approaches. Given the complexity in performing catalytic measurements, the amount of data available for selecting ‘optimal’ catalysts for specific reactions is limited. The work described here develops an analysis framework suitable to the small number of measurements available, while also developing a large relevant descriptor-base. We have performed the foundational work needed to develop a catalyst discovery toolkit. Using volcano plots as a platform, we have fused manifold learning methods and graph network methods from which one can rapidly explore new chemistries for single atom alloy (SAA) catalysts. We use single atom systems for testing our robustness, with the added benefit that prior work on single atom systems has not utilized machine learning. Using SAAs allows for a rapid screening of the combinatorial design space. We developed a machine learning logic for screening chemistries to define necessary detailed DFT calculations and have identified 28 alloys which are most promising for further exploration.

9:00 AM MT02.07.04/MT03.08.04
Graph Theory and Machine Learning Uncover Zeolite Transformation Pathways Daniel Schwalbe Koda, Wujie Wang and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

Zeolites are inorganic nanoporous materials with broad industrial applications as catalysts, ion exchangers, and separators. Despite sustained research, controlling polymorphism is still a critical challenge in their design, relying mostly on trial-and-error. First-principles calculations could aid the search for new frameworks, but the number of theoretically accessible topologies and the complexity of their kinetic mechanisms render this approach computationally prohibitive. Here, we employ a suite of computational tools such as big-data, graph theory, structural kernels, density functional theory (DFT), and machine learning to explain and predict zeolite transformations. We first relate solid-state transformations to materials descriptors by combining crystallography with a graph-theoretical metric. Supported by exhaustive literature, we then show that interzeolite diffusionless transformations occur only between graph-similar pairs. Moreover, all known instances of intergrowth take place between either structurally- or topologically-similar structures. Our metric suggests hundreds of low-distance pairs between known frameworks and thousands of hypothetical frameworks for realizing novel transformations and intergrown crystals. Such insights are further refined by atomistic simulations. Building on millions of DFT calculations, we parameterize interatomic interactions in pure-silica zeolites using neural network models and active learning. The method enables accurate structural optimizations and off-equilibrium energy sampling with low computational cost, allowing the selection of favorable graph-driven phase transitions between frameworks and uncovering new synthetic pathways for zeolites.

9:15 AM MT02.07.05/MT03.08.05
Automatic Processing of the Scientific Literature to Accelerate Nanomaterials Design and Discovery Anna M. Hiszpanski, Brian Gallagher, Karthik Chellappan, Peggy Pk Li, Shusen Liu, Hyojin Kim, Jinkyu Han, Bhavya
A significant challenge in utilizing machine learning approaches to accelerate materials development is the lack of large and structured data sets. While there are ongoing community efforts to create collaborative materials databases and repositories for this purpose, the diversity and breadth of data types, length scales, and applications still makes it challenging to create such all-encompassing materials databases that are of broad practical use. However, if tools are developed to automatically process the vast scientific literature and extract and structure information of interest to a given user, then such tools can enable the easy creation of personalized databases with user-specified relevant information to which data mining approaches can then be applied.

We developed such tools for the automated extraction of a suite of information from the text of articles pertaining to nanomaterials synthesis and demonstrate their utility for nanomaterials synthesis. Attaining nanomaterials of desired composition, dimension, and morphology is critical for end-use applications but challenging to do, often requiring time-consuming iterations of synthesis and characterization. Using a corpus of 35k nanomaterials-related articles, we first use a simple unsupervised classification algorithm based on the frequency of occurring terms to identify the primary nanomaterial composition and morphology in each article. Classifying and analyzing articles based on their targeted nanomaterial composition and morphology by itself provides a bird’s eye view and can help identify “hot topics” in the field or alternatively under-studied or challenge-to-synthesize nanomaterials. Next, we apply a supervised machine learning approach to our corpus to identify and extract from articles’ text the sentences related to the nanomaterials’ synthesis protocols, thereby yielding a useful synthesis reference library. Interestingly, we find that function words (i.e., to, in, for, of, at) commonly omitted in natural language processing of non-scientific text are in fact a characteristic trait in discriminating between synthesis- and non-synthesis-related sentences in scientific text. With synthesis protocols in-hand, we further process these via chemical entity recognition (CER) to identify and extract the chemicals used in various nanomaterials’ syntheses. We evaluate a variety of open-access CER tools, as well as our own in-house developed CER tool, that each utilize different tokenizers for parsing the text and techniques for identifying chemicals, and we find that, despite the variety of approaches undertaken, most tools have comparable performance with a peak f1 score of 87%. Normalizing the chemicals names extracted from articles, we then have the opportunity to compare the frequency of use of chemicals for various nanomaterial morphologies. We demonstrate how such analysis provides useful insights as to the importance of chemicals in directing the growth of nanoparticles during synthesis to desired morphologies, like for example nanowires versus nanospheres versus nanocubes. We package this database created entirely by extracting information from existing nanomaterials literature into a browser-based visualization tool we developed that enables easy exploration of the data, thereby helping guide hypothesis generation and reduce the potential parameter space during experimental design.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-777678

9:30 AM BREAK

10:00 AM *MT02.07.07/MT03.08.07*
High Throughput Experimental Materials Research Methods at NREL. Andriy Zakutayev; National Renewable Energy Laboratory, United States

Bridging the gap between computational predictions and industrial applications requires acceleration and automation of experimental synthesis, characterization and data analysis. High Throughput Experimentation (HTE), also known as combinatorial experiments, is one possible approach to accelerate materials research. Thus, HTE combinatorial methods have been regarded as a promising approach to fulfill the promise of the materials genome initiative (MGI)[1], complementary to high throughput computations and industrial research and development. This presentation will focus on the state of high throughput experimental materials research methods at National Renewable Energy Laboratory (NREL). First, I will discuss methods for creating later gradients of thin film sample properties, in particular going beyond chemical composition of metals [1]. Then, I will talk about spatially-resolved characterization methods, including interlaboratory exchange of samples [2]. Finally, I will highlight our efforts in streamlining data analysis in combinatorial materials science, including a recently published COMB1gor software package [3]. These methods will be illustrated by a broad range of materials examples, including oxides, chalcogenides, and nitrides.

10:30 AM MT02.07.08/MT03.08.08
Machine Learning-Assisted High Throughput Synthesis and Characterization of Hybrid Polymer-Carbon Nanotubes Composites for Thermoelectric Application Daniil Bash1,2, Anas I. Abutaha2, Yang Xu2, Yee Fun Lim2, Vijila Chellappan2, Zekun D. Ren3, Isaac S. Tian1,1, Pawan Kumar2, Swee Liang Wong2, Jose Recatela Gomez2,4, Jayce J. Cheng2, Tonio Buonassisi5,3 and Kedar Hippalgaonkar2; 1National University of Singapore, Singapore; 2Institute of Materials Research and Engineering, Singapore; 3Singapore-MIT Alliance for Research and Technology (SMART), Singapore; 4University of Southampton, United Kingdom; 5Massachusetts Institute of Technology, United States

The so-called 4th revolution in science began with the advent of machine learning (ML), as well as high-throughput (HT) experimentation and robotization. Herein, we describe a workflow that enables rapid screening of a parameter space of hybrid composites, comprised by carbon nanotubes and poly-3-hexylthiophene (CNTs:P3HT) for thermoelectric (TE) applications, with Bayesian optimization embedded in the feedback loop in order to explore the space in a more efficient fashion.

The parameter space under scrutiny includes 4 types of nanotubes (both single- and multiwall), 16 CNTs:P3HT ratios, 2 solvents (o-DCB, and chloroform) and 3 doping conditions, which result in 384 unique synthetic parameters. The setup used involves a robotic pipettor and the microfluidic flow reactor with XY stage for automatic drop casting. We synthesize more than 150 samples per hour, as compared to 4 samples per hour with traditional manual procedures. Characterization was done with means of hyperspectral imaging and 4-point-probe measurements to ascertain optical properties and electrical conductivity.

The conductivity data of the initial experiments was used to train the ML algorithm. After training, the algorithm inferred new experimental conditions for achieving highest possible conductivity, closing the feedback loop. In the end, 3 iterations of the experiments yielded the value of conductivity higher than 150 S cm⁻¹.

Further work includes the optimization of the experimental setup as well as the ongoing effort to use hyperspectral imaging to bypass the bottleneck step i.e. profilometry, as it is the main source of error.

10:45 AM MT02.07.09/MT03.08.09
Data-driven Materials Design of Halide Perovskites for Photovoltaic Applications Shijing Sun1, Noor Titan Putri Hartono1, Felipe Oviedo1, Zekun D. Ren1, Janak Thapa1, Zhe Liu1, Armi Tiihonen1, Ian Marius Peters1, Juan Pablo Correa Baena2, Tonio Buonassisi1 and Savitha Ramasamy3; 1Massachusetts Institute of Technology, United States; 2Georgia Institute of Technology, United States; 3Institute of Infocomm Research, Singapore

To meet increasing global energy demand, it is critical yet challenging to explore new methods to accelerate the development of novel energy materials. In recent years high-throughput experimentation (HTE) and machine-learning techniques have become increasingly accessible to scientific researchers. We herein demonstrate a case study on the data-driven design of perovskite-inspired materials for photovoltaic applications, where we employed machine-learning techniques to guide the synthesis of new halide perovskites for photovoltaic applications. Halide perovskites (ABX₃, where A = Cs, methylammonium (MA), formamidinium (FA); B = Pb, Sn; and X = Cl, Br, I) have shown great promise as light absorbers. Solar cells based on perovskites have surprised the energy community as an emerging low-cost photovoltaic technology with a record power conversion efficiency (24.2%) now exceeding polycrystalline Si cells (22.3%).[1] In this study, we developed a high-throughput experimental platform for thin-film synthesis and characterization, and investigated 75 unique perovskite compositions interest for energy-harvesting applications in a two-month period. To achieve desired optoelectronic properties, we established a set of selection criteria for screening. A deep neural network is employed to classify compounds into 0D, 2D, and 3D perovskite structures via X-ray diffraction patterns analysis. [2] The combination of fast synthesis and machine-learning assisted data diagnostics achieves an acceleration of over an order of magnitude per experimental learning cycle over our laboratory baseline. Among the 41 Pb-free perovskite compositions studied, we identified the optimised doping level in a multi-site alloy series, Csₓ(Bi₁₋ₓSbx)(I₁₋ₓBrx)₉, where a desired structural (2D) and optical properties (< 2 eV). [3] Our work contributes to the prospect of automated materials discovery and we envision an accelerated development in functional materials in the next decade aiming to provide new energy solutions.
11:00 AM MT02.07.10/MT03.08.10
Application of Variational Autoencoders to Create Thin Film Structure Zone Diagrams Lars Banko, Yury Lysogorskiy, Ralf Drautz and Alfred Ludwig; Ruhr-Universität Bochum, Germany

Structure zone diagrams (SZD) are frequently used to estimate thin film microstructures based on a few chosen synthesis parameters. Despite their usefulness, the predictive power of classical SZD is very limited due to the complexity of the synthesis-microstructure relationship of thin films. Furthermore, the complicated interplay of many synthesis parameters and compositional complexity hinders a generalisation. Classical SZD have in common that they are based on a small number of observations. Underlying trends were extracted by the scientists’ expertise and in a creative process abstracted into a diagram representation of microstructural features. Several refined SZD were proposed, which implemented more physical parameters. With emerging developments in combinatorial thin film synthesis and high-throughput characterization a fast, high-quality acquisition of microstructure data is now possible. This and progress in machine learning of images now provides tools to handle complex image data and improve SZD: We present a dataset containing > 100 samples of SEM surface images from Cr-Al-O-N material libraries, each featuring a different chemical composition and synthesis condition such as deposition temperature, ion energy and sputter frequency of high power impulse magnetron sputtering (HiPIMS). We train convolutional variational autoencoders (VAE) on this dataset of augmented SEM surface image data. Results show that VAEs can cluster microstructure data through latent space representations. The performance of different neural network architectures is discussed. The VAEs generative capabilities to predict SEM surface images from chemical composition and synthesis parameters are investigated. By sampling of the latent representation, we are able to generate SZDs for different variations and combinations of input parameters like temperature, ion energy and chemical composition. The qualitative trends which we observe demonstrate the prediction of microstructure by generative deep learning models.

11:15 AM MT02.07.11/MT03.08.11
Generative Adversarial Networks with Molecular Graph Convolution for Learning Secondary Structures of Functional Biomolecules Siddharth S. Rath1,1,1, Oliver Nakano-Baker1,1, Jonathan Francis-Landau1,1, Ximing Lu1,1, Kevin Jamieson1,1, Burak B. Ustundag1,2 and Mehmet Sarikaya1,1,1; 1University of Washington, United States; 2Istanbul Teknik Universitesi, Turkey

Generative models, a recent paradigm in machine learning has revolutionized the industry by generating ‘natural looking’ data. While such models have found limited applications in the domain sciences, they display untapped potential in generating materials or molecular structures commensurate with target properties and desired functionalities. While the protein folding problem has been addressed previously by multilevel computational methods and various deep convolutional neural networks, unfortunately, the key step of encoding atomic structures for computational treatment is a challenge. Historical efforts have focused on pre-process featurization that relies upon traditional string representation without any structural information, expert-designed heuristics-based inputs, or on volumetric modeling that presumes a specific predetermined conformation without associated functionality. Here we demonstrate the first implementation of generative models, more precisely, generative adversarial networks with graph encoding of atomic connectivity within the biomolecules, for data-driven prediction of peptide and protein conformations associated with particular functionalities such as binding to atomically flat surfaces and biomineralization. In the graph input, atoms are considered as nodes and the bonds are considered edges, while angles in the molecule are encoded as a third order tensor between any three nodes. The generator tries to output secondary structures in terms of the bond edges and angle tensors while the discriminator network learns from

existing sequences and their secondary structures from pdb files and MD simulations. We test the predicted results with MD simulations as well as circular dichroism experiments. Results show that the generative model developed herein is generalizable to any functionality and more accurate than existing methodologies for predicting functionality-associated peptide conformations for practical implementations in disease diagnostics, drug screening, biosensing and bioelectronic devices. As part of the Materials Genome Initiative, the research is supported by NSF-DMREF program through the grant DMR-1629071.

SESSION MT02.08/MT03.09: Joint Session: Machine Learning Augmented High-Throughput Experimentation II
Session Chairs: Ichiro Takeuchi and Andriy Zakutayev
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 210

1:30 PM *MT02.08.01/MT03.09.01
Prediction Interpretability in Data-Driven Materials Development Julia Ling, Astha Garg, James Peerless, Erin Antono, Edward Kim, Yoolhee Kim, Nils Persson and Malcolm Davidson; Citrine Informatics, United States

Sequential learning is a data-driven workflow for accelerating materials development. In this iterative workflow, machine learning models are used to explore a “design space,” the set of possible experiments that could be performed, to surface promising candidate materials. Experimental data for those candidate materials are used to retrain the models so that they can provide successively better-informed suggestions.

For sequential learning to be effective, a relevant design space of candidate materials must first be constructed. These design spaces often include complex constraints, as well as a mix of continuous and categorical variables. The machine learning model can be used to sift through the design space to surface the most promising candidates. For these top candidates, it is valuable to have insights into how the model made its predictions and why it predicts high performance. Interpretability analysis can increase confidence in the model predictions, uncover sample bias in the underlying training data, and provide information on the robustness of the predicted performance. This talk will discuss approaches for constructing relevant design spaces and for interpreting model predictions, and show how these approaches fit into the overall sequential learning workflow.

2:00 PM *MT02.08.02/MT03.09.02
Network Theory Meets Materials Science Vinay Hegde1, Muratahan Aykol2 and Christopher Wolverton1;
1Northwestern University, United States; 2Toyota Research Institute, United States

One of the holy grails of materials science, unlocking structure-property relationships, has largely been pursued via bottom-up investigations of how the arrangement of atoms and interatomic bonding in a material determine its macroscopic behavior. Here we consider a complementary approach, a top-down study of the organizational structure of networks of materials, based on the interaction between materials themselves. We demonstrate the utility of applying network theory to materials science in two applications: First, we unravel the complete “phase stability network of all inorganic materials” as a densely-connected complex network of 21,000 thermodynamically stable compounds (nodes) interlinked by 41 million tie-lines (edges) defining their two-phase equilibria, as computed by high-throughput density functional theory. We find that the node connectivity in the materials network has a lognormal distribution, and the connectivity decreases with the number of elemental constituents in a material. Analyzing the topology of this network of materials has the potential to uncover new knowledge inaccessible from traditional atoms-to-materials paradigms. Using the connectivity of nodes in this phase stability network, we derive a rational, data-driven metric for material reactivity, the “nobility index”, and quantitatively identify the noblest materials in nature. Second, we apply network theory to the problem of synthesizability of inorganic materials, a grand challenge for accelerating their discovery using computations. We combine the above phase stability network with timelines for the first experimental synthesis of each compound from literature citations. This allows us to create a time-dependent network, and from the time-evolution of the underlying network properties, we use machine-learning to predict the likelihood that hypothetical, computer generated materials will be amenable to successful experimental synthesis. **In collaboration with S. Kirklin, L. Hung, S. Suram, P. Herring, and J. Hummelshoj
2:30 PM BREAK

3:30 PM MT02.08.03/MT03.09.03
A Database to Enable the Discovery and Design of Atomically Precise Nanoclusters
Sukriti Manna, Peter Lile, Alberto Hernandez and Tim Mueller; Johns Hopkins University, United States

Atomically precise nanoclusters can be used for numerous applications due to the unique properties they possess. Despite their wide range of applications, the structures and properties of many small elemental clusters remain unknown. We present the “The Quantum Cluster Database,” an open-access source containing the structures and properties of tens of thousands of cluster structures of up to 55 atoms for 55 elements. The structures are compared against previous computational and experimental data where available. We discuss the methods that are being used to accelerate the construction of the database and describe how the database can be accessed for cost-effective, data-driven materials design.

3:45 PM MT02.08.04/MT03.09.04
Data Driven Experimental Discovery of New Nitride Materials
Sage Bauers1, Elisabetta Arca1, Wenhao Sun2, Chris Bartel3, John D. Perkins1, Aaron Holder3, Stephan Lany1, Gerbrand Ceder2 and Andriy Zakutayev1; 1National Renewable Energy Laboratory, United States; 2University of California, Berkeley, United States; 3University of Colorado Boulder, United States

New materials enable new technologies, so discovery of new materials is one of the most important directions in materials research. Oxides and some other materials chemistries, which have been extensively explored in the past, yielded many spectacular properties. Other chemistries, such as nitrides, have been barely touched: for every 14 documented oxides there is only 1 known nitride.

We will present on data-driven experimental discovery of new nitride materials, focusing on experimental synthesis and characterization, while also featuring computational predictions and machine learning. The data mining efforts followed by first-principles calculations and machine learning analysis indicated that there are 93 unexplored ternary metal nitride chemical spaces, with 244 new predicted stable ternary materials, and explained the stability trends among these and other nitrides [1].

Experimental synthesis using high-throughput combinatorial methods realized 7 of these compounds, including Zn-M-N (M= Sb, Mo, W) with wurtzite-derived crystal structures and Mg-TM-N (TM = Nb, Ti, Zr, Hf) with rocksalt-derived crystal structures. Physical property characterization results of the ternary rocksalts indicate that they are semiconductors with 1.8-2.1 eV optical absorption onsets and large dielectric constants [2]. The Zn-Sb-N wurtzite is the first ever reported Sb-containing nitride, with Sb in unusually high 5+ valence state, and measured room-temperature photoluminescence near 1.6-1.7 eV solar matched band gap [3].

Overall, these results both demonstrate the power of data-driven materials discovery, and suggest that many new previously unreported nitride materials remain to be synthesized.


4:00 PM *MT02.08.05/MT03.09.05
Active Learning for Nanophotonic Design via Multi-Fidelity Physical Models
Harry A. Atwater1, Jialin Song1, Yury S. Tokpanov1, Yuxin Chen1, Dagny Fleischman1, Katherine T. Fountaine2 and Yisong Yue1; 1California Institute of Technology, United States; 2Northrop Grumman Corporation, United States

We have explored the design of nanophotonic structures, such as subwavelength-scale spectral filters, using an advanced active machine learning algorithm that efficiently explores multiple physical models with different approximation fidelities and costs. Our method, which is applicable to a variety of nanophotonics optimization problems, employs a novel strategy consisting of a mutual information based multi-fidelity Gaussian process optimization algorithm (MF-MI-Greedy). It consists of two components: an exploratory procedure to gather information about the target (i.e., the highest fidelity) function via querying lower fidelity functions, followed by an exploitative procedure to optimize the target level fidelity with the previously gathered information. Our results on
several pre-collected nanophotonics datasets demonstrate the compelling performance of the multiple-fidelity Bayesian optimization approach. These experiments suggest that there is a significant potential in utilizing cheap, multi-fidelity simulations to aid the discovery of optimal photonic nanostructures.

4:30 PM MT02.08.06/MT03.09.06
Accelerating Materials Discovery through Rapid Construction of Processing Phase Diagrams
Duncan Sutherland, Aine Connolly, Sebastian Ament, Michael O. Thompson, Carla Gomes and Bruce van Dover; Cornell University, United States

Exhaustive experimental mapping of non-equilibrium processing phase diagrams demands a prohibitively huge allocation of resources for even a single realistic system with more than two compositional degrees of freedom, even with current state-of-the-art high-throughput techniques. Advanced data analysis methods are thus called for to accelerate such explorative efforts, focusing on multimode analysis of critical boundary points in the phase diagram where transitions are observed. Here, we present a hierarchical, prioritized data analysis structure to optimize usage of costly experimental resources. By combining data analysis methods based on optical characterization and x-ray diffraction with sophisticated active learning algorithms, we can efficiently map phase boundaries in composition-time-temperature processing phase diagrams. We demonstrate the utility of our approach by constructing processing phase diagrams for spike annealed multicomponent oxide materials.

4:45 PM MT02.08.07/MT03.09.07
High-Throughput Screening of Perovskite-Inspire Materials Using Steady-State Photoconductivity and Bayesian Optimization
Jose D. Perea, Felipe Oviedo, Han Yin, Janak Thapa, Armi Tiihonen, Zhe Liu, Ian Marius Peters, Shijing Sun, Rafael Jaramillo and Tonio Buonassisi; Massachusetts Institute of Technology, United States

Hybrid organic-inorganic perovskites solar cells have recently increased scientific interest for their manufacturing simplicity and high performance, challenging the best thin-film photovoltaic devices. Perovskites solar cells have broad and strong light absorption along with excellent transport properties that partly explain their record power conversion efficiency above 24% [1, 2, 3]. Compositional engineering of perovskites is a time-consuming effort. Reaching high efficiency in compositions with complex and diverse dopants that usually requires significant trial and error and hundreds of measurements of full solar cells [4]. In addition to the abundance of applied research on this subject, there is great interest in understanding the fundamentals of transport and photophysical properties of various perovskites compositions [5]. High-throughput methods for screening compositions at the film level could be a potentially powerful alternative to investigate the complex perovskite composition space efficiently. Nevertheless, screening for high-efficiency perovskite compositions with high-throughput methods is not yet firmly established, in part due to the complexity of photophysical characterization experiments at the film level. In this work, we report for the first time a combination of high-throughput conventional steady-state photoconductivity method, (SS-PC) to determine diffusion lengths and Bayesian optimization methodology. This approach allows us to investigate the complex compositional space efficiently by just making films and not full solar cells. By using QSS-PC as a proxy for efficiency, we use Bayesian optimization to guide compositional changes and obtain the best solar cell efficiency for a given material, accelerating material screening by 10X.

[5] Y. Chen et al. NATURE COMMUNICATIONS | 7:12253 | DOI: 10.1038/ ncomms12253 |
MT02.09.01
Machine Learning for Revealing Aging Mechanisms of Perovskite Solar Cells
Armi Tiihonen, Shijing Sun, Jose D. Perea, Felipe Oviedo, Zhe Liu, Noor Titan Putri Hartono, Janak Thapa and Tonio Buonassisi; Massachusetts Institute of Technology, United States

Perovskite solar cells are among the most promising new photovoltaic technologies, boasting with rocketing efficiency records and raising interest as a component of tandem solar modules. Although the stability of perovskite solar cells is steadily improving and the most stable perovskite devices already pass 1000-hour aging tests under operating conditions [1], insufficient lifetime still remains a major bottleneck of the technology.

The aging mechanisms of perovskite solar cells need to be understood better for suppressing them. Several aging mechanisms, such as perovskite decomposition or ion migration in the device [1], have been identified in literature, and the observed aging mechanisms depend highly on the environmental conditions the devices are facing, such as temperature, humidity, and visible or ultraviolet illumination. More information about the activation and ground causes of the degradation of the devices is still needed, but the majority of aging tests in the literature do not demonstrate clear degradation of the devices [2]. The next step is to shift the focus of research community towards longer aging tests producing clear degradation with detailed analysis [1-2], and new working methods, such as machine learning, are required for extracting all the possible information from the laborious aging test.

In this contribution, we create a comprehensive mapping of the degradation of perovskite solar cells by aging devices until clear degradation under several different combinations of environmental stress conditions, such as illumination, increased humidity, and high temperature. Automated measurement systems are utilized for collecting densely sampled aging data with sample sizes that are statistically significant. We utilize machine learning methods for analyzing the relatively large data set our approach produces. This way, we are able to extract more refined information on the activation and interlinking of the detected aging mechanisms.

Reference:

MT02.09.02
High-Throughput Discovery of Next Generation Sequencing-Based Peptide-Guided New Materials via Machine Learning
Jacob Rodriguez, Deniz T. Yucesoy, Siddharth S. Rath, Jason Stephany, Doug Fowler and Mehmet Sarikaya; University of Washington, United States

A crucial problem in the development of nanobiotechnology is control of the interface between the organic molecule and the substrate. Mastery of the field would enable highly sensitive biosensors capable of detecting disease biomarkers, affinity-tunable drugs, and efficient synthesis of solid biomaterials, among many other applications. Peptides are short amino acid sequences (4-40 long) that can have diverse conformational states when placed near a bias (i.e., 2-D materials, e.g., MoS2, electrical fields, etc.) and/or in solution (i.e., PBS, deionized water, etc.). These sequences can be found in larger proteins or designed in silico when the conformational behavior is often well-defined. Machine learning approaches may be used in many applications including drug design and continues to produce successful results. However the large data sets are required to train the ML algorithms to enable them to identify the dominant features. In a convergent science approach, here we identified three biological replicas of ~2.5 million unique 12-amino acid long peptide sequences with affinity for MoS2 using a novel method that combines Next-Generation Sequencing and Phage-Display directed evolution approaches. The massive size of this dataset grants a much greater understanding of why peptides bind to MoS2 upon development of the correct model or a large amount of experimental validation. We have developed a multitude of machine learning applications for the prediction of binding behavior including linear regression and recurrent neural network methods. Both methods seek to predict the functional affinity of this massive MoS2 binding set using the data from the combinatorial libraries that
are indirectly related to the solid-binding affinity. Further, the diversity in our approach yielded informative conclusions about the types of ML applications appropriate for this genetic dataset. Our results show that the functionality of peptides can be predicted using linear regression within and across replicates with high accuracy (0.75 to 0.9 Pearson/Spearman Rank Correlation). Encouraged by the preliminary results, we are currently implementing ML-assisted directed evolution experiment along with recurrent neural networks to determine the evolution path for high throughput labelling towards creating custom libraries. The research is supported by NSF-DMREF program through the grant DMR-1629071 as part of the Materials Genome Initiative.

**MT02.09.03**  
**Data Driven Analysis of Dielectric Constants in Inorganic Materials**  
Kazuki Morita¹, Daniel W. Davies¹, Keith Butler²,¹ and Aron Walsh¹,³; ¹Imperial College London, United Kingdom; ²Rutherford Appleton Laboratory, United Kingdom; ³Yonsei University, Korea (the Republic of)

Dielectric constants are crucial to understanding optical and electric properties of materials. A low-cost predictor of dielectric behaviour would be highly valuable in materials science. Models such as Clausius-Mossotti and Penn's model are well known and have been used intensively, however, they are known to only hold for limited types of compounds. Previously, Han and co-workers have screened ~2000 compounds to find high dielectric constant materials with a large band gap[1,2]. They reported several materials that do not follow the existing models. Simple physical models are generally inadequate to capturing the trends in dielectric constants, which derive from many-body interactions. We propose the use of statistical approaches to describe them. We train multiple machine learning models using database of 1636 compounds. Our analysis show that some models were successful in capturing the complex trends in dielectric behaviour. Comparing with conventional models, the machine learning model gave an order of magnitude improvement in predictive power. The chemical trends in dielectric constants will also be discussed.

[1] Novel high-κ dielectrics for next-generation electronic devices screened by automated ab initio calculations. NPG Asia Mater. 7, e190 (2015); https://doi.org/10.1038/am.2015.57


**MT02.09.04**  
**A Semi-Automatic Pipeline for Efficient and Sustained Polymer Data Capture**  
Pranav Shetty and Rampi Ramprasad; Georgia Institute of Technology, United States

Machine Learning (ML) has enabled huge strides to be made in fields as diverse as Computer Vision, Natural Language Processing, Robotics etc [1][2]. Materials Science has also seen a flurry of work in recent years involving use of statistical techniques to predict material properties. ML models are data-hungry and their predictive accuracy improves asymptotically with the amount of data fed into it. As most materials property data is in journal papers and not in an easy to use database, prospective researchers must painstakingly extract this data manually. We hope to address this issue in the polymer space by building a framework that can automatically extract polymer property data from published literature. Data can be extracted systematically from 1000’s of papers to generate insight that would be very difficult to do manually.

Our framework aims to capture data from text in published literature and from tables. We generate word vectors [3], a mathematical way of representing words in a high dimensional space, from our corpus of polymer papers and use those to tokenize the text and thus extract polymer property information. We extract properties such as glass transition temperature, polymer melting temperature, dielectric constant, refractive index etc from tens of thousands of papers to generate ~1000’s of data points for each property. Similar work has been done in the space of extracting synthesis parameters for inorganic materials from literature [4][5] but this is the first such framework for the polymer domain. With the extracted data, we can power ML models that can be used to accelerate materials discovery and design new polymers.

**References**

SESSION MT02.10: High-Throughput Experimentation and Machine Learning I
Session Chairs: Brian DeCost and John Perkins
Thursday Morning, December 5, 2019
Hynes, Level 2, Room 210

8:30 AM *MT02.10.01
Beyond Just Fitting Numbers—Artificial Intelligence for Identifying Statistically Exceptional Materials
Matthias Scheffler1,2 and Luca Ghiringhelli1; 1Fritz-Haber-Institut der MPG, Germany; 2Humboldt-Universität zu Berlin, Germany

Several issues hamper progress in data-driven computational science. In particular, these are a missing FAIR [1] data infrastructure and appropriate data-analytics methodology [2].

Significant efforts are still necessary to fully realize the A and I of FAIR. Here the development of metadata, their intricate relationships, and data ontology need more attention. Obviously, a FAIR data infrastructure – for being accepted by the community – should work without bureaucratic hurdles or the needs for special training. In this talk, I will discuss the challenges and progress, focusing on computational materials science.

Concerning the data-analytics, we note that the number of possible materials is practically infinite, but only 10 or 100 of them may be relevant for a certain science or engineering purpose. In simple words, in materials science and engineering, we are often looking for “needles in a hay stack”. Fitting or machine-learning all data (i.e. the hay) with a single, global model may average away the specialties of the interesting minority (i.e. the needles). I will discuss methods that identify statistically-exceptional subgroups in a large amount of data, and I will discuss how one can estimate the domains of applicability of machine-learning models. [3]

1) FAIR stands for Findable, Accessible, Interoperable and Re-usable. The FAIR Data Principles; https://www.force11.org/group/fairgroup/fairprinciples

9:00 AM MT02.10.02
Crystallographic Information and Thermoelectric Properties Obtained from High-Throughput Experiments of Ca1-xBixMnO3 Powder Kenjiro Fujimoto1, Yusuke Yamada1, Akihisa Aimi1, Keishi Nishio1 and Shingo Maruyama2; 1Tokyo University of Science, Japan; 2Tohoku University, Japan
Material prediction by machine learning in recent years requires huge data, and in many cases it is supplemented by text mining and computational chemical simulation. I think that development of high-throughput experimental tools should also be continued in order to interpolate diversity in data and to construct a new database. In case of high-throughput materials preparation and evaluation, we treat about several hundred samples in one day. As an example, in conventional method for synchrotron powder X-ray diffraction, we have to fill fine capillaries (c.a. 0.2 mmΦ) with well-grounded powder. We need at least 10 hours for only sample filling when we measure 100 sample in one day. Therefore, we have made a prototype for effective and high-throughput evaluation in synchrotron X-ray powder diffraction measurements. Tools made with 3D printers made it possible to continuously measure powder libraries transferred to tape. In this study, as an example, powder library of perovskite-type Ca$_{1-x}$Bi$_x$MnO$_3$ was prepared and obtained X-ray diffraction data using the our developed high throughput evaluation tool. Then, we studied which parameter contributed to the improvement of the thermoelectric performance from crystallographic information obtained our developed automated Rietveld analysis program.

As the amount of Bi substitution increased, lattice constant was linearly increased based on Vegard's law. From the change of the bond length of Mn-O and the tilt angle of MnO$_6$ octahedron depending on the Bi substitution amount, the decrease of the electrical conductivity is ideally expected. However, the power factor ($PF = S^2 \times \sigma$) increased as the substitution amount increased. From these results, it was thought that the increase in $PF$ value was related to the carrier concentration more strongly than the other parameters.

Acknowledgements:
These XRD and XAFS experiments were conducted at the BL5S1 and BL5S2 of Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation, Aichi, Japan (Approval No.2018P0104).
as well as single and co-alloying compositions of each of the 5 alloying elements, resulting in a high dimensional dataset that is not amenable to manual analysis. Interpretation of this high dimensional dataset is facilitated by analyzing the trained CNN model by evaluating local partial derivatives (Gradient Analysis), revealing key data relationships that are not readily identified by human inspection or traditional analyses. Statistical analysis of the ensemble of ~1 million gradients provides quantitative composition-structure-property and structure-property relationships as well as the similarity of the chemical role of different alloying elements, which collectively provide insight into the fundamental material science. Furthermore, automated reporting of these key data relationships illustrates a key mechanism by which machine learning methods accelerate scientific discovery.


9:45 AM MT02.10.05
A Data Driven Approach for the Accelerated Discovery of Photocathode Materials Evan Antoniuk¹, Yumeng Yue¹, Yao Zhou², Bruce Dunham³, Piero Pianetta³, Theodore Vecchione² and Evan J. Reed¹; ¹Stanford University, United States; ²Google, United States; ³SLAC National Accelerator Laboratory, United States

In this work, we utilize a data driven approach for the development of photocathode materials, which have served an integral part in developing modern x-ray light sources. In turn, these high-brightness light sources have enabled exciting discoveries. Recently, the hard x-ray free electron laser (FEL) at SLAC National Accelerator Laboratory has enabled researchers to monitor bond formation in the active site of proteins, optically tune the interlayer interactions in two-dimensional materials and probe the formation of diamonds from laser-compressed hydrocarbons. Through the further development of ultra-high brightness light sources, previously unthinkable experiments may be imagined.

Perhaps the most cost-effective method for improving the performance of FELs is through the discovery of new photocathode materials that can produce higher-brightness beams. However, past efforts for the discovery of photocathode materials have primarily used trial and error approaches with very low throughput. To date, less than 30 materials have been reported in the literature for photocathode applications. In this work, we screen over 10,000 bulk crystals in the Materials Project database to discover candidate photocathode materials. We utilize the Materials Project calculated electronic band structures as well as a newly developed photoemission model to rapidly identify materials with ideal photoemission properties. To ensure our candidate materials can be readily integrated into photocathode devices, we then filter out materials that have not yet been synthesized.

Following this filtering process, we discover over 300 candidate photocathode materials with a predicted brightness that is 10x larger than the current state-of-the-art photocathodes. We further characterize these high-brightness photocathode materials by performing high-throughput DFT work function calculations including multiple surface terminations and Miller indices. The photoemission properties of the photocathode materials are then further explored by utilizing DFT to calculate the photoexcitation probability of all possible optical excitations in a material. Through close partnerships with experimental collaborators, we discuss the possibilities for these newly discovered photocathode materials to shape the next generation of FELs.

10:00 AM BREAK

10:30 AM *MT02.10.06
Adding Domain Knowledge and Causality to Materials Informatics Vladan Stevanovic; Colorado School of Mines, United States

Today’s materials science deals with data sets that are much smaller than what would be desired by the contemporary statistical methods. Historically, this problem has been dealt with using “modern” scientific method – formulation, via induction, of causally related hypotheses and their measurement-based testing through deduction. However, the complexity of materials’ behavior and the insufficient knowledge of all factors influencing experimental outcomes, in combination with the successes of AI in other fields (e.g. targeted advertising) motivated recent surge of activities in utilizing machine learning, neural networks, random forests and other methods in materials science. While of unquestionable practical value, the statistically obtained relationships suffer from the absence of causality and non-uniqueness. In this talk I will discuss ways of adding domain knowledge and causality to the data driven materials discovery and design. The approach we recently adopted starts from the appropriate theory and the analytically deduced relationships between quantities of interest. In the next step we replace hard-to-access physical quantities appearing in those relationships with physically motivated proxies that are easily
accessible from materials data bases or are inexpensive to compute from first-principles. The price for this replacement is the introduction of free parameters into the models, which are then obtained by fitting to existing, usually experimental data. In this way one integrates domain knowledge with materials informatics and creates causal and interpretable models of relevant materials properties. I will review successes in applying such an approach to the discovery and design of novel semiconductors for thermoelectric, photovoltaic and power electronics applications.

11:00 AM MT02.10.07
Mapping and Understanding Large-Scale Stability Trends across the Ternary Metal Nitrides
Wenhao Sun\textsuperscript{1,2}, Chris Bartel\textsuperscript{2,3}, Elisabetta Aca\textsuperscript{4}, Sage Bauers\textsuperscript{4}, Bethany Matthews\textsuperscript{4}, Janet Tate\textsuperscript{5}, Bor-Rong Chen\textsuperscript{6}, Michael F. Toney\textsuperscript{6}, Laura T. Schelhas\textsuperscript{6}, Andriy Zakutayev\textsuperscript{4}, Stephan Lany\textsuperscript{4}, Aaron Holder\textsuperscript{4} and Gerbrand Ceder\textsuperscript{2}; 1University of Michigan–Ann Arbor, United States; 2Lawrence Berkeley National Labs, United States; 3University of Colorado Boulder, United States; 4National Renewable Energy Laboratory, United States; 5Oregon State University, United States; 6SLAC National Accelerator Laboratory, United States

Exploratory synthesis in novel chemical spaces is the essence of solid-state chemistry. However, uncharted chemical spaces can be difficult to navigate, especially when materials synthesis is challenging. Nitrides represent one such space, where stringent synthesis constraints have limited the exploration of this important class of functional materials. Here, we employ a suite of computational materials discovery and informatics tools to survey, visualize, and explain stability relationships across the inorganic ternary metal nitrides. First, we use crystal structure prediction algorithms to probe the stability landscapes of previously unexplored ternary nitride spaces, identifying hundreds of promising new ternary nitrides for further exploratory synthesis. Next, we use unsupervised machine-learning algorithms to cluster together cations with a similar propensity to form stable or metastable ternary nitrides. To visualize these clustered nitride families, we construct a large and comprehensive stability map of the inorganic ternary metal nitrides. Our map reveals broad overarching relationships between nitride chemistry and thermodynamic stability, and inspires us to rationalize these trends from their underlying chemical origins. To do so, we extract from the DFT-computed electron density the mixed metallicity, ionicity, and covalency of solid-state bonding, which we use to formulate data-driven insights into the thermochemical and electronic origins of ternary nitride stability.


11:15 AM MT02.10.08
Combinatorial Synthesis and High-Throughput Characterization of Microstructure and Phase Transformation in NiTiCu-X Quaternary Thin-Film Libraries for Elastocaloric Cooling
Naila Al Hasan\textsuperscript{1}, Huilong Hou\textsuperscript{1}, Jonathan Counsell\textsuperscript{2}, Tieren Gao\textsuperscript{1}, Suchismita Sarkar\textsuperscript{3}, Sigurd Thienhaus\textsuperscript{4}, Apurva Mehta\textsuperscript{3}, Alfred Ludwig\textsuperscript{5} and Ichiro Takeuchi\textsuperscript{1}; 1University of Maryland, United States; 2Kratos Analytical Ltd., United Kingdom; 3SLAC National Accelerator Laboratory, United States; 4Ruhr-Universität Bochum, Germany

Ni-Ti based shape memory alloys (SMAs) have found widespread use in the last 70 years but improving their functional stability remains a key quest for more robust and advanced applications. Named as such due to their ability to retain their processed shape as a result of a reversible martensitic transformation, they are highly sensitive to compositional variations. Alloewing with ternary and quaternary elements to fine tune the lattice parameters and the thermal hysteresis of an SMA, therefore, becomes a challenge in materials exploration. Combinatorial materials science allows streamlining of the synthesis process and data management from multiple high throughput characterization techniques. In this study, composition spreads of Ni-Ti-Cu-X (X = V, Fe, Co) thin film libraries were synthesized by magnetron co-sputtering on thermally oxidized Si wafers. Composition dependent phase transformation temperature and microstructure were investigated and determined using high throughput wavelength dispersive spectroscopy, synchrotron x-ray diffraction, and temperature-dependent resistance measurements. Composition-structure-property phase maps for the quaternary systems are used to discuss correlations of functional properties with respect to local microstructure and composition of the thin film libraries. This work was supported by the National Science Foundation Graduate Research Fellowship Program under Grant No. DGE 1322106.

11:30 AM MT02.10.09
Discovery of Promising Salt Hydrates for Thermal Energy Storage Using High Throughput Computation and Machine Learning
Steven G. Kiyabu and Donald Siegel; University of Michigan, United States
Salt hydrates demonstrate promise as heat storage materials as they possess high energy densities and reversibility at moderate temperatures. Despite their promise, a great number of salt hydrate compositions have not been explored. The goal of this work is to identify new salt hydrates that can outperform known materials in terms of energy density and are predicted to be thermodynamically stable. A total of 5,292 hypothetical salt hydrates were generated by systematically substituting cations and halides into 76 salt hydrate crystal structures mined from the Inorganic Crystal Structure Database. These hypothetical hydrates were characterized according to their enthalpy of dehydration (from which stability, energy density, and heat-storing temperature are derived) in one of two ways. 2,954 of these hydrates were characterized using high-throughput density functional theory calculations. A machine learning model with extensive feature selection was then developed and trained on these hydrates. The initial set of structural and ionic features was expanded to a set of several thousand physically meaningful combinations of the original features. A two-step feature selection process using LASSO and a genetic algorithm was then employed before the final model was trained. The remaining 2,338 hypothetical salt hydrates were then characterized using this predictive model. Several promising hypothetical hydrates were identified with higher energy densities than experimentally-known salt hydrates. Furthermore, the machine learning model illuminated several new property-performance relationships in salt hydrates.

11:45 AM MT02.10.10
Accelerating the Search for Lithium-Ion Conductors with Machine Learning Interatomic Potentials
Koutarou Aoyagi1,2, Chuhong Wang1 and Tim Mueller1; 1Johns Hopkins University, United States; 2Toyota Motor Corporation, Japan

All-solid-state lithium-ion batteries are leading candidates for the next generation of batteries, but interfacial resistance needs to be improved for commercialization. Interfacial impedance can be improved through the use of cathode coating materials between the active electrode material and the solid state electrolyte. As experimentally exploring candidate coating materials is time-consuming and resource-intensive, the development of new coating materials can be accelerated by computationally screening candidate materials in a high-throughput manner. One of the most important criteria for coating materials is lithium-ion conductivity. As the mechanism for lithium-ion conduction is generally not known for a candidate coating material, computational assessment of lithium-ion conductivity is best accomplished through molecular dynamics simulations. Sufficiently accurate simulations can be performed using density functional theory, but the computational cost of this approach limits its use to materials that are fast ionic conductors. We demonstrate that this problem can be addressed through the use of machine learning to develop interatomic potentials on the fly. We present a method for using moment tensor potentials, a recently developed class of machine learning interatomic potentials [1], for automatically calculating lithium-ion conductivity with molecular dynamics simulations and demonstrate that this approach results in improved agreement with experiments over ab-initio molecular dynamics while requiring less computing time.

discuss the surprising difficulty of this problem and introduce efficient, nonmyopic policies to solve it, demonstrating our method on large-scale materials and drug discovery experiments. Nonmyopic active search increases search efficiency dramatically across a wide range of settings, suggesting it may be a promising approach to automating discovery pipelines.

2:00 PM MT02.11.02
Pan-Sharpening Algorithm for Spectral Map Reconstruction Nikolay Borodinov¹, Natasha Bilkey², Alison Pawlicki¹, Marcus Foston², Anton V. Ievlev¹, Alex Belianinov¹, Stephen Jesse¹, Rama K. Vasudevan¹, Sergei Kalinin¹ and Olga S. Ovchinnikova¹; ¹Oak Ridge National Laboratory, United States; ²Washington University in St. Louis, United States

Recent advances in chemical imaging allow material composition characterization at the nanoscale. Such methods (optical spectroscopy, secondary ion spectrometry, mass spectrometry to name a few) vary in data acquisition, sample preparation, and spatial resolution; and thus offer common yet nonidentical applicability for different samples [1].

Coupling atomic force microscopy with infrared spectroscopy is a recent addition to the chemical imaging toolkit. A pulsed infrared laser triggers periodic thermal expansion of the sample, which is then detected by an AFM tip. Recent advances in AFM-IR allow imaging of polymer blends and nanocomposites, biological tissue, and ion migration; which makes it a highly relevant technique [2]. Currently there are two operational modes: an acquisition of a single wavenumber map, which has full AFM resolution, and an acquisition of a sparse arrays at full spectral resolution. A direct attempt to measure full spectral response at each point of an AFM scan would be prohibitively long, and very likely to be disturbed by sample drift. In order to yield a full resolution dataset which could be used for correlative analysis, the two types of data – a spectral array and a set of single wavenumber maps, have to be combined in a physically meaningful way. Methods for combining multiple data channels with different spectral and spatial resolution have been intensively explored and overall are commonly referred to as pan-sharpening. One of these approaches, which is very suitable for the case of AFM-IR, relies on coupled non-negative matrix factorization (CNMF) of the data.

We demonstrate the applicability of CNMF-PS algorithm for synthetic data, experimental AFM-IR with known ground truth and an experimental AFM-IR with unknown ground truth. We analyze the algorithm parameters (downsampling rate, number of NMF components, number of single wavenumber maps used) on the quality metrics of the PS operation. We use our method for the analysis of plant cell wall materials and derive the correlation between the spatial distributions of chemically dissimilar components provided by CNMF-PS and local physical property (mechanical stiffness measured as the shift in AFM tip contact resonance). In addition, we use this method for the chemical characterization of tribofilms which are easily destroyed by exposure to the IR. These examples highlights the utility of PS algorithm for in-depth nanoscale characterization of various materials. This work can be readily adopted by other chemical imaging techniques generating spectral images.

References:
[3] The authors acknowledge the Center for Nanophase Materials Sciences, which is a US DOE Office of Science User Facility supported under Contract DE-AC05-00OR22725, (N.B., A.P., A.V.I, A.B., S.V.K, O.S.O). A portion of algorithm development was a part of the AI Initiative, sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (S.J., R.K.V), managed by UT-Battelle, LLC, for the U.S. Department of Energy (DOE). The plant sciences portion of this work was supported by the Center for Engineering MechanoBiology (CEMB), an NSF Science and Technology Center, under grant agreement CMMI: 15-48571 (N.B. and M.F.).

2:15 PM MT02.11.03
Accelerated Catalyst Discovery through Gaussian Processes and Active Learning Kiran Vaddi, Olga Wodo and Krishna Rajan; University at Buffalo, United States

We introduce an active learning procedure to query and uncover highly catalytic regions within a design space. We
have identified key challenges related to the high dimensional responses of cyclic voltammetry experiments and derived a Bayesian Model Selection (BMS) method to efficiently label the responses and to guide the active learning within the identified design space. Applying the proposed methodology on a simulated kinetic zone diagram as the design space, we show that actively learning within the design space can improve the design of experiments for catalyst discovery and characterization. We have reduced the total number of experiments required to discover the high catalytic zones in the design space by an order of magnitude, thereby significantly accelerating design and minimizing experimental requirements. Using an active batch search, we derive a mechanism to actively learn highly catalytic zones in a high-throughput combinatorial search for catalyst.

2:30 PM MT02.11.04
Insights in Chemical Features Impacting the Quality and Lifecycle of 3D Printed Model System—An Integrated Experimental, Modeling and Data Sciences Approach Amra Peles, William S. Rosenthal, Francesca C Grogan, Yulan Li, Erin I Barker, Zachary C Kennedy, Timothy Pope, Christopher Barrett and Marvin Warner; Pacific North West Laboratory, United States

Additive manufacturing is causing fundamental changes in the way complex 3D objects are produced from their digital designs. It is well known that product quality, ease of reproducibility and often open-source nature of digital model design possess pressing concern about utilizing this fast-developing technology to produce safety and security critical parts. Our ability to understand additive manufacturing process from conceptual design to the life-long printed part performance and to uncover critical features that are the best indicators of future failure of the part is critical. Here the elements forming a part of the holistic integrated approach are presented, which are also the backbone for the materials discovery framework.

We employ the polymer nylon 12 as the feedstock to print the specimens for the mechanical testing and as a model system. We report on initial polymer feedstock characterization for the details of compositional chemistry and powder-specific qualities; the mathematical model for powder geometry and material property representation; the implementation of phase-field models to study sintering and aging properties of selective laser sintering (SLS) process; few-shot learning strategy to train and characterize micro-CT images; and coupled to the uncertainty quantification an implementation of long short term memory (LSTM) algorithm to optimize error back flow in time dependent aging study. The insights into sensitivity analysis and the adaptive inference modeling to guide the design of build experiments, aging of printed specimens and set of static and dynamic mechanical tests will be presented. The micro-CT studies are used to look at structural features and their changes due to variable processing and aging of printed specimens. The experimental micro-CT images and details of experimentally aged specimens serve as the ground truth for the structural and aging study features from phase-field model.

2:45 PM BREAK

3:15 PM *MT02.11.05
The Machine Learning Route to Accelerated Discovery and Inverse Design Johannes Hachmann; University of New York, Buffalo, United States

The use of modern machine learning, informatics, and data mining approaches is a relatively new development in the chemical and materials domain. These techniques have been exceedingly successful in other application fields, and since there is no fundamental reason why they should not have a similarly transformative impact on chemical and materials research, there is now a concerted effort by the community to introduce data science in this new context. They hold tremendous promise for the practical realization of accelerated discovery and inverse design. However, adapting techniques from other application domains for the study of chemical and materials systems requires a substantial rethinking and redevelopment of the existing methods.

In this presentation, we will discuss our work on designing advanced, physics-infused neural network architectures, the fusion of unsupervised clustering with supervised regression for local ensemble models, active and transfer learning techniques, bootstrapping approaches to minimize our training data footprint, methods to increase the applicability domain of data-derived models, and automated hyperparameter optimization.
Predictive materials modeling can provide properties of real and virtual compounds and will be available on demand, thereby enabling rapid iteration time in materials design. However, the allure and necessity of accelerated discovery that motivates computational materials design is diminished by the prevalent heuristic approaches to materials synthesis and optimization. This presentation will outline our collaborative work to extract information from peer reviewed academic literature across a range of materials science texts. We have demonstrated not only the potential of the natural language processing (NLP) approach to assemble materials data from the literature, but we have also shown that one can develop hypotheses for what synthesis conditions drive a particular target material outcome using learning approaches. The presentation will describe application of NLP and machine learning to a few cases of materials discovery as well as issues with current and historical writing conventions in materials science literature to propose a structured way to facilitate reproducibility, clarity, and machine readability.

We present a computing and data science effort at PNNL for an end-to-end analysis pipeline for chemical dynamics studies using High-Performance Computing (HPC) resources. The current computing model uses DIRAC (Distributed Infrastructure with Remote Agent Control) for its workflow and data management. A detailed meta-data assignment using the DIRAC File-Catalog is used to automate the stages of data processing. The DIRAC system is deployed on containers managed using a Kubernetes cluster to provide a scalable infrastructure. A modified DIRAC agent provides the ability to submit jobs using singularity on dedicated and opportunistic HPC sites. The data products from this pipeline are feed into a graphics processing unit (GPU) cluster that runs various Machine Learning (ML) tasks, such as 3D convolution networks and/or physics aware temporal models.

The performance of most organic electronics is critically dependant on the bulk morphology. Subsequently it becomes important to identify distributions of morphologies that have high performance. While computational studies and high-throughput analysis promise drastic improvement of time to delivery, they are nonetheless limited in several aspects, primarily two-fold — (a) the size of morphology space, even for simplistic descriptions (2D, binary) is practically unlimited and (b) the resources required for quantification are still limited (limited physics models) and time consuming. In this work, we address the first issue of efficiently exploring the practically infinite morphology space using state-of-the-art machine learning and artificial intelligence algorithms. More specifically, we take a completely data-driven approach to generate morphologies that show high performance. We used a combination of invariance obeying generative adversarial networks along with robust and interpretable CNN based structure-property map to generate extremely high performing morphologies. The generated morphologies consistently showed high performance and simultaneously sampled remote regions of the morphology space that were previously not reported. Finally, we quantified the generated morphologies against full physics simulations to find that the novel AI approach predicts high performing morphologies in most of the cases.

Materials informatics (MI) has attracted a great deal of interest over the past decade in efforts to accelerate materials discovery. Virtual screening is a frequently employed MI procedure to link a target property to an explanatory feature of materials, i.e., a descriptor. The model is then applied to predict and rank the target property in materials
registered in the database. However, a major bottleneck of the MI model is an insufficient amount of supervised data. To overcome this issue, we took three approaches, namely, high-throughput (HT) computations for an extension of the database,\textsuperscript{1,2} a newly developed ensemble-scope descriptor for the virtual screening with a limited supervised data,\textsuperscript{3} and a HT experiment that facilitates efficient materials discovery within a certain chemical search space MI suggested.\textsuperscript{4} In this presentation, we demonstrate applications of the method to an exploration of oxygen ion conductors, aiming to find new materials superior to the conventional high-temperature conductor, yttria-stabilized zirconia (YSZ), which is used for solid oxide fuel cells.

The ensemble-scope descriptor includes the physical and chemical knowledge, and short- and long-range representations of the crystal structure. This multifaceted feature augments information acquired from a relatively small number of supervised data to improve the prediction power; in addition, it provides physical insights in the prediction, which facilitate to get new knowledge and extend a search space. Given only 29 supervised data, we successfully discovered more than 5 compounds, such as EuKGe\textsubscript{2}O\textsubscript{6} and Ca\textsubscript{3}Fe\textsubscript{2}Ge\textsubscript{3}O\textsubscript{12}, which were verified by experiment. The MI prediction was then used to focus a chemical search space where the HT experiment performed. We implemented HT combinatorial synthesis, HT-XRD measurement, and HT conductivity measurement. The application of the method to oxygen ion conductors led to the discovery of materials in the Ca-(Nb,Ta)-Bi-O system that exhibited high conductivity and durability.

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SESSION MT02.12: Poster Session IV: Experimentation and Machine Learning

Session Chairs: Jason Hattrick-Simpers, Barnabas Poczos and Aleksandra Vojvodic
Thursday Afternoon, December 5, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

**MT02.12.01**

**Effect of Dielectric Particle Heterogeneity on Capacitance—A Machine Learning Biased Genetic Algorithm Approach**

Venkatesh Meenkshisundaram\textsuperscript{1,2}, David Yoo\textsuperscript{1,2}, Andrew S. Gillman\textsuperscript{1} and Phil Buskohl\textsuperscript{1}, \textsuperscript{1}Air Force Research Laboratory, United States; \textsuperscript{2}UES, Inc., United States

Microscale spatial and material heterogeneities in 3D printed electrical devices present significant challenges to predictable electrical performance and device reliability. Dielectric particles are often added to dielectric inks to tailor the macro level permittivity of printed dielectric substrates and coatings. In these inks, the combined role of particle morphology, discrete spatial arrangement and material properties on variance is difficult to distinguish experimentally and hence poorly understood. This is primarily due to the large parameter space of processing variables as well as electrical sensitivity to local heterogeneities. We address this challenge by combining a finite element capacitor model with a neural network biased genetic algorithm (NBGA) to optimize the volume fraction, particle size and permittivity distributions of dielectric particles to identify systems with high capacitance variance. Comparison of the optimized system to an equivalent system with monodisperse particles revealed that heterogeneity in particles could be key to achieving larger variance that is not available to system with monodisperse particles. A closer look at the optimized system revealed that variance in distance between particles and the electrodes was larger than the monodisperse system. This can be attributed to larger packing configurations accessible to the system with polydisperse particles as compared to system with monodisperse particles. Classification-based machine learning techniques were also applied to the NBGA-created database to extract correlations between the spatial/material distributions of the dielectric particles and the capacitance variance. Collectively, the study provides a useful framework to correlate electrical performance with both macro- and microstructural variation sources, which is key to accelerating the development of 3D printing materials.
Machine Learning Based Data Driven Approach for Optimized Inkjet Printed Electronics Fahmida Pervin
Brishty, Ruth Urner and Gerd Grau; York University, Canada

Machine Learning (ML) has not been explored extensively to optimize printed electronics manufacturing. As a predictive methodology, it has the potential to efficiently minimize printing configuration workload. Inkjet printing is a promising method of additive manufacturing due to its attractive attributes including low-cost, scalability, non-contact printing and microscale on-demand customization. It generates droplets of electronic materials with a piezoelectrically actuated dispenser controlled through voltage pulse and timing parameters. This will enable novel electronics development on flexible plastic and paper substrates such as wearable sensors, RFID tags or flexible displays in a drop-on-demand (DOD) way. A major challenge in inkjet printing is the rapid optimization of stable jetting conditions. Several problems can occur: no ejection, perturbation, satellite drop, multiple drops, drop breaking, nozzle clogging etc. These non-idealities can lead to significant uncertainty in the behavior of mass-produced electronic devices and circuits. Steady drop speed and volume generation requires numerous time and material consuming trial and error experiments. Theoretical modeling and prediction is limited and difficult due to the complexity of the printing process. Here, an intelligent ML algorithm is demonstrated to forecast the jetting window based on machine and material properties.

Optimal inkjet system parameters vary from material to material and printer to printer, so stable jetting is interpreted here as a data-driven optimization problem. A major challenge was the lack of an established dataset in this context. Data was extracted from academic papers as well as experimentally collected in our lab. Printers from different manufacturers and different inks (pure solvents and nanoparticle inks) were included in the dataset. The input factors were printer-dependent (printer make, nozzle size), material-dependent (density, viscosity, surface tension) and printing control parameters (dwell time, echo time, rise time, fall time, jetting frequency, dwell voltage, echo voltage and waveform shape). The measured outputs were drop velocity and volume.

The merged dataset has 13 features out of which the 9 most important features were identified during a first stage of exploratory data analysis. A detailed analysis was then performed to compare various (linear and non-linear) regression models with the goal to identify a type of model with high predictive capacities while at the same time allowing for interpretation of the underlying implied dependencies of the involved features. The models were trained on 80% of the data and the mean absolute error was calculated on 20% test data. Simple linear relationship consideration between the input and output features did not yield accurate predictions. Instead, small ensembles of decision trees (boosted decision trees and random forests) were explored further to estimate jet drop velocity, and volume. The models were applied to an experimentally collected data set with a material that was not included in the training set. The learned regression model predicted drop velocity with test root mean square error (RMSE) of 0.53 m/s. Drop volume was forecasted for the same dataset with RMSE of 14.88 pico-liter.

In conclusion, we demonstrated that employing machine learning for drop behavior prediction can be used for forecasting new fluid drop formation which were not available at training time. This will enable more efficient materials selection as well as tuning of printing parameters. It has the potential to considerably speed up the development of novel materials and inks for printed electronics by eliminating extensive jetting experiments that are costly in terms of money, time and material.

MT02.12.03
Scientific Data Infrastructure for Combinatorial Material Science Lars Banko, Sigurd Thienhaus and Alfred Ludwig; Ruhr-Universität Bochum, Germany

Data mining by statistical/machine learning methods is an emerging topic in material science. Advanced algorithms are able to find patterns in large datasets beyond human capabilities. Additionally, these techniques can accelerate the analyses of complex data. Combinatorial material science generates large, comparable data sets of materials libraries that are designated for data mining applications. Aggregation of those data sets within a research group or even within a certain scientific community provides the opportunity to generate knowledge based on non-trivial correlations. The basis for this approach is a solid data management which ensures a high degree of reusability by appropriate data curation. Here, we demonstrate our recent achievements in the development of a customized scientific data infrastructure. The solution consists of a commercially available, customizable document management system, a terminal server-based IT infrastructure and in-house developed software tools. The main purpose of this data infrastructure is to track all data and information about a materials library throughout the whole sample lifecycle, from experimental planning and synthesis over processing to characterization and analyses. It is demonstrated that standardization of data acquisition, pre-processing and storage promote time efficient, machine assisted data analyses. The use of terminal servers guarantees access from various devices (computers, tablets,
smartphones) and operating systems (Windows, Linux, OS X, iOS, android etc.) and improves data security at the same time. Maintenance is reduced by remote applications which are easy to deploy and update. An additional benefit is the structured storage of knowledge which counteracts fast personnel cycles in university research.

MT02.12.04
Machine Learning Prediction of Glass-Forming Ability and Elastic Modulus for Bulk Metallic Glasses Jie Xiong, San Qiang Shi and Tong-Yi Zhang; The Hong Kong Polytechnic University, Hong Kong; Shanghai University, China

There is a genuine need to shorten the development period for new materials with desired properties. Bulk metallic glasses (BMGs) are a unique class of materials that are gaining attention in a wide variety of applications due to their attractive physical properties. One limitation to the wide-scale use of these materials is the lack of predictable tools for understanding the relationship between alloy composition and ideal properties. In this work, machine learning (ML) approach was applied on a dataset of 6312 alloys. The resulting ML model predicted the glass forming ability and elastic moduli of unseen alloys in good agreement with most experimentally measured values. It will promote the development of basic theories of metallic glasses to reveal the intrinsic correlation of physical properties through material big-data mining. This work indicates the great potential of ML in the design of advanced materials with target properties.

MT02.12.05
Accelerated Development of High-Performance Nanocomposite Solar Absorbers Using Bayesian Optimization Qiangshun Guan, Afra S. Alketbi, Aikifa Raza and TieJun Zhang; Khalifa University of Science and Technology, United Arab Emirates

Machine learning-based approach is desired for accelerating materials design, development and discovery, especially when it is coupled with high-throughput experiments and simulations. In this work, we propose to apply the Bayesian optimization to design ultrathin multilayer W-SiC nanocomposite absorbers for high-temperature solar power generation. The optical properties of nanocomposite depends on the filling factors as predicted by the effective medium theory. The spectrally averaged solar absorptance of various absorber designs is evaluated with a semi-analytical scattering matrix method. The design of spectrally selective nanocomposite absorber is optimized over a range of filling factors and layer thicknesses to maximize the overall solar absorptance. Our nanofabrication and experimental characterization results demonstrate the capability of the proposed close-loop approach for solar energy materials development. Comparison with other global optimization methods (Random Search, Simulated Annealing and Genetic Algorithm) shows that the Bayesian optimization can expedite the design of multilayer nanocomposite absorbers and hence reduce their development cost significantly. This work sheds light on the high-throughput discovery of materials for solar energy and sustainability applications.

MT02.12.06
Recommender System of Processing Conditions for Inorganic Compounds Based on a Parallel Experimental Dataset Hiroyuki Hayashi, Atsuto Seko and Isao Tanaka; Kyoto University, Japan; PRESTO, Japan; National Institute for Materials Science, Japan

Studies on high throughput material-screening through calculations based on density functional theory and/or machine-learning methods have increased rapidly in the last decade. However, data-centric approaches for successful processing conditions are still in the very early stage. Little works have yet been reported except for literature-data based approaches [1,2]. In this study, we propose a machine-learning approaches for successful processing conditions for inorganic compounds based on parallel experiments [3]. Initially, an experimental database was constructed for 67 pseudobinary oxides registered in the Inorganic Crystal Structure Database (ICSD) [4] by parallel experiments using 23 starting materials and 23 cation mixing ratios. Precursor powders were obtained by four synthesis methods (solid-state reaction, polymerized complex, cyclic ether sol-gel, and spray co-precipitation), which were fired at five different temperatures. This resulted in 1,648 unique chemical synthesis conditions and database entries. The reactants were characterized sequentially using powder X-ray diffraction equipment with an automatic sample exchanger. The synthesis results were rated as a score, which was placed into a fifth-order tensor with 243,340 elements. The Tucker decomposition method was used to predicted yet-to-be-rated scores for unexperimented processing conditions. Good predictive performance of the present model was demonstrated by leave-one-experimental-composition-out cross validation. It was further evaluated by examining
the presence of highly rated compositions in another database, ICDD-PDF (International Center for Diffraction
Data-Powder Diffraction File) [5]. The prediction performance was about twice when the compositions are chosen
randomly and was as good as the existing method of the composition-recommender system [6]. Moreover, the
present method can recommend not only the compositions that are likely to exist stably but also successful synthesis
conditions of them at the same time. The chemical similarities regarding the chemical processing conditions
evaluated through the tensor decomposition seem to be consistent with our heuristics. Superiority of the
recommender system with the synthesis data to accelerate the discovery of as-of-yet-unknown compounds can be
demonstrated.

References

MT02.12.07
Designing Stretchable MoS2 Kirigami Using Deep Reinforcement Learning Pankaj Rajak1, Beibei Wang2, Ken-
ichi Nomura2, Aiichiro Nakano2, Rajiv Kalia2 and Priya Vashishta2; 1Argonne National Laboratory, United States;
2University of Southern California, United States

Mechanical properties of 2-D materials such as MoS2, MoSe2, WS2 and WSe2 can be tuned by the ancient art of kirigami. Experiments and atomistic simulations show that these 2-D materials can be stretched more than 50% by strategic insertion of cuts. However, designing kirigami structures with desired mechanical and thermal properties is highly sensitive to the pattern and location of kirigami cuts on a flat sheet. Furthermore, the search space of kirigami design increases exponentially with an increase in the system size. We have used a reinforcement learning (RL) model, which after training can generate a wide range of MoS2 kirigami structures with high stretchability. Our model consists of an RL agent, whose goal is to design kirigami cut patterns, and a convolution neural network-based reward model. The latter is trained using molecular dynamics simulation data, which gives no reward to patterns generated by the RL agent if the stretchability is less than 30%. The remaining structures are given rewards proportional to their stretchability. The RL model is trained for a MoS2 kirigami structure state space of 4,826,809 candidates, and after training the model is able to synthesize structures with more than 50% stretchability from a space consisting of up to 6 cuts.

Acknowledgment
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MT02.12.08
Materials Discovery by Machine Learning and Single Particle Diagnosis Yukinori Koyama1, Atsuto Seko2,1, Isao Tanaka2,1, Shiro Funahashi1 and Naoto Hirosaki1; 1National Institute for Materials Science, Japan; 2Kyoto University, Japan

Discovery of new materials often leads to breakthroughs in a variety of applications, and thus exploration of new materials is a major subject in materials research. Space of chemical compositions is too wide to search for novel compounds without convincing guidelines. Therefore, it is important to establish a reasonable methodology for materials exploration. In this study, we propose an approach of materials exploration using a machine-learning technique to estimate relevance of chemical compositions followed by single-particle-diagnosis experiments. We also demonstrate discovery of novel nitrides by this approach.

First, we developed a machine-learning model of a descriptor-based recommender system to estimate relevance of chemical compositions, i.e. whether the compositions form stable structures or not. Training dataset includes
chemical compositions registered in the Inorganic Crystal Structure Database (ICSD) as positive cases, and compositions not registered in the ICSD as negative cases. A set of descriptors composed of means, standard deviations, and covariances of elemental representations are used to define similarity of chemical compositions. Random forest classifier is used to estimate probabilities of chemical compositions as the positive cases. The expectant probabilities can be used as indicators of the relevance.

After screening by the machine-learning model, we tried to synthesize compounds of the relevant chemical compositions. Then, we analyzed crystal structures of the obtained samples by the single-particle-diagnosis approach, as follows. The samples are first analyze by a conventional powder X-ray diffraction (XRD). If XRD patterns are not fitted well by known crystals, the samples might contain unknown structures. Then, particles of about several micrometers in size, which are like single crystals, are picked up. Single-crystal XRD data of the individual particles are collected and their crystal structures are refined.

The proposed approach is efficient for materials exploration. We have found novel nitrides having new crystal structures.

**MT02.12.09**

**Predicting Carbon Nanotube Forest Synthesis-Structure-Property Relationships Using Physics-Based Simulation and Deep Learning** Taher Hajilounezhad, Zakariya Oraibi, Ramakrishna Surya, Filiz Bunyak, Kannappan Palaniappan, Prasad Calyam and Matthew R. Maschmann; 1University of Missouri-Columbia, United States; 2University of Cincinnati, United States

Carbon nanotubes (CNTs) are promising candidate materials for numerous advanced applications due to their significant mechanical, thermal, optical and electrical properties. CNT forests represent population of CNTs that self-assemble into arrays, with CNTs oriented perpendicular to their growth substrate. Unfortunately, a remarkable performance degradation is observed when individual CNTs self-assembled into CNT forests. Structural disorder plays a major role in this performance gap. To date, there is a lack of understanding about how numerous CNT synthesis processing parameters influence structural disorder and the relationship of CNT structural morphology to CNT forest properties. Further, physical experiments can sample only a limited number of CNT forest growth parameter combinations because of time and financial restrictions. A comprehensive and multidimensional exploration of all synthesis growth parameters is impractical.

The recent advances in high-performance computing, parallel computing and artificial intelligence has opened a new door to employ simulation modeling and computational approaches to prevent costly and frequently biased interpretation of physical experiments. The integration of artificial intelligence and high-throughput physical experiments has given rise to autonomous materials research systems that can direct smart material synthesis experiments via reinforcement learning algorithms. This approach may vastly accelerate material discovery, understanding, and adoption into various industrial applications. We foresee that numerical simulations that compliment physical experiments will provide a vital new data pipeline to train deep learning (DL) algorithms for such systems moving forward. By utilizing coupled physical and numerical experimental campaigns, autonomous research systems may operate faster and at a reduced cost.

In this work, we develop DL models that analyze CNT forest image data prepared by a timeresolved and physics-based numerical simulation. The DL models are used to predict both the CNT synthesis attributes (CNT diameter, CNT areal density) and the resultant mechanical stiffness based on the structural morphology of the CNT forest. The physics-based finite element simulation first models the growth and self-assembly of CNT forests based on stochastic CNT physical parameters and then models the compression of the resultant CNT forest. The simulated CNT forest structural morphology images train the DL models to predict synthesis parameters. Different machine learning algorithms and deep learning architectures are used to find underlying processstructure correlations. The trained model then predicts CNT synthesis attributes based on forest characteristics. Classification accuracies of up to 95.5% are achieved by applying deep convolutional neural networks. This study represents an early step to implement a highthroughput computational and experimental synthesis set-up that yields application-tailored CNT forests with prescribed properties.

**MT02.12.10**

**Automation of Electron Microscopy to Enable Atomic Datasets for Machine Learning** Matthew Hauwiller, Abinash Kumar and James M. LeBeau; Massachusetts Institute of Technology, United States
Theory, synthesis, and characterization form the essential components of the materials informatics cycle. While significant emphasis has been placed on theory and synthesis, comparatively limited progress has been made in the area of materials characterization. Preliminary efforts to apply machine learning to characterization have focused largely on the backend data analysis, but capturing reproducible data in a statistically significant way remains a major challenge. Although electron microscopy can provide atomic-level structural measurements of materials to unravel structure-property relationships, there are some critical limitations to the current workflow that severely limit the current usage and future potential for materials informatics. The largely manual nature of the technique requires a significant amount of time to characterize an extremely small volume of material. This makes it difficult to collect large enough datasets that truly represent the material, especially when the material is inhomogenous or contains various defects. The human input in collecting images and spectroscopic data inherently contains both bias and random error that is undesirable for any comprehensive and systematic study.

In this presentation, we will present a core component to enable the autonomous electron microscope, the Universal Scripting Engine for Transmission Electron Microscopy (USETEM). We will show that this scripting engine is widely applicable and simplifies scripting to enable high-throughput atomic-level imaging of materials. The object-oriented code allows the microscope, detector, and any other components to be controlled through either a visual build tool (similar to LabView) or simple python scripts. We will discuss how the USETEM framework can make it easier to foster collaborations between microscopists at different universities, national laboratories, and industry as researchers develop creative ways to use their instruments to study materials. Machine learning for instrument control will also be discussed with insight into how it opens new opportunities in autonomous image acquisition. As a first step towards this vision, a deep convolutional neural network is demonstrated that can be used to automate convergent beam electron diffraction pattern analysis. The process enables, for example, autonomous determination of sample thickness to within 1 nm and tilt to within a fraction of a milliradian, at real-time speeds. Automating the electron microscope using artificial intelligence will address data size, bias, and documentation concerns, providing improved inputs for machine learning algorithms for faster discovery of emergent materials.

Small-Data Driven Machine Learning Screening Framework for Accelerated Discovery of Ferroelectric Oxides

Yang Hao and Achintha Ihalage; Queen Mary University of London, United Kingdom

The application of machine-learning (ML) to accelerate materials discovery, synthesis, optimization and characterization has significantly reduced the time and resource consumption of first principal calculations or experimental measurements. Especially after the launch of programs such as Materials Genome Initiative and the recent popularity of data science, many open access materials databases have now reached “big data” status, resulting an exponentially growing trend in ML based materials discovery. However, some technologically important materials such as ferroelectrics are scarce in nature and therefore the available datasets do not reveal much information about these materials. Ferroelectric materials can be electrically, mechanically or thermally excited which makes them intriguing candidates for many device applications. The shortage of data has hindered the applicability of ML, or more specifically deep learning (DL), in discovering new ferroelectric materials. The use of “small data” to train a machine learning algorithm and yet achieving state-of-the-art results has been a popular research topic. Specifically, in the field of ferroelectrics and tunable materials where the data is very scarce, machine learning algorithms that perform well even with a small amount of data can be fairly effective and can make it as an effective platform for new material discovery. The available material datasets, either first principle calculated (MP, OQMD), experimental (ICSD, HTEM) or both (CSD, Citrination), despite being huge, however, lack of ferroelectric information.

Most of the regularly updated databases contain over 100,000 materials which makes it tedious to search and discover new ferroelectric materials manually. Another important point to note is that significant portion of first principle calculated materials available in the datasets have not yet been synthesized and their ferroelectric behaviour is not reported in the calculations. Hence, we adopt two machine learning methods for accelerated screening of large databases to find previously unreported ferroelectric oxides. The emphasis of this work is to use an extremely small dataset to train the two machine learning algorithms and later combine the results to discover new ferroelectric oxide materials.

In this work, we propose a combined ML – DL framework for accelerated discovery of ferroelectric oxide materials by learning from an extremely small dataset, thus breaking the shackles between ML and big data.
classification algorithms are trained on a small literature-collected database and the classification is performed on the materials project (MP) database. By combining the results, we report 24 promising ferroelectric candidate materials along with their structure, band gap, chemical stability status and ferroelectric likelihood information. Our results suggest that the developed framework is able to identify ferroelectric materials at an accuracy of 89% and the results were mutually confirmed by the two algorithms. Materials are synthesized, processed and measured with results to be presented at the conference.

Acknowledgments
The authors acknowledge Engineering and Physical Sciences Research Council (EPSRC) for providing funding for Software Defined Materials for Dynamic Control of Electromagnetic Waves (ANIMATE) project (Grant No. EP/R035393/1). A.I. acknowledges IET AF Harvey Research Prize for funding the PhD studentship.

MT02.12.12
Creating Glasswing Butterfly-Inspired Durable Antifogging Superomniphobic Supertransmissive, Superclear Nanostructured Glass through Bayesian Learning and Optimization Sajad Haghanifar and Paul Leu; University of Pittsburgh, United States

The creation of durable superomniphobic surfaces with optical functionality has been extremely challenging. Major challenges have included low optical transmission, low optical clarity, lack of scalable fabrication, condensation failure, and inability to self-heal. Inspired by recent research on the transmission advantages of the random nanostructures on the glasswing butterfly, we report on a strategy to create self-healing, random re-entrant nanostructured glass with high liquid repellency and antifogging properties with supertransmission (99.5% at 550 nm wavelength for double-sided glass) and superclarity (haze under 0.1%). Our approach to creating these random nanostructures is to utilize a multiobjective learning and Bayesian optimization approach to guide the experiments of glass substrate fabrication. The surface demonstrates static water and ethylene glycol contact angles of 162.1 ± 2.0° and 155.2 ± 2.2°, respectively. The glass exhibits resistance to condensation or antifogging properties with an antifogging efficiency more than 90% and demonstrates the departure of water droplets smaller than 2 μm. The surface can restore liquid-repellency after physical damage through heating for 15 minutes. We envision that these surfaces will be useful in a variety of optical applications where self-cleaning, antifouling, and antifogging functionalities are important.

MT02.12.13
Machine Learning and Optimization in Shape Memory Alloys Using a Large Experimental Database William F. Trehern and Ibrahim Karaman; Texas A&M University, United States

Shape memory alloys (SMA) are martensitically transforming materials that exhibit interesting functional properties when undergoing transformation. One of the most well-known of SMA functional properties, the shape memory effect, can be observed when an SMA is deformed in the lower temperature martensitic phase and then heated to the austenitic phase, recovering the original shape and reversing the deformation strains. Upon cooling the material back to martensite, a twinned martensitic structure forms to accommodate for Bain strains that would otherwise change the shape of the sample. Another functional property, superelasticity, occurs when the SMA is deformed in the higher temperature austenitic phase. In this case, the austenite will transform to martensite through the applied strain, forming a detwinned martensite structure allowing for large amounts of deformation. Upon unloading, the material returns to the austenitic phase, recovering the deformation strains and returning to the pre-deformed shape. Both of these functional properties are subject to many different variables (such as material composition, production method, forming processes, and heat treatments) that influence the property characteristics (transformation temperatures, transformation strain, irrecoverable strain, enthalpy of transformation, and fatigue life to name a few). The test parameters also have a great influence on these properties, thus should also be accounted for. In this study, more than 80 independent variables coupled with nearly 30 different response variables are used to find hidden correlations or patterns in 6,000 raw, real experimental data entries. Through exploitation of this database, important and highly influential variables were extracted and utilized in a prediction process for a targeted material property to use in an application. These predictions are then selected based on expected improvement and experimentally validated. I will discuss the
methodology used for database development, necessary data cleaning steps, model development and feature extraction, model prediction, prediction selection using optimization, and experimental procedures for prediction validation. Assessment of related research and possibilities of this informatics approach in other systems will also be discussed.

MT02.12.14

Discovery Paradigm for Novel Organic-Inorganic Halide Perovskites for Optoelectronic Applications through Automated Synthesis Katherine N. Higgins¹, Maxim Ziatdinov², Rama Vasudevan², Sergei Kalinin² and Mahshid Ahmadi¹; ¹University of Tennessee, Knoxville, United States; ²Oak Ridge National Laboratory, United States

Hybrid organic-inorganic perovskites (HOIPs) are rapidly emerging as one of the most fascinating materials for photovoltaic, light emission, lasing, and sensing applications¹-⁴. In general, three-dimensional (3D) HOIPs adopt the typical perovskite crystal structure of ABX₃, where A, B, and X denote monovalent organic or inorganic cations (e.g., CH₃N⁺ (MA⁺), CH₅N₂⁺ (FA⁺), guanidinium (GA⁺), Cs⁺ and Rb⁺), divalent inorganic cations (Pb²⁺, Sn²⁺), and halide anions (I⁻, Br⁻, Cl⁻), respectively. These compounds are among more than one thousand perovskite-inspired candidate compounds that have been theoretically predicted during the last few years⁵-⁶. However, despite extensive theoretical studies, only a small fraction of predicted compounds has been experimentally realized since synthesis of each new material involved complex and time-consuming optimization cycle for synthesis. In addition, optimizing these materials for specific applications requires careful balance between intrinsic properties such as bandgap, defect chemistry, charge transport and crystal structures that affects material microstructure, and poorly understood parameters such as chemical stability of surfaces and interfaces. In this presentation we will demonstrate the first results on the automated synthesis and characterization for the combinatorial libraries of HOIPs. Using automated laboratory synthesis, we demonstrate formation of the library of HOIP compositions. Next, an automated characterization tool with capability of UV-Vis absorption and photoluminescence (PL) spectroscopy is used to rapidly measure the band gap energy and PL properties across the composition library. Finally, machine learning applied to the optical properties allows rapid elucidation of property evolution along 2- and 3-dimensional phase fields. We further discuss application of Gaussian process optimization for evolutionary search in the high dimensional composition spaces and balance between exploration and exploitative searches targeting individual aspects of figure of merits and their combinations. The synergy of compositional, and optical properties such as band gap and photoluminescence spectroscopy developed here allows a comprehensive picture of the functionality evolution across the composition series and attempts to establish predictive relationships across the composition in these material systems.

References:
8:30 AM *MT02.13.01
ML-Aided Thermal Management Materials Design and Small Data Strategy Yibin Xu; National Institute for Materials Science, Japan

Materials informatics has been expected to accelerate the process of materials design and development. More and more research results have been reported recently on study of material property prediction and material design using materials data and machine learning method. We have developed some machine learning models to predict thermal properties and design new materials with ultra-high/low thermal conductivities. In this talk, our recent work on development of thermal insulating coating and high thermal conductive polymer will be introduced. These results demonstrate the effectiveness of machine learning, meanwhile show that data availability and quality are the key issues of this method. A “small data” strategy is proposed to decrease the amount of data needed in machine learning and to make the best use of existing data.

9:00 AM MT02.13.02
Using Advanced Decision Policies in Bayesian-Optimized Machine Learning to Control Carbon Nanotube Growth Rahul Rao1, Pavel Nikolaev1, Ahmad E. Islam1, Kristofer Reyes2 and Benji Maruyama3; 1UES Inc Air Force Research Laboratory, United States; 2University at Buffalo, The State University of New York, United States; 3Air Force Research Laboratory, United States

Control over the properties (length, defect densities) and structure (diameter, semiconducting/metallocratic type) of carbon nanotubes (CNTs) is highly desirable for a number of applications. In this regard, we developed ARES (Autonomous Research System), which utilized a Random Forest algorithm to optimize carbon nanotube growth rate by evaluating in situ feedback from Raman spectroscopy during the growth process.1 Here we utilize Bayesian Optimization (BO) to control carbon nanotube diameters, which are critical for electronics applications. Previous implementations BO in materials development often use statistical models such as Gaussian Processes (GPs) to represent the experimental response function of interest. GPs make it difficult to specify fine-grained structure in the response function other through the specification kernel functions, which are often used to identify smoothness and periodicity of the function. In materials applications, however, other important structures of the response function must be considered. For example, the kinetics of materials synthesis can be parameterized through input variables such as temperature and gas flow rates, which affect certain kinetic processes over others. Hence, such a kinetic response is best modeled locally so that each local model captures only the relevant physics specific to input variables such as temperature. Here we demonstrate the use of local approximation belief models for to control CNT diameters. We show how to use such Bayesian beliefs inside the Knowledge Gradient (KG) decision policy to select information-rich experiments to run inside a closed-loop experimental system. Through this combination of local approximation belief models and the KG decision policy, we show how specific CNT properties such as diameter can be tuned and optimized over a small number of experiments.

9:15 AM MT02.13.03
Predicting Solid-Solution Formation—Machine-Learning and a New Physics-Based Rule Zongrui Pei1, Junqi Yin2, Jeffrey Hawk1, David Alman1 and Michael Gao1; 1National Energy Technology Laboratory, United States; 2Oak Ridge National Laboratory, United States

There are various empirical rules proposed to predict the formation of single-phase solid solution, but they are based on very small datasets and of very limited predictability. In the present work, we perform a machine-learning (Gaussian Process Classification) study on a large dataset consisting of 1252 alloys, including binary and high-entropy alloys, and we achieved a success rate of 93% in predicting single-phase solid solution. More importantly, the present machine-learning results also identify the most important features, among which are the Molar Volume and Bulk Modulus. Inspired by this machine-learning insight, a new physics-based thermodynamic rule is constructed. The new rule is nonetheless slightly less accurate (73%) than the machine learning algorithm, but employs only the elemental properties, which is in line with the spirit of Hume-Rothery rules. Therefore, it has advantages of simplicity and efficiency that render it very useful for high throughput application.
freud—Powerful Particle Simulation Analysis Tools for Machine Learning and Materials Design
Bradley D. Dice, Vyas Ramasubramani, Eric S. Harper, Matthew Spellings, Joshua A. Anderson and Sharon C. Glotzer;
University of Michigan, United States

Although particle simulations span a wide range of length and time scales, most well-established analysis tools are strongly focused on biomolecular simulations, and few tools exist for studying colloidal and coarse-grained material simulations. This presentation will showcase freud, a Python package that aids in calculating quantities that are frequently of interest in colloidal and nanoparticle simulations. We will discuss machine learning applications, including crystal structure identification in both supervised and unsupervised settings, which are enabled by the wide range of particle environment descriptors that freud implements. The freud library scales to extremely large systems, which has been crucial to studying complex phenomena such as the hexatic phase transition in systems of hard polygons that becomes most evident in simulations of over one million particles. It is also well-suited for building user-defined, computationally efficient analysis methods that can be adapted for analyzing new systems. We will show how the package’s efficiency and flexibility have enabled its use in such diverse applications as the inverse design of isotropic pair potentials and the optimization of shape-driven solid-solid phase transitions. Finally, we will demonstrate how output from freud can be coupled with visualization tools such as OVITO to render per-particle quantities in complex systems. Its flexibility allows freud to be used to engineer materials by design, including in cutting-edge applications such as analyzing simulations on-the-fly to study complex phenomena as they occur.

Revealing the Spectrum of Unknown Layered Materials with Super-Human Predictive Abilities
Gowoon Cheon¹, Ekin D. Cubuk², Evan Antoniuk¹, Joshua E. Goldberger³ and Evan J. Reed¹; ¹Stanford University, United States; ²Google Brain, United States; ³The Ohio State University, United States

We use semi-supervised learning to discover over 1000 new two-dimensional layered materials that have yet to be discovered or synthesized. We accomplish this by combining physics with machine learning on experimentally obtained data and verify a subset of candidates using density functional theory. Our model accelerates the discovery of layered materials by 13 times compared to random trial-and-error approaches. Even compared to expert scientists working in the field of two-dimensional materials, it is five times better than practitioners in the field at identifying layered materials and is comparable or better than professional solid-state chemists. We also of course find that our model is orders of magnitude faster than any human.

To achieve super-human performance, we employ semi-supervised learning techniques for the first time in materials discovery. Semi-supervised learning utilizes unlabeled data in addition to labeled data, which is powerful in cases where labels are expensive to obtain or are noisy. We find that semi-supervised learning provides benefits over supervised learning in identifying layered materials. In the field of materials physics, labeled data can be scarce, such as rare materials known to possess certain properties; they can also be noisy, such as property measurements with large errors. Semi-supervised learning may be applicable to a wide range of problems in materials science.

Microstructure Informatics—Expanding Descriptors from Molecular to Microstructural Level
Olga Wodo;
State University of New York at Buffalo, United States

The holy grail of materials science is to discover the mechanism governing the material properties and describe them in terms of a small set of physically meaningful descriptors. The discovery and exploration of materials and their properties critically depend on the availability of easily computable descriptors. At the atomistic level, descriptors played a key role in the area of materials design via first-principle combinatorial methods for photovoltaic, battery, or catalytic materials. More than a dozen software is available to calculate descriptors at the electronic and atomistic level. Descriptors at the next scale – microstructure– are relatively less explored and consist of various application specific and disparate clusters of descriptors. Most frequently, descriptors are tailored for characterizing specific mechanisms. In this talk, we present our unified framework to compute a library of generic descriptors. We describe our microstructure representation that facilitates the descriptor calculation. Our representation is based on the graph and skeleton and enables microstructure characterization in terms of shape (i.e., morphology), geometry, and
connectedness (i.e., topology). We explain how this work lays the foundation for machine learning of microstructure-property relationships and enables information fusion between multiple scales. We showcase our framework using examples from organic electronics.

11:00 AM MT02.13.07
High-Throughput Electron Microscopic Analysis of Nanomaterials Based on Machine Learning Techniques
Byoungsang Lee¹, Seokyoung Yoon¹ and Jung Heon Lee¹,²; ¹Sungkyunkwan University, Korea (the Republic of); ²SKKU Advanced Institute of Nanotechnology (SAINT), Korea (the Republic of)

Many important physical and chemical properties of nanomaterials, such as their optical, electronic, and catalytic properties, are strongly influenced by their morphological characteristics such as their shape, structure, and size.¹-⁵ Although it is desirable to synthesize mono-disperse nanomaterials for many applications, poly-disperse nanomaterials with substantially different shapes, structures, and sizes are generally obtained. Therefore a method suitable for precise characterization of the morphological properties of nanomaterials is highly demanded. Furthermore, it would be very important for this method to fulfill statistical analysis of the morphological characteristics of the nanomaterials as well.

Spectroscopy techniques such as UV-vis spectrometry, small-angle X-ray scattering (SAXS), and dynamic light scattering (DLS) are commonly used to assess morphological characteristics of nanomaterials. But it is very difficult to find exact morphological characteristic of nanomaterials using these techniques.

On the other hand, as electron microscopy (EM) allows images of individual nanomaterials to be taken, it is one of the best ways to analyze the morphological characteristics of nanomaterials. Furthermore, as the images of hundreds of nanomaterials can be easily obtained at the same time, if EM characterization is taken at low magnification, it can be a powerful way to acquire morphological characteristics of nanomaterials in a statistical manner. However, morphological analyses of nanomaterials are still carried out manually by individual researcher as the size of nanomaterials are generally measured from only several of the hundreds of nanomaterials collected from the researcher and the shapes and structures of nanomaterials can only be described in a qualitative manner. Thus, an innovative method to analyze the morphological characteristics of nanomaterials in a quantitative manner is highly demanded.

Here we have developed highly precise method to analyze the morphological characteristics of nanomaterials from EM images. [precise/facile/simple] Among over 50,000 nanomaterials we tested, this method were capable to identify the size and shape of nanomaterials with high precision of 99.7% and low false discover rate of 0.2%. This method was also capable to automatically identify and either separate or exclude overlaid nanomaterials to minimize misidentification of their morphological characteristics. To achieve this, we processed individual EM images of nanomaterials in various routes, including diverse pre- and post- treatments and varied edge detection (multiple thresholds), using machine learning and stacked all the processed.

On the other hand, it is impossible to measure all the population of nanoparticles with EM equipment. Therefore, we tried to find the number of samples needed through repeated measures multivariate analysis, but it was difficult to find the point to be saturated. The significance (p-value) in the multivariate analysis only affects the null hypothesis (effect size = 0), not only the correlation but also the size of the sample. On the other hand, the effect size is expressed in standard deviation units, which can be compared between any studies and utilized in meta-analysis. Therefore, we calculated the effect size using Hedges' g according to the number of repeated measurements and the number of particles per measurement and found a point where the decreasing slope saturates.

In addition, it was possible to cluster nanoparticles effectively using Fourier transform and Gaussian mixer models, and to classify optical effects according to morphological characteristics analyzed by EM through comparison of far-field optical responses of nanoparticles through clustering there was. As a result, we propose the need for new analytical techniques using EM.

11:15 AM MT02.13.08
Inverse Learning of Material Physics Through In Situ Image Data and Continuum Modeling
Hongbo Zhao and Martin Z. Bazant; Massachusetts Institute of Technology, United States

With the availability of spatio-temporal imaging data of energy materials at the nano to micron scale, there is a tremendous amount of information about the material properties that can be extracted. As an example, we show that the thermodynamic model, or free energy landscape of a phase-separating system can be learned through inversion of models such as Cahn-Hilliard or Allen-Cahn equations. Other models that involve reaction kinetics can also be used to model the dynamics of imaged particles when they are chemical driven. Here, we demonstrate that the
inverse problem technique can be applied to lithium-iron phosphate (LFP). By imaging the evolution of lithium concentration in the particle, we are able to extract its free energy and reaction kinetics, which typically are difficult to obtain through electrochemical measurements alone due to mosaic phase separation at the porous electrode scale.

11:30 AM MT02.13.09
Evaluating Machine Learning as a Tool for Segmentation of In Situ TEM Data James Horwath¹, Dmitri Zakharov² and Eric A. Stach¹; ¹University of Pennsylvania, United States; ²Brookhaven National Laboratory, United States

In situ and operando experimental techniques afford scientists the ability to observe dynamic processes in material systems with high spatial and temporal resolution. However, such experiments can generate enormous amounts of data in very short amounts of time. Without frameworks to efficiently and quickly analyze data, the benefits of these novel experimental techniques cannot be fully realized. Simultaneously, while the field of deep learning for image classification and segmentation has developed to a point where non-experts can implement and extend models to a variety of applications, we face a need for reproducibility and physical understanding of the results these models provide. Here, we evaluate the use of machine learning as a segmentation tool for the measurement and localization of supported nanoparticles in a high temperature Environmental Transmission Electron Microscopy (ETEM) experiment. Our methods are capable of segmenting high-resolution images at rates greater than one image per second, with only minimal post-processing steps required for quantitative analysis.

To begin, we have developed a method to automate the creation of reliable training labels for high resolution ETEM images using traditional computer vision techniques. With this training data in hand, we study the role of convolutional neural network (CNN) architecture on the practical utility of different models, and the learnability of our dataset. We also demonstrate the impact of image resolution on the ability of a standard CNN model to learn seemingly simple image features. Our experiments show the importance of regularization, particularly for image analysis, and we expose the danger in engineering machine learning architectures to better fit data rather than learning features of physical importance. In a final test case, we exhibit the use of a simple, single-layer CNN to process high resolution images which confirms that important image features are learned in the earliest layers of a deep learning model, and promotes the notion of scaling back the depth of a model in favor of increased interpretability and extensibility. The use of deep learning to solve physical problems is an area of active research, however a bridge is needed to relate learning theory and development to practical approaches for applying these techniques in other fields. In this work we attempt to systematically determine and investigate important features of machine learning models and datasets so that general tools for high-throughput data analysis can be developed.

11:45 AM MT02.13.10
Robust Microstructure Representation Devyani G. Jivani and Olga Wodo; SUNY Buffalo, United States

Microstructure quantification and design require a detailed and informative representation that uses a small number of design variables and at the same time allow to explore large microstructure spaces. The representation should capture the material features that are critical for establishing quantitative microstructure-property relationships. This work introduces skeletal-based microstructure representation that has capabilities to address all the above requirements. The modeling with skeletons is analogous to vertebrate animals and trees where the skeleton represents the underlying structure. Skeletons allow for the distillation of shape, size, and topological information. In principle, this paradigm allows the creation of models of arbitrary geometry and topology. The shape recognition algorithm – SpeedSeg is used to segment the skeleton into basic primitives to further decrease the design/storing space. In this set-up, a combination of arcs and line-segments is used.

The research demonstrates that using this representation shapes can be constructed incrementally and stored compactly. Moreover, the flexibility of this representation is demonstrated by modeling microstructures with a high level of spatial heterogeneity. The Cahn-Hilliard equation is used to model microstructure evolution between two polymers in the thin film. The microstructures are synthetically generated for varying blend ratios and interaction parameters. The study reveals that this representation leads to two orders of magnitude reduction in terms of storage required and associated number of variables. A similar analysis is performed for several other types of microstructures, including fibrous and cellular structures.
SYMPOSIUM MT03

Automated and Data-Driven Approaches to Materials Development—Bridging the Gap Between Theory and Industry
December 2 - December 5, 2019

Symposium Organizers
Tonio Buonassisi, Massachusetts Institute of Technology
Kedar Hippalgaonkar, Institute of Materials Research and Engineering
Kristin Persson, Lawrence Berkeley National Laboratory
Edward Sargent, University of Toronto

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SESSION MT03.01/MT02.01: Joint Session: Autonomous Science I
Session Chairs: Tonio Buonassisi, Jason Hattrick-Simpers, Kedar Hippalgaonkar and Benji Maruyama
Monday Morning, December 2, 2019
Hynes, Level 2, Room 210

8:00 AM *MT03.01.01/MT02.01.01
Autonomous Research Systems for Materials Development—2019 Workshop Summary Benji Maruyama1, Eric A. Stach2, Gilad Kusne3, Jason R. Hattrick-Simpers3 and Brian L. DeCost3; 1Air Force Research Laboratory, United States; 2University of Pennsylvania, United States; 3National Institute of Standards and Technology, United States

This presentation will summarize the results of our “Autonomous Research for Materials Development Workshop,” where a multidisciplinary group of materials researchers, computer scientists and AI/ML experts explored the opportunities, barriers and future investments. Closed-loop autonomous research systems are disrupting the research process.

The current materials research process is slow and expensive; taking decades from invention to commercialization. Researchers are now exploiting advances in artificial intelligence (AI), autonomy & robotics, along with modeling and simulation to create research robots capable of doing iterative experimentation orders of magnitude faster than today.

We propose a “Moore’s Law for the Speed of Research,” where the rate of advancement increases exponentially, and the cost of research drops exponentially. We consider a renaissance in “Citizen Science” where access to online research robots makes science widely available. This presentation will highlight advances in autonomous research and consider the implications of AI-driven experimentation on the materials landscape.

8:30 AM *MT03.01.02/MT02.01.02
Self-Driving Laboratories for Accelerating Discovery of Thin-Film Materials Curtis P. Berlinguette1,1,1, Jason E. Hein1, Alan Aspuru-Guzik2,3,3, Benjamin P. MacLeod1, Fraser G. Parlane1 and Brian Lam1; 1The University of British Columbia, Canada; 2Canadian Institute for Advanced Research (CIFAR), Canada; 3The University of Toronto, Canada

This presentation will focus on our self-driving laboratory for thin film materials discovery and optimization. Discovering high-performance, low-cost materials is an integral component of technology innovation cycles, particularly in the clean energy sector. The linear methodology currently used to develop optimal materials can take decades, which impedes the translation of innovative technologies from conception to market. Our interdisciplinary
team is utilizing advanced robotics and machine learning to overcome this challenge. We are closing the feedback loop in thin film materials research by enabling our self-driving robotics platform named “Ada” to design, perform, and learn from its own experiments efficiently and in real time. As a proof-of-principle set of experiments, we will show how Ada discovers and optimizes high-performance, low-cost hole transport materials for use in advanced solar cells. I will also showcase how Ada’s modular design can enable the automated and autonomous discovery of materials for other clean energy technologies.

9:00 AM MT03.01.03/MT02.01.03
An Inter-Laboratory High Throughput Experimental and Open Materials Data Study of Sn-Zn-Ti-O Jason R. Hattrick-Simpers¹, Andriy Zakutayev², Sara Barron¹, Zachary Trautt¹, Nam Nguyen¹, Kamal Choudhary¹, John D. Perkins², Caleb Phillips², Gilad Kusne¹, Feng Yi¹, Apurva Mehta¹ and Martin Green¹; ¹National Institute of Standards and Technology, United States; ²National Renewable Energy Laboratory, United States; ³SLAC National Accelerator Laboratory, United States

We present the results of an inter-laboratory high-throughput experimental (HTE) study which focused on measurement reproducibility and data exchange. Over the past 20 years, a great number of HTE techniques for synthesizing and characterizing thin-film oxides have been developed and reported. To date, however, there has not been a comprehensive study of how values measured for a series of properties (e.g. conductivity or optical band gap) on the same library compare across labs. Nor has there been a study that has attempted to normalize the hand-off of HTE samples and data. Here we report on the first such study using the Sn-Zn-Ti-O transparent conducting oxide system.

A series of Sn-Zn-Ti-O samples were deposited via Pulsed Laser Deposition and magnetron co-sputtering. At each institution a set of HTE measurements were made for typical properties including structure, thickness, conductivity, and optical bandgap. The samples were then exchanged between the two labs and the same set of properties were measured at the other lab and the data exchanged via an agreed upon uniform format.

A few lessons learned and several scientific observations regarding the reproducibility of HTE results gathered during this process will be discussed. An important lesson was the importance of deciding upon, and using, consistent measurement grids within a lab (and during exchanges) for all measurements, as this will impact future data archiving and retrieval. It was observed that qualitative trends are well reproduced even when two labs use very different methods for measuring a property, for instance ellipsometry versus transmission-reflection UV-VIS spectroscopy. However, quantitative comparisons were found to be measurement specific and spanned from excellent (bandgaps measured within a mean absolute error < 0.1 eV) to relatively poor (log resistivity measurements within a mean absolute error of 2). In the latter case, we believe that differences in sample probe geometries coupled to large changes in the properties of small composition regions were the most likely source of the poor correlation. The lessons learned and best practices obtained will be discussed.

9:15 AM MT03.01.04/MT02.01.04
Automatic Microcrack Inspection in Photovoltaics Silicon Wafers by Unsupervised Anomaly Detection via Variational Auto-Encoder Zhe Liu, Felipe Oviedo, Emanuel M. Sachs and Tonio Buonassisi; Massachusetts Institute of Technology, United States

The presence of microcracks in silicon wafers significantly reduces wafer strength, yielding wafer breakage during the manufacturing process, transportation and field operation. With the trend of decreasing wafer thickness for cost reduction purposes, thinner wafers are more prone to breakage in the presence of microcracks [1]. To enable a smooth transition to thin wafers for even cheaper photovoltaic modules, we recently developed a high-throughput prototype for in-line crack detection for silicon wafers [2]. This tool scans silicon wafer in the near-edge regions for micro-cracks and outputs linescan signals from a linescan camera, where no crack shows a smooth, undisrupted profile. As an in-line detection tool, it also requires a rapid and reliable algorithm that automatically identifies the presence of a micro-crack within a second after wafer scanning. In this work, we adopted an unsupervised machine learning method for anomaly detection, because the presence of microcracks above the critical length is typically a statistically rare event in the current PV production line (typically less than 5%). Specifically, a generative machine learning algorithm variational auto-encoder (VAE) is used to identify scans with microcracks [3]. The working principle of this algorithm is that: (1) VAE encodes the linescan profiles into lower-dimension vectors of latent variables, and then the latent variables are reconstructed back to linescan profile with the goal of minimized error; (2) because of most linescan profiles are very similar smooth curves without any cracks, the VAE model is trained to be biased toward linescan without cracks; (3) whenever a linescan profile for a crack appears, the trained VAE
model generates a vastly different profile with a significant reconstruction error; (4) the crack is then detected by monitoring anomalous reconstruction error. The advantage of this unsupervised VAE method over the previous neural network method [4] is that it does not require a large amount of labelled crack data with different crack shapes (which can be very difficult to obtain). We demonstrate successful crack detections with several different wafer types (e.g., multi, mono, as-cut, and textured) and crack shapes (e.g., line-shape, cross-star, L-shape). We show that, with statistical analysis, this VAE-based anomaly detection could be a reliable and versatile method to enable the rapid detection of microcracks in silicon wafers.

Reference:

9:30 AM MT03.01.05/MT02.01.05
Screening of High-Capacity Oxygen Storage Materials with Machine Learning Approach Nobuko Ohba1, Takuro Yokoya2, Seiji Kajita1 and Kensuke Takechi1; 1Toyota Central R&D Laboratories, Inc., Japan; 2Toyota Motor Corporation, Japan

The oxygen storage material (OSM), such as CeO2 or pyrochlore type CeO2-ZrO2 (p-CZ), is used as a catalyst support for a three-way catalyst in automotive emission control systems. It has oxygen storage capacity (OSC) that is an ability to release and store oxygen reversibly by the fluctuation of cation valence depending on the reducing and oxidizing atmosphere. In this study, we explore high-capacity OSMs by using materials informatics (MI), which combines material science with inference algorithms in machine learning. The OSC of 60 metal oxides supported Pd were experimentally estimated by the amount of produced CO2 while switching between oxidizing (O2) and reducing (CO) atmosphere every 2 minutes at temperature of 973, 773, and 573K. These experimentally measured OSC data were used as supervised data in our MI scheme. The support vector machine regression model was trained for the prediction of the OSC at each measured temperature. This model uses descriptors in which physical properties are considered to represent the features of the OSC. These features were automatically extracted using grid search to achieve each model with the highest accuracy. It is found that the features related to the stability of the oxygen atoms in the crystal and the crystal structure itself such as cohesive energy, which is obtained from the first-principles calculation, are highly correlated with the OSC. The present model predicts the OSC of 1,300 existing oxides registered in the in-house electronic structure calculation database. Several dozen materials with promising high OSC were proposed through this virtual screening. We synthesized one of the screened materials and experimentally confirmed that it indicates higher OSC than the conventional OSM, p-CZ.

9:45 AM BREAK

10:15 AM *MT03.01.06/MT02.01.06
The Metaphysics of Chemical Reactivity and Materials Discovery Lee Cronin; University of Glasgow, United Kingdom

Discovery in chemistry falls mainly into one of four types of areas with the discovery of new molecules, new reactions, new reactivity, and finally new physical properties of the resulting compounds or materials. Establishing new reactivity leads to new reactions which also leads to new molecules. This is therefore the order of impact for discoveries in terms of the amount of chemical knowledge that they contribute. Such findings must, by definition, belong outside the known or predictable; and they are outliers and as such can oppose conventions, assumptions and
biases. By developing the meta-physics of chemistry and chemical reactivity we should be able to establish a new set of ontologies in chemistry that relate back to the practical core operations, but also can be translated into molecular structures and the discovery of function. The truth of chemistry lies with finding the intrinsic reactivity of the input chemicals, and then encouraging or enabling reactivity by process control. Whilst the new discovery and reaction should be translatable to chemical bonding theory, chemists need to grapple with the fact that the application of the current rules will not allow discovery, instead they will act to restrict it to the known rules. So chemical discovery requires that the current rules are updated, broken, or new ones are made where before there were none. The discovery of Diels-Alder or cross-coupling reactions are excellent examples of new rules that were just discovered without any prior warning.

Without a deeper development of a meta-physics of chemistry the use of big data and artificial intelligence will just tell us what we already know we know, and maybe predictable extensions, rather than enabling discovery. The challenge for the chemist is not the use of artificial intelligence, but the intelligent use of algorithms and automation for novel discoveries. In this talk I will explain how this might be possible.

References

10:45 AM MT03.01.07/MT02.01.07
Robot-Accelerated Perovskite Investigation and Discovery (RAPID)—A High-throughput Approach Towards Metal Halide Perovskite Single Crystal Discovery
Zhi Li1, Mansoor Ani N. Nellikkal2, Liana Alves2, Peter Parrilla2, Ian M. Pendleton2, Matthias Zeller2, Joshua Schrier2, Alexander Norquist2 and Emory Chan3;
1Lawrence Berkeley National Lab, United States; 2Haverford College, United States; 3Purdue University, United States; 4Fordham University, United States

Metal halide perovskites have emerged as promising materials for next-generation photovoltaic and optoelectronic devices. The discovery and full characterization of new metal halide perovskite-derived materials have been limited by the difficulty of growing high quality single crystals needed for single crystal X-ray diffraction studies. The formation of large single crystals is non-trivial, owing to the vastness of the chemical search space with enormous compositional degrees of freedom. We present the first automated, high-throughput approach for metal halide perovskite single crystal discovery based on inverse temperature crystallization (ITC) as a means to rapidly identify and optimize synthesis conditions for the formation of high quality single crystals. Using our automated approach, we have carried out a total of over 5000 metal halide perovskite synthesis reactions spanning six chemical systems. Through this unbiased search of the experimental space, we have more than doubled the number of metal halide perovskite materials accessible by ITC method and discovered a new perovskite structure. Combining machine learning and other statistical methods, we quantify the total experimental space and the likelihood of large single crystal formation. Moreover, machine learning models have been constructed for each chemical system, in which single crystal formation is modeled. This work is a proof of concept that a combined approach of high throughput experimentation and machine learning can be effective in the study of metal halide perovskite crystallization. The approach presented here is designed to be generalizable to different synthetic routes for the acceleration of materials discovery.

11:00 AM MT03.01.08/MT02.01.08
Optimizing Hole Transport Materials with a Self-Driving Thin-Film Laboratory
Benjamin P. MacLeod1,1, Fraser G. Parlane1,1, Thomas D. Morrissey1,1, Florian Häse2,3,4, Loïc M. Roch1,3,4, Kevan Dettelbach1, Raphael Moreira1, Lars Yunker1, Michael Rooney1, Joseph Deeth1, Verónica Lai1, Gordon Ng, Henry Situ1, Ray Zhang1, Alán Aspuru-Guzik1,2,3,4, Jason E. Hein1 and Curtis P. Berlinguette1,1,1; 1The University of British Columbia, Canada; 2Harvard University, United States; 3University of Toronto, Canada; 4Vector Institute for Artificial Intelligence, Canada

Self-driving laboratories combine algorithmic data analysis and experiment planning with robotic workflows to
autonomously optimize one or more experimental figures of merit. This approach is applicable to challenging multi-parameter and multi-objective optimization problems such as the optimization of thin film materials within the vast design space of composition, deposition, and processing conditions. Here we describe a self-driving laboratory capable of formulating inks, depositing films via spin-coating, characterizing the resulting thin films using multiple techniques, and planning new experiments based on previous experimental data using the ChemOS experiment orchestration software. The utility of this self-driving laboratory is demonstrated by autonomously optimizing optical and electronic properties of hole transport materials, which are crucial to the operation of a variety of thin-film-based optoelectronic devices. The autonomous optimization manipulates the film composition and annealing protocol to maximize a hole-mobility surrogate obtained by fusing data from transmission-reflection UV-Vis-NIR spectroscopy and 4-point probe conductivity measurements.


11:15 AM MT03.01.09/MT02.01.09

In the development of next-generation photovoltaics and light-emitting diodes, colloidal inorganic perovskite quantum dots (QDs) have drawn notable attention for their highly tunable bandgap properties, high-charge carrier mobility and defect tolerance, and adaptability towards solution phase processing. However, studies of this material group and other colloidal semiconductor nanocrystals requires extensive exploration of their massive reaction parameter space within highly controlled reaction environments. Conventional flask-based, trial-and-error approaches are, therefore, highly unlikely to effectively capture the full potential and optimal synthesis conditions of these high-priority materials. Further complicating this process, across the accessible bandgap range, optimal synthesis parameters will vary significantly. Flow synthesis platforms have recently been demonstrated as a time-and material-efficient reaction monitoring strategy for synthesis, screening, and optimization of colloidal nanomaterials. The high sampling rate, low chemical consumption, and precise process control (automation) of flow reactors greatly reduces the challenges in exploring complex reaction spaces; however, high-throughput reaction screening technologies alone are likely not able to make significant breakthroughs, due to the massive scope of relevant colloidal synthesis conditions.

In this work, we present a modular microfluidic platform integrated with a machine learning (ML)-enhanced reaction optimization algorithm for on-demand synthesis of high-quality inorganic perovskite QDs with desired optical properties using a homogeneous anion exchange reaction. The intelligent QD synthesis platform consists of multiple computer-controlled pumps for on-demand reagent delivery/dosing, a flow path selector valve for automated selection of the halide salt source, and an in-line flow cell for automatic UV-Vis absorption and photoluminescence spectroscopy. Utilizing a utility function, an array of trained neural networks, and a global optimization algorithm, the intelligent QD manufacturing platform, approaches a target emission bandgap, while minimizing emission linewidth and maximizing quantum yield by tuning the concentrations of the precursors. Halide salt precursors are mixed within a highly efficient inline micromixer before combining with the perovskite QDs and gas-liquid segmentation. Monitoring each halide exchange condition requires less than 180 uL of total halide salt precursor and 170 uL of starting perovskite QDs per sample.

Integration with a ML-enhanced optimization algorithm enables the system to reach optimized synthesis conditions, across all six variables, for a target emission energy of 2.2 eV in 238 samples and 83 mL of chemicals without any prior training. More advanced optimization methods and pre-training with archived experimental data will further reduce this optimization time and cost. The versatility and modularity of the developed intelligent QD synthesis platform make it readily adaptable for on-demand synthesis of other colloidal nanomaterials.

11:30 AM MT03.01.10/MT02.01.10
Autonomously Optimizing Thin Film Morphologies Using Machine Vision Fraser G. Parlane¹, Benjamin P. MacLeod¹, Nina Taherimakhsousi¹, Alan Aspuru-Guzik², Jason E. Hein¹ and Curtis P. Berlinguette¹; ¹The University of British Columbia, Canada; ²University of Toronto, Canada

The morphologies of solution-deposited thin films are frequently governed by complex combinations of processes from domains including multi-phase fluid flow, heat transfer, nucleation, solid mechanics, and interfacial...
phenomena. This complexity can frustrate both theoretical and empirical attempts to understand and control the morphologies of such films. Here we report an autonomous robotic system that uses machine vision feedback to determine optimal experimental parameters to achieve homogeneous, high-quality films via spin coating. An ink-formulating and spin-coating robot equipped with an imaging system provides images of thin films to a computer vision algorithm which grades the quality of the thin films. This grading assessment provides input to an optimization algorithm that chooses the next ink formulation with the goal of identifying regions in the parameter space of ink formulation and spin-coating conditions that result in high-quality films.


SESSION MT03.02/MT02.02: Joint Session: Autonomous Science II
Session Chairs: Gilad Kusne, Markus Reiher and Aleksandra Vojvodic
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 210

1:30 PM *MT03.02.01/MT02.02.01
Quantum Machine Learning in Chemical Space Anatole von Lilienfeld and Guido Falk von Rudorff; University of Basel, Switzerland

Many of the most relevant chemical properties of matter depend explicitly on atomistic and electronic details, rendering a first principles approach to chemistry mandatory. Alas, even when using high-performance computers, brute force high-throughput screening of compounds is beyond any capacity for all but the simplest systems and properties due to the combinatorial nature of chemical space, i.e. all compositional, constitutional, and conformational isomers. Consequently, efficient exploration algorithms need to exploit all implicit redundancies present in chemical space. I will discuss recently developed alchemical perturbation theory and quantum machine learning based approaches for interpolating quantum mechanical observables in compositional and constitutional space. Numerical results of our models indicate controlled accuracy and favourable computational efficiency.

2:00 PM *MT03.02.02/MT02.02.02
AI for Automating Materials Discovery Carla Gomes and Bruce van Dover; Cornell University, United States

Artificial Intelligence (AI) is a rapidly advancing field. Novel machine learning methods combined with reasoning and search techniques have led us to reach new milestones with increasing frequency, from self-driving cars to computer vision, machine translation, computer Go trained on human play, to Go and Chess world-champion level play using pure self-training strategies. These ever-expanding AI capabilities open up exciting new avenues for automating scientific discovery. I will discuss our work on using AI for accelerating and automating materials discovery. In particular, we have focused on high-throughput structure determination for combinatorial materials discovery and on solving the phase map diagram problem for composition libraries. While standard statistical and machine learning methods are important to address this challenge, they fail to incorporate relationships arising from the physics of the underlying materials. I will introduce an effective approach based on a tight integration of machine learning methods, to deal with noise and uncertainty in the measurement data, with optimization and inference techniques, to incorporate the rich set of constraints arising from the underlying physics. Finally, I will describe our vision and progress concerning Scientific Autonomous Reasoning Agent (SARA), a multi-Agent system to accelerate materials discovery integrating in a synergistic and complementary way, first principles quantum physics, experimental materials synthesis, processing, and characterization, and AI based algorithms for reasoning and scientific discovery, including the representation, planning, optimization, and learning of materials knowledge.

2:30 PM MT03.02.03/MT02.02.03
Machine Learning Methodologies to Enhance Automated Synthesis of New Materials Jonathan Fine, Armen Beck and Gaurav Chopra; Purdue University, United States
Functional groups link analytical, physical, organic, and materials chemistry and are therefore central to the chemical sciences. In both analytical and organic chemistry functional groups are used to predict the reactivity of molecules, select a solvent for a given reaction, and validate a reaction using measurable changes in the properties of a molecule. Current approaches to incorporate functional groups in the prediction, planning and verification of reaction conditions rely on human intervention and input. For example, the solvent used for a given transformation is chosen by a skilled organic chemist using intuition gained from the study of how the functional groups in a molecule dictate its solubility in a solvent. To verify if the reaction took place resulting in an unknown chemical entity, the state-of-the-art method is to accurately identify all functional groups of the reactants and products. This process is time-consuming, involves manual or database dependent analysis and interpretation of a Fourier Transform Infra-Red (FTIR) spectrum or Mass Spectroscopy (MS) data using previously established rules and experience of a skilled spectroscopist. These processes are subject to trial and error for compounds with multiple functional groups and for compounds that are not well characterized in the literature. Such issues hinder the automated development and characterization of truly new materials with minimal human intervention. We present fast deep learning methods to select the optimal solvent for a given reaction in a transformation-free manner and identify all the functional groups for both the products and reactants for any given reaction. Our methods do not use any database, pre-established rules or procedures to perform either task and use the general definition of functional groups as a ‘collection of atoms’ instead of simple chemical groups traditionally assigned by chemists. We use Artificial Neural Networks (ANNs) to derive patterns and correlations between these collections of atoms and the solvents used to carryout a given chemical reaction using 2.3 million patented reactions available from the United States Patent and Trademark Office. Our methodology is the first to differentiate solvents by their precise chemical structure instead of simply choosing a solvent class and yields a 5-fold cross-validated average F1-score greater than 0.9. Solvent predictions obtained from this model have been validated both in silico using Density Functional Theory and using experimental in situ techniques. To verify that a reaction has occurred, we trained separate ANNs on 7393 publicly available FTIR and MS combined spectra obtained from the NIST Webbook. Instead of using multiple binary classifiers used in previous works to assign functional groups, our approach treats the classification problem in a multi-class, multi-label fashion. The model has a cross-validated F1 score higher than 0.82 for 14 out of 17 defined functional groups. To showcase the practical utility of our method, we introduce two new metrics (Molecular F1 score and Molecular Perfection rate) to measure the performance of identifying all functional groups on molecules. The optimized model has a Molecular F1 score of 0.92 and a Molecular Perfection rate of 72%. Additionally, backpropagation of our model reveals IR patterns typically used by human chemists to identify standard groups, suggesting a convergence of the model on known spectral features that are diagnostic of particular functional groups. We further show that the introduction of additional functional groups does not decrease the performance of our model. Finally, we show redundancy in FTIR and MS data by encoding all our features in a latent space that retains the accuracy of the original model. These results reveal the importance of using machine learning for automated identification of new reaction conditions and functional groups to achieve autonomous processes in the future.

2:45 PM MT03.02.04/MT02.02.04
Autonomous Research Systems—Phase Mapping & Materials Optimization Gilad Kusne; National Institute of Standards and Technology, United States

The last few decades have seen significant advancements in materials research tools, allowing researchers to rapidly synthesize and characterize large numbers of samples - a major step toward high-throughput materials discovery. Machine learning has been tasked to aid in converting the collected materials property data into actionable knowledge, and more recently it has been used to assist in experiment design. In this talk we present the next step in machine learning for materials research - autonomous materials research systems. We first demonstrate autonomous measurement systems for phase mapping, followed by a discussion of ongoing work in building fully autonomous systems. For the autonomous measurement systems, machine learning controls X-ray diffraction measurement equipment both in the lab and at the beamline to identify phase maps from composition spreads with a minimum number of measurements. The algorithm also capitalizes on prior knowledge in the form of physics theory and external databases, both theory-based and experiment-based, to more rapidly hone in on the optimal phase map. The phase map is then exploited for functional material optimization.

3:00 PM BREAK

3:30 PM *MT03.02.05/MT02.02.05
Information Extraction and Learning by Large-Scale Text-Mining of the Scientific Literature  
Gerbrand Ceder; University of California, Berkeley, United States

The overwhelming majority of scientific knowledge is published as text, which is difficult to analyze by either traditional statistical analysis or modern machine learning methods. In contrast, the main source of machine-interpretable data for the materials research community has come from structured property databases which encompass only a small fraction of the knowledge present in the research literature. Beyond property values, publications contain valuable knowledge regarding the connections and relationships between the data items as interpreted by the authors. I will show multiple ways to extract useful information from scientific text in both supervised and unsupervised ways. I will show that materials science knowledge present in the published literature can be efficiently encoded as information-dense word embeddings (vector representations of words) without human labelling or supervision. These embeddings capture complex materials science concepts such as the underlying structure of the periodic table and structure-property relationships in materials. Furthermore, we demonstrate that an unsupervised method can recommend materials for functional applications several years before their discovery. This suggests that latent knowledge regarding future discoveries is to a large extent embedded in past publications. In a more supervised way, we have also demonstrated the extraction of codified synthesis recipes from text. Extraction the details of synthesis, including precursor compounds, synthesis operations and their numerical details, requires a very high precision of information extraction, and a tolerance to deal with imprecise and non-standard language. I will show how a large data set of codified solid-state synthesis reactions has been obtained and be queried to obtain interesting information on choice of synthesis operations and precursors is related to the target material.

4:00 PM *MT03.02.06/MT02.02.06
Autonomous Scanning Droplet Cell for On-Demand Alloy Electrodeposition and Characterization  
Brian L. DeCost, Howie Joress, Trevor Braun, Zachary Trautt, Gilad Kusne and Jason R. Hattrick-Simpers; National Institute of Standards and Technology, United States

We are developing an autonomous scanning droplet cell (ASDC) capable of on-demand electrodeposition and real-time electrochemical characterization for investigating multicomponent alloy systems for favorable corrosion-resistance properties. The ASDC consists of a millimeter-scale electrochemical cell and an array of programmable pumps that can be used to electrodeposit an alloy film and immediately acquire polarization curves to obtain electrochemical quantities of interest, such as the passive current density and oxide breakdown potential. We model these quantities using Gaussian Process regression to select the most informative series of alloys to synthesize and characterize, continuously updating the model as new electrochemical data is acquired. Our initial studies focus on systems that are likely to form corrosion-resistant metallic glasses (MGs) and single-phase multi-principle element alloys (MPEAs).

The ASDC is an open exemplar autonomous system that provides insight into both technical and methodological aspects of building and deploying robust closed-loop synthesis and characterization platforms. Our approach is to build loosely-coupled modular experimental, automation, and communications systems to 1. support rapid prototyping, debugging, and verification while producing meaningful scientific output and 2. enable integration into future large-scale multi-user and multi-instrument distributed laboratory systems. We address both of the main challenges that autonomous science systems face: learning to reliably synthesize materials and mapping material specification and processing to structure and properties. We will discuss the incorporation of prior knowledge in the form of theoretical and data-driven predictive models, as well as the integration of online and offline multi-modal experimental data streams. Ultimately, closed-loop automated materials synthesis and characterization platforms offer much more than a means of engineering materials properties and performance through black-box optimization algorithms: they offer the potential to develop and deploy new algorithms for generating and testing scientific hypotheses.

4:30 PM MT03.02.07/MT02.02.07
Autonomous Electrolyte Discovery for Batteries with Experimentally Informed Bayesian Optimization  
Adarsh Dave, Sven Burke, Jared Mitchell, Kirthivasan Kandasamy, Biswajit Paria, Barnabas Poczos, Venkatasubramanian Viswanathan and Jay F. Whitacre; Carnegie Mellon University, United States

An autonomous battery electrolyte experimental platform capable of mixing multi-component electrolyte systems
and characterizing the transport and electrochemical properties in a high-throughput manner is disclosed. A Bayesian optimization software package found novel electrolyte compositions through optimization of the high-dimensional electrolyte design space over key design objectives like electrochemical stability and conductivity. Electrolyte optimization is difficult because 1) electrolyte evaluation is expensive and takes time, and 2) the space of possible electrolytes is expansive, formed by many possible choices for solvents (often in ternary blends), salts (often in binary mixtures), and trace additives. Bayesian optimization methods are well suited for the optimization of high-dimensional functions with costly evaluations, often producing an efficient design-of-experiments to converge on multi-objective optimal formulations in few experiments. To expedite the optimization over the expansive design space, theoretical predictions of electrolyte properties via the Advanced Electrolyte Model were utilized as “priors” in the statistical model.

Implementation of the novel experimental platform was carried out by two novel test stands developed to automate the mixing and characterization of electrolytes: Otto (for aqueous systems) and Clio (for aprotic/organic systems). The test stands characterized the ionic conductivity and electrochemical stability of electrolyte systems, featuring a four-electrode conductivity probe, pH meter, and a flow-through three-electrode cell and potentiostat. Clio also integrated electrochemically active electrodes for optimization of electrolyte/electrode systems. The active electrode systems used were common functional ceramic metal oxides.

A software orchestration and data layer linked the test-stands to human experimenters and machine-learning packages through a web-services architecture; all experiment data and meta-data is saved in a database. Additional out-of-the-loop characterization was conducted on cathodic systems to validate composition, structure, and oxidation state. The aqueous design space consisted of aqueous blends of lithium and sodium salts, including nitrates, sulfates, and other commonly-used battery salts. High-concentration aqueous electrolyte candidates were discovered by optimizing of electrochemical voltage stability and conductivity, including low-cost, high-performing alternatives to known but costly aqueous electrolytes (e.g. LiTFSI). Clio’s design space includes blends of both aprotic organic solvents and solutes in additional to various compositions of electrochemically active electrodes. The test-stands are demonstrated to be significantly faster than common human experimentation techniques, converging on novel, optimized electrolyte mixtures in mere hours or days of experimentation.

SESSION MT03.03: Poster Session I: Autonomous Science
Session Chairs: Tonio Buonassisi, Kedar Hippalgaonkar and Kristin Persson
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

MT03.03.01
A Comparative Study of Experiments and Simulations on Grain-Boundary Formation of Polycrystalline Ba122 Phase Iron-Based Superconductors

Yuki Okada1, Shinnosuke Tokuta1, Yusuke Shimada2, Akimitsu Ishii1, Akinori Yamanaka1 and Akiyasu Yamamoto1; 1Tokyo University of Agriculture and Technology, Japan; 2Tohoku University, Japan

Iron-based superconductors are promising materials for high magnetic field applications because of their high transition temperature, high upper critical filed and small electromagnetic anisotropy [1]. Grain-boundaries (GBs) play a dominant role on the transport current performance of superconducting materials. Katase et al. reported that the critical current density through artificial bicrystal grain boundary is strongly dependent on grain boundary misorientation GB angles (θGB) and nearly constant up to a critical angle θc of ~9 degrees, which is substantially larger than the θc of ~5 degrees for YBa2Cu3O7−δ. [2]. Foreseeing the future applications such as long-length wires and large bulk materials, it is important to understand the mechanisms of the grain-boundary formation during the solid-state sintering of polycrystalline iron-based superconductors. However, the mechanism of grain-boundary formation during the solid-state sintering has not been elucidated because in situ observation of grain-boundary at high temperature is technically not easy. In this sense, the numerical modeling of grain-boundary formation is a promising approach for understanding and controlling the grain-boundary structure in the sintered materials. In particular, phase-filed modeling [3,4] is a powerful tool to solve free boundary problems, such as the grain-boundary migration in polycrystalline materials. In this study, we performed the comparative study of experiments and phase-
field modeling on grain-boundary formation of polycrystalline K-doped Ba122 iron-based superconductors. K-doped Ba122 polycrystalline bulk samples at different stages of sintering were fabricated by systematically changing heating conditions of mechanically alloyed powder. Their microstructure was analyzed by SEM and STEM to understand the mechanisms of grain-boundary formation during sintering. These experimental results were compared with the extended multi-phase-field modeling of solid-state sintering based on the model proposed by Wang [5].


MT03.03.02
Raman Mapping of Graphene-Based Materials—a Statistical Guide to Significance Stuart Goldie and Karl Coleman; Durham University, United Kingdom

Recent publications analysing some commercially available graphene and GNP (graphite nanoplatelets) samples have highlighted the need for a robust metrology if graphene and related technologies are to develop. Raman spectroscopy is a widely used tool for probing carbon due to the wealth of information that can be gained, however it is a highly localised probe and recording a single spectrum over a wide area often produces a distorted result dominated by minor features. This can be problematic when measuring inhomogeneous materials that contain a mixture of graphite flake sizes, thicknesses and various degrees of functionalization and defect concentrations.

To overcome these limitations, spectra can be recorded from a number of different points on a sample surface; however this poses a new question: how many points are needed? To answer this we have measured a selection of common graphitic materials including commercial GNPs and liquid exfoliated graphene to generate large data sets of Raman spectra from many points. A bespoke computer program has been developed in this study and was used to automatically fit the Raman signals for each independent spectrum; these parameters can then be used to infer some of the properties of the material. For example the heights of the D peak and G peak are often compared to estimate the concentration of defects in the sp² network.

The convergence of these parameters is used to identify the approximate sample size required for robust characterization by plotting summary statistics (mean, interquartile range and P10 & P90) against the size of the data set; followed by a Monte Carlo based approach to resample data in smaller sets and probe the potential error when using an insufficient number of measurements. Whilst the focus of this work was on Raman spectroscopy, the methodology is applicable to other analysis techniques that require multiple measurements. Whilst different materials behave differently, in most cases it is clear that an average value can be derived after approximately one hundred data points however a full distribution describing the variety of materials present is only obtained after many hundreds of spectra are analysed. We also find many of these distributions are not normal, and simple metrics like mean and standard deviation fail for graphene materials, as reported previously.

It is hoped this statistical approach can be applied in a variety of settings, both academic and industrial to inform the careful characterization and reporting of graphene materials. Raman spectroscopy is a non-destructive technique that is already in routine use and the spectral fitting program developed to accurately process these data sets will be freely available.

References
(4) Ferrari, A. C. Raman Spectroscopy of Graphene and Graphite: Disorder, Electron–Phonon Coupling, Doping and


**MT03.03.03**

**High-Throughput Screening of p-Type Transparent Oxide Semiconductors**

*Miso Lee*¹, Yongs Youn¹, Kanghoon Yim² and Seungwu Han¹; ¹Seoul National University, Korea (the Republic of); ²Korea Institute of Energy Research, Korea (the Republic of)

The transparent devices require complementary pairs of n-type and p-type transparent semiconductors to fabricate high efficient electronic devices. However, only a few p-type transparent oxide semiconductors were identified while there are a lot of n-type transparent oxide semiconductors like ZnO and In₂O₃, and InGaZnO with good device performances. Recently, several studies have been performed to search for p-type oxides using high-throughput screening with the band gap and effective mass (or branch point energy) as descriptors. However, these descriptors do not well distinguish the n-type and p-type oxide groups. Furthermore, none of suggested materials was verified experimentally, which means we need a better theoretical predictor. In this presentation, we propose a reliable descriptor for the p-type dopability based on the formation energy of hydrogen impurity (FEH). The predictive power of FEH is validated by that it can distinguish well known p-type and n-type oxides. Using FEH, we screen binary oxides and selected ternary compounds by considering the known design principles of p-type oxides (containing Sn²⁺ and Cu¹⁺ as well as oxychalcogenides). Considering FEH, band gap, and hole effective mass, we suggest La₂O₂Te and CuLiO as promising p-type oxides, which are validated through the full intrinsic defect calculations. [1] Furthermore, to enable high-throughput screening, we identify two coarse but simple descriptors - the band gap and oxygen partial weights at valence band maximum which correlate with FEH. Using the simplified descriptors, we screen over 17,700 oxygen-containing compounds in AFLOW database and select 426 compounds for the calculation of FEH. Finally, we identify 156 oxide semiconductors with the band gap larger than 1.1 eV and good p-type dopability. Furthermore, we classify the identified p-type oxides according to their valence band character and reveal chemical principles underlying the p-type dopability. [2]

**References**


**MT03.03.05**

**Spectrum Adapted Expectation-Maximization Algorithm for High-Throughput Peak Shift Analysis in Synchrotron X-Ray Operando Spectromicroscopy**

*Naoika Nagamura*¹², Tarojiro Matsumura³, Shotaro Akaho³, Kenji Nagata¹² and Yasunobu Ando³; ¹National Institute for Materials Science, Japan; ²Japan Science and Technology Agency, PRESTO, Japan; ³National Institute of Advanced Industrial Science and Technology, Japan

Recently, various kinds of high resolution and multi-parameter spectral analysis is available by using high brilliant quantum beams like synchrotron radiation X-rays. Such advanced spectroscopy measurements potentially produce huge number of datasets. Developing the efficient method for the spectral data analysis is an urgent issue in the multi-dimensional measurements.

For example, operando SR X-ray scanning photoelectron microscopy system, called “3D nano-ESCA” (three-dimensional nanoscale electron spectroscopy for chemical analysis)[1], provides spatial, time and electric field dependence of photoemission spectra. This equipment has bias voltage application circuit for “operando analysis”, i.e. spectroscopy analysis during device operation, so we perform electric potential mapping by detecting the spatial distribution of XPS core-level peak shift in microscopic device structures under operation with high spatial resolution (~ 70 nm). However, the 3D nano-ESCA has been performed only for the pin-point or line-scan analysis that deals with few tens of spectral datasets by the inefficiency of peak fitting procedure, although spatial and time resolved measurement potentially provides over thousands of the datasets.

The method of spectral data analysis using machine learning technique has been studied to improve the resorting to the manual trial and error, e.g. applying a Bayesian peak separation with the exchange Monte Carlo method[2]. However, the computational cost was paid little attention because the number of datasets was not so large in conventional spectroscopy measurements.

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Here we introduce the spectrum-adapted expectation-maximization (EM) algorithm for the high-throughput peak shift detection analysis of the large number of spectral datasets by considering the weight of the intensity corresponding to the measurement energy steps\[3\].

The EM algorithm is one of the machine learning techniques for estimating the parameters of the mixture model, including latent parameters, based on maximum likelihood estimation with iterative calculation between the expectation (E) step and the maximization (M) step. When ordinally EM algorithm is applied to the peak separation using a linear superpositions of distributions such as Gaussian distributions, the analyzed data are required to be one-dimensional, but the spectral data consists of N measurement steps of energy \( (x = \{x_1, \ldots, x_n, \ldots, x_N\}) \) corresponding to the intensity \( (w = \{w_1, \ldots, w_n, \ldots, w_N\}) \). So we solved this disadvantage by using the intensity \( (w) \) as a weight for each measurement step \( (x) \).

We applied the proposed method to the experimental datasets taken by the 3D nano-ESCA. Spectral datasets were collected from FETs using atomically thin films such as graphene and MoS\(_2\) monolayer sheets. We confirmed drastic acceleration of peak fitting in comparison to the manual approach. In the presentation, we show concrete applications to the synthetic data of graphene field effect transistors (FETs) and other semiconductor fine devices.

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**MT03.03.06**

**Fabrication of Composition Gradient Polymer Films at Elevated Temperatures for High-Throughput Characterization**

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Materials informatics has been a relevant focus for accelerated materials development in an industry where traditional research methodologies demand a considerable investment in time and resources. In order to implement these informatics-enabled approaches, curation of well-structured datasets can be facilitated via high-throughput methods\(^1\). An effective combinatorial screening procedure can be constructed with the fabrication of composition gradient polymer thin-film libraries via solution processing. High-throughput property characterization can then be applied to these gradient libraries to rapidly map the composition space for the response variable of interest. Here, we present work toward the high-throughput discovery of process-structure-property relationships in polymer composites. Many such polymer systems present challenges in solution processing due to low ambient solvent interactions and high viscosities. An automated flow system capable of high temperature operation was constructed for the solution-casting of polymer films. This system includes a custom-designed serpentine grooved-channel mixing component suitable for flow of high viscosity solutions and filler particles, allowing for fabrication of gradient films with spatial variations in composition. We discuss high-throughput characterization on these gradient libraries, which demonstrates the feasibility of our solution processing apparatus and gradient film approach.


**MT03.03.07**

**Enabling Correlative Spatially-Resolved Non-Uniformity Analysis of Perovskite Degradation via Machine Learning**

Zhe Liu, Shijing Sun, Noor Titan Putri Hartono, Armi Tiibonen, Janak Thapa, Felipe Oviedo and Tonio Buonassisi; Massachusetts Institute of Technology, United States

Despite a rapid ramp-up of record efficiencies of lab-scale solar cells, perovskite as an absorber for solar cells has a great challenge to achieve large-area spatial uniformity \([1]\), and long-term operation stability \([2]\). Both spatial uniformity and operation stability are important metrics to scale up the perovskite solar cells toward industrial commercialization. Particularly, during the degradation tests, the non-uniform film changes \((e.g., local color change)\) are observed. We hypothesize this non-uniformity of degradation is likely due to process-induced defects acting as the degradation seed point \((e.g., water ingression)\), which could be reduced by a capping/buffer layer \((e.g., ammonia salt 2D thin layer)\) on perovskite absorber. We examine this hypothesis by correlating multiple spatially resolved characterization tools along with the degradation tests. First, photoluminescence (PL) imaging is used to reveal the location of structural and electrical defects in the perovskite films. Second, calibrated red-green-blue
(RGB) camera imaging is used to monitor spatial differences of degradation under various harsh environmental conditions (e.g., humid, hot and illuminated). Third, X-ray diffraction (XRD) mapping is used to identify the material phase change over time at different locations in the film. As a comparison, the experiments are repeated for the perovskite samples with a thin capping layer. With the correlative dataset of spatially resolved characterization results, we develop a machine learning method (i.e., convolutional neural network) that predict the material phase change (i.e., the results of XRD maps) from the fast and easy-to-implement PL and RGB images, because XRD mapping is a relatively slow process. Hence, we will be able to gain more understanding of the mechanism of non-uniform degradation by this correlative analysis.

Reference:

MT03.03.08
Data-Driven Sliding Mode Control for Pulses of Fluorescence in STED Microscopy Based on Förster Resonance Energy Transfer Pairs Maison Clouatre and Makhin Thitsa; Mercer University, United States

Pairs of conjugate donor-acceptor fluorescent probes have proven themselves useful in stimulated emission depletion (STED) microscopy in recent years. For instance, it has been shown that the lifetime of said probes directly correlates to the resolution of the microscope [1]. However, once the lifetimes of the probes have been optimized, it is desirable to control their fluorescence in order to improve the resolution further. Here, we propose combining model-free control with sliding mode control to track nanosecond pulses of blue-shifted acceptor fluorescence in order to inhibit visible light emitted from the image plane, shrink the point spread function, and subsequently improve the resolution of the microscope. This is achieved by automatic adjustment of the STED laser beam pump power. This controller is numerically simulated against a generic model created from Förster resonance energy transfer (FRET) theory. However, since it is innately model-free and data-driven, it can be easily applied to various physical systems with drastically different dynamics. It is the goal of this paper to demonstrate that common fluorescent dyes can be used to increase the resolution in modern super resolution microscopy—paving way for biological imaging previously unachievable.

References

MT03.03.09
Realizing Bulk, Stable Low Work Function Materials Lin Lin, Ryan Jacobs, Dane Morgan and John Booske; University of Wisconsin--Madison, United States

The work function is a fundamental property defined as the minimum energy to remove an electron from the material, and depends sensitively on the bulk electronic structure and surface chemistry, such as surface orientation, surface termination, and presence of surface adsorbates. The work function is a crucial parameter to understand and control in numerous applications, including electron emitters, thermionic energy converters, oxide electronics, solar photovoltaics, (photo)electrochemical reactions and memristors.[1] In particular, there has been tremendous interest in the engineering of low work function materials, such as metals with adsorbed alkali species, semiconductors with functionalized organic species, and 2D materials such as graphene and MXene compounds which are both doped and functionalized with surface species. However, all of these solutions to create low work function materials rely on utilizing surface functional species or monolayers of electropositive elements which are unstable, particularly at elevated temperatures above room temperature. Therefore, a fundamental materials science research question is the following: How does one engineer a material with low work function (e.g. less than 2 eV), and have this low work function realized in a bulk, stable monolithic material?

To answer this question we turn our focus to perovskite oxides, a class of materials with applications ranging from catalysis to piezoelectrics to light absorbing layers in solar cells, which possess broad compositional flexibility.
enabling the tunability of many properties, including the work function.[2, 3] In particular, engineering of perovskite oxides presents the unique opportunity for realizing low work functions in a bulk, monolithic material by virtue of the intrinsic polar and stable \{001\} surfaces of the perovskite structure. Our recent work used Density Functional Theory (DFT) calculations to explore a representative set of 20 perovskite oxides for the dual purpose of (1) searching for perovskites which possess a low work function and (2) gaining an improved fundamental understanding of the factors governing the work function in perovskite oxides. From this work, we discovered that pure and Ba-doped SrVO3 could exhibit low work functions of about 1.9 and 1.1 eV, respectively.[2]

Following this path, we have performed detailed experiments on pure, bulk polycrystalline samples of SrVO3. The sol-gel method is used to produce high purity SrVO3 powder, which is pressed into pellets and sintered in a reducing atmosphere. X-ray photoelectron spectroscopy (XPS) measurements indicate that bulk SrVO3 exhibits a low work function of 1.8-2 eV, and similar values are obtained across the entire bulk sample surface to within +/- 0.2 eV, and is consistent with our DFT predictions. These results suggest that SrVO3 is the first example of a bulk, monolithic material with an intrinsically low work function, potentially impacting a large array of technological applications and suggesting that engineered perovskite materials are a new class of low work function compounds.

References:

MT03.03.10
OpenKIM—Reliable Interatomic Models for Multiscale Simulations Ryan S. Elliott and Ellad B. Tadmor; University of Minnesota, United States

Multiscale and Atomistic simulations of materials using empirical interatomic potentials (also called "force-fields", or more generically "models") play a key role in realistic scientific and industrial applications. The Open Knowledgebase of Interatomic Models project (https://OpenKIM.org) includes an automated user-extendable framework for testing the predictions of models for a host of material properties. Visualization tools have been developed to compare model predictions to help select the most appropriate one for a given application. Verification checks ensure the integrity of the models. Models in OpenKIM that conform to the KIM application programming interface (KIM API) can be seamlessly used with several major molecular simulation codes. Although KIM's objective is to have all models conform to the KIM API, this is not always immediately possible or practicable. So, OpenKIM also supports "Simulator Models" (SMs), i.e., models that are currently only available within a single molecular simulation code. SMs are treated just like any other model in OpenKIM so that results for verification checks, material properties predictions, and visualizations are available for SMs as well. This talk will describe the OpenKIM project and how the testing framework can assist materials researchers.

MT03.03.11
Density Functional Theory Simulation on Material Science—Bridging the Gap Between Theory and Experiment ChunYu Lu, Srinivasa R. Tamalampudi, Nitul S. Rajput, Boulos Alfakes, Tuza Olukan and Matteo Chiesa; Khalifa University, United Arab Emirates

Thanks to the consistent effort in making DFT simulation more reliable and bringing this powerful tool to the engineer, first-principles quantum physics calculations can reliably be utilized to design materials and further to give insights into the material characterization results. In this work, we perform DFT simulation and experimental characterization on 2D material layers, such as InSe and graphene, and doped semiconductor ZnO, to explore and design material properties for different applications. We combine the DFT-atomic force microscopy (AFM)[1], DFT-Optical/Raman spectroscopy[2], DFT-predicted macroscopic surface wettability[3] and DFT device simulation[4] as an integration tool to directly compare the experimental results, such as AFM characterization, contact angle measurement, reflectance/Raman/FTIR spectroscopy, and solar cell IV curve. These full set of comparisons offer a great opportunity to allow the bottom-up realization of material structures that are tailored to deliver the desired device performances.

References
Interest in the application of big data and artificial intelligence to the manufacturing industry is increasing. However, this is feasible when all the structures of facilities/environment - sensor - communication - data acquisition - analysis are balanced. It is difficult to expect remarkable achievement in a short time considering the situation of small and medium-sized manufacturing companies. Especially in the foundry industry, there are many difficulties in introducing big data and artificial intelligence technology because it traditionally tends to depend on worker's know-how in controlling processing parameters. Nevertheless, there is still a need to build a smart factory, so it is necessary to study IoT sensing system for collecting big data of processing parameters and machine learning technique for prediction.

In this presentation, the difference of concepts between artificial intelligence, machine learning and deep learning is introduced. In connection with data acquisition using IoT sensors, an example of application to the centrifugal casting field using an Arduino-based module is introduced. In addition, a case study of machine learning model for prediction of hydrogen concentration in molten aluminum is introduced. The development of machine learning technology is very fast and it is necessary to grasp the flow while applying it in the manufacturing field even though it is quite simple case.

Current piezoelectric materials rely on a unique resilience of the polar response to disorder which produces a stable structure near a morphotropic phase boundary (MPB). However, many piezoelectric materials are not amenable to disorder, and are thus unusable in MPB systems. In this work, we apply a sensitivity analysis approach to ab initio calculated piezoelectric properties to determine the effect of disorder on the piezoelectric response. Vibrational properties are found to drive degradation in the piezoelectric effect with disorder, rather than the dielectric, or internal strain components. In well-known piezoelectric systems, (perovskites and tungsten bronze structures) multiple stable optical phonon modes are found to contribute to the piezoelectric response, providing a fingerprint for disorder tolerance. Hence, a multiple-phonon mode criteria is used to evaluate candidate materials suggested by the Materials Project and to screen the database for novel, disorder-tolerant piezoelectrics. Eight prototype structures are altered through chemical substitution to generate novel systems with high piezoelectric effect. These structural families may be explored to replace PZT as MPB systems beyond perovskites.

Laser Aided Additive Manufacturing (LAAM) is a kind of metal additive manufacturing process using the high-powered laser beam to melt the powdered or wire feedstock to build the near-net three-dimensional components. Studying thermal field induced by different laser parameters is important to evaluate and optimize the resultant residual stress and distortion distribution. However, it is very computationally expensive to simulate multi-bead deposition process using existing numerical model to analyze and select appropriate process parameter. This work proposed a laser process parameter planning frame to design an appropriate laser process parameter sequence for the
LAAM process. The frame utilizes a recently developed finite element (FE) model to predict the thermal behaviour during the deposition process, and a reinforcement neural network to modify the laser process parameter based on the temperature field in process. The optimized process parameter is able to improve the temperature distribution homogeneity of the deposited part.

MT03.03.18
Classifying and Predicting the Electron Affinity of Hydrocarbons Using Machine Learning

Dooman Akbarian1, Behzad Damirchi1, Hunter Woodward2, Jonathan Moore2 and Adri van Duin1; 1The Pennsylvania State University, United States; 2The Dow Chemical Company, United States

Hydrocarbons include a wide range of chemical substances that can be found in many products ranging from oil extracted directly from the reservoir to drug products and occur in a range of mixtures, degrees of purity and molecular size. Electron Affinity (EA) has been identified as an important factor for predicting the chemical properties of hydrocarbons. For instance, previous investigations found that the EA is a principle descriptor for modeling the gas phase oxidation rates of polyaromatic hydrocarbons (PAH) in diesel combustion which indicates that the initial step in the destruction of PAHs is capturing an electron. Additionally, previous studies could find a non-linear correlation between the phototoxicity and the EA of the PAHs. There are experimental and Quantum Mechanics (QM) techniques to calculate the EA of species. However, due to high experimental and computational costs, it is beneficial to develop machine learning (ML) methods based on reasonable amount of available data that can accurately and quickly estimate the EA of hydrocarbons. Supervised ML can be implemented on available data sets to predict properties based on individual structural features. In this study, we used Density Functional Theory (DFT) to calculate the EA of more than 1500 hydrocarbons including PAH, alkanes, cycloalkanes and alkenes. Then a ML technique was developed to explore the relationship between the EA and the physical structure of the species. Using this method, we could reveal the role of different geometrical features and functional groups on the EA of the hydrocarbons.

SESSION MT03.04: Cognitive Materials Discovery
Session Chairs: Sergey Barabash and Jason Hattrick-Simper
Tuesday Morning, December 3, 2019
Hynes, Level 2, Room 208

8:00 AM *MT03.04.01
Accelerated Materials Discovery Using Theory, Computation, Optimization and Natural Language Processing

Anubhav Jain; Lawrence Berkeley National Laboratory, United States

For the past several decades, the standard method of materials discovery has involved a combination of research intuition and comprehensive experimental investigation. Recently, a variety of new computational and experimental tools have been introduced to go beyond this standard paradigm. In this talk, I will describe our group's effort in creating an automated pipeline for suggesting and discovering new materials in silico. We have recently coupled our capability to perform high-throughput density functional theory calculations for a variety of materials properties (software implementation: https://atomate.org) with inverse optimization techniques that allow machine learning surrogate models to suggest the most promising compounds for exploration. This allows a computational optimization to be performed on supercomputing resources in a closed loop without any human intervention (software implementation: https://github.com/hackingmaterials/rocketsled). The machine learning model used for the optimization can be provided by the user, be chosen from a set of standard optimization routines, or use a new machine learning surrogate that we have developed that can be trained automatically and without any human intervention on any materials composition-property or structure-property data set (software implementation: https://github.com/hackingmaterials/automatminer). Finally, I will outline a collaborative effort at LBNL in which we analyze text data from materials abstracts to predict "gaps" in the research literature, and use this information to power an algorithm to suggest promising new compounds for functional applications. These tools make it possible to leverage large computing resources and the past scientific literature to focus and accelerate the experimental phases of materials discovery.
8:30 AM MT03.04.02

**Machine Learning of Reaction Pathways in Chemical Vapor Deposition for Directed Synthesis of Two-Dimensional Chalcogenides**

Aravind Krishnamoorthy\(^1\), Pankaj Rajak\(^1\)\(^2\), Sungwook Hong\(^1\), Ken-ichi Nomura\(^1\), Aiichiro Nakano\(^1\), Rajiv Kalia\(^1\) and Priya Vashishta\(^1\); \(^1\)University of Southern California, United States; \(^2\)Argonne National Laboratory, United States

Scalable synthesis of two-dimensional (2D) materials is a major bottleneck to more widespread adoption of layered material-based devices. Chemical vapor deposition (CVD) has emerged as a viable method for large-scale synthesis of 2D materials. However, neither experiment nor theory has been able to decipher mechanisms and selection rules for different growth scenarios or make predictions of optimized growth parameters. Experimental challenges stem from the use of atomic-resolution probes like TEM to characterize CVD growth reactions *in situ* under elevated temperatures and pressures. Computational synthesis, which simulates CVD processes using reactive molecular dynamics simulations provides the atomistic resolution necessary for the identification of reaction mechanisms and synthesis pathways. Here we use recurrent neural networks and reinforcement learning methods trained on trajectories from several hundred simulations of computational synthesis of a prototypical two-dimensional semiconductor, monolayer MoS\(_2\), to uncover the dependence of product stoichiometry, crystallinity and phase distribution on reaction parameters like temperature, sulfur and hydrogen partial pressures, thus paving the way for rational design of CVD synthesis techniques for MoS\(_2\) and other layered materials.

This work was supported as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC0014607. Simulations were performed at the Argonne Leadership Computing Facility under the DOE INCITE program and at the Center for High Performance Computing of the University of Southern California.

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8:45 AM OPEN DISCUSSION

9:00 AM MT03.04.04

**High-Throughput Design of Organic Friction Reducers in Engine Oils**

Jing Yang, Jon Paul Janet, Fang Liu and Heather J. Kulik; Massachusetts Institute of Technology, United States

Computational modeling and high-throughput techniques have the promise to enable the atom-by-atom design of nanoscale properties that give rise to essential changes in macroscale properties. In the quest for increasing energy efficiency and resource utilization, energy losses remain an outstanding challenge that can be solved in part through computational materials design. For example, during the operation of a car engine, only 15% of the fuel energy is used for car movement, whereas the remaining is lost. Friction reducers (FRs) additives can minimize the friction loss in these engines by reducing friction between moving parts at the contact area. Traditional FRs contain metals, sulfur, and phosphorus, which can poison exhaust system catalysts and diesel particulate filters. Thus, if suitably designed, organic friction reducers (OFRs) present a promising alternative solution. Here, we apply non-equilibrium molecular dynamics simulations together with density functional theory methods under a high-throughput workflow to enable the atom-by-atom design of OFRs. We directly compute the coefficients of friction (COFs) of OFRs on model-engine iron oxide surfaces. This atomistic simulation allows us to develop direct physical insight into the nanoscale properties of OFRs that give rise to the criteria of friction reducing characteristics. By carrying out coverage- and temperature-dependent simulations, we can explore several conditions not easily probed during experiments. These studies allow us to build a quantitative-structural-property relationship for predicting good OFR characteristics, enabling an iteratively improving materials design workflow.

9:15 AM MT03.04.05

**High-Throughput Computational Discovery of In\(_2\)Mn\(_2\)O\(_7\) as a High Curie Temperature Ferromagnetic Semiconductor for Spintronics**

Wei Chen\(^1\), Janine George\(^1\), Joel B. Varley\(^2\), Gian-Marco Rignanese\(^1\) and Geoffroy Hautier\(^1\); \(^1\)Université catholique de Louvain, Belgium; \(^2\)Lawrence Livermore National Laboratory, United States

Ferromagnetic semiconductors are valued for their potential applications in spintronics. For spin-polarized transport, combining strong ferromagnetism and attractive semiconducting properties in one material is highly desirable, but yet this remains an open problem. Here we conduct a search for concentrated ferromagnetic semiconductors through high-throughput computational screening. Our screening reveals the limited availability of semiconductors combining ferromagnetism and a low effective mass. Among the identified ferromagnetic semiconductors are Eu
chalcogenides, Cr spinel chalcogenides, Bi manganites, Mn pyrochlore oxides, and Mn double perovskites. In particular, we show that the manganese pyrochlore oxide In$_2$Mn$_2$O$_7$, hitherto unknown to spintronic applications, is a promising candidate for spin transport as it combines low electron effective mass ($0.29 m_0$), a large exchange splitting of the conduction band (1.1 eV), good stability in air, and a Curie temperature (about 130 K) which is among the highest of concentrated ferromagnetic semiconductors. We rationalize the high performance of In$_2$Mn$_2$O$_7$ by the unique combination of a pyrochlore lattice favoring ferromagnetism with an adequate alignment of O-2p, Mn-3d, and In-5s, forming a dispersive conduction band and enhancing the Curie temperature. We further find that Sn and Mo can be incorporated on the In site while acting as shallow donors, suggesting that In$_2$Mn$_2$O$_7$ can be effectively n-doped.

9:30 AM *MT03.04.06
Cognitive Materials Discovery and Onset of the New Discovery Paradigm Dmitry Zubarev; IBM Almaden Research Center, United States

The discovery of novel materials can generate immense technological, economic, and social benefits. However, these are slow, challenging, expert-intensive efforts. Our thesis is that new capabilities of cognitive computing – particularly natural language processing, knowledge representation, and automated reasoning – are poised to transform the process of materials discovery and take us from our current discovery paradigm driven by data science and machine learning to the next stage where cognitive systems seamlessly integrate information from human experts, experimental data, physics-based models, and data-driven models to speed discovery. We discuss the key bottlenecks to discovery that need to be removed to enable this new approach and illustrate progress towards this cognitive future with examples from IBM research efforts in Accelerated Materials Discovery.

10:00 AM BREAK

SESSION MT03.05: Machine Learning Augmented High Throughput Characterization I
Session Chair: Dmitry Zubarev
Tuesday Morning, December 3, 2019
Hynes, Level 2, Room 208

10:30 AM *MT03.05.01
Bridging the Electronic, Atomic and Mesoscopic Scales Using Machine Learning Subramanian Sankaranarayanan$^{1,2}$; $^1$Argonne National Laboratory, United States; $^2$University of Illinois at Chicago, United States

The ever-increasing power of modern supercomputers, along with the availability of highly scalable atomistic simulation codes, has begun to revolutionize predictive modeling of materials. Molecular dynamics (MD), in particular, has led to breakthrough advances in diverse fields, including tribology, energy storage, catalysis, sensing. Furthermore, recent integration of MD simulations with X-ray characterization has demonstrated promise in real-time 3-D atomistic characterization of materials. The popularity of MD is driven by its applicability at disparate length/time-scales, ranging from ab initio MD (hundreds of atoms and tens of picoseconds) to all-atom classical MD (millions of atoms and tens of nanoseconds), and coarse-grained (CG) models (microns and tens of micro-seconds). Nevertheless, a substantial gap persists between AIMD, which is highly accurate but restricted to extremely small sizes, and those based on classical force fields (atomistic and CG) with limited accuracy but access to larger length/time scales. The accuracy and predictive power of classical MD is dictated by the empirical force fields, and their capability to capture the relevant physics.

In this talk, I will present some of our recent work on the use of machine learning (ML) to seamlessly bridge the electronic, atomistic and mesoscopic scales for materials modeling. Our automated ML framework aims to bridge the significant gulf that exists between the handful of research groups that develop new interatomic potential models (often requiring several years of effort) and the increasingly large user community from academia and industry that applies these models. Our ML approach showed marked success in developing force fields for a wide range of materials from metals, oxides, nitrides, hetero-interfaces to two-dimensional (2-D) materials and even water (arguably the most difficult system to capture from a molecular perspective). This talk will also briefly discuss our
ongoing efforts to integrate such cheap yet accurate atomistic models with (a) AI techniques to perform inverse design and construct metastable phase diagrams of materials (b) Deep learning to improve spatiotemporal resolutions of ultrafast X-ray imaging.

11:00 AM *MT03.05.02
Accelerating Development of Materials for Industrial and High-Tech Applications with Data-Driven Analysis and Simulations Sergey V. Barabash; Intermolecular Inc, United States

The development of advanced materials via high-throughput experimentation at Intermolecular is accelerated using guidance from modeling and machine learning (ML). Rapid materials development at a reasonable cost implies that a large number of parameters describing the deposition outcome and materials performance (including composition, phase, texture, defects, stability/degradation) and the knobs that directly and indirectly affect those outcomes (including deposition method, precursors and ambients, temperature and other conditions, film thickness, and the identity of other materials included in the stack) form a vast space that needs to be efficiently navigated. This talk primarily focuses on methods, with a few examples of specific findings from our internal R&D.

Accessing external DFT databases (such as MaterialsProject) together with high-performance computing (HPC) resources for new DFT simulations and pymatgen-enabled workflows permits rapid on-demand theoretical modeling and thermodynamic analysis. This can be used to screen materials in a stack based on compatibility, allowed chemical potentials, possibility of templating, and wetting, so as to identify most promising combinations of material layers that make up the device stack, together with desired deposition conditions. For instance, additional material layers can be identified, deposition of which ensures high quality (e.g. low vacancy concentration) of preceding layers despite the use of aggressive chemistries in depositing subsequent layers. One can further theoretically pre-screen “dopants” that help stabilizing a given phase of a given material. While relatively straightforward in the case of stabilization of TiO2 phases, such a theoretical pre-screening needs be more involved in the case of HfO2. We compare different approaches to identifying regions of thermodynamic stability in multicomponent systems, including CALPHAD, theoretical models of disordered alloys used together with DFT database queries, phenomenological selection rules and recursive partitioning based on experimental data. Unexpected phases such as alloys between ordered compounds can be predicted using thermodynamic modeling with effective Hamiltonians such as cluster expansions (CEs).

HPC-enabled, DFT-driven search for novel material phases can help building a better reference set for phase identification in thin films; e.g. our analysis during development of ferroelectric HfO2 films accounts for the novel rhombohedral phase, predicted by our DFT study[1] and independently demonstrated in recent experiments[2]. Combining DFT simulations with phenomenological modeling and data-driven search allows us to identify materials with better intrinsic properties, such as materials combining high band gap $E_g$ with high dielectric constant $\kappa$. Some materials identified by our workflows combine attractive ($\kappa, E_g$) values with possibility of synthesis at ambient conditions, even though showing smaller improvement over the common high-$\kappa$ materials than the exotic materials such as the high-pressure BeO phase predicted in literature[3] (that is yet to be stabilized at the ambient conditions). We discuss practical considerations that limit materials development based on such predictive workflows.

Finally, we illustrate co-optimization of multiple target material properties using ML based on experimental data. We discuss issues that may arise due to human pre-selection of promising phase space regions: ML algorithms readily pick up pre-detected trends, but may draw unjustified conclusions, particularly in the presence of noise/measurement errors. Use of physically meaningful descriptors, including those obtained using DFT simulations and data mining, leads to detecting important trends, improving predictions, and identifying optimal compositions.


11:30 AM MT03.05.03
Exploring Large Scale ToF-SIMS Data Matrices Using Artificial Neural Networks: Polymers and Biointerfaces Paul Pigram1, Robert Madiona1,2, Wil Gardner1,2, Nicholas Welch2, David Winkler1,2,3 and Benjamin Muir2; 1La Trobe University, Australia; 2CSIRO Manufacturing, Australia; 3University of Nottingham, United
Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is continuously advancing. The data sets now being generated are growing dramatically in complexity and size. More sophisticated data analytical tools are required urgently for the efficient and effective analysis of these large, rich data sets. Standard approaches to multivariate analysis are being customised to decrease the human and computational resources required and provide a user-friendly identification of trends and features in large ToF-SIMS datasets.

We demonstrate the generation of very large ToF-SIMS data matrices using mass segmentation of spectral data in the range 0 – 500 m/z in intervals ranging from 0.01 m/z to 1 m/z. No peaks are selected and no peak overlaps are resolved. Sets of spectra are calibrated and normalized then segmented and assembled into data matrices. Manual processing is greatly reduced and the segmentation process is universal, avoiding the need to refine peak lists for different sample types or variants.

ToF-SIMS data for standard polymers (PET, PTFE, PMMA and LDPE) and for a group of polyamides are used to demonstrate the efficacy of this approach. The polymer types of differing composition are discriminated to a moderate extent using PCA. PCA fails for polymers of similar composition and for data sets incorporating significant random variance.

In contrast, artificial neural networks, in the form of self organising maps (SOMs), deliver an excellent outcome in classifying and clustering different and similar polymer types and for spectra from a single polymer type generated using different primary ions. This method offers great promise for the investigation of more complex bio-oriented systems.

We compare the analysis of large scale mass segmented matrices with those formed using conventional selection of ToF-SIMS peak lists. SOMs are used to cluster and discriminate antibody fragments bound at surfaces and to demonstrate antibody orientation in optimised ELISA format assays.

Integrate Machine Learning in Describing Radiation-Assisted Microstructural Evolution Miaomiao Jin¹², Penghui Cao³ and Michael P. Short¹; ¹Massachusetts Institute of Technology, United States; ²Idaho National Laboratory, United States; ³University of California Irvine, United States

The evolution of materials microstructure driven by radiation in nuclear applications poses an imminent need to describe the behavior for system reliability, safety and economics. Radiation effects on materials such as void swelling and embrittlement have been long standing complex phenomena yet to be well characterized under different conditions. Specifically, radiation-induced void swelling is a unique mode of degradation in nuclear materials. Serious efforts have been spent to increase radiation tolerance, which is to postpone the consequence of radiation damage. However, the behavioral sensitivity to a number of parameters such as chemical compositions and the irradiation environment makes the conventional trial-and-error experimental approach highly inefficient. Meanwhile, the physics-based computational models are also subject to inefficiency and critique of fidelity due to the complex underlying defect dynamics on multi-scales. In the era of increasing data resources from resource-consuming nuclear materials experiments, machine learning (ML) as an alternative could prove useful in more efficiently and accurately predicting macroscale materials response and guiding experiment testing. It is then applied to perform prediction of the incubation period of void swelling based on manually collected experimental data. By training decision tree based ensemble models, it delivers very good performance in prediction, and the identified main contributing factors such as temperature, Fe and Cr content, and dose rate are fairly consistent with established understandings. Ultimately, establishing a well-performed ML model is a promising route to radiation resistant material design. It is thus our plan to construct a public web platform to crowdsource more data for nuclear materials exploration. And from the methodology point of view, ML can be utilized as a subroutine in a physics-based modeling technique for acceleration. Such types of reduced-order model can constitute a future research direction, by exploring a hybrid of ML methodology and physical framework to alleviate current computational constraints in characterizing radiation-induced microstructural evolution.
1:45 PM **MT03.06.01**
*Towards Automated Information Extraction from High Resolution Transmission Electron Microscopy Images*  
Mary Scott1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

Transmission electron microscopy (TEM) is the characterization method of choice to observe the atomic-scale and microstructural local features within materials that play a critical role in material performance. Current TEM capabilities include a wide variety of imaging modalities to probe a material’s structure. It is possible to resolve structures with 0.39 angstrom resolution [1], to perform rapid nanodiffraction experiments to characterize the microstructure of hard and soft materials [2], to resolve local chemistry and bonding [3], and much more. Furthermore, recent advances in fast electron detection enable imaging at nearly 100 KHz rates, enabling extremely rapid data acquisition. Directly incorporating these TEM capabilities for structural validation into a high throughput materials prediction, design and synthesis routine would profoundly speed up the materials discovery process.

However, a bottleneck exists between image acquisition and the extraction of relevant information that can be used in a materials design feedback loop. While image analysis of individual images can easily identify regions of interest and determine whether they contain defects, it is prohibitively time-consuming to manually perform this analysis on large numbers of images. This means that, for example, in a given nanoparticle synthetic optimization process, only a small number of successful end products are studied in detail. Failure cases are typically not characterized, and population heterogeneity statistics are not captured. Therefore, to automatically identify and quantify defects, size and shape statistics, and other key structural features which can dominate a material’s mechanical, electronic, and catalytic properties, a new approach is required.

Advances in machine learning and computer vision have made high accuracy automated image interpretation possible. While widely applied in the life sciences, this approach is only recently being applied to atomic resolution TEM images. Here, we present application of machine learning and other high-throughput methods to TEM images for nanoparticle identification and microstructural characterization. When combined with existing automatic image acquisition protocols, this approach is a viable option to close the materials design loop and incorporate TEM into high-throughput materials design and synthesis in a way not currently possible.


2:15 PM **MT03.06.03**
*Feature Extraction from SEM Images to Predict Materials Performance Using Computer Vision and Deep Learning Methods*  
T. Yong-Jin Han; Lawrence Livermore National Laboratory, United States

Visualization techniques, such as scanning and transmission electron microscopy, electron diffraction, X-ray computed tomography and magnetic resonance imaging, among others, are widely used providing high spatial resolution images of atomic arrangements, crystallographic information, material’s shapes, sizes and other microstructure information including defects and voids within materials. Significant advancements in materials characterization methods are providing higher resolutions images, complex information and faster data collection capabilities. With these breakthroughs in visualization techniques, the bottleneck in advancements in materials characterization will no longer be the capability limitations of the characterization tools themselves, but rather, the ability to rapidly analyze and interpret the large amount of complicated (high dimensional), high-quality data. To address this challenge, we are implementing machine learning approaches to accelerate image analysis process,
extracting images features to correlate to mechanical performance.

Breakthroughs in machine learning have shown us that deep learning (DL) has significant advantages over traditional machine learning (ML) and computer vision (CV) techniques for a variety of applications, most notably: improved predictive performance and automated learning of feature representations with minimal human guidance. However, important limitations remain. In particular, DL typically requires more labeled training examples than traditional ML approaches, and it is often difficult to explain model performance. In order to assess application of computational tools for materials science, we chose to compare the two approaches: (1) a traditional ML approach (random forest) using state-of-the-art computer vision features and (2) an end-to-end deep learning approach. In this presentation, approaches taken to extract image features from SEM images of molecular solid crystals and using these features to predict materials performance will be discussed. We show that our image-based ML approach reduces root mean square error (RMSE) by an average of 51% over a non-image-based baseline.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and was supported by the LLNL-LDRD Program under Project No. 19-SI-001.

2:30 PM OPEN DISCUSSION

2:45 PM MT03.06.05
High Throughput Transmission Electron Microscopy—Closing the High Throughout Material Discovery Paradigm Catherine Groschner1 and Mary Scott1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

The past decade has seen a rise in the concept of automated materials discovery. A large majority of the work in this area has focused around computation of intrinsic material characteristics and the creation of material property libraries1. This has been paired with methods to search for suitable candidates from these libraries. However, these predictions still require experimental validation. To this end, high throughput synthetic methods have followed both in the area of organic and inorganic materials2. The missing piece to automated materials discovery is then in high throughput characterization of materials. High throughput materials characterization represents the final feedback step to both computational predictions and high throughput syntheses.

High resolution transmission electron microscopy (HR-TEM) is particularly suited to the materials discovery pipeline because of its high resolution and local information. Most computational libraries are based on DFT calculations which are directly tied to atomic structure. By providing atomic structural information, TEM could be used to verify structural information in computation. This information is also critical to the synthesis of materials to verify the intended atomic structure is being created.

Since nanomaterials are particularly suited to analysis by HR-TEM characterization, in this talk we will address the current state of high throughput HR-TEM characterization of nanomaterials. The first fundamental problem which must be solved to allow for automation is segmentation of nanoparticle regions from the micrograph background. This is particularly challenging since the signal to noise of the particle above the background is extremely low in HRTEM micrographs. However, we have developed a convolutional neural network (CNN) which is able to segment nanoparticles with a 94% pixel-wise accuracy. The neural network is shown to be robust to changes in contrast and is sensitive to the presence of lattice fringes. We will also discuss automated detection of crystal structure and defects.


3:00 PM BREAK
3:30 PM *MT03.07.01
How Do We ESCALATE Lab Automation and Data Collection for RAPID Discovery of Perovskites? Joshua Schrier; Fordham University, United States

Laboratory data collection should be comprehensive but adaptable. An ideal system should provide a mechanism for specifying unambiguous machine-readable experiment that enable remote operation and replicability, presenting these as instructions to human operators and machines, capturing comprehensive data and metadata during experiment, and performing extraction, transformation, and loading (ETL) to facilitate machine learning. Yet, existing tools require significant development time that is incompatible with rapidly evolving scientific needs.

In this talk, I will describe ESCALATE (Experiment Specification, Capture and Laboratory Automation Technology) an adaptable open source package for experiment description and data collection. As a specific example, I will describe its application to Robotic-Accelerated Perovskite Investigation and Discovery (RAPID). The first generation of RAPID uses inverse temperature crystallization (ITC) to grow halide perovskite single crystals for x-ray structure determination and bulk characterization using commercial liquid handling robots. All experiment plans for the syntheses are contributed remotely, by both human scientists and algorithms trained on the reaction data. More >25 compounds have been produced by the RAPID:ITC (compared to only 4 known ITC-grown halide perovskites prior to our work), including >10 new compounds or polymorphs. Incoming data collected by ESCALATE is used to automatically train machine learning models, evaluate model performance and feature influence, and quantify reproducibility. A live web dashboard communicates these insights to the scientist and management in visual form. I will conclude by describing case studies about new scientific insights extracted from the comprehensive RAPID dataset, and discuss ongoing deployments of ESCALATE to perovskite thin film and vapor diffusion experiments.

4:00 PM *MT03.07.02
AI–Based Learning Machines to Accelerate Discovery of New Materials Apurva Mehta; Stanford Synchrotron Radiation Lightsource, United States

With over a hundred elements in the periodic table, there exists a large number of potential new materials. Some of these new materials and rational optimization of devices based on them can provide solution to many of the growing and daunting challenges we face today, from climate change to water shortage and from faster internet to longer-lasting orthopedic implants. However, in spite of major investments in the last two decades resulting in dramatic advancement in performance of the material science tools, rate of discovery of new materials is still sluggish; it still takes over 20 years for development of a new technological material. The rate of new material discovery lags the performance enhancement of material synthesis and characterization tools because the traditional material discovery approaches based on human curation and perception are unable to cope with the revolution in data generation. They are unable to fully harness accelerating rate of data (both computational and experimental) into discovery of new materials.

Another way of looking at the problem is that the three stages of the discovery cycle, starting with predicting new experiments, performing measurements efficiently, and ending with finding new insights and discoveries in the measurements, are performed sub-optimally. Furthermore, these three stages are isolated from each other halting the discovery cycle. Suboptimal performance and broken links between the stages delay discoveries. The first stage is suboptimal because human curators are finding it increasingly difficult to find trends hidden in rapidly growing and increasingly complex materials data. Overwhelmed researchers are unable to make accurate predictions of experimental conditions (and or compositions) where new desired material may be located. Absence of reliable prior hypotheses, combined with the inability of a human curator to keep pace with information contained in high throughput measurements in real-time, forces a strategy of rapid, but blind searches of vast experimental space, resulting in increasingly large fraction of data of poor quality and of little scientific value. In a blindly cast search, even when the grid catches evidence for a new material, it often takes human researcher weeks of frustrating work wading through large number of poor quality measurements to find it. It is like searching for a needle in a
haystack in a lightless barn. The performance of the final stage of the discovery cycling is becoming worse as materials become more complex and role of processing becomes more significant, making experimental search space too complex (multi-dimensional) for a human curators, using traditional approaches, to find subtle but significant signatures of new discoveries even after prolonged data analysis.

Here, we use the search for new compositional complex alloys, to illustrate a new material discovery approach that leverages recent advances in big-data analytics, machine-learning, and artificial intelligence to link and accelerate performance of each of the three stages of the discovery cycle. The approach is based on two key learning machines: the first makes extraction of new knowledge from large and complex dataset fast, sophisticated, and independent of human curation; and the second engine then uses rapidly extracted information in a Bayesian approach to make decision-making smarter and automated. Data-driven decision-making can not only accurately predict the next experiment to perform, but optimize the experimental data collection measurement-by-measurement so only high quality measurements of with higher scientific content are collected. Close coupling of these two learning machines will bridge gaps that stall discovery cycle, and rapid iteration of one to the other will accelerate discoveries of new technological materials and devices.

4:30 PM MT03.07.03
Accurate and Explainable Machine Learning of Chemical Reactivity in Transition Metal Complexes

Pascal Friederich1,2, Gabriel dos Passos Gomes1, Riccardo De Bin3, David Balcells3 and Alan Aspuru-Guzik1,4; 1University of Toronto, Canada; 2Karlsruhe Institute of Technology, Germany; 3University of Oslo, Norway; 4Vector Institute for Artificial Intelligence, Canada

Homogeneous catalysis using transition metal complexes is ubiquitously used for organic synthesis, as well as technologically relevant in applications such as water splitting and CO2 reduction. The key steps underlying homogeneous catalysis require a specific combination of electronic and steric effects from the ligands bound to the transition metal atom. Finding the optimal combination is a challenging task due to the exceedingly large number of possibilities and the non-trivial ligand-ligand interactions. In this work, we show how high-throughput density functional theory (DFT) and machine learning methods can be combined to accurately predict activation energies for H2 splitting within large chemical spaces containing thousands of derivatives of the Vaska’s complex (trans-[Ir(PPh3)2(CO)(Cl)]. A hybrid approach combining Gradient Boosting Regression with Gaussian Processes allows reach high accuracies (MAE = 0.59 kcal/mol). In contrast with DFT calculations requiring several days to be completed, the machine learning models were trained and used on a laptop on a time-scale of minutes. By using interpretable representations and ranking the feature importances, our approach allows us to interpret the machine learning models and extract design rules to systematically control activation energies. We will give an outlook on how this model can be generalized to other chemical reactions and to derive non-trivial application specific design rules in a fully automated way.

4:45 PM MT03.07.04
Reliability Prediction and Diagnosis of Next-Generation Photovoltaics Using Sparse Datasets and Semi-Supervised Machine Learning

Felipe Oviedo1, Hansong Xue2, Jose D. Pereal1,2, Thomas Heumüller3, Zekun D. Ren2, Zhe Liu1, Shijing Sun1, John Fisher1, Christoph J. Brabec3 and Tonio Buonassisi1; 1Massachusetts Institute of Technology, United States; 2Solar Energy Research Institute of Singapore (SERIS), Singapore; 3Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander University Erlangen-Nürnberg, Germany

Next-generation photovoltaics require high reliability to scale up to market applications. Although a number of promising novel solar cell materials, such as organic solar cells or perovskites, have shown promising performance, improving reliability remains a difficult and time-consuming challenge due to complex and lengthy characterization, and challenging decoupling of dominant degradation mechanisms [1]. Furthermore, common degradation mechanisms among similar samples are often difficult to identify, due to the dynamic nature of degradation and the use of sparse experimental datasets. In this context, we propose a methodology to accelerate 10X–100X the reliability characterization and improvement of solar cell materials and devices by combining a semi-supervised machine learning approach, used for prediction of degradation, and an inference approach based on a device numerical simulator, used to identify root-causes of degradation. First, we adapt the Latent Dirichlet Allocation (LDA) [2] algorithm to identify common degradation trends and regimes in a set of current–voltage (JV) measurements of various unlabeled and weakly-labeled solar cells. Second, using the common degradation regimes extracted by LDA and the initial few hours of degradation, we develop and train a recurrent machine learning model
[2] to predict the \( JV \) characteristics of the sample of interest at the 1000\(^{th} \) hour of degradation. Finally, we use the predicted \( JV \) degradation as function of time to infer, via a device model in a Bayesian setting, the degradation time–series of the intrinsic material and device properties, such as electron and hole mobility of the active layer, or the interfacial properties. By comparing the change in time of various material and device properties, the knowledge of these time–series allows us to quickly identify the main drivers of degradation and suggest improvements for solar cell reliability. To test our methodology, we synthesize, degrade and measure 300 samples of organic photovoltaic materials: established P3HT–PCBM, and next-generation PBDBT–ITIC and P3HT–IDTBR. Each sample in the dataset presents various degradation trends due to varying active layer compositions, hole and electron transport layer combinations, process variation and interfacial properties. Given, the high number of sources of variables, the dataset is inherently sparse. In this context, our methodology successfully determines the final degraded \( JV \) characteristics using less than 10\% of the degradation measurements, on average, and successfully decouples the root-causes of degradation across the sparse dataset. Based in our results, we propose and test potential reliability improvements for PBDBT–ITIC and P3HT–DTBR solar cell materials and architectures.

Reference:


systematic means to identify the shortest path toward a material with some desired properties or the experiments that maximize knowledge of the explored space. In many materials science tasks, however, the goal is to obtain a mapping between two or more experimentally measured quantities. Standard active learning algorithms may not be optimal for such complex scientific problems. Reducing the experimental effort to obtain such mappings can be optimized not by independently running several active learning tasks but rather by a strategy coordinating different experiments performed simultaneously. In this talk I will present the idea of cooperative learning, and illustrate it with examples from several different high-throughput studies.

8:45 AM MT03.08.03/MT02.07.03
Exploring Catalyst Chemistries beyond Scaling Laws using Statistical Learning Scott Broderick, Aparajita Dasgupta, Thaicia Stona and Krishna Rajan; University at Buffalo, United States

We have significantly expanded the knowledge-base of metal catalysts through a unique combination of manifold learning, Gaussian process regression and clustering approaches. Given the complexity in performing catalytic measurements, the amount of data available for selecting ‘optimal’ catalysts for specific reactions is limited. The work described here develops an analysis framework suitable to the small number of measurements available, while also developing a large relevant descriptor-base. We have performed the foundational work needed to develop a catalyst discovery toolkit. Using volcano plots as a platform, we have fused manifold learning methods and graph network methods from which one can rapidly explore new chemistries for single atom alloy (SAA) catalysts. We use single atom systems for testing our robustness, with the added benefit that prior work on single atom systems has not utilized machine learning. Using SAAs allows for a rapid screening of the combinatorial design space. We developed a machine learning logic for screening chemistries to define necessary detailed DFT calculations and have identified 28 alloys which are most promising for further exploration.

9:00 AM MT03.08.04/MT02.07.04
Graph Theory and Machine Learning Uncover Zeolite Transformation Pathways Daniel Schwalbe Koda, Wujie Wang and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

Zeolites are inorganic nanoporous materials with broad industrial applications as catalysts, ion exchangers, and separators. Despite sustained research, controlling polymorphism is still a critical challenge in their design, relying mostly on trial-and-error. First-principles calculations could aid the search for new frameworks, but the number of theoretically accessible topologies and the complexity of their kinetic mechanisms render this approach computationally prohibitive. Here, we employ a suite of computational tools such as big-data, graph theory, structural kernels, density functional theory (DFT), and machine learning to explain and predict zeolite transformations. We first relate solid-state transformations to materials descriptors by combining crystallography with a graph-theoretical metric. Supported by exhaustive literature, we then show that interzeolite diffusionless transformations occur only between graph-similar pairs. Moreover, all known instances of intergrowth take place between either structurally- or topologically-similar structures. Our metric suggests hundreds of low-distance pairs between known frameworks and thousands of hypothetical frameworks for realizing novel transformations and intergrown crystals. Such insights are further refined by atomistic simulations. Building on millions of DFT calculations, we parameterize interatomic interactions in pure-silica zeolites using neural network models and active learning. The method enables accurate structural optimizations and off-equilibrium energy sampling with low computational cost, allowing the selection of favorable graph-driven phase transitions between frameworks and uncovering new synthetic pathways for zeolites.

9:15 AM MT03.08.05/MT02.07.05
Automatic Processing of the Scientific Literature to Accelerate Nanomaterials Design and Discovery Anna M. Hiszpanski, Brian Gallagher, Karthik Chellappan, Peggy Pk Li, Shusen Liu, Hyojin Kim, Jinkyu Han, Bhavya Kailkhura, David Butler and T. Yong-Jin Han; Lawrence Livermore National Laboratory, United States

A significant challenge in utilizing machine learning approaches to accelerate materials development is the lack of large and structured data sets. While there are ongoing community efforts to create collaborative materials databases and repositories for this purpose, the diversity and breadth of data types, length scales, and applications still makes it challenging to create such all-encompassing materials databases that are of broad practical use. However, if tools are developed to automatically process the vast scientific literature and extract and structure information of interest to a
given user, then such tools can enable the easy creation of personalized databases with user-specified relevant information to which data mining approaches can then be applied.

We developed such tools for the automated extraction of a suite of information from the text of articles pertaining to nanomaterials synthesis and demonstrate their utility for nanomaterials synthesis. Attaining nanomaterials of desired composition, dimension, and morphology is critical for end-use applications but challenging to do, often requiring time-consuming iterations of synthesis and characterization. Using a corpus of 35k nanomaterials-related articles, we first use a simple unsupervised classification algorithm based on the frequency of occurring terms to identify the primary nanomaterial composition and morphology in each article. Classifying and analyzing articles based on their targeted nanomaterial composition and morphology by itself provides a bird’s eye view and can help identify “hot topics” in the field or alternatively under-studied or challenge-to-synthesize nanomaterials. Next, we apply a supervised machine learning approach to our corpus to identify and extract from articles’ text the sentences related to the nanomaterials’ synthesis protocols, thereby yielding a useful synthesis reference library. Interestingly, we find that function words (i.e., to, in, for, of, at) commonly omitted in natural language processing of non-scientific text are in fact a characteristic trait in discriminating between synthesis- and non-synthesis-related sentences in scientific text. With synthesis protocols in-hand, we further process these via chemical entity recognition (CER) to identify and extract the chemicals used in various nanomaterials’ syntheses. We evaluate a variety of open-access CER tools, as well as our own in-house developed CER tool, that each utilize different tokenizers for parsing the text and techniques for identifying chemicals, and we find that, despite the variety of approaches undertaken, most tools have comparable performance with a peak F1 score of 87%. Normalizing the chemicals names extracted from articles, we then have the opportunity to compare the frequency of use of chemicals for various nanomaterial morphologies. We demonstrate how such analysis provides useful insights as to the importance of chemicals in directing the growth of nanoparticles during synthesis to desired morphologies, like for example nanowires versus nanospheres versus nanocubes. We package this database created entirely by extracting information from existing nanomaterials literature into a browser-based visualization tool we developed that enables easy exploration of the data, thereby helping guide hypothesis generation and reduce the potential parameter space during experimental design.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-777678

9:30 AM BREAK

10:00 AM *MT03.08.07/MT02.07.07
High Throughput Experimental Materials Research Methods at NREL Andriy Zakutayev; National Renewable Energy Laboratory, United States

Bridging the gap between computational predictions and industrial applications requires acceleration and automation of experimental synthesis, characterization and data analysis. High Throughput Experimentation (HTE), also known as combinatorial experiments, is one possible approach to accelerate materials research. Thus, HTE combinatorial methods have been regarded as a promising approach to fulfill the promise of the materials genome initiative (MGI)[1], complementary to high throughput computations and industrial research and development. This presentation will focus on the state of high throughput experimental materials research methods at National Renewable Energy Laboratory (NREL). First, I will discuss methods for creating later gradients of thin film sample properties, in particular going beyond chemical composition of metals [1]. Then, I will talk about spatially-resolved characterization methods, including interlaboratory exchange of samples [2]. Finally, I will highlight our efforts in streamlining data analysis in combinatorial materials science, including a recently published COMBigor software package [3]. These methods will be illustrated by a broad range of materials examples, including oxides, chalcogenides, and nitrides.


10:30 AM MT03.08.08/MT02.07.08
Machine Learning-Assisted High Throughput Synthesis and Characterization of Hybrid Polymer-Carbon Nanotubes Composites for Thermoelectric Application Daniil Bash1,2, Anas I. Abutaha3, Yang Xu2, Yee Fun Lim2, Vijila Chellappan2, Zekun D. Ren1, Isaac S. Tian1,1, Pawan Kumar2, Swee Liang Wong2, Jose Recatala
The so-called 4th revolution in science began with the advent of machine learning (ML), as well as high-throughput (HT) experimentation and robotization. Herein, we describe a workflow that enables rapid screening of a parameter space of hybrid composites, comprised by carbon nanotubes and poly-3-hexylthiophene (CNTs:P3HT) for thermoelectric (TE) applications, with Bayesian optimization embedded in the feedback loop in order to explore the space in a more efficient fashion.

The parameter space under scrutiny includes 4 types of nanotubes (both single- and multiwall), 16 CNTs:P3HT ratios, 2 solvents (o-DCB, and chloroform) and 3 doping conditions, which result in 384 unique synthetic parameters. The setup used involves a robotic pipettor and the microfluidic flow reactor with XY stage for automatic drop casting. We synthesize more than 150 samples per hour, as compared to 4 samples per hour with traditional manual procedures. Characterization was done with means of hyperspectral imaging and 4-point-probe measurements to ascertain optical properties and electrical conductivity.

The conductivity data of the initial experiments was used to train the ML algorithm. After training, the algorithm inferred new experimental conditions for achieving highest possible conductivity, closing the feedback loop. In the end, 3 iterations of the experiments yielded the value of conductivity higher than 150 S cm⁻¹.

Further work includes the optimization of the experimental setup as well as the ongoing effort to use hyperspectral imaging to bypass the bottleneck step i.e. profilometry, as it is the main source of error.

Data-driven Materials Design of Halide Perovskites for Photovoltaic Applications

Shijing Sun¹, Noor Titan Putri Hartono¹, Felipe Oviedo¹, Zekun D. Ren¹, Janak Thapa¹, Zhe Liu¹, Arni Tiihonen¹, Ian Marius Peters¹, Juan Pablo Correa Baena¹, Tonio Buonassisi¹ and Savitha Ramasamy¹; ¹Massachusetts Institute of Technology, United States; ²Georgia Institute of Technology, United States; ³Institute of Infocomm Research, Singapore

To meet increasing global energy demand, it is critical yet challenging to explore new methods to accelerate the development of novel energy materials. In recent years high-throughput experimentation (HTE) and machine-learning techniques have become increasingly accessible to scientific researchers. We herein demonstrate a case study on the data-driven design of perovskite-inspired materials for photovoltaic applications, where we employed machine-learning techniques to guide the synthesis of new halide perovskites for photovoltaic applications. Halide perovskites (ABX₃, where A = Cs, methylammonium (MA), formamidinium (FA); B = Pb, Sn; and X = Cl, Br, I) have shown great promise as light absorbers. Solar cells based on perovskites have surprised the energy community as an emerging low-cost photovoltaic technology with a record power conversion efficiency (24.2%) now exceeding polycrystalline Si cells (22.3%).[1] In this study, we developed a high-throughput experimental platform for thin-film synthesis and characterization, and investigated 75 unique perovskite compositions interest for energy-harvesting applications in a two-month period. To achieve desired optoelectronic properties, we established a set of selection criteria for screening. A deep neural network is employed to classify compounds into 0D, 2D, and 3D perovskite structures via X-ray diffraction patterns analysis. [2] The combination of fast synthesis and machine-learning assisted data diagnostics achieves an acceleration of over an order of magnitude per experimental learning cycle over our laboratory baseline. Among the 41 Pb-free perovskite compositions studied, we identified the optimised doping level in a multi-site alloy series, Csₓ(Bi₁₋ₓSbx)(I₁₋ₓBrx), where a desired structural (2D) and optical properties (< 2 eV). [3] Our work contributes to the prospect of automated materials discovery and we envision an accelerated development in functional materials in the next decade aiming to provide new energy solutions.

Application of Variational Autoencoders to Create Thin Film Structure Zone Diagrams  

Lars Banko, Yury Lysogorskiy, Ralf Drautz and Alfred Ludwig; Ruhr-Universität Bochum, Germany

Structure zone diagrams (SZD) are frequently used to estimate thin film microstructures based on a few chosen synthesis parameters. Despite their usefulness, the predictive power of classical SZD is very limited due to the complexity of the synthesis-microstructure relationship of thin films. Furthermore, the complicated interplay of many synthesis parameters and compositional complexity hinders a generalisation. Classical SZD have in common that they are based on a small number of observations. Underlying trends were extracted by the scientists’ expertise and in a creative process abstracted into a diagram representation of microstructural features. Several refined SZD were proposed, which implemented more physical parameters. With emerging developments in combinatorial thin film synthesis and high-throughput characterization a fast, high-quality acquisition of microstructure data is now possible. This and progress in machine learning of images now provides tools to handle complex image data and improve SZD: We present a dataset containing > 100 samples of SEM surface images from Cr-Al-O-N material libraries, each featuring a different chemical composition and synthesis condition such as deposition temperature, ion energy and sputter frequency of high power impulse magnetron sputtering (HiPIMS). We train convolutional variational autoencoders (VAE) on this dataset of augmented SEM surface image data. Results show that VAEs can cluster microstructure data through latent space representations. The performance of different neural network architectures is discussed. The VAEs generative capabilities to predict SEM surface images from chemical composition and synthesis parameters are investigated. By sampling of the latent representation, we are able to generate SZDs for different variations and combinations of input parameters like temperature, ion energy and chemical composition. The qualitative trends which we observe demonstrate the prediction of microstructure by generative deep learning models.

Generative Adversarial Networks with Molecular Graph Convolution for Learning Secondary Structures of Functional Biomolecules  

Siddharth S. Rath1,1,1, Oliver Nakano-Baker1,1, Jonathan Francis-Landau1,1, Ximing Lu1,1, Kevin Jamieson1,1, Burak B. Ustundag1,2 and Mehmet Sarikaya1,1,1; 1University of Washington, United States; 2Istanbul Teknik Universitesi, Turkey

Generative models, a recent paradigm in machine learning has revolutionized the industry by generating ‘natural looking’ data. While such models have found limited applications in the domain sciences, they display untapped potential in generating materials or molecular structures commensurate with target properties and desired functionalities. While the protein folding problem has been addressed previously by multilevel computational methods and various deep convolutional neural networks, unfortunately, the key step of encoding atomic structures for computational treatment is a challenge. Historical efforts have focused on pre-process featurization that relies upon traditional string representation without any structural information, expert-designed heuristics-based inputs, or on volumetric modeling that presumes a specific predetermined conformation without associated functionality. Here we demonstrate the first implementation of generative models, more precisely, generative adversarial networks with graph encoding of atomic connectivity within the biomolecules, for data-driven prediction of peptide and protein conformations associated with particular functionalities such as binding to atomically flat surfaces and biomineralization. In the graph input, atoms are considered as nodes and the bonds are considered edges, while angles in the molecule are encoded as a third order tensor between any three nodes. The generator tries to output secondary structures in terms of the bond edges and angle tensors while the discriminator network learns from existing sequences and their secondary structures from pdb files and MD simulations. We test the predicted results with MD simulations as well as circular dichroism experiments. Results show that the generative model developed herein is generalizable to any functionality and more accurate than existing methodologies for predicting functionality-associated peptide conformations for practical implementations in disease diagnostics, drug screening, biosensing and bioelectronic devices. As part of the Materials Genome Initiative, the research is supported by NSF-DMREF program through the grant DMR-1629071.
Prediction Interpretability in Data-Driven Materials Development Julia Ling, Astha Garg, James Peerless, Erin Antono, Edward Kim, Yoolhee Kim, Nils Persson and Malcolm Davidson; Citrine Informatics, United States

Sequential learning is a data-driven workflow for accelerating materials development. In this iterative workflow, machine learning models are used to explore a “design space,” the set of possible experiments that could be performed, to surface promising candidate materials. Experimental data for those candidate materials are used to retrain the models so that they can provide successively better-informed suggestions.

For sequential learning to be effective, a relevant design space of candidate materials must first be constructed. These design spaces often include complex constraints, as well as a mix of continuous and categorical variables. The machine learning model can be used to sift through the design space to surface the most promising candidates. For these top candidates, it is valuable to have insights into how the model made its predictions and why it predicts high performance. Interpretability analysis can increase confidence in the model predictions, uncover sample bias in the underlying training data, and provide information on the robustness of the predicted performance. This talk will discuss approaches for constructing relevant design spaces and for interpreting model predictions, and show how these approaches fit into the overall sequential learning workflow.

Network Theory Meets Materials Science Vinay Hegde1, Muratahan Aykol2 and Christopher Wolverton1; 1Northwestern University, United States; 2Toyota Research Institute, United States

One of the holy grails of materials science, unlocking structure-property relationships, has largely been pursued via bottom-up investigations of how the arrangement of atoms and interatomic bonding in a material determine its macroscopic behavior. Here we consider a complementary approach, a top-down study of the organizational structure of networks of materials, based on the interaction between materials themselves. We demonstrate the utility of applying network theory to materials science in two applications: First, we unravel the complete “phase stability network of all inorganic materials” as a densely-connected complex network of 21,000 thermodynamically stable compounds (nodes) interlinked by 41 million tie-lines (edges) defining their two-phase equilibria, as computed by high-throughput density functional theory. We find that the node connectivity in the materials network has a lognormal distribution, and the connectivity decreases with the number of elemental constituents in a material. Analyzing the topology of this network of materials has the potential to uncover new knowledge inaccessible from traditional atoms-to-materials paradigms. Using the connectivity of nodes in this phase stability network, we derive a rational, data-driven metric for material reactivity, the “nobility index”, and quantitatively identify the noblest materials in nature. Second, we apply network theory to the problem of synthesizability of inorganic materials, a grand challenge for accelerating their discovery using computations. We combine the above phase stability network with timelines for the first experimental synthesis of each compound from literature citations. This allows us to create a time-dependent network, and from the time-evolution of the underlying network properties, we use machine-learning to predict the likelihood that hypothetical, computer generated materials will be amenable to successful experimental synthesis. **In collaboration with S. Kirklin, L. Hung, S. Suram, P. Herring, and J. Hummelshoj

A Database to Enable the Discovery and Design of Atomically Precise Nanoclusters Sukriti Manna, Peter Lile,
Alberto Hernandez and Tim Mueller; Johns Hopkins University, United States

Atomically precise nanoclusters can be used for numerous applications due to the unique properties they possess. Despite their wide range of applications, the structures and properties of many small elemental clusters remain unknown. We present the “The Quantum Cluster Database,” an open-access source containing the structures and properties of tens of thousands of cluster structures of up to 55 atoms for 55 elements. The structures are compared against previous computational and experimental data where available. We discuss the methods that are being used to accelerate the construction of the database and describe how the database can be accessed for cost-effective, data-driven materials design.

3:45 PM MT03.09.04/MT02.08.04
Data Driven Experimental Discovery of New Nitride Materials Sage Bauers¹, Elisabetta Arca¹, Wenhao Sun², Chris Bartel³, John D. Perkins¹, Aaron Holder¹, Stephan Lany¹, Gerbrand Ceder² and Andriy Zakutayev¹; ¹National Renewable Energy Laboratory, United States; ²University of California, Berkeley, United States; ³University of Colorado Boulder, United States

New materials enable new technologies, so discovery of new materials is one of the most important directions in materials research. Oxides and some other materials chemistries, which have been extensively explored in the past, yielded many spectacular properties. Other chemistries, such as nitrides, have been barely touched: for every 14 documented oxides there is only 1 known nitride.

We will present on data-driven experimental discovery of new nitride materials, focusing on experimental synthesis and characterization, while also featuring computational predictions and machine learning. The data mining efforts followed by first-principles calculations and machine learning analysis indicated that there are 93 unexplored ternary metal nitride chemical spaces, with 244 new predicted stable ternary materials, and explained the stability trends among these and other nitrides [1].

Experimental synthesis using high-throughput combinatorial methods realized 7 of these compounds, including Zn-M-N (M= Sb, Mo, W) with wurtzite-derived crystal structures and Mg-TM-N (TM = Nb, Ti, Zr, Hf) with rocksalt-derived crystal structures. Physical property characterization results of the ternary rocksalts indicate that they are semiconductors with 1.8-2.1 eV optical absorption onsets and large dielectric constants [2]. The Zn-Sb-N wurtzite is the first ever reported Sb-containing nitride, with Sb in unusually high 5+ valence state, and measured room-temperature photoluminescence near 1.6-1.7 eV solar matched band gap [3].

Overall, these results both demonstrate the power of data-driven materials discovery, and suggest that many new previously unreported nitride materials remain to be synthesized.


4:00 PM *MT03.09.05/MT02.08.05
Active Learning for Nanophotonic Design via Multi-Fidelity Physical Models Harry A. Atwater¹, Jialin Song¹, Yury S. Tokmanov¹, Yuxin Chen¹, Dagny Fleischman¹, Katherine T. Fountaine² and Yisong Yue¹; ¹California Institute of Technology, United States; ²Northrop Grumman Corporation, United States

We have explored the design of nanophotonic structures, such as subwavelength-scale spectral filters, using an advanced active machine learning algorithm that efficiently explores multiple physical models with different approximation fidelities and costs. Our method, which is applicable to a variety of nanophotonics optimization problems, employs a novel strategy consisting of a mutual information based multi-fidelity Gaussian process optimization algorithm (MF-MI-Greedy). It consists of two components: an exploratory procedure to gather information about the target (i.e., the highest fidelity) function via querying lower fidelity functions, followed by an exploitative procedure to optimize the target level fidelity with the previously gathered information. Our results on several pre-collected nanophotonics datasets demonstrate the compelling performance of the multiple-fidelity Bayesian optimization approach. These experiments suggest that there is a significant potential in utilizing cheap, multi-fidelity simulations to aid the discovery of optimal photonic nanostructures.

4:30 PM MT03.09.06/MT02.08.06
Accelerating Materials Discovery through Rapid Construction of Processing Phase Diagrams **Duncan Sutherland**, Aine Connolly, Sebastian Ament, Michael O. Thompson, Carla Gomes and Bruce van Dover; Cornell University, United States

Exhaustive experimental mapping of non-equilibrium processing phase diagrams demands a prohibitively huge allocation of resources for even a single realistic system with more than two compositional degrees of freedom, even with current state-of-the-art high-throughput techniques. Advanced data analysis methods are thus called for to accelerate such explorative efforts, focusing on multimode analysis of critical boundary points in the phase diagram where transitions are observed. Here, we present a hierarchical, prioritized data analysis structure to optimize usage of costly experimental resources. By combining data analysis methods based on optical characterization and x-ray diffraction with sophisticated active learning algorithms, we can efficiently map phase boundaries in composition-time-temperature processing phase diagrams. We demonstrate the utility of our approach by constructing processing phase diagrams for spike annealed multicomponent oxide materials.

4:45 PM MT03.09.07/MT02.08.07

**High-Throughput Screening of Perovskite-Inspire Materials Using Steady-State Photoconductivity and Bayesian Optimization** Jose D. Perea, Felipe Oviedo, Han Yin, Janak Thapa, Armi Tiihonen, Zhe Liu, Ian Marius Peters, Shijun Sun, Rafael Jaramillo and Tonio Buonassisi; Massachusetts Institute of Technology, United States

Hybrid organic-inorganic perovskites solar cells have recently increased scientific interest for their manufacturing simplicity and high performance, challenging the best thin-film photovoltaic devices. Perovskites solar cells have broad and strong light absorption along with excellent transport properties that partly explain their record power conversion efficiency above 24% [1, 2, 3]. Compositional engineering of perovskites is a time-consuming effort. Reaching high efficiency in compositions with complex and diverse dopants that usually requires significant trial and error and hundreds of measurements of full solar cells [4]. In addition to the abundance of applied research on this subject, there is great interest in understanding the fundamentals of transport and photophysical properties of various perovskites compositions [5]. High-throughput methods for screening compositions at the film level could be a potentially powerful alternative to investigate the complex perovskite composition space efficiently. Nevertheless, screening for high-efficiency perovskite compositions with high-throughput methods is not yet firmly established, in part due to the complexity of photophysical characterization experiments at the film level. In this work, we report for the first time a combination of high-throughput conventional steady-state photoconductivity method, (SS-PC) to determine diffusion lengths and Bayesian optimization methodology. This approach allows us to investigate the complex compositional space efficiently by just making films and not full solar cells. By using QSS-PC as a proxy for efficiency, we use Bayesian optimization to guide compositional changes and obtain the best solar cell efficiency for a given material, accelerating material screening by 10X.

[5] Y. Chen et al. NATURE COMMUNICATIONS | 7:12253 | DOI: 10.1038/ ncomms12253 |
Machine learning is often used in materials design nowadays. They are called as Materials Informatics [1] and Material Genome [2]. Recent progress of the technology to predict physical properties of materials is remarkable, especially in metal material [3] and small organic molecule consisting of a single raw material [4].

By contrast, in the case of thermosetting resins, mixed raw materials are often used to synthesize. In such a case, it is hard to predict the material properties due to the existence of missing data derived by the difference in the number of raw materials in each resin. Thus, we suggest a method of machine learning using explanatory variables incorporating raw material information concerning chemical structure.

First, we predicted the classification of raw materials by the random forest, where the extended circular fingerprint (ECFP) [5] was used as the explanatory variable. Then, we aggregated ECFP for each classification predicted by the random forest. After that, we constructed the prediction model by using the aggregated ECFP, feature quantities of reaction intermediates, and curing conditions of resin as explanatory variables. As a result, the model was able to predict in high accuracy ($R^2 = 0.8$), for example, the elastic modulus of thermosetting resins. Furthermore, we show the result of verification of prediction accuracy in first step, such as using the one-hot-encoding.

Therefore, we confirmed that the properties of thermosetting resins could be predicted using mixed raw materials by the proposed method.

a comprehensive quantification of its structure is necessary. In this study, through a combination of high-resolution and high-throughput imaging of the membrane, across several location and depths of the membrane, we quantitatively estimated several physical parameters such as pore area, fiber diameter, network topology, and fiber orientation of these heterogeneous membranes. Scanning Electron Microscope and atomic force microscope images were acquired to provide micron-level details of the mycelium network. These images were sampled across a range of magnifications, and image processing techniques such as statistical region mapping and axial thinning were employed for feature extraction. By obtaining a distribution of the fibers radii, Gaussian mixed models were used to identify three unique fibers indicating bifurcation as the main network growth mechanism. Additionally, unsupervised learning tools were employed to appropriately identify pores from the processed images, which showed a positively skewed data with an average pore area of 4 µm² and a mode of 0.5 µm² across the growth. These pore areas put mycelium in the magnitude for PM2.5 filtration, verifying mycelium’s potential as an air filtration membrane. The results accelerate the development of mycelium-based biofiltration products by establishing a feedback loop with Ecovative Design to optimize their growth conditions and species selection to generate optimized microstructures for filtration.

MT03.10.04
Reinforcement Learning Based 3D Molecular Structure Prediction of Aromatic Hydrocarbon Family Soo Kyung K. Kim, Youngwoo Cho, Piyush Karande, Joanne Taery Kim, Peggy Pk Li and T. Yong-Jin Han; Lawrence Livermore National Laboratory, United States

Conventional methods to predict 3D structures of the molecule are based on iterative stochastic optimization techniques by moving each atom based on energy calculation using physics-based electronic structure modeling such as DFT or MD. Therefore, computing cost of physics-based modeling of 3D molecular structure is significantly increasing with the number of iterations to calculate energy until the total energy of structure is converged, and so with the number of atoms in the target molecule. Therefore, the conventional iterative stochastic optimization may not be optimal for the molecules with a large number of atoms but relatively simple structure. Specifically, for the molecules containing multiple same substructures, such as aromatic hydrocarbon family which has derivative structures of benzene rings, the number of atoms tends to be very large compared with the simple structural pattern of aromatic hydrocarbon family.

As the cost-efficient alternatives, we propose a novel reinforcement learning algorithm to optimize 3D structure of molecules in aromatic hydrocarbon family based on DDPG (Deep Deterministic Policy Gradient) method. There are three main contributions of our proposed approach: (1) To fasten the computation, we applied novel technique to reduce the degree of freedom to move atoms by grouping repetitive substructures in aromatic hydrocarbon family as a unique entity and move them as a unit, (2) We developed the general strategy to build action space applicable to any small aromatic hydrocarbon molecules, (3) We tested whether the knowledge obtained from several aromatic hydrocarbon molecules can be transferred to new aromatic hydrocarbon molecules. To demonstrate the efficiency of our model, we predicted the 3D structure of 13 aromatic hydrocarbon molecules and compared with results from the conventional DFT calculation. Our experiments show that our model succeed to predict 3D structure of our 10 target molecules with the faster convergence than DFT calculation.

MT03.10.05
Comparison of Neural Networks Based Models and Molecular Fingerprints for the Accurate Density Prediction of Small Molecules Joanne Taery Kim, Soo Kyung K. Kim, Piyush Karande, Peggy Pk Li, Youngwoo Cho, T. Yong-Jin Han and Donald Loveland; Lawrence Livermore National Laboratory, United States

Prediction of stoichiometric properties of small molecules is an important process in developing and designing new materials having the desired properties. Specifically, fast screening to identify a promising density of the molecules is significant to develop high performance explosive and high energy molecule. To calculate the density property of molecules, sophisticated quantum level electronic structure calculations, such as DFT or MD simulation, have been employed in optimizing 3D molecular structure and find the energy minimum. However, there are two problems in employing quantum level calculation. First, it requires a significant amount of computing resources which polynomially increases as the size of the molecule. Therefore, it is computationally expensive and not scalable. Second, there are many cases the results from calculation is different with experimental value. Therefore, finding an efficient computational method to accurately predict experiment density of large number of small molecules is of great value. Recent advances in deep learning lead to rise in numerous neural networks based architectures, and they have recently been applied to various tasks in material science domain, such as small molecular design, predicting
Despite the impressive performances of previous works, there have been only a few work to predict structural properties of molecules which requires through featurization of 3D structure of the target molecule. Specifically, density prediction requires careful selection of input data and sophisticated featurization method to represent both 3D structure and physical property accordingly. In this work, we propose methods to predict experimental density value of small molecules employing various combinations of molecular featurization techniques and neural net based architectures. We used published experimental density values and 3D structure of molecules from cambridge structural database. Comparison study between different neural net architectures and different molecular fingerprint is presented and accuracy of density prediction is reported. Several preprocessing techniques including various fingerprints are also compared and discussed with the results. To the best of our knowledge, this is the first work to predict experimental density using deep learning.

**MT03.10.06**

**Predicting Accurate Adsorption Energies of Mono and Diatomic Gases on Transition Metal Surfaces Using Machine Learning**

Sanjay K. Nayak, Satadeep Bhattacharjee and Seung Cheol Lee; Indo-Korea Science and Technology Centre, Bengaluru, India

Finding the “ideal” catalyst is a matter of great interest in the communities of chemists and material scientists, partly because of its wide spectrum of industrial applications. Information regarding a physical parameter termed “adsorption energy”, which dictates the degrees of adhesion of an adsorbate on a substrate is a primary requirement in selecting the catalyst for catalytic reactions. Both experiments and in-silico modeling are extensively being used in estimating the adsorption energies, both of which are Edisonian approach and demands plenty of resources and are time consuming. In this work, employing a data-mining approach, we predict the adsorption energies of monoatomic and di-atomic gases on the surfaces of many transition metals (TMs) in no times. With less than set of 10 simple atomic features, our predictions of the adsorption energies are within a root-mean-squared-error (RMSE) of 0.4 eV with the quantum many-body perturbation theory estimates, a computationally expensive with good experimental agreement. We minimized the RMSE further up to 0.11 eV by using the pre-computed adsorption energies obtained with conventional exchange and correlation (XC) functional as one component of the feature vector. Based on our results, we developed a set of scaling relation between the adsorption energies computed with many-body perturbation theory and conventional DFT XC-functionals.

**MT03.10.07**

**Machine Learning-Directed Navigation of Synthetic Design Space—A Statistical Learning Approach to Controlling the Synthesis of Perovskite Halide Nanoplatelets in the Quantum-Confined Regime**

Erick Braham; Texas A&M University, United States

Understanding and developing maps of chemical synthesis using machine learning has the potential to revolutionize efficient synthesis. The design of a chemical synthesis often relies on a combination of chemical intuition and Edisonian trial-and-error methods which are not just inefficient but inherently limited in their ability to quantitatively predict synthetic outcomes, easily defeated by complex interplays between variables, and oftentimes based on suppositions that are limited in validity. The synthesis of nanomaterials has been especially prone to empiricism given the combination of complex chemical reactivity as well as mesoscopic nucleation and growth phenomena spanning multiple temporal and spatial dimensions. Here, utilizing the synthesis of two-dimensional CsPbBr₃ nanoplatelets as a model system, we demonstrate an efficient machine learning navigation of reaction space that allows for predictive control of layer thickness down to sub-monolayer dimensions. Support vector machine (SVM) classification and regression models are used to initially separate regions of the design space that yield quantum-confined nanoplatelets from regions yielding bulk particles and subsequently to predict the thickness of quantum-confined CsPbBr₃ nanoplatelets that can be accessed under specific reaction conditions. The SVM models are not only just predictive and efficient in sampling the available design space but also provide fundamental insight into the influence of molecular ligands in constraining the dimensions of nanocrystals. The results illustrate a quantitative approach for efficient navigation of reaction design space and pave the way to navigation of more elaborate landscapes beyond dimensional control spanning polymorphs, compositional variants, and surface chemistry.

**MT03.10.08**

**Computational Design of Iron-Based Amorphous Magnetocaloric Alloys and Exploration of Vast Material...**
Search Spaces Adam M. Krajewski\textsuperscript{1,2} and Matthew A. Willard\textsuperscript{1}; \textsuperscript{1}Case Western Reserve University, United States; \textsuperscript{2}The Pennsylvania State University, United States

Solid-state magnetic refrigeration employing the magnetocaloric effect (MCE) is a field of very active research. Compared with conventional gas compression-expansion refrigeration, magnetic refrigeration based on MCE offers improved energy efficiency, reduced environmental impact, and noise-free operation. In this study, we performed data-driven predictions of complex iron-based amorphous alloys laying in the 18-dimensional composition range: $\text{Fe}_{100-\Sigma}\text{Ni}_{0-38}\text{Co}_{0-40}\text{Cu}_{0-10}\text{Zr}_{0-11}\text{B}_{0-29}\text{Cr}_{0-10}\text{Nb}_{0-10}\text{Gd}_{0-22}\text{Mo}_{0-10}\text{Si}_{0-10}\text{Nd}_{0-15}\text{Ce}_{0-13}\text{Sm}_{0-3}\text{Mn}_{0-24}\text{Ti}_{0-8}\text{V}_{0-14}$. To design alloys that would achieve higher-than-ever reported performance in refrigeration at a desired operating temperature, we employed a combination of Machine Learning and Search Algorithms. The framework aims to maximize the magnitude of peak magnetic entropy change $|\Delta S_M|_{\text{peak}}$ and tune Curie temperature $T_C$ to value the granting of the highest performance. Based on the contents of the database we collected, our predictive tool is expected to be useful when designing alloys for applications requiring any $T_C$ between 200K and 500K. This temperature range includes room temperature (298K), which is considered to be the most important, as it would allow the creation of MCE-based household refrigerators.

Since April, we have been experimentally validating our predictions, first by testing a state-of-the-art alloy reported in the literature and then testing novel alloys designed with our predictive framework based on that alloy. Results obtained so far show excellent agreement between our predictions and experimental results. In our MRS presentation, we pay particular attention to the design of Search Algorithms. Based on our experience, this step is by far the most challenging due to the considerable dimensionality of composition and vast search space, which in our case included up to $10^{34}$ possible alloys. It is also the most crucial step to the prediction of alloys that are reasonable and are feasible to be made in the lab. We not only report our final method of search but also elaborate on challenges we overcame along the way. This knowledge should be useful to any group working on the design of high-entropy amorphous metals.

MT03.10.09
Modeling Transport Current in Polycrystalline Superconducting Materials Akiyasu Yamamoto and Takuya Obara; Tokyo University of Agriculture and Technology, Japan

Transport current is one of the critical parameters for practical applications of superconducting materials, such as transmission cables and strong magnets. On the other hand, early studies have shown that there is a large gap between the intrinsic physical properties and the macroscopic transport properties obtained as a material due to “weak-link” effects at grain-boundaries, vortex pinning performance and microstructural defects [1,2]. Establishing the prediction model of transport properties is an important issue for the utilization of automated and/or data-driven approaches to superconducting materials research and development. Connectivity is a useful parameter that represents the effective cross-sectional area of the transport current [3]. Matsushita \textit{et al}. has proposed a mean-field model that quantitatively links connectivity and microstructural defects [4]. In this study, we studied transport property prediction method based on numerical modeling. The transport mechanism of polycrystalline materials composed of crystals with electrical anisotropy and containing voids as microstructural defects was investigated by means of a random resistance network based on a three-dimensional cubic site percolation model. The local current distribution and the macroscopic connectivity of the system were obtained by numerical simulation using the finite element method. In addition, the simulated result was compared with the measured electrical resistivity of the synthesized samples.


MT03.10.10
High-Throughput Computation and Evaluation of Raman Spectra Qiaohao Liang\textsuperscript{1}, Shyam Dwaraknath\textsuperscript{2} and Kristin A. Persson\textsuperscript{1,2}; \textsuperscript{1}University of California, Berkeley, United States; \textsuperscript{2}Lawrence Berkeley National Laboratory, United States

Raman spectroscopy is used ubiquitously in the characterization of condensed materials, spanning from minerals, polymers, to biomaterials, as it provides a unique fingerprint of local bonding and environment. In this work, we demonstrate a robust and automatic computational workflow for Raman spectra that employs first-principle
calculations based on density functional perturbation theory. Sets of calculated Raman spectra peaks was compared to those obtained from established experimental databases to estimate the accuracy of the calculated properties across chemical systems and structures. Our work, consisting 55 mineral compounds and 205 pairs of matched peaks, shows that the mean wavenumber deviation is -9.66 cm\(^{-1}\) with a standard deviation of 18.58 cm\(^{-1}\), indicating our calculations tend to slightly underestimate the Raman peak locations. With a mean absolute relative error (MARE) of -2 % for wavenumbers and the low bias exhibited by the intensities, we conclude that our computational data set is in reasonably good agreement with the experimental data and have explored potential reasons for the deviations.

**MT03.10.11**

Alkyltin Keggin Clusters as Photoresist Material for Extreme Ultraviolet Lithography

Rebecca Stern\(^1\), Danielle Hutchinson\(^2\), Morgan Olsen\(^2\), Lev Zakharov\(^2\), Kristin A. Persson\(^1,3\) and May Nyman\(^2\); \(^1\)University of California, Berkeley, United States; \(^2\)Oregon State University, United States; \(^3\)Lawrence Berkeley National Laboratory, United States

With integrated circuit manufacturers aiming to produce sub-10nm feature sizes, extreme ultraviolet lithography (EUV) is the next developing technology for the job. The challenges with using polymer-based photoresists for EUV can be eliminated by using oxohydroxo metal nanoparticle photoresists instead. Oxohydroxo metal clusters have the potential to provide faster writing speeds, higher resolutions, and better etch resistance than chemically amplified polymer resists. In a joint computational-experimental effort we examine the stability of organotin Keggin clusters for use as sensitive high-resolution photolithographic resists. A one-step synthesis obtained the β-isomer (β-NaSn12), the γ-isomer (γ-NaSn12), and a γ-isomer capped with a butyltin (γ-NaSn13). The Sn Keggin ions crystallized readily without counterions which increased the simplicity of the synthesis as well as improved the yield, purity, and reproducibility. Solution characterization (SAXS, NMR, ESI-MS) verified that solutions contained only the Na-centered dodecamers. Computational modeling was used to determine the ground state electronic structure of the three butyltin Keggin structures, as well as the capped β-isomer (β-NaSn13), and the hypothetical α-isomers (α-NaSn12 and α-NaSn13). The computed hydrolysis Gibbs free energy and HOMO-LUMO gap provided the stability ranking: β-NaSn12 > γ-NaSn12 > α-NaSn12 which was consistent which experimental observations. The uncapped isomers were computationally evaluated to be more stable than their respective capped analogues. In-depth structure-energy analysis reveals a balance between corner-linking to minimize cation-cation repulsion, and edge-lining to maximize stability via bond formation. Therefore, this sodium centered tin Keggin ion represents the only Keggin ion family so far, that favors the isomers of lower symmetry. Finally, the system’s neutral charge makes it a valuable model system for understanding the fundamental patterning mechanisms at play.

**MT03.10.12**

Symmetry in *Ab Initio* Prediction of Metal Organic Frameworks

James Darby\(^1\), Mihails Arhangelskis\(^2\), Athanassios Katsenis\(^2\), Joseph Marrett\(^2\), Tomislav Fričić\(^2\) and Andrew J. Morris\(^3\); \(^1\)University of Cambridge, United Kingdom; \(^2\)McGill University, Canada; \(^3\)University of Birmingham, United Kingdom

First-principles crystal structure prediction (CSP) is a well established technique which is routinely used to predict crystal structure in a diverse range of systems such as periodic solids, interfaces, encapsulated nanowires etc. However, one downside of CSP is that the number of minima in the potential energy surface scales exponentially with system size. As such, it rapidly becomes computationally unfeasible to search for more complex structures with larger unit cells. Here we discuss how ligand symmetries can be exploited to accelerate the prediction of Metal Organic Frameworks (MOFs).

Symmetry is often imposed during CSP to reduce the dimension of the search space and expedite energy evaluations. When atoms are used as the constituent units of the structure it is simple to apply symmetry constraints. However, if, as with MOFs, we start with extended units then imposing symmetry constraints is not trivial. Our method, Wyckoff Allowed Molecules (WAM), makes use of molecule symmetries to generate trial structures with molecules on special Wyckoff sites, as well as on the general site.

To test our approach we searched for a variety of Zinc based MOFs \(^1\) using the *ab initio* random structure searching method with WAM and the CASTEP plane wave DFT code. These results will be presented and used to highlight strengths and weaknesses of the approach.

**MT03.10.13**

**Development of Machine Learning Potential for Si Clusters**

Minkyu Park1, Seokmin Lim1,2, Seungchul Kim1,2 and Yong-Sung Kim3,2; 1Korea Institute of Science and Technology, Korea (the Republic of); 2University of Science and Technology, Korea (the Republic of); 3Korea Research Institute of Standards and Science, Korea (the Republic of)

Recently, the breakthrough developments of artificial neural network (ANN) accelerate the in the field of materials science. In the last few years, J. Behler and M. Parrinello introduced a method, which is a new kind of neural-network representation of density functional theory potential-energy surfaces, called “symmetry function (SF)”.

Here, we calculate the total energies and atomic forces of variety Si clusters, which is fundamental and significant material in modern semiconductor industry, by using ANN. More than 11,000 training set data are generated by carrying out trajectories of ab initio molecular dynamic simulations with canonical ensembles at 300 and 700 K, and the static calculations of randomly positioned coordination of Si clusters. To describe chemical atomic environment properly, we carefully determined number of radial and angular SFs with different parameters. The hyper-parameters in ANN have been tuned by random search and grid search method. To evaluate accuracy of ANN models, we addressed root mean square errors between value of the DFT calculations and ANN calculations through decent-gradient algorithm. The calculated error of total energy for training and test data-sets are less than 0.08, 0.18 eV/atom, and error of atomic force for training and test-sets are less than 0.10 and 0.74 eV/A, respectively. For applications of machine learning based potential, we compared the mechanical and crystallographic properties with density functional theory calculations.

**MT03.10.14**

**Model-Based Optimization of Laser-reduced Graphene with Sparse Datasets**

Hud Wahab, Alexander Tyrrell, Vivek Jain, Lars Kotthoff and Patrick Johnson; University of Wyoming, United States

A major challenge towards efficient materials discovery is the reliance on human intuition in the experimental design. Currently, the navigation in the search space for targeted material properties using high-throughput experiments and computations often necessitates large resources. Here, we investigate how machine learning accelerates the search and discovery of new materials using sparse datasets. In particular, model-based search explores iteratively key parameters to guide the experiments and computations. The approach utilizes uncertainties and makes predictions from a surrogate model together with a utility function that prioritizes the decision making process on unexplored data in multidimensional space. We demonstrate this approach on the fabrication of laser-reduced graphene circuits on flexible substrates. The surrogate model is fed with surface characterizations with a view to automate the manufacturing process in a closed-loop. We demonstrate effective explorations and rapid optimizations even with sparse data and discuss the integration of machine learning in advanced manufacturing.

**MT03.10.15**

**High-Throughput Data Generation and Analysis with the Signac Software Framework**

Carl Simon Adorf, Vyas Ramasubramani, Bradley D. Dice and Sharon C. Glotzer; University of Michigan, United States

Computational resources for high-throughput data generation offer incredible potential for accelerating scientific discovery, especially if used in conjunction with well-managed computational workflows. The open-source signac data management framework enables researchers to maintain well-formed, sharable, and reusable data spaces from early exploration through production runs on supercomputers. This is achieved through a transparent, application-agnostic data and workflow model, as well as a simple and unobtrusive programmatic interface. The framework has been applied to molecular simulations, quantum chemistry, photonics, computational fluid dynamics, machine learning, graph mining, and even the management of experimental data. Implemented in Python, signac interoperates organically with other well-established libraries within the scientific software ecosystem such as NumPy and pandas, and it integrates naturally into Jupyter notebooks for data presentation and exploration. The framework readily supports the use of HDF5 files for the storage of large hierarchical numerical data. With special emphasis on enabling rapid prototyping, workflows implemented with signac are easily executed both on local...
resources and powerful supercomputing clusters like OLCF’s Summit. We will present representative examples of scientific applications that demonstrate the efficacy and versatility of signac across a range of materials research domains.

*MT03.10.16
Autonomous Research Systems ARES™ for Materials Development

Benji Maruyama1, J. Daniel Berrigan1, Rahul Rao2, Ahmad E. Islam2, Jennifer Carpena2, Michael A. Susner2, Thomas J. Hardin2, Megan Creighton3, Kristofer Reyes4, Jay Myung5 and Mark Pitt5; 1Air Force Research Laboratory, United States; 2UES Inc., United States; 3National Research Council, United States; 4University at Buffalo, The State University of New York, United States; 5The Ohio State University, United States

Autonomous Research Systems like ARES™ are disrupting the research process by using AI and Machine Learning to drive closed-loop iterative research. ARES™ is our autonomous research robot capable of designing, executing and evaluating its own experiments at a rate of up to 100 iterations per day. Previously ARES taught itself to grow carbon nanotubes at controlled rates (NPJ Comp Mat 2016). Here we discuss recent research campaigns on maximizing carbon nanotube growth rates using a Bayesian optimization planner. We also use HOLMES and knowledge gradient descent to introduce advanced decision policies with local parametric models to control nanotube diameter. Implications for nanotube materials development will be discussed. Finally, we have developed a new research robot for additive manufacturing, AM ARES™, which is at the early stages of teaching itself to print structures with unknown inks. We plan to make the AM ARES™ Robot available online so that a broad community of researchers can test concepts and approaches for AI/ML and experimental design as applied to 3D printing, thus building to the larger goal of enhancing citizen science.

MT03.10.17
A New Cure Kinetic Model of Polymeric Sealants and Its Application to Simulating their Mechanical Behaviour in Industrial Processes

Jae-Hyuk Choi1, Wonbo Shim1, Doyoung Kim1, Chul Hong Rhie2 and Woong-Ryeol Yu1; 1Seoul National University, Korea (the Republic of); 2Hyundai Motor Company, Korea (the Republic of)

Accurate cure kinetic model of polymeric sealants is essential to determine processing conditions of industrial processes, e.g., an automotive painting process involving a body sealant because their mechanical behaviour is highly dependent on their degree of cure during processes. Sourour-Kamal model with seven kinetic parameters is the most widely used cure kinetic model, but it cannot describe the degree of cure in both isothermal and dynamic process conditions. In this study, additional parameters related with the temperature rate were introduced and its validity was proved by carrying out a series of cure experiments of an epoxy-base automotive sealant using a differential scanning calorimetry, finally demonstrating that the degree of cure can be calculated under arbitrary time and temperature profile. Later, the thermal expansion, the cure shrinkage, and the rheological and viscoelastic properties of the sealant were characterized with a function of the degree of cure using a thermomechanical analysis, rheometry and dynamic mechanical analysis, respectively. The developed cure kinetic model and the four properties were incorporated into ABAQUS through a user material subroutine. Finally, the mechanical behavior of the sealant under various time-varying temperatures in automotive heating and coating processes was simulated to determine whether the sealant fails or not during and after the process.

MT03.10.18
PDPep: Protein-Derived-Peptides for Materials Science and Biomedical Device Applications—a Machine Learning Approach

Siddharth S. Rath, Jonathan Francis-Landau, Chris Pecunies, Jacob Rodriguez, Deniz T. Yucesoy, Rene Overney, Sami Dogan and Mehmet Sarikaya; University of Washington, United States

Manipulating physicochemical and structural properties of materials by customizing their microstructures has been the pivotal element in materials science. However, where purely artificial efforts, e.g., heat-and-beat, usually involve complicated materials processing, nature’s design process, evolution, achieves similar functionality for materials at ambient conditions. While enantioselective directed evolution of enzymes has become recently popular in chemistry, the potential for directed-evolution in manipulating materials’ microstructure has been largely untapped. Here we demonstrate how millions of peptide sequences collected from combinatorial libraries and next-generation-sequencing paradigms, can not only be used to de-novo predict materials science relevant peptide sequences (for example, biomineralization), but also be used to scan naturally occurring pan-functional proteins for deriving
peptides with targeted functionalities (e.g., target binding). As examples to PDpep approach, we derive hydroxyapatite biomineralizing peptides from Amelogenin and use these *Amelogenin-Derived-Peptides* for developing formulations towards a utility in repairing defective dental tissues; ice-inhibiting peptides, *AFpep* (antifreeze peptides), from antifreeze proteins for controlling ice nucleation and growth; and magneto-receptive peptides, *MRpep*, from crytochrome-4 for biosensing applications, we demonstrate here that the methodology can be used to mineralize tailored microstructures with predictable materials phases as well as interface these structures with biology and materials science at the molecular level towards genetic design of functional materials in practical technological systems. As part of the Materials Genome Initiative, the research is supported by NSF-DMREF program through the grant DMR-1629071.

**MT03.10.19**

**Computational Design of Solid-State Electrolytes for All-Solid-State Li Batteries** Wonseok Jeong¹, Youngho Kang² and Seungwu Han¹; ¹Seoul National University, Korea (the Republic of); ²Korea Institute of Materials Science, Korea (the Republic of)

The growing research efforts have been put into developing solid-state electrolytes (SSEs) that can alleviate many of the issues of Li-ion batteries arising from the utilization of the organic liquid electrolytes. Up to date, several SSEs such as Li₁₀GeP₂S₁₂, Li₃La₂Zr₂O₁₂, and Li₁₁₃Al₀₃Ti₁₇(PO₄)₃ have been proposed as candidates in previous experiments. However, none of those SSEs are fully satisfactory due to the insufficient ionic conductivity or chemical and mechanical stability or high electronic conductivity. Nevertheless, the capability of numerous materials for SSE has been unexplored, and thus we might be able to discover new interesting candidates by a systematic investigation of relevant properties of thousands of materials. In particular, owing to the high accuracy of first-principles calculations as well as recent advances in computing power, computational screening approaches have been applied to searching publicly available materials databases for a new type of SSEs.[1,2] In this work, we take one step further toward discovering potential SSEs; in addition to simply exploring a pre-existing materials database, we try to design new materials with aliovalent substitution of cations. This aliovalent substitution is known to facilitate kinetics of Li diffusion.[3,4] We first screen potential materials, which maybe be useful in themselves or become mother materials for generating new ones by aliovalent substitution, considering fundamental properties such as the presence of transition metals, thermodynamic stability, and band gap. Afterward, we crudely examine the potential energy surface (PES) around the Li ion at interstitial sites. The materials with the most smooth PES are then chosen for the further studies. Starting from 42,337 structures from the Materials Project database, we find and design a number of new[i] Li ionic conductors, some of them are predicted to exceed the Li ionic conductivity of the state-of-the-art Li₁₀GeP₂S₁₂.


**SESSION MT03.11: High Performance Computing and Screening of Materials**

Session Chairs: Mohamed Eddaoudi and Yousung Jung
Thursday Morning, December 5, 2019
Hynes, Level 2, Room 208

**8:00 AM *MT03.11.01**

**Reproducibility of Materials Simulations and Accessibility to Data** Giulia Galli; University of Chicago, United States

We discuss a strategy and present a simple tool to facilitate scientific data reproducibility by making available, in a distributed manner, all data and procedures presented in scientific papers, together with metadata to render them searchable and discoverable [1]. We also discuss accessibility to data presented in scientific papers and in general material simulation data generated by diverse groups and communities.

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**SESSION MT03.10: Computational Design of Solid-State Electrolytes for All-Solid-State Li Batteries**

Wonseok Jeong, Youngho Kang, and Seungwu Han
Seoul National University, Korea (the Republic of)

The growing research efforts have been put into developing solid-state electrolytes (SSEs) that can alleviate many of the issues of Li-ion batteries arising from the utilization of the organic liquid electrolytes. Up to date, several SSEs such as Li₁₀GeP₂S₁₂, Li₃La₂Zr₂O₁₂, and Li₁₁₃Al₀₃Ti₁₇(PO₄)₃ have been proposed as candidates in previous experiments. However, none of those SSEs are fully satisfactory due to the insufficient ionic conductivity or chemical and mechanical stability or high electronic conductivity. Nevertheless, the capability of numerous materials for SSE has been unexplored, and thus we might be able to discover new interesting candidates by a systematic investigation of relevant properties of thousands of materials. In particular, owing to the high accuracy of first-principles calculations as well as recent advances in computing power, computational screening approaches have been applied to searching publicly available materials databases for a new type of SSEs.[1,2]

In this work, we take one step further toward discovering potential SSEs; in addition to simply exploring a pre-existing materials database, we try to design new materials with aliovalent substitution of cations. This aliovalent substitution is known to facilitate kinetics of Li diffusion.[3,4] We first screen potential materials, which maybe be useful in themselves or become mother materials for generating new ones by aliovalent substitution, considering fundamental properties such as the presence of transition metals, thermodynamic stability, and band gap. Afterward, we crudely examine the potential energy surface (PES) around the Li ion at interstitial sites. The materials with the most smooth PES are then chosen for the further studies. Starting from 42,337 structures from the Materials Project database, we find and design a number of new[i] Li ionic conductors, some of them are predicted to exceed the Li ionic conductivity of the state-of-the-art Li₁₀GeP₂S₁₂.

8:30 AM MT03.11.02
Niobium Oxide Dihalides NbOX2—A New Family of Two-Dimensional van der Waals Layered Materials with Intrinsic Ferroelectricity and Antiferroelectricity Yinglu Jia1,2, Min Zhao1, Gaoyang Gou1, Xiao C. Zeng2 and Ju Li3; 1Xi’an Jiaotong University, China; 2University of Nebraska-Lincoln, United States; 3Massachusetts Institute of Technology, United States

Two-dimensional (2D) ferroelectric (FE) materials displaying spontaneous polarizations are promising candidates for miniaturized electronic and memory devices. However, stable FE orderings are only found in a small number of 2D materials by experiment so far. In the current work, based on high-throughput screening of a 2D van der Waals layered materials database and first-principles calculations, we demonstrate niobium oxide dihalides NbOX2 (X = Cl, Br and I), a group of experimentally synthesized yet underexplored van der Waals layered compounds, as a new family of 2D materials that simultaneously exhibit intrinsic in-plane ferroelectricity and antiferroelectricity. Similar to FE perovskite oxides, polar displacement of Nb cations relative to the center of the anion octahedral cage can lead to experimentally measurable FE polarizations up to 27 μC cm−2 in layered NbOCl2. The presence of low-lying antiferroelectric (AFE) phases can effectively reduce the energy barrier associated with polarization switching, suggesting switchable ferroelectricity is experimentally achievable. In addition, the mechanism driving FE phase transitions in NbOX2 monolayers around Curie temperature $T_C$ is clearly revealed by our finite-temperature simulations. NbOCl2 monolayer is predicted to be a stable ferroelectric with $T_C$ above room temperature. Moreover, application of NbOBr2 and NbOI2 monolayers as 2D dielectric capacitors is further developed, where electrostatic energy storage of nearly 100% efficiency can be achieved in the 2D single-layer regime.

8:45 AM MT03.11.03
Virtual High-Throughput Screening of Photoactive Quaternary Oxides Daniel W. Davies1, Keith Butler2 and Aron Walsh1; 1Imperial College London, United Kingdom; 2STFC, United Kingdom

The discovery of earth abundant, functional materials is critical for sustainable technological advancement. There is a concerted global effort to reduce the time it takes to realize such materials via databases, high-throughput screening and informatics,[1] but forming a four-component compound from the first 103 elements results in excess of $10^{12}$ potential compositions.[2] Such a search space is intractable to high-throughput experiment or first principles calculations.

In this work, we present a low-cost, virtual high-throughput materials design workflow and use it to identify earth-abundant materials for solar energy applications from the quaternary oxide chemical space. A statistical model that predicts bandgap from chemical composition is built using supervised machine learning and the trained model forms the first in a hierarchy of screening steps. Further data-driven algorithms are used to assign crystal structures and to discard unlikely chemistries based on oxidation state information.[3]

We demonstrate the utility of this process by screening over 1 million oxide compositions generated using the open-source SMACT package.[4] We find that, despite the difficulties inherent to identifying stable multi-component oxides, several compounds produced by our workflow are calculated to be thermodynamically stable or metastable and have desirable optoelectronic properties according to first-principles calculations. The predicted phases are Li₂MnSiO₅, MnAg(SeO₃)₂ and two polymorphs of MnCdGe₂O₆, all four of which are found to have direct electronic bandgaps in the visible range of the solar spectrum.


One of the conventional approaches of materials informatics (MI) is on the basis of supervised learning, which expects a property of unknown materials from known materials. In other words, the learning process is appropriate for accurate and broad prediction within a search space where a supervised dataset covers. In this study, to discover truly new materials by a MI approach, we present a search system to explore outside of what we have known so far. Recently, Yang and Tsuda group proposed an automatic-design framework for organic materials, by using Monte-Carlo tree search (MCTS) to select a prospective molecular fragment. This search process is driven by iterative evaluations in optimization of a target property. However, long-simulation time to evaluate the property is a major bottleneck in MCTS. In the case of engine oils, for example, a molecular dynamics (MD) method using Green-Kubo formalism is a proper evaluator for viscosity property. This MD-based evaluation of viscosity requires a large number of MD time steps, which is the bottleneck of the search system.

We present an ultra-fast MD evaluation method of viscosity, which realizes the automatic oil-molecular design. This acceleration is achieved by an idea from a theoretical model of glass transition, in which viscosity can be represented by Arrhenius-type equation. This model states that viscosity can be estimated by a small number of MD steps compared to a direct evaluation methodology. We combine this fast MD evaluation with the MCTS, and examine this search system, by setting viscosity index (VI) as a target property. The VI is an indicator of viscosity susceptible to temperature; typically, high VI oil is regarded to high quality in machinery equipment. In this closed-loop search, the total number of the evaluated molecules is 55,000, which is done in the “K” super computer. We select one prospective molecule as a motif, and make it modified so as to synthesis. This MI-designed oil molecule is experimentally confirmed that it indicates high VI essentially comparable to high-VI base oils in the commercial market.

Metal oxide semiconductors, which support equilibrium populations of electron and hole charge carriers, have widespread applications including batteries, solar cells, and display technologies. It is often difficult to predict in advance if a redox process will result in localized or delocalized charge carriers; the former is associated with polaron transport and the latter with band transport. Determining polaron ground states directly within the density functional theory (DFT) framework is a formidable task and invariably requires careful parameter control of multiple expensive calculation runs[1].

Thanks to the existence of extensive databases covering calculated properties of known and hypothetical systems[2], we are able to utilize data from routine DFT calculations to predict the energetic driving force for carrier localization. By considering the competition between the loss in kinetic energy (from wavefunction localization) and gain in potential energy (from dielectric polarization), the net polaron binding energy can be determined in line with the early work of Pekar[2] and Frölich[3]. We demonstrate how this data can parameterise a simple screening metric for predicting the nature of charge carriers, circumventing the need for explicit polaron modelling in high-throughput studies. Our results are consistent with observations regarding carrier dynamics and lifetimes. We apply our screening metric to identifying p-type metal oxides (targeting low hole polaron binding energy) yielding a number of promising candidates including LiAg3O2 and Ca4Bi2O, in addition to recovering known p-type oxides such as the Delafossite structure CuRhO2.

This study highlights the utility of modern materials datasets to facilitate rapid screening of hard-to-access properties. By comparison with new data generated from hybrid DFT calculations, we explore current limitations in
terms of data quality and availability of necessary properties.


9:30 AM *MT03.11.06
What Does “Cheap” Materials Property Prediction Enable? Shyue Ping Ong, Chi Chen, Xiangguo Li, Zhi Deng and Yunxing Zuo; University of California, San Diego, United States

In the recent decade, materials science has seen a huge growth in available data from combinatorial experiments as well as high-throughput first principles calculations. With this data explosion, we now stand at the cusp where machine learning techniques can make meaningful predictions of many properties of materials almost instantaneously. In this talk, I will discuss the potentially transformative impact that this “instant” materials property prediction can have on materials research, from providing new chemistry insights that will greatly improve our ability to “guess” new materials with superior properties to accessing large length / time scales at near DFT accuracy. I will highlight some of the most promising machine learning approaches thus far, focusing, in particular, on techniques to address fundamental data size and diversity limitations in materials science. Finally, I will outline some of the key obstacles that still remain to ML-enabled materials science.

10:00 AM BREAK

SESSION MT03.12: High Performance Computing, DFT with Machine Learning
Session Chairs: Giulia Galli and Shyue Ping Ong
Thursday Morning, December 5, 2019
Hynes, Level 2, Room 208

10:30 AM *MT03.12.01
Solid State Materials Discovery Using Computational and Data-Driven Approaches Yousung Jung; KAIST, Korea (the Republic of)

Discovery of a new material with desired properties is the ultimate goal of materials research. To date, a generally successful strategy has been to use chemical intuition and empirical rules to design new materials, but these conventional approaches require a significant amount of time and cost due to almost unlimited combinatorial possibilities of materials to explore in chemical space. A promising way to significantly accelerate the latter process is to incorporate all available knowledge and data to plan the synthesis of the next material. In this talk, I will present a few initial frameworks we have developed along this line to perform machine-learned density functional calculations, to predict the properties of a material using simple representations, and to generate new materials for a given property using materials deep generative model.

11:00 AM MT03.12.02
Pawpyseed—Post-Processing Tools for PAW Wavefunctions Kyle W. Bystrom¹, Danny Broberg², Shyam Dwaraknath¹, Kristin A. Persson¹² and Mark Asta²¹; ¹Lawrence Berkeley National Laboratory, United States; ²University of California, Berkeley, United States

Post-processing tools for PAW wavefunctions are important for the automation of DFT studies. For example, calculating the overlap operator between wavefunctions from different structures is critical for electron-phonon coupling calculations as well as new formation energy correction methods being developed for point defect calculations. PAW augments plane-wave pseudo wavefunctions with atom-centered orbitals on a radial grid to minimize the size of the plane-wave basis set needed for accurate calculations. This also makes calculating these
overlap operators nontrivial. To overcome this difficulty and enable arbitrary overlap calculations, we developed a general formalism for doing so and implemented it in an open-source code called Pawpyseed. Pawpyseed provides a powerful, parallelized C backend for handling large systems and a flexible Python front-end that takes advantage of cutting-edge research tools like the Python Materials Genomics (pymatgen) package. This performance-usability balance is ideal for automated post-processing of DFT calculations. We demonstrate one potential use of pawpyseed by implementing a perturbation theory-inspired formation energy correction for point defect calculations that improves upon previously proposed band edge shifting techniques.

11:15 AM MT03.12.03
ARTEMIS—Ab Initio Restructuring Tool Enabling the Modelling of Interface Structures Ned T. Taylor, Francis H. Davies, Shane G. Davies, Conor J. Price and Steven P. Hepplestone; University of Exeter, United Kingdom

From metal contacts to batteries, interfaces dominate the physics of devices. Whilst modelling of the individual components of such systems is well understood, the modelling of interfaces is limited due to the structure of the interface being relatively unknown. Prediction of these interfaces is driven by human intuition and computational ease, which is fraught with problems. We have developed a structural prediction approach for exploring interface structures with the goal of eliminating human bias. Here, using two test cases; 1) metal contacts of 2D systems, and 2) oxide-graphite batteries, we show how we can produce interface structures for these complicated systems in order to find the lowest energy interface.

Here, we present our software package, ARTEMIS (Ab initio Restructuring Tool Enabling the Modelling of Interface Structures), developed to ease the generation and modelling of interfaces in order to explore the energy space of interfaces and find the lowest energy interface. We model various metal contacts on a set of transition metal dichalcogenides, investigating different termination planes and surface stoichiometries. The software also enables the exploration of intermixing and plane shifting in order to find the lowest energy interface between any two materials. Hence, by using ARTEMIS, we show how a variety of metal contacts for 2D systems could be explored, as well as understanding electronic properties of graphitic/oxide mixtures for applications such as batteries.

11:30 AM *MT03.12.04
Design Strategies for the Construction of Metal-Organic Frameworks Mohamed Eddaoudi; King Abdullah University of Science and Technology, Saudi Arabia

Demand for functional materials targeted for specific applications is ever increasing as societal needs and demands mount with advancing technology. One class of inorganic-organic hybrid materials, metal-organic frameworks (MOFs), has burgeoned in recent years due, in part, to effective design strategies (i.e. reticular chemistry) for their synthesis and their inherent [and readily interchangeable] hybrid, highly functional character. Metal-organic materials, specifically metal-organic frameworks (MOFs), have emerged as a unique class of materials amenable to design and manipulation for desired function and application. Several design strategies have been utilized and developed to target viable MOF platforms, from the single-metal-ion molecular building block (MBB) approach to the hierarchical supermolecular building block and supermolecular building layer approaches (SBB and SBL, respectively) to our newly introduced merged net approach allowing for the construction of intricate MOFs with multiple ligands, . This inherent built-in information allows access to highly stable and made-to-order porous materials toward applications pertaining to energy and environmental sustainability.
Designing energy conversion materials with simultaneous satisfying activity and stability properties is a challenge especially for electrochemical reaction such as the water splitting reaction. Often, high electrocatalytic activity of a catalyst material is accompanied by structural instability. In this presentation, I will discuss a core-shell oxide catalyst material design, where an active core catalyst is covered with a stable shell, as an attractive solution to the problem of catalyst instability. So far, the influence of the core during electrocatalytic reactions on the surface of the shell of oxide systems is not well understood. In this contribution, we demonstrate how ultrathin heterostructures composed of unstable active and stable inactive layers can be used for studies of model core–shell oxide architectures. In particular, we show that as little as a one unit cell subsurface layer of an active perovskite SrRuO$_3$ “core” can activate a SrTiO$_3$ “shell” surface layer towards oxygen evolution reaction (OER). While, as little as a two unit cell shell layer is enough to completely protect the inherently unstable catalyst against corrosion during OER. Using density functional theory calculations and a simplified electronic structure model, we unravel the mechanism for the subsurface activation for a class of oxide heterostructures and rationalize the choice of the SrTiO$_3$-SrRuO$_3$ system, which is realized experimentally.$^{1}$


2:00 PM MT03.13.02
Data-Driven Approach for Core-Loss Spectroscopy—Prediction of Spectra and Quantification of Properties
Shin Kiyohara$^1$, Masashi Tsubaki$^2$ and Teruyasu Mizoguchi$^1$; $^1$The University of Tokyo, Japan; $^2$Artificial Intelligence Research Center, Japan

In materials development, a structural analysis of materials is indispensable to understand the structure property relationships. Especially, with increasing demand for nanoscale devices, in which peculiar atomic arrangements influence the material properties more than those in bulk, the importance of the local structure analysis is rapidly increasing. Among a variety of analytical techniques, core-loss spectroscopy, that is, electron energy loss near edge structure (ELNES) and X-ray absorption near edge structure (XANES), is strongly authentic with nano- or sub nanoscaled spatial resolution and nano- or femto-scaled time resolution, enabling to analyze the lattice defects and chemical reaction. Due to their superior spatial- and time-resolutions, huge number of spectra, several thousands and million, can be observed in one experiment.

On the other hand, interpreting the core-loss spectra is not straightforward. Although theoretical simulations of ELNES/XANES have been performed to interpret the spectra, calculating just single spectrum requires huge computational time, such as tens hours and days. The one-by-one simulation is quite difficult for the large spectrum data-set.

In this situation, we need an alternative approach to analyze a thousand of spectra. Here, we developed new data-driven approaches to predict the core-loss spectra and quantify the material properties by the machine learning [1-3]. First, we have used the machine learning to predict the core-loss spectra. A spectral database of O-K edges of silicon dioxides, including 1,171 spectra, was constructed by the theoretical calculation. Then, we constructed a neural network model, whose input layer is the partial density of states (PDOS) at the ground state and output layer is the core-loss spectra. After training, the prediction model can produce the core-loss spectra only by the PDOS. Different from the core-loss spectrum, the PDOS at the ground state can be obtained within a few minutes.

Furthermore, the prediction model constructed by the "crystalline" silicon dioxides was applied to predict the O-K edge spectra of "amorphous" silicon dioxides. Based on this investigation, we revealed the critical difference between the crystalline and amorphous silicon dioxides [2].

In addition to the spectrum prediction, we used the machine learning to find the connections between the ELNES/XANES and the materials structures and properties. The same database as above was used and considered mean bond length, bond angle and Voronoi volume as geometrical features, and bond overlap population, Mulliken charge and excitation energy as chemical bonding features. As the results, we achieved to predict the geometrical properties and the chemical bonding properties correctly. Furthermore, our prediction model constructed by the simulation was applied to an experimental spectrum, and we found that our model could predict the properties correctly from the experimental spectrum even though it had large noise.

The details of the two studies will be discussed in my presentation.

References
Rapid Inference of Optical Constants and Thickness of Thin Films by Supervised Machine Learning

Siyu I. Tian1,2, Zhe Liu1, Vijila Chellappan4, Yee Fun Lim4, Felipe Oviedo3, Benjamin P. MacLeod3, Fraser G. Parlane5, Curtis P. Berlinguette5 and Tonio Buonassisi3; 1Singapore-MIT Alliance for Research and Technology, Singapore; 2National University of Singapore, Singapore; 3Massachusetts Institute of Technology, United States; 4Agency for Science, Technology and Research, Singapore; 5The University of British Columbia, Canada

The use of machine learning (ML) and automation has recently emerged to accelerate material development and optimization. This automated closed-loop cycle of material development requires accurate and rapid characterization to provide feedback for the optimization of subsequent syntheses. In this study, we propose an ML-based method to rapidly extract optical constants and thickness of thin films from transmittance and reflectance (TR) spectra. The TR spectra of a thin film capture convoluted information of its optical constants (i.e., refractive index $n$ and extinction coefficient $k$) and thickness $t$. Today, a trained expert fits measured TR spectra with a material-specific parametric model and optical model to indirectly extract optical constants and thickness, and validates with low-throughput measurements (e.g., profilometry or scanning electron microscopy). Hence, the extraction of $n$, $k$, and $t$ from TR spectra becomes a bottleneck for a high-throughput experiment loop.

This study demonstrates semi-automatic extraction of $n$, $k$, and $t$ from TR spectra. First, we generate our training dataset using optics simulations. Values for $n$ and $k$ are simulated by combining several optical oscillator models (e.g., Tauc-Lorentz model); then, transfer matrix formulation of Fresnel equations are used to simulate TR spectra. The simulated data are augmented to reflect the noise and imperfection of experimental measurements, following the strategy in [1]. Second, we use a variational autoencoder (VAE) to reduce the dimension of the dataset, and then we feed the dimensionally-reduced latent variables into a deep neural network (NN) to estimate the optical parameters and thickness of the film. We found a 95% confidence interval is within ±30 nm for the whole range of 100-nm- and 2000-nm-thick films. Third, after training of the machine learning model is complete, we apply the pre-trained ML model to simulated and experimental TR spectra of organic and inorganic metal-oxides. The NN-predicted parameters are further used as the inputs to a forward-fitting Bayesian inference model to accurately extract $n$, $k$, and $t$. Lastly, we discuss how this approach might generalize to other material systems and characterization methods.

[1] https://www.nature.com/articles/s41524-019-0196-x

Act Locally—Tuning PV Materials to Local Climate
Erin Looney, Tonio Buonassisi and Ian Marius Peters; Massachusetts Institute of Technology, United States

Recently, machine learning (ML) has emerged as a useful tool for photovoltaics (PV) system design and performance evaluation [1]. However, many PV materials have been demonstrated, with different sensitivities to the solar spectrum and operating temperatures. In this contribution, we seek to demonstrate how ML can accelerate the adoption of PV technology, by customizing it to the local environment, leveraging a technology-dependent energy-yield model that uses open-source satellite information [2]. First, we apply ML to classify PV operating conditions (spectra + temperature) globally, using an unsupervised clustering approach with embedded physics domain knowledge. Then, on the basis of this classification, we envision a way to more accurately determine power ratings and predict energy yield for PV modules made from different materials in each climate zone, identifying opportunities for R&D innovation with strong future market pull.

Beyond-Expert-Level Prediction of Battery Performance by Feature-Engineering-Free Machine Learning
Xi Chen and Xin Li; Harvard University, United States

Predicting the performance of functional materials systems such as rechargeable batteries in real-time is of great importance to both scientific research and industry. Due to the large capacity and power needed for batteries in electric vehicles and the relatively closed environment of cars, the safety of Li-ion batteries has become the paramount concern, since failure due to short circuit or leakage of chemicals can easily catch fire. Also, a typical battery test in battery research and development can be quite time-consuming. For example, up to thousands of charge/discharge cycles are needed for a cycling performance test. Thus, there is strong interest across both the academic and industrial community in predicting the cycling performance, life and critical failure event based only on the first cycle, the initial cycles, or the few cycles before battery failure, which holds great potential of accelerating the research and development of battery materials and improving the safety control procedures of electric vehicles. Previously, sophisticated apparatus is required in order to measure indicator properties of performance, while machine learning approaches based on feature engineering procedures require a priori expertise, which impedes the application in the complicated real-world environment. Here we show a novel end-to-end machine learning approach, free of feature engineering, toward effective real-time prediction of the battery life and failure, using just the raw images of the charge-discharge voltage profiles. Our method can make unsupervised real-time automatic extraction of latent physical factors that control the battery performance beyond human expertise. We demonstrated the real-time classification of cyclability using just the first cycle, and the real-time prediction of battery malfunction up to 20 cycles prior to the catastrophic failure. Our results show significant effectiveness even for just a proof-of-concept level dataset, which paves the way toward the real-world application.

3:00 PM BREAK

3:30 PM *MT03.13.06
Enabling Data Science Methods for Catalyst Design and Discovery
Zachary W. Ulissi; Carnegie Mellon University, United States

Increasing computational sophistication and resources can enable a larger and more integrated role of theory in the discovery and understanding of new materials. Most materials studies start in a data-poor regime where the material of interest is unrelated to previous to studies (new structure, composition etc) or the computational methods are incompatible with previous studies (different exchange-correlation functionals, methods, etc). Efficient methods to quickly define, schedule, and organize necessary simulations are thus important and enable the application of online design of experiments approaches. I will discuss on-going work and software development to enable data science methods in catalysis including open datasets for the community. I will describe applications of our approach to ordered bimetallic alloy catalysts, with applications to several electrochemical catalyst discovery efforts including CO2 reduction, oxygen reduction, and water splitting chemistry. I will also discuss the methods and approaches we use to share data among group members and educate new students with the necessary skills to pursue these research directions (including statistics, machine learning, computer science, etc). Finally, I will discuss the transition from data-poor to data-rich regimes and our experiences when data-intensive deep-learning methods become more appropriate than simpler models based on chemical intuition.

4:00 PM MT03.13.07
Estimating Carrier Injection Barriers at Metal-Polymer Interfaces Using Multi-Fidelity Information-Fusion Method
Deepak Kamal1, Lihua Chen1, Rohit Batra1, Yifei Wang2, Zongze Li2, Yang Cao2 and Rampi Ramprasad1; 1Georgia Institute of Technology, United States; 2University of Connecticut, United States

The long term electric insulating behavior of polymers critically depends on the electronic structure at polymer-metal interfaces. Particularly, injection of charged particles (electrons/holes), from the electrodes (metals) to the dielectric (polymer) at these interfaces are known precursors to dielectric aging which culminates in the breakdown of the dielectric. In the absence of defect states on the interface, the probability of this charge injection is decided by the energy difference between the Fermi level of the electrode and the edges of valence and conduction bands of the dielectric. Conventionally, to bypass the need for laborious experimental measurements, computational schemes based on density functional theory (DFT) are employed to calculate these properties. But, computing these properties to match experimental observations requires calculations to be performed on large metal-polymer interfacial structures containing hundreds of atoms. This is computationally expensive and limits the chemical space.
one can explore to find a suitable combination for a given application. Here, we try to overcome this limitation by using a Multi-Fidelity Information-Fusion approach \[1\] to create a model that can predict the charge injection barrier, given a metal-polymer pair. To develop this model, we use charge injection barriers calculated at three different levels of fidelity. In the lowest level of fidelity, band edges positions of isolated single-chain of polymers and Fermi level of isolated metal slabs are computed to obtain the charge injection barriers. These calculations are cheap and hence a database of these values are created from quick calculations performed on a large number of metal-polymer systems. Further, property values obtained from expensive computations, considering large polymer-metal interfaces, are performed on a subset of these systems and are used as data for the second level of fidelity. Finally, the experimentally observed values of the property are used as the highest fidelity data. A co-kriging method is then used to model the relationship between a numerical representation of the metal-polymer system and values of the property at different fidelities. This approach provides an accurate, inexpensive and flexible alternative to expensive DFT calculations to obtain reliable values of charge injection barriers. These models can be readily used for screening metal-polymer systems for insulating applications.

### 4:15 PM MT03.13.08
**Data Mining of Layered Crystalline Perovskites—Structure, Energetic and Electronic Properties and a Comparison with the ABC3 Counterparts**

**Yaoding Lou\(^1\), Junkai Deng\(^2\) and Zhe (Jefferson) Liu\(^1\); \(^1\)The University of Melbourne, Australia; \(^2\)Xi’an Jiaotong University, China**

Perovskite is a classic class of materials that have been studied for a long time. Their interesting properties, such as ferroelectricity, have been enabled a wide range of applications. Recently, the Ruddlesden-Popper (RP) phase of perovskites is becoming an exciting research topic, owing to the interesting properties like superconductivity and optoelectronics. The RP perovskite has layered crystalline structure, consisting of alternated ABC\(_3\) and AC layers with a compound formula of A\(_{n+1}\)B\(_n\)C\(_{3n+1}\) where \(n = 1, 2, \ldots\) (Note that the conventional ABC\(_3\) can be seen as \(n = \infty\)). However, our understanding of RP perovskite is limited. It is highly desirable to gain an overall picture of the structure, energetic, and electronic structures of RP perovskites, particularly how the size confinement effect (i.e., the finite \(n\)) could differentiate their physical properties from the conventional ABC\(_3\). In this work, we did data-mining for the RP perovskites based on the Materials Project database (including over 100 000 inorganic compounds). It is well recognised that octahedra rotation plays a critical role in the electronic, ferroelectric, and magnetic properties of perovskites. We, therefore, carried out in-depth structure and energy analysis of octahedra rotation of RP perovskite and compared them with the conventional ABC\(_3\). Some physical insights are obtained to understand the physical origins of octahedra rotation. The detailed observations and conclusions are listed below.

1. 254 RP perovskite or inverse perovskite crystal structures are identified.
2. The RP perovskites cover diverse chemical species, such as oxide, halide, hydride, and have a wide composition range.
3. The majority of RP perovskite compounds with \(n=1\), i.e., 38 out of 56, have a larger band gap than ABC\(_3\) counterparts. There are 12 semiconductor RP compounds whose ABC\(_3\) counterparts are metallic.
4. Most of the RP perovskites inherit the octahedra rotation patterns of the ABC\(_3\) counterparts.
5. Five RP perovskites have multiple stable octahedra rotation patterns.
6. For most RP perovskites, there is a clear trend that the total energy difference between the rotated and non-rotated configurations are reduced. For some RP perovskites, the non-rotated configurations even become the ground states.
7. Our in-depth analysis suggests that the pseudo-Jahn-Teller effect could be the driving force of octahedra rotation and the relative A-site ion size (concerning B-site as expressed by tolerance factor) could serve as a resistance force for the octahedra rotation.
8. As for RP perovskites, the existence of interface moves the d-orbital of B-site ion to lower energy levels, weakening the pseudo-Jahn-Teller effect and thus the tendency of octahedra rotation.

Our work provides an overview of the structure, energetic, and electronic properties of RP perovskites, which could lay the ground for further investigation of properties of novel two-dimensional perovskites exfoliated from RP phase.

### 4:30 PM MT03.13.09
**Automated Coarse Graining Procedure for Molecular Dynamics, Preserving Rare Events**

**Blake Duschatko, Jonathan Vandermause, Nicola Molinari and Boris Kozinsky; Harvard University, United States**

Molecular dynamics is an essential computational tool for the development and discovery of new materials. However, large length and time scale systems can be computationally intractable. In particular, integration times must be small enough to capture the most rapid motions in the system. In addition, computational expense increases with system size, making it impossible to observe the dynamics of protein folding events, for example. In light of
this, coarse graining procedures to explicitly replace atoms with coarser “beads” are often needed to simulate
dynamics even at millisecond timescales.

While predominantly guided by chemical and physical intuition, recent works have been aimed at designing
automated procedures for determining coarse grained units [1,2,3]. To this end, we demonstrate the efficacy of
spectral clustering algorithms in coarse graining a variety of systems that have not been previously explored with
these methods. Alternative metrics for comparing atomic trajectories are considered that can preserve rare-events at
the coarse grained level, and we explore the physical intuition of the latent space that is afforded by these procedures
as opposed to other machine learning methods.

In addition, we consider the coupled problem of finding a force model for the coarse grained units along with that of
“fine graining” - given a latent space representation of the atomic system, how do the units interact, and how can we
go back to the atomic representation despite the dramatic loss of information? Recent work using Gaussian process
regression for \textit{ab initio} molecular dynamics [4] has demonstrated the advantage of Bayesian methods for force field
construction, and we extend these ideas to the dynamics of latent space force fields. The variance of force
predictions provides a natural indicator of when the coarse grained system is insufficient for capturing the system
dynamics, from which we consider a method for going between the atomic and coarse grained representations.

reduction approach for identifying dynamical domains in protein complexes from limited structural datasets,”
Bayesian Active Learning of Interpretable Force-Fields for Atomistic Rare Events,” arXiv preprints

4:45 PM MT03.13.10
\textbf{Molecular Design Strategy of $\lambda^{5}\sigma^{6}$-Phosphorous Compounds for OLED Applications} Jonas Köhling, Gerd-Volker Röschenthaler and Veit Wagner; Jacobs University Bremen, Germany

Organic light emitting diodes (OLEDs) are one of the leading technologies used as active optoelectronic device in
displays. Currently, in OLED displays the most challenging quest is to synthesize and design efficient and new
stable blue emitters or improve already existing emitters. To achieve this goal it is of great interest to evaluate a
large number of possible molecules prior to synthesis and to optimize their molecular design.

In this study a large amount, i.e. 151 derivatives, of phosphorous fluorescent compounds were evaluated with first
principle simulations regarding their light emitting properties and molecular orbital alignment. As basic structure the
central phosphorous atom is bound to one derivative of 8-Quinolinol as well as 4 fluorine atoms. 8-Quinolinol was
systematically varied by introduction of substituents from strong electron withdrawing groups (EWG) towards
strong electron donating groups (EDG). Besides the mesomeric and inductive electron withdrawing and donating
effects also the position of the substituent has a crucial influence on the calculated emitting wavelength of these
fluorophores. To determine the emitting wavelength of an isolated molecule time-dependent density functional
theory (B3LYP/6-31+G(d,p)) was employed. EWGs tend to increase the bandgap if placed on the benzene ring of
the ligand, where EDGs show the same effect when substituted on the pyridine ring of the ligand. This allows to
tune the calculated bandgap between 3.2 - 4.1 eV and to choose configurations with energetically aligned molecular
orbitals.
TUTORIAL: Advanced Materials Exploration with Neutrons
December 1 - December 1, 2019

* Invited Paper

TUTORIAL
Advanced Materials Exploration with Neutrons

Sunday Morning, December 1, 2019
Hynes, Level 2, Room 207

This tutorial will give an overview/introduction of a few commonly-used materials characterization techniques using neutrons, such as SANS, NSE, BS/TOF, PDF, etc. In the Topical Outlines, we have detailed the contents of the lectures. Prevailing materials development requires detailed structural and dynamic information down to the atomic or molecular level. Neutron scattering includes a collection of techniques, both elastic and inelastic, complimentary to X-rays, which are unique in providing the ensemble-averaged information of the atomic spatial distributions and movements with sub-angstrom spatial and sub-picosecond temporal resolution. Compared to in-house materials characterization techniques, neutron scattering requires high intensity neutron beams, which are only available at large accelerators or research reactors hosted at the national labs. We hope to give an overview of this technique for the materials scientists who do not have ready access to it.

8:30 AM
Welcome Yang Zhang, University of Illinois at Urbana-Champaign

8:35 AM
Small Angle Neutron Scattering Yun Liu, National Institute of Standards and Technology

The lecture will discuss the applications of small angle neutron scattering to study a wide range of soft matter materials such as biological and polymeric materials.

9:10 AM
SASView Wojciech Potrzebowski, European Spallation Source

An introduction to the SAS data analysis capabilities of the community developed SASView package with information on how to contribute to its further enhancement.

9:45 AM BREAK

10:15 AM
Neutron Reflectometer John Ankner, Spallation Neutron Source Oak Ridge National Laboratory

The lecture will cover the fundamental principles underlying neutron reflectivity measurements and how the technique can be applied to the study thin films of soft matter, energy materials, biomaterials, and magnetic systems.

10:50 AM
Neutron Pair Distribution Function Katharine L. Page, University of Tennessee
This lecture will give an introduction to the technique and applications of pair distribution function (PDF) analysis, with an emphasis on nanostructure and disorder in bulk functional materials.

1:30 PM
**Time-of-Flight and Backscattering Spectroscopy** Madhusudan Tyagi, National Institute of Standards and Technology

The lecture will cover basics of backscattering and time of flight spectroscopy. Some scientific examples from backscattering and time of flight will be presented to illustrate data analysis and its interpretation.

2:10 PM
**Neutron Spin Echo** Antonio Faraone, National Institute of Standards and Technology

This lecture will cover the basic principle of operation of NSE as well as data reduction. Some relevant scientific examples of NSE work will be covered and will be used to exemplify the basic ideas of data analysis and interpretation.

2:45 PM BREAK

3:15 PM
**Simulation and Software** Anibal (Timmy) Ramirez-Cuesta, Oak Ridge National Laboratory

This lecture will cover simulations of inelastic neutron scattering spectra from atomistic models.

3:50 PM
**How to Write Winning Neutron Scattering Proposals** Victoria Garcia-Sakai, Science and Technology Facilities Council

This lecture will cover basic skills of writing successful neutron scattering proposals.

4:25 PM
**Conclusion**

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**SYMPOSIUM MT04**

Advanced Materials Exploration with Neutrons
December 2 - December 5, 2019

**Symposium Organizers**
Victoria Garcia Sakai, Science and Technology Facilities Council
Kenneth Herwig, Oak Ridge National Laboratory
Despina Louca, University of Virginia
Yang Zhang, University of Illinois at Urbana-Champaign

* Invited Paper

**SESSION MT04.01: Quantum Materials I**
Session Chairs: Despina Louca and Yang Zhang
Monday Morning, December 2, 2019
Hynes, Level 2, Room 207

9:00 AM *MT04.01.01
Quantum Spin-Nematic State in Layered Vanadophosphates Andrey Zheludev; ETHZ, Switzerland

Conventional magnetic order spontaneously produces a static periodically modulated magnetization in the sample. It thus breaks rotational and time-reversal symmetries of the underlying spin Hamiltonian. A spin nematic is an exotic state that only breaks rotational but not time reversal symmetries. The spins remain disordered and fluctuating, but these fluctuations are spontaneously anisotropic. Theory predicts a spin nematic ground state for quantum spin systems with competing ferromagnetic (FM) and antiferromagnetic (AFM) interactions in high magnetic fields. The simplest model is a FM-AFM S=1/2 square lattice. To date there seems to be only one family of materials that approximate this scenario, namely the layered vanadophosphate. Unfortunately, our understanding of these compounds has been severely limited by a lack of single crystal samples. This is particularly problematic for experiments in magnetic fields where any features or phase transitions are smeared out by the powder averaging of the material's anisotropic properties.

In my talk I will present breakthrough magnetic, thermodynamic, ESR, NMR and neutron scattering studies on single crystals of two vanadophosphate species, namely BaCdVO(PO₄)₂ and Pb₂VO(PO₄)₂. Neither turned out to be quite the proximate FM-AFM square lattice that it was advertised to be. Nevertheless, in both systems we find clear indications of "hidden" nematic order, just below saturation in high magnetic fields.

9:30 AM *MT04.01.02
Emergent Quantum Phenomena in Frustrated Quantum Magnets—Application of External Tuning Parameters Sara Haravifard; Duke University, United States

What are the experimental signatures of exotic Spin Liquid states? What is the best approach in solving the Hamiltonian of the systems with disordered ground states? What is the role of chemical disorder and how can it be addressed? What part can the external tuning parameters play in shedding light on the mystery of long-sought Quantum Spin Liquid state and other emergent phases of matter in real materials? These are some of the pressing questions intriguing the researchers for the past decades, creating a rich and diverse arena in the field of Quantum Materials. In this talk, I will discuss how chemical composition, external pressure, and application of magnetic field, can regulate the underlying electronic and magnetic interactions in frustrated quantum magnets, ultimately driving the ground state across the phase diagram, and providing key information. As examples, I will present our recent results for neutron scattering studies performed under extreme sample environments on 2D and 3D rare-earth based geometrically frustrated antiferromagnets.

10:00 AM BREAK

10:30 AM *MT04.01.03
Overview of the Neutron Scattering Program at DOE’s Office of Basic Energy Sciences Pappannan Thiyagarajan; Department of Energy, United States

The presentation will provide an overview of the DOE’s Office of Basic Energy Sciences (BES) Neutron scattering programs for the fundamental materials research. The programs support basic research on the unique interactions of neutrons with matter to achieve a fundamental understanding of the atomic, electronic, and magnetic structures and excitations of materials and their relationship to macroscopic properties. Major focus is on the transformative research that uniquely requires neutron scattering as a major tool and serves as a driver for the concomitant advancement of neutron scattering techniques and capabilities for materials research at the two BES world-leading neutron scattering facilities. Research opportunities identified by the recent BES workshops and roundtables will be discussed. The application process and opportunities for white papers will be overviewed, as well as the on-line resources for principal investigators.

For additional information, visit the BES Web page at: https://science.energy.gov/bes/
Identification and Control of Domain Wall Patterning in Spinel Ferrimagnets
Gregory J. MacDougall
University of Illinois at Urbana-Champaign, United States

Spinel antiferromagnets have long been at the center of research into strong spin-lattice coupling and orbital effects. Among other properties, these materials frequently demonstrate concomitant magnetic and structural phase transitions, heightened magneto-elastic or dielectric response functions, and low-temperature multiferroism. There is very little agreement on the microscopic picture to be associated with these effects, but recent work has shown that mesoscale inhomogeneity can play a key role in raising the susceptibilities of complex materials to external perturbations.

In this talk, I will be discussing recent work at the University of Illinois which establishes the importance of mesoscale heterogeneity in determining bulk magnetic properties of spinel ferrimagnets Mn₃O₄ and MnV₂O₄. This will first include a review of Raman scattering, magnetic force microscopy and muon spin rotation data from our group, which reveal the existence of stripe-like magnetic domains in these materials that include ordered and disordered regions. The majority of the talk will then focus on our recent work performed using small angle neutron scattering (SANS), with which we observe Bragg signatures of the same domain wall patterning in the bulk with a typical length scale of ~100nm. Variation with temperature associate these domains with known low-temperature magnetostructural transitions, and measurements taken in applied field reveal a highly anisotropic response associated with domain wall motion. I will correlate key features of our SANS data with observations of nonequilibrium behavior in our magnetization data, and discuss the implications for the properties of other magnetic materials.

Research was supported by the National Science Foundation under Grant NSF DMR 1455264.

Anharmonic Effects on Phonon Eigenvectors and S(Q,E) in Quantum Paraelectric SrTiO₃
Xing He¹, Dipanshu Bansal², Barry Winn³, Songxue Chi³ and Olivier Delaire¹; ¹Duke University, United States; ²Indian Institute of Technology Bombay, India; ³Oak Ridge National Laboratory, United States

The quantum paraelectric behavior and strongly anharmonic lattice dynamics of SrTiO₃ have attracted interest for decades [1]. Reflecting the incipient ferroelectric instability near the quantum critical point and anharmonic couplings between acoustic and optic phonons, anomalous temperature-dependent phonon intensities were observed in multiple Brillouin zones (BZs) from inelastic neutron scattering (INS) experiments on SrTiO₃. The Hybrid Spectrometer (HYSPEC) and HB3 triple-axis spectrometer at Oak Ridge National Laboratory (ORNL) were used to track phonon intensities over a wide temperature range and for a large volume in reciprocal space. The $S(Q,E)$ data reveal a strong softening of the zone-center transverse optic (TO) mode, congruent with ferroelectric (FE) incipient, and simultaneously a strongly anomalous evolution of the intensity of transverse acoustic (TA) modes, which decreases dramatically on cooling. The experimentally observed trends are confirmed and rationalized using ab initio molecular dynamics (AIMD) and anharmonically renormalized phonon methods [2], which achieve quantitative agreement with the INS experiments. By analyzing the simulated temperature-dependent force constants (FC) and eigenvectors, it is found that the structure factors $|F|^2$ of TA and TO modes change dramatically with temperature, as a direct consequence of the strong anharmonicity in this system. Moreover, we identify that the changes of Ti and O eigenvectors are responsible for these striking observations, which originates from Ti-O interatomic FC changes on cooling. These results explain the long-standing question of the origin of the phenomenon first observed by Yamada and Shirane [1]. Our results also systematically extend this observation to multiple BZs and different high-symmetry directions ([1,0,0] and [1,1,0]). These results establish how temperature-dependencies of phonon intensities beyond the harmonic picture can be quantitatively measured through INS mapping of $S(Q,E)$ volumes, providing direct insights into the behavior of phonon eigenvectors in real space, and also show how first-principles simulations including anharmonic effects can reproduce and rationalize such anharmonic effects. These findings are also valuable to understand other perovskite materials with a variety of phase transitions, such as KTaO₃ and EuTiO₃, and related ferroelectricity/paraelectricity and quantum effects [3-6].

Phonons are the main source of total entropy, thermal expansion, and thermophysical properties of most materials, so it is essential to know the temperature-dependent lattice dynamics. We measured phonon dispersions in silicon by inelastic neutron scattering at elevated temperatures. We determined the thermal shifts of phonon frequencies and broadenings of phonon linewidths throughout the Brillouin zone from these experiments. Large phonon anharmonicities manifested through shifts and broadenings go beyond the quasiharmonic model even at low temperatures. Although the quasiharmonic model (harmonic phonons renormalized by volume) predicts the experimental thermal expansion of silicon well, it does not correctly depict the temperature-dependent lattice dynamics. The necessity to include anharmonicities and nuclear quantum effects to describe the lattice dynamics throughout the temperature range was verified by state-of-the-art ab-initio calculations using the stochastically initialized temperature-dependent effective potential method. The quasiharmonic model correctly predicts the macroscopic values due to a cancelation of phonon shifts, but its validity should not be assumed because it predicts average quantities. The pure anharmonicity included ab-initio calculated phonon lifetime changes and thermal conductivity correctly predict the experimentally determined lifetimes and thermal conductivity as well as previously reported values.

SESSION MT04.02: Quantum Materials II
Session Chairs: Kate Ross and Stephen Wilson
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 207

1:30 PM *MT04.02.01
Nature of Magnetic Excitations in 2D and 3D Spin Liquids Martin Mourigal; Georgia Institute of Technology, United States

Magnetism is a fascinating phenomenon: it is rooted in relativistic quantum mechanics and yet an integral component of the technologies we use every day. In magnetic insulators, where atomic-scale magnetic dipoles carried by electrons are closely bound to a crystal lattice, novel phases of matter with no classical analogues are possible. Chief among these phases are spin-liquids, in which strong fluctuations of magnetic dipoles preclude conventional magnetic order even for temperatures low compared to the average interaction between spins. Such exotic magnetic matter is of great fundamental interest because it features a wealth of coherence and entanglement phenomena – the hallmarks of the quantum world – and is often amenable to theoretical and computational predictions. In this talk, I will present experimental research that brings together materials chemistry, neutron scattering and computer modeling to understand the magnetic excitations in a range of frustrated oxide compounds with triangular, kagome and pyrochlore lattice structures. My talk will emphasize the importance of neutron scattering instrumentation to probe complex materials behavior in which chemical disorder, geometrical frustration

2:00 PM *MT04.02.02
Neutron Scattering of Molecular Nanomagnets Tatiana Guidi1, Stefano Carretta2, Elena Garlatti2, Alessandro Chiesa2, Paolo Santini2, Giuseppe Amoretti2, Béatrice Gillon3, Grigore Timco4 and Richard Winpenny4; 1ISIS STFC, United Kingdom; 2Università’ di Parma, Italy; 3LLB-CEA, France; 4University of Manchester, United Kingdom

Molecular nanomagnets (MNMs) are clusters made of a finite number of magnetic ions coupled by a strong exchange interaction within the clusters and with a negligible magnetic interaction between adjacent clusters in the crystal lattice. They are promising systems for technological applications in the fields of high-density magnetic memory devices, quantum information processing and spintronics. They are also model systems to study the fundamentals of quantum mechanics as they display quantum mechanics effects at the macroscopic level. The advances in the chemical engineering of these molecules have allowed the synthesis of tailor-made systems displaying several interesting quantum phenomena and to improve their properties to bring them closer to technological applications. Neutron scattering techniques have been intensively and successfully used to study the microscopic properties of molecular magnets and have enabled to reveal the signatures of their quantum behaviour. I will show how advanced neutron scattering experiments have been pivotal for the understanding of the magnetic properties and quantum behaviour of a selection of molecular magnets model systems. The new generation of neutron instruments equipped with position sensitive detectors together with the availability of large single crystals has allowed us to reveal the microscopic details of prototypical MNMs unambiguously characterising their Spin Hamiltonian [1,2], to reveal finite size effects on the magnetic properties of linear antiferromagnetic chains [3] and the entanglement between complex spin systems [4].


2:30 PM MT04.02.03
Observation of Near-Surface Diffusion of Isotopically Labelled Iron in Magnetite Steffen Tober1,2, Marcus Creutzburg1,2, Björn Arndt1,2, Konstantin Krausert1,2, Stefan Mattauch3, Sabine Pütter1, Alexandros Koutsioubas3, Amir Syed Mohd3, Lukas Volgger4, Herbert Hutter4, Heshmat Noei1, Vedran Vonk1, Dieter Lott5 and Andreas Stierle1,2; 1Deutsches Elektronen-Synchrotron DESY, Germany; 2Universität Hamburg, Germany; 3Forschungszentrum Jülich GmbH, Germany; 4TU Wien, Austria; 5Helmholtz-Zentrum Geesthacht, Germany

The defect structure in the near surface region of magnetite (Fe3O4) is particularly important for a better understanding of the material’s electronic properties and catalytic activity. Hence, the mobility of Fe in Fe3O4 is a key ingredient towards a better understanding of near surface processes. Recent scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) studies of the (√2×√2)R45° reconstructed (001) surface suggested a subsurface vacancy stabilisation model for this surface, later proved by surface x-ray diffraction (SXRD) [1,2]. The surface reconstruction is reported to get lifted by formic acid adsorption at room temperature [3]. Low energy electron microscopy (LEEM) experiments under oxidising conditions showed a regrowth process of Fe3O4-layers on (001) surfaces [4]. These observations indicate an interesting interplay between cation vacancy formation and diffusion processes. The role of near surface cations was investigated by neutron scattering using 57Fe as a marker. A 25 nm thick 57Fe3O4 marker layer was homoepitaxially grown on top of a (001) polished natural Fe3O4 single crystal substrate by reactive molecular beam epitaxy (MBE). The interdiffusion of iron ions across the film-substrate interface was followed by neutron reflectivity (NR) [5]. Due to the lower scattering length of 57Fe:FeO compared to natural Fe3O4, Kiessing fringes were observed by NR. Comparison with NR simulations assuming a perfectly smooth interface between the film and the substrate showed that a notable intermixing of the iron isotopes already occurred during the growth of the marker layer at only 420 K. The diffusion process was followed by successive annealing steps in ultra-high vacuum (UHV) and the subsequent acquisition of NR curves. In the course
of the annealing, the Kiessing fringes faded out due to interfacial diffusion. The diffusion process is already observed to take place in the temperature range of 500 K-600 K over the probed depth of several tens of nanometers, which shows that substantial mass transport happens in the near-surface region at much lower temperatures as previously observed by bulk diffusion experiments [6]. Diffusion lengths and the respective diffusion constants obtained from fitted scattering length density (SLD) profiles will be compared to the results of earlier studies on bulk Fe₃O₄ at 800 K-1600 K [6,7]. The NR results are complemented by time of flight secondary ion mass spectroscopy (TOF-SIMS) data and x-ray data characterising the structural changes of the samples during the diffusion experiments.


2:45 PM MT04.02.04
Characterization of Local Atomic Structure and Dynamics in Pb-Free Relaxor Ferroelectrics Abhijit Pramanick; City Univ of Hong Kong, Hong Kong

Relaxor ferroelectrics are of great importance in many modern technologies, including high energy density capacitors, electrocaloric cooling and energy harvesting. Due to environmental concerns regarding the current Pb-based relaxors, it is necessary to develop new Pb-free alternatives. Characterization of composition-structure-property relationships is a prerequisite first step towards rational and efficient design of new materials. Nevertheless, structural understanding of relaxor ferroelectrics is challenging because of their highly disordered nature. For the new Pb-free relaxors, the polar atomic displacements are correlated over only nanometer length scales and THz frequencies, although the details of such nanoscale correlations are yet to be fully resolved. In this talk, I will present our recent findings on the nanoscale orderings of polar atomic displacements in the newly designed Pb-free relaxors, which are measured using pair distribution function analysis of neutron and X-ray total scattering patterns. In addition, I will show that while conventional pair distribution function study offer insights into the instantaneous snapshots of local atomic correlations, they do not inform about the timescales over which such correlations become stable. I will demonstrate the application of the dynamic pair distribution function (DyPDF) method to elucidate the timescales over which such nanoscale atomic orderings become stable in some Pb-free relaxor systems. The implication of nanoscale atomic ordering and dynamics towards the dielectric, ferroelectric and electrothermal properties of Pb-free relaxors will be discussed.

3:00 PM BREAK

3:30 PM *MT04.02.05
Field-Tunable Quantum Disordered Ground State in NaYbO₂ and Related Compounds Stephen Wilson; University of California, Santa Barbara, United States

In this talk, I will present our recent results exploring the magnetic ground state and field-induced phase behavior in the triangular lattice compound NaYbO₂. The triangular lattice decorated with J_{eff}=1/2 moments has enjoyed renewed interest due to recent reports of quantum spin liquid formation in YbMgGaO₄ and related materials. One ambiguity however remains the role played by structural/exchange disorder in generating this behavior, which motivates the exploration of alternate lattice types hosting the same equilateral triangles of J_{eff}=1/2 moments. Here we establish NaYbO₂ as one such alternative with an ideal R-3m structure and minimal lattice disorder. Yb moments experience an enhanced exchange field due to smaller Yb-Yb distances, yet they fail to order at temperatures as low as 20 mK and demonstrate a frustration parameter f>400. The resulting quantum disordered state can be quenched via the application of a magnetic field that drives the formation of a fluctuation stabilized up-up-down spin state. Interlayer frustration of the native, zero-field 120 deg antiferromagnetic order on the triangular lattice is proposed as a critical ingredient for realizing this phase behavior. If time permits, recent results on related materials will also be presented.

Final Program 1/13/2020  1972
This work is supported by DOE, Office of Science, Basic Energy Sciences under Award DE-SC0017752.

4:00 PM *MT04.02.06
Origin of Long Lifetime of Band-Edge Charge Carriers in Organic-Inorganic Lead Iodide Perovskites
Tianran Chen; National Institute of Standards and Technology, United States

Long carrier lifetime is what makes hybrid organic-inorganic perovskites high performance photovoltaic materials. Several microscopic mechanisms behind the unusually long carrier lifetime have been proposed, such as formation of large polarons, Rashba effect, ferroelectric domains, and photon recycling. Here, we show that the screening of band-edge charge carriers by rotation of organic cation molecules can be a major contribution to the prolonged carrier lifetime. Our results reveal that the band-edge carrier lifetime increases when the system enters from a phase with lower rotational entropy to another phase with higher entropy. These results imply that the recombination of the photo-excited electrons and holes is suppressed by the screening, leading to the formation of polarons and thereby extending the lifetime. Thus, searching for organic-inorganic perovskites with high rotational entropy over a wide range of temperature may be a key to achieve superior solar cell performance.

4:30 PM *MT04.02.07
Neutron Scattering Studies of Strong Anharmonicity and Phonon Breakdown Near Phase Transitions
Olivier Delaire; Duke University, United States

Anharmonic phonon-phonon interactions are critical to rationalize and design both ferroelectrics and thermoelectrics, in which strong anharmonicity may be found near lattice instabilities. Large deviations from harmonic potential energy surfaces, as in the Landau double-well picture, give rise to interesting phonon properties characterized by extensive interactions between phonon quasiparticles and pronounced renormalization effects. Similarly, in superionic crystals, where ionic mobilities are comparable to those of liquids, the atomic dynamics are strongly anomalous but remain debated. A central question is whether phonon quasiparticles -which conduct heat in regular solids- can survive in the superionic state, where a large fraction of the system exhibits liquid-like behavior. I will present results from inelastic neutron scattering (INS) measurements of lattice dynamics in strongly anharmonic materials. Combined with large-scale first-principles simulations, such as ab-initio molecular dynamics, these INS experiments enable a detailed understanding of how peculiar atomic dynamics give rise to useful material properties. In thermoelectrics PbTe and SnSe near soft-mode transitions, large thermal conductivity suppressions are achieved by anharmonic scattering [1,2]. In superionics CuCrSe2 [3] and Na/Li solid-state electrolytes, our studies show how anharmonic phonon dynamics are at the origin of low thermal conductivity and superionicity. Yet, long-wavelength acoustic phonons capable of heat conduction remain in the superionic regime. Our studies of lattice dynamics and diffusion will help rationalize the emergence of ultralow thermal conductivity for thermoelectrics and facilitate the design of high-performance solid-state electrolytes for next-generation batteries.

The plasticity of Zr-Cu-Al bulk metallic glasses (BMGs) can be significantly improved by introducing nanoscale heterogeneous structure with the addition of Fe. However, the crystallization pathways of the phase-separated Zr-Cu-Fe-Al BMG is still unclear. The neutron and synchrotron pair distribution function (PDF) analysis illustrates that the phase-separated Zr-Cu-Fe-Al BMG behaves two-step crystallization behavior. Compared with the homogenous Zr-Cu-Al BMG with a single crystalline product tetragonal \( \text{Zr}_2\text{Cu} \), the crystalline products of the phase-separated BMG are more complicated. Upon heating the phase-separated BMGs above the crystallization temperatures, the first crystalline products of the phase separated BMG, i.e., the cubic \( \text{Zr}_2\text{Cu} \) and \( \text{Zr}_2\text{Fe} \) with \( \text{Fd}-3m \) space group, form firstly, and then transform to simpler tetragonal \( \text{Zr}_2\text{Cu} \) phase with \( \text{I}4/m \text{mm} \) space group and orthorhombic \( \text{Zr}_3\text{Fe} \) phase with \( \text{Cmcm} \) space group. Our experiments, by taking advantage of the phase contrast difference of the neutron and synchrotron PDF, reveal that there is a specific sequence of the appearance of the copper-rich and iron-rich crystalline phases during each stage. Our study would shed light on developing BMGs of a controllable heterogeneous structure with potentially tunable mechanical properties.

DYNASOR—A Tool for Extracting Dynamical Structure Factors and Current Correlation Functions from Molecular Dynamics Simulations

Diffraction techniques provide access to dynamical structure factors, which contain detailed information about dynamic processes in materials. The extraction and decoding of this information is, however, non trivial and can greatly benefit from atomic scale simulations. To this end, we here present a flexible and powerful tool that enables the calculation of static and dynamical structure factors from trajectories from molecular dynamics (MD) simulations. The DYNASOR software can readily handle input from several major open source MD packages and thanks to its C/Python structure can be readily extended to support additional software. DYNASOR is hosted as open source on gitlab [1] and can easily be installed via PIP. In addition to dynamical structure factors the code enables computation of current correlation functions and separating contributions in the form of partial correlation functions. The performance and potential of DYNASOR is demonstrated for both solids and liquids, in particular focusing on the possibility to extract the full temperature dependence of both phonon frequencies and lifetimes.

Neutron Powder Diffraction and Inelastic Scattering Studies of Different Types of H\(_2\) Coordination in Molecular Organic Framework Materials

Variable temperature neutron diffraction studies of certain molecular organic framework (MOF) materials reveal that different types of H\(_2\) can be coordinated based on the temperature of first exposure. Both neutron powder diffraction (NPD) and inelastic neutron scattering (INS) have been implemented to best describe this phenomenon. Rietveld refinements of the NPD data provides crystallographic evidence of the adsorbed H\(_2\) locations, and INS provides descriptions of the dynamics of the H\(_2\). Temperature dependent data indicates that a pseudo-chemisorbed state can transform into a physisorbed state upon warming. Furthermore, certain materials studied display NTE that can be modulated based on the different types of H\(_2\) adsorbed.

A Mass-Selective View of Local Binding and Nuclear Dynamics in a BaZr\(_{0.7}\)Ce\(_{0.2}\)Y\(_{0.1}\)O\(_{3+\delta}\) Proton Conductor as Observed by Neutron Diffraction and Compton Scattering

Concurrent neutron Compton scattering and neutron diffraction experiments at temperatures between 70 K and 300 K have been performed on proton conducting hydrated BaZr\(_{0.7}\)Ce\(_{0.2}\)Y\(_{0.1}\)O\(_{3+\delta}\) (BZCY72) fabricated by spark plasma sintering. A combined neutron data analysis, augmented with density functional theory modelling of lattice
dynamics, has enabled, for the first time in this technologically important family of proton conducting perovskite oxides, a mass-selective view of the combined thermal and nuclear quantum effect on local effective binding. The emerging picture is the one of increased anharmonic character of the lattice dynamics and local binding of the framework atoms above the orthorhombic to rhombohedral phase transition at 85 K, whereby a subtle interplay between mode hardening and softening with increased temperature tunes the effective local binding of nuclear species. Importantly, these anharmonic effects seem to be most pronounced in the case of oxygen and cerium. For the latter, the obtained results may shed more light on the origins of high sensitivity of the mixed conductivity observed in $\text{BaZr}_0.7\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-δ}$. With increased Ce doping level. For the former, together with the neutron data on protons, our analysis strongly suggests the existence of a single type of trapped protons and trap proton sites in the room-temperature non-conducting phase of $\text{BZCY72}$. The protons at room temperature possess insufficiently high kinetic energy to overcome the local barrier for long-range diffusion but enough to perform transfer between different trap sites. A plausible explanation of the origins of the onset of ionic conduction would then involve distinct proton types, the ones trapped around the edges of YO6 octahedra, and the remainder formed of protons located near the ZrO6 and CeO6 octahedral edges, the sites that would favour mobile protons. The apparent proton conductivity would then result from a subtle interplay between the population size and mobility of the trapped and free proton fraction as a function of temperature.

MT04.03.05
Quantifying Doping Concentrations in Neutron Transmutation Doped GaN
Richard T. Barber¹, Quang Nguyen¹, Jae Kwon¹, John Brockman¹,² and John Gahl¹,²; ¹University of Missouri, United States; ²University of Missouri Research Reactor Facility, United States

Doping of gallium nitride (GaN) has become an important topic in the field of wide bandgap semiconductors. We have recently introduced a method for uniform doping of GaN using neutron transmutation doping (NTD). In NTD, gallium inside GaN is transformed into germanium through the use of neutron irradiation. Because of radioactivity after irradiation, measurement of doping concentration has been very challenging. Thus, we employed gamma-ray spectroscopy to accurately measure concentrations of the germanium doping in NTD GaN. This method relies on the gamma-rays outputted by decaying Ga-72 atoms before they beta decay into Ge-72. However, due to a difference in half life, the Ga-70 activity cannot be safely measured this way. An estimate of Ga-70 activity was calculated based on the theoretical amount of Ga-72 and the measured amount of Ga-72. We have confirmed the accuracy of the measurement by comparing data from inductively coupled mass spectroscopy (ICP-MS) and secondary ion mass spectroscopy (SIMS). We have successfully confirmed that our gamma-ray spectroscopy measurements turn out to be a highly accurate method for doping concentration measurement of NTD GaN.

MT04.03.06
Melanin and Neutrons—Towards Simulating Vibrational Spectra of Disordered Macromolecules
Hamish Cavaye¹, Jose Martinez-Gonzalez¹ and Albertus B. Mostert²; ¹Science and Technology Facilities Council, United Kingdom; ²Swansea University, United Kingdom

Melanin is a common and naturally occurring pigment that plays a number of important roles in the human body. Due to its biocompatibility and proton-conducting properties, melanin is a material of great interest in the field of electroceuticals; electronic devices that can interface with biological systems. Development of such devices would pave the way for personalised healthcare and for advanced health informatics, which was listed among the grand challenges for the 21st century by the National Academy of Engineering in the USA. However, there is still much that is unknown about melanin and it remains an area of active research in particular for its conducting properties and associated proton dynamics in the solid state.

Inelastic neutron scattering (INS) is a technique that is uniquely suited to investigating proton dynamics within materials, as the vibrational spectra obtained from INS are particularly sensitive to modes involving hydrogen. Unlike optical methods such as Raman and IR spectroscopies, there are no selection rules for INS and so all modes are allowed. Additionally, as melanin lacks long-range order, it is not amenable to study by diffraction techniques and INS can indirectly offer structural information by virtue of comparison with theoretical spectra produced from calculations.

Peak intensities in INS can be wholly described by the neutron scattering cross-sections and absolute quantities of the atoms involved. This means that predicting INS spectra is often a much more reliable process than for other techniques. For small, isolated molecular species or materials with well-characterised crystal structures, agreement between predicted and experimental spectra can be very good, thus leading to full assignment of the features in the
spectra. However, for larger and less well-characterised macromolecular materials such as melanin, performing the
theoretical calculations necessary to predict the associated INS spectrum is non-trivial and in most cases the
computational cost is prohibitively expensive.
We present our recent work towards a method by which the experimental INS spectrum of a melanin sample can be
analysed by the combination of several short and simple first-principles calculations to gain insight into the system
for a reasonable computational cost.
In the first stage we perform density functional theory (DFT) calculations for a range of expected monomeric
moieties, which are used to obtain vibrational frequencies and atomic displacements for each of their vibrational
modes. These calculations can then be interpreted by AbINS, a module within Mantid which was developed to
generate predicted INS spectra from such calculation outputs. Lastly, we create a linear combination of these
“monomer spectra” in order to replicate the experimentally measured spectrum of melanin itself. From here, the
main features of the spectrum can be identified and characterised, leading to insight into its structure.

SESSION MT04.04: Engineering Materials I
Session Chairs: Brent Heuser and Boris Khaykovich
Tuesday Morning, December 3, 2019
Hynes, Level 2, Room 207

9:00 AM *MT04.04.01
Advances in Neutron Radiography for Materials Science Hassina Z. Bilheux1, Jean-Christophe Bilheux1,
Yuxuan Zhang1, Jiao Lin1, Gian Song2, Qingge Xie1, Paris Cornwell1, Erik Stringfellow1, Jamie Molaison1, Louis J.
Santodonato1, Ke An1, Alexandru D. Stoica1, Ryan Dehoff3, Michael Kirka1 and Sarma Gorti1; 1Oak Ridge National
Lab, United States; *Kongju National University, Korea (the Republic of); 3ASTAR, Singapore

Abstract: Neutron radiography is a non-destructive non-invasive technique capable of characterizing materials in-
situ. At reactor facilities, this method is capable of measuring defects such as porosity or cracks in advanced alloys
and engineering components, water movement in geomaterials and plant roots, lithium transport in functioning
batteries, etc. At these facilities, novel techniques such as grating interferometry have recently been developed as a
mean to change contrast and to increase sensitivity to smaller features. Spatial resolutions of tens of µm can be
achieved over a field-of-view of several cm². Moreover, in the past decade, the development of time-of-flight (TOF)
imaging capabilities at spallation neutron sources have enabled the characterization of microstructures and isotope
mapping using Bragg edge and resonance imaging, respectively. Spalled neutrons offer novel imaging contrast
mechanisms in both the thermal/cold and epithermal range that are not easily attainable at reactors. This presentation
aims at giving an overview of neutron radiography and computed tomography techniques at both reactor and
spallation sources, followed by selected research examples such as lithium transport in batteries, hydrogen content in
engineering materials, 3D mapping of additively manufactured (AM) components, microstructure evolution in AM
samples as a function on temperature and stress, isotope mapping in nuclear materials, etc. A brief overview of the
VENUS project, a TOF imaging beamline in construction at the Spallation Neutron Source of Oak Ridge National
Laboratory, will also be given.

Acknowledgments:
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9:30 AM *MT04.04.02
Advances in Neutron Imaging Nikolay Kardjilov1, Ingo Manke1, Robin Woracek2, Henning Markoetter1, André Hilger1, Tobias Arlt1, Robert Bradbury1 and John Banhart1; 1Helmholtz-Zentrum Berlin, Germany; 2European Spallation Source (ESS), Sweden

Imaging techniques based on neutron beams are rapidly developing and have become versatile non-destructive analysing tools in many research fields. Due to their intrinsic properties, neutrons differ strongly from electrons, protons or X-rays in terms of their interaction with matter: they penetrate deeply into most common metallic materials while they have a high sensitivity to light elements such as hydrogen, hydrogenous substances or lithium. This makes neutrons perfectly suited probes for research on materials that are used for energy storage and conversion, e.g. batteries, hydrogen storage, fuel cells, etc. Moreover, their wave properties can be exploited to perform diffraction, phase-contrast and dark-field imaging experiments. Their magnetic moment allows for resolving magnetic properties in bulk samples. This presentation will focus on recent applications of neutron imaging techniques in both materials research and fundamental science illustrated by examples selected from different areas.

10:00 AM BREAK

10:30 AM *MT04.04.03
Application of Advanced Neutron Scattering Techniques to Study Hydrogen Behavior in LWR Nuclear Fuel Cladding Brent Heuser1, Jun-Li Lin1, Timothy Prisk2, Tanya J. Dax2, Alexander Kolesnikov3, Changwoo Do4, Hassina Z. Bilheux1, Brianne J. Heisinger1, Yongfeng Zhang4 and Garrett Granroth3; 1University of Illinois at Urbana-Champaign, United States; 2National Institute of Standards and Technology, United States; 3Oak Ridge National Laboratory, United States; 4Idaho National Laboratory, United States

Light water nuclear reactor (LWR) technology and the development of advanced nuclear reactors depend on materials innovation and mitigating deleterious environmental effects. This talk will focus on the utility of neutron scattering techniques to interrogate LWR structural materials. Emphasis will be placed on the study of hydrogen behavior in LWR cladding. We use the newest generation of neutron sources and instruments to study hydrogen at low concentration; novel experiment results will be presented that demonstrate the utility of neutron scattering as applied to nuclear materials.

11:00 AM MT04.04.04
Advanced Characterization of Nuclear Materials Using Neutron Imaging Yuxuan Zhang1, Hassina Z. Bilheux1, Kristian Myhre1, Jean-Christophe Bilheux1, Jiao Lin1, Jared Johnson1, Andrew Miskowiec1, Rodney Hunt1, Louis J. Santodonato2, Jamie Molaison1, Paris Cornwell1 and Erik Stringfellow1; 1Oak Ridge National Laboratory, United States; 2Advanced Research Systems, Inc., United States

Advanced fuel materials for nuclear energy systems are being investigated using neutron imaging at both the High Flux Isotope Reactor (HFIR) and the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). Research efforts have specifically focused on understanding how production processes impact elemental distributions within the tristructural-isotropic (TRISO) fuel kernels. Conventional characterization techniques (i.e. scanning electron microscopy with energy dispersive spectroscopy, optical microscopy, etc.) often require significant and destructive sample preparations, are greatly limited by the penetration depth, and thus are unable to extract bulk information. In our work, attenuation-based neutron computed tomography at CG-1D beamline at HFIR was performed on TRISO fuel kernels to evaluate the presence of carbon agglomerates in 3 dimensions. Additionally, at the SNAP beamline at SNS, neutron resonance computed tomography was performed to map the isotopic content of the kernels contain uranium and gadolinium. Neutrons with energies higher than 1 eV are absorbed by the nucleus of an atom. Absorption as a function of neutron energy can be mapped from the radiographs and display isotope-specific peaks that can be fitted to quantify the amount of isotope present in the material in 3 dimensions. This presentation presents the characterization of nuclear fuel materials using both the attenuation-based and resonance computed tomography techniques. These two techniques can be utilized in unison to provide unique insight on the material’s manufacturing processes.

Acknowledgments
Neutron Characterization of Boron-Containing PDMS Composites for Space and Nuclear Applications

Joseph H. Dumont¹, Samantha J. Talley¹, Eamonn C. Murphy¹, Zachary Brounstein¹, Alexander M. Long¹, Tom Robison², Kwan-Soo Lee¹ and Andrea Labouriau¹; ¹Los Alamos National Laboratory, United States; ²National Security Campus, United States

Polydimethylsiloxane (PDMS) or silicone, is widely used in both industrial applications and academic research area due to its low cost, easy manufacturability, backbone flexibility, low surface energy, and chemical and thermal stability. PDMS elastomers are typically prepared by a hydrosilylation reaction between the hydride groups and the vinyl groups in PDMS. Alternatively, it has been used to synthesize foams vulcanized at room temperature for cushioning applications by reacting a hydride-functional PDMS with a hydroxyl-terminated PDMS at room temperature.¹⁻³

There is an increased demand in aerospace, nuclear reactors, and other neutron-producing sources for neutron shielding materials to mitigate ionizing radiation damage.⁴⁻⁵ The attenuation from neutrons radiation in space and nuclear applications can be performed using isotopically-enriched boron (¹⁰B) because of its large neutron cross-section.¹⁰B has previously been successfully incorporated in a PDMS and other polymer matrices for these types of applications.³,⁶ However, compliant PDMS composites with high concentrations of ¹⁰B (≥ 70 wt%) have not been proposed.

The Energy-Resolved Neutron Imaging (ERNI) Flight Path at the Los Alamos Neutron Science Center (LANSCE) allows to probe boron-containing materials and obtain an energy resolved transmission spectra on a pixel-by-pixel bases. This allows 3D reconstructions via Computed Tomography (CT) of the samples and verifies the filler distribution.

In this work, we study the neutron attenuation and boron distribution of highly-filled boron-containing PDMS composites (50-70% by weight) using the capabilities at LANSCE and CT. Additionally, the chemical, thermal and mechanical properties will be studied using a wide range of experimental techniques are used including Fourier transform infrared spectroscopy, mass spectroscopy, differential scanning calorimetry, thermogravimetric analysis, nuclear magnetic resonance spectroscopy, and mechanical testing. The resistance of the composite materials to solvents will be investigated through solvent swelling experiments and exposure to high humidity. The presented work lays the foundation for highly-filled composite polymer foams to be considered for space and nuclear applications.

References
(6) Harrison, C.; Weaver, S.; Bertelsen, C.; Burgett, E.; Hertel, N.; Grulk, E. Polyethylene/boron nitride composites
11:30 AM MT04.04.06
Mapping Porosity, Crystal Phases and Material Phases with Multi-Scale and Multi-Modal Imaging D.S. Hussey¹, V. DiStefano¹, J.M. LaManna¹, L.G. Butler², L.M. Anovitz³ and D.L. Jacobson¹; ¹National Institute of Standards and Technology, United States; ²Louisiana State University, United States; ³Oak Ridge National Laboratory, United States

Neutron imaging has seen rapid development in new methods. These methods exploit neutron diffraction, refraction, and magnetic precession, to generate novel image contrasts. Dark field image acquired over a broad range of autocorrelation lengths (nm to µm) provides a quantitative measure of the porosity in the sample and in 3 dimensions. By acquiring images as a function of wavelength, and determining the wavelength at which a particular lattice plane no longer contributes to scattering (so-called Bragg edges), one can infer crystal phase. If the scan is made with sufficiently fine wavelength resolution, one can measure the average strain along the beam direction. Another recent advance comes from combining neutron and X-ray tomography (NeXT) in a simultaneous fashion. NeXT provides researchers with a unique tool to study complex structures, as the bivariate histogram of attenuation values makes the problem of segmentation slightly easier. Because the two probes interact differently for a broad range of materials that are difficult to separate with one probe alone. As an example, in fluid flow in geological specimens, water and void space can be difficult to distinguish in an X-ray tomogram, while the matrix and void space can be difficult to distinguish in neutron tomograms. By combining both views simultaneously, the problem of segmenting flow is straightforward. This presentation will discuss dark field imaging in geology and additive manufacturing, the Bragg edge imaging system at NIST using the analysis of austenite vs martensite in TRIP steel, as well as introduce the NIST-NeXT system highlighting the analysis of concrete and shale rocks.

11:45 AM MT04.04.07
In Situ Neutron Diffraction of Strain Path Change Effects in Cold-Rolled MgAZ31B Sheet Karl Sofinowski¹,², Steven Van Petegem¹, Jan Capek¹, Tobias Panzner¹ and Helena Van Swygenhoven-Moens¹,²; ¹Paul Scherrer Institute, Switzerland; ²École Polytechnique Fédérale de Lausanne, Switzerland

There has been growing interest in wrought magnesium alloys (most commonly, AZ31) for strong, lightweight structural components in cars, aircraft, and electronics. These components are subjected to non-linear loading conditions during cold-forming and use, which is known to have significant effects on the mechanical properties of metals. It is therefore important to study the microstructural evolution during strain path changes in these alloys to understand their macroscopic response under such conditions.

In situ neutron diffraction has been used extensively to investigate the evolution of intergranular strain during loading to provide insight on the relative behavior of different magnesium alloy deformation modes during uniaxial tension/compression tests. In this work, we report on the results from in situ neutron diffraction experiments combined with in situ acoustic emission of strain path changes of cold-rolled Mg AZ31B sheets. It is found that, while dislocation slip prevails as the main deformation mechanism, the twinning activity strongly depends on the nature of the strain path change. Post mortem EBSD is also presented to characterize the twin variant selection, which depends heavily on the strain path change angle as well.

This research is performed within the ERC Advanced Grant MULTIAX (339245).
Complex hydrides have been found to exhibit variety of functionalities that can be utilized for many applications. One of the important applications of hydrides is for energy storage such as hydrogen storage due to the high hydrogen capacities of the light weight complex hydrides and superionic battery application due to the fast ionic mobility in some small ion-containing hydride systems. In this talk, I will present some of our recent work on rational development of novel complex hydrides, e.g. inorganic-organic combined complex hydride systems for hydrogen storage, including metal guanidinates, borohydride guanidinium complexes, and novel salts comprised of alkali cations and large polyhedral boron-hydrogen-based anions for superionic conduction. I will focus on the structural studies of these materials with aspects of crystal structure determination of novel hydrides using the combined x-ray/neutron powder diffraction and neutron vibrational spectroscopy. The rich information obtained from the structural and dynamic analysis and their implications for hydrogen storage and ionic conductivity will be discussed.

2:00 PM *MT04.05.02
A View into Adsorption and Separations Processes within Metal-Organic Frameworks through Neutron Scattering Craig Brown1,2; 1National Institute of Standards and Technology, United States; 2University of Delaware, United States

Adsorption of molecules in functionalized and high surface area metal-organic frameworks (MOFs) is of emergent technological importance in a multitude of areas ranging from chemical separations to energy storage. We have been studying the properties of MOFs for storage and separations of industrially important small molecules such as hydrogen, oxygen, carbon dioxide, noble gases, and short chain organics. Besides the geometrical and porosity control available in MOF chemistry, the properties of the frameworks can be tweaked to elevate electrostatic interactions by exposing open metal cation sites or functionalizing ligands. Here, we discuss the information accessible from neutron scattering experiments on a selection of nominally rigid MOFs. The results illustrate the power, and limitations, of diffraction and spectroscopy in elucidating the governing characteristics of these material properties and the interactions with the guest molecules.

2:30 PM MT04.05.03
Determining Electron/Phonon Interactions in Organic Semiconductors Using Inelastic Neutron Scattering Harrelson F. Thomas1, Varuni Dantanarayana1, Makena Dettmann1, Luke Daemen2, John Anthony3, Enrique D. Gomez4, Alessandro Troisi5, Nir Goldman6, Roland Faller1 and Adam J. Moule1; 1University of California, Davis, United States; 2Oak Ridge National Laboratory, United States; 3University of Kentucky, United States; 4The Pennsylvania State University, United States; 5University of Liverpool, United Kingdom; 6Lawrence Livermore National Laboratory, United States

Organic semiconductors (OSCs) provide the unprecedented ability to tailor properties like electronic band gap, mechanical flexibility, processability, and biocompatibility. Recent theories suggest that low frequency dynamic intra- and intermolecular motions are critical to determining localization of the charge carrier, and thus, control the hole mobility. We used inelastic neutron scattering (INS) to probe thermal disorder directly by measuring the high resolution phonon spectrum in multiple small molecule OSCs. We achieved near perfect agreement between the INS spectra of OSC crystals and first principle electronic simulations. This simulation is used to generate a set of electron-phonon coupling parameters, which are used to compute hole mobility using transient localization theory. The charge mobility, calculated from first principles, is in excellent quantitative agreement with macroscopic measurements.

We note however, that most OSCs are not extended crystals. Instead most OSCs are a mixture of multi-crystalline and amorphous domains. The electronic simulation method used in our first study (plane-wave DFT) is much too computationally expensive to include chemical, structural, or even orientational disorder. So even though it is possible to measure a low energy phonon spectrum using INS in a polymeric or multi-crystalline sample, it was until now not possible to model the spectrum. We developed two multi-scale modeling techniques to model phonons in disordered samples and allow us to quantitatively validate the models using INS spectra. For modeling disordered crystals we developed the use of density functional tight binding to model phonons and INS spectra. For fully amorphous samples we developed the use of molecular dynamics to model INS spectra in amorphous small molecules and polymers. This presentation will detail the use of these modeling techniques.
Advanced Neutron Scattering in the Service of Advanced Manufacturing Technology
Markus Strobl\textsuperscript{1,2}, Efthymios Polatidis\textsuperscript{1}, Pavel Trtik\textsuperscript{1}, Jan Capek\textsuperscript{1}, Jacopo Valsecchi\textsuperscript{1}, Roland Loge\textsuperscript{1}, Kilian Wasmer\textsuperscript{1}, Nikola Kalentics\textsuperscript{3}, Rita Drissi Daoudi\textsuperscript{3}, Manuel Morgano\textsuperscript{1} and Hossein Tabasi\textsuperscript{3}; \textsuperscript{1}Paul Scherrer Institut, Switzerland; \textsuperscript{2}Copenhagen University, Switzerland; \textsuperscript{3}EPFL, Switzerland; \textsuperscript{4}EMPA, Switzerland

The Neutron Imaging and Applied materials Group at the Paul Scherrer Institut (PSI) in Switzerland has a long tradition of supporting industry and industrial R&D with neutron imaging and diffraction investigations. Often results have an impact on advancing and improving manufacturing. In particular also the development of metal additive manufacturing (AM) can profit from the ability of neutrons to penetrate deep into and to hence non-destructively assess bulk metal materials.

Conventional neutron imaging is applied at the imaging beamlines NEUTRA and ICON to provide insight into produced porosities and geometric integrity of required structures inside a built part. The results are to validate predictions and build strategies and to guide e.g. sensor developments for in-situ AM process control. While neutron imaging at PSI provide spatial resolutions down to below 5 micrometers, with novel advanced methods structural variations on sub-micrometer length scales can be resolved.

The fact that in additive manufacturing the material is established simultaneously together with the geometry of a specific part, enables to tune the material properties with respect to loading states it undergoes during service. At POLDI, a neutron diffractometer for engineering materials research, the mechanical behavior of TRIP and TWIP steels is investigated, in order to determine the crystallographic textures to be locally produced by AM for either promoting or suppressing the TWIP or TRIP effects with respect to the applied loading.

While neutron diffraction is routinely applied to study local residual stresses generated during the build process, respectively their relief during post build treatments, also advanced neutron imaging techniques provide sensitivity to local crystallographic features such as microstructure and residual stresses. For example, the residual stress variations in the critical surface regions achieved through laser shock peening (LSP), displaying a strong gradient towards the bulk reaching to depths of millimeters, have been shown to be best probed by Bragg edge imaging. The method provides sufficient spatial and crystallographic resolution while being able to provide large area views of treated specimen.

A number of recent examples of neutron measurements in the service of advanced manufacturing technology shall be presented and discussed.
coupled. Therefore we use several incident energies and combine the data to obtain \( S(Q, E) \) with high resolution. We plan to apply this approach to the study of local dynamics of liquids with important applications, such as aqueous solution of salts and liquid electrolytes for energy storage and as insulator in field-effect-transistors. The knowledge garnered shall contribute to the bottom-up design of better functional liquids.

4:00 PM *MT04.05.06
Capturing Functional Nanostructures and Their Interfaces with Neutron Total Scattering Katharine Page\(^1,2\);
\(^1\)The University of Tennessee, Knoxville, United States; \(^2\)Oak Ridge National Laboratory, United States

It is widely recognized in catalysis, fuel cell and battery chemistry, bio- and geochemical processes, and a host of additional functional materials areas that unique properties and characteristics are governed by intricate structural-chemical relationships. Uncovering the identity and role of locally ordered motifs, including those of surface species and interfaces, remains a challenge because experimental tools to observe materials at atomic length-scales, in relevant operating conditions, or within sufficiently fine time scales are limited. We present our efforts to apply and extend neutron total scattering and related probes towards capturing the interplay of crystal chemistry and functionality in nano- and nanostructured materials. Examples include: (1) exploration of internal dipole-dipole ordering in ferroelectric nanocrystals, demonstrating the enhancing effects of cubic particle shape and polar surface termination; (2) investigation of layered manganese oxide structures, where interlayer water molecules, hydrogen bonding, and the nature of vacancies/intercalants strongly impact electrochemically active variants; and (3) demonstrated abilities to probe the structure and dynamics of gas-solid interfaces in catalytic materials, where the signatures of interfacial species are enhanced through the use of neutron isotope contrast techniques. These examples improve understanding of technologically significant materials and highlight a broader theme of our research aimed at extracting crystal structure models from experimental data with the detail needed to guide and validate modern nanoscale theories, and design new and improved functional materials. Current challenges and future opportunities in this arena will be discussed.

4:30 PM MT04.05.07
Local Structure Analysis and Modeling of Lignin-Based Carbon Composite Anodes through the Hierarchical Decomposition of the Radial Distribution Function Software – HDRDF Dayton G. Kizzire, Valerie García-Negrón, David Harper and David Keffer; The University of Tennessee, Knoxville, United States

High performance Li-ion batteries manufactured with bio-based and renewable materials are a necessity in a market focused on efficiency, sustainability and cleaner energy. Previous studies have suggested a solution through lignin, a low-cost, renewable bio-feedstock with a high carbon content. Processing and pyrolysis of the lignin produces a graphitic composite composed of nanoscale crystallite spheres dispersed in an amorphous matrix and have shown success in uses as high-performance anodes in Li-ion batteries. These bio-based composite structures have proven to have superior charge capacity, high reversible capacity, low irreversible capacity loss, and high cycle life when compared to traditional intercalated Li-ion anodes. Understanding the structure of the bio-based anode is critical to explaining the exceptional anode properties. The local atomic environment is often characterized via a radial distribution function calculated from neutron and x-ray scattering experiments, but when studying complex materials, interpretation of the RDF can present a significant challenge due to the nature of scattering from the amorphous phase. Traditionally, large scale molecular dynamics (MD) simulations are used to form a hypothetical structure and generate a corresponding RDF to be compared to experiment. Alterations to the material’s structure and constituent particle size in MD simulations is an expensive and time-consuming process. A significantly more efficient approach for the interpretation of RDFs of complex materials is the Hierarchical Decomposition of the RDF (HDRDF), in which the total RDF is decomposed into components, some of which are modeled with static atomic structures and others of which are modeled as continuous mesoscale objects. The HDRDF software generates a real-space model of the complex nanomaterial and correlates the RDF to a set of material descriptors, such as crystalline domain size, crystalline volume fraction, total density, etc. and compares its RDF to experiment. The HDRDF approach has been shown to use roughly one million times less computational resources compared to MD simulation. We report progress on the development of a second generation of the HDRDF software, which extends the capability to arbitrary domain geometries and we apply the HDRDF technique to the interpretation of neutron and x-ray scattering of lignin-based nanostructured carbon composites. This work implements HDRDF to quantitatively determine how choice of lignin feedstock and pyrolysis temperature impacts the nano- and mesoscale structures of the resulting graphitic composites. Initial results have shown crystallite radius increases and crystalline
volume fraction decreases as pyrolysis temperature increases.

4:45 PM MT04.05.08
Creepy Concrete—Understanding Concrete Creep In Situ Using Neutron Scattering Nishant Garg; University of Illinois Urbana Champaign, United States

The phenomenon of creep in concrete, even after 40 years of experimental and theoretical research, is not fully understood. While it is commonly agreed that the viscoelastic nature of the primary hydration product, calcium-silicate-hydrate (C-S-H) gel, is largely responsible for concrete creep, the physical, nano-scale origin behind this viscoelastic nature is not clear. In order to determine if atomic-scale structural reorganization of C-S-H occurs during creep, in situ neutron scattering was used to continuously examine cementitious samples subject to uniaxial compression over a period of 9 months. For this in situ study, a custom load-frame was designed and implemented at the Nanoscale Ordered Materials Diffractometer (NOMAD) beamline at the Spallation Neutron Source (SNS), Oak Ridge National Lab. Pair distribution function (PDF) analysis of total neutron scattering was performed to follow the evolution of changes in the local structure of C-S-H, resulting in novel insights for the mechanism of concrete creep.

SESSION MT04.06: Instrument/Facilities
Session Chairs: Victoria Garcia Sakai and Kenneth Herwig
Wednesday Morning, December 4, 2019
Hynes, Level 2, Room 207

9:00 AM *MT04.06.01
A Novel Strongly Spin-Orbit Coupled Quantum Dimer Magnet: Yb2Si2O7 Kate A. Ross; Colorado State University, United States

The quantum dimer magnet (QDM) is the canonical example of "quantum magnetism". This state consists of entangled nearest-neighbor spin dimers and often exhibits a field-induced "triplon" Bose-Einstein condensate (BEC) phase. We report on a new QDM in the strongly spin-orbit coupled, distorted honeycomb-lattice material Yb2Si2O7 [1]. Our single crystal neutron scattering, specific heat, and ultrasound velocity measurements reveal a gapped singlet zero field ground state with sharp, dispersive excitations. We find a field-induced magnetically ordered phase reminiscent of a BEC phase, with exceptionally low critical fields of Hc1 ~0.4 T and Hc2 ~1.4 T. Using inelastic neutron scattering we observe a Goldstone mode (gapless to within = 0.037 meV) that persists throughout the entire field-induced magnetically ordered phase, suggestive of the spontaneous breaking of U(1) symmetry expected for a triplon BEC. However, in contrast to other well-known cases of this phase, the high-field (H > 1.2T) part of the phase diagram in Yb2Si2O7 is interrupted by an unusual regime signaled by a change in the field dependence of the ultrasound velocity and magnetization, as well as the disappearance of a sharp anomaly in the specific heat. These measurements raise the question of how anisotropy in strongly spin-orbit coupled materials modifies the field induced phases of QDMs.


9:30 AM *MT04.06.02
Perspectives of the European Spallation Source—The Next-Generation Neutron Facility Ken Andersen; European Spallation Source ERIC, Sweden

The European Spallation Source is currently under construction in Lund, Sweden. It is designed to provide world-leading performance, with instruments optimized for the long-pulse time structure of the facility, making full use of what will be the world’s brightest neutron beams for the study of materials ranging from biological systems and soft matter to engineering materials, structural chemistry and magnetism.

An overview will be given of the state of the construction project, as well as key design features of the facility,
allowing an unprecedented degree of flexibility and performance for the instruments. 15 instruments are under construction, covering SANS, reflectometry, imaging, engineering diffraction, powder and single-crystal diffraction, chopper spectrometers, and crystal-analysyer spectrometers. Highlights of instrument design aspects will be raised, which further enhance the scientific impact of the instruments.

10:00 AM BREAK

10:30 AM *MT04.06.03
First Experiments at the Second Target Station of the Spallation Neutron Source Paul Langan; Oak Ridge National Laboratory, United States

Neutron scattering has become a vital tool for studying materials across many scientific fields and applications, including automotive engines, batteries, data storage, geology, polymers, and biomedicine. In the United States, the Office of Science of the US Department of Energy (DOE) supports two major neutron scattering user facilities at Oak Ridge National Laboratory (ORNL): the High Flux Isotope Reactor (HFIR) and the Spallation Neutron Source (SNS). SNS is currently undergoing a proton power upgrade (PPU) to double its power capability to 2.8 MW. This upgrade, which will be completed in 2024, will deliver 2 MW of proton beam to the existing First Target Station (FTS) at the SNS, resulting in a significant increase in thermal neutron brightness to enable new capabilities for materials research in the thermal energy (shorter wavelength) range. The PPU project will also provide the addition power required to operate a planned Second Target Station (STS) for SNS. STS will provide pulsed beams of cold (longer wavelength) neutrons with unprecedented peak brightness and containing broad ranges of neutron energies. These beams will provide wholly new capabilities for the study of a broad range of materials using neutron scattering and support users in many fields of research—materials science, physics, chemistry, geology, biology, and engineering, among others—and in industry. When it is fully built out, the capabilities offered by the twenty-two instruments planned for the STS will complement those of HFIR and the FTS. The STS has a pivotal role to play in extending the reach of neutron scattering to new transformative opportunities for discovery science and applications that require time-resolved examination of nonequilibrium processes in dynamic hierarchical systems over greatly increased length, energy, and time scales. To illustrate the extraordinary potential of the STS to impact a broad spectrum of scientific fields, examples of first experiments to be conducted at the STS will be described.

11:00 AM *MT04.06.04
WASP the Wide Angle Neutron Spin Echo Instrument Peter Falus and Bela Farago; Inst Laue Langevin, France

The first Neutron Spin Echo (NSE) instrument has been in user operation for 40 years now and the newest one: WASP at ILL has just started commissioning. I will use this occasion to review how the basic design of the NSE spectrometers have developed during these years. The technical and scientific capabilities of the new instrument will be presented as well.

All functioning Neutron Spin Echo spectrometers use the basic IN11A design where the precession field is generated by long solenoids along the neutron beam. This construction limits the angular coverage and count rate of the instruments. Last century there have been two tries to make a wide angle coverage neutron spin echo instrument. IN11C at ILL is equipped with a flattened solenoid and has been in use since its creation. It has a 30 degree-wide angular coverage but a very limited resolution. This instrument was practically trading intensity for resolution. The SPAN instrument at HZB used a pair of coils in the anti Helmholtz configuration creating an azimuthally symmetric magnetic field; which, in theory, could allow a nearly 360 degree detector coverage. WASP uses an improved SPAN construction, and it aims to have a 500 times higher detected intensity than IN11A while the resolution remains the same.

The long construction has finished in 2018, and the three weeks of commissioning were promising. We have echo in all detectors up to one third nominal field integral, and the detected intensity is 500x of IN11A. By the time of the conference we hope to present detailed characterisation of the instrument.

11:30 AM *MT04.06.05
Examples of Materials Research at ESS Using Neutrons—From Construction towards Operation Monika Hartl¹, Luke Daemen² and Yongjoong Lee¹; ¹European Spallation Source ERIC, Sweden; ²Oak Ridge National Laboratory, United States
The European Spallation Source ESS in Sweden is currently in construction and will receive first neutrons in 2021. The start of the user program will be in 2023. Even now, during construction of the facility, we are encountering interesting material problems, some of which can be solved best using neutron scattering. This presentation will show examples for ESS material research that supports construction and leads towards operation. The data shown throughout the contribution has been recorded at currently operating spallation sources such as SNS, ISIS and JPARC.

Material degradation due to radiation is a limiting factor for the lifetime of high power spallation sources. This well-recognized fact leads to increased research efforts in finding the best materials for construction of ESS and understanding what happens with the materials on the atomic scale when exposed to a radiation field. These material investigations are greatly aided by the use of neutrons. Examples given are connected to understanding the radiation hardness of greases and oils, investigating the effect of purity and grain size of beryllium on its effectiveness as neutron reflector as well as solving issues related to the ortho- to parahydrogen conversion in the cold moderators. With ESS moving towards the start of the user program in 2023, we are beginning to collaborate with local scientists and small local industry on scientific projects using neutron scattering as main analysis tool. This helps to educate the local user community in the usefulness of neutrons and us in preparing the user laboratory infrastructure for the future. We will show an example using neutron vibrational spectroscopy to observe bisphenol A adsorbed on sand and clay. This is currently an area of great interest to the water industry as these materials are part of water filters potentially suitable to remove bisphenol A from sewage water. This project benefited from the use of neutrons as the bisphenol A adsorbed on clay and sand cannot easily be detected using optical spectroscopy or X-ray methods.

SESSION MT04.07: Soft Materials I
Session Chairs: Mark Dadmun and Changwoo Do
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 207

1:30 PM *MT04.07.01
**Measuring and Modeling In Situ SANS from Complex Fluids Under Programmable Flow Histories** Patrick T. Corona¹, Nino Ruocco¹, Kathleen M. Weigandt², L. Gary Leal¹ and Matthew Helgeson¹; ¹University of California, Santa Barbara, United States; ²National Institute of Standards and Technology, United States

In situ small angle neutron scattering under flow (flow-SANS) has become a critical tool for developing processing-structure-property relationships of complex fluids and soft matter. However, sample environments and associated measurement methods for flow-SANS have largely limited these measurements to steady state flows and simple rheometric deformations (pure shearing or elongation) that fail to capture the complex nonlinear and time-varying deformations encountered during processing. To bridge this gap, we have developed a novel fluidic four-roll mill (FFoRM) that, in combination with recent capabilities for spatiotemporal measurements, enables in situ SANS measurements under programmable quasi-two dimensional flows within a single device.[1] Here, we highlight the unique capabilities of “FFoRM-SANS” by its application to understand flow-induced ordering during the processing of rod-like polymeric and colloidal fluids. Interpretation of the rich data sets obtained are interpreted using a new, general framework for model-free estimation of orientation probability distribution functions (OPDFs) from scattering of orientable particles. Doing so enables parameter-free quantification of the effective structure factor that captures the dominant contributions of flow-interaction coupling on orientational order. We find that the effective structure factor depends significantly on the flow history of the fluid, and thus provides rational criteria for designing processing flows for improved or controlled ordering.


2:00 PM MT04.07.02
**Identifying the Conformational Characteristics of Sheared Wormlike Micelles from Anisotropic Scattering Profiles** Yuva Shinohara¹, Wei-Ren Chen¹, Guan-Rong Huang¹, Changwoo Do¹, Yun Liu², Lionel Porcar² and Takeshi Egami³; ¹Oak Ridge National Laboratory, United States; ²National Institute of Standards and Technology, United States; ³Institut Laue-Langevin, France; ⁴The University of Tennessee, Knoxville, United States
Wormlike micelles (WLMs) are self-assembly systems formed by amphiphilic surfactants immersed in water. Understanding the structural origin of their rheological properties is important for scientific as well as technological reasons. Small-angle neutron scattering (SANS) has been used to investigate the conformational characteristics of WLMs under macroscopic deformations. Upon increasing the applied stress, the angular dependence of SANS intensities develops progressively due to the flow-induced alignment at a molecular level. In existing analysis schemes, an assumption of the angular distribution function is often required to extract the orientation of aligned WLMs from their anisotropic SANS spectra. The validity of the assumption is, however, not known a priori.

To bypass this intrinsic constraint, we have developed a rigorous approach based on the spherical harmonics expansion (SHE); this approach allows us to extract the conformational information of the aligned WLMs from their scattering intensity profiles without any model fitting. The feasibility of this approach is verified theoretically. Based on a case study of the hexadecyltrimethylammonium bromide (CTAB)/sodium salicylate WLM system, we demonstrate that our method not only facilitates the quantitative scattering studies of deforming materials but also provides insightful information regarding their deformation behavior at the molecular level based on the symmetric properties of real spherical harmonics.

*YS and TE acknowledge support from the US Department of Energy, Office of Science, Basic Energy Science, Materials Science and Engineering Division.

2:15 PM MT04.07.03
Theoretical Framework for Determining the Structural Characteristics of Deforming Objects from Their Scattering Signature
Guan-Rong Huang1, Yangyang Wang2, Yuya Shinohara2, Changwoo Do1, Takeshi Egami2,3 and Wei-Ren Chen1,2; 1Neutron Scattering Division, Oak Ridge National Laboratory, United States; 2Oak Ridge National Laboratory, United States; 3The University of Tennessee, Knoxville, United States

There has been much interest in understanding the structural characteristics of deforming materials that are manifest on different length scales. In the context of scattering investigation, the domain of interest can be decomposed into a microscopic region within which the local configurational translation and rotation can be treated in detail, and a larger regime where the description of global shape envelope is appropriate. From a perspective of geometric interpretation at either the microscopic or the macroscopic level, a central issue is how to quantitatively determine the structural characteristics from the anisotropic scattering intensity in a model-free manner.

We present a general approach to deal with this problem, which is valid to different deformation conditions and mathematically rigorous. In the mean-field limit, we first demonstrate that the radius of gyration is indeed the source term of intra-particle structure factor. By expanding the spectral anisotropy using the real spherical harmonic expansion (RSHE), we derive the exact mathematical expression of 2nd order gyration tensor in terms of the anisotropic spatial correlation functions. Based on the same RSHE scheme, we derive the orientational distribution functions to describe the local configurational alignment. Theoretical benchmark studies demonstrate that our developed approach not only facilitates quantitative scattering studies of flowing materials based on the symmetric properties of real spherical harmonics, but also provides insightful information regarding the deformation behavior of materials at the molecular level.

2:30 PM BREAK

3:30 PM *MT04.07.04
Advancing Neutron Scattering to Explore Nano-Scale Physics in Energy Systems and Engineering Materials
Li Liu, Kemal Ramic and Jinghua Feng; Rensselaer Polytechnic Institute, United States

We look into methodology development based on neutron scattering techniques to “visualize” complex phenomena. This visualization must integrate scattering experimental analysis, simulation, and theory to provide real space images of such phenomena. And their potential use in exploring energy and engineering processes is highly promising. Exploratory neutron scattering methodology development for the fields of Nuclear Data and Concentrating Solar Power will be discussed in the presentation.

In Nuclear Data, improvements in determination of the thermal scattering law of moderator materials (measuring, calculating, and validating) are important for accurate prediction of neutron thermalization in nuclear systems. In
this work a new methodology for producing thermal scattering libraries from the experimental data for polyethylene (C2H4)n is discussed and expanded to other systems such as Lucite and water. Double differential scattering cross section (DDSCS) experiments were performed at the Spallation Neutron Source of Oak Ridge National Laboratory (SNS ORNL). New scattering kernel evaluations, based on phonon spectrum for (C2H4)n, are created using the NJOY2016 code. Two different methods were used: direct and indirect geometry neutron scattering at ARCS and SEQUOIA, and VISION instruments, respectively, where the phonon spectrum was derived from the dynamical structure factor S(Q,ω) obtained from the measured DDSCS. In order to compare and validate the newly created library, the experimental setup was simulated using MCNP6.1. Compared with the current ENDF/B-VII.1, the resulting Rensselaer Polytechnic Institute (RPI) (C2H4)n libraries improved both double differential scattering and total scattering cross sections. A set of criticality benchmarks containing (C2H4)n from HEU-MET-THERM resulted in an overall improved calculation of Keff, although the libraries should be tested against benchmarks more sensitive to (C2H4)n. The Density Functional Theory (DFT)+oClimax (a package provided by ORNL) method is used and is shown to be most comprehensive method for analysis of moderator materials. The importance of DFT+oClimax method lies in the fact that it can be validated against all data measured at VISION, ARCS and SEQUOIA, and experimental total scattering cross section measurements.

In Concentrating Solar Power, we are developing neutron measurements for in-situ interface corrosion kinetics and molten salt properties. This research will provide fundamental data for material selection including the molten salt systems for both nuclear and solar applications. The presentation will focus on the development of in-situ neutron techniques for fundamental understanding of the mechanisms of molten salt corrosion, and the micro-structural response of containment alloys thereto, to measure the surface corrosion kinetics. We are working on realization and initial application of in-situ techniques for measuring molten salt fundamental properties including molten salt structure, dynamics, and salt density, etc. and the micro-structural and -chemical response of containment alloys to corrosive molten salt environments. The two neutron techniques involved are Vibrational Spectroscopy and Neutron Reflectometry. They both have unique characteristics for complex liquids at high temperatures. Moreover, while we are designing and manufacturing sample environments for harsh environments (high temperature and corrosive), they will provide great first-of-the-kind experimental data for molten salt systems.

4:00 PM *MT04.07.05
Neutron Optics to Enable Polychromatic Neutron Imaging and Powder and Stress-Strain Diffraction Boris Khaykovich1, Alexandru D. Stoica2, J. T. Cremer3, Muhammad Abir1 and D.S. Hussey4; 1Massachusetts Institute of Technology, United States; 2Oak Ridge National Laboratory, United States; 3Adelphi Technology, Inc., United States; 4National Institute of Standards and Technology, United States

We are developing neutron optical devices whose task is to increase the throughput of neutron instruments. For neutron imaging, we demonstrate designs of two types of neutron microscopes. Like an optical microscope, the neutron microscope consists of a condenser and an image forming optics. Neutrons are focused on the sample by the condenser mirrors while the image forming mirrors focus transmitted neutrons on the detector [1]. The condenser is designed to maximize the neutron flux and to obtain desired beam divergence at the sample. The condenser consists of axisymmetric confocal paraboloid and a hyperboloid mirrors, which are concentrically nested. The image-forming optics are designed using different combinations of the confocal nested ellipsoid and hyperboloid mirrors called Wolter mirrors. Both optics are being manufactured for installation at NIST. The design of magnification-10 mirrors should achieve the spatial resolution of about 10 μm. Importantly, the resolution of the microscope is determined by the mirrors rather than by the beam collimation as in conventional pinhole imaging, leading to possible dramatic improvements in the signal rate and resolution. Also, in contrast with pinhole imaging, in the microscope, the samples are placed far from the detector to allow for bulky sample environment. For diffraction, we are developing analyzers for polychromatic cold and thermal diffractometers. Polychromatic incident beam allows for multiplexing analyzer crystals in order to cover relatively large solid angles. Specifically, we optimized axisymmetric PG analyzers inspired by the very first neutron-diffraction experiment by Mitchell and Powers [2]. In addition, we are adopting bent single-crystal wafers following the developments of the so-called “thickness focusing” [3,4]. The combination of the polychromatic beam [5] and focusing geometry allows increasing both the signal rate and resolution. The proposed instruments will have much higher throughput than existing instruments and thus enable diffractometers at compact neutron sources.


Final Program 1/13/2020 1987

4:30 PM MT04.07.06
Characterization of Colloidal Nanocrystal Surface Structure Using Small Angle Neutron Scattering and Efficient Bayesian Parameter Estimation
Samuel W. Winslow¹, Wenbi Sheherbakov-Wu¹, Yun Liu², William Tisdale¹ and James W. Swan¹; ¹Massachusetts Institute of Technology, United States; ²University of Delaware, United States

Complete structural characterization of colloidal nanocrystals is challenging due to rapid variation in the electronic, vibrational, and elemental properties across the nanocrystal surface. While traditional characterization techniques such as electron microscopy and X-ray scattering can provide detailed information about the inorganic nanocrystal core, these techniques provide little information about the molecular ligands coating the nanocrystal surface. Moreover, because most models for scattering data are parametrically nonlinear, uncertainty estimates for parameters are challenging to formulate robustly. Using both PbO- and PbCl₂-derived, oleate-capped PbS quantum dots as a model system, we demonstrate the capability of small angle neutron scattering (SANS) in resolving core, surface layer, ligand-shell, and solvent structure for well-dispersed nanocrystals using a single technique. We quantify a ~0.3 nm thick surface PbClₓ layer on the PbCl₂-derived quantum dots, previously only hypothesized. Global fitting of the SANS data across a solvent deuteration series enables unique determination of the spatial distribution of each material. Molecular dynamics simulations were used to develop a coarse-grained form factor describing the scattering length density profile of ligand-stabilized nanocrystals in solution. We introduce an affine invariant Markov chain Monte Carlo method to efficiently perform nonlinear parameter estimation for the form factor describing such dilute solutions. This technique yields robust uncertainty estimates. This experimental design is broadly applicable across colloidal nanocrystal material systems including emergent perovskite nanocrystals and the parameter estimation protocol significantly accelerates characterization and provides new insights into the atomic and molecular structure of colloidal nanocrystals.

4:45 PM MT04.07.07
Understanding Formation of Chitosan-Gold Gels using Small Angle Neutron Scattering
Radha Perumal Ramasamy¹ and Vinod K. Aswal²; ¹Anna University Chennai, India; ²Bhabha Atomic Research Centre, India

Biopolymers are very important class of materials as they are environmentally friendly. Chitosan is a very popular biopolymer and it has several advantages such as excellent film forming capacity, biodegradability and nanoparticle forming capability as it has reducing and stabilizing effect on metal ions. Understanding the interactions between ions and chitosan can help us make better membranes that can be potentially used in battery technology. Here, the use of Small Angle Neutron Scattering (SANS) in chitosan gels is explored. SANS is a useful technique for the characterization of biological materials. SANS experiments involve scattering of a monochromatic neutron beam from the sample and measures the scattered neutron intensity as a function of scattering vector. The wavelength of the neutron beam used was 5.2 Å with a resolution (Δλ/λ) of about 15%. All of the data were collected in the accessible Q range of 0.017–0.35 Å⁻¹. All of the SANS data were corrected for the background, the empty cell contribution, and solvent contribution, and were normalized using standard procedure. Chitosan solution was prepared by adding 1% (w/v) of chitosan powder, 1.5% (w/v) of acetic acid to D₂O. Previous study by us has shown that we can use neutron scattering to determine the radius of gyration (Rg) of chitosan and the size of the gold nanoparticles. Using SANS and SEM images we could show that the size of the gold nanoparticles templated on chitosan is comparable to that of the Rg of chitosan when the chitosan solution contained 1Mm HAuCl₄ and was heated to form red colored solution. Also, we have shown that increasing the concentration of gold in chitosan solution to 3mM and more resulted in the formation of gels. When the gels where heated it resulted in the formation
of rose red colored liquid. When chitosan-HAuCl₄ gels where incubated at 25° C the gels collapsed in time. After ten days when the samples where imaged it was observed that micron sized gold particles had formed. The particles where mostly hexagonal in shape. The size of these particles are much larger than the Rg of the chitosan and therefore this result implies that chitosan acts as a template for the gold ions to nucleate and form micron sized particles. The formation and the collapse of the gels was attributed to the electrostatic interactions between the gold ions and the chitosan unit with the gold ions acting as bridges. This in turn made the liquid viscous thus forming gels. SANS was used to study the formation of the gels. SANS results showed that the Rg for chitosan film is lesser than that for chitosan in solution. Also, the Rg for chitosan-gold gels was the same as that of chitosan in solution. There was no correlation length observed in chitosan solution, however it was present in chitosan-gold gels. This result indicates that the chitosan units are localized in the gel phase. These gels have potential applications in detectors.

SESSION MT04.08: Soft Materials II
Session Chairs: Antonio Faraone and Victoria Garcia Sakai
Thursday Morning, December 5, 2019
Hynes, Level 2, Room 207

8:45 AM MT04.08.01
Insights into the Structural Dynamics of Polyfluorene β Phase Using Neutron Spectroscopy Nicholas D. Siemons¹,², Anne Guilbert², Jenny Nelson², Mohamed Zbiri¹ and Christian Nielsen³; ¹Institut Laue-Langevin, France; ²Imperial College London, United Kingdom; ³Queen Mary University, London, United Kingdom

Within the polymer semiconductor family, poly(9,9-dioctylfluorene) (PFO) has attracted interest for applications such as light emitting diodes and lasers due to its efficient pure-blue electroluminescence. It has been shown that PFO can adopt a unique and interesting conformer termed as ‘β phase’.¹,² This conformer exhibits efficient light emission and spontaneous emission.³–⁵ However it also emits light at different wavelengths to the other blue emitting material conformers, and therefore can pose challenges in the creation of polymer LED’s. It has also been shown to act as a charge transport trap,⁶ therefore electron-phonon coupling and slower dynamics are likely to impact photoemission. We look to provide insight into the β phase dynamics to help with characterisation. We use temperature-resolved neutron diffraction and spectroscopy techniques to study β phase and to propose a crystal structure for it. We explore the dynamics using quasi-elastic and inelastic neutron spectroscopy in combination with molecular dynamics simulations and quantum chemical calculations. Combining the neutron data with computational methods allows us to test various polymer-solvent compound/co-crystal structures as candidates for β phase and explore its dynamical features.

9:00 AM *MT04.08.02
Impact of Encapsulated Species on Block Copolymer Micelle Self-Assembly and Dynamics Megan Robertson¹, Tyler Cooksey¹, Xiuli Li², Bryce Kidd² and Louis Madsen²; ¹University of Houston, United States; ²Virginia Tech, United States

Block copolymer micelles enable the formation of widely tunable self-assembled structures in liquid phases, with applications ranging from drug delivery to personal care products to nanoreactors. In order to understand fundamental aspects of micelle assembly and dynamics, the structural properties and solvent uptake of biocompatible poly(ethylene oxide-b-ε-caprolactone) (PEO-PCL) diblock copolymers in deuterated water (D₂O) / tetrahydrofuran (THF₈) mixtures were investigated with a combination of small-angle neutron scattering (SANS), nuclear magnetic resonance (NMR), and transmission electron microscopy. PEO-PCL block copolymers, of varying molecular weight yet constant block ratio, formed spherical micelles through a wide range of solvent compositions. We investigated the effect of solvent composition on the unimer content, aggregation number, degree of solvent swelling of the micelle core, and micelle size parameters. Furthermore, we explored the impact of guest molecules, such as model drug compounds, on the micelle self-assembly. Finally, we are developing a time-resolved NMR technique, complemented by existing time-resolved SANS methods, to quantify chain exchange dynamics in these systems.
**Small Angle Scattering Studies of Hierarchically Self-Assembled Binary Nanoparticle Superlattices** Sung-Min Choi; Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of)

The nanoparticle superlattices (NPSLs) can provide new emerging properties through collective coupling between nanoparticles, which are strongly dependent on the lattice symmetry of NPSLs as well as nanoparticle composition. Various methods have been developed for the synthesis of NPSLs, which include slow solvent evaporation, DNA-mediation, electrostatic interaction and others. In our group, we developed for the first time a micelle-assisted method for forming exceptionally ordered NPSLs which are inherently sensitive to environmental conditions, and used it to demonstrate the thermally reversible structural symmetry transitions of NPSLs. We applied this method for one-dimensional [1] and spherical [2] nanoparticles, respectively, which show a spectrum of lattice symmetries depending on particle size ratio, composition, and temperature. The structural details and phase transitions are investigated by neutron and x-ray small scattering techniques. The maximization of free volume entropy is considered as the main driving force for the formation of superlattices, which is well supported by theoretical free energy calculations.


**Elucidation of Buried Polymer Interfaces through Contrast Variations** Wei Chen1,2, Zhang Jiang1 and Matthew V. Tirrell2,1; 1Argonne National Laboratory, United States; 2The University of Chicago, United States

Soft interface characteristic of a strong response to external stimuli represents a grand challenge central to many technical applications, ranging from electrochemistry to colloidal science, heterogeneous catalysis, nanoscience, corrosion, tribology, surface science, biology, and energy production. However, there is a dearth of techniques capable of probing both spatial arrangement and chemical property at interfaces, especially if the solution contains a mixture of ions and organic and biomolecules. As complementary to contrast variation neutron scattering, resonant x-ray scattering (RXS) by merging x-ray scattering and x-ray absorption spectroscopy in a single experiment has developed into an important technique, which yields orders of magnitude more contrast between materials than non-resonant x-ray scattering and provides the unique sensitivity to chemical configurations and spatial relationships of organic functional groups (resonant scattering centers) at important 1–1000 nm length scales. This added resonant sensitivity represents a qualitatively different scattering mechanism than those active in non-resonant x-ray, neutron, and electron scattering.

Here we applied RXS to investigate a breadth of interfaces from Hard-Soft to Soft-Soft: solid-solid interfaces of polystyrene (PS) films on the silicon substrate, solid-liquid interfaces of silica nanoparticles surface grafted poly (2-methacryloyloxyethyl phosphorylcholine) (PMPG) zwitterionic polymer brushes (SiO2-PMPG) in solutions, and polymer interfaces of symmetric polystyrene-block-poly(methyl methacrylate) (PS-b-P(MMA)) diblock copolymers. It is found that the chemical interfacial width of PS thin film at the substrate interface arising from the preferential orientation is about one order of magnitude of the polymer radius of gyration (Rg). Moreover, although the ion-induced changes of PMPC thickness are not apparent in aqueous solutions, their chain conformations like zwitterion distribution and correlation varied, dependent on salt types, ionic strengths and ion valences. As each monomer has no net charge, the chains are not in extended configurations at low salt concentrations. In contrast to simple polyelectrolytes, they expand when salt is added since the local attractions between positive and negative ions are screened, thereby producing a rich science base in understanding the configurations, ionic distribution, and in interfacial interactions of zwitterionic polymer brushes in a variety of relevant and important ionic environments. Regarding the PS-b-P(MMA) diblock polymers with lamellar microdomains normal to the substrate, their even order scatterings should be significantly reduced or extinct as a result of symmetric extinction. By adjusting beam energies
close to the absorption edge of the constituent atoms, the intensity of odd order scatterings remains intact, while that of even order scatterings changes as a function of beam energies. Quantitative analyses on these RXS data around the individual absorption edge of constituent components allow us to determine electron density profiles at interfaces, independent of the models. This, in turn, establishes the relationships of interfacial structures and physical properties of polymers and soft condensed matter, which can be strongly influenced by inherent structural disorder ranging over length scales from molecular functional groups to characteristic conformation and crystallization scales up to sample dimensions.

11:00 AM MT04.08.05
**Exploring Protein-Polymer Interactions with Neutron Scattering** Bradley Olsen¹, Helen Yao¹, Chris Lam², Aaron Huang¹ and Wei-Ren Chen²; ¹Massachusetts Institute of Technology, United States; ²Oak Ridge National Laboratory, United States

Proteins form the basis for important materials in today’s society, including a wide variety of biocatalysts and biosensors that are critical to the production of chemicals, medicine, and national defense. In many of these materials as well as in other applications such as antifouling coatings, self-assembled biomaterials, and protein crystallization, the interactions between proteins and polymers are critical to the functioning of the device. However, measurement of these interactions has traditionally been quite difficult, requiring arduous thermodynamic measurements to estimate interaction parameters in a variety of different competing theoretical frameworks.

Here, we explore several approaches to better understand protein-polymer interactions through the use of neutron scattering methods. First, we explore measurements of the form factor of protein-polymer bioconjugates, where the shape of the flexible polymer coil attached to the protein can provide information on the protein-polymer interaction. Measurements on a series of different polymers are performed, and data fitting allows the general behavior of these molecules in solution to be understood. Measurements are interpreted in the light of coarse-grained molecular simulations of the bioconjugate materials.

Second, cross structure factors are measured for protein-polymer blends at relatively high concentration in order to provide insight into the physics under more strongly interacting conditions. Measurements were performed for three different model systems using contrast variation small-angle neutron scattering (CV-SANS), and cross structure factors were extracted from the data. These were analyzed through systematic comparison to the dilute solutions of protein and polymer as well as through inverse Fourier transforms to provide real space information.

Finally, several experiments suggest that hydration plays a key role in governing interactions between proteins and polymers, especially at high concentration where there is a competition for water. SANS measurements of high concentration solution, combined with a new analysis method, enable estimation of hydration numbers from the traditional dilute regime through the semidilute and into a relatively concentrated regime, allowing an understanding of how hydration number changes with concentration to be gained. Comparison of this neutron data with other spectroscopic data and self-assembly measurements provides insight into how hydration governs the molecular interactions that drive these processes.

11:30 AM MT04.08.06
**Mapping Structural Dynamics of Conjugated Polymers** Anne Guilbert¹, Mohamed Zbiri², Peter Finn³, Christian Nielsen² and Jenny Nelson¹; ¹Imperial College London, United Kingdom; ²Institut Laue-Langevin, France; ³Queen Mary University of London, United Kingdom

Conjugated polymers have attracted a keen interest over the past decade for their potential applications as semiconductors in various types of devices: organic light emitting diodes, organic solar-cells, organic field-effect transistors, etc. One of the potential advantages of polymeric semiconductors over their inorganic counterpart is the possibility of processing them from solution. To increase solubility, alkyl side chains are added to the conjugated backbones of the polymers. The side chains are therefore not involved in the frontier molecular orbitals. Thus, they do not impact directly optoelectronic properties. However, they do impact the polymer conformation and the polymer packing, which in turn impact the optoelectronic processes and the subsequent emergent macroscopic properties of the material. Recently, the side chains have also been engineered to transport ions in the solid-state, opening a new range of applications such as batteries or bio-sensors. Because polymers are soft materials, a range of
dynamics occurs over an extended time scale, from femtosecond to millisecond, and are likely to modulate the impact of microstructure on the optoelectronic properties of the material. Vibrational dynamics have been evidenced to impact absorption, inner reorganization energy, charge transfer between similar molecules and between different molecules at an heterojunction, delocalization, and so more generally charge transport and charge separation processes. Slower dynamics on the picosecond to nanosecond time-scale include side-chain reorientation and backbone torsion. These dynamics are impacted the conformation of the chains and thus, modulates the efficiency of the opto-electronic processes. It has been shown for instance that the global charge transport network changes over timescale competing with charge carrier lifetime. Furthermore, these slow dynamics are temperature-dependent and therefore, can be activated during device operation. For instance, molecular diffusion becomes predominant above the glass transition of the material and is a known degradation mechanism.

We present a detailed microscopic study of the structure-dynamics relationship of both regio-regular (RR) and regio-random (RRa) poly(3-hexylthiophene) (P3HT) using elastic, quasielastic, spin-echo and inelastic neutron scattering techniques. We use deuteration to modulate the coherent and incoherent cross-sections of the materials, beyond a contrast variation purpose, allowing particularly to access both self-motions and collective dynamics of the materials. Measurements are underpinned by quantitative numerical simulations using classical molecular dynamics (MD) simulations, as well as molecular and periodic density functional theory based quantum chemical (QC) calculations. MD simulations reproduced well the large structural features and slow motions, but provided a limited description of molecular vibrations. MD shed light on differences in collective dynamics between Q-values linked with the π-π stacking and the lamellar stacking of the polymer, with the crystalline phase being the most impacted. Molecular QC described well the high-energy vibrational features, while periodic QC allowed to describe the mid-energy vibrational range. We show that this extensive combined approach of neutron-based measurements and multi-computational calculations allows to fully map the structural dynamics of conjugated polymers such as P3HT.

11:45 AM MT04.08.07
Composition of Polyimide Aerogels Saturated with Ionic Liquids by SANS Samantha Rinehart1, Rocco Viggiano2, Baochau Nguyen2, Maryann Meador2 and Mark Dadmun1; 1University of Tennessee, United States; 2NASA Glenn, United States

Polymeric aerogels, more specifically polyimide aerogels (PIA), provide excellent mechanical properties relative to traditional silica aerogels while maintaining thermal stability. NASA has investigated PIA paired with ionic liquids as novel mechanically robust electrolyte systems for next generation batteries. Common laboratory techniques provide insight into the relationship between polyimide structure and surface area, porosity, and pore volume of the aerogel; however, these measurements are traditionally conducted sans solvent. Because of this, the impact of the ionic liquid on the nanoscale structure of PIA is unclear. To determine the impact of solvent presence, we use small angle neutron scattering to determine the skeletal size and composition of solvated PIA. Careful analysis of SANS data from PIA/ionic liquid constructs surprisingly shows that the ionic liquid penetrates the polyimide skeleton. This unexpected structure clearly impacts charge transport and therefore performance of the aerogel as a battery component. This mixing behavior must be more fully understood to rationally utilize these promising materials in devices and further experiments are planned to elucidate the impact of polyimide and ionic liquid structure, as well as fabrication procedure on the pore size, structure, and mixing behavior in PIA/ionic liquid aerogels. These results therefore broaden the characterization tools of polymeric aerogels and provide pathways to correlate a broad range of their structural characteristics to their performance.
Experimentally exploring the molecular exchange in polyelectrolyte complexes is crucial to understanding the kinetic behaviors of many ionic systems. Polyelectrolyte complex (PEC) micelles are a type of nanoscale assemblies whose core is usually composed of ionic complexes and corona is constituted by neutral and hydrophilic polymers. Here, we present the employment of time-resolved small-angle neutron scattering (TR-SANS) technique to assess the chain exchange rate in polyelectrolyte complex micelles in aqueous solutions. The aim is to explore the dependency of the molecular exchange rate on polymer block length, system temperature, and solution salinity. We investigate two micelle systems that are prepared through the ionic complexation between poly (styrene sulfonate) (PSS) and a polypeptide, poly (ethylene oxide)-block-poly (L-lysine) (PEO-b-PLL), or a synthetic diblock polyelectrolyte, poly (ethylene oxide)-block-poly (vinyl benzyl trimethyl ammonium chloride) (PEO-b-PVBTMA). Neutron contrast is obtained by deuterium labeling the PVBTMA block and PSS block. Measurements performed up to 34 hours after the mixing of deuterium-rich micelles and hydrogen-rich micelles imply that the PEC micelles may not exchange molecules with their surroundings due to the strong ionic interaction between oppositely charged groups. Neither the elevation of system temperature nor increase of solution salinity, two common ways to weakening the strength of electrostatic interactions, seem to unlock the molecular exchange at the experimented time scale. We postulate that it is the large energy barrier stemming from the breakup of ionic pairs in polyelectrolyte complexes that prevents the chain expulsion or micelle fusion from happening. We anticipate these findings would provide fundamental insights on the origin of morphological complexities and nonequilibrium phenomena in polyelectrolyte-based self-assemblies.

2:00 PM MT04.09.02
QENS Insights on the Nanoscopic Origin of Rheological Properties in Some Well-Dispersed Polymer Nanocomposites
Antonio Faraone1 and Erkan Senses2; 1National Institute of Standards and Technology, United States; 2KOÇ University, Turkey

Polymer nanocomposites (PNCs) with attractive polymer–nanoparticle (NP) interactions, are often reported to disperse individually, enabling the investigation of interfacial effects on the rheological properties without contribution from particle percolation. By taking advantage of selective isotope labeling of the chains, neutron scattering techniques uniquely allow the possibility of investigating the structural and dynamical properties of the polymers in the matrix. In particular, high-resolution QuasiElastic Neutron Scattering (QENS) techniques, such as backscattering and Neutron Spin Echo, allow directly observing the chain motions at the nanoscale by simultaneously accessing a broad range of time-scale (from sub-nanoseconds to hundred nanoseconds), and length-scales (from monomer size to entanglement mesh sizes); specifically important for polymers are the localized fast dynamics on sub-monomer level, the segmental dynamics at the monomer level and the entangled/collective dynamics at larger scales. These information, as well as those obtained using X-ray Photon Correlation Spectroscopy (X-PCS), provide microscopic insight relevant for the understanding of the rheological properties of the PNC.

Here, I will present results on the nanoscale dynamics of polymer chains in composites with dynamically asymmetric interphases, [1] with NPs of sizes comparable to that of the polymer coils in the matrix, [2] and which have been subject to large deformation. [3]


2:15 PM MT04.09.03
Neutron Scattering Investigations on Structure and Dynamics of Architecturally-Engineered All-Polymer Nanocomposites
Erkan Senses1, Madhusudan Tyagi2 and Antonio Faraone2; 1Koc University, Turkey; 2National Institute of Standards and Technology, United States

Recent advances in synthetic chemistry made it possible to precisely control the topology of polymers that determines many of their physical properties. Ring, star, comb, bottlebrush and hyperbranched polymers exhibit structural relaxation that is not observed in their linear chain counterparts. In particular, star shaped polymers in which many linear chains share a common center are particularly interesting as the monomer density towards the center increases dramatically at high functionalities, making a portion of a star macromolecule dense and impenetrable, akin to hard-spheres. Thus, depending on the number and the length of arms, these polymers can
display both soft and hard nanoparticle character, making them ideal to study the effect of interphases in polymer nanocomposites. In our work [1], we used high-glass transition temperature (\( T_g \)) deuterated star shaped polymers as nanofillers and dispersed them in miscible low-\( T_g \) hydrogenated linear matrices to create a new kind of polymer nanocomposites in which the interpenetration between the fillers and the matrix, and therefore, the bulk rheological properties, are systematically varied via filler architecture at the same particle concentration. The resulting ‘architecturally engineered’ nanocomposites transition from the well-known simple linear blends to conventional hard sphere-polymer nanocomposites. We investigated these nanocomposites using static (SANS) and quasielastic neutron scattering (backscattering and spin-echo) measurements over a wide range of time and length scales in the glassy and melt state of the composites. The localized and segmental dynamics as well as chain-chain entanglements are all modified by compactness of star-shaped fillers. The observed microscopic changes manifest at the macroscopic level as softening and stiffening depending on the functionality and sizes of the macromolecules, thus offers a novel approach for tuning the physical properties of polymer based nanocomposites for advanced materials applications.


2:30 PM MT04.09.04
Bicontinuous Structure Gel from Binary Solvent Spinodal Decomposition Stabilized by Nanoparticles Jamming within One Liquid Phase Yuyn Xi\(^1,2\) and Yun Liu\(^1,2\); \(^1\)National Institute of Standards and Technology, United States; \(^2\)University of Delaware, United States

In this work, nanoparticles with preferential wetting to one of the liquid phases are demonstrated to arrest the spinodal decomposition of binary solvent mixture. A physical gel is formed and thus termed as solvent segregation driven gel (SeedGel). Small angle neutron scattering (SANS) experiments are conducted to identify the partition of particles by contrast matching the scattering length density of one liquid component to that of the nanoparticles. During the solvent phase separation, nanoparticles are found to be jammed within the phase that is rich in one of the liquid components. Compared to bicontinuous interfacially jammed emulsion gel (Bijel), SeedGel greatly relaxes the rigid restriction on the neutral wettability of the nanoparticles to the two solvents. Additionally, SeedGel shows reversible thermal response to quasi-static temperature ramping. The multi-length scale characterizaton by SANS and ultra-small angle neutron scattering (USANS) reveal that both the particle-particle distance and the domain size can be directly manipulated by temperature change and are strongly correlated with the gel transition. The SeedGel formation mechanism is also applicable to sub-10 nm particles, which possesses a great potential to link the self-assembled structure with the unique properties of small particles, such as quantum dots. Moreover, SeedGel can be molded to various shapes due to the enhanced mechanical strength. Subsequent drying of the solvents results in nano-porous medium up to centimeter size with neither nanometer nor micrometer cracking. In conclusion, a new mechanism of arresting liquid-liquid spinodal decomposition with colloidal particles is proposed. The strategy for preparing SeedGel can serve as a versatile, yet simple method to assemble particles to porous materials that can be implemented to various applications that favor high surface area.

2:45 PM MT04.09.05
Application of Artificial Intelligence and Machine Learning for Accelerated Data Collection and Analysis of Small Angle Neutron Scattering Changwoo Do\(^1\), Ming-Ching Chang\(^2\), Yi Wei\(^2\) and Wei-Ren Chen\(^2\); \(^1\)Oak Ridge National Laboratory, United States; \(^2\)University at Albany, State University of New York, United States

Pursuing hardware upgrades to provide brighter beams for material studies has been the paramount goal of every neutron scattering facility. Here, we present an alternative route to circumvent the limitation of neutron flux using recent advancements in artificial intelligence (AI), namely image super-resolution deep convolutional neural network (CNN). The feasibility of accelerating data collection has been demonstrated by using small angle neutron scattering data collected from the Extended Q-range Small Angle Neutron Scattering (EQ-SANS) instrument at Spallation Neutron Source (SNS). Data collection time can be reduced by increasing the size of binning of the detector pixels at the sacrifice of resolution. High-resolution scattering data is then reconstructed by using AI deep super-resolution learning method. This technique can not only improve the productivity of neutron scattering instruments by speeding up the experimental workflow but also enable capturing kinetic changes and transient phenomenon of materials that are currently inaccessible by existing neutron scattering techniques. Then, we will show how Machine Learning can be used to assist users in selecting appropriate scattering models.
3:00 PM BREAK

SESSION MT04.10: Bio-Materials
Session Chair: Yun Liu
Thursday Afternoon, December 5, 2019
Hynes, Level 2, Room 207

3:30 PM *MT04.10.01
Towards Understanding the Role of Lipid Complexity in Tuning Biomembrane Properties
Elizabeth Kelley; National Institute of Standards and Technology, United States

A 5 nm thick membrane separates the cell from its surrounding environment. Life places extreme demands on the material properties of these thin membranes by requiring that they are both rigid enough to define the cell structure yet flexible enough to undergo dramatic changes in cell shape during processes like endocytosis and cell division. In turn, the properties of the biomembranes are determined by the unique characteristics of the thousands of chemically distinct lipid molecules that make up the membrane. A long-standing challenge in biophysics is to link the complex and highly regulated lipid diversity to the membrane properties and ultimately cell function. This talk will highlight new insights from neutron scattering towards understanding the role of lipid diversity in tuning the properties of model biomembranes. We will demonstrate how subtle changes in lipid composition, such as mixing hydrophobic tail lengths or adding charged headgroups, can have significant and unexpected effects on the membrane elastic properties. The results reveal the complex and interwoven relationship between lipid membrane composition, structure and dynamics.

4:00 PM *MT04.10.02
Biomimetic Lipid Membranes—A Neutron Scattering and Simulations Perspective
Rana Ashkar1,1, Milka Doktorova2,3, Haden Scott4, Frederick Heberle4, Elizabeth Kelley5, Michihiro Nagao5,6, Jan-Michael Carrillo5, Bobby Sumpter7, Francisco Barrera4, George Khelashvili3 and John Katsaras7; 1Virginia Tech, United States; 2University of Texas Health Center at Houston, United States; 3Weill Cornell Medical College, United States; 4The University of Tennessee, United States; 5National Institute of Standards and Technology, United States; 6Indiana University, Bloomington, United States; 7Oak Ridge National Laboratory, United States

Lipid bilayers, the main matrix of cell membranes, host a wide range of vital biological processes and are ubiquitous in a variety of research areas at the interface of biophysics, health care, and biotechnology. In order to understand the function of lipid membranes and fully utilize their potential in pharmaceutical and biotechnological applications, it is imperative to understand the phenomena that control key membrane functions, such as domain formation and protein recruitment. Among such phenomena, membrane dynamics, manifested in mechanical and diffusive membrane properties, remain poorly understood despite evidence of their active role in various cellular processes. This talk will focus on recent advances in neutron scattering characterization and MD simulations for interrogating molecular and collective dynamics in lipid membranes and their response to cholesterol content, lateral rearrangement, and protein binding events. The synergistic integration of neutron scattering and simulations, and the inherent capabilities of both techniques to probe selective dynamics, is offering significant insights into the delicate spatiotemporal functions of biomimetic lipid membranes.

4:30 PM MT04.10.03
Tuning Interactions between Modular Coiled Coil Bundles via Computational Sequence Design—A Small Angle Neutron Scattering (SANS) Study
Nairiti J. Sinha1,2, Rajkumar Misra1, Rui Guo3, Christopher J. Kloxin1, Jeffery G. Saven1, Grethe V. Jensen1 and Darrin J. Pochan1; 1University of Delaware, United States; 2National Institute of Standards and Technology, United States; 3University of Pennsylvania, United States

Computational sequence prediction is a powerful design tool that has enabled discovery of non-natural peptide sequences that can assemble into coiled coil bundles that are antiparallel homotetramers containing strategically-placed solvent-exposed amino-acid side groups and chemically-reactive complementary functional groups. By taking advantage of the tunable interaction landscape coupled with orthogonal chemical-assembly pathways, the
artificial coiled coils can be utilized as tunable anisotropic *Molecular Legos* or modular building-blocks to construct artificial biomaterials that display a rich hierarchical nanostructure. In this talk, we will discuss the design and construction of new sequences of robust 4 nm x 2 nm cylindrical coiled coil forming peptides that have been computationally designed to carry different net charge as a result of the dissociable amino-acid side-groups in the peptide sequence. Thus, an entire spectrum of charged bundles has been studied, consisting of bundles that carry a high net positive charge (+32) to those with a high net negative charge (-32) in order to systematically investigate the impact of the net charge and also local charge distribution on inter-bundle interactions as a function of solution conditions such as pH and ionic strength. We have employed Small Angle Neutron Scattering (SANS) extensively to characterize the computationally designed bundle dimensions and inter-bundle interactions since SANS is uniquely suited to studying soft-matter systems in their native solution state in a non-intrusive and non-destructive manner. SANS along with Small Angle X-ray scattering (SAXS) has yielded insight into the rich interaction landscape of charged bundles at the nanoscale. We show that all bundles at dilute concentrations yield a form-factor scattering profile that can be fit using a cylinder model to extract the bundle dimensions. The experimentally measured dimensions are directly compared to the expected dimensions calculated using the bundle PDB file. As the bundle concentration increases, a correlation peak or ‘ionomer peak’ is observed in the scattering profile, the strength of which increases with net charge and bundle concentration and is responsive to the presence of salt. The electrostatic repulsion interactions between bundles resulting in the correlation peak are modeled using both Effective Hard-Sphere (EHS) and the Hayter-Penfold (HP) structure factor, with the latter giving better fit results especially for highly charged bundles at higher concentrations. Lastly, we will show that the coiled coil bundle stability and solubility in water, i.e. the formation of stable coiled coil homotetramers in aqueous solution is dependent on a number of factors such as the net charge on the bundle, type of charge (negative versus positive), temperature and ionic strength, which is characterized for a specific peptide sequence via contrast-matching SANS measurements.

4:45 PM MT04.10.04
Internal Dynamics and Hydrodynamics of the NISTmAb 8670 and Its Comparison with Industrial Monoclonal Antibodies Jannatun Nayem1,2, José R. Villanueva-Valencia3, Norman Wagner1 and Yun Liu2,1; 1University of Delaware, United States; 2National Institute of Standards and Technology, United States; 3University of Guanajuato, Mexico

Internal dynamics such as the movements of hinge-bending domain motions of therapeutic monoclonal antibodies (mAb) are crucial for important bio-functionalities during targeted immune therapies. However, determining these functional dynamics via traditional spectroscopic techniques (e.g. NMR) at the spatial and temporal scales pertinent to a mAb is highly nontrivial primarily due to their anisotropic shape and large molecular weight. Currently, the commonly used theories have inaccurate assumptions and often do not apply to anisotropic proteins at high concentrations. Here, we have established a substantiated methodology using a unique combination of the neutron spin echo spectroscopy, an accurate dynamic decoupling theory, and the semi analytic colloidal theories for dilute suspensions to probe the internal dynamics of NISTmAb, RM 8670. Our findings show that at the short time limit when the contribution of the rotational motion is negligible, the effective diffusion coefficients obtained by NSE is intrinsically different from the long-time diffusion coefficient obtained by the dynamic light scattering, which is primarily due to the anisotropic shape of a mAb. A prominent difference between a rigid-body mAb diffusion and the overall effective diffusion of a NISTmAb at 3-5 nm length scales is observed. This concludes that the intra-particle domain motions contribute ~15% to the total effective diffusion of a NISTmAb within the NSE correlation time window. Our analysis also provides a theoretical description of the hydrodynamic parameter. The hydrodynamic effects of many different mAbs were evaluated and a universal method was established that describes the concentration dependence of the diffusion coefficients with different types of solution interactions. To our surprise, when the hydrodynamic volume fraction is considered, the hydrodynamic parameters collapses from values ranging from 7.6 to 11.2 to that of 2.5 to 3.3 approaching the hard sphere (HS) value, 1.83. This elucidates the importance of hydration and shapes in solution stability. Though a qualitative agreement is achieved between NSE experiments and atomistic molecular dynamic simulations, their intra-particle dynamics are overestimated. We attribute the difference to the force fields and water models used in the simulation. The findings of this work provide foundation for future theoretical and simulation work for predicting diffusion properties and their related macroscopic solution properties for proteins with various shapes, sizes, and interactions.
Segregational Behavior of d-Transition Elements at Different Grain Boundaries in Tungsten—First-Principles Study

Ahmed Tamer A. AlAsqalani1,2 and Tomas Polcar1; 1University of Southampton, United Kingdom; 2Assiut University, Egypt

Owing to their excellent physical properties such high melting temperature, significant high-temperature strength and good thermal conductivity, tungsten and tungsten-based alloys are promising candidates in various applications. They are commonly used as potential plasma-facing material in fusion reactors and electrical contacts. In literature, several experimental observations by TEM revealed the improved thermal stability of W-based binary alloys upon addition of Ti, Ag and Ta atoms [1,2]. These observations have been attributed to the segregation of solute atoms to grain boundaries (GB). The propensity for segregation of these alloying elements is different as indicated by formation of enrichment/depletion regions around GBs. However, the segregants behavior, enhanced stability and its underlying mechanisms are not fully understood. In this work, an extensive DFT calculations have been performed to explore the GB morphological effects on the segregation behavior of Ti, Ag and Ta as examples of 3d, 4d and 5d elements, respectively. Six different GB structures consisting of low/high-angle symmetric tilt [001] GBs are considered. It is found that Ag atoms exhibit substantial tendency of segregation to both types of GBs. In contrast, both Ta and Ti atoms exhibit preferential propensity to segregate to high-angle STGB. The highest segregation energy values obtained for Ti, Ag and Ta are -0.017, -1.53 and -0.2, respectively. The change of metallic bond nature between solute and W atoms are responsible for the variation of the segregation energy for each element. Furthermore, segregation energy results indicate that while Ag atoms tend to segregate within and around the GBs plane, whereas Ti and Ta atoms energetically prefer to reside within the GB core. This behavior was explained using density of states (DOS) and charge transfer analysis. We found that d-d hybridization and charge transfer between solute and host atoms play important role in determining segregation/anti-segregation character for each GB site. A comparison of our DFT results with existing thermodynamical and atomistic models have been made and some improvements should be included for further development.

References

SESSION MT05.01: Overview of Emerging FIB-Based Research
Session Chairs: Frances Allen and Silke Christiansen
Monday Morning, December 2, 2019
Hynes, Level 2, Room 204

10:30 AM *MT05.01.01
Unravelling the Origins of Functionality through Correlative Multimodal Chemical Imaging Olga S. Ovchinnikova, Anton V. Ievlev and Alex Belianinov; Oak Ridge National Laboratory, United States

The key to advancing energy materials and biological systems is to understand and control the structure and chemistry at interfaces. While much of the dynamic chemistry can be studied on macro-scale systems, there is a lack of means to localize chemical measurements and correlate them to nanoscale structure of the material. Through a unique merger of advanced scanning probe and ion microscopy with mass spectrometry techniques rooted in innovative data processing and control algorithms, we are now able to understand the interplay between chemical and physical functionality at the fundamental length scales using multimodal chemical imaging. This multimodal imaging transcends existing techniques by providing nanoscale structural imaging with simultaneous chemical analysis. Here, I will discuss how we have developed and used this capability to visualize dynamic material transformations at interfaces, to correlate these changes with chemical composition, and to distill key performance-centric material parameters. One exciting capability is to drive materials away from equilibrium at the nanoscale with highly localized fields. This allows field confinement effects on localized chemistry in materials to be locally probed, especially at interfaces. This in turn yields direct information on key energy related questions such as electron and ion motion distribution and transport at and between interfaces. Overall, I will focus on ways to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental and molecular characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

11:00 AM *MT05.01.02
Exploring a FIB-SEM Research Data Ecosystem Keana Scott, Alline Myers and Peter Bajcsy; National Institute of Standards and Technology, United States

In the past decade, focused ion beam scanning electron microscopy (FIB-SEM) has transformed from a niche technique for semiconductor and materials science research into a broadly useful processing, analysis and characterization technique of choice for many disciplines. Although, Ga+ FIB-SEM instruments are the most commonly used FIB-SEMs, plasma FIB-SEMs have enabled routine 3D structural analysis of (relatively) large volumes. And the availability of multiple ion species is enabling application specific uses of different FIB instruments and renewing interests in techniques such as FIB-SIMS (Secondary Ion Mass Spectrometry). Additionally, advances in the instrument hardware and software have resulted in increased system stability and robustness, as well as ease of use and maintenance that have significantly lowered the barrier to entry into FIB-SEM techniques. However, as the FIB-SEM instrumentation becomes increasingly automated and complex, the challenges associated with the resulting data volume and complexity are increasing. The current trend towards open
and re-usable data also requires added effort to provide necessary meta data and curate the research data into a consumable format.

In this presentation, examples of materials characterization applications that are uniquely enabled by FIB-SEM are described, and how the resulting data fits into various overlapping research data ecosystems is explored [1]. For example, a material characterizations study such as carbon fiber ultrastructure analysis can generate a large number of images. These image data sets can be used and re-used by materials scientists to explore structure property relationships while the same set of data, with an appropriate meta data, can be re-purposed as test data sets by computational imaging scientists for their algorithm development. We will explore some of the currently available data infrastructures supporting the findable, accessible, interchangeable, and reusable (FAIR)[2] data ecosystems and how the FIB-SEM community can effectively adapt these.


11:30 AM *MT05.01.03
Ultra-High Precision Engineering of 2D Nanomaterials Using Energetic Focused Ion Beam Technologies
Songkil Kim; Pusan National University, Korea (the Republic of)

An emerging paradigm in engineering is the design of materials to act as simple building blocks in order to achieve complex functionality at multiple scales. The discovery of new nanomaterials such as low-dimensional nanomaterials, new metal alloys and functional polymers, has been leading these developments, and more material and engineering design options have been given to scientific and engineering societies, with demands to overcome the challenges of the current existing technologies. However, challenges persist in integration of nanomaterials to device architectures, control of material properties, and realization of functional devices, for practical applications. To tackle these challenges, it is crucial to develop multidisciplinary, integrated approaches, to enable precise manipulation of these materials compatible with integrating them into existing engineering systems as well as for the development of new concepts of device architectures.

Developments of cutting edge technologies in manufacturing enabled to programmatically transform materials into real engineering components by ‘direct digital printing’ with high degree of controls, making it possible to manufacture complex multi-dimensional components on demand in micro- and macro-scales. As the similar concept of manufacturing, directing matter on atomic-to-nanoscales, termed as ‘focused electron or ion beam induced processing’, is being developed to achieve atomically precise manufacturing of nanomaterials and 3D structures in solids, liquids and at interfaces. Focused electron or ion beam induced processing is a resist-free advanced nanomanufacturing technique for ‘direct-write’ processing of a wide range of structural and functional nanomaterials. Focused charged particle beam-based techniques involve in electron-matter or ion-matter interaction, enabling additive/subtractive nanofabrication as well as doping and functionalization of nanomaterials, along with the in-situ nanoscale imaging in the scanning or transmission electron/ion microscope environments. Thus, these techniques provide unique opportunities in materials design to address many challenges in nanoengineered systems. In this research presentation, recent advancements of energetic focused ion beam technologies will be introduced, especially for their applications to direct manipulation of 2D nanomaterials such as graphene and molybdenum disulfide (MoS2). Among the several technological developments, the synergistic theoretical and experimental research work will be presented to introduce the promise of the focused helium ion beam and argon molecular cluster ion beam technologies in atomic manipulation, multi-mode nanofabrication, defect engineering and chemical imaging as a next-generation nanofabrication tool.

SESSION MT05.02: Novel FIB Sources and Nano-Fabrication
Session Chairs: Frances Allen, Alex Belianinov and Shane Cybart
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 204

1:30 PM *MT05.02.01
New Light and Heavy Ion Beams from Liquid Metal Alloy Ion Sources for Advanced Nanofabrication and Ion Implantation Paul Mazarov, Lars Bruchhaus, Fabian Meyer, Achim Nadzeyka, Torsten Richter, Ralf Jede, Yang Yu, Jason E. Sanabia, Lothar Bischoff, Wolfgang Pilz, Nico Klinger, Gregor Hlawacek and Jacques
Focused Ion Beam (FIB) processing has been developed into a well-established and still promising technique for direct patterning and prototyping on the nm scale, high resolution imaging or high resolution ion lithography\(^1\). Exploring the Liquid Metal Alloy Ion Sources (LMAIS) potential represents a promising alternative to expand the global FIB application fields. Thanks to this, nearly half of the elements of the periodic table are made available in the FIB technology as a result of continuous research in this area during the last fifty years\(^2\). Recent developments could make these sources an alternative technology feasible for nanopatterning challenges.

Concerning ion beam resolution and minimization of unwanted damage, light ions like He or Li are preferred candidates. Liquid metal alloy ion sources (LMAIS) with a lifetime of more than 1000 µAh on the basis of Ga\(_{35}\)Bi\(_{60}\)Li\(_{5}\) and Sn\(_{95}\)Li\(_{5}\) alloys were developed, characterized and tested in a commercial mass-separated VELION FIB-SEM system (Raith GmbH)\(^3\). In the case of Li ions from the mass separated FIB a lateral resolution of 5.6 nm could be obtained in first experiments and the sputter yield was determined to 0.4 for 35 keV Li ions on Au. For reference, the helium ion microscope (HIM) has a lateral resolution of about 0.5 nm and 1.8 nm, for He and Ne respectively, He has a sputter yield of 0.1\(^4\). For sub-10 nm focused ion beam fabrication and microscopy, the GaBiLi-FIB or the SnLi-FIB could therefore be considered as alternatives to the HIM with the benefit of providing additional ion species in a mass separated FIB without changing the ion source.

In this contribution the operation principle, the preparation and testing process as well as prospective domains for modern FIB applications will be presented\(^1,5\). As an example we will introduce a GaBiLi LMAIS in detail. It enables high resolution imaging with light Li ions and sample modification with Ga or heavy polyatomic Bi clusters, all coming from one ion source. Moreover we will discuss the main properties of a modern LMAIS like long life-time, high brightness and stable ion current. The physical basics and experimental results of LMAIS, their physical properties (I-V characteristics, energy spread) and questions of the preparation technology using elementary as well as binary and ternary alloys as source material will be covered.


2:00 PM *MT05.02.02*  
**Gas Assisted Plasma FIB—A Delaying Tool** Anne Delobbe\(^{1,2}\), Gregory Goupil\(^2\), Sharang Sharang\(^3\) and Pascal Gounet\(^4\); \(^1\)Tescan Orsay Holding, Czechia; \(^2\)Orsay Physics, France; \(^3\)TESCAN Brno s.r.o., Czechia; \(^4\)ST Microelectronics, France

Initially launched in 2011 by Orsay Physics, Xe Plasma FIB-SEM is currently used to save operation time for many applications which were up to now realized by Ga FIB. Ga FIB and Xe FIB instruments are the go-to tools for chip material analysis in the semiconductor industry for applications like TEM lamella preparation, circuit editing, and physical inspection by sample preparation.

With the downscaling of the technologies, delaying, which consists of perfect layers by layer de-processing, is one particular very demanding application which was developed using the plasma FIB. The goal is to localize a failure in a fully integrated circuit included in a few hundreds of nanometers thick area. The demand for suitable and nano-accurate polishing techniques are in growing demand to reveal buried interest areas with the assurance of matching to the reference sample with no modification due to the preparation technique used. Many trials have been attempted to use a FIB to remove homogeneously different metal/insulator layers. A solution is to work on ion species, ion energies, spot size, scanning strategy… But ion beam etching alone is not able to achieve planar surface on interconnect technologies. The milling rate of different materials is too unequal and their architecture is too tricky to reach deep layers with the minimum roughness on the sample. Thus, due to a constant evolution of the material used in the semiconductors and their intrinsic tangle at the nanometric level, it becomes an increasingly pressing demand to reach, without alteration, a specific area in such complex structures. To overcome these artifacts, a solution is to control FIB milling rates of all the different as-constitutive elements of the SC’s surface by adding a specific chemistry near the area of interest during operation. In this perspective, we developed a new reliable, fast and accurate Gas Injection System (OptiGIS) and its devoted precursors. The chemistry used for homogeneous milling needs also to overcome the production of residues and particulates.
which are undesirable for electrical characterization and are caused by milling of surface materials such as the case of plasma FIB delayering. Conductive residues can redeposit on sample surface, shorting metal lines to one another and creating false electrical signals, while non-conductive residues may cover metal lines and result in bad electrical contact. To mitigate this issue, gases etchant are used in delayering process to produce volatile by-products when reacting with the surface easily removed by the vacuum pump instead of redepositing on sample surface. A successful Xe FIB delayering on sub-14 nm technology from metal 8 to transistor contacts in combination with special gas chemistry will first be presented.

In a second part, this case will be compared to the performance of this process with a Ga FIB. The differences between the two use cases will then be exposed for comparison.

Experimentally, top-down delayering of sub-14 nm technology nodes were performed with both Ga and Xe FIBs using special gas precursor. GIS was inserted to inject gas on to the area of interest. Suitable current density, beam shape and gas delivery was prepared to conduct planarity and the process was monitored using end point detection based on the SE signal being generated during the etching process. The parameters will be discussed.

In a third part the focus will be on the end pointing. This end pointing recognizes each peak as the metal layer and the trough as via layer which gives full control to the operator to start and stop the process in any layer of interest. A final fine polishing is performed once the specific layer is entered to get rid of residual precursor or carbonated compounds before the final analysis such as probing.

2:30 PM MT05.02.03
Comparison of Gallium and Neon Ion Beam Milling on GaAs Deving Xia\textsuperscript{1}, John A. Notte\textsuperscript{1}, Ying-Bing Jiang\textsuperscript{2} and Brett Lewis\textsuperscript{1}; \textsuperscript{1}Carl Zeiss, United States; \textsuperscript{2}The University of New Mexico, United States

Microscale and nanoscale structuring are important processing steps for prototyping advanced semiconductor devices from III-V materials such as GaAs and GaN. For example, the self-assembly of group III metallic nanodots and other nanostructures of III-V compound semiconductors has become a topic of much interest \cite{1}. Also, the controlled growth of III-V materials shows interesting optical qualities with the prospect of negative index of refraction materials \cite{2}. Traditionally, ion beam milling with a gallium focused ion beam instrument (Ga-FIB) has been used to structure these materials. The same Ga-FIB is also routinely used for sample preparation for subsequent transmission electron microscopy (TEM) imaging or analysis steps. However, the use of the Ga-FIB can significantly alter these materials through ion beam induced damage effects, including the implantation of gallium. In some cases, there is evidence of Ga-rich “droplets” that seem to form on the surface of these materials.

The ZEISS ORION NanoFab serves as a useful platform for the prototyping of advanced III-V materials for semiconductor, optical, and other device researches. This instrument provides a traditional Ga-FIB, but helium and neon focused ion beams with 0.5 and 2.0 nm probe sizes (respectively). Together these ion beams can offer sub-nanometer imaging resolution, as well as device fabrication with no artifacts associated with gallium residue. The same platform also offers secondary ion mass spectrometry (SIMS) based elemental analysis with a magnetic mass spectrometer, and a lateral resolution on the order of 15 nm.

In this talk, we compare the effects of Ga and Ne ion beam milling into a GaAs substrate. These two ion beams are used over a range of areal dosages (ions/cm\textsuperscript{2}) to explore the milling rate, milling artifacts, and pattern formation. On the same platform, the helium focused ion beam is used to assess the milling rate, and for detailed examination of the milled patterns and surface morphology. As expected, experimental results show that the milling rate with a 30 keV Ga-FIB is much faster than that with a Ne ion beam. However, the gallium beam tends to induce a progressive formation of Ga-rich nanodots or nanodroplets on the bottom and sidewalls of the milled pits. In contrast, when using a Ne beam with the same 30 keV energy, the bottom surfaces of the milled pits show a porous texture. With a lower Ne ion beam energy, such as 10 keV, the bottom surface appears to be much less porous without any significant decrease of milling rate. The neon beam with its small probe size and easy operation at low probe currents, enables high fidelity patterning of the GaAs. We further examine the milled samples using TEM to assess damage, implantation, and structural changes below the surface. Further investigations include the effects of an etchant gas (XeF\textsubscript{2}) for material removal using both the Ga and Ne beams. Additional experimental results include the milling of GaN substrates with both Ga and Ne ion beams.

Ne-FIB Fabrication of Tips for Atom Probe Tomography
Frances I. Allen\textsuperscript{1,2}, John A. Notte\textsuperscript{3}, Paul T. Blanchard\textsuperscript{4}, Norman A. Sanford\textsuperscript{4}, Ruopeng Zhang\textsuperscript{1,2}, Andrew M. Minor\textsuperscript{1,2} and Soeren Eyhusen\textsuperscript{3}; \textsuperscript{1}University of California, Berkeley, United States; \textsuperscript{2}Lawrence Berkeley National Laboratory, United States; \textsuperscript{3}Carl Zeiss Microscopy, United States; \textsuperscript{4}National Institute of Standards and Technology, United States

Focused ion beam (FIB) milling using gallium ions is routinely used for the site-specific preparation of sharp tips for Atom Probe Tomography (APT), in which atoms are evaporated from the tip and detected using a mass spectrometer to enable 3D reconstruction of the needle-shaped volume atom by atom. Artifacts from the Ga-FIB milling process include near-surface implantation of gallium and the accumulation of gallium along grain boundaries and between phases. With the advent of novel FIB sources, alternative ion species for precision milling are now available. For example, Ne-FIB-milling as the final polishing step in the preparation of electron-transparent samples for Transmission Electron Microscopy (TEM) has been demonstrated as an alternative approach for samples in which contamination effects from gallium cannot be tolerated \cite{1}.

Here we use the neon beam generated by the gas field-ionization source of a Helium/Neon Ion Microscope (HIM/NIM) for the final trimming of APT tips that have been extracted from bulk samples by Ga-FIB lift-out. Materials investigated include a titanium alloy and a sample comprising aluminum/aluminum oxide layers on a silicon substrate. High-resolution TEM analysis of Ne-FIB-milled tips reveals that implanted gallium from the pre-milling steps is successfully removed. A thin amorphous layer of < 5 nm is observed, beneath which the crystallinity of the tip is well-preserved. The experimental workflows for the Ne-FIB technique will be discussed and the 3D reconstructions from the APT measurements presented.

\begin{thebibliography}{1}
\bibitem{1} T. C. Pekin, F. I. Allen, and A. M. Minor, \textit{J. Microscopy}, 264 (2016) 59-63
\end{thebibliography}

**3:00 PM BREAK**

**3:30 PM *MT05.02.05*
Electro-Hydro Dynamic Ion Sources and Focused Ion Beam Machines
Jacques Gierak\textsuperscript{1}, Paul Mazarov\textsuperscript{2} and Lothar Bischoff\textsuperscript{3}; \textsuperscript{1}Centre de Nanosciences et de Nanotechnologies, France; \textsuperscript{2}Raith GmbH, Germany; \textsuperscript{3}Helmholtz-Zentrum Dresden-Rossendorf, Germany

In this talk we will review and detail the current status of EHD ion sources, also commonly referred as Liquid Metal Ion Sources, their development perspectives and their ever present expanding applicative domains. We will review the roots of this technology born in the early 70’s, deriving from space propulsion research, when physicists applied EHD phenomena onto liquid metal meniscus to create high brightness ion sources. Since then the LMIS qualities based on a remarkable brightness, excellent emission stabilities (current emission and emitting area invariance), ease of operation, lifespan and compactness small size were at the origin of the focused ion beam (FIB).

As a deeply involved team in the pursuing quest aiming at investigating the full applied potential of the direct-write Focused Ion Beams technology since the mid-80’s, we will analyze and comment the never interrupted major effort invested around the world aiming at developing alternative ion sources. As a complement to the development of high current sources or atomic-sized emitters, we will show that high performance Liquid Metal Ion Sources and Liquid Metal Alloys Ion Sources exhibit definitive advantages at the prototyping level.

We will analyze, quantify and describe the potential gains still to be expected from the widely used gallium LMIS and other alloy ion sources, that add a large number of ion species and patterning schemes.

In conclusion we will summarize our vision on the future of FIB technology based on electro-Hydro Dynamically (EHD) driven emitters operating in the cone-jet mode, both in terms of performances, versatility and on the science frontiers these might help to push. My presentation will be an attempt to provide an overview on this FIB continuous evolution and future capabilities.


**4:00 PM MT05.02.06**
Focused Ion Beam Preparation of Strain Microscopy Samples for Coherent X-Ray Imaging of 3D Nano-Scale
Structure and Lattice Strain Felix Hofmann1, Nicholas Phillips1, Gareth Hughes1, James Douglas1, Ross Harder2 and Wenjun Liu2; 1University of Oxford, United Kingdom; 2Argonne National Laboratory, United States

Focused Ion Beam (FIB) machining has emerged as a transformational tool for microscopy, making it possible to extract samples of particular features of interest with high spatial specificity. A challenge in this context is the damage FIB inevitably causes and the consequences this damage has for subsequent microscopy. Multi-reflection Bragg Coherent Diffraction Imaging (MBCDI) is an exciting, new coherent X-ray diffraction technique that allows the imaging of 3D structure and lattice strain in crystalline materials with 10s of nanometers 3D spatial resolution. However, to function, MBCDI requires samples less than one micron in size. This constraint has thus far limited MBCDI to materials that naturally form isolated micro-crystals of this size. The vast majority of technologically important materials have thus remained out of reach.

Here we present a new FIB-based fabrication approach that allows the manufacture of micron-sized strain microscopy samples for MBCDI. Importantly these can be manufactured with high spatial specificity, such that they contain specific defects or microstructural features of interest. A very important challenge is how to manage the damage cause by FIB milling. Our previous MBCDI work on initially pristine gold micro-crystals showed that milling with 30 keV Ga ions can cause large lattice strains that extend up to hundreds of nanometers into the sample. While these strains can be reliably probed using MBCDI, they obscure the subtle strain fields associated e.g. with crystal defects of interest. Using MBCDI we demonstrate that the strains from high energy FIB milling can be reliably removed by low energy FIB polishing. This is a key aspect of the new FIB-based strain microscopy sample preparation.

Several examples of strain-microscopy sample preparation using FIB will be presented, concentrating on materials not normally suited to coherent X-ray diffraction imaging. We show that, using the new approach, the full, 3D resolved strain fields of specific, pre-selected dislocation structures can be probed. We can also study in detail irradiation-induced lattice strains in samples extracted from macroscopic armor for future fusion reactors, or local strains in a nickel superalloy. These examples highlight the general applicability of the new FIB preparation routine, transforming MBCDI to a nano-scale microscopy tool for real-world engineering materials.

4:15 PM MT05.02.07
Comparison of Several Focused Ion Beam Fabrication Methods for Quantitative In Situ Small-Scale Mechanical Testing Yang Yang1, Frances I. Allen1,2 and Andrew M. Minor1,2; 1Lawrence Berkeley National Laboratory, United States; 2University of California, Berkeley, United States

Quantitative in situ TEM small-scale mechanical testing has attracted broad interest over the past 20 years. Through these techniques, one can not only directly visualize the microstructure/defects evolution during mechanical deformation, but also measure the mechanical properties of nanostructured materials. Typically, the small-scale coupons for these tests are fabricated by Gallium focused gallium ion beam (Ga-FIB). It is well-known that Ga-FIB may introduce radiation damage and gallium contamination at the sample surface. Although these artifacts may only exist at the surface layer which is usually less than 30 nm, their effects on the mechanical behavior may be significant. In addition, the sample geometry may also impact the measured mechanical properties. For example, it is difficult to control the length of the cylinder-shape pillar; thus, measuring strain accurately can be difficult. In this presentation, we will systematically compare several focused ion beam fabrication methods for quantitative in-situ small-scale mechanical testing, with an emphasis on the ion type (Ga, Ne, or Ar) and sample geometry (round-/square- shaped cross-section). We hope to provide insights into choosing appropriate FIB fabrication methods that enable more reliable quantitative in-situ small-scale mechanical testing.

4:30 PM MT05.02.08
Beam Exit Cross-Sectional Polishing (BEXP) and Functional SPM—New Approach for 3D Mapping of Physical Properties of Nanostructures Marta Mucientes1, Leonardo Forcieri1, Pamela Jurczak2, Mingchu Tang2, Huiyun Liu2, Yipin Gong3, Tao Wang3, Samuel Jarvis1, Kunal Lulla1 and Oleg V. Kolosov1; 1Lancaster University, United Kingdom; 2University College London, United Kingdom; 3The University of Sheffield, United Kingdom

The modern technology demands the miniaturization of devices and the discovery of novel materials, both requiring matching characterization methods possessing nanoscale resolution and able to the three-dimensional physical properties of these devices and structures. Scanning Probe Microscopies (SPM), could allow the nanoscale mapping
of the sample morphology, as well as local mechanical, electrical and thermal properties being a relatively easy to use and efficient tool for exploration of inorganic surfaces. However, studying 3D structures in SPM provides significant challenge, with mechanical sectioning of the samples ruled out as it creates too rough surface, focused ion beam (FIB) creates cuts that are usually too narrow for the SPM probing tip, as well as implanting Ga ions strongly modify the properties of the materials studied and damage the surface, with mechanical cleavage can only be applied to the narrow subset of epitaxial layers with minimal defects.

Here, we present the novel Beam Exit Cross-sectional Polishing (BEXP) approach, creating nanoscale near-atomically flat sections of layers from few nm to the surface down to several micrometres deep, and minimal damage to the sections device or material. BEXP uses triple broad 1 mm wide Ar-ion beams intersecting in the cut area and shaped by the edge mask to define a cut plane. This plane oriented in such a way that it intersects the sample surface at small negative angle, with beam exiting the sample (hence the BEXP name) keeping intact the sample surface. The glancing angle and inert nature of Ar results in minimal Ar-ions implantation and modification of the sample as well as fairly flat surfaces (roughness ~1nm RMS)\(^1\), providing optimal geometry for accessed via the material sensitive SPM\(^2,3\).

The BEXP has been implemented in the nanomechanical and electrical studies of III-V compound semiconductor structures commonly employed in the manufacturing of optoelectronic devices – photovoltaics, LED and lasers.\(^4\) Due to the shallow angle of the BEXP section, the projection of the multi-layered structures increases approximately 1 to 10 the thickness of the layers, facilitating the visualization of the material defects, such as, the propagation of the antiphase domains across the structure, creating a charge separation in multiple quantum wells - one of the key problems in the efficiency of the devices. SPM maps of nanoscale sections of GaN NWs on Si revealed the electron affinity dependence with the material thickness and unexpected domain reversal in individual NW. In summary, tandem of BEXP with materials sensitive SPM provide a very efficient tool for exploring 3D structure and physical properties of solid state materials with true nanoscale resolution.


4:45 PM MT05.02.09
Transfer of Sub-10 nm Patterns to Substrate Using Helium Ion Beam Lithography and Reactive-Ion Etch
Matthew Hunt\(^1\), S. Lewis\(^{1,2,1}\), N. Lee\(^1\), H. Alty\(^2\), J. Yang\(^{1,3}\), A. Wertheim\(^1\), G. DeRose\(^1\), Stephen Yeates\(^2\), Richard Winpenny\(^2\) and A. Scherer\(^{1,1}\), California Institute of Technology, United States; \(^2\)The University of Manchester, United Kingdom; \(^3\)Stanford University, United States

While focused ion beams (FIB) of light ion species such as He\(^+\) and Ne\(^+\) are often pursued for high-resolution, direct-etch patterning, their low sputtering rates – relative to heavier ion species like Ga\(^+\), Xe\(^+\) and Cs\(^+\) – limit such uses to low-volume-removal applications. In this work, we present two light ion FIB techniques that are useful for etched patterning on orders-of-magnitude larger scales than typical, while still maintaining the high-resolution capability (e.g. sub-10 nm for He-FIB and sub-20 nm for Ne-FIB) that is most attractive about them. In the first, helium ion beam lithography (HIBL) is used to create structures as small as 6 nm wide and 20 nm tall in silicon, spaced less than 20 nm apart, which represents a new lowest published benchmark for creating Si fins for e.g. FinFET technology. This is done by exposing a novel, metal–organic resist material with 35 keV HIBL, then transferring the pattern to the substrate with a pseudo-Bosch reactive-ion etch (RIE). Requisite exposure times are on the same order of magnitude as those needed in conventional 100 keV electron beam lithography (EBL), which makes producing sub-10 nm structures as scalable with HIBL as any other process is with EBL. The second technique involves the use of He- or Ne-FIB to create nanowires as thin as 20 nm, 60 nm tall, and as long as several millimeters. To do so, a sub-10 nm thick atomic layer deposition (ALD) hard mask is patterned by direct-etch FIB, followed by the transfer of the pattern through the underlying, thicker substrate material via RIE. Patterning times by this technique can be two orders of magnitude lower than are necessary to remove the same volume of material by direct-etch only. The benefits and drawbacks to these two nanofabrication techniques are discussed, as are their underlying mechanisms and potential applications.
SESSION MT05.03: FIB Property Engineering I
Session Chairs: Frances Allen, Alex Belianinov and Shane Cybart
Tuesday Morning, December 3, 2019
Hynes, Level 2, Room 204

9:00 AM *MT05.03.01
Local and Macroscale Property Control of Ferroic Thin-Film Materials with Ion Beams Lane W. Martin1,2;
1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

Ferroic materials including oxide ferroelectrics, magnets, and multiferroics are of great interest for a range of modern applications. What’s more, these materials stand poised to revolutionize next-generation applications, if we can determine ways to overcome inherent limitations in their function. Because of their complex chemistry, propensity for defect formation, etc. these materials – especially in the thin-film form required for many advanced applications – often have performance that lags behind that of their bulk counterparts. In turn, researchers working on advanced thin-film synthesis approaches have attempted to treat these ternary, quaternary, and more complex systems more-and-more like semiconductor systems. Efforts to make cleaner, more precise versions of these materials were envisioned to produce ever better properties – but alas, these efforts have not always play out as desired.

In recent years, however, it has been seen that we can borrow other lessons from the semiconductor community to control and improve the properties of these complex, functional materials. Namely, ion bombardment approaches are seeing a renewed interest as researchers better understand how ion beams can be used to manipulate the electronic and defect structures of materials and, in turn, how this affects the evolution of the physical properties. In this talk, we will explore recent efforts focused on the use of both low- (~30 keV) and high- (~3 MeV) energy ion beams can enable control of the concentration and type of defects in ferroic oxides and, in turn, how these beams can be used to enhance material properties. Using systems like helium-ion microscopes and pelletron accelerators, we are afforded access to a range of species and bombardment conditions. Specifically we will highlight examples of work done on materials such as the canonical ferroelectrics PbTiO3 and PbZr1-xTixO3, relaxor ferroelectrics such as (1-x)PbMg1/3Mg2/3O3-(x)PbTiO3, and the multiferroic BiFeO3. Here, among other things, we will show how the controlled introduction of ion-beam-induced knock-damage creates intrinsic defects that can, in surprising fashion, improve the electrical resistance (by orders of magnitudes) of these materials, how implantation and ion-beam-induced damage can provide a pathway to control local switching enabling emergent function like multi-state functionality, and how ion-beam-induced damage can even tune the competition of energies such that one can alter the ferroic nature of these materials. To end, we will discuss where these ideas could lead us next in using ion beams to manipulate properties in materials.

9:30 AM *MT05.03.02
Fabrication of Single Atom Devices by Direct Write Nanofabrication Edward Bielejec; Sandia National Laboratories, United States

We will present our results on the fabricate of single atom devices via direct write nanofabrication using Sandia National Laboratories nanolmplanter. This focused ion beam (FIB) implantation capability is part of Sandia’s Ion Beam Laboratory and is a multi-species 10-100 kV FIB system with a minimum spot size of 10 nm with both mass resolution using an ExB filter and single ion implantation capability using fast blanking and chopping. The combination of high spatial resolution, variable energy and the ability to implant a range of elements from the periodic table makes this a versatile machine for a range of topics from deterministic seeding of TaOx memristor devices, high resolution ion beam induced charge collection (IBIC) for probing the structure of defect cascades, deterministic single donor devices for quantum computing research, to the formation of individual defect centers in wide bandgap substrates including diamond, SiC, hBN, etc… using in-situ detectors. Here we concentrate on FIB implantation into diamond nano-structures for the creation of color centers.

Color centers in diamond including NV, SiV and GeV are used for a range of applications from metrology to single
photon sources. We demonstrate the ability to deterministically implant ions into diamond photonic nanostructures with high spatial resolution, <40 nm. This enables high resolution arrays for yield testing as well as the development of strong coupling between the resulting color center and the nanophotonic cavities. Separately, we have demonstrated single ion detection using an in-situ diamond detector with signal-to-noise-ratio approaching 10.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

10:00 AM BREAK

10:30 AM *MT05.03.03
Neuromorphic MoS2 Memtransistors Fabricated by Localised Helium Ion Beam Irradiation Jakub P. Jadwiszczak¹, Darragh Keane¹, Gregor Hlawacek², Hongzhou Zhang¹ and Shane Cybart¹; ¹Trinity College, Ireland; ²Institute of Ion Beam Physics and Materials Research, Germany; ³University of California, United States

Two-dimensional layered semiconductors have recently emerged as attractive building blocks for next-generation low-power non-volatile memories. However, challenges remain in the controllable sub-micron fabrication of bipolar resistively switching circuit components from these novel materials. In this work, we demonstrate lateral on-dielectric memtransistors from monolayer single-crystal molybdenum disulfide (MoS2) utilizing a focused helium ion beam. The site-specific irradiation with the probe of a helium ion microscope (HIM) allows for the creation of charged defects in the MoS2 lattice. The reversible drift of these locally seeded defects in the applied electric field modulates the resistance of the semiconducting channel, enabling versatile memristive functionality on the nanoscale. The asymmetric nature of the ion irradiation plays a crucial role in controlling the resistive switching behaviour and hence optimising the device performance. This work has potential to advance the down-scaling of memristive devices with low power consumption and applicability for synaptic emulation in next-generation flexible electronic applications.

11:00 AM MT05.03.04
Large Scale Automated Fabrication Using a Helium Ion Microscope Ethan Cho, Jay C. LeFebvre, Hao Li and Shane Cybart; University of California, Riverside, United States

We have fabricated a variety of high-transition temperature superconducting (HTS) Josephson devices with properties that exceed prior-art devices using a focused helium ion beam (FHB). These FHB Josephson junctions have exceptional qualities such as a resistance greater than 1 kohms as well as superconducting quantum interference devices with voltage close to 1 mV. These high figures of merit make HTS devices appealing for many applications. Unfortunately, these demonstrations are small scale devices with few junctions contained in small 100 micron areas due to the field of view of the FHB at high resolution. To bring this technology to the next level, innovations are needed for large area patterning such as those implemented in commercial electron beam lithography equipment. We present our efforts in bringing this to fruition using our Orion plus microscope equipped with a Raith ELPHY pattern generator system. We developed an automated direct-write Josephson junction process where large-scale areas are broken into smaller write fields that are compatible with the field of view of the FHB. The smaller areas are individually written and stitched together. Since the FHB is not equipped with a laser interferometer stage, it is necessary to account for stage backlash and other sources of stitching error using auto-alignment marks in the circuit design. Using the Raith ELPHY pattern generator we maintain a small field of view for high resolution patterning and control the stage to stitch the device with errors less than a few micrometers per movement. Additionally, while setting up the coordinate system to match the design and the patterned device, a focal plan is fitted in the coordinate system to keep the beam in focus even after long stage movements. This further reduces the action needed by a human operator. To test the automation process, we designed a large area wide-bandwidth, high-dynamic range sensor which consists of a large number of long Josephson junctions in an array. The array, typically several millimeters long, is much larger than common lithography write fields (typically a hundred micrometers) making the fabrication process excessively long and tedious. The signal voltage output scales with the number of junctions contained in the series array which is an important metric for determining the device performance. Previous designs were limited to a few hundred junctions with output voltage of less than 5 mV. By automating the process, we are
now capable of making arrays with over 2600 junctions in series with voltage output over 100 mV! This circuit was installed into a prototype receiver for signals intelligence research and is one of the first FHIB Josephson circuits to be transferred out of the university.

11:15 AM MT05.03.05
Pulsed Laser-Assisted Helium Ion Nanomachining of Monolayer Graphene—Direct-Write Kirigami Patterns
Cheng Zhang1,2, Ondrej Dyck2, David A. Garfinkel1, Michael Stanford1,2, Alex Belianinov2, Jason D. Fowlkes2, Stephen Jesse2 and Philip Rack1,2; 1The University of Tennessee, Knoxville, United States; 2Oak Ridge National Laboratory, United States; 3Rice University, United States

A helium gas field ion source has been demonstrated to be capable of realizing higher milling resolution relative to liquid gallium ion sources. One drawback, however, is that the helium ion mass is prohibitively low for reasonable sputtering rates of bulk materials, requiring a dosage that may lead to significant subsurface damage. Manipulation of suspended graphene is, therefore, a logical application for He⁺ milling. We demonstrate that competitive ion beam-induced deposition from residual carbonaceous contamination can be thermally mitigated via a pulsed laser-assisted He⁺ milling. By optimizing pulsed laser power density, frequency, and pulse width, we reduce the carbonaceous byproducts and mill graphene gaps down to sub 10 nm in highly complex kirigami patterns. The experimental observation is qualitatively in line with the Finite Element Method simulation results. This technique enables complex features to be direct written on suspended membranes, opening the gate to a variety of applications such as fabricating heterostructure carbon-based devices.

11:30 AM MT05.03.06
Phase Transitions in He⁺ FIB-Irradiated VO₂ Observed with 4D-STEM Imaging
Steven Zeltmann1, Lei Jin1, Frances I. Allen1, Junqiao Wu1 and Andrew M. Minor1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

The metal-insulator transformation in vanadium dioxide (VO₂) at ~340K is accompanied by a spontaneous strain of ~1%, which can be used to create nano-scale sensors and actuators. The ability to grow homogeneous single-crystal nanostructures, the large change in lattice parameters (orders of magnitude greater than typical thermal expansion), and low transition temperature are advantageous in applications, and highly sensitive nano-thermometers and microscale solid engines have been previously demonstrated. In this work, we demonstrate nano-scale local patterning of the transition temperature of 100 nm thick VO₂ nanowires by 30 kV He⁺ focused ion beam irradiation. Doses in the range of 10¹⁵-10¹⁶ ions/cm² do not evidently disturb the VO₂ lattice, but rather are believed to introduce oxygen vacancies that modify the transformation behavior. Spatially resolved measurement of the transition temperature is accomplished using four-dimensional scanning transmission electron microscopy (4D-STEM), a technique where a convergent electron probe is rastered across an electron-transparent sample and the full diffraction pattern is acquired at every probe position. In each of the diffraction patterns we find the position of the Bragg scattered electrons, which are used to determine the local lattice parameters.

We performed 4D-STEM scans of VO₂ nanowires with different patterned He⁺ doses using an in situ heating stage to reveal the monoclinic-rutile transformation as a function of space and temperature. We found that the transition temperatures measured by the structural distortion match those separately measured by electrical resistivity on homogenously irradiated nanowires with the same He⁺ doses. We also observe sharp interfaces between the rutile and monoclinic phases at the boundaries between different He⁺ doses. These results demonstrate the possibility of fine-tuning of the transformation temperature for precisely controlled actuation, as well as graded structures that allow for smooth onset of the actuation or sensing signal, by local irradiation with the He⁺ FIB.

11:45 AM MT05.03.07
Use of Helium-FIB to Study Helium Ion Irradiation Effects for a Tungsten Target
Mehdi Balooch, Frances I. Allen and Peter Hosemann; University of California, Berkeley, United States

The interactions of 25 keV helium ions with a tungsten (100) single crystal target at room temperature for doses ranging from 1x10¹⁵ to 1x10¹⁸ ions/cm² are investigated using a helium Focused Ion Beam (FIB) microscope to perform the irradiations in a site-specific dose-controlled manner. The swelling and surface topographic changes of the exposed surfaces are initially observed using Helium Ion Microscopy (HIM) and Atomic Force Microscopy
At a dose of about $5 \times 10^{17}$ ions/cm$^2$, blisters abruptly appear and randomly rupture. Channeling phenomena along 110 orientations becomes evident on W(100) blisters in the HIM micrographs. Blisters are found to grow to a maximum of 1 micron in diameter before rupture. Cross-sections through blisters prepared by gallium FIB milling and imaged by Transmission Electron Microscopy (TEM) reveal the formation of a blister cavity with helium nanobubbles of around 1 nm in diameter found in the material above and below the cavity. The formation of nano-cracks connecting nanobubbles is also observed, in agreement with the mechanism of blister formation involving the inter-bubble fracture of highly over-pressurized helium bubbles proposed decades ago by Evans [1], which until now, to the best of our knowledge, had not been experimentally verified. We also apply nanoindentation to measure the reduced modulus and hardness values versus indentation depth for areas implanted to different doses and propose a phenomenological equation to describe the experimentally-determined hardness and swelling values.


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**SESSION MT05.04: FIB Property Engineering II**

**Session Chairs:** Frances Allen and Shane Cybart

**Tuesday Afternoon, December 3, 2019**

**Hynes, Level 2, Room 204**

**1:30 PM *MT05.04.01***

**Nanoscale Superconducting Quantum Devices Based on High Transition Temperature Superconductor Materials Fabricated by Focused Helium Ion Beam** Hao Li, Ethan Cho and Shane Cybart; University of California, Riverside, United States

Focused helium ion beam (FHIB) fabrication of high transition temperature superconductor (high-$T_c$) Josephson junctions has opened up new opportunities in both basic science and applications due to the much smaller critical dimensions afforded by the process. The displacement of critical element atoms such as oxygen or amorphization of the polycrystalline film directly introduced by FHIB can change the electrical property of high-$T_c$ superconductor to normal metal, even insulator at low temperature. The controllable changes of the electrical properties within nanometers provides the basis to investigate the quasiparticle tunneling density of states at different angles, which is highly related to the cooper pairing mechanism where scientist are expecting breakthrough for decades. Versatile nanoscale quantum devices by combining the nanoscale functional features, such as very narrow barrier (at the order of the coherence length in a-b plane, ~2 nm), sub-10 nm insulating lines and area have also been designed and made. Scaling down the size of the features of basic also benefits the superconducting electronics technology for higher detector sensitivity, higher circuit integration density, and higher circuit performance. In this presentation, we show how helium ion junctions can be used for spectroscopic studies of the superconducting energy gap and its anisotropy in the a-b plane. In addition, we demonstrate applications of nanojunctions in high-frequency applications, digital circuits, and quantum sensing.

**2:00 PM MT05.04.02***

**Superconducting Nanoscale Detectors Fabricated Using Precision Dislocation Engineering** Ilya Charaev, Glenn Martinez, Denis Bandurin, Andrew Dane, Reza Baghdadi, Marco Colangelo and Karl K. Berggren; Massachusetts Institute of Technology, United States

We present an alternative approach to creating nanowires through local damage by a focused He ion beam (HIM). Motivated by the successful realization of Josephson junctions (JJ) after the introduction of dislocations into an otherwise orderly atomic arrangement [1], we have fabricated nanoscale detectors on superconducting films using He$^+$ ion beam irradiation < 0.5 nm diameter. The ion beam propagates through the thin film and leaves a very narrow damage track. It benefits from a reduced interaction volume compared to that of an electron beam of similar energy and archives higher resolution without needing resist. Furthermore, this He$^+$ beam technique allows for control of the atomic layer in three dimensions due to low dose and high collimation. We have performed an analysis of critical dose for different materials and have characterized patterned nanostructures. Our results suggest HIM may have advantages over e-beam lithography for some applications.

Ion Beam Induced Damage in MgB2 and Co-Doped Ba(FeAs)2 Thin Films for Josephson Junctions

Leila Kasaei1, Hussein Hijazi1, Mengjun Li1, Ryan Thorpe1, Hongbin Yang1, Philip E. Batson1, Ke Chen2, Torgny Gustafsson1, Xiaoxing Xi2 and Leonard C. Feldman1; 1Rutgers University, United States; 2Temple University, United States

Josephson junctions (JJs) are widely used in many superconducting circuits. Focused He+ ion beam irradiation has the potential of direct writing JJ multi-junction circuits. We have used 30 KeV He+ focused ion beam (He-FIB) with beam diameter of less than 0.5 nm to create nano-scale “normal” barriers, fabricating planar Josephson junctions in superconducting MgB2 [1,2] and Co-doped Ba(FeAs)2 (Ba122) thin films. Results show excellent device-to-device reproducibility. Accurate descriptions of the ion beam created normal state are critical to the development of beam created JJs and superconducting devices. By exploiting TRIM, TEM, and channeling RBS analysis, we have explored several means to obtain experimental information of the final state of the irradiated materials, so as to correlate these structural results with the electronic properties of the resulting film.

1] L. Kasaei et al. AIP Advances 8, 075020 (2018); https://doi.org/10.1063/1.5030751
2] L.Kasaei et al. IEEE Transactions on Applied Superconductivity, 29 (2019); https://doi.org/10.1109/TASC.2019.2903418

Nanoscale Devices Fabricated by Focused Ion Beam Irradiation of YBa2Cu3O7 Thin Films

Max Karrer; University Tübingen, Germany

Recent advances in focused ion beam (FIB) techniques have opened new opportunities for nanoscale milling and local modification of thin film superconductors. We present various FIB-based approaches to produce devices in thin films of the cuprate superconductor YBa2Cu3O7 (YBCO). By Ga FIB milling, we fabricated YBCO nanoSQUIDs on bicrystal substrates with ultra-low flux noise in the thermal white noise limit [1]. Such devices offer detection of magnetization reversal processes in individual magnetic nanoparticles or nanowires [1-3]. By He FIB irradiation, it is possible to locally drive YBCO from the superconducting to the insulating state, with high spatial resolution, and hence to “write” Josephson barriers into thin films [4]. We present here a comprehensive analysis of the electric transport properties at 4.2 K of He-FIB produced YBCO Josephson junctions [5]. The critical current density $j_c$ can be adjusted by irradiation dose $D$, with an exponential decay of $j_c(D)$. For Josephson devices we find an approximate scaling of the characteristic voltage $V_c \propto j_c^{1/2}$, and current-voltage characteristics that are well described by the Resistively and Capacitively Shunted Junction model, without excess currents for $V_c < 1$ mV. The He-FIB technique provides the possibility to place junctions at arbitrary location, with different orientation and shape, and even with different $j_c$ on the same chip. Moreover, He-FIB irradiation with high dose produces highly resistive walls or areas. We used this feature to produce dc SQUIDs with sub-μm loop sizes and very low flux noise. As a further He-FIB application, we demonstrate the creation of ultradense tailored periodic pinning arrays for Abrikosov vortices in YBCO thin films, with lattice spacing down to 70 nm. By electric transport measurements and molecular dynamics simulations, we study unconventional commensurability effects of the vortex lattice with the fabricated quasi-Kagomé pinning lattices. Altogether, the He-FIB technique provides a promising tool for nanoscale patterning of advanced devices, e.g. Josephson junction arrays, in YBCO thin films.

References

Nanocluster Formation In Silica via Microbeam-Focused MeV Ion Implantation

John D. Demaree1 and Daryush Ilia2; 1CCDC Army Research Laboratory, United States; 2FSU, United States

2:45 PM MT05.04.05

Nanocluster Formation In Silica via Microbeam-Focused MeV Ion Implantation

John D. Demaree1 and Daryush Ilia2; 1CCDC Army Research Laboratory, United States; 2FSU, United States
Nanometer-scale metallic clusters of Ag and Au can be formed via implantation of 0.785 MeV Ag and 1.450 MeV Au ions into high-purity optical quality fused quartz silica (Infrasil), followed by thermal annealing at temperatures from 500-700°C (Ag nanocluster formation) or 900-1100°C (Au nanocluster formation). The optical properties of the resulting material – specifically, the intensity and wavelength of the plasmonic absorption bands from 400-530 nm, as well as the off-resonance absorption – are strongly affected by the total ion fluence, the particular metallic ion(s) implanted, and the details of the annealing process (temperature, time, and implantation/annealing processing order). In past studies, we have shown that ion beams focused to a 2mm diameter and stepped slowly in 0.5mm increments laterally across a silica surface results in significantly different nanocluster formation than when ion beams are rastered across a much larger area in a conventional way. We have speculated that the increased ionization and/or localized thermal load in a moderately-focused process can lead to the acceleration of metal atom diffusion and nucleation of metallic nanoclusters, even at relatively low overall sample temperatures. In this work, we will extend these studies to more tightly focused beams using an electrostatic quadrupole lens recently installed on a National Electrostatics 5SDH-2 accelerator. Focusing Ag and Au beams down to less than 100 micrometers in diameter, we will explore the limits of MeV ion implantation into such small areas without unacceptable damage to the silica host. The implanted surfaces will be examined with 3D wide area microscopy and 3D laser microscopy and optical absorption photo spectrometry, as well as Rutherford Backscattering Spectrometry (RBS) to confirm the implantation dose. To reach the implantation fluences needed for nanocluster formation (10^{16} atoms/cm^2 to 10^{17} atoms/cm^2) in reasonable times, it is likely that the current density in the microscopic area will be very high, which may lead to damage via melting, plastic flow, electric microdischarges, or even ablation. If, however, we can form nanoclusters with tailored optical properties in these small areas, this technique could be used to create regimented structures with interesting and useful optical properties.

3:00 PM BREAK

SESSION MT05.05: FIB In Situ Stages and Nanotomography
Session Chairs: Frances Allen and Silke Christiansen
Tuesday Afternoon, December 3, 2019
Hynes, Level 2, Room 204

3:30 PM *MT05.05.01
Expanding the FIB/SEM Toolkit—Taking a Look at Various In Situ Sample Processing and Characterization Possibilities
Andrew J. Smith, Andreas Rummel, Klaus Schock, Matthias Kemmler and Stephan Kleindiek; Kleindiek Nanotechnik, Germany

FIB/SEM tools have become commonplace in many university, industry, and research labs and are employed for a wide range of applications in a variety of research and industrial fields. From preparing samples for Transmission Electron Microscopy (TEM) and Atom Probe Tomography (APT), to milling specific test structures for further analysis or mechanical/electrical characterization, to failure analysis and circuit edit tasks in semiconductors - FIB/SEMs are an integral part of many problem-solving and research workflows. Injecting process gases is an important part of many FIB/SEM processes. Precursor materials are introduced into the microscope's vacuum chamber and are decomposed by either the ion or electron beam. This results in material deposition, enhanced etching of specific materials, or the generation of very smooth surfaces on mixed-material substrates. A compact, flexible gas injection system will be introduced. In addition, injecting liquids (at high chamber pressures) can also be of interest for specific research topics. Another important topic is sample agility. For one, when milling into samples with the goal of preparing cross sections or large TEM lamella, so-called curtaining effects can be very bothersome. An approach for mitigating these effects will be discussed. In addition, some sample analysis methods require the ability to tilt and rotate samples to specific angles - beyond what the microscopes' stages allow by default. One such analysis is Electron Channeling Contrast Imaging (ECCI), which will be introduced briefly. Finally, there are assembly tasks which require a high degree of sample motion, not accessible with standard microscope stages. An example of such an assembly task will be provided. In addition, FIB/SEMs are often used in materials characterization. Tensile and compression tests can be performed on FIB-milled structures. Or, the FIB can be a tool that allows preparing/retrieving micro- or nano-sized objects and
Atomic Force Microscopy is popular among a wide range of research fields as it provides 3D topography information. Combining AFM with FIB/SEM tools yields the ability for multi-modal tests e.g. by combining the AFM technique with electron-based analysis methods (e.g. EDX).

**4:00 PM *MT05.05.02***  
**Advances in FIB Nanotomography—Towards 1 nm³ Voxel**s Michael W. Phaneuf, Alexandre Laquerre and Ken G. Lagarec; Fibics Incorporated, Canada

For about 20 years gallium FIB systems have been used to produce precise serial section datasets for the purpose of 3D analysis and reconstruction [1,2,3,4]. In this technique, volume pixels (voxels) with dimensions on the nanometer scale in x, y and z are acquired by "slicing" with a "machining beam" and detecting signals stimulated by an "imaging beam", resulting in datasets that can readily span one hundred micrometers or more in at least one dimension. In our lab, we have demonstrated 1,000,000 cubic micrometers of aluminum alloy can be analyzed (with 40 nm voxels) in about 48 hours.

While the initial published efforts typically achieved slice thicknesses on the order of 100 to 500 nm, across just a few dozen slices, more recent efforts have accomplished thicknesses (and voxels) below 5 nm in size [5] and many thousand slices in a dataset. Achieving precision, accuracy and information fidelity under these conditions has become a complex task. This presentation will outline our experiences performing precision sectioning with gallium ions and imaging with either low energy electrons (in our ZEISS Crossbeam 550) or helium ions (in our ZEISS Orion NanoFab), coupled with precise beam control and dynamic measurements of slice thickness and beam position to achieve these goals.

Recent advancements towards the goal of 1 nm³ voxels will be demonstrated in the analysis of a range of materials systems. Multi-resolution analysis encompassing high voxel resolution imaging coupled with intermediate resolution analytics using EDS and EBSD will also be presented. The trade-offs necessary between various instrument parameters in order to enable successful implementation, the challenges of the existing technologies, and the requirements for future instrumentation and analysis development will also be discussed.


**4:30 PM MT05.05.03***  
**In-Situ Correlative Analysis of Ion-Beam Treated Nanostructures by Combination of AFM and FIB**  
Christian H. Schwalb¹, Stefan Hummel¹, Robert Winkler², Jurgen Sattelkow², Pinar Frank¹, Gregor Hlawacek³, Peter Hosemann², Georg E. Fantner¹ and Harald Plank²; ¹GETec Microscopy, Austria; ²Technical University Graz, Austria; ³Helmholtz-Zentrum Dresden-Rossendorf, Germany; ⁴University of California, Berkeley, United States; ⁵EPFL, Switzerland

During the last decade the combination of different microscopic and spectroscopic methods into one instrument gained increasing importance due to the simultaneous acquisition of complementary information. Especially highly...
localized probing of mechanical, electrical, magnetic, chemical and crystallographic properties on the nanoscale represents a key success factor for gaining new insights in the micro and nano world.

We present a unique atomic force microscope (AFM) – the AFSEM™ - designed for seamless integration into scanning electron microscopes (SEM) or FIB systems. Its open design and the use of self-sensing cantilevers with electrical readout allows for simultaneous operation of SEM, FIB and AFM inside the vacuum chamber to perform correlative in-situ AFM/SEM/FIB analysis of ion-beam treated nanostructured materials. We present correlative AFM/EBSD data of a FIB polished ZrO₂ ceramic of phase transformed regions. While EBSD allows for locally identifying areas where the phase transformation has occurred, in-situ AFM can now be utilized to analyze phase-transformation-induced topographic changes with sub-nm resolution.

In a further step, we demonstrate how in-situ correlative analysis with the AFM in an SEM and dual-beam system can be extended into the third dimension to measure nanomechanical properties of soft material. To achieve this, FIB slicing and mapping of nanomechanical properties using the AFSEM™ is performed in repetitive steps to build up a 3-dimensional elasticity map. Finally, we present, for the first time, in-situ correlative AFM results of helium treated surfaces inside the Zeiss ORION Nanofab. These experiments include the detailed study of a broad variety of samples. The dose-dependent creation of helium bubbles is shown on silicon, copper and steel surfaces. In addition, in-situ correlative MFM analysis of helium treated samples are shown. We observed the creation of magnetic domains on helium treated steel surfaces as well as the modification of multi-layered magnetic structures by ion-beam treatment.

Based on the broad variety of applications regarding the characterization of different materials and devices we anticipate the AFSEM to be one of the driving characterization tools for correlative SEM/FIB/AFM analysis in the future.

4:45 PM MT05.05.04
Focused Ion Beam Processing for Practical 3D Analysis of Hard and Soft Biomaterials Meltem Sezen and Busra Tugba Camic; Sabanci University, Turkey

In this study, strategical nanostructuring, patterning and characterization routes were applied to determine morphological, chemical and structural features of biomaterials, ranging from nanocomposite biocompatible ceramics and biodegradable polymer coatings to soft neural tissues. Studies concerning serial sectioning which is followed by high resolution imaging/EDS mapping were performed at Focused Ion Beam - Scanning Electron Microscope (FIB-SEM) platforms for revealing biomaterials’ inner structures (morphological and chemical distribution data e.g. porosity, dopant/matrix, networking) in three dimensions down to the nanoscale. Novel biodegradable and biocompatible polymer nanocomposites were developed by doping silver nanowires (AgNWs) and boron nitride (BN) nanoparticles inside biopolymer (e.g. PLA, PCL) matrices, and three-dimensional characteristics of these samples were investigated at the micro/nano-scale by the use of proper processing methodologies and instrumental parameters. In addition, different natural tissues and synthetic biocomposites; such as human tooth, human brain and ceramic bone-graft materials were processed and analyzed by using serial ion slicing applications provided by FIB-SEM platforms. This study showed the versatility of using case-specific strategies for instant and simple processing of a variety of both hard and soft biological samples, which can be coupled with simultaneous imaging and chemical analysis procedures.

SESSION MT05.06: Theory and Simulations
Session Chairs: Frances Allen and Shane Cybart
Wednesday Morning, December 4, 2019
Hynes, Level 2, Room 204

9:00 AM *MT05.06.01
Free-Standing and Supported Two-Dimensional Materials under Ion Irradiation Arkady Krasheninnikov; Helmholtz-Zentrum Dresden-Rossendorf, Germany
Ion irradiation has successfully been used for introducing impurities and creating defects in two-dimensional (2D) materials in a controllable manner. Moreover, focused ion beams, especially when combined with in-situ or post-irradiation chemical treatments, can be employed for patterning and even cutting 2D systems with a high spatial resolution. The optimization of this process requires the complete microscopic understanding of the interaction of energetic ions with the low-dimensional targets. In my presentation, I will dwell upon the multi-scale atomistic computer simulations of the impacts of ions onto free-standing (e.g., suspended on a TEM grid) and supported (deposited on various substrates) 2D materials, including graphene and transition metal dichalcogenides (TMDs), such as MoS$_2$ and WS$_2$. The theoretical results will be augmented by the experimental data obtained by the coworkers. Finally, I will touch upon the interaction of highly-charged [3] and swift heavy ions [4] with 2D systems and overview recent progress in modelling this using non-adiabatic approaches including time-dependent density functional theory and Ehrenfest dynamics [5].


9:30 AM MT05.06.02
First-Principles Study of Charge Equilibration and Electronic Stopping in Self-Irradiated Silicon Cheng-Wei Lee and Andre Schleife; University of Illinois at Urbana-Champaign, United States

Charged energetic particle radiation has technological interest in applications including nuclear energy, outer space, medicine, and fundamental research. As a result of irradiation, damage, including point defects, forms and ultimately determines the material properties. Therefore, understanding the underlying interactions between charged particles and a material is important. When using the semi-empirical SRIM model to describe the interaction of charged ions with target materials as well as defect formation, one particularly severe drawback is that the model assumes an equilibrium charge state for the projectile. However, the Lindhard-Winter model predicts that the charge state of the projectile strongly affects electronic stopping and recent experimental results show that channeling U$^{91}$ in Si indeed experiences larger stopping power than off-channeling U ion. The underlying mechanism is not fully understood.

We use first-principles simulations, based on real-time time-dependent density functional theory, to study charge equilibration and electronic stopping for projectiles in multiple initial charge states. Our simulations for heavy (silicon) projectiles traversing crystalline bulk silicon indeed showed a pronounced dependence of electronic stopping on the initial projectile charge state. This effect was not observed in computational data for light projectiles impacting metal or semiconductor targets, but is qualitatively similar to the experimental results of channeling U$^{91}$ in Si.

To provide detailed understanding, we analyze the dynamics of charge equilibration, influence of the impact parameter, and contributions of core and valence electrons to electronic stopping. We observe that the equilibrium charge state of the Si projectile primarily depends on the impact parameter and ultimately dominates electronic stopping. Our results provide insights for future application of multi-charge ion source and can be integrated with multi-scale models, e.g. two-temperature molecular dynamics, to more accurately predict the defect formation during primary knock-on events.

9:45 AM MT05.06.03
Interrogation of the Nano-Beam and Nano-Target Effects in Ion Radiation Using IM3D Yang Yang1,2, Yong Gang Li3, Michael P. Short1 and Ju Li1,1; 1Massachusetts Institute of Technology, United States; 2Lawrence Berkeley National Laboratory, United States; 3Institute of Solid State Physics, Chinese Academy of Sciences, China

Nanoscale ion implantation represents an expanding, interdisciplinary field that combines radiation effects with nano-engineering to control matter on the atomic level. In so doing, it offers the potential to create novel nano-devices such as quantum computers, magnetometers, nanowire pn junctions, etc. In particular, ion implantation enables more precise control of the spatial distribution and concentration of dopants/defects, making it highly desirable to fabricate nano-devices reproducibly. However, confidently taking advantage of it hinges upon the accurate and precise knowledge of the spatial distribution of dopants and defects created by ion implantation. Widely used, modern 1D simulations, such as SRIM (the Stopping Range of Ions in Matter) for example, may fail to predict this distribution because of the breakdown of key assumptions, including a large ion beam and target homogeneity in at least one dimension. Full three dimensional (3D) simulations of ion implantation are necessary in a wide range of nanoscience and nanotechnology applications to capture the increasing effect of ion leakage out of surfaces [Handbook of Materials Modeling. https://doi.org/10.1007/978-3-319-50257-1_115-2]. Using a recently developed 3D Monte Carlo simulation code IM3D [Scientific Reports 5 (2015) 18130], we first quantify the relative error of the 1D approach in three applications of nano-scale ion implantation: (1) nanobeam for nitrogen-vacancy (NV) center creation, (2) implantation of nanowires to fabricate p–n junctions, and (3) irradiation of nano-pillars for small-scale mechanical testing of irradiated materials. Because the 1D approach fails to consider the exchange and leakage of ions from boundaries, its relative error increases dramatically as the beam/target size shrinks. Lastly, the “Bragg peak” phenomenon, where the maximum radiation dose occurs at a finite depth away from the surface, relies on the assumption of broad beams. We discovered a topological transition of the point-defect or defect-cluster distribution isosurface when one varies the beam width, in agreement with a previous focused helium ion beam irradiation experiment. We conclude that full 3D simulations are necessary if either the beam or the target size is comparable or below the SRIM longitudinal ion range [Nanoscale 10 (2018) 1598].

10:00 AM BREAK

SESSION MT05.07: FIB-SIMS I
Session Chairs: Alex Belianinov and Silke Christiansen
Wednesday Morning, December 4, 2019
Hynes, Level 2, Room 204

10:30 AM *MT05.07.01
FIB-SIMS—Recent Advances in Secondary Ion Mass Spectrometry for Analytical Dual Beam Focussed Ion Beam Instruments Lex Pillatsch, Agnieszka Priebe and Johann Michler; Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Secondary ion mass spectrometry (SIMS) is a well-known technique for 3D chemical mapping at the nanoscale, with detection sensitivity in the range of ppm or even ppb. Energy dispersive X-ray spectroscopy (EDS) is the standard chemical analysis and imaging technique in modern scanning electron microscopes (SEM), and related dual-beam focused ion beam (FIB/SEM) instruments. Contrary to the use of an electron beam, in the past the ion beam in FIB/SEMs analytical instruments has predominantly been used for local milling or deposition of material. In this talk we will review the emerging FIB-SIMS technique which exploits the focused ion beam as an analytical probe, providing the capability to perform secondary ion mass spectrometry measurements within FIB/SEM instruments: secondary ions, sputtered by FIB, are collected and selected according to their mass by a mass spectrometer. In this way a complete 3D chemical analysis with high lateral resolution < 50 nm and a depth resolution < 10 nm is attainable. We first report on the historical developments of both SIMS and FIB techniques and review recent developments in both instruments. Next, the components of modern FIB-SIMS instruments, from the primary ion generation in the liquid metal source in the FIB column, the focussing optics, the sputtered ion extraction optics, to the different mass spectrometer types are all detailed. The advantages and disadvantages of parallel and serial mass selection in terms of data acquisition and interpretation are highlighted, while the effects of
pressure in the FIB/SEM, acceleration voltage, ion take-off angles and charge compensation techniques on the analysis results are then discussed. The capabilities of FIB-SIMS in terms of sensitivity, lateral resolution, depth resolution and mass resolution are reviewed including measurements conducted on standard calibration samples such as BAM and VCSEL samples and also metallic nanoparticles incorporated into an inorganic matrix. Different data acquisition strategies related to dwell time, binning and beam control strategies as well as roughness and edge effects are discussed. Application examples are then presented for the fields of thin films, polycrystalline metals, batteries, solar cells, metallic multilayers, and biological samples. These are followed by studies towards enhancing secondary ion yields, and therefore TOF-SIMS signal quality, using supplementary gases. Two approaches are presented – one using a novel Cs evaporator prototype and the other based on supplying water vapour and fluorine gas using a commercial in-situ Gas Injection System (GIS). The potential of fluorine gas for increasing the spatial resolution of TOF-SIMS data (elemental distribution images and depth profiles) and de-coupling mass interference is demonstrated. Finally, FIB-SIMS is compared to EDS, and the potential of the technique for correlative microscopy with other FIB/SEM based imaging techniques is discussed.

11:00 AM *MT05.07.02
NanoFab-SIMS—A Promising Tool for the Characterization of Nanofeatures Christelle Guillermier, Brett Lewis and Fouzia Khanom; Carl Zeiss SMT, Inc., United States

The rapid development and evolution of the nanotechnology market has triggered an increased demand for advanced characterization techniques at the nanoscale level. As of today, nanofeatures characterization requires the use of multiple ex-situ correlative techniques. For instance, Transmission Electron Microscopy (TEM) or Scanning Electron Microscopy (SEM) is often combined with Secondary Ion Mass Spectrometry (SIMS). SEM/TEM can uniquely reveal the nanofeature’s morphology, size and specific location on a sample (sub-organelles of a cell for example) while SIMS, a well-established sensitive surface analytical technique, will provide the chemical information. Although essential, ex-situ correlative techniques comes with the caveat of requiring adaptative sample preparation and the non-trivial task of identifying features of interest for the subsequent elemental characterization technique. TEM combined with Energy-Dispersive X-ray spectroscopy (EDX), on the other hand, offers in-situ characterization; but unlike SIMS, EDX cannot provide chemical information at sub-micrometric resolution and lacks the ability to detect light elements (H and Li).

A promising new technology for the characterization of nanofeatures has emerged with the configuration of the NanoFab with a SIMS detector. The ORION NanoFab is an ion microscope that allows high resolution secondary electron (SE) imaging with a He⁺ focused ion beam which can be focused to a 0.5 nm probe size. This same instrument also provides a Ne⁺ ion beam with a focused probe sizes of 2 nm. Recently, this platform has been configured with a custom-designed magnetic sector spectrometer equipped with four Channel Electron Multipliers (CEMs) positioned in the same focal plane. The accessible mass range is 1 to 250 amu and the mass resolution M/DM exceeds 400. Importantly, SIMS with neon provides elemental imaging with spatial resolution smaller than 15 nm. The combination of high resolution He⁺ secondary electromaging (0.5 nm) with Ne⁺ SIMS elemental mapping yields a direct correlative technique particularly attractive for exploring nanoparticles, as well as nanofeatures in general, in their macroscopic environment.

The NanoFab-SIMS has demonstrated recent success for the characterization of nanofeatures in the fields of perovskite materials, CIGS solar cells, nanotoxicology, batteries and nano-analytics in life science. We will present novel applications of this technology in the fields of nanomedicine, photonics and biology. More specifically we will show results on the characterization of biogenic nanoparticles (size in the 20 to 200 nm range) whose properties provide alternative treatment for bacterial resistance to antibiotics. We also investigated the elemental composition of doped phase-separated dielectric nano-particles in optical fibers and demonstrated that their composition varies with the particle size (size range 30-700 nm). Biology examples will include visualization of cells sub-organelles tagged with osmium antibodies.

11:30 AM MT05.07.03
Enhancing Sensitivity with NeFIB-SIMS—A Material and Parameter Study Brett Lewis, Fouzia Khanom and Christelle Guillermier; Carl Zeiss SMT Inc, United States

Recently, the ZEISS ORION NanoFab has been equipped with a double focusing magnetic sector secondary ion
mass spectrometer (SIMS) capable of chemically mapping features on the order of 10 nm[1-3] using a highly focused neon ion beam produced from a tuned gas field ion source. Initial results are extremely promising, already demonstrating usefulness in applications ranging from defect localization for semiconductor chips, chemical endpointing, and depth profiling to nanotoxicology[4], battery research[5], and characterizing solar cells[6, 7] and optoelectronics[8].

However, the utility of such an instrument is limited by its ability to detect trace elements which at small dimensions can be comprised of a limited number of atoms. Ultimately, the sensitivity of the SIMS is determined by the secondary ion (SI) current produced via the primary ion beam sputtering away the target material. This SI current is dependent on the sputter yield of the material, the collection efficiency of the detector, and, importantly, the ionization cross section of the species of interest.

In this study, we present a method for increasing the ionization cross section of different materials via the introduction of an in-chamber oxygen co-flow on a prototype tool, demonstrating in some cases a more than 2 order of magnitude increase in the SI useful yield. It is shown that oxygen can significantly enhance the positive ion yield of neighboring ions due to the readily forming oxide bond. When this bond is broken by the incoming primary ion, the oxygen tends to accept electrons due to its high electron affinity leaving the ion of interest more likely to be positively charged. Evidence shows that the ion yield enhancement is directly related to the surface coverage of the oxygen.

To study mechanistic effects and dependencies, we present data showing the effect of varied oxygen partial pressure, pixel dwell time, refresh time, beam current, and material type. The effect of the gas co-flow on sputter rate is also noted and presented.

Finally, we demonstrate the effect on the ultimate resolution that results from enhanced sensitivity with metallic nanoparticle contaminants on a silicon surface as well as on the BAM L200 standard. The future implications and challenges of increased sensitivity are also discussed.


11:45 AM MT05.07.04
High-Resolution Cs+ Ion Beam for FIB and SIMS Applications Brenton Knuffman, Andrew D. Schwarzkopf and Adam V. Steele; Zerok Nanotech Corporation, United States

The Low Temperature Ion Source (LoTIS) produces a beam of Cs+ ions that can be focused to nanometer spot sizes. This capability enables LoTIS to provide value in FIB applications where excellent machining acuity is required, such as circuit edit, as well as analytical applications where a high yield of secondary ions is desirable, as in secondary ion mass spectrometry (SIMS). The combination in a single beam will enable process control of nanomachining applications using simultaneous FIB machining and SIMS analysis.

We present the latest results from a prototype Cs+ Low Temperature Ion Source (LoTIS) retrofitted to a commercial FIB platform. Spot sizes as small as (2.1 ± 0.2) nm (one standard deviation) are observed with a 10 keV, 1.0 pA beam. Brightness values as high as (2.4 ± 0.1) × 107 A m-2 sr-1 eV-1 are observed near 8 pA [1]. We will also discuss plans for a new FIB+SIMS platform and examples of applications that are enabled by this unique combination.

Compared with the gallium liquid metal ion source (LMIS) utilized in most FIB systems today, LoTIS can provide a similar range of currents (pA to several nA), smaller spot sizes, and a reduced subsurface affected volume. These benefits have been utilized in the prototype system to perform circuit edits on 10 nm node chips. When compared with the standard Cs ion source used in commercial SIMS systems, LoTIS can deliver 100x more current into an
equivalent spot. Additionally, LoTIS can deliver a few pA into few nm spot sizes, enabling SIMS material analysis at the ~4nm fundamental physical limits of the technique. This also enables the use of SIMS in problem domains where x-ray dispersive spectroscopy has been used traditionally.


SESSION MT05.08: FIB-SIMS II
Session Chairs: Silke Christiansen and Shane Cybart
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 204

1:30 PM *MT05.08.01
Analytical Capabilities on FIB Instruments Using SIMS—Applications, Current Developments and Prospects
Tom Wirtz, Jean-Nicolas Audinot, Jelena Lovric, Alexander Ost and Olivier De Castro; Luxembourg Institute of Science and Technology, Luxembourg

Secondary Ion Mass Spectrometry (SIMS) is an extremely powerful technique for analyzing surfaces, owing in particular to its ability to detect all elements from H to U and to differentiate between isotopes, its excellent sensitivity and its high dynamic range. SIMS analyses can be performed in different analysis modes: acquisition of mass spectra, depth profiling, 2D and 3D imaging. Adding SIMS capability to FIB instruments offers a number of interesting possibilities, including highly sensitive analytics, in-situ process control during patterning and milling, highest resolution SIMS imaging (~10 nm), and direct correlation of SIMS data with data obtained with other analytical or imaging techniques on the same instrument, such as high resolution SE images or EDS spectra [1,2].

Past attempts of performing SIMS on FIB instruments were rather unsuccessful due to unattractive detection limits, which were due to (i) low ionization yields of sputtered particles, (ii) extraction optics with limited collection efficiency of secondary ions and (iii) mass spectrometers having low duty cycles and/or low transmission. In order to overcome these limitations, we have investigated the use of different primary ion species and of reactive gas flooding during FIB-SIMS and we have developed compact high-performance magnetic sector mass spectrometers operating in the DC mode with dedicated high-efficiency extraction optics. We installed such SIMS systems on different FIB based instruments, including the Helium Ion Microscope [3-5], a FIB-SEM DualBeam instrument and the npSCOPE instrument, which is an integrated Gas Field Ion Source enabled instrument combining SE, SIMS and STIM imaging with capabilities to analyse the sample under cryo-conditions [6].

Here, we will review the performance of the different instruments with a focus on new developments such as cryo-capabilities and new detectors allowing parallel detection of all masses, showcase methodologies for high-resolution 3D chemical imaging, present a number of examples from various fields of applications (nanoparticles, battery materials, photovoltaics, micro-electronics, tissue and sub-cellular imaging in biology, geology,...) and give an outlook on new trends and prospects.

[6] This project has received funding from the European Union’s Horizon 2020 Research and Innovation Programme under grant agreement No. 720964.

2:00 PM MT05.08.02
Development of an In Situ Cryo High Resolution Instrument for Multimodal Analysis in Nano-Toxicology
Olivier De Castro1, Jelena Lovric1, Rachid Barrahma1, Olivier Bouton1, Eduardo Serralta2, Nico Klinger3, Gregor Hlawacek2, Peter Gnauck3, Serge Duarte Pinto5, Falk Lucas3 and Tom Wirtz1; 1Luxembourg Institute of Science and
Nowadays many consumer products contain nanoparticles in order for them to have certain desired properties. However, with the addition of nanoparticles these products can have potentially unknown health risks to humans, animal and plant species, and to the environment in general. The nanomaterial risk identification involves their physico-chemical characterization currently employing a variety of techniques and separate instruments. This makes the characterization an expensive and time-consuming process.

In the framework of the Horizon2020 project npSCOPE, we are developing a new integrated instrument for the characterization of nanoparticles. The aim is to improve the efficiency of the nanomaterial characterization workflow by integrating several techniques in one single instrument. The npSCOPE instrument is equipped with the ultra-high resolution Gas Field Ion Source (GFIS) technology [1] allowing the sample to be irradiated with very finely focused He+ and Ne+ ion beams at the nano-scale. Furthermore, the instrument incorporates detectors for secondary electron imaging, a secondary ion mass spectrometer (SIMS) for chemical analysis [2-4] and a detector allowing the detection of transmitted ions/atoms to obtain in-situ structural/3D visualisation data. The instrument will allow the characterization of nanoparticles in their native state as well as embedded in complex matrices (e.g. biological tissue, liquid, etc.). A further key feature of the instrument is cryo-capability, including a 5 axis cryo-stage, in order to perform analyses of biological samples in a frozen-hydrated state and thus avoid artefacts caused by classical sample preparation (e.g. chemical fixation) used for HV or UHV imaging of biological specimens at room temperature.

Beside analyses of nano-toxicological samples we are planning to use this instrument in different material science fields as well as other life science domains that require high resolution imaging in cryo-conditions (e.g. lipid research) [5].

(For further information please visit www.npscope.eu)


[5] This project has received funding from the European Union’s Horizon 2020 Research and Innovation Programme under grant agreement No. 720964.
dynamics. Thus, KPFM only detects the small remainder of the photoinduced field, suggesting that the large photoinduced chemical changes are shielded as such less visible in traditional indirect measurements like KPFM. These pieces of knowledge—which are critical for further developments of HOIPs optoelectronics—were unknown previously, suggesting the importance of the direct observation of ion dynamics in HOIPs using tr-ToF-SIMS.

SESSION MT05.09: Biological Applications of FIB
Session Chairs: Alex Belianinov and Silke Christiansen
Thursday Morning, December 5, 2019
Hynes, Level 2, Room 204

9:00 AM *MT05.09.01
Cryo-FIB Sample Preparation Methods for Tissue and Cells in Structure Biology Studies at Molecular Resolution
Miroslava Schaffer1, Stephan Kleindiek2, Benjamin D. Engel1, Stefan Pfeffer1, Michael Heymann1, Tim Laugks1, Julia Mahamid1, Andrew J. Smith2, Juergen M. Plitzko1 and Wolfgang Baumeister1; 1Max Planck Institute of Biochemistry, Germany; 2Kleindiek Nanotechnik GmbH, Germany

In situ cryo-electron tomography (cryo-ET) has become a central technique in structural biology over the last decade, facilitating studies of molecular structures directly within the native cellular environment. This progress was to a large extent driven by ground-breaking developments in sample preparation of frozen-hydrated specimen by cryo-focused-ion-beam microscopy (cryo-FIB) [1-4]. Standard FIB millings routines for homogeneously thick, electron-transparent lamellas from plunge-frozen specimen are nowadays well established and regularly carried out [5]. Lamellas are created directly on the frozen TEM grid by completely removing all material on both sides of the volume of interest.

However, this technique is limited to samples which can be vitrified in toto by plunge-freezing TEM grids, preventing a wide range of biological questions from being addressed by cryo-ET. Large specimens such as tissue samples from multicellular organisms require vitrification by high-pressure-freezing (HPF) to prevent the formation of crystalline ice. These samples are then too thick for the standard cryo-FIB lamella milling.

Overcoming this limitation is thus the next milestone for in situ cryo-ET. Several FIB techniques from materials science have been proposed for adaptation to cryo-preparation of thick biological samples, and proof of principle studies showing the feasibility of the FIB milling at cryogenic temperatures have been published. However, due to the stringent sample quality requirements of cryo-ET at molecular resolution, successful application of these techniques has so far not been demonstrated.

In this presentation we will show our recent cryo-FIB sample preparation development which enabled the first molecular resolution cryo-ET studies of HPF vitrified tissue [6]. Utilizing a cryo-adapted micromanipulator ‘gripping’ tool developed especially for this application, this novel cryo-FIB lift-out technique completely avoids localized material deposition and associated contamination issues. Fluorescently-labelled volumes of interest are selectively extracted from large HPF bulk samples and transferred onto special customized TEM grids for final thinning and subsequent use in the cryo TEM. We will discuss the optimization steps of each part of the complete workflow from HPF freezing to final cryo-ET experiment which were required to obtain meaningful tomographic data at molecular resolution.

References:

9:30 AM *MT05.09.02
Multimodal Analysis of Calcified Biological Materials  
Lasse M. Kling; Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

In ageing societies all over the globe, the number of people suffering from bone disease, e.g. osteoporosis (OP) in the first place, has increased dramatically. OP considerably impairs patients' life quality, and results in high societal costs. However, current understanding of bone disease is still insufficient due to the lack of appropriate high resolution tools that permit a thorough analysis of scale bridging bone architectures from macro to nano with statistical significance to support the development of better treatments by drugs or surgical intervention.

Cutting-edge correlative workflows starting from X-ray microscopy (XRM) volume analysis, with voxel sizes of <1µm, over light sheet fluorescence microscopy (LSFM) and large scale scanning electron microscopy data acquisition, to dual beam microscope analysis (focused electron- and ion beams) permit the scale bridging investigation of bone architectures and thus merging the “big picture” and the underlying ultrastructure with statistical significance. Together with advanced data analysis even including machine learning approaches permit reaching the next, so far unprecedented level of understanding.

I will show an examplary correlative workflow from sample collection over sample preparation and the acquisition of bone fine structures, composed of trabecular-, vascular-networks as well as a three-dimensional arrangement of osteo-lacunae (OL) that host osteocytes and the interosteocyte lacuno-canalicular network (LCN). Blood vessel and OL volume can be assessed quantitatively with statistical significance in a new generation of lab-based XRM and LSFM. For investigation of the more delicate LCN we conduct dual beam microscope analysis (focused electron- and ion beams) in combination with additional analytical add-ons and demonstrate how this correlatation of various image modalities utilizing correlated data from electron-, ion-beam imaging and analytics, probes and focused laser light will permit to advance the current understanding of scale bridging bone architectures and their function. [ref1, ref2, ref3].

References:
[ref2] A. Grüneboom et al., A network of trans-cortical capillaries forms the mainstay for blood circulation in long bones, Nature Metab. Published online (02/2019)  

10:00 AM BREAK
based scheme will be presented that makes it possible to compensate for heat induced deposit distortions. If left uncorrected, this type of artifact/error prevents CAD replication during deposition when using a typical organometallic precursor for deposition. The compensation strategy will be demonstrated for electron-based nanoprinting using both simulations and experiments. However, the CAD capability that will be presented is also compatible with the use of an ion beam for deposition. Select applications of functional 3D nanoprinted structures will also be presented.

11:00 AM *MT05.10.02
Direct-Writing Nanofabrication of Complex 3D Superconducting Nanostructures Rosa Córdoba1,2, Alfonso Ibarra3, Dominique Mailly4 and Jose M. De Teresa2,3; 1Molecular Science Institute (ICMol), Spain; 2Aragon Material Science Institute (ICMA), Spain; 3University of Zaragoza, INA, LMA, Spain; 4University Paris Saclay, Univ Paris Sud, CNRS, Ctr Nanosci & Nanotechnol, France

Nowadays, superconductors are commonly utilized in several applications such as energy generators and storage due to their unique capability of transferring electricity without energy losses. In some applications, their nanoscale patterning enhances their performance and gives rise to new physical phenomena. Innovative schemes have taken advantage of the third dimension (3D) for the development of advanced superconducting electronics. Thus, 3D nanosuperconductors could promote a change in the next generation of electronic components. Nevertheless, their fabrication and characterization are still challenging and only a few works addressing the growth of real 3D nanosuperconductors have been reported so far 1-4.

In this contribution, we introduce a template-free nano-lithography method to fabricate in a single-step 3D nano-elements on-demand with arbitrary geometry. The fabrication of complex 3D nano-architectures opens fascinating novel routes in the fields of material science, physics and nanotechnology. This specific technique called focused ion beam induced deposition (FIBID) is based on chemical vapour deposition process assisted by a charged particle beam focused to a few nanometers. Particularly, by using tungsten hexacarbonyl molecules with a He+ ion beam focused to 0.3 nm, complex 3D W-C nanostructures have been fabricated 5. As a proof of concept, we report for the first time the fabrication and characterization of 3D superconducting crystalline WC hollow nanowires with outer diameters down to 32 nm and inner ones down to 6 nm56. In addition, by modifying the ion beam current, hollow nanowires with controllable inner and outer diameters have been achieved 7. The growth of the vertical WC nanowire occurs around the ion beam spot, mainly due to the interaction of secondary electrons with the adsorbed precursor molecules, whereas a cavity at the center of the nanowire is created due to the He+ beam milling effect on the growing material. As shown by transmission electron microscopy, nanowires microstructure displays grains of large size fitting with face-centered cubic WC1-x phase. By studying their magnetotransport properties, we have found that nanowires exhibit 1.5 times higher superconducting critical temperatures (6.4 K) as well as 1.5 times higher upper critical magnetic fields (≈14 T) (Fig. 1(c)) when compared to nanowires grown by a Ga+ FIBID.

The fabrication of such nanomaterials with excellent properties makes this technique at the cutting edge of nanofabrication methods based on focused beams of charged particles.

Acknowledgement:
“This project has received funding from the EU-H2020 research and innovation programme under grant agreement No 654360 NFFA-Europe.”

References
5. Córdoba, R. et al., manuscript in preparation.
A Focused Ion Beam (FIB) can be combined with precursor materials to grow deposits, the technique being referred to as Focused Ion Beam Induced Deposition (FIBID). In the standard FIBID configuration, a gas injection system delivers a precursor material in the gas phase, which becomes adsorbed to the substrate surface. The FIB irradiation decomposes the precursor molecules, creating a local deposit. The primary application of FIBID is the growth of metal lines, used to perform electrical connections during circuit edit [1] or utilized to contact nano-objects such as nanowires [2]. More recently, FIBID has found applications for the direct growth of functional materials in the fields of magnetism [3], superconductivity [4] and nano-optics [5]. Typical disadvantages when using FIBID include the long processing times and the appearance of side effects in the deposit and in the substrate: ion-induced defects, implantation, amorphization and milling [6]. New advances in FIBID aiming to lower the required ion doses would have a beneficial impact by decreasing the processing time and by minimizing the detrimental side effects caused by the ion irradiation.

In the present contribution, we will introduce FIBID under cryogenic conditions (Cryo-FIBID), which has been found to be an ultra-fast method to grow metal layers, nanowires and contacts [7]. Cryo-FIBID relies on FIB irradiation of a condensed layer of a precursor material formed on the substrate under cryogenic conditions. The technique implies cooling the substrate below the condensation temperature of the gaseous precursor material, subsequently irradiating with ions according to the wanted pattern, and posteriorly heating the substrate above the condensation temperature.

It will be shown that by using W(CO)6 as the precursor material, a Ga+ FIB, and a substrate temperature of -100 °C, W-C metal layers and nanowires with resolution down to 38 nm can be grown by Cryo-FIBID [8]. The most important advantages of Cryo-FIBID are the fast growth rate (about 600 times higher than conventional FIBID with the precursor material in gas phase) and the low ion irradiation dose required (~ 50 μC/cm2), which gives rise to very low Ga concentrations in the grown material and in the substrate (≤ 0.2 %). This approach gives solution to the typical problems of the FIB technique: ion implantation, ion milling, ion-induced creation of defects and amorphization. Electrical measurements indicate that W-C layers and nanowires grown by Cryo-FIBID exhibit metallic resistivity. These features pave the way for the use of Cryo-FIBID in circuit editing and photomask repair in the semiconductor industry and, more generally, for the local growth of metal layers, nanowires and contacts, with various applications in nanotechnology.

[8] R. Córdoba et al., manuscript submitted

**11:45 AM MT05.10.04**

**Atomistic Insights into Self-Fold Process of Nanostructures Induced by Focused Ion Beam**

Cheng-Lun Wu and Chun-Wei Pao; Academia Sinica, Taiwan

Focused Ion Beams (FIB) are versatile tools with cross-disciplinary applications from the physical and life sciences to archaeology. Nevertheless, the nanoscale patterning precision of FIB is often accompanied by defect formation and sample deformation, which brings opportunities in fabricating nanostructures with complicated three-dimensional geometries, as well as challenges in controlling the degree of deformation. In this study, we revealed the fundamental mechanisms governing the self-folding of nanostructures undergoing FIB processes by a series of GPU-accelerated, large-scale molecular dynamic simulations. We revealed that the primary mechanism leading to nanostructure deformation during FIB processes is the mass transport to the free surface of nanostructures induced...
by energetic ion bombardment. We revealed a surprisingly simple linear correlation between atomic volume removed from the film interior and film deflection angle, regardless of incident ion energies and currents, by quantitatively analyzing the amount of volume removed from film interior. Hence, the present study demonstrates that it is possible to control the self-folding of nanostructures by controlling the direction of mass transport via carefully manipulating incident ion energy, and direction, thereby allowing fabricating nanostructures with complex three-dimensional geometries.

SYMPOSIUM MT06

In Situ Characterization of Dynamic Phenomena During Materials Synthesis
December 2 - December 6, 2019

Symposium Organizers
Amy Clarke, Colorado School of Mines
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* Invited Paper

SESSION MT06.01: Imaging of Crystal Nucleation and Growth
Session Chairs: Patrick Grant and Ashwin Shahani
Monday Morning, December 2, 2019
Hynes, Level 2, Room 209

8:30 AM *MT06.01.01
Capturing Crystal Nucleation in 4D at Atomic Resolution Jianwei Miao1, Jihan Zhou1, Yongsoo Yang1, Yao Yang1, Dennis S. Kim1, Andrew Yuan1, Xuezeng Tian1, Colin Ophus2, Fan Sun1, Andreas K. Schmidt2, Michael Nathanson3, Hendrik Heinz3, Qi An4, Hao Zeng5 and Peter Ercius2; 1University of California, Los Angeles, United States; 2Lawrence Berkeley National Laboratory, United States; 3University at Buffalo, The State University of New York, United States; 4University of Colorado Boulder, United States; 5University of Nevada, Reno, United States

Nucleation plays a critical role in many physical and biological phenomena ranging from crystallization, melting and evaporation to the formation of clouds and the initiation of neurodegenerative diseases1-3. However, nucleation is a challenging process to study in experiments especially in the early stage when several atoms/molecules start to form a new phase from its parent phase. Here, we advance atomic electron tomography to study early stage nucleation at 4D atomic resolution4,5. Using FePt nanoparticles as a model system, we reveal that early stage nuclei are irregularly shaped, each has a core of one to few atoms with the maximum order parameter, and the order parameter gradient points from the core to the boundary of the nucleus6. We capture the structure and dynamics of the same nuclei undergoing growth, fluctuation, dissolution, merging and/or division, which are regulated by the order parameter distribution and its gradient. These experimental observations differ from classical nucleation theory (CNT) and to explain them we propose the order parameter gradient (OPG) model6,7. We show the OPG
model generalizes CNT and energetically favours diffuse interfaces for small nuclei and sharp interfaces for large nuclei. We further corroborate this model using molecular dynamics simulations of heterogeneous and homogeneous nucleation in liquid-solid phase transitions of Pt. We anticipate that the OPG model is applicable to different nucleation processes and our experimental method opens the door to study the structure and dynamics of materials with 4D atomic resolution.

References

9:00 AM *MT06.01.02*
Recent Advances in 3-4D In Situ X-Ray Imaging of Solidification Dynamics and Microstructure Formation
Ragnvald Mathiesen; Norwegian University of Science and Technology, Norway

Over the last decade, we have seen a vast development in X-ray imaging techniques, methods and instrumentation, both at synchrotron facilities and in the home laboratory. At present, X-ray imaging experiments can be carried out with spatial resolutions < 10 nm, or with time resolutions down to ~100 ns. It is also becoming more feasible to use other channels than those typical in transmission-based imaging (attenuation, phase contrast), such as diffraction or scattering to form the image contrast, also when studying dynamic systems. In solidification science, X-ray radiography, topography and tomography are well-established methods for studies solidification dynamics and microstructure formation. The presentation will show recent advances in fast high-resolution quantitative in situ imaging in 3 and 4D, with examples on how experimental output may be used to evaluate and guide computer modelling efforts within the field. Furthermore, some recent and near-future advances within X-ray imaging will be presented, allowing to combine ultra-fast imaging with high spatial resolutions to study governing process dynamics at mesoscopic scales. These advances also include image modalities new to solidification science, that may open for novel studies. Finally, the talk will present some preliminary results from dynamical dark-field imaging studies of dendritic mushy zones and growing eutectics, demonstrating a method that can provide completely new insight into thermomechanical effects in solidification processes.

9:30 AM BREAK

SESSION MT06.02: Solidification and X-Ray Analysis
Session Chairs: Amy Clarke and Ragnvald Mathiesen
Monday Morning, December 2, 2019
Hynes, Level 2, Room 209

10:00 AM *MT06.02.01*
In Situ X-Ray Investigations of Thin Binary Metallic Alloys and the Interplay of Confinement and Growth
Maike Becker1,2, Jonathan Dantzig1, Laszlo Sturz2, Matthias Kolbe1, Stefan Klein1,2 and Florian Kargl1; 1German Aerospace Center (DLR), Germany; 2Aix-Marseille Univ., Université de Toulon, CNRS, IM2NP, France; 3University of Illinois at Urbana-Champaign, United States; 4Access e.V., Germany; 5Deutsche Gesellschaft für
Materialkunde (DGM), Germany

X-radiography enables the observation of the solidification process in a few hundred microns thin samples of metallic alloys in real-time. Therefore, growth characteristics like solidification velocities or concentration changes can be determined and analyzed. The choice of thin samples avoids a superposition of the solidification structures and exploits the X-ray contrast through a clear distinction between the solid and liquid phases. Another advantage of the thin sample geometry is the possibility to arrange the main surfaces of the sample horizontally in the measurement apparatus, so that large scale fluid flows are reduced. However, radiography is only a 2D representation of a 3D process in which the radiography images display a projection of the 3D sample. Hence, what happens in the thickness direction remains largely hidden. Therefore, the question remains how the confined geometry influences the solidification process and the final microstructure.

We present our results on X-radiography studies of equiaxed dendrite growth in a near-isothermal temperature field with a focus on Al-Ge alloys. We have discovered a dendrite orientation transition (DOT) with increasing Ge concentration in this alloy system. Supplementary post mortem EBSD analysis of the in situ processed samples revealed that the dendrites change their growth directions from the crystallographic <100> to the <110> direction. In addition we found that the thin sample geometry influences the selection of the primary growth directions, so that different growth morphologies develop depending on the orientation of the crystals in the sample. Indeed, confinement in one direction forces the dendrites to select in-plane growth directions. Furthermore, the detailed study of the crystal orientations helped to identify certain 3D growth structures from the transmission contrast in situ images of the dendrites, although the images only represent a projection.

Additional important growth characteristics for dendritic growth are tip growth rates and liquid concentration fields. Both parameters are accessible in our in situ experiments. Tip growth rate measurements typically show a transient, an accelerating and a decelerating regime. However, acceleration occurs only when either the dendrites nucleate far from each other so that they have sufficient time to grow, or when they nucleate in a more undercooled melt. Concentration measurements show that deceleration clearly coincides with the overlap of solute fields from neighboring dendrites. Furthermore, we determined the profile of the solute concentration in front of a dendrite tip. These observations are used to elucidate the influence of confinement on the growing microstructure. To better understand the influence of the thin sample geometry and of important material properties on microstructure formation, a comparison of our experimental data with simulations is also pursued.

10:30 AM MT06.02.02
Investigating Nucleation and Initial Grain Growth in the Alloy System Al-Ge Observed in Real Time with In Situ Techniques Mareike Wegener1, Paul Kamm2, Francisco Garcia-Moreno2 and Florian Kargl1; 1German Aerospace Center (DLR), Germany; 2Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany

In-situ techniques like X-ray radiography at thin samples or tomography in the bulk material has become a powerful tool to investigate solidification process in metals in real time [1-3]

We use laboratory based X-ray radiography and fast synchrotron X-ray tomography to analyze nucleation and the initial growth of the nucleated grain depending on the level of added grain refiner, alloy composition and cooling rate, for the alloy system Al-Ge.

The influence of solute segregation and nucleation undercooling is characterized and parameters for the development of dendritic or globu-dendritic morphology of the grain studied. Fast synchrotron X-ray tomography enables 3D time-resolved observation of dendritic growth. With 50 topographies per second (tps) the destabilization of the solid-liquid interface and the transition from spherical growth towards dendritic morphology, in the early stage of the grain growth, was observed and a critical radius for the transition determined.

Nickel-based superalloys are nowadays still the reference material family to produce blades for advanced turbine engines. Creep-resistant turbine blades and vanes are produced by lost-wax casting and directional solidification, enabling an accurate control of the microstructure and therefore the manufacturing of single-crystal parts. Need for a higher efficiency of turbines motivates the use of materials resistant to higher temperatures. Nevertheless, selecting materials with improved mechanical properties sometimes increases the challenges to process them. For instance, CMSX-4 single crystal superalloy is known to be sensitive to the occurrence of freckles, defects causing the affected parts to be rejected.

Understanding the impact of thermo-solutal convection during alloy solidification is of central importance in the casting industry because convective flow generated from density variations in the liquid is at the origin of many casting defects, such as chemical segregations and freckles. Direct observation of metal alloy solidification by X-ray imaging is an invaluable tool to reveal the dynamics of microstructure formation. Among the various X-ray imaging techniques available using laboratory or synchrotron sources, X-ray radiography is an attractive method that simply consists in illuminating a thin sample with X-ray radiation. The transmitted image is collected on a detector to obtain a projected image of the solidification front, in situ and in real-time.

The present communication reports observations of the solidification of CMSX-4 and binary Ni-11wt.%Al alloys by using fast synchrotron X-radiography. Experiments have been carried out at the ID19 beamline of ESRF (European Synchrotron Radiation Facility) using a new high temperature furnace allowing materials with a high melting temperature to be studied. The use of a high-temperature directional solidification furnace along with the combination of an intense monochromatic beam and a high-speed X-ray sensitive camera allowed us to carry out the direct observation of the development of solutal flow during dendritic growth for Ni-based alloys. The formation of a dendritic network will be studied for directional solidification experiments carried out at various growth velocities using two solidification configuration: (i) the power-down technique consisting of concomitantly decreasing the temperature of the heating element and (ii) by pulling allowing us to follow the solidification of the whole sample from the bottom to the top. Interaction of the dendritic network with solute plumes will be reported, along with the development of convective flow in the mushy zone. The formation of liquid pockets on the sample side lead to the formation of equiaxed structures during their solidification. The processing of images recorded during pulling experiments allowed us to reveal the segregation pattern forming at the sample scale. In addition, measurements of characteristic parameters (primary, secondary dendrite spacings) will be compared to analytical models.

Since the discovery of quasicrystals (QCs) in 1984 [1], QCs have attracted substantial interest due to their unique structure. For instance, QC patterns exhibit long range order without short range periodicity, and classically forbidden rotational symmetry (e.g. 5-, 8-, 10-, and 12- fold). There exist two classes of QCs with different dimensions of quasiperiodicity: 2D (decagonal, $d$-) and 3D (icosahedral, $i$-) QCs. In the former case, the $d$-QC is stacked periodically along a decagonal ($i.e.$, ten-fold) axis [2]. In contrast, the $i$-QC shows quasiperiodicity in all directions. While the exceptional structural aspects of QCs have been reasonably well described in the literature, there are still remaining questions in terms of why and how they form in the first place.

In our talk, by leveraging state-of-the-art dynamic imaging techniques, we present our efforts on tracking the nucleation and growth of both classes of QCs near- and far-from-equilibrium, as well as the structural relaxation of QCs upon prolonged annealing. Our research was conducted with the aid of time-resolved synchrotron-based X-ray
microscopy (XRM) and dynamic transmission electron microscopy (DTEM). By coupling these two techniques, we have investigated a broad range of length-scales (from tens of nm to hundreds of μm) and solidification pathways (1 K/s to 10^6 K/s cooling rates). The results provide a wealth of knowledge on the emergence of QCs in deeply undercooled melts; the influence of phasons on QC stability; the growth mode of the QCs from a liquid (solidification) as well as a solid phase (precipitation); and similarities and differences in the crystallization signatures between the QCs and periodic approximant phases. We anticipate that our real-time experiments can provide guidance for simulations on this exotic form of matter.

References

11:15 AM MT06.02.05
Radiographic Investigations of the Formation and Growth of Primary Intermetallic Compounds in Liquid Aluminium Alloys Shikang Feng1, Enzo Liotti1, Christoper Gourlay2, Yi Cui2 and Patrick Grant1; 1Oxford University, United Kingdom; 2Imperial College London, United Kingdom

X-ray radiography and tomography imaging studies have been applied widely to study solidifying alloys in order to understand the effect of cooling conditions, alloy composition and presence of external fields such as gravity, electromagnetic pulses, extrinsic additions, etc on crystal formation and growth. However, these studies have predominantly concerned understanding primary phase formation whereas the properties of many engineering alloy castings are more generally (and more dramatically) controlled by the size, morphology, distribution, volume fraction and nature of minority, dispersed secondary phases. These phases may be present in concentrations of only a few volume percent, and are frequently formed at temperatures close to the formation of the majority phase or at lower temperature by eutectic reaction, which makes studying the dynamics of their formation and growth more difficult. These secondary intermetallic compound (IMC) phases are also often ordered structures that exist only over a comparatively narrow range of compositions. In contrast to the disordered primary phases, such as a-Al in aluminium alloys, the way in which the formation and growth dynamics of these ordered IMCs can be affected by changes to casting conditions is much less well-understood.

This investigation applies equipment and software tools developed for the radiographic study of the dynamics of primary phase formation using synchrotron X-rays in aluminium alloys and applies them to model alloys in which normally secondary minority IMCs, known to have a controlling effect on toughness and ductility, are contrived to appear directly from the cooling liquid as primary phase, unconstrained by any prior formation of a conventional primary phase. The formation and growth of two alloy classes are studied in detail: (i) Al-3wt%Fe in order to study the important β-Fe IMCs found in may commercial aluminium alloys, and (ii) an Al-Pt-Er model alloy chosen to have similar morphology IMCs to β-Fe but where the presence of Pt and Er enable the use of a novel pixellated spectrometer detector that spatially resolves the distribution of Pt and Er in the forming IMCs, and in the surrounding liquid. In the former alloy, a technique for estimating the formation temperature of every β-Fe IMC particle directly from the radiographic image sequences is also described.

Real-time observations are combined with detailed post-solidification microscopy including high resolution electron back-scatter diffraction (EBSD) to confirm similarities of the IMCs in both alloy systems, and to identify a common twin plane re-entrant (TPRE) growth mechanism. Extrinsic additions to the alloy such as grain refiners are also investigated to show how IMC formation dynamics and temperatures can be manipulated in a manner similar to that of α-Al dendrites. Examples are given of how the different data from these experiments can be fused to improve our understanding of the factors controlling the formation and growth of IMCs. These insights may ultimately allow better exploitation of the beneficial effects of IMCs on properties such as tensile strength, while minimising their detrimental effects on toughness and ductility, and so enable the development of “tolerant” processing of alloys to enable greater metal recirculation.

11:45 AM MT06.02.06
A Joint Machine Learning and Multi-Stage Thresholding Approach to Automated Dendrite Analysis within In Situ X-Ray Videos of Isothermal Equiaxed Alloy Solidification in Microgravity Jonathan S. Mullen, Mert Celikin and David Browne; University College Dublin, Ireland
The automated assessment of growing dendrites within in situ X-ray videos of alloy solidification can be vulnerable to errors stemming from the underlying traits of the frames provided. Specifically, the high degree of image difference between the start and the end of the observed process, along with factors such as noise and the effective shutter speed used, can lead to a reduction in assessment accuracy. The approach demonstrated here seeks to address and mitigate these issues through a combination of machine learning and multi-stage thresholding, balancing the adaptability of the former with the processing capabilities of the latter. This solution was developed and tested using a video of spatially isothermal, equiaxed solidification of a thin Al-20wt%Cu alloy sample during the 2015 MASER 13 sounding rocket microgravity flight within the on-board XRMON-SOL furnace.

SESSION MT06.03: Rapid Solidification and High Undercooling
Session Chairs: Jianwei Miao and Damien Tourret
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 209

1:45 PM *MT06.03.01
Dynamic Transmission Electron Microscopy for In Situ Studies of Irreversible Materials Processes Joseph McKeown; Lawrence Livermore National Lab, United States

The dynamic transmission electron microscope (DTEM) at Lawrence Livermore National Laboratory (LLNL) was developed to enable imaging of rapidly evolving, irreversible materials processes with nanometer spatial and nanosecond temporal resolutions. DTEM uses electron pulse trains generated by UV-stimulated photoemission to provide multiple (up to 9) image acquisitions across temporal ranges from hundreds of nanoseconds to microseconds, yielding frame rates that are on the order of 10^6 times higher than conventional in situ TEM frame rates. This pulse train is accomplished with a laser based on an arbitrary waveform generator (AWG) to shape laser pulses to square temporal profiles, producing a user-defined (pulse duration and spacing) UV pulse train that is delivered to the instrument’s photocathode to generate an electron pulse train. Each electron pulse captures an image at a specified delay time, and a high-speed electrostatic deflector directs each image to a different segment of a CCD camera. A multi-frame image (i.e., a movie) is obtained at the end of the experiment. Here, an overview of the DTEM instrument and its operation will be presented.

The majority of DTEM work has focused on imaging of microstructure evolution and precise measurement of kinetics during non-equilibrium phase transformations. As a representative example, studies of rapid alloy solidification (RS), in which solid-liquid interface evolution is monitored and the solidification dynamics are determined, will be discussed. RS occurs in numerous manufacturing processes, such as laser welding and additive manufacturing (AM). Recently, the growth of metals-based AM has led to renewed interest in developing predictive modeling capabilities to describe microstructure evolution under RS conditions (i.e., large deviations from equilibrium solidification due to high interface velocities). Calibration and validation of models to describe these non-equilibrium solidification conditions has proved challenging, largely due to the difficulties associated with acquiring in situ experimental measurements. DTEM results (measured interface velocity and morphology) will be presented in conjunction with efforts to calibrate and validate phase field models to describe RS.

Finally, future directions of research using DTEM will be discussed, with particular focus on efforts to develop an experimental platform to image microstructure evolution and defect formation and propagation during in situ high-strain-rate tensile testing of metals with the goal of understanding the dynamic mechanical properties of materials.

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2:15 PM *MT06.03.02
In Situ High-Energy X-Ray Diffraction Studies of Undercooled Solidification Jianrong Gao; Northeastern University, China
Liquid metals can be undercooled significantly below their melting temperatures and bring about formation of a rich variety of metastable microstructure. It is of fundamental and technical interest to understand thermodynamics and kinetics of undercooled solidification. In the past twenty years, solidification velocity-undercooling relationships in pure substances and alloys have been established by means of in situ observations of a traveling thermal front on the surface of the solidifying bulk liquid using a camera or a photodiode. Those relationships have been used to test various theories on rapid solidification and provided insights into metastable microstructure formation under non-equilibrium processing conditions. However, primary solids nucleated from the undercooled liquid may differ from those predicted by an equilibrium phase diagram suggesting metastable or even new solidification pathways. They are more often than never remelted or decomposed in a late stage of solidification or through solid-state cooling leading to difficulties in identification of their crystal structure and changes of solidification pathways. In situ monitoring of undercooled solidification using the time-resolved X-ray diffraction technique can ease these difficulties and provide critical knowledge of solidification pathways, stable or metastable, as well as ripening or decomposition of primary solids. In this talk, I shall present two examples of the use of this technique in in situ monitoring of non-equilibrium solidification of undercooled Nd–Fe–B and Co–Si alloys. In both alloys, metastable solids are formed at medium bulk undercoolings but are decomposed prior to completion of solidification of a bulk liquid. With such knowledge, microstructure formation in as-solidified samples can be well understood. I shall also talk about potential of this technique in advancing current understanding of other non-equilibrium solidification phenomena or in combination with other techniques.

2:45 PM BREAK

SESSION MT06.04: Solidification—Interface Pattern Dynamics
Session Chairs: Maike Becker and Guillaume Reinhart
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 209

3:15 PM *MT06.04.01
In Situ Observation of Crystal Orientation Effect on Lamellar-Eutectic Solidification Microstructures in Thin Al-Al2Cu Samples Sabine Bottin-Rousseau; Sorbonne University, France

We present an in situ experimental study of crystallographic effects during nonfaceted eutectic growth in thin Al-Al2Cu samples. Thin (about 10 µm thick) near-eutectic Al-Al2Cu films were prepared by plasma sputtering on flat sapphire (Al2O3) substrates. The thin-sample geometry allows one to observe lamellar-growth patterns in real time without convection in the liquid. We used a reflected-light long distance optical microscope that focuses the contact surface of the metallic film with one of the transparent walls of the sample container during directional solidification.

We recall that in bulk solidification, in brief, the Al-Al2Cu alloy usually forms lamellar microstructures. The two eutectic phases are also known to present special, or heteroepitaxy crystal orientation relationships (ORs). Marked crystallographic effects, i.e., a dependence of the growth microstructure on the OR, have been reported for a long time in Al-Al2Cu. More recently, a theory of such crystallographic effects, which takes into account the anisotropy of the surface free energy of the interphase boundaries in the solid, has been proposed, and essentially validated by experimental and numerical studies using model systems [1-3]. This analysis casted light on the distinction that exists between a « floating » dynamics, which is characteristic of an essentially isotropic system, and a « locked » dynamics, during which the lamellae follow a direction that is determined by the OR-dependent anisotropy, and thus possibly grow inclined with respect to the thermal-gradient axis.

Our observations, combined with ex situ crystallographic analysis (X-ray diffraction and EBSD), provide additional evidence for this statement. We studied 8 different eutectic grains of large (typically 4 mm) lateral extension. Most of (7 out of 8) were of the locked type. At low velocity, that is when the lamellar spacing is larger than the sample thickness, the solidification dynamics is essentially 2D. In locked grains, the interphase boundaries appear then as straight lines under the optical microscope, and follow an essentially uniform locking direction. Here are our main findings: 1-Al2Cu crystals were not arbitrarily oriented with respect to the sample walls, namely, a {001} plane and a {100} plane were both nearly perpendicular to the sapphire plate (within 10°); 2-The apparent trace of the
interphase boundaries followed a direction that was systematically belonging to the \{100\} plane in question; 3-We found some reproducible ORs, but none of them were close to the so-called Beta-6 or Alpha-4 ones that are frequently found in bulk samples [4,5]. It seems therefore that a heuristic density criterion that was successfully invoked for predicting the prevailing coincidence planes in the In-In₂Bi eutectic alloy is of poor help in the present case [6]. Our results also raise new questions about the selection dynamics of the ORs during the early stages of eutectic solidification.


3:45 PM MT06.04.02
Emergence of Faceted Spiral Patterns During Eutectic Crystallization
Saman Moniri¹, Hrishikesh Bale², Tobias Volkenandt³, Yeqing Wang⁴,¹, Jianrong Gao⁴, Tianxiang Lu¹, Kai Sun¹ and Ashwin J. Shahani¹; ¹University of Michigan, United States; ²Carl Zeiss Microscopy Inc., United States; ³Carl Zeiss Microscopy GmbH, Germany; ⁴Northeastern University of China, China

Engineered self-organization presents a future approach to manufacture multi-phase materials with superior properties. In particular, non-equilibrium routes to emergent metastable states could unveil novel functionalities not present in equilibrium states. Herein, we demonstrate the spontaneous formation of metastable, two-phase spiral microstructures during crystallization of a eutectic alloy system. Despite recent reports of spiral self-assembly in both metallic and organic systems, the underlying growth mechanism remains elusive. To reveal the origin of spiral growth, we pursue a multiscale investigation encompassing 3D measurements – X-ray nano-tomography aided by machine learning and electron backscatter diffraction – along with in situ synchrotron X-ray diffraction and atomic-resolution electron microscopy. The results show that crystallographic defects within 'hidden' polytetrahedral phases provide a template for spiral eutectic crystallization. Our findings demonstrate the ubiquity of defect-mediated growth in multi-phase materials and establish a pathway towards bottom-up synthesis of 3D chiral microstructures beyond the scope of existing approaches.

4:00 PM MT06.04.03
Diffusion Controlled Dynamics of Faceted Solidification Front Patterns
Silvere Akamatsu¹,²; ¹CNRS, France; ²INSPI-CNRS-SU, France

During solidification of a faceted alloy, the growth shape of the crystalline solid is primarily determined by the strongly anisotropic mobility of the interface between the solid and the melt. In a given system, it is not rare to observe facets that grow extremely slowly at finite undercooling, and even appear "frozen" or "blocked" on the spatial scale of the optical microscope, and other ones that grow as fast as if they were atomically rough. During solidification of a dilute alloy, the interplay between such a facet growth kinetics and the diffusion of chemical species in the liquid is then very complex, and achieving a steady-state growth regime, if possible at all, depends critically on the orientation of the crystal and boundary conditions.

Here, we present an experimental study of faceted growth patterns in dilute transparent alloys. We used thin-sample directional solidification techniques that permit to control the orientation of large single crystals with respect to the setup, and observe the evolution of the solid-liquid interface in real time with an optical microscope as a function of the growth rate. We will successively consider two cases. First, in impure biphenyl, the platelike growth shape of the monoclinic crystals includes two low-mobility (001) facets and four high-mobility (110) facets. We found that if a thin crystal is oriented with the (001) facets parallel to the sample walls, steady faceted cells and dendrites form for solidification velocities \( V \) above the threshold \( V_c \) of the Mullins-Sekerka instability. Both acute-angle [100] and obtuse-angle [010] cells are observed. As previously predicted theoretically, the presence of mobile facets on both sides of the dendritic finger does not strongly affect the regular dendritic scalings. For \( V < V_c \), large single crystals undergo a plastic deformation during growth due to long-range thermal stresses. Second, we considered a cyano-bicyclohexane molecule called CCH4 in the scientific literature. In this system, the interface between a nematic liquid and the so-called smectic B phase (a historical, but misleading name that designates a hexagonal molecular-
crystal solid with both orientational and positional long-range orders) presents a single facet plane parallel to the basal plane of the hexagonal stacking. We could bring evidence that the facets have practically no mobility at undercoolings smaller than about 0.1 K. In configurations where the CCH4 molecular layers are perpendicular to the sample walls, but tilted with respect to the main solidification axis, we observed drifting shallow cells (V>Vc) and a type of solitary wave, called faceton (V<Vc). A faceton consists of a localized traveling pattern with an asymmetric faceted shape, which propagates laterally, along the solidification front, in a stationary or oscillatory way. This dynamics casts light on the microscopic growth mechanisms of the facets in this system. It also has some striking similarities with the growth dynamics of silicon polycrystals.

4:15 PM MT06.04.04
Effect of Subgrain Boundaries on Microstructure Evolution During Directional Solidification of Binary Alloys Kaihua Ji1, Fátima Mota2, Younggil Song1, Jorge Pereda2, Bernard Billia2, Nathalie Bergeon2, Rohit Trivedi3 and Alain Karma1; 1Northeastern University, United States; 2Aix-Marseille Université and CNRS, France; 3Iowa State University, United States

Alloy microstructures formed by directional solidification are often polycrystalline, made up of several large grains of different crystallographic orientations with respect to the temperature gradient. While strongly misoriented grains are generally eliminated at early stages of growth, grains with misorientations less than about 15 degrees can persist to late stages and form subgrain boundaries (SBs), which can influence microstructure selection by mechanisms that are still not well understood. Here we combine experimental, phase-field, and analytical methods to investigate the coupled spatiotemporal evolution of SBs and cellular array structures, including the selection of the primary spacing and the lateral drift velocity induced by the grain misorientation. Experiments were carried out in the DECLIC/DSI experimental set-up aboard the International Space Station where a transparent (Succinonotriile-0.24wt%Camphor) alloy contained within a 3D crucible is solidified under purely diffusive growth regime. The in situ observations exhibit both convergent and divergent SBs, where two grains drift laterally to converge on and diverge from each other, respectively. Near a convergent SB, grains usually inter-penetrate, and the primary spacing of cells decreases in a relatively short range as cells are suppressed and eliminated at the SB. Near a divergent SB, however, a peak accompanied by a long tail is observed in the spacing distribution along the direction normal to the SB. Meanwhile, a divergent SB drifts laterally with a non-trivial velocity comprised between the drifting velocities of individual grains. State-of-the-art phase-field simulations reproduce those novel phenomena observed in the microgravity experiments.

We further develop a discrete nonlinear advection-diffusion equation to describe quantitatively the spatiotemporal evolution of the primary spacing in the presence of SBs. Our results show that advection alone, previously found to describe well the spacing evolution within a single misoriented grain, is insufficient to model quantitatively this evolution in the neighborhood of spacing extrema caused by SBs. We find that incorporation of phase diffusion, which tends to uniformize the spacing, is essential to quantitatively predict both the spacing evolution near extrema and the apparent drifting velocity of SBs that is comprised between the drifting velocities of individual grains. The non-trivial prediction of this apparent velocity directly links phase diffusivity to an experimentally observable quantity. Those insights into polycrystalline directional solidification provide an improved basis for controlling alloy microstructures.

4:30 PM MT06.04.05
Grain Competition in Polycrystalline Columnar Dendritic Solidification—Scale Bridging by Handshake between Phase Field and Dendritic Needle Network Methods Amir Molavi, Kaihua Ji and Alain Karma; Northeastern University, United States

Dendritic microstructures are the most frequent among cast metallic alloys. Understanding their formation has been a problem of long-standing interest because of their profound influence on mechanical properties. During columnar solidification, spatially extended dendritic grains of different misorientations with respect to the temperature gradient growth competitively. This growth competition has been recently investigated using 2D and 3D phase-field simulations. The results have highlighted the limitation of using a traditional minimum undercooling criterion to predict grain selection and the importance of considering details of grain interactions. However, results to date remain limited to moderate growth rates and large temperature gradient that form weakly branched cellular/dendritic array structures. Here we report the results of a study that combines phase-field (PF) and the dendritic needle network (DNN) methods to investigate grain competition in the well-developed dendritic regime relevant for casting.
of concentrated alloys. The PF model of alloy directional solidification exploits a novel rotationally invariant finite-difference discretization of the anti-trapping current to accurately resolve the dendrite tip operating state of misoriented grains. PF simulations are used to investigate the growth dynamics of secondary and tertiary branches, which play a key role in grain competition. In turn, DNN simulations with branching parameters calibrated by PF simulations, are used to characterize experimentally measurable grain boundary (GB) trajectories on larger length and time scales and to construct GB orientation selection maps as a function of GB bi-crystallography. The results reveal how the grain competition on the macroscale is influenced by the sidebranching dynamics on the dendrite tip scale, which is itself controlled by the magnitude of crystalline anisotropy and noise amplification. Results are compared to available experimental data.

4:45 PM MT06.04.06
Mechanisms of Structure Formation in Ice-Templated Materials—Experimental Observations Kaiyang Yin1, Kaishua Ji2, Moises Silva1, Louise L. Strutzenberg3, Rohit Trivedi4, Fridon Shubitidze5, Alain Karma2 and Ulrike G. Wegst1; 1Dartmouth College, United States; 2Northeastern University, United States; 3Northwestern University, United States; 4NASA Marshall Space Flight Center, United States; 5Iowa State University, United States

The basis of freeze casting is a phase-separation-induced templating of a second phase (e.g. polymers or particles, or both). The process is complex, a large number of parameters determine the structure and properties of the resulting freeze-cast material: i) the chemistry of the solution or slurry system (e.g. polymer and/or particle composition and properties such charge, size and shape), ii) additives and impurities (and their effect on either the solvent, polymer or particles), iii) processing conditions (e.g. cooling rate, temperature field), and iv) the physics of the strongly anisotropic faceted growth of ice. Empirically over the past 15-20 years, strategies have been developed to control some of these parameters in an attempt to custom-design and manufacture in a single processing step materials over several length-scales. However, while many different materials compositions have been investigated over the years — e.g. ceramic- and metal-based systems, both typically processed with the addition of polymeric dispersants and binders, and polymeric ones, both fibrillated and "smooth" — few have been analyzed with the intent to gain a better understanding of the mechanisms by which the ice crystal growth drives structure formation and self-assembly processes. The latter is what we attempt in this study.

Collating structural features found in the cell walls of freeze-cast ceramics (platelets versus particles), fibrillated biopolymers (collagen, nanocellulose), and "smooth" biopolymers (chitosan, trehalose), we can capture the ice crystal growth process and analyze it "post-mortem." Further assessment of the cell-wall structure using a variety of characterization techniques provides unique insights into the effects and their significance on cell wall assembly of anisotropic ice crystal growth, shear flow generated by the volumetric expansion of ice, and other forces, such as those exerted by the mold, for example. Combining these experimental observations with 3D Phase-field simulations of structure formation in ice-templated materials, detailed in a companion presentation, it becomes possible to gain fundamental science insights and obtain the desired structure-property-processing correlations not only at the more traditional macroscopic, but also at the meso- and microscopic scales.

SESSION MT06.05: Poster Session I: Solidification, Processing and Phase Transformations
Session Chairs: Ashwin Shahani and Manas Upadhyay
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

MT06.05.01
Analysis of Strain Aging of Steel Sheets by In Situ Electrical Resistance Measurement Mai Nagano1, Kotaro Hayashi1 and Masato Ueda2; 1Nippon Steel Corporation, Japan; 2Kansai University, Japan

The observation of the dynamic dislocations-carbon atoms interaction is important in the steel material design. BH steel sheets are bake hardened in the manufacturing process. It is said that solute carbon atoms are segregated in dislocations after bake hardening. Solute carbon atoms are observed by atom probe method [1]. However, there are few examples observed directly including the behavior of dislocations after bake hardening. An electrical resistance measurement method is able to observe both the solute carbon atoms and the state of dislocations [2]. The electrical
resistivity measurement can not only be measured on bulk samples, but also the in-situ measurement of the process of deformation after pre-deformation, baking, and hardening after baking. In this study, we developed in-situ measurement methods of electrical resistance in the bake hardening test. And we considered the metallurgy of BH steel sheets in the process of thermomechanical treatment of BH steel sheets.

Cold rolled sheets of Fe-0.02 mass% C-0.1 mass% Mn alloy, Fe-0.002 mass% C-0.1 mass% Mn alloy, and Fe-0.002 mass% C-0.1 mass% Mn-0.03 mass% Ti alloy were prepared. The respective alloys are called carbon steel, low carbon steel and ultra-low carbon steel. These cold rolled sheets were held at 1073 K for 120 seconds and then water cooled. From the test steel, a tensile test specimen with a load axis perpendicular to the rolling direction was cut out. The length of the gauge portion was 50 mm and the width was 2 mm. In tensile deformation, the electrical resistance of each specimen was measured at room temperature. In order to measure the electrical resistance of the test piece only, the test piece was electrically isolated from the device and the electrical resistance was measured in distilled water ice water. When tensile deformation was applied, the stroke speed was 0.25 mm / min. The electrical resistance was measured at a current value of 100 mA by the four-point DC method. In addition, after pre-deformation was applied to some of the test pieces as the bake-hardening treatment, the test pieces were immersed in a bath furnace at 443 K for 20 minutes. After that, the electrical resistance of the same test piece was measured again in tensile deformation.

The structure after water cooling was observed with an optical microscope, and the carbon steel was a composite structure of pearlite and ferrite. Low carbon steel, ultra-low carbon steel has ferrite structure. The average grain sizes of carbon steel, low carbon steel and ultra-low carbon steel were 11 μm, 17 μm and 16 μm respectively.

In carbon steel, the electrical resistance was measured during tensile deformation before bake hardening. As a result, the stress increased with the increase of stroke and the electrical resistance. The gradient of electrical resistance to stress is different in elastic deformation, Lüders deformation, and uniform plastic deformation area. The gradient of the electrical resistance to stress is called a stress-electrical resistance factor. The stress-electric resistance factor is larger in the order of Luders deformation, uniform plastic deformation and elastic deformation. In addition, the electrical resistance during tensile deformation was measured for the sample that had undergone the bake hardening process. As a result, the stress-electric resistance factor after the end of elastic deformation increased more rapidly than the pre-deformation. The increase in electrical resistance may correspond to the increase in lattice defects and the solute carbon concentration.

Thus, we developed a series of methods to measure the electrical resistance in situ in the bake-hardening test, and it became possible to capture microscopic information on the structure of dislocations and solute carbon atoms.

Reference

MT06.05.02
Effect of Solid-State Diffusion on Morphological Evolution During Liquid Metal Dealloying Longhai Lai and Alain Karma; Northeastern University, United States

Liquid metal dealloying (LMD) is a novel technique to produce nano-/meso-scale composite and open nanoporous structures with ultra-high interfacial area for diverse applications. This method exploits the selective dissolution of one element of a binary alloy into a metallic melt. Previous experimental and modeling studies have revealed that the kinetics of LMD is diffusion limited and that interfacial pattern formation can be understood in the framework of interfacial spinodal decomposition and diffusion-coupled growth. However, quantitative discrepancies exist between experiment and modeling predictions. Here, we report the results of a phase-field modeling study that reveals a surprisingly strong influence of solid-state diffusion on dealloying morphologies. Even though the solid-state diffusivity is four to five orders of magnitude smaller than the liquid-state diffusivity, it is found to stabilize the diffusion-coupled growth of lamellar structures, thereby favoring the formation of this aligned structure over high-genus topologically connected structures. The results also reveal that solid-state diffusion enables the solid-liquid interface to relax to local chemical equilibrium, thereby influencing the concentrations of alloy elements on the liquid side of the interface and in turn morphological evolution. We also present long-time simulations of dealloying kinetics that shed light on the origin of existing discrepancies between modeling and experiment.

MT06.05.03
X-Ray Photon Correlation Spectroscopy Studies of Spinodal Decomposition in TiO2-VO2: Epitaxial Thin Films Jeffrey A. Eastman1, G B. Stephenson1, Carol Thompson2, Matthew J. Highland1, Jyotsana Lal2, Irene Calvo-
Almazán¹, Hoydoo You¹, Yue Cao¹ and Hua Zhou¹; ¹Argonne National Laboratory, United States; ²Northern Illinois University, United States

TiO₂-VO₂ alloys are known to undergo spinodal decomposition when cooled below 557°C at a critical composition of 34 mol % Ti.¹ Since the misfit between the rutile-structured TiO₂ and VO₂ lattices is significantly smaller along the a-axis than along the c-axis of the tetragonal unit cell, annealing samples in the spinodal region of the phase diagram results in development of a composition modulation along the [001] direction, with an average quasi-periodicity varying from 15-50 nm, depending on composition and annealing conditions.¹,² Since the VO₂-rich regions of the resulting nanostructure exhibit a metal-insulator transition and a correspondingly large change in magnetic susceptibility near room temperature, while the TiO₂-rich regions remain insulating at all temperatures and exhibit very different optical behavior than VO₂-rich regions, these alloys are of interest as possible tunable metamaterials.² Full control of the synthesis of such metamaterials requires detailed understanding of their phase separation behavior as functions of temperature, composition, epitaxial strain, and surface orientation. To obtain this information, we recently initiated an x-ray photon correlation spectroscopy (XPCS) study of epitaxial TiO₂-VO₂ alloy thin films. XPCS is a coherent x-ray technique that can provide unique insight into the dynamical behavior of materials. Films with controlled composition, thickness, and surface orientation are grown epitaxially on TiO₂ substrates. Samples are illuminated with a partially coherent monochromatic x-ray beam at Sector 12-ID-D of the Advanced Photon Source. The time- and Q-dependences of the diffuse intensity that develops along [001] directions near Bragg reflections during spinodal decomposition are monitored in situ, while annealing samples. At temperatures in close proximity to the critical temperature for phase separation we are attempting to characterize equilibrium composition fluctuations for the first time in a crystal with a conserved order parameter (Model B in the notation of Hohenberg and Halperin³). At somewhat lower temperatures, e.g., 400°C, XPCS can reveal new information on atomic-level dynamics as the sample undergoes spinodal decomposition. Closer to room temperature, the metal-insulator transition associated with a tetragonal-to-monoclinic phase transition provides another opportunity to use XPCS to observe equilibrium critical fluctuations.

This work is supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.


MT06.05.04

In Situ TEM Investigation of the Electroplasticity Phenomenon in Metals Xiaqing Li¹,², Andrew M. Minor¹,², John Turner², Rohan Dhall² and Karen Bustillo²; ¹University of California, Berkeley, United States; ²National Center for Electron Microscopy, United States

Electroplasticity (EP) is a phenomenon in which applied pulsed electric fields during deformation result in increased formability in metals. This phenomenon has been studied since the 1950’s [1] and researchers have proposed two possible origins of this nearly-universal effect: (1) localized Joule heating at lattice defects and (2) the electron wind effect leading to vacancy migration [2]. However, there is no clear evidence of the true origin of this behavior at the level of individual defects [3]. In this work, in situ Transmission Electron Microscope (TEM) electromechanical tests were performed in order to correlate direct observations of dislocation motion with both mechanical data and applied electrical pulses in an effort to provide clarity on the true origin of this interesting phenomenon.

In this study we have systematically studied the way electrical fields alter the structure and mobility of dislocations in Ni. The controlled electromechanical experiments were performed during in situ testing in a JEOL 3010 TEM, an electrical push-to-pull device (E-PTP) and a Bruker, Inc. Picoindenter with Nanoscale Electrical Contact Resistance (nanoECR). Specific loading and observation directions were selected for the specimens, which were attached via focused ion beam (FIB) lift-out to the E-PTP device. The specimens were deformed uniaxially in tension with the motivation to correlate dislocation behavior and applied current pulses. A sequence of tests was carried out by load control and with variable electrical current pulsing during the mechanical test.
After each test, videos of the dislocation behavior could be directly compared to the electrical and mechanical data. Our initial studies resulted in two types of dislocation motion. The first type of motions happened in less than 0.1 sec where pre-existing dislocations escaped from the sample upon pulsing. The other type of motion was slower, with dislocations remaining in the sample for more than 1 second. In the latter case, dislocation motion could be observed through several consecutive steps.

Our observations found that during plastic deformation, relatively large slip traces with dislocations nucleated from the edges could be triggered by the pulses, contributing to large displacement increases in the sample. One example of dislocation motion in Al shows the motion of a dislocation could be correlated directly with the applied current when it was turned on, which can be explained by small changes in the applied electrical current that enabled the dislocation to overcome barriers. In addition, dislocations tend to move with a faster speed and a longer distance during the pulsing period, compared to the purely mechanically-triggered movement. We will also discuss results such as these in the context of local joule heating which can be measured indirectly through expansion of the lattice measured using TEM diffraction.

It is our ultimate goal to quantitatively measure the strain fields and local lattice change around dislocations to understand the external current effects in the plastic deformation of metals and alloys. Comparisons between the lattice strain fields, dislocation behavior and applied electric filed will provide valuable data to further improve atomistic models describing the dislocation motion change with electroplasticity. These experimental and theoretical frameworks will provide a scientific foundation for the design and optimization of alloys with enhanced electroformability for targeted manufacturing applications.

MT06.05.05
Laue Microdiffraction Measurements in Directionally Solidified Al-Al2Cu Eutectic Microstructures in Thin Samples Mehdi Medjkoune; Sorbonne Université, France

We present the first study by Laue microdiffraction (LMD) of the crystal orientation relationships in lamellar microstructures obtained by thin-sample directional solidification of the eutectic Al-Al2Cu alloy. The two eutectic phases are the Al-rich cubic solid solution (α) and the tetragonal intermetallic Al2Cu (θ). Thin Al-Al2Cu samples (12 µm thick) were fabricated by plasma sputtering on a clean, optically flat, sapphire single crystal. Eutectic growth was performed in our laboratory by using standard directional solidification (DS) at constant velocity in a fixed temperature gradient, and rotating directional solidification (RDS). The RDS method allows one to rotate the sample with respect to the temperature gradient, and therefore vary continuously the orientation of the eutectic solid during solidification. Both DS and RDS setups are equipped with a long-distance optical microscope for real-time observation of the growth front. Laue microdiffraction has been carried out ex situ on the BM32 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. In this technique, a thin “white” x-ray beam (typically 5 to 22 keV) of lateral extension in the 100 nm range is sent to the surface of the sample. Selected areas (typically 100X100 µm²) were investigated by using a step-wise scanning motion of the sample holder. At each position (sample pixel) the camera detector records a full Laue pattern, which includes diffracted spots emitted by the metallic film and the sapphire substrate (nondestructive method). The signal coming from the sapphire single crystal was observed to remain unchanged during a scan. The alternation of the aand q lamellae could be clearly seen, and the corresponding sets of diffraction spots univocally indexed.

We investigated 5 samples containing each 2 to 3 large eutectic grains. Here, we will mainly focus on a reference sample that has also been investigated by x-ray diffraction (XRD pole figures) and EBSD. That sample contained three distinct eutectic grains of the so-called locked type. Our XRD, EBSD and LMD results are in full quantitative agreement with each other: 1-In the three grains, the Al2Cu crystals are oriented with a(100)θ plane nearly parallel, and the (001)θ plane nearly perpendicular to the sample wall; 2-The distinct crystal orientation relationships (ORs) that we could identified in the three grains (and in the other samples) are different from those that are most commonly found in bulk Al-Al2Cu samples; 3- There are strong indications that the interphase boundaries follow a (010)θ plane, independently of the OR. As a main conclusion, we found that the structure of the Al2Cu phase dominates the determination of the free energy of the interphase boundaries, and selects the lamellar growth direction. Further investigations will be needed for elucidating the OR-selection mechanism at play (nucleation, grain competition). Finally, LMD measurements can be used to measure the mosaicity of the crystals. This work is in progress.
3D Phase-Field Simulations Explain Experimental Observations of Structure Formation in Ice-Templated Materials

Kaihua Ji¹, Kaiyang Yin², Louise L. Strutzenberg³, Rohit Trivedi⁴, Fridon Shubitidze⁵, Ulrike G. Wegst⁵ and Alain Karma¹; ¹Northeastern University, United States; ²Dartmouth College, United States; ³Marshall Space Flight Center, United States; ⁴Iowa State University, United States

Recent improvements to quantitative phase-field simulations now make it possible to model microstructure formation in three dimensions (3D) on experimentally relevant length and time scales, but quantitative modeling remains so far limited to materials that solidify with atomically rough non-faceted solid-liquid interfaces such as metallic alloys and transparent analogs. We developed a quantitative phase-field formulation for the faceted ice-water system with anisotropic solid-liquid interface energetic and kinetic properties calibrated against existing experimental observations of free dendritic growth of pure water under microgravity conditions. Using 3D phase-field simulations of directional solidification of water with a dilute impurity, we reproduce for the first time salient features of freeze-cast templated structures including the formation of lamellae and undulated ridges. The formation of ridges is shown to be caused by the breakdown of ice platelets, which grow in between lamellae in the basal plane of ice, into linear arrays of cells with rounded tips. The cell spacing determines the ridge spacing and undulations are generated by secondary oscillatory instabilities of cell growth. Our results highlight the crucial role of the anisotropy of both the solid-liquid interface free-energy and the interface kinetics in structure formation. They also demonstrate that other potentially important physical effects neglected in the phase-field model, such as fluid flow generated by the expansion of ice, may play a more secondary role in structure formation. The value of such 3D phase-field simulations is immense since they enable us to investigate little studied and not yet modeled mechanisms of hierarchical microstructure formation and cell wall material self-assembly, both of which define anisotropy, property profile, and overall performance of freeze-cast materials. A companion presentation highlights the experimental results that motivate our work.

Tracking the Initial Stages of Grain Boundary Formation in Bi₂O₃-Doped ZnO Polycrystalline Materials—Dynamics and Structures

Marcelo A. Martinho, Gabriel D. Rocha, Marco Aurelio L. Cordeiro and Edson R. Leite; Federal University of São Carlos, Brazil

Owing to the structural and chemical nature of polycrystalline materials, grain and phase boundaries play a fundamental role in these materials properties by tailoring desired material features (e.g., mechanical, electrical, optical properties). In spite of the evident importance, the basic understanding of these interfaces is still in its beginning, and lacks an essential correlation of its structure and materials properties. In order to provide fundamental insights into the structure and chemical nature of the grain boundary in oxides, grain boundaries of Bi₂O₃-doped ZnO polycrystalline materials in earlier sintering stages were analyzed by Aberration-corrected Transmission Electron Microscopy (FEI Titan Themis Cubed TEM operating at 300kV), where inelastic electrons from the beam were used as a source for mild temperature increasing in the system. Polycrystalline Bi₂O₃-doped ZnO samples were produced by solid-state synthesis route, consolidate by simple uniaxial pressure and sintered at 1100 °C for 2 hours. By using a Helios Nanolab Dualbeam 660 (Thermo Scientific), grain boundaries were identified and prepared in thin lamella form, which were studied by TEM. The first feature observed is the Bi-rich (nano)interphase region, where several atomic organizations could be identified. These structures formation was correlated to the complexions (phase-like behavior) [1,2] and their neighboring crystals orientation. Besides, during the analyses, electron beam promoted mild temperature increasing in the sample, which was enough to induce Bi migration, which was possible to observe at atomic resolution and real-time. According to the time-resolved images, the Bi diffusion followed a chemical potential gradient path over the sample, i.e. from higher (bulk) to lower (grain boundary region) chemical potential gradient, inferring it was the driven force for the phenomenon. Moreover, the temperature increasing promoted the Bi-rich phase acting as a liquid-like behavior on the sample surface, following the same chemical potential gradient path over the sample. The interface between ZnO crystals and Bi-rich interfaced also played an important role in the dynamics, where the Bi atoms could crystallize (oxide form) and then incorporated to the grain boundary region. Hence, by following the myriad of phenomena at atomic scale and real-time, this study demonstrates the complexity of grain boundary formation and provides new venues towards the development of advanced materials by grain boundary engineering.

We follow an Al-12\%at.pct Cu alloy sample from the liquid state to mechanical failure, using in situ X-ray radiography during directional solidification and tensile testing, as well as three-dimensional computed tomography of the microstructure before and after mechanical testing. The solidification processing stage is simulated with a multi-scale dendritic needle network model, and the micromechanical behavior of the solidified microstructure is simulated using voxelized tomography data and an elasto-viscoplastic fast Fourier transform model. This study demonstrates the feasibility of direct in situ monitoring of a metal alloy microstructure from the liquid processing stage up to its mechanical failure, supported by quantitative simulations of microstructure formation and its mechanical behavior.
dislocation density, texture, stress field, etc. These two in situ/operando synchrotron diffraction techniques can not only help us understand the unique microstructures of AM materials, but also enable many other exciting research opportunities. These include, but not limited to, the establishment of precise time-temperature-transition diagrams (particularly in the time domain below ms) of structural and functional alloys, and the development of kinetics-driven synthesis routes for novel metastable alloys with hierarchical microstructures and tailored functionalities.

9:15 AM MT06.06.02
In Situ Observation of Laser Additive Manufacturing with High-Speed X-Ray Diffraction Seunghee Oh1, Joseph Pauza1, Christopher Kantzos1, Joseph Aroh1, Rachel Lim1, Sidi Feng1, Andrew Chuang2, Niranjan Parab2, Cang Zhao2, Tao Sun2, Robert M. Suter1 and Anthony D. Rollett1; 1Carnegie Mellon University, United States; 2Argonne National Laboratory, United States

Laser powder bed fusion (LPBF) is a standard technique in additive manufacturing (AM) of metal because of its capability to build complex and precise parts. The laser-based processing is accompanied by rapid heating and cooling, and abrupt changes in phase and structure. Applying the high-speed synchrotron X-ray diffraction of the Advanced Photon Source (APS) provides essential insights into AM processing. In this study, we used high energy monochromatic X-rays and a high-speed Pilatus detector to probe the dynamics of the rapid evolution of the microstructure of AM metals under laser exposure. Various physical phenomena, including phase transformation, thermal effects, and evolving microstructure, are quantified using high-resolution x-ray diffraction. Based on the temperature and phases present, the Bragg rings expand, broaden, vanish, and re-appear. We have applied this in-situ synchrotron x-ray technique to various materials, including Al-, Ti-, Fe-, and Ni-based alloys. In Ti-6Al-4V, phase transformation between liquid, HCP α phase, and BCC β phase can be clearly identified. Movement of the (110) peak of BCC during the transformation indicates recalescence caused by the exothermic process from BCC to HCP. Although the phase composition is generally as expected from the relevant phase diagram, the kinetics often vary from typical experience. In Inconel 718, e.g., precipitate formation takes place within a few milliseconds after solidification, which conflicts with standard TTT diagrams. The in-situ analysis shows that a few milliseconds are enough for Laves and carbide phases to form. The temperature of specimens is also inferred from the coefficient of thermal expansion (CTE) and the instantaneous lattice parameter(s) value. In addition, high-speed X-ray in-situ imaging technique provides geometric information on vapor cavities, melt pools, and cracking. The coupling of these two in-situ techniques will improve our understanding of the physics underpinning metal LPBF process.

9:30 AM MT06.06.03
In Operando Direct Metal Laser Printing of Ti6Al4V During X-Ray Diffraction Samy Hocine1,2, Sin Ting Cynthia Chang2, Daniel Grolimund3, Nicola Casati4, Steven Van Petegem2 and Helena Van Swygenhoven-Moens1,2; 1École Polytechnique Fédérale de Lausanne, Switzerland; 2Paul Scherrer Institute, Switzerland; 3PSD/MicroXAS Paul Scherrer Institute, Switzerland; 4PSD/MS Paul Scherrer Institute, Switzerland

Laser based additive manufacturing allows building layer by layer a designed shape offering versatility and flexibility to many metallurgical sectors. The obtained microstructures depend however strongly on the laser and scanning parameters. Trial-and-error methods to determine the optimal SLM processing parameters for a desired microstructure are time consuming. Numerical modeling approaches can help predicting and understanding the role of individual parameters, but because of the multiple length and time scale character of the physical processes involved, the models become rapidly very complex.

To speed up the selection of parameters, to help validating computational models and to improve our understanding on the link between process parameters and microstructure in SLM, we have developed a miniaturized SLM device (MiniSLM) that allows printing 3D samples during synchrotron X-ray diffraction. The design of the SLM device was driven by specific requirements that are related to its implementation at synchrotron beam lines; the requirement to be portable and to be small and light enough to fit at various beam lines. Furthermore, the X-ray beam needs direct access to the powder bed, minimizing interference with absorbing or diffracting material. The constructed MiniSLM has all basic functionalities of commercial available SLM machines.

We report on Ti-6Al-4V samples that were manufactured in operando during X-ray diffraction at the MicroXAS and MS beamlines of the Swiss Light Source. By varying the laser power, scanning speed and hatch distance, various energy densities were obtained. The dynamics of the alpha and beta phases during fast heating and solidification are
tracked with a time resolution of 50µs. We reveal the influence of laser and scanning parameters on the temperatures reached during the process, the cooling rates of α and β phases and the duration the β phase exists during processing. By performing experiments with different scanning strategies including those required for making open lattice structures, we demonstrate that printing of short scan lines, as used in an island scanning strategy, result in coarsening of the prior β grains, lowering of the cooling rates after solidification, and therefore leading to a substantial different microstructure.

The time resolved measurements obtained from in operando xray diffraction provides information averaged over the volume probed by the x-ray beam (varied between 40µ and 200µ). We demonstrate how the in operando results can be used for validation of FEM-based models. Tuning the xray beam profile to the mesh size or vice versa, will optimize the synergetic aspect.

9:45 AM *MT06.06.04
Fast Synchrotron Imaging of Force Regime Transition in Arc Weld Pools
Fan Wu¹, Ken V. Falch¹,², Michael Drakopoulos³,⁴ and Wajira Mirihanage¹; ¹The University of Manchester, United Kingdom; ²Deutsches Elektronen-Synchrotron, Germany; ³Diamond Light Source, United Kingdom; ⁴Brookhaven National Laboratory, United States

Welding is considered as the most efficient and economical route for joining metals. In fusion welding processes, metals coalesce via extremely rapid melting and subsequent solidification. The melt pool evolution during this melting and solidification sequence determines formation of the final weld joint shape, microstructure and defects. So that scientific insight on weld pool evolution and related phenomena is vital to enhance structural integrity and resilience of the welded structures or components. However, inherent complexity with multi-physics phenomena, associated high temperatures and the rapidness of the welding processes make direct experimental investigations extremely demanding. In this contribution we report the observation of solid-liquid-solid phase transformation and related melt pool dynamics that take place during electric arc welding, obtained through in situ synchrotron imaging at millisecond scale. The analysis flow patterns along with the quantified weld pool surface dynamics revealed us to how different contributing forces dictate the flow conditions over the distinct durations of the relatively short existence of the liquid phase. Our preliminary results suggest the existence of arc, surface tension and gravity dominant regimes during the evaluation of the weld pool. Further, we present our observations on how different welding parameters influence these regimes and develop into different transient conditions.

10:00 AM BREAK

SESSION MT06.07: Thermal Processing of Metals
Session Chairs: Joseph McKeown and Damien Tourret
Tuesday Morning, December 3, 2019
Hynes, Level 2, Room 209

10:30 AM *MT06.07.01
Towards Multiscale Observations of Dynamics in Polycrystalline Microstructures—High Energy X-Ray Diffraction Microscopies
Robert M. Suter; Carnegie Mellon University, United States

High energy x-ray diffraction microscopies make possible the in-situ observation of internal microstructural evolution during processing in a wide variety of polycrystalline materials. Using distinct but compatible methods, length scales from millimeters to tens of nanometers can be accessed. Currently, crystalline grain unit cell orientations and strain fields are mapped over cubic millimeter volumes using high energy diffraction microscopy (HEDM). Bragg coherent diffractive imaging (BCDI) is sensitive to Angstrom scale atomic displacement fields that are resolved to a few tens of nanometers inside nano-particles; individual dislocations and their motions have been resolved. Dark field x-ray microscopy (DFM) also is able to image individual defects and their motions. Soon to come upgrades to synchrotron radiation facilities such as the Advanced Photon Source and the European Synchrotron Radiation Facility will accelerate and broaden the applicability of these techniques while also posing significant data volume challenges. Current efforts seek to combine these capabilities to allow mapping macroscopic volumes of a sample at micron resolution and then to zoom in on chosen regions of interest for studies of underlying
nanoscale dynamics. Such multiscale measurements have the potential to lead to development of validated multiscale models that are based on fundamental mechanisms and therefore can be predictive rather than being tailored to a specific sample. This talk will present an overview of experimental methods and their capabilities and progress towards integration. Example applications to in-situ studies of mechanically and thermally induced evolution will be demonstrated.

11:00 AM MT06.07.02

X-Ray Reflectivity with a Twist—Quantitative Time Resolved X-Ray Reflectivity Using Monochromatic Synchrotron Radiation

Howie Joress1,2, Shane Q. Arlington3, Timothy P. Weihs3, Joel D. Brock2 and Arthur R. Wolf1; 1National Institute of Standards and Technology, United States; 2Cornell University, United States; 3Johns Hopkins University, United States

We present our work on the development, demonstration, and application of a new method of quantitative time resolved specular x-ray reflectivity (XRR) for use with monochromatic synchrotron radiation. Our method utilizes a polycapillary x-ray optic to create a convergent beam, illuminating the sample surface with x-rays over a range of incident angles. An area detector collects scattered intensity over a range of exit angles. By altering the geometry, rotating the sample normal out of the plane of the incident beam, we can greatly reduce the effect of diffuse scatter, significantly improving the quality of the measured XRR compared to previous convergent beam XRR methods. We demonstrate our technique with time resolution up to 10 ms and show XRR with intensity over 5 orders of magnitude with $q_z$ resolution sufficient to measure Kiessig fringes from films as thick as 105 nm. Our optic, with a working distance of 22 cm, makes this measurement compatible with many in situ processes. After demonstrating this method, we applied it to the study of interdiffusion in metal-metal multilayers. By measuring the intensity of the first multilayer diffraction peak during rapid sample heating at up to 90 °C/s, we were able to extract the activation energy for interdiffusion in an Al/Ni multilayer system.

11:15 AM MT06.07.03

In Situ Thermal Cycling in TEM of an Additively Manufactured Steel

Manas V. Upadhyay1, Eva Héripré2, Alexandre Tanguy1, Sylvain Durbecq1, Lluis Y. Cardona2, Thien-Nga Lê1 and Simon Hallais1; 1LMS, CNRS, Ecole Polytechnique, Institute Polytechnique de Paris, France; 2Laboratoire MSSMat, UMR CNRS 8579 CentraleSupélec, Université Paris-Saclay, France

Additive manufacturing (AM), also known as 3D-printing, of metals and alloys involves reading a 3D part geometry from a computer-aided design file and building it in a layer-by-layer manner by locally melting the material using a moving heat-source (laser or electron beam). Based on the material feeding approach, metal AM processes can be divided into: (a) direct energy deposition (DED) and (b) powder-bed fusion methods. In DED, the feedstock material in powder/wire form is directly fed into the heat-source as it scans the build surface whereas in PBF, the powder feedstock is deposited onto a powder-bed between two successive layer scans. For both processes, the final as-built part contains surface and volumetric defects, and a heterogeneous non-equilibrium microstructure. These phenomena depend on the AM process parameters, composition of the feedstock, and the desired final part geometry which together determine the material properties, the residual stresses and the subsequent part performance. AM holds the potential to revolutionize the metal and alloy manufacturing sector through its ability to simultaneously synthesize the material from powder/wire form and manufacture the desired part geometry without the need of tooling.

In recent years, increasing number of research efforts are being dedicated to better understand, control and improve the process-microstructure-properties-performance relationship of AM metals and alloys. However, nearly all experimental and modeling efforts in this field have been directed towards studying the heat-matter interactions in the melt-pool and rapid solidification. While these are important topics to study, it is equally important to understand the microstructure evolution in the heat-affected solid zone which undergoes thermal cycling. Consider the layer-by-layer building of a single-track (one heat-source scan per layer) wall and focus on the material at a point X on a deposition layer \(L(>1)\). Immediately after the localized deposition, the material at X cools down at a very high temperature rate (ranging from \(10^3\) to \(10^6\) °C/s). Addition of more layers (i.e. \(L+1, L+2, \ldots\)) results in thermal cycling at X with varying temperature rates and amplitudes. The transient thermal gradients result in the formation of high-amplitude cyclic thermal stresses which must affect the microstructure at X, for example, through dislocation density evolution, recrystallization, precipitation, etc. At later stages of thermal cycling (i.e. during deposition of layer \(N >> L\)), a steady-state heat transfer could occur at X resulting in additional microstructural...
changes. Furthermore, material points at different locations in the as-built part are subjected to different thermal histories resulting in heterogeneous microstructural evolution. To our knowledge, there have been no coherent studies dedicated towards understanding the microstructural evolution during thermal cycling of the material. The main difficulty is tracking the microstructural changes in-situ during the AM process.

In this study, we are particularly interested in understanding the microstructural changes at the intragranular length scale due to thermal cycling during the AM processing of 316L stainless steel. Instead of following the building of this steel inside the AM processing chamber, we thermally cycle TEM lamellae inside a transmission electron microscope and follow their evolution in-situ. The lamellae are prepared from the material synthesized during the building of a wall of 316L stainless steel using a Laser Metal Deposition machine (a DED process). Once inside the TEM, the lamellae are subjected to the temperature vs time history obtained from thermal measurements at a given point-of-interest on the 316L wall during its processing. This thermal cycling results in some very interesting changes in the microstructure which will be presented during this talk.

11:30 AM MT06.07.04
Influence of Controlled Cooling Rates During Thermomechanical Processing of Ti 6%Al 4%V Alloys Using In Situ Scanning Electron Microscopy Genevieve A. Kane, M. David Frey, Daniel Lewis and Robert Hull; Rensselaer Polytechnic Institute, United States

We describe novel experimental approaches to examine the microstructural evolution of Ti 6%Al 4%V upon cooling from above the beta transus (~995 °C) while imaging in the scanning electron microscope. Ti 6%Al 4%V is a two phase, α+β titanium alloy with high strength and corrosion resistance. The existence of the α/β transformation gives rise to different microstructures and properties through various thermomechanical treatments. Fully lamellar microstructures, bi-modal microstructures, and equiaxed microstructures can each be obtained by accessing different cooling rates upon the final treatment above the beta temperature, each resulting in uniquely enhanced material properties.

Utilizing the capabilities of a heating/ tensile stage developed by Kammrath & Weiss Inc., that also incorporates in-situ nano-indentation capability, we are able to apply real-time imaging techniques in the scanning electron microscope to monitor and control the development of the microstructure. Annealing temperatures up to 1100 °C are attainable, with cooling rates ranging from .01 ° C per second to 4 °C per second. This has allowed us to directly observe the formation of lamellae at different annealing temperature/ cooling rate combinations to determine the lamellar microstructure width, separation, and colony size.

Applying a cooling rate (0.1 °C per second) to samples annealed to 1100 °C showed that lamellar microstructures initiate and form within alpha colonies at temperatures of ~ 920-930°C. When held at the temperature where lamellar formation initiates, the lamellae continue to propagate and lengthen by 50% from their initial length in two minutes time throughout the parent grains. Upon further cooling, the lamellae widen from 3.5- 7 µm to 8-15 µm. Extensive analysis of lamellar microstructure formation and growth will be presented, comparing different temperature regimes, cooling rates and times at temperature.

The ability to further refine thermomechanical processing conditions allows for an assessment of mechanical properties associated with the presence of both phases, and their final microstructure, particularly given the in-situ indentation capabilities available in our system. As such, the ability to deconvolute temperature and time considerations in the formation of lamellar and also bi-modal microstructure is vital, and will be discussed in detail during this presentation.

Acknowledgments: This research is sponsored through grants from the National Science Foundation, Awards CMMI-1647005, and CMMI-1729336. This work was performed with the use of clean room and characterization facilities within the Center for Materials, Devices and Integrated Systems at Rensselaer Polytechnic Institute. We also acknowledge collaborations with Dr. Antoinette Maniatty, Dr. John Wen, Arun Baskaran, Sagar Bhatt, Anant Kekre, and Michael Allahua. Additionally, we acknowledge the help and expertise of Kammrath and Weiss with equipment development.
1:30 PM *MT06.08.01
The Synergy of Tomography and Simulation—A Method to Determine Grain Boundary Properties Jin Zhang¹, Henning Poulsen² and Peter W. Voorhees¹; ¹Northwestern University, United States; ²Technical University of Denmark, Denmark

An approach is proposed to measure grain boundary properties by comparing the evolution of experimentally determined 3D grain structures to that derived from simulation. Grain evolution in pure iron is determined in three dimensions and as a function of time using diffraction contrast tomography at a synchrotron source. The temporal evolution of over 1300 grains is quantified. This provides information on the morphology and kinetics of a large number of grain boundaries in a single experiment. Using a time step from these data as an initial condition in a phase-field simulation, the computed structure is compared to that measured experimentally at a later time. An optimization technique is then used to find the reduced grain boundary mobility that yields the best match of the simulated microstructure. We find a strong variation of the reduced mobility for a given grain boundary misorientation. A strong dependence of the reduced mobility on location in Frank-Rodrigues space is also observed.

2:00 PM MT06.08.02
The Dynamics of Abnormal Grain Growth in a Particle-Containing System—New Insights from Multimodal Three-Dimensional X-Ray Imaging Jiwoong Kang, Ning Lu, Nancy Senabulya and Ashwin J. Shahani; University of Michigan, United States

Since the intrinsic grain structure of a polycrystal has significant impact on its properties, investigators have focused intently on studying the dynamics of the grain network under various external stimuli, e.g., heat. Upon annealing the material may undergo abnormal grain growth (AGG), in which a few grains grow more rapidly compared to the others. AGG is a common grain coarsening phenomenon that has been observed in a vast array of metallic and ceramic systems. To capture AGG, past experimental studies have relied heavily on two-dimensional (2D) experiments, such as surface characterization via electron backscatter diffraction (EBSD) and optical microscopy. However, such experiments have had limited success in developing a comprehensive model of AGG due to lack of information below the sample surface. Furthermore, these characterization techniques are destructive in nature, and thus it is impossible to follow the individual grain trajectories as a function of time (in the same specimen). As a result, it is impossible to determine the sequence of events that led to AGG in the first place.

Integrating X-ray absorption- and diffraction-contrast tomography (denoted ACT and DCT, respectively) in the laboratory can provide in-depth information on microstructures that are simultaneously polycrystalline and multiphase. Here, we have harnessed this non-destructive method to gain new insights into the problem of AGG in a particle-containing system. We investigate an Al-Cu alloy as a model system. The prepared specimen was imaged through the combination of ACT and DCT on a laboratory X-ray microscope in situ and as AGG proceeds. The 3D data provided an unprecedented opportunity to uncover what determines the expansion and shrinkage of grains — including the abnormal grain — as a function of the initial grain size and topology [5, 6]. However, both of these metrics do not correlate with grain growth rate. Instead, we find a strong correlation between the locations of secondary phase particles (obtained via ACT) and grain boundaries (imaged via DCT). As the specimen is annealed, the distribution of grain boundaries becomes more closely correlated to the distribution of AlCu particles, suggesting that the abnormal grain nucleates in a relatively particle-free region of the sample volume. Meanwhile, the normal grains are pinned by a dense particle cloud. Once it has attained its size advantage, the abnormal grain persists to grow due to an exceptionally large capillary driving force. This study provides new understanding on the origin of AGG with implications for the production of single crystals.

Bulk nanocrystalline alloys possess many unique physical properties with tremendous potential for various applications. However, ultra-nano grains of sub-4 nm dimension are extremely difficult to create and stabilize. This research proposes a spontaneous and reversible approach to nanocrystallize Cu-Sn bimetallic alloy by taking advantage of the polymorphic phase transition of Cu$_6$Sn$_5$. During temperature increase, and starting from a temperature 275 °C lower than the melting point of bulk Cu$_6$Sn$_5$, ~10 nm Cu$_6$Sn$_5$ nanoparticles were coarsened to tens of nanometers, as observed by in situ TEM. The particle growth continued even during the initial cooling stage. Interestingly, when the cooling process went through the polymorphic phase transition temperature of Cu$_6$Sn$_5$, η-Cu$_6$Sn$_5$ was transformed to η$'$-Cu$_6$Sn$_5$, and massive grain refinement occurred spontaneously as confirmed by atomic level monitoring in TEM. The final grain size reached a mean value of ~2.5 nm, sufficient small to be in a regime with enhanced ductility, offering highly improved ductility because of inverse Hall-Petch phenomenon, and excellent thermal, electrical and mechanical properties. This process is also reversible, offering an unprecedented method to stabilize extremely small nanograins. Such an ultra-nano material can be technically useful for a variety of applications including as a unique circuit interconnection material which can serve at higher temperatures than its processed temperature. We successfully demonstrated using nano-Cu$_6$Sn$_5$ as the interconnection material for the packaging of SiC high-power devices. Because of the significantly depressed sintering temperature of ultra-fine Cu$_6$Sn$_5$ nanoparticles, the SiC can be successfully packaged at a temperature lower than its actual working temperature. Because of the enhanced ductility of the inverse Hall-Petch sub-4 nm nanocrystalline joints, nano-Cu$_6$Sn$_5$ has a very promising potential to be used in the packaging of flexible devices. It can offer two attractive advantages simultaneously: processing at low temperature to prevent the damage of the flexible substrate; but working at a relatively high temperature to allow the usage of high-power flexible electronics. Like Cu$_6$Sn$_5$, other alloys such as Cu-Al, Fe-Zr, Al-Ni, etc. also possess such a capability of phase transition-induced grain refinement. This work will inspire other researchers to create many additional, sub-4 nm type nanocrystalline alloys, offering unprecedented pathway to realize ultra-nano-grained alloys and more interesting functions which were difficult to gain before.

2:30 PM *MT06.08.04
Grain Growth in Metallic Films—Experiments, Simulations and Data Analytics Katayun Barmak$^1$ and Yekaterina Epshteyn$^2$; $^1$Columbia University, United States; $^2$The University of Utah, United States

Most technologically useful materials are polycrystalline microstructures composed of a myriad of small monocristalline cells/grains separated by grain boundaries/interfaces. Grain boundaries play a crucial role in determining the properties of materials across a wide range of scales. A grand challenge problem in engineering of polycrystals is to develop prescriptive process technologies capable of producing an arrangement of grains that provides for a desired set of materials properties. One method by which the grain structure is engineered is through grain growth or coarsening of a starting structure.

Grain growth can be viewed as the evolution of a large metastable network, and can be mathematically modeled by a set of deterministic local evolution laws for the growth of an individual grain combined with stochastic models to describe the interaction between grains. Thus, to develop a predictive and prescriptive theory, investigation of a broad range of statistical measures for microstructure evolution during grain growth in polycrystalline materials are needed and must be obtained using experiments, simulations, data analytics and mathematical modeling. One of the goals of our current research presented here is thus to use data-driven numerical simulations closely integrated with experiments in order to improve upon mathematical models of grain growth and guide design of new experiments.

In this talk, we will report the results of in situ experiments of grain growth in thin films of Pt conducted using a heating holder in a transmission electron microscope (TEM). Our interest here is the dynamics of grain boundary motion. In addition, we will report on ex situ experiments of grain growth in Al, Al-0.2 at% Mn and Cu thin films, with thicknesses in the range of 25-150 nm and annealing temperatures in the range of 150-600 °C. A variety of
geometric and topological metrics of the grain structure were extracted from bright-field or dark-field (TEM) images or precession electron diffraction crystal orientation maps, including not only the grain size, but also the dihedral angles, the number of neighbors (i.e., side class) and the side class of nearest neighbors of grains.

The experimental grain size distributions for the Al and Cu films were found to be remarkably similar to each other despite the many and significant differences in experimental conditions, which include sputtering target purity, presence of an alloying element, substrate type, film thickness, deposition temperature, actual as well as homologous annealing temperatures, annealing time, absolute grain size, and the twin density within the grains. This similarity argues for a universal experimental grain size distribution, which for grain diameters is lognormal as found previously for thin films at stagnation. Comparison of the experimental grain size distribution with that for two-dimensional, sharp-interface grain growth simulations with isotropic boundary energy shows the distributions to differ in two regions, termed the “ear” and the “tail”. It is shown that the excess small grains in the region of the “ear” are primarily the 3 and 4-sided grains, whereas the excess of large grains in the “tail” region are grains with more than 9 sides. The excesses in the ear and tail regions of the experimental distributions are necessarily balanced by a deficiency in the mid-sized grains with 6-8 sides. We will also present the grain boundary character distributions in the films and compare and contrast our findings with those for bulk samples with grain sizes in the micrometer range.

3:00 PM BREAK

SESSION MT06.09: Additive Manufacturing—Inks and Polymers
Session Chairs: Ashwin Shahani and Tao Sun
Tuesday Afternoon, December 3, 2019
Hynes, Level 2, Room 209

3:30 PM MT06.09.01
Unveiling Fundamentals of Ink-Based 3D Printing by Operando X-Ray Photon Correlation Spectroscopy
Maria A. Torres Arango1, Yuyang Zhang1, Gregory Doerk1, Ruipeng Li1, Chonghang Zhao2, Yu-chen Karen Chen-Wiegart1, Andrei Fluerasu1 and Lutz Wiegart1; 1Brookhaven National Laboratory, United States; 2Stony Brook University, The State University of New York, United States

Central to the advances in functional materials and their processing is the thorough understanding of the fundamentals governing the processing-properties relationships. In additive manufacturing, understanding these relationships is necessary since anisotropy is inherent to the processing techniques, compromising the components quality, performance and reliability. For continuous-flow direct writing (CDW) the materials are formulated as viscoelastic colloidal inks and extruded through a nozzle forming a component. Therefore, these inks are subjected to multiple stimuli during the deposition and post-processing stages, which affect the way these materials self-assemble, store/release stress, and subsequently form and propagate defects.

Seeking to unveil such fundamental relationships, we conduct operando synchrotron x-ray photon correlation spectroscopy (XPCS) studies to investigate the inks’ structural and dynamical evolution during the out-of-equilibrium stages associated with the 3D printing process. During the shearing and relaxation of the inks multiple phenomena take place including loss and recovery of the gel structure, solidification and jamming to name a few. Our setup combines XPCS and CDW at the Coherent Hard X-ray Scattering beamline (CHX-11ID) at the National Synchrotron Light Source II. XPCS is especially suited for investigating the nano-scale spatio-temporal evolution of materials processed by CDW, covering its relevant length and time scales, from tens to hundreds of nanometers, and milliseconds to the hundreds-of-seconds range. We observe the ink’s nanoscale structure and dynamics as a function of the spatial position within the printed filaments, which may further be related to the printed-structures’ solvent evacuation, colloid re-arrangement, and substrate properties (ink/substrate interactions). Additionally, we investigate the dependence on compositional variation, including inks from branched vs. monodisperse colloids and inks containing solvents with different vapor pressures, to expose fundamental differences in the structural and dynamic evolution. While our work serves to enlighten fundamental processes in CDW, it may be extended to other 3D printing techniques. Moreover, it constitutes the basis for the discovery of new pathways for the engineering of materials that exhibit novel properties and unprecedented performance, as well as shedding light onto solving...
relevant issues in additive manufacturing, including cracking, delamination and poor layer-to-layer adhesion.

3:45 PM MT06.09.02
“Sintering” Models and In Situ Experiments—Data Assimilation for Microstructure Prediction of Nylon Component SLS Additive Manufacturing William S. Rosenthal, Francesca C Grogan, Yulan Li, Erin I Barker, Josef Christ, Timothy Pope, Christopher Barrett, Marvin Warner and Amra Peles; Pacific Northwest National Laboratory, United States

Selective laser sintering (SLS) methods are workhorses for the additive manufacturing of polymer-based components. The ease of rapid prototyping and short-run manufacturing by anyone with a laptop and machine access also means it is easy to produce illicit or counterfeit components. It is necessary to have a data-calibrated in-situ physical model of the build process in order to predict expected and defective microstructure characteristics that inform the provenance of these components.

Toward this end, we calibrate 2D and 3D phase-field sintering models for material microstructure evolution and its kinetics during synthesis. We seek to understand and predict microstructure characteristics such as pore structure and layer interfaces in components built by a Formiga P100 SLS printer using PA 2200 Nylon 12 feedstock. This is accomplished by assimilating multiple in-situ data streams, post-hoc imaging analysis, and computational model predictions in an adaptive Bayesian parameter estimation algorithm. In-situ data sources include infrared thermal imaging, built-in printer environmental sensors, and laser pathing guidance, including experimental uncertainty estimates. These are supplemented by post-hoc conical and synchrotron X-ray computed tomography, from which we infer bulk porosity and distributions for local and global pore characteristics. Similar predictions for porosity distributions are provided by the stochastically-driven phase-field sintering model. Randomized feedstock configurations are explored by a stochastic model for Nylon particle deposition and composition, which has been calibrated to bulk particle size analyses from a laser diffractometer. Additional model parameters such as system free energy, interfacial energy, and sintering kinetics are first constrained to physically-relevant search directions by global and local sensitivity analysis, and then explored using an adaptive sampling algorithm to match predictions.

Using this feedback loop, we obtain data-constrained estimates of sintering model parameters along with uncertainty bounds. We conclude by combining these predictions with the infrared thermal maps, and quantitatively relate the in-situ build environment to the resulting microstructure in sintered nylon components.

SESSION MT06.10: Processing of Ceramics
Session Chairs: Ashwin Shahani and Tao Sun
Tuesday Afternoon, December 3, 2019
Hynes, Level 2, Room 209

4:00 PM MT06.10.01
Kinetic Pathways of Layered Oxide Formation are Templated by Low-Temperature Intermediates Wenhao Sun1, Jianming Bai2, Gerbrand Ceder1 and Feng Wang2; 1Lawrence Berkeley National Labs, United States; 2Brookhaven National Labs, United States

Solid-state ceramic synthesis is often believed to equilibrium process, as the high temperatures of calcination are expected to minimize kinetic limitations associated with nucleation and growth. Despite this intuition, non-equilibrium phases are often observed during solid-state synthesis, prompting questions regarding the mechanistic origins of these metastable intermediates. Here, we use in situ synchrotron XRD to compare the multistage phase evolution of three important Li-ion cathode materials, LiCoO2, LiNiO2 and LiNi0.8Co0.2O2, during a hydrothermal-assisted ceramic synthesis process. While all three systems ultimately crystallize in the stable Rm layered phase after heating, a metastable spinel phase is observed to form prior to LiCoO2, and disordered rocksalts prior to the Ni-based compounds. We demonstrate that these metastable intermediates are kinetically-facile lithiation products of stable binary oxides that originate during low-temperature synthetic preparation. Our findings highlight newopportunities to engineer low-temperature phases to topotactically template the ceramic synthesis of target crystalline phases.
X-Ray Synchrotron Investigations of the Away from Equilibrium Crystallization of ZrO2 under Electromagnetic Excitation

Nathan Nakamura1, Laisuo Su1, Han Wang2, Shikhar K. Jha1, Haiyan Wang2, Simon J. Billinge3, C. Stephen Hellberg4 and B. Reeja Jayan1; 1Carnegie Mellon University, United States; 2Purdue University, United States; 3Columbia University, United States; 4U.S. Naval Research Laboratory, United States

Electromagnetic (EM) fields can significantly affect crystallization and phase transitions in ceramic materials, leading to low-temperature phase transitions and compositions not observed using conventional furnace-based techniques. Specifically, the application of 2.45 GHz microwave radiation (MWR) during ceramic synthesis has been found to crystallize unexpected phases and influence local atomic ordering. However, the mechanisms underlying how EM fields impact phase stability and promote far-from-equilibrium phases are not well understood. To fully understand the role of EM fields in ceramic nucleation and growth, it is necessary to characterize the relationship between the applied field and the resultant atomic structure. Due to the away from equilibrium nature of EM field-assisted phase transitions, it is necessary to characterize effects on both long range crystalline atomic order and short range atomic order which deviates from the crystalline phase. An understanding of the local atomic distortions induced by MWR and how they impact relative phase stability and the free energy space is especially critical to understanding these processes. An improved understanding of these effects will create the opportunity to utilize EM fields as an additional thermodynamic parameter to access regions of phase space not accessible via conventional synthesis routes.

We utilize a combination of synchrotron X-ray pair distribution function (PDF) analysis, synchrotron X-ray absorption spectroscopy, and density functional theory (DFT) calculations to investigate the impact of MWR on defect formation, phase transitions, and phase stability in ZrO2 thin films. Through PDF and extended X-ray absorption fine structure (EXAFS) analysis, we demonstrate that the application of MWR promotes defects on the oxygen sublattice, leading to local structural distortions which stabilize a long-range cubic atomic structure. This defective cubic ZrO2 structure forms at 225°C in the presence of MWR, significantly lower than the temperature conventionally required to synthesize cubic ZrO2 (>2400 °C). DFT calculations reveal that point defects on the oxygen sublattice can significantly alter the free energy landscape of ZrO2, and we find that the low-energy defective atomic configurations predicted by DFT correspond well to the experimental ZrO2 atomic structure observed. This combined experimental and computational study provides direct evidence for the role of EM fields in promoting defect-mediated phase transitions which deviate from the conventional free energy space of ZrO2, and creates the opportunity to further utilize MWR-assisted synthesis as a means to access away-from-equilibrium phases in ceramic oxide materials.

Defect-Mediated Anisotropic Lattice Expansion in Ceramics as Evidence for Non-Thermal Coupling between Electromagnetic Fields and Matter

B. Reeja Jayan1, Shikhar K. Jha1, Nathan Nakamura1, Shuyan Zhang1, Laisuo Su1, Phil M. Smith1, Xin L. Phua2, Han Wang2, Haiyan Wang2, John S. Okasinski3 and Alan J. McGaughey1; 1Carnegie Mellon University, United States; 2Purdue University, United States; 3Argonne National Laboratory, United States

Electromagnetic (EM) fields have been known to stimulate a range of surprising responses in materials. Microwave radiation is a type of EM field in the frequency range of 0.3 -300 GHz that can lower the synthesis temperature required for ceramics like TiO2 and induces mixed amorphous-crystalline phase compositions. To better understand the effects of microwave radiation on matter, we study structural changes during microwave heating and microwave radiation-assisted synthesis using in-situ synchrotron X-ray diffraction. We observed anisotropic expansion-contraction of lattice parameters, ‘a’ and ‘c’ of the tetragonal anatase phase, which contradicts the results from conventional thermal heating. When the as-received anatase powders are heated with microwave radiation, an instantaneous decrease in the intensities of diffraction peaks indicates loss of long-range atomic order (decrystallization), which is supported by high-resolution electron microscopy and selected area diffraction patterns. Ex-situ Raman spectroscopy and X-ray photoemission spectroscopy of microwave-heated and microwave-synthesized anatase powders indicate increased defect-generation under microwave exposure. Molecular dynamics simulations on the anatase phase of TiO2 suggests that introducing an oxygen vacancy can lead to the formation of an interstitial-vacancy pair. So, if microwave radiation can affect defect nucleation in the structure, the generation of defect-pairs away from equilibrium can explain the anisotropic lattice expansion, crystallization at lower...
temperatures, and/or stabilization of metastable phases under electromagnetic fields. Anisotropic lattice expansion and decrystallization under externally applied fields provide direct evidence for non-thermal coupling between EM fields and matter. Understanding such non-thermal, field-driven processes has implications in engineering low temperature processes for integrating ceramics with delicate polymeric materials for flexible electronics and in tailoring ceramic properties for energy storage, photovoltaic, and catalytic applications.

4:45 PM MT06.10.04

In Situ TEM Observation of Structure Evolution During Ceramics Sintering Kai He; Clemson University, United States

In situ transmission electron microscopy (TEM) has gained rapid growth in the past decade and attracted tremendous attention in diverse scientific research because it can acquire dynamic information and allow for the mechanistic understanding of various physical and chemical processes in a broad range of materials systems. Specifically, the advancement of in situ TEM in physical and/or chemically reactive environments has enabled the direct observation of structure evolution during materials synthesis. The sintering that transforms the precursor powders into the dense solid phase is the critical fabrication process for ceramic materials. To overcome the limitation of conventional long-holding techniques, recent efforts have been put toward flash sintering, which represents a solid-state synthesis far from equilibrium and shows great technical importance relevant to additive manufacturing. In this regard, to provide an in-depth understanding of the fundamental level, we employ in situ TEM techniques to study the dynamic structure evolution during the sintering of ceramic materials.

Here, we primarily focus on simple transition metal oxides (such as TiO2, Fe2O3, etc.) to investigate their sintering behaviors under various sintering rates. We use a TEM holder capable of in situ heating via MEMS-based devices, on which pristine metal oxide nanoparticles are uniformly dispersed. By tuning the input current density, we can control the power and heating speed that is applied to the nanoparticles, and simultaneously observe their morphological and structural changes in real time. From enormous in situ TEM observations, we found distinct sintering mechanisms relating to sintering rate: the slow sintering include stages of grain rotation, agglomeration, and growth, whereas the flash sintering proceeds directly through abrupt densification and subsequent growth, which is governed by the surface diffusion at different heating load. The effect of grain size and surface orientation also plays an important role in sintering kinetics. Our findings provide valuable insights into understanding the flash sintering mechanism and also show potential implications for developing fast additive manufacturing techniques for ceramic materials.

SESSION MT06.11: Semiconductors—Solidification
Session Chairs: Sabine Bottin-Rousseau and Damien Tourret
Wednesday Morning, December 4, 2019
Hynes, Level 2, Room 209

8:45 AM MT06.11.01

Role of Evolving Interface Instabilities in the Genesis and Evolution of Extended Defects During Epitaxial Growth of Cubic SiC Giuseppe Fisicaro1, Corrado Bongiorno1, Ioannis Deretzis1, Marcin Zielinski2, Silvia Scalese1, Francesco La Via1, Massimo Zimbone1 and Antonino La Magna1; 1CNR Institute for Microelectronics and Microsystems, Italy; 2NOVASiC, Savoie Technolac, France

The growth of high-quality Silicon Carbide (SiC) substrates and nanoparticles is a topic of extreme technological interest due to the importance of this material for current and future technologies. Concurrently, such growth process is challenging due to the meta-stability of different crystal symmetries (polytypes) in the usual growth conditions. Atomic mechanisms ruling the extended defects kinetics in cubic SiC material, manifesting both stacking and anti-phase instabilities, have been investigated by means of cross correlations between simulated evolution and in-situ micro-structural characterizations of crystal growth processes. First we explored the configurational space of cleaved and defective (adatoms and vacancies) surfaces with ab-initio structure predictions algorithms at density functional theory level. Then the atomistic configurations and energetics are input of a Kinetic superlattice Monte Carlo code which simulates the growth kinetics of SiC substrates and nanoparticles. Ab-initio calibrated Kinetic Monte Carlo simulations in super lattices evidence a mutable and complex kinetic behaviour which has been
validated by transmission electron microscopy analyses of experimental samples. Both simulations and characterizations show that anti-phase boundaries generate single stacking faults with different symmetries or sequences of them. Moreover, boundaries interact with the extended defects of the stacking fault class promoting their annihilation or polarity changes. Defect-defect correlations are mediated by surface instabilities, since a clear interplay between the modifications of the growing surface morphology and the bulk defects occurs and ones cause and influence each others.

9:00 AM *MT06.11.02
In Situ Observation of Melt Growth Processes of Silicon Kozo Fujiwara; Institute for Materials Research, Tohoku University, Japan

Multicrystalline silicon (Mc-Si) ingots for solar cells are manufactured by unidirectional solidification method. In general, since semiconductor materials are not subjected to structure control by a method such as thermo-mechanical treatment after solidification, structure control must be performed in a unidirectional solidification process. However, it has not been well understood how the microstructures in Mc-Si, such as, crystal grains, grain boundaries, twin boundaries, sub-grain boundaries, etc. behave at the crystal-melt interface. We have attempted to understand the crystal growth mechanisms by directly observing the crystal-melt interface of silicon.

We have developed a lab-scale in situ observation system which is composed with a crystal growth furnace and a digital optical microscope. To date, we have successfully observed crystal-melt interfaces of materials including Si, Ge, Sb, Cu, Sn, GeSn, GaSb, and so on. This presentation will focus on dendrite growth, crystal-melt interface instability, and grain boundary dynamics of silicon. The results of other materials will also be discussed.

9:30 AM MT06.11.03
Simultaneous In Situ X-Ray Diffraction Topography and Radiography Imaging for Defect Characterization During Silicon Growth Maike Becker, Gabrielle Regula, Serge Neves Dias, Hadjer Ouaddah, Guillaume Reinhart and Nathalie Mangelinck-Noël; Aix-Marseille Univ., Université de Toulon, CNRS, IM2NP, France

A new imaging device for the characterization of silicon during high temperature processing is installed at beamline ID19 at the European Synchrotron (ESRF). We demonstrate the great potential of this imaging setup for the detailed investigation of the interaction and generation of grains and defects that influence the growth process and the final crystalline structure of silicon. Better knowledge of the formation and interaction of defects in silicon is essential in order to improve defect engineering during the manufacturing step of silicon used for photovoltaic applications. In particular, defects like dislocation bunches or sub-grain boundaries reduce the photovoltaic performance and should be therefore analyzed.

In our experiments, two individual camera system that are fully synchronized record the topography and the radiography images in real-time during silicon sample processing in a Bridgman furnace. Compared to previous studies, where the topographs were recorded on X-ray sensitive films, it significantly increases the image acquisition rate allowing a detailed analysis of defect dynamics in the sample.

Topography is the analysis of the fine internal structure of an X-ray diffraction Laue spot in real space that provides information on the crystal quality by the display of lattice distortions. As dislocations and strain fields deform the crystal structure, they can be observed in a topography image by contrast changes. In our experiments, one Laue spot (topograph) is selected and recorded with one of the cameras. The transmitted beam is recorded at the same time by a second camera constituting the radiography images. The radiography contrast originates from the density difference of the solid and the liquid silicon phases and provides information on the morphology and kinetics of the interface. This supplementary information is used to identify new grain nucleation and grain competition events. The in situ studies are complemented by ex situ methods like electron backscatter diffraction and etch pitch measurements, to get information on the grain boundary character and on the dislocation density.

The combination of all techniques allows to analyze the mechanisms responsible for grain and dislocation generation and strain formation. Our work focuses on 300 µm-thin single-crystal silicon float zone samples that contain no visible defects at the beginning of an experiment. During heating, dislocations are generated at the sample edges and their motion intensifies with increasing temperature. We measure their velocities up to the melting
point and observe their interactions. In fact, little is known on the nucleation and mobility of dislocations at temperatures beyond 1373 K. When solidification starts, dislocations initially present in the seed propagate in the regrown crystal with the solid-liquid interface. It is important to learn more about dislocation extension from the seed to the regrown crystal, to explore the role of the seed used for example in recent process developments. At the sample edges (solid-liquid-vapor triple point) twin nucleation occurs, which leads to grain competition in the center, which in turn can trigger new grain nucleation. Even dislocation multiplication by the activation of Frank-Read sources can be observed, which underlines the efficiency of the new imaging device for a thorough and comprehensive characterization of silicon processing.

9:45 AM MT06.11.04
Synthesis of 100 Micron Scale Single Crystals of Ge$_2$Sb$_2$Te$_5$ via Femtosecond Optical Excitation Marc Zajac$^1$, Aditya Sood$^1$, Taeho Roy Kim$^1$ and Aaron Lindenberg$^{2,1}$; $^1$Stanford University, United States; $^2$SLAC National Accelerator Laboratory, United States

Phase change materials, including Ge$_2$Sb$_2$Te$_5$ (GST), can rapidly and reversibly switch between an amorphous, or glassy, state and a crystalline, or ordered, state via electrical or optical pulses. The amorphous phase and the crystalline phase have very different electrical and optical properties, which means that they can be used in rewritable optical data storage media and in fast, non-volatile electronic memory devices. Using in-situ electron diffraction techniques, we observed that excitation above a threshold fluence with a single femtosecond, 800 nm pulse induces sharp Bragg peaks indicative of large crystalline grains on the order of the probe beam size (80-100 μm). This was confirmed by transmission electron microscopy (TEM). Further analysis with the TEM showed that these large single crystalline grains are dendrites located in the center of the laser excitation with a face-centered cubic (fcc) crystal structure. It was determined via energy dispersive X-ray spectroscopy (EDX) that the large single crystalline dendrites are the same composition as the initial amorphous phase. This eliminates constitutional undercooling as a plausible mechanism to explain the formation of the dendrites. The observation of the large grains and the fact that the composition does not change indicates a large crystal growth velocity regime and opens up new opportunities for the growth of single crystal phases of the phase-change materials.

10:00 AM BREAK

SESSION MT06.12: Semiconductors—Processing
Session Chairs: Guillaume Reinhart and Peter Voorhees
Wednesday Morning, December 4, 2019
Hynes, Level 2, Room 209

10:30 AM MT06.12.01
Atomic-Scale Observation of Dynamic Processes of SrTiO$_3$ (001) Surface Reconstruction at High Temperatures Zhen Wang$^1$, Bumsu Park$^1$, Jong Chan Kim$^2$, Hu Young Jeong$^2$ and Sang Ho Oh$^2$; $^1$Sungkyunkwan University, Korea (the Republic of); $^2$Ulsan National Institute of Science and Technology, Korea (the Republic of)

The atomic structure of (001) SrTiO$_3$ surface has been studied for a long time by various surface sensitive diffraction and spectroscopy techniques. The exotic physical properties exhibited by this surface have been of particular interests since the discovery of a two-dimensional electron gas (2DEG) at the surface [1]. Although atomic-scale surface profile imaging using high-resolution transmission electron microscopy (HRTEM) or scanning transmission electron microscopy (STEM) techniques have been used to visualize the surface structure, assessing the dynamic atomic processes leading to the surface reconstruction still remains challenging.

Here we designed an in-situ HRTEM experiment at elevated temperatures in a Cs-corrected TEM (GRAND ARM 300 CF). TEM samples were prepared from a (001) SrTiO$_3$ single crystal along the [100] and [110] cross-sectional zone axes by using FIB and attached to a DENSsolutions MEMS heating chip. A negative spherical aberration (Cs) imaging (NCSI) HRTEM condition was applied to observe the surface structure in real-time with all atoms (including strontium, titanium, and oxygen) being clearly resolved with minimal contrast delocalization [2]. In addition to the surface profile imaging at NCSI HRTEM mode, STEM high-angle annular dark-field and annular
bright-field imaging have been carried out at room temperature, 300 °C, 500 °C, 700 °C, and 950 °C. In order to determine the chemical composition and the valence state of the outermost surface atoms, atomic-resolution STEM energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) elemental mapping have been performed, respectively.

We observed that the (001) SrTiO3 surface was terminated predominantly by SrO layer throughout all temperature ranges studied by in-situ TEM. Interestingly, the SrO surface layer showed a unique surface reconstruction largely deviating from the bulk-truncated (1×1) structure with titanium (Ti) ions in the surface SrO layer, particularly occupying the oxygen-oxygen bridge sites (i.e. corresponding to the octahedral interstitial sites in bulk SrTiO3). The presence of the Ti interstitials was confirmed directly by atomic-scale STEM EDS and EELS elemental mapping. As temperature increases, the interstitial Ti atoms were displaced increasingly upward from the surface plane and caused a pronounced rumpling of the SrO layer. When the temperature is reached 950 °C, a layer-by-layer sublimation occurred from the surface by the formation and migration of atomic step with a unit cell step height. We directly observed that the Ti atoms from the moving step edge migrate and occupy the interstitial sites immediately when the sub-surface SrO layer is exposed as free surface during sublimation. From the Ti-L2,3 and O-K EELS edges, we observed that the formal valence of the interstitial Ti is mainly +3 and the surface SrO and sub-surface TiO layers contain a significant amount of oxygen vacancies. The observed surface structure of (001) SrTiO3 with Ti interstitials in the SrO termination has not reported before and we believe this unique surface structure is closely related to the formation mechanism of surface 2DEGs by oxygen vacancies. Our real-time surface profile imaging of the dynamic processes of surface reconstruction provides new insight into the surface science and has the potential to reveal the emergent phenomena such as the formation mechanism of 2DEG at oxide surfaces.

References

10:45 AM MT06.12.02
Low-Temperature Growth of Epitaxial BaTiO3 Ultrathin Film by Molecular Beam Epitaxy and Its Structural Properties Yeongjae Shin1, Juan Jiang1, Yichen Jia2, Frederick J. Walker1 and Charles H. Ahn1,2; 1Yale University, United States; 2Yale, United States

BaTiO3 (BTO) is a promising candidate for lead-free electronic devices for applications using piezoelectric or ferroelectric thin films. To achieve large-scale integration of BTO with existing semiconductor technology, however, the synthesis of high-quality BTO films at suitably low temperatures is required to reduce the thermal budget during device fabrication. Here, we report a successful synthesis of ultrathin epitaxial BTO films on SrTiO3 (001) by molecular beam epitaxy with a substrate temperature as low as 280 °C. X-ray diffraction and in-situ reflection high-energy electron diffraction are performed to investigate the structural properties and relaxation of the BTO film during growth. This result paves the way toward the realization of novel nanoelectronic devices using epitaxial BTO films.

11:00 AM MT06.12.03
Investigating Thin Film Growth Mechanisms in Real Time Using RBS and XRD Andre R. Vantomme1, Jelle Demeulemeester1, Annelore Schrauwen1, Dries Smeets1, Koen van Stiphout1, Christopher B. Mtshali2, Christophe Detavernier1, Kristiaan Temst1 and Lino M.C. Pereira1; 1KU Leuven, Belgium; 2Materials Research Group, South Africa

Thin films formed by solid phase reaction often exhibit a complex composition of several atomic species. The (re)distribution, diffusive and reactive properties of the individual species as well as their relative motion upon thermal treatment have a distinct influence on the formation properties and thus on overall thin film properties. Rutherford backscattering spectrometry (RBS) and X-ray diffraction (XRD) measurements have proven extremely valuable in the study of thin film formation as a function of thermal treatment. RBS is an ideal technique to unravel the compositional depth profile of thin films. On the other hand, X-ray diffraction provides complementary information on the lattice structure (hence the phase!) and texture of the material.

In conventional studies, several specimens are typically subjected to different heat treatments and subsequently analyzed one by one, in order to obtain a complete overview of the reaction sequence. However, due to the discrete
character of this approach, critical stages for the understanding of the development of thin film properties (e.g., formation of transient phases) are easily overlooked. This problem is circumvented by determining the specimen properties in real time, i.e. in situ during annealing/reaction with a high sampling rate. Additionally, real-time measurements drastically decrease the workload, as kinetic parameters, redistribution properties and phase sequence during thin film reaction, for example, can be obtained from a combined ramped RBS or XRD annealing, while numerous specimens have to be analyzed in the conventional approach.

The strength and complementarity of these in situ techniques will be illustrated with a number of typical examples. These will include:
- Growth mechanism of binary and ternary silicide and germanide thin film by thermal annealing. Particular attention will be devoted to the (re)distribution of Pt or Pd during solid phase reaction of Ni<sub>x</sub>Pt<sub>1-x</sub> and Ni<sub>x</sub>Pd<sub>1-x</sub> alloys with Si, and the role of Pt/Pd on the growth kinetics.
- Determining the dominant diffusing species during nickel and palladium germanide formation, two of the most promising candidates for use as ohmic contacts when anticipating germanium-based devices. By continuously monitoring the movement of a thin (inert) marker in situ during phase formation by RBS, the relative contribution of the atomic species to diffusion can be directly deduced.
- Metallization of GeSn, a material which is used to enhance the charge transport properties in the MOSFET channel via strain engineering. Ge<sub>x</sub>Sn<sub>1-x</sub> with Sn concentrations required for device operation (of the order of 6-9 at.%) are metastable. Further treatment such as annealing, implantation or metallization often results in phase separation, i.e. Sn precipitation. Therefore, particular attention has to be paid to the Sn redistribution during metallization, for example Ni/GeSn reaction. A combination of in situ RBS and in situ XRD enables us to follow the (meta)stability and reaction kinetics during reaction.

An additional comment that should be made is that, in order to extract the compositional depth profile embedded in the RBS data, dedicated analysis of each individual spectrum, one by one, is required. Since a single real-time measurement easily contains a hundred or more spectra, analyzing a full data set can be extremely time consuming. To this end, we have implemented a novel analysis technique, i.e. artificial neural networks (ANNs), to tackle the quantitative analysis of large real-time RBS data sets. This approach, which is based on pattern recognition, allows to analyze vast amounts of data without compromising the integrity of the results, thus enabling to conduct systematic real-time RBS studies on large batches of samples or experiments.

11:15 AM MT06.12.04
Coherent X-Ray Measurement of Local Step-Flow Propagation During Growth on Polycrystalline Organic Semiconductor Thin-Film Surfaces
Randall Headrick<sup>1</sup>, Jeffrey Ulbrandt<sup>1</sup>, Peco Myint<sup>2</sup>, Jing Wan<sup>1</sup>, Yang Li<sup>1</sup>, Andrei Fluerasu<sup>3</sup>, Yugang Zhang<sup>4</sup>, Lutz Wiegart<sup>3</sup>, Karl Ludwig<sup>2</sup>; 1University of Vermont, United States; 2Boston University, United States; 3Brookhaven National Laboratory, United States

Vacuum physical vapor deposition of C<sub>60</sub> on a graphene-coated surface is investigated in real-time by utilizing 9.65 keV X-rays from the CHX coherent hard X-ray synchrotron beamline at NSLS-II. X-ray Photon Correlation Spectroscopy is performed in the Grazing Incidence Small Angle X-ray Scattering (GISAXS) mode to achieve surface-sensitive conditions. Local step-flow is monitored through the observation of oscillatory correlations in the GISAXS intensity. The experimental results show that the step-flow velocity is nonuniform, and we model the velocity of each step-edge as being a simple function of the lengths of the terraces above and below it. This model predicts that the steps become almost stationary near the edges of the mounds, and the average slope of the surface is large. It was not previously known that such nonuniform and disordered step arrays as we have observed would follow such a simple growth law. We also find that the sensitivity to local step-flow is increased due to coherent mixing of X-rays scattered from the average mound structure with those scattered from the step array. This effect is a version of heterodyne scattering, where the scattering from the average step array can be considered to be a quasi-static reference signal. This work shows that the use of coherent X-ray scattering provides an approach to better understand surface dynamics and fluctuations during crystal growth. We have also extended these measurements to additional materials systems, including the growth of organic semiconductor small molecules with a lower symmetry than C<sub>60</sub>, such as diindenoperylene.
The continued demand for power efficient and high-performance microelectronics components is the key driver for the increase in the density and miniaturization of transistors. The performance of these nanoscale transistors depends on their architecture and materials properties. Controlled fabrication of the nanoscale semiconductors materials tailored for microelectronics application requires detailed insight into the chemical and physical processes that take place during their fabrication. Optimization of these nanofabrication processes is currently based on trial-and-error approaches, and these structures are only characterized post processing limiting the insight into how materials evolve during the fabrication.

Here, we describe our development approach, which is based on our in situ liquid phase TEM imaging platform, to directly visualize the semiconductor fabrication related processes occurring in solutions with nanometer resolution in real-time. In my talk, I will show how we can study the etching of Si and SiGe nanowires, which will be an essential element in the next generation gate-all-around field effect transistors (GAAFET). Moreover, I will show an in situ TEM based test platform for studying the effects of anisotropic etching that is often present for many semiconductor materials and describe how different crystallographic Si planes etch.

Our results highlight the importance of visualizing the processes relevant to nanofabrication in order to understand and improve the nanofabrication related processes.

Hafnia based memristive devices are promising candidates as next generation non-volatile memory devices and are appealing because of the compatibility with back-end-of-line processes in the current semiconductor fabrication process and the good chemical and thermal stability. [1-2] One major issue with current devices is the large device-to-device variability [3] which could be resolved by highly textured hafnia where grain boundaries, interconnecting top and bottom electrode, serve as predefined pathways locally constricting the formation of the conductive filament as shown by conductive AFM [4].

In this study, a TiN/HfO2/Pt stack grown on c-cut sapphire is investigated by monitoring structural changes of the dielectric layer with automated crystal orientation mapping (ACOM) during in situ heating in the TEM. The 50 nm TiN layer has been grown by using reactive molecular beam epitaxy (RMBE) followed by in situ growing 12 nm amorphous hafnia and ex situ sputter deposition of 100 nm Pt. From one stack, a cross sectional focused ion beam (FIB) lamella has been prepared and transferred onto a Micro Electrical Mechanical System (MEMS) based heating chip. Laterally resolved structural information has been acquired by ACOM in order to track structural changes in the dielectric layer. The structural changes have been compared to another stack which has been ex situ annealed.

A temperature dependant study has been performed to monitor the growth process, thus giving insight into the growth mechanism and formation of grain boundaries in this system. Furthermore, we show, that the transformation from amorphous to the polycrystalline state lowered forming voltages and device-to-device variability serving as basis for a direct structure-property correlation.

References:
Nanostructured Au films resulting from supersonic cluster beam deposition of bare gold clusters show a non-ohmic electrical behavior and complex and reproducible resistive switching with characteristics suitable for neuromorphic applications [1, 2]. In order to achieve a deeper understanding of the modification induced at the nanoscale by joule heating in a gold cluster-assembled film due to the flow of an electrical current, we performed an in situ HRTEM characterization of the dewetting of the nanostructured films under thermal annealing.

Gold cluster-assembled films were fabricated by supersonic beam deposition on silicon nitride membranes, with nominal thickness of 1, 3, 12 and 18 nm respectively. Their initial morphology depends on the deposited amount of gold: while the samples 1 and 3 nm-thick are constituted by isolated and branched gold nanosized polycrystals, those with the higher thickness show a quite more branched, and percolating. The TEM/HRTEM/STEM measurements showed that the samples’ in situ heating leads to the dewetting of the gold polycrystals, and to the depercolation of those initially percolated, via the retraction of all the branches constituting the Au crystals. Such an evolution, common to all samples, was studied in terms of collective behavior, by low-magnification TEM imaging, HAADF-STEM and electron diffraction (ED) pattern collection of large ensembles of gold polycrystals. In particular, the global evolution under thermal in situ stimulus of the gold polycrystals not giving rise to a percolating network was quantified investigating the change of typical features such as their sizes, the latter expressed by their maximum (length) and minimum (width) mean Feret diameter, and the area fraction of the substrate covered by them. With regards to the Feret length and width, as well as to the covered area fraction, both not percolating samples showed that, as a consequence of the branches retraction, these parameters decreased with the thermal increase, bringing to smaller, still polycrystalline but spheroidal nanoparticles, showing a log-normal distribution of their size and with the mean one increasing with the nominal thickness. The same behavior was observed even for the percolating structure, but due to the fact that they were initially connected among them, the determination of the Feret parameters was achievable only after their dewetting. As well, the concomitant thickness increase of the gold nanocrystals during their branches’ retraction was qualitatively observed by HAADF-STEM imaging. The ED diffraction patterns indicated that: i) the as-deposited gold nanostructures did not grow following any preferential crystalline direction, and that ii) while the dewetting gave rise to the size increase of the central parts of the originally branched gold nanostructures, the crystal structure of those zones did not change with the heating and then again no any preferential crystal orientation was found after their thermally-driven evolution’s completion. Finally, the spherical aberration(Cs)-corrected HRTEM allowed determining the atomically-resolved in situ thermal evolution of single gold nanocrystals in the direct space, showing that the branches retraction is accompanied by the most peripheral crystal grains’ boundary movement, bringing to the formation of final, thicker, separate and more regular gold nanocrystals, in agreement with what observed on large ensemble of nanostructures.


A Stochastic Simulation Model for Understanding the Dynamics of Au-Seeded III-V Nanowire Growth Erik Mårtensson1,2, Carina Babu Maliakkal1,2, Sebastian Lehmann1,2, Marcus Tornberg1,2, Daniel Jacobsson2,3, Axel R. Persson2,3, Reine Wallenberg2,3, Jonas Johansson1,2 and Kimberly A. Dick1,2,3; 1Solid State Physics, Lund University, Sweden; 2NanoLund, Lund University, Sweden; 3National Center for High Resolution Electron Microscopy and Centre for Analysis and Synthesis, Lund University, Sweden

Direct observation of growing Au-catalyzed III-V nanowires via in-situ transmission electron microscopy can give crucial insights into the theoretical understanding of the growth process, through monitoring the dynamic behaviour of the catalyzing seed particle as well as the resulting nanowire it gives rise to. [1,2] However, the theoretical
framework of nanowire growth is to a large extent built on physical quantities which are not directly measurable in a microscope (e.g. the supersaturation of the growth species in the seed particle), often lack the dynamic aspect of the growth process, and rely on material properties and interface energies which are not always well known. This can make it difficult to correlate observations from *in-situ* experiments with nanowire growth theory.

Here, a stochastic simulation model of III-V nanowire growth is presented, which captures the dynamic processes of nanowire growth in a theoretical framework.[3] The model is based on the material flow of the growth species through the seed particle to follow the composition of the seed over time. Knowing the composition in turn allows for the calculation of nucleation rates using classical nucleation theory. Then, the moment when nucleation occurs, as well as the type (meaning crystal structure/composition), is decided using these nucleation rates and random numbers. Nucleating a new layer in turn affects the composition of the seed which allows the model to capture the dynamics of nanowire growth.

The model is designed to have the same input parameters as those used for experimental growth, such as the flow of growth species and temperature of the system. The output of the simulation include the temporal evolution of the physical quantities used in theoretical works, but also the size and composition of the seed, the crystal structure and composition of the growing nanowire and other properties which can be directly compared with observations from *in-situ* microscopy. This makes stochastic simulations and *in-situ* microscopy mutually beneficial. The simulations can provide explanations to experimentally observed trends due to the output of additional physical quantities, while the observations provide real time correlated measurements of the growth dynamics which can be used to improve the model.

An example of this synergistic nature will be presented, where experimental *in-situ* growth of GaAs nanowires using metalorganic precursors in an environmental transmission electron microscope was combined with simulations.[4] Experiments showed that the two distinct steps in nanowire growth, meaning the incubation period and the step flow growth, occurred on similar time scales and were found to be controlled by different parameters for most of the tested parameter space. Because of this, a step flow process was added to the model, and analyzing the simulations gave insights to how these processes can be limited by one or both of the growth species in different regimes. The experimental values for the step flow times in turn allowed us to tune and improve upon some of the parameters used in the simulations which are not well known, such as the interface energy between the liquid seed particle and the GaAs nanowire.

The flexibility of the simulation framework allows for many uses beyond analyzing step flow times in GaAs nanowire growth. As an example, the input variable corresponding to the flow of growth species can be changed throughout the course of the simulation. This gives the model the freedom to theoretically evaluate growth of heterostructures with different crystal structures for binary nanowires or different compositions for ternary nanowires.

2 - J. -C. Harmand et al., Phys. Rev. Lett. 121, 166101
3 - E. K. Mårtensson et al., Nano Lett., 19, 2, 1197-1203
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2:00 PM MT06.13.03

*In Situ* Observation of Surface-Diffusion-Assisted, Solid-State Oriented Attachment to Platinum-Based Nanowires

Yanling Ma\(^1\), Wenpei Gao\(^2\), Hao Shan\(^1\), Wenlong Chen\(^1\), Xiaqing Pan\(^2\) and Jianbo Wu\(^1\); \(^1\)Shanghai Jiao Tong University, China; \(^2\)University of California, Irvine, United States

One-dimensional platinum-based nanowires (NWs) have been demonstrated to possess improved activity and stability towards oxygen reduction reaction (ORR) for proton-exchange membrane fuel cells. Sufficient understanding on the growth mechanism at atomic level and seeking approaches for facile synthesis of platinum-based NWs are emerging. Here we report a novel scalable synthesis of surfactant-free thin platinum-based nanowires network electrocatalysts based on a generic solid state method. The growth stages and formation mechanism are investigated by in situ transmission electron microscopy (TEM). It reveals that the enhanced surface diffusion of Pt atoms due to the H\(_2\) adsorbate, especially on \{100\} planes, can establish a liquid-like behavior which facilitates the diffusion. Surface coalescence then prefers to occur on this specific plane, until the exposed Pt (100)
Surface is attached by other nanoparticles. In situ atomic observation demonstrated that four stages are included among this solid state orientated attachment: 1) H₂ adsorption, preferentially on Pt {100} facets, 2) higher local diffusion on Pt {100}, 3) attachment and formation of necking area between Pt nanoparticles, and 4) coalescence to form a short NW. The resulting catalysts demonstrated enhanced ORR performance: the as-prepared platinum-based NWs delivered the mass activity of 0.71 A/mgPt for Pt NWs and 1.52 A/mgPt for Pt-Ni alloy NWs, and the specific activity of 2.20 mA/cm²Pt for Pt NWs and 3.58 mA/cm²Pt for Pt-Ni alloy NWs, showing promising improvement over the commercial Pt/C catalyst. This newly developed solid state H₂-assisted method with the atomic understanding from in situ TEM observation provides an applicable path for scalable production of surfactant-free Pt-based NWs with excellent activity towards ORR. It is prone to better understand the surface adsorbate-promoted growth mechanism in gas at the atomic scale thus presents the possibility to synthesize flexible shape-controlled nanostructures in gas, similarly as in liquid phase.


2:15 PM MT06.13.04
Theory Meets Experiment to Understand the Sintering Processes of Ag Nanoparticles Edison Z. da Silva¹, Giovanni M. Faccin², Thales Machado³, Marcelo de Assis³, Nadia G. Macedo³, Elson O. Longo³, Juan Andres⁴ and Miguel A. San-Miguel⁵; ¹UNICAMP, Brazil; ²Universidade Federal da Grande Dourados, Brazil; ³Federal University of São Carlos (UFSCar), Brazil; ⁴University Jaume I (UJI), Spain; ⁵Instituto de Química, UNICAMP, Brazil

A novel process, the formation and growth of metallic Ag nanowires (NWs) and nanoparticles (NPs) on α-Ag₂WO₄ upon electron beam irradiation has been discovered and was extensively investigated by different experimental techniques including transmission electron microscopy (TEM) [1-3]. A combination of long time atomistic molecular dynamics (MD) simulations [4] and in situ transmission electron microscopy (TEM), was used to probe the coalescence of Ag nanoparticles (NPs). In the experiments we were able to observe and analyze rarely seen in situ Ag NPs growth produced by irradiation of an α–Ag₂WO₄ crystal by electrons from a TEM electron beam in vacuum, which were observed in real-time. This phenomenon can be considered as a clear example of surface plasmon resonances (SPR), in which the electron beam creates Ag NPs that become SPR electric dipoles. Nearby Ag NPs undergo coalescence processes that are controlled by dipole-dipole interactions, forming larger clusters [4]. The welding and sintering of Ag NPs analyzed with computer simulations, provided meaningful insights at atomistic level and show the role of the crystallinity and shape of the Ag NPs, lattice plane matching, and also the effect of stacking faults during these processes helping the understanding of the experiments. They uncovered an interface evolution process displaying a disorder to order transition [5] which was also verified experimentally, supporting the conclusions of this study.

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2:30 PM BREAK

SESSION MT06.14: Nanowires, Nanotubes and 1D Structures
Session Chairs: Katayun Barmak and Amy Clarke
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 209

3:30 PM *MT06.14.01
Mechanisms Involved in GaAs Nanowire Formation Explored by In Situ Transmission Electron Microscopy
Jean-Christophe Harmand1, Gilles Patriarche1, Federico Panciera1, Frank Glas1, Laurent Travers1 and Vladimir Dubrovskii2; 1C2N/CNRS/Université Paris-Saclay, France; 2ITMO University, Russian Federation

We investigate several mechanisms involved in GaAs nanowire formation, using an aberration-corrected transmission electron microscope (TEM) equipped with beam sources of Ga and As4 molecules. The molecular beams are supplied to a heated SiC membrane and the GaAs nanowires form by vapor-liquid-solid growth, with or without Au catalyst particles. Growth is observed in real-time with the atomic resolution.

We adjust the As4/Ga beam flux ratio to control the geometry of the catalyst droplet. The contact angle of the droplet on the nanowire top facet has a strong influence on the stacking of the GaAs atomic layers: wurtzite (WZ) or zinc-blende (ZB) crystal structures can be obtained [1]. Both structures form layer by layer, but specific features are associated with the growth of each of these crystalline phases. WZ phase stacking systematically corresponds to nucleation events occurring at the periphery of the interface between the droplet and the nanowire. In such a case, this interface is perfectly flat and the step flow is relatively slow [2]. ZB stacking is obtained mainly at large droplet contact angles, the top facet being truncated and the step flow much faster (instantaneous at a camera acquisition rate of 10 frames per s). In this situation, the truncation volume varies periodically, at the frequency of monolayer formation as already reported in other systems [3].

We show that the previous features are not intrinsically related to the crystal structure which grows. Indeed, at contact angle below 90°, ZB monolayers can form with a slow step flow and no facet truncation at the liquid/solid interface. Moreover, we use an artifice to produce a truncation of the top facet while the droplet contact angle leads to WZ formation. In this situation, the WZ stacking is maintained but the monolayer step flow becomes fast. This shows that the truncation of the top facet acts as a reservoir of atomic species which can accelerate the completion of a monolayer, whatever the crystal structure being formed.

Finally, we will show that a fine control of the beam sources allows us to switch abruptly from one crystalline phase to another and thereby, to fabricate crystal phase superlattices.

We acknowledge the French National Research Agency (ANR) for funding the TEMPOS/NanoMAX project within the EQUIPEX "Investissements d'Avenir" programme.


4:00 PM MT06.14.02
Limits of III-V Nanowire Growth Based on Real-Time Observations of Droplet Dynamics Marcus Tornberg1,2, Carina Babu Maliakkal1,2, Daniel Jacobsson1,2, Kimberly A. Dick1,2, and Jonas Johansson1,2; 1Lund University, Sweden; 2NanoLund, Sweden

Crystal growth of III-V semiconductor nanowires assisted by a liquid droplet requires, apart from successful nucleation, that the particle continuously wet the top of the nanowire. Recent TEM observations have shown that with increasing droplet volume, the interface between the nanowire and the liquid may become truncated [1,2], and eventually the droplet may be displaced from the top facet [3]. While this has been observed and discussed from the nucleation point of view, it has not been addressed from the droplet dynamics perspective.

Here we compare in-situ transmission electron microscopy observations of the droplet-nanowire interface during growth of Au-assisted GaAs nanowires, with calculations of the stability of the droplet on the nanowire top facet by comparing the capillary forces. By expanding the Young’s equation for droplet on a surface to include a truncated facet, we find limits for the solid-vapor and liquid-vapor surface energy ratio with respect to the contact angle of the droplet. These limits confine an interval of surface energy rations between which the droplet remain on top of the nanowire. In addition, it is predicted that formation of a truncation of the solid-liquid interface increases the stability for having a droplet on the top of a nanowire.
From the experimental observations, based on real-time imaging of the crystal growth at ~20 frames/s, we observe the dynamic droplet-nanowire interface as the droplet is filled with Ga which results in a truncated interface from time to time. Along with these observations, we estimate the surface tension and contact angle of the droplet based on the projected droplet volume. These experimental data and observations are then combined with our theoretical calculations in order to experimentally estimate the surface energy of the GaAs wurtzite \{10-10\} solid-vapor interface. We get an experimental prediction of the surface energy for the crystal growth conditions of GaAs (pressures and temperatures) in comparison to the existing theoretical predictions made for ideal environments and reconstructions [4, 5]. The comparison can further be used to hypothesize if, or how, the surface of interest has been reconstructed.

To conclude, using high frame-rate in-situ TEM imaging in conjunction with theoretical estimations we will present a reasoning for the formation of a truncation at the droplet-nanowire interface. In addition, we will show the observed droplet dynamics and how they are used to experimentally estimate the surface energy of the wurtzite GaAs nanowire sidewall.

**References**

catalytic chemical vapor deposition (ACCVD) using Co and Ni catalysts. C K-edge, and Co and Ni L-edge XANES measurements were performed at BL-7A in KEK PF and BL-5S1 at Aichi SR, respectively. In CNT growth by thermal decomposition, CNTs are formed on SiC(000-1) surface by heating above 1200°C in a vacuum, due to the desorption of Si atoms from SiC surface. C K-edge XANES results showed that the orientation of C-C bond changed with the increase of the sample temperature. When the temperature was 1100°C, C-C bonds were parallel to the surface. However, they were aligned to perpendicular to the surface above 1300°C. Taking into account the results of first-principles density functional theory/molecular dynamics (DFT/MD) simulation [2], at the beginning, the graphene flakes were formed at ~1200°C, which were parallel to the SiC surface. As the temperature rose, they were curved by the formation of bonds with the dangling-bonds on SiC(000-1), and hemispherical structures (“carbon nanocaps”) were formed. When the temperature was above 1300°C, CNT growth was proceeded perpendicular to the surface [3]. Our results showed that the size and structure of graphene flakes formed at the initial stage would determine the structure (diameter, chirality and the number of walls) of CNTs.

Next, we performed Co and Ni XANES measurements to clarify the chemical states of these metal catalyst particles during SWCNT growth by ACCVD. Co and Ni L-edge XANES spectra showed that “as deposited” Co and Ni catalysts were both partially oxidized and they were reduced to metal particles during heating. However, after SWCNT growth started, Co catalysts were transformed to carbides, but Ni catalyst remained metallic. This indicates that, during SWCNT growth, carbon atoms dissolve into the Co catalyst particles, while carbon atoms diffused only on the surface of Ni catalyst particles. Taking into account the similarity in the bulk phase diagrams of C-Co and C-Ni, the difference in the chemical states of Co and Ni catalyst particles is due to the specific property of nano-sized particles, which is consistent with the DFT simulation [4].

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4:45 PM MT06.14.05
Using In Situ Spectroscopy Techniques to Isolate the Roles of Hydrogen Exposure and Trace Carbon Contamination on Catalyst Nucleation Success Rate for Carbon Nanotube Growth Jennifer Carpena1, Rahul Rao1, J. Anibal Boscoboinik2, Sammy Saber1, Jiang-Qiang Zhong2, Matthew R. Maschmann3, Piran Ravichandran Kidambi4, Nick T. Dee5, Dmitri Zakharov2, Anastasios J. Hart5, Eric A. Stach6 and Benji Maruyama6; 1Air Force Research Laboratory (UES Inc.), United States; 2Brookhaven National Laboratory, United States; 3University of Missouri, United States; 4Vanderbilt University, United States; 5Massachusetts Institute of Technology, United States; 6Air Force Research Laboratory, United States

Limited understanding of the factors influencing the yield of CNTs relative to the number of catalyst particles remains an important barrier to their large-scale production with high quality and to tailoring CNT properties for applications. This lack of understanding is evident in the frequent use of Edisionian approaches for achieving high-yield CNT growth, and the sometimes confusing influence of trace residues on the reactor walls. In order to grow CNTs reproducibly and enable large-scale growth, it is imperative to understand, fundamentally, how these common practices impact catalytic activity and thus nucleation success rate. Herein, we use ambient pressure-X-ray photoelectron spectroscopy (AP-XPS) and in situ Raman spectroscopy to study the influence of carbon and hydrogen on the coupling between catalyst reduction and CNT nucleation, from an iron catalyst film. The XPS results reveal a positive correlation between the degree of catalyst reduction and the density and quality of the CNTs, verifying that effective catalyst reduction is critical to CNT nucleation, and to the resulting CNT growth yield. We also show that hydrocarbon by-products from consecutive growths can facilitate catalyst reduction and increase nucleation success rates significantly. The in situ Raman studies reveal that the addition of carbon decreases the incubation time, thereby enabling a higher CNT nucleation density. Our findings suggest that common practices used in the field, such as reactor preconditioning, aid in the reduction of the catalyst population, thus improving nucleation success rates and enabling growth of dense forests.
MT06.15.01
Direct-Design Approach for Reversible Tuning of the Optoelectronic Properties of Doped Metal-Oxide Semiconductors Pragathi Darapaneni and James A. Dorman, Louisiana State University, United States

Tuning the optoelectronic responses of metal-oxide semiconductors in a stable, but reversible manner is identified as the limiting factor for their deployment in real-world flexible electronic devices. Currently, external stimuli (e.g. pressure, temperature) are applied on these inorganic semiconductors to modify their optoelectronic response, ultimately reverting to their initial state upon relaxation. Therefore, this work demonstrates the effect of polarized molecules for reversibly manipulating the optical, electrical, and magnetic transport properties of transition metal (TM) doped metal-oxides and is validated computationally. As a proof-of-concept, the electronic properties of TM dopants and their coupling with rare earths (RE) are probed using time-resolved optical spectroscopy. While these materials have applications in bio-sensors and flexible displays, the results of which have potential for quantum computing.

Functionalized Ni doped TiO$_2$ thin films were characterized to identify effect of surface dipoles (para-substituted benzoic acid ligands) on their optoelectronic and structural properties. The ligand-induced local structural and electronic changes around Ni$^{2+}$ were investigated via neutron scattering (NS) and soft x-ray absorption spectroscopy (XAS). Upon functionalization, a distinct shift in the $t_{2g}$-$e_g$ filling and energy levels were observed in the Ni L$_2$ edge XAS spectra and was attributed to a local geometry distortion. Our real time (RT) time-dependent density functional theory (TDDFT) calculations further confirm that the applied ligand field changes the 3d metal orbitals hybridization, resulting in the observed variation in the Ni L$_2$ edge XAS. Additionally, in situ ultraviolet photoelectron spectroscopy (UPS) measurements on functionalized TiO$_2$:Ni films reveal that the direction of charge transfer and band bending is reversible and proportional to the dipole moment. Next, TiO$_2$:Ni$^{2+}$ shell layer with controlled thickness, is coated on the core β-NaYF$_4$:Er$^{3+}$ nanoparticles to facilitate Ni$^{2+}$-Er$^{3+}$ energy transfer for dynamic upconversion luminescence via adaptive Ni$^{2+}$ absorption. UV-Vis and in situ photoluminescence (PL) measurements on these surface-modified RE core-TM shell phosphors indicate a clear shift in the optical absorption (~ 50 nm) and emission spectra, demonstrating the ligand-dependent luminescence of core-shell phosphor. This direct design method of combining experiments and theory will provide a robust approach for designing weak field dependent optoelectronic materials. More importantly, this ability to reversibility manipulate interfacial charge transfer processes of doped semiconductors has direct implications in the development of quantum computing type materials and memory-storage devices.

MT06.15.02
Fold 2D Woven DNA Origami to Origami+ Structures Chao Wang, Yiyang Zhang and Dongsheng Liu; Tsinghua University, China

DNA origami strategy has greatly promoted the development of DNA nanotechnology as it can construct delicate 2D/3D nanostructures. The current method to prepare DNA origami is through a woven approach to fix a long strand DNA into certain shapes. This article describes a novel strategy to fold the same 2D DNA sheet into multiple complex structures driven by introducing hydrophobic interaction. The pathway of the folding process can be adjusted by tuning the distribution and chronic order of cholesterol, resulting in different complicated structures. This method has been proved efficient for constructing variable nanostructures based on the same DNA origami sheet, and termed as origami+. This work represents a new strategy in DNA nanotechnology and will improve the ability to manipulate objects at nano-scale.

Reference:

MT06.15.03
In Situ TEM Operation of a Copper-Based 3-Terminal Synaptic Cell Baoming Wang$^1$, Teodor Todorov$^2$, John
As an alternative computing architecture, neuromorphic computing has drawn enormous attention worldwide. Various analog switching devices have been demonstrated as synapses for neuromorphic computing. A particularly promising design involves an analog neural network accelerator based on a cross-point array of non-volatile memory elements. However, these devices often show non-ideal switching characteristics that will limit the accuracy in neural network training. Improved control of analog switching can be achieved by replacing each 2-terminal memory element with a 3-terminal memristor structure that has a channel with a “read” terminal on each end, plus a control electrode that is analogous to the gate in a transistor. We are particularly interested in memristor structures that do not use lithium as the diffusing species, due to its sensitivity to air and humidity. We have therefore developed a fast-switching memory element based on the use of a copper superionic conductor, Cu₁₆Rb₄Cl₁₅I₇. This unusual compound has the highest reported room temperature conductivity of any solid electrolyte, 0.34 S/cm. Ex situ measurements suggest that a voltage at the control electrode causes Cu⁺ to migrate through the solid electrolyte and deposit onto the channel, changing its resistivity, as measured using the two read terminals. However, ex situ measurements cannot directly address failure modes and the physical factors limiting reliability, even when structural and electrical characteristics are correlated before and after operation of the device. We therefore describe the use of transmission electron microscopy, with structural and analytical (EDS/EELS) capabilities, to investigate the operation mechanism and limitations of copper-based 3-terminal synaptic cells. We have fabricated electron-transparent thin film samples on commercial TEM window chips with a copper control electrode and various materials for the channel. The chips are accommodated in a Hummingbird TEM holder with biasing capability. We will describe the characteristics of these devices and correlation of their electrical performance with microstructural evolution. We will also compare the device operation with liquid cell TEM observations of the cyclic pulse deposition of copper from a liquid electrolyte, which has been proposed as an alternative synaptic cell design. For both liquid and solid electrolytes, we believe that in situ TEM techniques have a vital role to play in the material and architecture design of memristor-based 3-terminal devices.

**MT06.15.04**

*In Situ Gas-Cell TEM Studies of Alloyed Nanoparticles*

Boao Song¹, Yuzi Liu² and Reza Shahbazian-Yassar¹;

¹University of Illinois at Chicago, United States; ²Argonne National Laboratory, United States

Corrosion is the interaction between service materials and environments that involves chemical or electrochemical reactions at interfaces. The corrosion-induced deteriorate of proper material functions is the most common cause of the failure during service. Alloyed nanoparticles (NPs), an emerging material compound involving several elements in the form of disordered solid solutions, is attracting increased attentions since their novel properties in applications of catalysis and superior structural alloys. The corresponding service environment for such materials usually involves super critical conditions such as exposure to chloride-containing solutions, acidic, high-temperature, high oxidative gases, which requires in depth understanding of corrosion behaviors at both structural and chemical level. In contrast to alloys in bulk phase, the corrosion-resistant properties of nanoparticle phase is poorly studied due to the relatively fresh discovery of such materials system and the challenge of obtaining nanoscale information regarding to the typical few nanometer sizes of NPs. With the reduced size of alloys from bulk to NPs, it is crucial to utilize advanced characterization techniques like TEM to gain atomic resolution information during oxidation process. *In situ* TEM, with combined sub-nanometer resolution and real time observation capabilities, is essential for such study.

The oxidation behavior is specifically essential to be investigated for alloyed NPs with working conditions expose to atmospheric pressure gases at elevated temperature. To do so, an *in situ* gas-cell TEM holder is utilized to allow the alloyed NPs expose to various of gases environment. The distance between two Si microchips can be adjusted as small as 50 nm or as large as 2 μm, accommodating the major size range of synthesized NPs. Air, H₂, and water vapor gases are used to flow into the cell with a constant volumetric flow rate. A temperature controller is used to set the temperature from RT to 800 °C. The *in situ* gas-cell allows atomic resolution imaging at both room and elevated temperatures, and the structural evolution during oxidation is observed in real time. The oxidation states for various elements are evaluated by electron energy loss spectroscopy (EELS) at different temperatures. The observation is further investigated by density functional theory (DFT) calculation to gain fundamental understanding of oxidation behavior. The present study provides insights into how oxidation initiated at the surface of alloyed NPs, and help gain deeper understanding of designing anti-oxidation composition for next generation functional alloys.
Melanins are ubiquitous biopigments responsible of manifold functionalities in living organisms. Eumelanin is a hygroscopic, black-brown biomacromolecule belonging to the family of melanin biopigments. It is synthesized by the oxidative polymerization of (5,6)-dihydroxindole (DHI) and (5,6)-dihydroxindole 2-carboxyl acid (DHICA) building blocks. Different available polymerization sites, a wide variety of supramolecular arrangements and co-existing redox states, bring chemical and physical disorder to the biopigment. There is a significant interest in eumelanin physicochemical properties such as broadband optical absorption, free radical scavenging, metal-ion chelation and hydration dependent electrical response, this last mainly attributed to protonic transport. Owing to the complex structural organization, a universal theory correlating supramolecular aggregation to fundamental optical and electrical properties of eumelanin does not exist yet. Furthermore, the charge transport properties of the biopigment, object of numerous studies, are still elusive. Our group is currently investigating the solid-state polymerization of spin coated DHI and DHICA thin films at surfaces. We observe that the monomers aggregate, possibly eventually polymerizing in a time scale of 48hr at ambient condition. Images obtained by Atomic Force Microscopy (AFM) show that after a few days at ambient condition DHI thin films grow into well defined fern-like structures on certain areas of the surface. This process, attributable to a diffusion limited aggregation (DLA), is followed by the growth of crystal-like agglomerations about 400 nm-high, on the fern structures. On the other hand, DHICA thin films do not form crystal-like agglomerations. We observe, instead, that regularly shaped nano-pillar structures, uniformly coating the substrate surface, grow in about 1hr at ambient condition. The pillars gradually undergo an in-plane and out-of-plane growth, reaching average width and height of 100 nm and 300 nm. UV-Vis spectra of DHI acquired over time, show an absorption peak at 305 nm that gradually shifts to 322 nm after one month at ambient condition. We tentatively interpret this red shift as an evidence of solid-state polymerization. Interestingly, both in DHI and DHICA spectra, we observe an increase of the absorbance both in the UV and Visible regions, this latter likely due to an improved -electron delocalization of oligomeric structures over time.

Being non-toxic, abundant, solution processable and quite biodegradable, eumelanin is a promising candidate for green electronics: as such our results are of paramount importance to exploit the full technological potential of the biopigment.

References
crystalline control, it is originated from the real-time imaging function of scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which allows localized crystallization (nanoscale phase change) with sub-10 nm precision. In addition, the crystallization leads to volume change, which generates stress in the thin film and triggers self-assembly of 3D nanostructures. Various complex three-dimensional (3D) functional nanostructures can be realized based on this scheme.

MT06.15.07

*In Situ* Transmission Electron Microscopy Characterization of High-Temperature Behavior of Metal Nanostructures Daan Hein Alsem, James Horwath, Khim Karki and Eric A. Stach; 1Hummingbird Scientific, United States; 2University of Pennsylvania, United States

The most common method for controlling structure through processing is through simple thermal excursions, as temperature causes atomic diffusion, and thus allows structural re-ordering. One of the primary experimental method used to determine the local internal structure of nanomaterials is that of transmission electron microscopy (TEM). Therefore, the most common dynamic *in situ* microscopy experiments revolve around the relatively simple act of heating nanomaterial samples.

Thin-film technology has allowed much more local heating of the specimen in TEM heating holders if one is studying nanomaterials, enabling more stable imaging during *in-situ* TEM heating experiments. More recently, direct temperature measurements on these thin-film heating systems have made temperature measurements at the sample become closer to becoming reality. Although double-tilt TEM heating holders have been available, they suffer from some of the same limitations as standard double-tilt TEM holders do. Specifically, backlash in the tilting mechanism and lack of repeatability of the tilt makes it difficult to get the sample in exactly the right orientation and to know the exact angle of rotation. In this work we will use an optimized double-tilt thin-film heating platform that minimizes mechanical artefacts in the tilting mechanism and provides very stable image performance when heated to temperatures up to 1000°C, where it can be run more than 150 hours. Outside of standard temperature characterization of these thin-film heating TEM systems using different high resolution optical thermal imaging techniques, we also used melting standards to confirm accurate temperature response of the on-chip temperature sensor to indicate the temperature at the sample. We can identify very local and discrete melting events of samples with known melting points and correlate this to the sensor response, where local melting happens at very discrete moments (typically within a few frames), and surface diffusion occurs in matters of seconds following that.

In addition to this, we used this new *in-situ* TEM sample heating system to characterize model nanomaterial systems. Specifically, we studied the behavior of gold nanoparticles and nanorods on SiN$_x$ substrates as function of temperature. Starting with characterizing of particle motion and stability under the beam and then the phase transformation and (rapid) shape change at the melting point. We will present rapid frame-to-frame phase transformation process of gold nanorods as we ramp the sample temperature to 1000°C and show that we can use the system to track phenomena in nanostructures over the full temperature range of the TEM heating system with good image stability. These results illustrate the optimized overall mechanical stability and temperature performance of this newly developed *in-situ* TEM double-tilt heating platform.

MT06.15.08

Acid Etching of ZnO Nanostructures—*An In Situ* TEM Study Fangyuan Liu, Xingxu Lu and Pu-Xian Gao; University of Connecticut, United States

In micromachining and nanoelectronic field, etching is an important method to selectively construct two-dimensional or three-dimensional nanostructure semiconductors by introducing etchants or sacrificing the surface with powerful force [1]. ZnO nanostructure has been one of the most popular nanomaterials being studied in the past decades due to its widespread potential applications in photovoltaics, catalysis, flexible electronics, and solid state lighting, etc. [2,3]. To improve the ZnO nanostructure based device performance, some research groups used acidic or basic wet etching to help to expose the high surface energy crystal planes such as the semipolar $\{10-11\}$ family surfaces [4]. However, it is hard to control the surface exposure regularity of the etched ZnO nanostructures. In this work, *in situ* liquid cell transmission electron microscope (LCTEM) is employed to help resolve the crystal shape change in the acid etching process and reveal the morphology transformation process. To mitigate and clarify the well-known electron beam effect in LCTEM [5], optical microscopy (OM) and scanning electron microscope (SEM) has been used in combination of the LCTEM method. By using such a combination method, the etching process of
ZnO nanostructures can be robustly and confidently analyzed from atomic to nanometer scales and the etching mechanism can be simulated. Controlling pH=1~5 and temperature from 20 °C to 60 °C, the nanostructure will be changed from pencil shape to crown shape, as well as the etching rate will be changed. And both {10-11} and {10-1-1} can be preferentially exposed. This etching study provides some insight into controllably surface etching for nanoscale crystal surfaces.

Hexagonal Palladium Hydride in Graphene Liquid Cell
Jaeyoung Hong1, Jee-Hwan Bae1, Hee-Young Park1, Sehyun Lee1, Sunjun Hong2, Hoje Chun2, Juyoung Kim1, Kyureung Lee1, Byungchan Han3, Jungwon Park3, SungJong Yoo3 and Dongwon Chun1; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Yonsei University, Korea (the Republic of); 3Seoul National University, Korea (the Republic of)

Unexpected high pressure phenomena have been reported in boron nitride, Na-Cl and water, which are not observed at ambient conditions, indicating pressure can determine the stability of crystal structure [1-3]. It is widely accepted that palladium and palladium hydride (Pd-H) have a face-centered cubic (FCC) crystal structure under environmental conditions, even at high temperature in the case of pure Pd. In this study, we firstly report hexagonal close-packed (HCP) Pd-H which is a new palladium hydride phase previously suggested by density functional theory (DFT) calculation in high pressure [4].

We synthesized hexagonal Pd-H by irradiating high energy electron beam on aqueous solution of Pd in a transmission electron microscope (TEM). We adopted graphene liquid cell (GLC) to acquire high resolution images in liquid. [5] The electron beam induced nanoparticle growth in liquid was traced by FEI Titan TEM equipped with Gatan OneView CCD camera, which can acquire a single image within 0.04 seconds. Crystal structure analysis of the Pd nanoparticles was performed by analyzing diffraction patterns generated by fast Fourier transform (FFT) of high resolution TEM images acquired during particle growth. Through the diffraction patterns obtained from various zone axis, it was revealed that synthesized Pd nanoparticles have HCP structure which is different from the structure of Pd and Pd-H at ambient conditions, FCC. From energy dispersive X-ray spectroscopy (EDS) analysis conducted with a TEM equipped with Bruker Super X-EDS system, no element except for Pd was detected, suggesting oxygen doesn’t influence on the formation of hexagonal structure. Given that EDS cannot detect elements lighter than boron and inter-planar distance of the particle is greater than that of an imaginary pure HCP Pd which has same interatomic distance with FCC Pd, created particle is assumed to be Pd-H.

Thermodynamic stability of HCP structure of Pd-H was verified with a computational study. A simulation show that Pd-H is likely to have hexagonal structure when pressure is applied and concentration of hydrogen in palladium is high. For PdH0.5, HCP is more stable than FCC only when it’s under pressure higher than a few GPa, while HCP phase is more stable even at ambient pressure in the case of PdH1. Considering the previous reports asserting that materials lying between two graphene layers experience high pressure up to a few GPa and that radiolysis of water produces hydrogen radicals, formation of hexagonal Pd-H is attributed to not only hydrogen radicals but high pressure applied by water trapped between graphene layers. [3,6] We tried to synthesize the HCP particles outside a TEM by irradiating electron on liter scale vessel under ambient atmosphere, but resulting products were mostly FCC particles, which might be due to the absence of high pressure.

Also, it was confirmed that the nanoparticle has hexagonal structure even at the beginning of the growth stage and inter-planar spacing of the particles does not change remarkably during in-situ observation, suggesting hydrogen radicals participate in both nucleation and growth reactions. It’s quite different from FCC Pd-H formation process where hydrogen is absorbed by an existing Pd matrix. In addition, we investigated thermal stability of hexagonal Pd-H by an in-situ TEM heating holder (Gatan heating holder model 652). It is known that hydrogen desorbs easily from FCC Pd-H at around 100°C even in hydrogen atmosphere [7]. Interestingly, hexagonal Pd-H maintained its crystal structure even when it’s annealed over 300°C under vacuum without noticeable lattice constant change.

References
storage and for electrocatalysis due to a combination of properties including high magneto-crystalline anisotropy, high Curie temperature, small superparamagnetic critical size and high chemical stability. Solution phase techniques provide an excellent strategy for preparing monodisperse FePt NPs with a narrow size distribution, good compositional control and well-defined shape. Traditional ex situ experiments using TEM and XRD analytic methods show that fct-FePt NPs pass through several intermediate stages during solution synthesis from Pt and Fe precursors. First, fcc-Pt and crystalline Fe3O4 (magnetite) phases appear, presumably formed by reduction of the Pt and Fe precursors, respectively, at lower temperature. Subsequently, the Fe3O4 phase disappears and the fcc-FePt phase appears. Finally, the fcc-FePt phase transforms into fct-FePt when the sample is heated to a higher temperature. Controlling these reactions is important for precise control of the resulting nanoparticles, but the mechanism of the formation of fcc-FePt from the fcc-Pt and Fe3O4 phases is difficult to characterize using only ex situ data. We have therefore used in situ liquid cell electron microscopy to explore the mechanism of the reaction between crystalline Fe3O4 NPs and Pt solution in an aqueous medium. We find that microstructural changes take place in crystalline Fe3O4 NPs upon flowing a Pt precursor solution. The size of the crystalline Fe3O4 NPs gradually decreases and they eventually disappear, followed by re-formation of small NPs. Under certain conditions we also observe the formation of unusual structures where the NPs develop hollow cores. We consider the effect of initial Fe3O4 NP size, Pt concentration and temperature on the morphological changes, and discuss a model in which the crystalline Fe3O4 NPs are reduced and alloy with Pt atoms to form fcc-FePt NPs. Understanding the intermediate reaction steps can contribute to a better control of the formation of fct-FePt NPs.

9:45 AM BREAK

SESSION MT06.17: Thin Films and 2D Structures
Session Chairs: Kozo Fujiwara and Ashwin Shahani
Thursday Morning, December 5, 2019
Hynes, Level 2, Room 209

10:15 AM *MT06.17.01
Opportunities for Imaging the Formation of Interfaces between 2D and 3D Materials Frances M. Ross;
Massachusetts Institute of Technology, United States

The interfacial structure that forms at the junction between a 2D layered material and a 3D crystal can dominate the physical phenomena exhibited by the combination of materials. In particular, epitaxial or low defect density 2D/3D interfaces minimize electrical contact resistance and allow efficient charge transfer, and are essential for achieving proximity-induced superconductivity for spintronics applications and for developing catalysts and field effect or optoelectronic devices. In situ TEM provides a unique tool for examining the structure, formation and evolution of 2D/3D interfaces by following along as 3D nanocrystals are grown on 2D substrates. The experiments require deposition capabilities as well as ultrahigh vacuum (UHV) to control the sample surface cleanliness and avoid extraneous reactions such as oxidation. We therefore use a custom TEM with base pressure in the 10⁻¹⁰ Torr range and an attached series of vacuum chambers with heating and deposition capabilities. We first transfer 2D layers or heterostructures onto substrates that can be cleaned by direct-current heating in the vacuum system. Without breaking vacuum we then deposit metals or semiconductors using evaporation or reactive gas precursors. Imaging can be carried out at the same time as, or immediately after deposition, to follow the evolution of the interfacial structure. We will illustrate the capability of TEM to analyze nanocrystal nucleation and evolution, orientation relations, interface dislocations, local strain fields and defects in several metals and semiconductors on 2D materials. We will discuss how parameters such as substrate temperature and defect density affect the morphology of deposited metals, including reactive systems such as Nb on transition metal dichalcogenides. We will show a strategy for achieving epitaxial growth of materials that show poor epitaxy, such as Ag, Ge or Si, by using a template made of another, epitaxial material such as Au. We can also measure the catalytic properties of individual metal nanocrystals as we use them to grow semiconductors using chemical vapor deposition. We finally describe the use of sequential deposition to form heterostructures and the effects of patterning the 2D material. We conclude by discussing the importance of recent developments in microscopy instrumentation in analyzing 2D/3D materials growth to help design functional nanoscale materials.
Real-Time Observations of Phase Transitions During Antimonene Epitaxial Growth
Matthieu Fortin-Deschenes1, Onur Mentes2, Andrea Locatelli2, Francesca Genuzio2 and Oussama Moutanabbir1; 1Polytechnique Montreal, Canada; 2Elettra Sincrotrone Trieste, Italy

Group V 2D materials are a new class of materials [1] which includes various allotropes of phosphorus, arsenic, antimony [2, 3] and bismuth. Amongst them, we find the α and β phases of antimonene, which display thickness dependent electronic and topological properties, including a single-layer semi-conducting phase and a quantum spin-hall state at multilayer thickness. Using Transmission Electron Microscopy (TEM) and real-time Low-Energy Electron Microscopy (LEEM) observations of the van der Waals growth of antimonene on graphene, we discuss the growth modes of α-antimonene and its transition to β-antimonene occurring at a critical thickness of ~5nm. Moreover, using synchrotron-based X-ray Photoemission Electron Microscopy (XPEEM), we discuss the environmental stability and bonding nature of both phases. These results are an important step towards developing large-scale epitaxial growth methods for group V 2D materials.


Structural Evolutions of Vertically-Aligned Two-Dimensional MoS2 Layers Revealed by In Situ Heating Transmission Electron Microscopy
Mengjing Wang1, Jung Han Kim1, SangSub Han1,2, Kyu Hwan Oh2, Hee-Suk Chung3 and Yeonwoong Jung1,1,1; 1University of Central Florida, United States; 2Seoul National University, Korea (the Republic of); 3Korea Basic Science Institute, Korea (the Republic of)

Benefited from a large density of 2D layer edges exposed on the surface, vertically-aligned 2D MoS2 layers have recently harvested excellent performances in the field of electrochemical catalysis and chemical sensing. With the increasing versatility for high-temperature demanding applications, it is vital to identify their thermal-driven structural and chemical stability as well as clarify its underlying principle. Despite various ex-situ and in-situ characterizations on horizontally-aligned 2D MoS2 layers, the direct in-situ heating of vertically-aligned 2D MoS2 layers and the real-time observation of their dynamics at the near-atomic scale have never been approached, leaving their thermal stability poorly understood. Moreover, the geometrical advantage of the surface-exposed vertically-aligned 2D MoS2 layers is anticipated to unveil the structural dynamics of interlayer van der Waals gaps and its correlation with thermal energy, unattainable with 2D MoS2 layers of any other structural forms. Herein, we report a comprehensive in-situ heating TEM study on cleanly transferred vertically-aligned 2D MoS2 layers up to 1000°C. Several previously unknown striking phenomena were observed in the course of heating; (1) formation and propagation of voids between the domains of vertical MoS2 layers with distinct grain orientations starting at about 900°C. (2) subsequent melting of 2D MoS2 layers accompanying a formation of Mo nanoparticles at about 945°C, much lower than the melting temperature of their bulk counterpart. (3) initiation of melting from the surface-exposed 2D layer vertical edge sites, congruently supported by density functional theory (DFT) prediction. These new findings obtained with vertically-aligned 2D MoS2 layers will offer critical insights into better understand the thermodynamic principle that governs the structural stability of general van der Waals 2D crystals as well as provides technological guidance for materials design and optimization in their potential high-temperature applications.

In Situ TEM of an Oxide Thin-Film Crystal Nucleation and Growth and Aberration-Corrected TEM of Oxygen Vacancy Ordering Kinetics
Robert Sinclair, Yunzhi Liu, Sangchul Lee and Kyung Hoon Min; Stanford University, United States

It is now well understood that careful in situ transmission electron microscope (TEM) experiments are required in order to reveal, at high resolution, materials phenomena which are representative of the true natural behavior. One such study, of the crystallization of high-k dielectric tantalum oxide (Ta2O5) thin films on a silicon substrate, has shown how the individual mechanisms of nucleation and growth contribute to the overall transformation and
processing behavior, and even allow in situ capacitance measurements on individual crystals. The determination of the reaction activation energy is an important component of this type of work [1]. This approach has been extended to describe the kinetics of oxygen ion-vacancy ordering in epitaxial thin films of ceria (CeO$_2$) grown on yttria stabilized zirconia single crystal substrates, as revealed by in situ aberration-corrected TEM [2].


11:45 AM MT06.17.05
*In Situ* SAXS, WAXS and Absorption Measurements on the Nucleation and Growth of CdSe Nanoplatelets

Johanna van der Bok$^1$, Paul T. Prins$^1$, Federico Montanarella$^2$, Daniel Vanmaekelbergh$^1$, Andries Meijerink$^1$, Celso de Mello Donega$^1$ and Andrei V. Petukhov$^1$; $^1$Utrecht University, Netherlands; $^2$ETH Zürich, Switzerland

A better understanding of the formation mechanism of nanoparticles is needed to control growth and fine-tune their properties for applications. SAXS, WAXS and absorption measurements are commonly used to obtain insight in the formation mechanism of nanocrystalline systems. However, these measurements are typically performed in capillaries or by taking aliquots, therefore represent particle growth under conditions that are different than the actual reaction conditions. We developed a reactor to reproduce the conditions under which nanoparticles are synthesized by using specially designed glassware. In this reactor it is possible to do in-situ SAXS, WAXS and absorption measurements in oxygen and water free environment, at high temperatures and with a time resolution on the order of milliseconds. Furthermore, we were also able to add solid reactants or inject a liquid at any time during the synthesis, while measuring.

Here we report in-situ measurements aimed at giving more insight into one of the most debated nanoparticle formation mechanisms: the formation of CdSe nanoplatelets. These platelets have a cubic crystal structure, which makes the non-isotropic growth in only two dimensions counterintuitive. Several seemingly contradicting mechanisms for the formation have been suggested, e.g. oriented attachment [1], ligand-induced two-dimensional growth [2] and nucleation on crystal facets [3]. There is a consensus that the platelets only form in solution when a mixture of short and long chain carboxylates is present. SAXS measurements show that the NPLs form after the short chain cadmium carboxylate has melted (240°C). The in-situ absorption measurements reveal a large effect of the temperature when the short chain carboxylate is introduced in the reaction mixture (190-240°C). This triggered us to investigate the effect of addition temperature and the melting point of the short chain carboxylates in more detail. The SAXS and WAXS measurements provide information on the size, shape, crystals structure and melting of the carboxylate, whereas the absorption measurements made it easier to distinguish between a mixture of quantum dots and nanoplatelets.

forces, and particle motion. Here we use in situ transmission electron microscopy and atomic force microscopy to
directly observe and measure the particle motion and interfacial forces, respectively. Integrating theoretical
calculations and simulations, we revealed the orientation dependent attachments of particles, interfacial structures,
and the factors that affect them, such as temperature, pH, ionic strength, particle shapes, and solvents, etc. In
addition, we also demonstrated that strain relaxation at the grain boundaries, induced via oriented attachments,
forming twin structures. The specific systems that we investigate are metal (Ag and Au), oxides (TiO₂), and
minerals (mica), etc. The work provides a deep understanding of mechanisms of oriented attachments and factors
control the process and thus provide a guide to design and fabricate the morphologies and structures, which are
closely related with material properties and functions.

2:00 PM MT06.18.02
X-Ray Dynamical Diffraction in Powder Samples with Time-Dependent Particle Size Distributions Adriana
Valerio, Sergio L. Morelhao, Alex J. Cabral, Marcio M. Soares, and Claudio M. Remedios; 1Institute of
Physics, University of São Paulo, Brazil; 2Universidade Federal do Oeste do Pará, Brazil; 3Instituto de Ciências
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Advanced synchrotron sources of high flux and detector systems capable of collecting, in just a few seconds, full X-
diffraction (XRD) patterns of powder samples create opportunities for in situ studies of a variety of processes
such as catalysis, energy storage and conversion, and crystallization of nanoparticles from amorphous precursors.
There will be thousands of XRD patterns containing information on structural changes along the processes.
Particularly in the case of crystallization, information on crystal phase, lattice strain, and particle size distribution
(PSD) as a function of time and temperature, covering the whole process from amorphous to fully crystalline phases.

Besides position of the diffraction peaks that can provide information on thermal expansion coefficients from
nanoscale to large particles with bulk properties, width and area of the diffraction peaks allow a detailed
investigation of the growth kinetics, including nucleation and coarsening processes in the time-dependent PSDs.
Particle size from diffraction peak widths stand for just one value that can be produced by an infinity of PSDs. In
situ measures of integrated intensities during growth of crystalline particles provide a direct route to access
fluctuation in the population N(t) of particles as a function of time t. Nucleation (dN/dt>0) and coarsening (dN/dt<0)
processes can be evidenced from the experimental integrated intensities when compared to theoretical values for
PSDs with constant number of particles and with imposed constraints to the determined particle sizes from
diffraction peak widths.

Coarsening (grains growing in size) under constant volume of diffraction is possible at the cost of small grains that
dissolve providing material to larger grains in a process widely known as the Ostwald ripening phenomenon. Since
first described by Wilhelm Ostwald in 1896, the phenomenon has been observed in a number of general nanocrystal
growth systems where broad spectrum of particle sizes are present [1]. This process play a fundamental role in
determining the evolution in time of the particle population, and it is crucial for controlled synthesis of nanocrystals.

For PSDs with broader distributions, particle sizes from diffraction peak widths has complex behavior with the PSD
parameters such as mode (most probable value) and standard deviation, and where dynamical diffraction corrections
can be indispensa. For strong Bragg reflections, neglecting dynamical corrections in broad PSDs with many
particles of sizes above a few hundred nanometers leads to an aberration regarding the actual mode value. Without
accounting for dynamical effects to suppress the kinematical intensity contribution of large particles, the position
and width of the PSDs would have to be much smaller than they actual are to reproduce the experimental peak
widths. In this work we developed a systematic procedure to solve time-dependent PSDs based on in situ XRD
experiments. It is based on the kinematical approach of x-ray diffraction, with proper integrated reflectivity
corrections from dynamical diffraction calculation [2]. As practical demonstration we applied this analytical
procedure to the single-phase crystallization process of bismuth ferrite [3]. In situ XRD data collection where carried
out with synchrotron x-rays of 12keV, acquisition time of 38 s per XRD pattern, and enough flux to monitor
diffracting particles as small as 20 nm.

[1] Z. Zhang, Z. Wang, S. He, C. Wang, M. Jin, and Y. Yin,
2016).
In Operando Scanning Electron Microscopy of Growth, Etch and Alloying Kinetics of Nanomaterials

Ryo Mizuta1, Maik Simon2,3, Ye Fan1, Thomas Mikolajick2,3, Walter M. Weber2,3 and Stephan Hofmann1; 1University of Cambridge, United Kingdom; 2Namlab gGmbH, Germany; 3Center for Advancing Electronics Dresden, Germany

The potential of environmental scanning electron microscopy (ESEM) as a versatile, in-operando technique that can accommodate many length scales, substrate geometries and reactive environments has been highlighted in the context of recent in-situ studies of catalytic graphene and hexagonal boron nitride (h-BN) chemical vapour deposition [1-3]. We have set up a dedicated new ESEM system based on a modified adoption of the ZEISS NanoVP aperture technology to facilitate improved high-resolution imaging, combined with heating capabilities of up to 1000°C and a customised local gas injector system. We present here our latest results using this new in-operando capability to foster an understanding of crystal growth and phase transformations on the nano-scale specifically for 1D and 2D materials. We show in-operando ESEM of the Ni silicidation of top-down patterned Si nanochannels revealing unexpected time-dependent phenomena that contribute to inhomogeneous silicidation lengths. This silicidation process plays an important role in VLSI transistor fabrication as it allows the formation of highly conductive metal silicide contacts very close to the gate [4,5]. However, while bulk silicidation is well understood, the altered kinetics for small diameters, which are increasingly applied in highly scaled transistors, are not fully understood [6]. We introduce strategies how such silicidation on the nano-scale can be much better controlled, offering new insights for scaled contact formation. We also show an in-situ ESEM study of localised etching of 2D materials addressing key questions on the nucleation and etch kinetics specifically of graphene, h-BN and TMD materials such as WS2.

References

Dynamic Perturbation of the Electrical Double Layer with an Electrochemical AFM for Confined Metal Electrodeposition

Mark Aarts and Esther Alarcon-Llado; AMOLF, Netherlands

Understanding and directing electrochemical reactions below the micrometer is a long-standing challenge in electrochemistry. In this respect, electrodeposition using scanning probe microscopy provides an attractive platform, not only for additive nanoscale manufacturing, but also for the investigation of local dynamics such as mass transport and reaction kinetics.

We report on the direct writing of copper nanostructures using an oscillating nanoelectrode operated with an Atomic Force Microscope (AFM) in aqueous solutions. The nanoelectrode is used to locally initiate electrochemistry, while the AFM allows for in-situ probing of the deposited material. We demonstrate the writing of arbitrary structures beyond cluster size with lateral dimensions in the order of the tip radius. Strikingly, this local writing is only possible in highly dilute electrolytes (~ 1 µM CuSO4). Moreover, we find a profound effect of the dynamic operation of the nanoelectrode on the deposition kinetics.

We explain our results by considering the extended screening length and slow charge dynamics of the dilute electrolyte, which allows the nanoelectrode to operate inside, and disturb, the electrical double layer (EDL) at the solid-liquid interface. We visualize these (dis)charging dynamics and their effect on the reaction directly through the electrodeposited structures, and experimentally observe the Debye time of the electrolyte as a threshold value for growth. Furthermore, we show that this threshold time increases as a function of applied potential.

Our results lead us to propose a reaction mechanism based on cyclic charging and discharging of the EDL, which
facilitates local electrodeposition through direct electrostatic interaction between ions in the liquid and the nanoelectrode.

2:45 PM MT06.18.05
Environmental TEM Study of Size- and Shape-Selected Cobalt Nanoparticles on the External Surface of MFI Nanosheets Jennifer Carpena1, Donghun Kim2, Dmitri Zakharov3, Rahul Rao1, J. Anibal Boscoboinik4, Eric A. Stach1, Michael Tsapatsis5,6, Dario Stacchiola3 and Benji Maruyama6; 1Air Force Research Laboratory (UES Inc.), United States; 2University of Minnesota, United States; 3Brookhaven National Laboratory, United States; 4University of Pennsylvania, United States; 5Johns Hopkins University, United States; 6Air Force Research Laboratory, United States

One of the factors limiting catalytic activity of nanoparticles is the lack of control over formation and evolution processes (i.e. coalescence and coarsening) and over size and shape selectivity at high temperature. Here, we show that zeolite nanosheets of the MFI type (MFI-nanosheets or MFI-Ns), formally known as the Zeolite Socony Mobil–five (ZSM-5), can be used to keep cobalt catalyst nanoparticles docked to the support external-surface and to help retain their small size when exposed to high-temperature reducing conditions for a prolonged time. In situ environmental transmission electron microscopy (ETEM) shows that the MFI-Ns can influence not only the size of nanoparticles but also their shape via catalyst/support registry. ETEM image analysis revealed the preferential docking of nanoparticles to energetically favored configurations –namely to four or less pores consequently regulating the resulting population of nanoparticles. We ascribe the observed registry to catalyst/support interactions and to the periodic surface of the MFI-Ns with local minima, which helped stabilize nanoparticles and suppress evolution. This study elucidates how a nano-porous support surface may provide a path forward for controlling nanoparticle formation and evolution kinetics and for achieving size- and shape-selectivity at high temperature.

3:00 PM BREAK

3:30 PM MT06.18.06
Optical Detection of Self-Assembly Dynamics Below the Diffraction Limit Hans Robinson, Zhixing He, Chengshuai Li and Yizheng Zhu; Virginia Tech, United States

The resolution of optical microscopy is generally limited by diffraction to approximately half a wavelength, which prevents close monitoring of the motion of nanoparticles with optical techniques. Moreover, the intensity of light scattered from a single nanoparticle scales as the square of the particle volume, making it difficult to detect the scattered light from small particles with sufficient speed to characterize particle dynamics. Various superresolution techniques exist that overcome these difficulties, but these generally require careful fluorescent labeling or else are applicable only in rather limited circumstances, and are often too slow to be of use in following the dynamics of self-assembly.

We introduce an interferometric optical technique that overcomes many of these difficulties, and therefore will allow the detailed characterization of the dynamics of self-assembly at the nanoscale. This technique measures the optical anisotropy in the scattering from individual nanoparticles or small assemblies of nanoparticles, which makes it possible to determine the three-dimensional alignment between pairs of particles or of a single anisotropic particle with time resolution on the order of a few microseconds. We will present a theoretical development of this technique, as well as experimental demonstrations on monitoring the rotational motion of individual gold nanorods and the assembly of superparamagnetic nanoclusters.

Looking forward, the technique could be straightforwardly combined with existing single-particle tracking techniques, and since it is interferometric in nature, particles as small as a few nanometers could potentially be tracked, both in position (x,y,z) and orientation (θ,φ). In addition, each measurement results in an optical spectrum, which has the added advantage that for the assembly of metal nanoparticles, the plasmon nanoruler effect could be used to determine the separation between particles with high accuracy. Taken together, these capabilities have the potential to afford in situ monitoring of nanoscale self-assembly with unprecedented detail in a straightforward, non-invasive, and affordable setup.

3:45 PM MT06.18.07
Formation of (MoO3)n Clusters and Nanoparticles in the Gas Phase Measured with Time-of-Flight and
Since the 1930s, molybdenum oxide (MoO$_3$) is in the scope of knowledge to be a very selective catalyst for the conversion of methanol to formaldehyde by oxidation [1]. It also has promising gas sensing properties and the utilization of MoO$_3$ nanorods in gas sensors exhibits a highly selective response to NO$_2$ and NH$_3$ [2]. Catalysis as well as sensing requires high surface area materials and thus a controlled formation of materials on the nanoscale. Gas phase synthesis is an established technology to produce small particles in high purity without any template. We investigated the nucleation and growth of molybdenum oxide nanoparticles in flames using time-of-flight mass spectrometry (TOF-MS) and particle mass spectrometry in combination with molecular-beam sampling. This sampling technique instantaneously interrupts all reactive gas-phase processes and thus allows a spatially resolved measurement of gas and particle-phase. TOF-MS can be used to identify the composition as well as the transient formation and growth of intermediate species such as clusters from various locations in a reactor. MoO$_3$ nanoparticles are synthesized by the decomposition of molybdenum hexafluoride (MoF$_6$) in a premixed hydrogen/oxygen flame. Due to low pressure (20–30 mbar), an almost one-dimensional, spatially extended flat flame is formed enabling spatially-resolved measurements along the reactor axis. The progress from the initial decomposition of the gaseous precursor to the formation and growth of (MoO$_3$)$_n$ clusters and nanoparticles has been studied by varying the distance between the burner head and the sampling nozzle position. The measurements show a sequential cluster formation followed by a subsequent particle nucleation. The number concentrations of differently sized clusters strongly vary indicating “magic” cluster sizes. In contrast to previously studied WO$_3$ nanoparticle formation [3], (MoO$_3$)$_n$ clusters with excess of oxygen are observed. Moreover, (MoO$_3$)$_n$ cluster and nanoparticle formation is much more prone to the flame chemistry during synthesis, which can be used to tune the nanoparticle growth process.

References:

4:00 PM MT06.18.08
**In Situ Ultrafast Electron Scattering to Measure Massively Enhanced Nucleation and Growth Driven by Highly Non-Equilibrium Ultrafast Laser Assisted Diffusion** Alex Sarracino, Abdul R. Ansari, Ben Torralva and Steven M. Yalisove; University of Michigan–Ann Arbor, United States

In-situ pump probe electron scattering to study the nucleation and growth of thin films is still a technique in the early stages of development. Unlike in 4-D microscopy, where a single electron scattering event is observed $10^6$ times where reversible phenomena is interrogated, most material self-assembly at the nanoscale evolves and requires a single packet of $10^6$ electrons to probe. We will present a different approach to ultrafast pump probe electron scattering by using a laser-pumped electron gun in a reflection geometry to collect the specular beam rather than a diffracted beam which allows for lower electron loss in the material.

We have developed this technique to directly measure the ultrafast laser assisted diffusion of self-interstitials that are generated by irradiating GaAs with a 150 fs laser operating at 780nm using a fluence below the melt threshold but above the High Spatial Fluence Laser Induced Periodic Surface Structure (HSFL) formation threshold (0.04 J/cm$^2$). We have described the defect generation mechanism in the literature [1]. Self interstitials are generated via an ultrafast, athermal process in less than 600 fs after the laser pulse irradiation. Subsequent 1 kHz irradiation for one second causes the formation a self-assembled grating that eventually has a wavelength of 180 nm consisting of ~90 x 200 nm walls and ~90 x 200 nm trenches (measured with Transmission Electron Microscopy). Preliminary pump probe experiments show that the growth does not continue after the last pulse. The growth rate of the material above the original surface is at least 2000 Å/sec assuming the process takes the full millisecond between pulses. However, we have much evidence that the ultrafast laser assisted diffusion stops somewhere between 100 ps to 50 ns, hence the actual growth rate is between $10^6$ and $10^7$ Å per second.

We will present results from a nonadiabatic quantum molecular dynamics calculation where we have studied the enhancement in mass transport of a self-interstitial atom during and after irradiation. The model couples the vector potential of the laser field directly to the Hamiltonian and allows us to directly monitor the bonding and electron-ion
coupling. The method, which requires 40 attosecond time steps, has revealed additional athermal, ultrafast atomic transport mechanisms that are consistent with the extremely large growth rates we observe.

This talk will present our electron gun design and performance as well as results from our pump probe electron scattering study of the nucleation and growth of the first islands that appear after ~300 to 400 exposures. These islands are ~0.5 nm tall and ~20 nm wide and require a probe with a commensurate wavelength. Our electron pulses have a temporal width of ~2 ps after acceleration to 30KV. Results will be shown for multiple experiments where the electron beam will be delayed from 50 ps after the 400th exposure to 50 ns after the 400th exposure. By observing the reduction in the specular beam intensity we will be able to extract an arrival rate of our subsurface interstitials assisted by the optical field.

References:

4:15 PM MT06.18.09
In Situ Study of the Formation Mechanism of CdSe Nanocrystals Paul T. Prins1, Federico Montanarella1, Kim C. Dümbsen2, Johanna van der Bok1, Andrei V. Petukhov1, Celso de Mello Donega1, Daniel Vanmaekelbergh1, Freddy T. Rabouw1 and Zeger Hens2; 1Debye Institute for Nanomaterials Science, Netherlands; 2Physics and Chemistry of Nanostructures Group, Belgium

Colloidal quantum dots have recently entered the consumer market as phosphor material for television screens. Over the past 30 years of research, an enormous variety of synthesis procedures has been developed for quantum dots of different chemical compositions, sizes, and shapes. In most cases, the metal and anion precursors are mixed at temperatures of 200–350°C in the presence of coordinating ligands. The outcome of the synthesis is determined by the chemical nature and concentrations of the precursors, the reaction temperature, the presence of additives, and other parameters. While for most synthesis procedures we have a reasonable model of the underlying formation mechanisms, this model is usually supported only by indirect evidence. For example, intermediate stages in the reaction may be studied by taking aliquots from the reaction mixture and analysing them ex situ using electron microscopy. Alternatively, optical spectroscopy has allowed the study of quantum dot formation mechanisms in situ, but this method relies on reference measurements that relate properties to structure. Recently, X-ray scattering experiments have been explored as a promising route to obtain in situ data on quantum dot formation. However, X-rays penetrate poorly through the reaction mixture, so the experiments could only be performed using thin capillaries as reaction vessels, which severely hinder reactant mixing compared to conventional reaction flasks.

Here, we follow the formation of colloidal CdSe quantum dots using in situ X-ray scattering under reaction conditions comparable to typical synthesis procedures used in academic labs. To this end, we have developed a reaction-flask design that allows for proper reactant mixing while minimizing attenuation of the X-ray probe beam. We can thus track the size, size dispersion, and concentration of quantum dots during growth, without the use of calibration curves. Even for the intensively studied system of CdSe quantum dots, we show that the conventional model of separated nucleation and growth fails to provide an accurate description of the quantum dot formation. Instead, we find that the nucleation phase extends for minutes, continuing while existing quantum dots in the ensemble are growing. Although nucleation and growth are not separated, we nevertheless achieve a narrow size distribution of the final product. Based on a comparison to simulations, we propose that this seemingly counterintuitive finding is evidence for a radius-dependent quantum dot growth rate. This allows smaller quantum dots to grow faster than bigger ones, resulting in a narrow size distribution. The origin of a radius depended growth rate has most likely to do with the different faceting of larger quantum dots compared to smaller ones.

Our method has provided unexpected insights into a synthesis procedure that has been studied in depth for over 25 years. This highlights the importance of in situ measurements of nanocrystal growth under realistic reaction environments. With follow-up experiments, we will investigate the synthesis of other types of nanocrystals, including NaYF4 upconversion nanocrystals and CdSe nanoplatelets.

4:30 PM MT06.18.10
Real-Time Coherent X-Ray Scattering Studies of Ion Beam Nano-Patterning Peco Myint1, Mahsa Mokhtarzadeh2, Jeffrey Ulbrandt3, Suresh Narayanan3, Randall Headrick3 and Karl Ludwig1,1; 1Boston University, United States; 2Shahid Beheshti University, Iran (the Islamic Republic of); 3The University of Vermont, United...
States; 4Argonne National Laboratory, United States

Broad ion beam bombardment of solid targets leads to the spontaneous formation of nanoscale structures, such as ripples or ultrasmoothened surfaces, but complete fundamental understanding of the phenomenon is still elusive. In this work, the surface sensitive X-ray technique of Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) is used to study the kinetics and dynamics of nanoscale surface evolution. While non-coherent X-rays can measure the averaged kinetics on a surface, coherent X-rays make it possible to differentiate the dynamics of fluctuations around the average kinetics. Real-time studies of ion bombarded Si, Ge, and SiO₂ surfaces have been conducted. The target materials were kept either below or above their recrystallization temperatures. In the early stage of room temperature ion bombardment, the evolution of averaged kinetics is well fit with a linear theory formalism employing a viscous relaxation term. The X-ray Photon Correlation Spectroscopy (XPCS) two-time correlation function shows a novel behavior in the early stage, with memory stretching back to the beginning of the bombardment. During the late stage where the average surface structure on a given length-scale is no longer evolving, dynamical processes exhibit compressed exponential correlation behavior. Ion bombardment experiments above the target materials’ recrystallization temperatures are ongoing and their results will also be reported.

4:45 PM MT06.18.11
In Situ and Operando X-Ray Scattering Studies of the Processing and Performance of Novel Three-Dimensional Tricontinuous Bulk Conductor/Insulator/Conductor Nanocapacitor for Ultra-High-Power Electrical Energy Storage Samuel S. Welborn1, John Corsi1,2 and Eric Detsi1,2; 1University of Pennsylvania, United States; 2Vagelos Institute for Energy Science and Technology (VIEST), United States

Three-dimensional (3D) electrostatic capacitors have the potential to outperform their conventional two-dimensional (2D) counterparts. In this talk, I will present our work on the use of real-time X-ray scattering techniques to aid the development of a novel class of 3D tricontinuous bulk conductor/insulator/conductor nanocapacitors using nanoporous gold (NP-Au), a 3D bicontinuous network synthesized by selective alloy corrosion (dealloying), as the scaffold and primary building block. These X-ray scattering experiments are performed at the University of Pennsylvania’s Dual-Source and Environmental X-ray Scattering Facility, an instrument capable of simultaneously probing the Ultra Small-Angle X-ray Scattering (USAXS) and Wide-Angle X-ray Scattering (WAXS) regimes in various experimental environments. In the first part of this talk, I will present a fundamental study on the synthesis of 3D NP-Au, the scaffold of our 3D nanocapacitor. In particular, we use in situ USAXS/WAXS to probe the evolution of microstructure, morphology, and crystal structure during electrochemical dealloying (synthesis) performed under potential control in neutral electrolyte. Our studies have revealed that both zero-dimensional (0D) Au nanoparticles and 3D NP-Au form during the dealloying process, an important and previously unknown finding. In the second part of my talk, I will present our studies on post-synthesis thermal coarsening in combination with X-ray scattering (in situ USAXS) to tailor the ligament/pore size distribution in the 3D NP-Au scaffold, which is used as the first conductor in the bulk conductor/insulator/conductor nanocapacitor. In connecting these in situ USAXS/coarsening results with in situ transmission electron microscope (TEM) observations, we have found that the abovementioned 0D Au nanoparticles play an important role in the initial stages of the coarsening process. Following the post-synthesis thermal coarsening, the insulator (alumina, Al₂O₃) and second conductor (aluminum-doped zinc oxide, AZO) are grown on the pore walls of the starting 3D NP-Au scaffold using atomic layer deposition (ALD), resulting in a 3D tricontinuous bulk NP-Au/Al₂O₃/AZO nanocapacitor. In the third part of this talk, I will discuss our use of operando Grazing Incidence SAXS (GISAXS) methods to probe the microstructural and morphological changes of the tricontinuous bulk nanocomposite during ultra-fast charge/discharge operation.
High-resolution imaging of electron beam-sensitive crystalline materials is one of the most difficult applications of transmission electron microscopy (TEM). The challenges are manifold, including the acquisition of images with an extremely low beam dose, the time-constrained search for crystal zone axes, the precise alignment of successive images, and the accurate determination of the defocus value.

We reported that using a direct-detection electron-counting camera, it is possible to acquire useful high-resolution TEM images with electron dose as low as a few electrons per square angstrom to ensure that the intact structure was captured before damage occurred [1]. In this talk, we will present a suite of new methods that we recently developed to address the rest challenges mentioned above. Our methods advance the HRTEM of extremely beam-sensitive materials from “occasionally possible” to “routine”. We demonstrate the effectiveness of our methodology by capturing atomic-resolution (~ 1.5 Å) TEM images of several metal organic frameworks (MOFs) that are generally recognized as highly sensitive to electron beams. In the case of MOF UiO-66, individual metal atomic columns, various types of surface termination, and benzene rings in the organic linkers, are clearly identified. We also successfully apply our methods to other electron beam-sensitive materials, and achieve atomic-resolution TEM imaging of the organic-inorganic hybrid perovskite CH3NH3PbBr3 for the first time [2]. More recently, we applied this new technology to prove the successful encapsulation of single molecule magnets in MOF NU-1000 [3], and to investigate the evolution and transformation of various defects in MOF UiO-66 [4]. We also found a new TEM specimen preparation technique particularly useful for beam-sensitive materials.


9:30 AM MT06.19.02
Controlled Manipulation of Individual Molecules on Surfaces with Advanced Scanning Probe Microscopy Techniques Omur E. Dagdeviren1, Chao Zhou1, Milica Todorovic2, Eric Altman1 and Udo Schwarz1; 1Yale University, United States; 2Aalto University, Finland

With the continued development of scanning probe microscopy techniques, manipulation of single molecules has become possible. Thereby, the manipulation path can be chosen at will and energy barriers between potential minima on that pathway can be quantified, as can the energy landscape around the molecule before and after manipulation. To explore the practicality of this novel pathway to catalysis research, we selected benzene molecules on a Cu (100) surface as a model system. We first choose a specific manipulation path and then move the tip at constant but continuously reduced heights while recording the oscillation amplitude A and phase phi with the microscope operated in our recently developed tuned-oscillator (TO) detection scheme [1]. To preserve the accuracy of recovered tip-sample interaction potentials and forces, we use oscillation amplitudes significantly larger than the decay length of the tip-sample interaction potential [2,3]. Analyzing the full (x, z, A, phi) data array then allows recovery of the potential energy U(x, z) acting between the tip and the sample, the force on the tip normal to the surface vertical tip-sample force Fz(x, z), and the force Fl(x, z) that acts on the tip along the manipulation path (i.e., lateral) with meV, pN, and pm resolution. In 54 distinct manipulation events, the molecules were either pushed, pulled, jumped to the tip, or did not move depending on the chemical surroundings of the molecule and the chemical identity of the tip. For further insight, we compared the experimentally measured energy landscapes and manipulation outcomes with computational results obtained using a Bayesian Optimization Structure Search (BOSS) protocol [4], which also delivers that the diffusion barrier evolves with the chemical identity of the tip and the surrounding of the molecule. This machine learning technique developed at Aalto University delivers the minimum energy pathways and entire energy landscapes with minimal computational effort.

References:

9:45 AM BREAK

10:15 AM MT06.19.03
Carving Pt-Based Bimetallic Nanoparticles under Electrochemical and Thermal Conditions Shu Fen Tan, Ainsley Pinkowitz, Baoming Wang and Frances M. Ross; Massachusetts Institute of Technology, United States

Pt nanoparticles (NPs) have been widely used as electrocatalysts for oxygen reduction reactions (ORR) in fuel cells of interest in the automotive industry¹ and hydrogen evolution reaction (HER) in alkaline electrolyzers.² However, the high cost as well as the high d-band center of Pt hinder its application as a cost-effective fuel cell material. Instead, Pt is combined with other metals. The resulting Pt-based bimetallic NPs are potential candidates to overcome the issues associated with pure Pt without compromising the electrochemical performance. Since the underlying electrocatalytic reactions, such as adsorption and desorption of reactants, intermediates and products, take place on the surface of the electrocatalysts, the performance is determined by the surface composition of the bimetallic NPs.³ Tremendous effort has been made in synthesizing Pt-based bimetallic NPs with precisely controlled surface structure and chemistry. In particular, chemical and electrochemical processes have both been used to tune the surface composition of bimetallic NPs.⁴ Chemical processing is often difficult to control due to random site etching, but electrochemical processing is relatively versatile and it can be straightforward to etch the non-noble metal away. However, important questions regarding this electrochemical tuning remain unresolved, regarding the interplay of kinetic etching phenomena and external parameters such as the NP shape, initial composition, surfactants, temperature and etching potential.

Here, we use in situ liquid cell electron microscopy as a direct probe of the electrochemical etching of oleylamine-capped Pt-based bimetallic NPs in aqueous sulfuric acid electrolyte solution at elevated temperatures with high temporal and spatial resolution. We have modified liquid cell chips in order to perform simultaneous electrochemical biasing and heating. We synthesize Pt-based bimetallic NPs in the shape of rhombic dodecahedra with well-defined facets.⁵ The particles contain a Pt skeleton covered by the non-noble metal, for example Ni, as well as a surface layer of Pt surrounding the entire NP. Our real-time observations reveal that the etching kinetics of these Pt-based bimetallic NPs upon application of a bias is dependent on the reaction temperature. Furthermore, the applied bias required to etch the NPs is also dependent on the reaction temperature. We will discuss the etching mechanism, taking account of the effects of the electron beam on the observations. Understanding the electrochemical behavior of these Pt-based bimetallic NPs at elevated temperatures potentially lays the foundation for rational design of desired structures for application as electrocatalysts.

References

10:30 AM MT06.19.04
Reversible Gas–Solid Reaction on Palladium Surface under an Electric Field Takehiro Tamaoka¹², Ryotaro Aso¹, Hideto Yoshida¹ and Seiji Takeda¹; ¹Osaka University, Japan; ²Kyushu University, Japan

Gas-solid reaction plays an important role in catalysis, gas sensing and gas storage. Therefore, reaction process on metal surface with gas has been extensively studied at the atomic scale. However, the reaction process on metal surface with gas under electric field remains poorly understood. In our study, we investigated the reaction process on metal surface under electric field by means of atomic-resolution in situ environmental transmission electron microscopy (ETEM), and found that an unexpected metal (Pd)-gas (N₂) compound was formed on the metal surface under an electric field.⁶

We studied Pd surface by using a pair of Pd electrode tips with nanometer separation. The reaction process on Pd surface in gases, such as O₂ and H₂, is well understood. Here, we performed systematic study on Pd surface in four typical environments (vacuum, O₂ (100 Pa), H₂ (100 Pa) and N₂ (100 Pa)) with and without an electric field. First, we studied Pd surface without an electric field.⁶ We found that the surface oxidation of Pd surface in O₂ has a
dependence of previous exposure to H₂: after prolonged exposure to H₂, the oxidation of Pd surface is suppressed. Based on the ETEM observation and electron energy loss spectroscopy (EELS) measurement, we concluded that subsurface adsorption of H atoms suppresses the oxidation of Pd surface. Then, we studied Pd surface pretreated in H₂ under an electric field. In vacuum, a tunneling current flowed across the nanogap between electrically biased Pd electrode tips. In O₂ and H₂, Pd atoms on the positive electrode tip were evaporated and then deposited to the negative electrode tip without any changes in the crystal structure.[1] In N₂, we found that a peculiar compound was formed on the positive electrode tip.[1] A PdN compound, which is predicted and confirmed only at extremely high pressure and temperature, was formed at low pressure and room temperature under an electric field. The gas-solid reaction was reversible with the change of the magnitude of an electric field. It is most likely that electrons passing through the nanogap induce the gas-solid phase transition. We will show the in situ movie of the dynamic phenomena including the gas-solid phase transition. In addition, we will show the result of ETEM observation of Pt surface. These findings obtained only by means of in situ ETEM observation have opened new route toward synthesizing nanomaterials.

References

10:45 AM MT06.19.05
Cross-Correlative X-Ray/TEM Liquid Cell Microscopy for Energy Applications Khim Karki¹, Joonsuk Park², Allen Y. Liang³, Tyler Mefford², Daan Hein Alsem¹, Eric A. Stach³, William C. Chueh² and Norman J. Salmon¹; ¹Hummingbird Scientific, United States; ²Stanford University, United States; ³University of Pennsylvania, United States

Cross-correlative techniques using transmission electron microscopy (TEM) and synchrotron transmission X-ray microscopy (STXM) are becoming more common and are used to study a wide range of electrochemical reaction-systems at the nanoscale. This approach has already started to produce new insights on the dynamics and structural changes during processes as lithium ion insertion/extraction, dendrite formation, metal nucleation, and metal corrosion. Despite the power of this approach, the challenges associated with replicating bulk-scale electrochemistry data in the environmental cell microscopy platform are well-known. First, the hardware components are not best optimized to perform in the reduced scale environment. Second, the chips configurations such as sizes and aspect ratios of different electrodes suitable for various electroanalytical measurements are poorly designed. Here, we use operando liquid cell TEM/STXM microscopy platform, validating cross-correlative electroanalytical bulk-scale measurements with model systems, to study the oxygen evolution reaction (OER) in the electrodeposited thin films of Ni(OH)₂/Co(OH)₂ for charge storage applications such as batteries and supercapacitors.

The studies presented here are performed using electrochemical cells, which consist of two microfabricated chips sandwiched with electron transparent SiNx membranes for viewing in TEM/STXM. Using a new developed hardware system with a specialized configuration of working, counter and reference electrode, we performed cyclic voltammetry studies in 0.1M CuSO₄ and 20 mM K₃Fe(CN)₆/20 mM K₄Fe(CN)₉ in 0.1M KCl solutions to validate the bulk-scale correlation between TEM and STXM. Next, we study nucleation mechanism during the electrodeposition of Ni(OH)₂/Co(OH)₂ film growth on the substrate electrode using TEM/STXM. We compare oxygen evolution on 50 μg cm⁻² geom Co(OH)₂ on glassy carbon in a macroscopic rotating disk electrode (RDE) cell at a rotation rate of ω = 1600 rpm and a scan rate of ν = 10 mV s⁻¹ and in the operando STXM cell with Co(OH)₂ on Pt at defined voltage scan rate and electrolyte flow rate. The current-potential relationship in the operando STXM cell shows similar Tafel slopes at the same potentials to the RDE tests validating the high electrochemical fidelity of the operando STXM cell. The liquid-electrochemistry hardware developed for this work can be used to study range of materials using cross-correlative imaging in TEM/SEM and X-ray microscopes.

11:00 AM MT06.19.06
Anisotropic Oxidation of Suspended Graphene—Etch Dynamics and Stability Beyond 1000 °C Joachim D. Thomsen¹,⁵, Jens Kling², Timothy J. Booth¹, David M. Mackenzie¹ and Peter Bøggild⁴; ¹Massachusetts Institute of Technology, United States; ²Technical University of Denmark, Denmark; ³Aalto University, Finland

We study the oxidation of clean suspended mono- and few-layer graphene in real-time by in situ environmental transmission electron microscopy [1]. In order to study the oxidative etching of suspended graphene, we have
developed a cleaning scheme that results in the near complete removal of hydrocarbon residues over the entire visible sample area (~50 µm²) [1, 2]. This etching process allows the top-down fabrication of graphene nanoribbons with lower edge roughness than can be achieved by electron beam lithography.

At pressures below 0.1 mbar we observe anisotropic oxidation and the formation of hexagonal holes with armchair-oriented edges, with an edge roughness below 1 nm. We see increasingly isotropic oxidation at higher pressures, eventually leading to irregular holes at a pressure of 6 mbar. We find that the growth rate of the initial defect is more stable than that of an extended hole. We show that this is due to re-arrangement of the edge atoms, leading to a stable defect which over time is broken by consecutive discrete and stochastic atomic removal events.

Finally, we find that few-layer suspended flakes are stable against oxidation at temperatures up to at least 1000 °C in the absence of impurities and electron beam-induced defects. These findings show (i) that the oxidation behavior of mono- and few-layer graphene depends critically on the intrinsic roughness, cleanliness and any imposed roughness or additional reactivity from a supporting substrate and (ii) that the activation energy for oxidation of pristine suspended few-layer graphene is up to 43% higher than previously reported for graphite. These results have implications for applications of graphene where edge roughness can critically affect the performance of devices, and more generally highlights the surprising (meta)stability of the basal plane of suspended bilayer and thicker graphene towards oxidative environments at high temperature.


11:15 AM MT06.19.07
Active and Stable Low-Platinum Catalysts—From In Situ Understanding to Rational Design Jianbo Wu and Yanling Ma; Shanghai Jiao Tong University, China

The core-shell catalysts with atomic layered surface Pt through liquid phase atomic layer deposition has been proven to be one of the most promising oxygen reduction (ORR) electrocatalysts with high activity and low consume of Pt.1-5 It is important to directly observe how the atomic layers grow via in situ technique. On the other hand, corrosion is a major and unavoidable challenge for the degradation of properties of multimetallic core-shell electrocatalysts during electrocatalysis, which restricts the practical application of this type electrocatalysts severely.6-7 Therefore, it has been an urgent issue to understand the evolution and mechanism of corrosion of Pt-based core-shell catalysts during the reaction with an aim to the effective utilization of the catalysts.8

In this presentation, we will first report a 3D growth mechanism for the formation of core−shell nanostructures involving a hybrid process with initial island growth and surface diffusion. The desired surface structure can be achieved by adjusting the competition between island deposition and surface diffusion.9 Then, we will show the corrosion behavior of Pd@Pt core-shell electrocatalysts in the etching solution, which depends on the effects of geometry and surface defect.10-11 Finally, we can demonstrate the capability of electrochemistry inside of TEM, showing both the oxidative etching and the re-deposition behaviors during the cyclic voltammetry in TEM.

References:

**11:30 AM MT06.19.08**

*In Situ* Imaging and Characterization of the Electrochemical Nucleation and Growth of Sulfur and Bromine Microdroplets inside Liquid Electrolytes Nian Liu and Po-Wei Huang; Georgia Institute of Technology, United States

Since the first discovery of supercooling in 1724, the study of supercooled matter has been mainly limited to varying temperature or pressure. Early this year we have demonstrated an electrochemical approach to generate supercooled sulfur and observe the dynamic process in situ (see Publication 1 below). Our methodology combines dark-field optical microscopy, a transparent electrochemical cell, and a fast camera to visualize the process at single microdroplet with millisecond time resolution. This platform may open up opportunities for studying supercooled liquids as the droplets approach either homogeneous nucleation to the crystalline state or enter into the glass transition. Relevant to understanding lithium-sulfur battery chemistry, liquid sulfur is observed to form in the electrochemical cell and elucidates a long-debated reaction pathway for sulfur redox reaction in this environment. In a follow-up work (see Publication 2 below), we applied the above methodology to image in situ the electrochemical formation of polybromide droplets, which is used in zinc-bromine flow batteries, a promising technology for stationary energy storage. Using our unique platform, we reveal the liquid nature, chemical composition, and strong interaction with the electrode, which cannot be done using conventional analysis tools. The results provide insights into the role of complexing agents and guide the future design of zinc-bromine flow batteries.

This presentation is based on the following two recent publications from my lab:
   [https://doi.org/10.1073/pnas.1817286116](https://doi.org/10.1073/pnas.1817286116)
   [https://doi.org/10.1002/ange.201906980](https://doi.org/10.1002/ange.201906980)

**11:45 AM MT06.19.09**

*In Situ* Multimodal Characterization of Lithium/Sodium-Ion Batteries by Using Electrochemical Liquid Cell Zhiyuan Zeng; City University of Hong Kong, Hong Kong

Lithium/Sodium ion batteries have high energy density and are extremely light and inexpensive to produce, thus the success of Li/Na ion batteries may help to achieve a major leap in green energy storage technology. Advancing our understanding necessitates the development of experimental tools capable of operando characterization that can discern mechanisms of operation and degradation in the native operating environment. The most illuminating and useful characterization methods are those capable of providing detailed mechanistic information of charge/discharge dynamics of individual grains and particles. TEM investigations specialize in revealing structural and compositional information with nanoscale spatial resolution and subsecond temporal resolution. By utilizing our newly designed electrochemical liquid cells, we devoted our effort to the in situ and operando multimodal study of the dynamic Electrode-Electrolyte Interface reactions.

For lithium ion batteries, we captured dynamic electrochemical lithiation and delithiation of Au anodes in a commercial LiPF<sub>6</sub>/EC/DEC electrolyte using transmission electron microscopy (TEM). The inhomogeneous lithiation, lithium metal dendritic growth, electrolyte decomposition, and solid-electrolyte interface (SEI) formation were observed in situ. In addition, the dynamic lithiation/delithiation of MoS<sub>2</sub> nanosheets in a LiPF<sub>6</sub>/EC/DEC commercial electrolyte were also observed. Upon discharge in a voltage range of 1.8-1.2 V, MoS<sub>2</sub> on the Ti electrode underwent irreversible decomposition resulting in fragmentation of the MoS<sub>2</sub> nanosheets into 5-10 nm MoS<sub>2</sub> nanoparticles. For sodium ion batteries, we report an in situ study of Na deposition with the development of electrochemical liquid cells, in which the electrodes within a cell are patterned in different configurations to produce a flat or sharp curvature. The Na deposition shows granular growth. Variations in the SEI thickness on a Na nano-grain introduce differences in the local growth rate and disparities in the morphology. The newly formed Na grains preferentially deposit at the base of existing grains close to the electrode.
* Invited Paper

SESSION MT07.01: Characterization of Dynamic Processes by Electron Microscopy
Session Chairs: Ursel Bangert and Michele Conroy
Wednesday Morning, December 4, 2019
Hynes, Level 2, Room 205

9:00 AM *MT07.01.01

Visualising Dynamic Nanomagnetism and Magnetostructural Transitions Using Lorentz Microscopy

Trevor Almeida¹, Adrian Muxworthy², Damien McGrouther¹, Rafal E. Dunin-Borkowski³, András Kovács³, Jamie Massey⁴, Christopher Marrows⁴ and Stephen McVitie¹; ¹University of Glasgow, United Kingdom; ²Imperial College London, United Kingdom; ³Research Centre Juelich, Germany; ⁴University of Leeds, United Kingdom

In order to better understand magnetic behaviour in naturally occurring or synthetic samples, it is often necessary to investigate the underlying processes on the nano-scale. Transmission electron microscopy (TEM) allows atomic spatial resolution imaging and combining in situ TEM experiments with techniques like off-axis electron holography or differential phase contrast (DPC) imaging allows for imaging of magnetisation in nanostructures whilst under the influence of external stimuli; e.g. gas atmospheres, biasing, temperature, etc. In this context, several examples of the use of in situ TEM and magnetic imaging will be presented.

Fe₃O₄ is the most magnetic naturally occurring mineral on Earth, carrying the dominant magnetic signature in rocks and providing a critical tool in palaeomagnetism. The oxidation of Fe₃O₄ to maghemite (γ-Fe₂O₃) influences the preservation of remanence of the Earth's magnetic field by Fe₃O₄. Further, the thermomagnetic behaviour of Fe₃O₄ grains directly affects the reliability of the magnetic signal recorded by rocks. Through combining electron holography with environmental TEM, in situ heating and liquid cell TEM, the effects of oxidation [1] and temperature [2] on the magnetic behaviour of Fe₃O₄ NPs are visualised successfully, as well as the magnetism within hydrated magnetotactic bacteria [3].

Equiatomic iron-rhodium (FeRh) has attracted much interest due to its magnetostructural transition from its antiferromagnetic (AF) to ferromagnetic (FM) phase and is considered desirable for potential application in a new generation of novel nanomagnetic or spintronic devices. Several scanning TEM techniques are performed to visualise the localised chemical, structural and magnetic properties of a series of FeRh films. The quantitative evolution of the growth and co-existence of AF and FM phases in the FeRh films are observed directly during in situ heating using DPC imaging [4]. In addition, combining DPC imaging with both heating and the application of electrical current pulses in situ within the TEM provides direct visualisation of the current-driven motion of magnetic DWs within planar FeRh thin films.
The main concerns during the polarization switching in nanosize ferroelectrics are the space charges on the oxide-electrode interfaces, trapping of the charged defects and strong domain wall pinning which readily increase the required switching field. To better understand and solve these problems, dynamic experiments are needed. In situ (heating and biasing) transmission electron microscopy (TEM) offers imaging and analytical tools at the relevant length-scales.

Thin lamellae samples with optimized geometry, prepared from a single crystal BTO (100), exhibit unusually stable and ordered 180° domain walls at room temperature [1]. Heating up to ~50 °C induces highly ordered 90° walls. Further heating above the Currie temperature (Tc) and then cool-down reintroduces the 180° domain structure. The transition from 180° to the 90° domain structure could originate due to the thermal strain release as the sample is heated. The appearance of the 180° domain-state is independent of the cooling rate below the Tc.

Further to the heating studies, we applied cyclic triangle wave-shape potential with a slope of 0.035 V/s. Due to the complex geometry of the sample, the electric field at the centre of the lamella was estimated by finite element calculations. The results show a homogeneous electric field distribution within the electron transparent region of ~3.1 kV/cm per 1 V applied to the electrodes. The operando response of weakly charged domain walls on the applied electric field revealed a tail to tail configuration [2]. Theoretically, in a bulk sample this tail-to-tail configuration is hindered by the polarizing surface effect, which leads the preferable direction of the polarization to point perpendicularly to the normal of the electrode [3]. In a thin lamella sample polarization direction pointing out of the lamella surface is electrostatically highly unfavourable, which could explain the appearance of the weakly charged domain walls.

By following the dynamics of the domain walls with respect to the applied voltage, clear hysteretic and non-linear behaviour is revealed. By recording the domain growth/shrinkage and nucleation, “P-E hysteresis-like” loops can be produced by appropriate image analysis. Additionally, application of cyclic voltage with various amplitudes reveals quadratic response of the domain growth with respect to the applied maximal voltage. This direct measurement complies with Rayleigh’s law P(E)~αE² [4] and shows its fulfilment even at the local scale.


9:45 AM MT07.01.03
**In Situ** TEM Observation of Reversible Structural and Resistive Phase Transitions in Magnetic Perovskite Films Driven by Voltage Pulses and Strain
Lide Yao, Sampo Inkinen and Sebastiaan van Dijken; Aalto University, Finland

Oxygen defects can have a profound effect on the physical properties of transition metal oxides. In complex oxides where magnetic, ferroelectric and superconducting phases emerge from strong correlations between localized transition metal electrons, oxygen vacancies can radically alter a plurality of quantum phenomena via valence changes and structural phase transitions [1]. The ability to control the concentration and profile of oxygen vacancies in oxide nanostructures would thus open up comprehensive prospects for new functional ionic devices. Here, we use in situ transmission electron microscopy (TEM) to demonstrate reversible switching between uniform structural phases in epitaxial La2/3Sr1/3MnO3 films. In our experiments, we employ a piezo-controlled probing holder to apply short voltage pulses and local strain. Simultaneous high-resolution imaging and resistance probing under zero strain reveals reproducible voltage-induced transformations between a low-resistance perovskite phase, a high-resistance La2/3Sr1/3MnO2.5 brownmillerite structure, and an intermediate-resistance perovskite-like phase [2]. Reversible horizontal migration of oxygen vacancies within the manganite film, driven by combined effects of Joule heating
and bias voltage, predominantly triggers the structural and resistive phase transitions. Concurrent application of perpendicular strain and voltage pulses produces an entirely new structural phase whereby oxygen vacancies order in regular 3D rather than 2D patterns.


10:00 AM BREAK

10:30 AM *MT07.01.04

In Situ High-Resolution EELS for Probing Insulator-to-Metal Transitions in Correlated Oxide Nanostructures

Laura Bocher1,2, Xiaoyan Li1,2, Ibrahim E. K. Koita1,2, Marcel Tencé1,2, Jean Denis Blazit1,2, Luiz H. G. Tizei1,2, Mathieu Kociak1,2, Alexandre Gloter1,2 and Odile Stéphan1,2; 1Laboratoire de Physique des Solides - CNRS, France; 2Université Paris-Sud, France

Transition metal oxides (TMOs) undergo a plethora of phase transitions in response to external perturbations (temperature (T), pressure...), and vice versa outstanding physical phenomena in TMOs can be fine-tuned under controlled external stimuli (T, electrical or magnetic fields, light...). For instance, two types of insulator-to-metal transitions (IMTs) can be activated in Mott insulators or correlated systems such as (V1-xCrx)2O3 in response to external perturbations such as pressure, electronic doping or temperature [1]. V2O3 presents a T-driven IMT from an antiferromagnetic insulator (AFI) to a paramagnetic metallic (PM) state at around 160 K associated with a symmetry change. A different paramagnetic Mott insulating (PI) state can be usually destabilized by pressure or chemical doping into a correlated metallic state via the isostructural Mott transition. An out of equilibrium Mott transition can even be electrically activated in Cr-doped systems at 300K by applying short electric field pulses to induce a non-volatile ultrafast resistive switching creating conductive filaments nanodomains in the insulating matrix [2]. This electrically activated RS has revealed its potential for non-volatile memories used in high-performance resistive random-access memories. So far, the insulating/metals (I/M) domain coexistence and the electronic phase separation in such oxides have only been investigated in situ by ARPES, nano-IR and STM/STS but with 10nm spatial resolution at best and not in cross-section so as to reveal buried interfaces. Moreover, additional properties can emerge solely in nanostructured TMOs where strain engineering and interfacial mechanisms play a key role. However the local mechanisms governing I/M domain formation, percolation, and dissolution may arise at boundaries as thin as an atomic column and be due to local structural defects, chemical clustering or interfacial mechanisms – all atomic scale phenomena.

Very recently, advanced monochromated electron spectromicroscopes (UHR-STEM/EELS) emerged as real game-changers for nanomaterials characterization where the improved EELS resolution, i.e. 5meV, extending a larger range of relevant electronic excitations (from IR to soft X-ray) available at the nanometer scale and below. Combining such remarkable instrumental capabilities with in situ (tunable temperature and electrical biasing) options open an entirely new avenue of experiments for monitoring TMO’s phase transitions, and provide an unique in situ characterization tool capable of mapping the I/M nanodomains at sub-nm scale. Hence the requirement to monitor the IMT switching effect by probing and mapping in situ their electronic, atomic and chemical structures at the finest scale under thermal and/or electrical stimuli to gain a full understanding of these nanostructures’ functionalities.

Here we will first present recent variable-T UHR-STEM/EELS experiments performed on a Cs-corrector monochromated NION microscope, CHROMATEM, equipped with a HennyZ stage holder providing tuneable temperature (from liquid nitrogen to 1000°C) and biasing capabilities. New insights into nanostructured V2O3 and Cr-doped systems are unveiled by probing their PM and AFI spectroscopic features upon low-T thermal cycling through both low-loss and core-loss signatures (interband plasmon excitation and V-L2,3 and O-K fine-structures) [3]. Mapping such electronic excitations down to the nm-scale could highlight nanoscale electronic phase separation mechanisms further correlated with their structural and chemical properties down to the atomic scale. Finally, first perspectives on the electrically activated IMT in Mott insulator will be introduced.

References:
[4] The authors acknowledge funding from the National Agency for Research under the program of future
In Situ TEM Electrical Biasing of LAO/STO Interface-Devices Revealing Charge Modulation and Associated Structural and Chemical Changes

Jinsol Seo1, Bumsu Park1, Christoph T. Koch2, Hyungwoo Lee3,4, Chang-Beom Eom4 and Sang Ho Oh1; 1Sungkyunkwan University, Korea (the Republic of); 2Humboldt-Universität zu Berlin, Germany; 3Korea Advanced Institute of Science and Technology, Korea (the Republic of); 4University of Wisconsin–Madison, United States

The recent discovery of a two-dimensional electron gas (2DEG) at the interface between insulating perovskite oxides SrTiO3 (STO) and LaAlO3 (LAO) was made possible by advances in atomic layer-controlled growth. It has been demonstrated that the 2DEG is localized within a few nm of the interface and that the carrier concentration can be altered with an electric field and/or lattice strain which allows possibility of device structures such as field effect transistor, diode and nonvolatile memory devices. Eventually, seeing such changes during the operation of devices helps us to improve our understanding and also provides a technical breakthrough for further optimization of devices.

In this study, in-situ inline electron holography biasing experiments have been carried out on the epitaxially grown LAO (10 u.c.)/STO (15 u.c.)/LAO (3 u.c.) devices to observe charge density modulation by electrostatic gating. TEM samples for in-situ biasing experiment were prepared by using focused ion beam (FIB). A thin TEM lamella prepared by FIB was attached to a MEMS biasing chip (DENSsolutionsTM) by depositing Pt to ensure electrical contact of the thin film electrodes of TEM sample to the MEMS chip. The top and bottom electrodes were electrically isolated by milling trenches. While negative/positive DC biases are applied to the SrRuO3 top electrode, inline electron holography was carried to visualize the modulation of local charge density, and STEM imaging and EELS line profile were also carried out at the same position to investigate the associated ionic displacement and change of the valence state of Ti ions using an aberration-corrected STEM operated at 300 kV (GRAND ARM 300 CF).

The in-situ TEM I-V curves of the device showed very low current level of only a few nA, indicating the leakage current through the sample surfaces has been suppressed sufficiently. The charge density maps obtained by inline electron holography clearly showed strong peaks at the interfaces of LAO/STO, which arises from both mean inner potential difference between the two materials and the interfacial space charges such as 2DEG. Therefore, to visualize the modulation of 2DEG induced by the applied bias, the charge density profiles were calibrated by subtracting that of 0 V to remove the contribution from the mean inner potential variation across the interfaces. The zero-bias calibrated charge density profiles obtained at each voltage showed an increase and decrease of 2DEG in response to negative and positive voltage, respectively. In addition to the charge density modulation, the change of valence state of Ti ion assessed by in-situ EELS and the related lattice strain by quantitative image processing of STEM images will be discussed in greater detail.

Direct Assessment of Surface Polarization of BaTiO3 (001) by In Situ Negative Cs HRTEM Imaging

Jeehun Jeong1, Zhen Wang1, Bumsu Park1, Jong Chan Kim2, Hu Young Jeong2 and Sang Ho Oh1; 1Sungkyunkwan University, Korea (the Republic of); 2Ulsan National Institute of Science and Technology, Korea (the Republic of)

BaTiO3 is one of the most promising candidate oxides for various devices due to ferroelectric polarization and/or resistive switching capability. For large data storage applications, the polarization of low dimensional material forms, especially the surface polarization, needs be characterized precisely to control its device characteristics. Recently, more attention has been paid to the (001) surface of tetragonal phase of BaTiO3 with perpendicular polarization to understand the evolution of surface deadlayer due to depolarization effects and the associated near-surface domain structure. Previously, STEM-HAADF and STEM-ABF have been used for unit-cell by unit-cell polarization mapping but for TEM study of the intrinsic surface properties a clean surface without contamination or protection should be prepared, which poses technical challenges for implementation.

Here, by means of in-situ high resolution transmission electron microscopy we observed the surface polarization of BaTiO3 (001) single crystal on the unit cell scale from 1000 °C to room temperature using a Cs-corrected TEM (Grand ARM300F). TEM samples were prepared from a (001) BaTiO3 single crystal along the [100] cross-sectional zone axis by using FIB and attached to a DENSsolutions MEMS heating chip. By using negative spherical aberration imaging (NCSI) technique, all atoms (including oxygen columns) were observed clearly with minimal contrast delocalization, so that complete and quantitative polarization maps were obtained for the BaTiO3 (001)
surface of cubic and tetragonal phases. From HRTEM surface profile imaging with minimal contrast delocalization, we found that the surface is stabilized by the BaO termination in most temperature ranges we studied. Interestingly, the surface BaO layer showed a rumpling with 4-5 unit cells period. At the peak of rumpling, the HRTEM image showed that the barium (Ba) atoms move upward from the surface plane and nearby oxygen columns are preferentially populated by oxygen vacancies. We also found that there are Ti ions in the surface BaO layer, particularly occupying the oxygen-oxygen bridge sites (i.e. corresponding to the octahedral interstitial sites in bulk BaTiO₃). The polarization maps showed that at the peak of surface rumple the polarization mostly points toward bulk region (P_{down}) and the in-plane polarization (P_{in}) dominates the neighboring unit cells with oxygen vacancies. This finding reveals that oxygen vacancies play a key role in the evolution of surface polarization. Although the surface structure and polarization observed after high temperature annealing in TEM and by using electron beam may deviate from the genuine surface properties of BaTiO₃, the observed periodic array of oxygen vacancies along in-plane direction is closely related to stabilizing mechanism of the polarization at surface. We will further show the real-time imaging of the dynamic processes of surface reconstruction occurring at various temperatures, which can be used to study how surface polarization and point defects intricately interplay with each other to result in distinct surface reconstruction, ferroelectric domain structure and ferroelectric size effects.

11:30 AM MT07.01.07
Atomic and Electronic Structures of a SrMoO₃-Based All-Oxide Epitaxial Ferroelectric Varactor Tunable at Low Voltages Leopoldo Molina-Luna, Alexander Zintler, Oscar Recalde, Patrick Salg, Phillip Komissinskiy and Lambert Alff; TU Darmstadt, Germany

In the field of oxide electronics, there has been tremendous progress in recent years in atomic engineering of functional oxide thin films with controlled interfaces at the unit cell level. The functionality of such perovskite oxides depends mostly on the electronic configuration of the B-site cations. Relevant devices such as tunable ferroelectric microwave capacitors (varactors) are based on dielectric BaₓSr_{1-x}TiO₃ and are stymied by the absence of suited compatible, very low resistive oxide electrode materials on the micrometer scale. This has been overcome by implementing highly conducting SrMoO₃ (SMO) thin-film electrodes as enabling material for all-oxide ferroelectric varactors [1]. By using scanning transmission electron microscopy (STEM) in combination with electron energy-loss spectroscopy (EELS) we were able to reveal the atomic and electronic structure in an all oxide ferroelectric epitaxial varactor heterostructure with a SMO thin-film bottom electrode. The remarkable result is that in spite of the contradicting thermodynamic oxidation conditions, the dielectric BaₓSr_{1-x}TiO₃ and the highly conducting SrMoO₃ can be effectively coupled under preservation of their physical properties in an epitaxial heterostructure with negligible cation intermixing and valence change. The resulting interface is atomically sharp down to the unit cell scale. Surprisingly, a few unit cells of SrTiO₃ are sufficient to engineer the interface, allowing the utilization of the Pt-like conducting SrMoO₃ in oxide electronics applications. Furthermore, we are currently exploring the use of microelectromechanical systems (MEMS) based in situ biasing chips to enable controlled ionic displacement studies directly inside a transmission electron microscope. We aim to link the atomic structure to the physical properties under working or so called operando conditions in electrically contacted electron transparent lamellae of the metal-insulator-metal (MIM) ferroelectric varactor structure by directly tuning the dielectric layer.

Reference:

11:45 AM MT07.01.08
Resolving Electric Field Induced Structural Transformations in the Time Domain Using MeV Electron Diffraction Aditya Sood¹,², Xiaozhe Shen², Suhas Kumar³, Suji Park², Marc Zajac¹, Yifei Sun⁴, Shriram Ramanathan⁴, William C. Chueh¹, Xijie Wang² and Aaron Lindenberg¹; ¹Stanford University, United States; ²SLAC National Accelerator Laboratory, United States; ³Hewlett-Packard Labs, United States; ⁴Purdue University, United States

Understanding the short timescale dynamic response of materials to electric fields is essential for the development of next generation electronic & photonic devices. Specifically, in ferroelectrics, a transient measurement of lattice response to E-field encodes key information about the nucleation and growth of domains, domain wall motion, and coupling to strain. Despite its scientific and technological importance, most previous work has focused on the separate characterization of electrical transport and structure. Here, we report the development of a time-resolved technique for the simultaneous measurement of electronic
transport and atomistic structure in response to an applied E-field. This is based on in situ diffraction using ~100 fs electron pulses with energies of ~3 MeV. Our setup has demonstrated a momentum transfer range of 9 Å\(^{-1}\), q-resolution of <0.17 Å\(^{-1}\) and a temporal resolution limited only by the rise time of the E-field pulse across the device. Devices are electrically excited using short voltage pulses while structural dynamics are probed in a stroboscopic manner as a function of delay time after the pulse is turned on. As a demonstration, we use this technique to investigate the dynamics of the electrically-induced insulator-metal phase transition in VO\(_2\). Through a simultaneous measurement of structure and electrical transport, we correlate the nucleation and growth of rutile domains with metallization of the channel. These experiments provide new insights into the fundamental processes governing the switching speed of VO\(_2\) devices, and elucidate the role played by nucleation, growth and percolation of phases.

SESSION MT07.02: Imaging, Probing and Control of Domains and Domain Walls
Session Chairs: Alexei Gruverman and Dennis Meier
Wednesday Afternoon, December 4, 2019
Hynes, Level 2, Room 205

1:30 PM MT07.02.01
Anomalous Domain Wall Motion in Copper-Chlorine Boracite—A New Opportunity in Negative Capacitance? Charlotte Cochard\(^1\), Joseph G. Guy\(^1\), Roger Whatmore\(^2\), Michele A. Conroy\(^3\), Kalani Moore\(^3\), Alan Harvey\(^3\), Ursel Bangert\(^3\), Amit Kumar\(^1\), Raymond G. McQuaid\(^1\) and Marty Gregg\(^1\); \(^1\)Queen's University Belfast, United Kingdom; \(^2\)Imperial College London, United Kingdom; \(^3\)University of Limerick, Ireland

By symmetry, all 90° domain walls in Cu-Cl boracite (Cu\(_3\)B\(_7\)O\(_{13}\)Cl) must be associated with either head-to-head or tail-to-tail polar discontinuities and are hence charged. As in other ferroelectric systems, charged walls have either enhanced or reduced electrical conductivities, compared to bulk, and so controlling their injection and movement could be of interest in the context of future domain wall nanoelectronics [1].

In this work, we show that repositioning these walls using electric fields can lead to an increase in the global electrostatic energy: changes in the microstructure can be such that regions with polarisation aligned against the field coarsen at the expense of those aligned with the field. Field-induced changes in polarisation which increase polar populations which are anti-aligned, imply a contribution to the effective permittivity from domain wall motion that is negative. This is extremely unusual and worthy of much more exploration and discussion [2].

The notion of this kind of anomalous domain wall motion seems impossible in proper ferroelectrics. However, in the case of improper ferroelectrics, such as the Cu-Cl boracites, the low spontaneous polarisation associated with strong coupling to the spontaneous strain makes the idea plausible, as local electrostatic energy increases might be offset by global strain energy decreases in the system.

After presenting evidence for the correct attribution of the nature of the domains, relying on several scanning probe techniques, the classical and anomalous motion of domain walls in Cu-Cl boracite studied through optical microscopy will be presented. The complexity of the energy landscape in this specific system will be discussed and finite element models quantifying the electrostatic work done will be presented, along with potential avenues to be pursued which could shed more light on the unique behaviour observed.

References

1:45 PM MT07.02.02
Deterministic Motion of Ferroelastic Domain Walls in Ferroelectric Bilayers Yangyang Zhang\(^1\), Myung-Geun Han\(^2\), Joseph A. Garlow\(^2\), Yueze Tan\(^3\), Fei Xue\(^3\), Long-Qing Chen\(^3\), Paul Munroe\(^1\), Nagarajan Valanoor\(^1\) and Yimei Zhu\(^2\); \(^1\)University of New South Wales, Australia; \(^2\)Brookhaven National Laboratory, United States; \(^3\)The Pennsylvania State University, United States

Efficient energy conversion and deterministic controllability are long-standing demand of novel miniaturized electromechanical devices [1]. Recent advancements in ferroelectric thin film synthesis provide a potential pathway
to apply interface engineering for favorable electrostatic and strain conditions for promotion of ideal ferroelastic domain switching and leads to enhanced electromechanical response in tetragonal PbZr$_{1-x}$Ti$_x$O$_3$ (T-PZT)/rhombohedral PbZr$_{1-x}$Ti$_x$O$_3$ (R-PZT) bilayer thin films \cite{2-3}. However, the dynamic evolution of their domain switching mechanism remains elusive.

In this work, we utilize \textit{in situ} transmission electron microscopy (TEM) to explore the interaction between two dissimilar ferroelectric layers (R-PZT and T-PZT). During the real-time domain switching process, the domain wall orientation in T-PZT can be determined by the external electric field. The interface of the PZT bilayer serves as the nucleation site for the controllable domain wall reorientation, which is revealed by both atomic resolution electron microscopy imaging and phase field simulation. Thus, the interplay between two ferroelectric polymorphs is the underlying physical mechanism for unprecedented electromechanical properties in the PZT bilayer, i.e., ferroelastic domain switching and its wall reorientation. The T-PZT/R-PZT heterostructure acts as a model system, which can stimulate further advances of electromechanical device design.

References
\begin{itemize}
  \item \cite{1} G. Catalan et al., \textit{Reviews of Modern Physics}, 84, 119-156 (2012)
  \item \cite{2} L.W. Martin, A.M. Rappe, \textit{Nature Reviews Materials}, 2, 16087 (2017)
  \item \cite{3} H. H. Huang et al., \textit{Advanced Materials Interfaces}, 2, 1500075 (2015)
\end{itemize}

\textbf{2:00 PM *MT07.02.03}
\textbf{Bulk- and Flexo-Photovoltaic Effects at Ferroelectric Domain Walls} Marin Alexe and Ming-Min Yang; University of Warwick, United Kingdom

Two years after the invention of modern prototype solar cells, it was found that BaTiO$_3$ exhibits a photovoltaic effect distinct from that of \textit{p-n} junctions, later called the bulk photovoltaic (BPV) effect. Under uniform illumination, a homogeneous ferroelectric material gives rise to a short-circuit current and produces an anomalously large photo-voltage well exceeding the bandgap energy. The microscopic origins of this effect supposed to originate from the asymmetric distribution of photoexcited non-equilibrium carriers in $k$-space, caused by absence of centrosymmetry.

The present talk will present the basics of the bulk photovoltaic effect, tip enhancement, as well as the electronic origin of the anomalous BPV in some materials such as BiFeO$_3$.I will show how the tip-enhanced effect may be used in optical switching of ferroelectric polarization. Finally, we will discuss the new flexo-photovoltaic effect which turns the BPV effect into a universal effect allowed in all semiconductors under strain gradient and how this effect does affect the local photoelectric effects at domain walls. \cite{1,2}

References
\begin{itemize}
  \item \cite{1} M.-M. Yang, D. J. Kim, \& M. Alexe, Flexo-Photovoltaic Effect, Science 360, 904 (2018).
  \item \cite{2} M.-M. Yang et al., Strain-Gradient Mediated Local Conduction in Strained BiFeO$_3$ Film, Nature Comms, in press.
\end{itemize}

\textbf{2:30 PM BREAK}

\textbf{3:00 PM *MT07.02.04}
\textbf{Anisotropic Polarization-Induced Conductance at a Ferroelectric Domain Walls and Heterointerfaces} Xiaoqing Pan; University of California, United States

Coupling between different degrees of freedom, i.e. charge, spin, orbital, and lattice, is responsible for emergent phenomena in complex oxide heterostructures. A notable example is formation of a two-dimensional electron gas (2DEG) at the polar/nonpolar LaAlO$_3$/SrTiO$_3$(LAO/STO) interface due to the polar discontinuity and as a means to counteract the electrostatic potential build-up across the LAO film. The polar discontinuity can also be produced by a ferroelectric polarization at the domain walls and ferroelectric/insulator interface. In this case, such a 2DEG can be controlled by switchable ferroelectric polarization, thus providing a new functionality. Depending on the polarization orientation, either electrons or holes are transferred to the interface, to form either a 2DEG or two-dimensional hole gas (2DHG). While the recent first-principles modeling predicts the formation of 2DEGs at the ferroelectric/insulator interfaces, experimental evidence of a ferroelectrically-induced interfacial 2DEG still remains elusive. Here, we report the emergence of strongly anisotropic polarization-induced conductivity at a
ferroelectric/insulator interface, which shows a strong dependence on the polarization orientation. By probing the local conductance and ferroelectric polarization over a cross-section of the BiFeO$_3$/TbScO$_3$(BFO/TSO) (001) heterostructure, we demonstrate that this interface is conducting along the 109° domain stripes in BFO, whereas it is insulating in the direction perpendicular to these domain stripes. Electron energy-loss spectroscopy (EELS) and theoretical modeling suggest that this extraordinary anisotropy of interfacial conduction is caused by alternating polarization associated with the ferroelectric domains, producing either electron or hole doping of the BFO/TSO interface. Similarly, we observed a spin-polarized 2DEG forms at the PZT/STO interface, which is strongly localized at the interfacial Ti atoms, due to the interplay between Coulomb interaction and band bending, and can be tuned by the ferroelectric polarization. Finally, we found that the intrinsic conductivity of domain walls in BiFeO$_3$ thin film grown (110) TbScO$_3$ is strongly dependent on the polarization configurations. We show that the 71° domain walls exhibit conductivity, which is about an order of magnitude larger than that of the 109° domain walls. The 71° domain wall conductivity is strongly anisotropic: more conductive along the [010] direction than along the [001] direction. High resolutions electron energy loss spectroscopy reveals that the origin of the anisotropic conductivity of the 71° walls stems from the potential discontinuity of the 71° domain walls along the [110] direction. Our findings in the ferroelectric interfaces and domain walls open a door for engineering ferroelectric/insulator interfaces toward the creation of tunable ferroic orders for magnetoelectric device applications and provide the opportunities for designing multiferroic materials in heterostructures.

3:30 PM MT07.02.05

Deconvoluting Conductance Contributions at Charged Ferroelectric Domain Walls Using Machine Learning

Theodor Secanell Holstad$^1$, Trygve Magnus Ræder$^{1,2}$, Donald Malcolm Evans$^1$, Didrik René Småbråten$^1$, Stephan Krohns$^3$, Zewu Yan$^{4,5}$, Edith Bourret$^5$, Tor Grande$^1$, Sverre Magnus Selbach$^1$, Joshua Agar$^2$ and Dennis Meier$^1$;

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Ferroelectric domain walls are spatially mobile interfaces that naturally occur in materials that develop a spontaneous electric polarization. Because of their unique electronic properties, such walls hold great promise as functional 2D systems, but the characterization of their intrinsic transport properties remains a challenging task.

Despite the significant progress in experiment and theory, most investigations on ferroelectric domain walls still fall into the basic research sector, aiming to understand their complex nano-physics and tailor their local electronic properties. One of the main challenges lies in the reliable characterization of emergent transport phenomena, which commonly is realized in terms of conductive atomic force microscopy (cAFM) measurements. However, cAFM is a two-probe measurement and, as such, susceptible to contributions from contact resistance that can obscure the data. Furthermore, as the resolution limit of cAFM ($\geq 20$ nm) is much larger than the width of typical ferroelectric domain walls ($\approx 10$ Å), it is often difficult to evaluate whether measured signals arise at the wall center, in adjacent accumulation and depletion regions, or due to displacement currents associated with domain wall movement.

In this talk, we will discuss how the physical property extraction from local conductance measurements can be improved by combining local I(V)-spectroscopy measurements with machine learning, employing a neural network autoencoder. Using the doped hexagonal manganite (Er$_{0.99}$Zr$_{0.01}$)MnO$_3$ as a model system, we conduct a comprehensive characterization, using different methods such as density functional theory (DFT), dielectric spectroscopy, piezoresponse force microscopy (PFM) and cAFM. To highlight different limitations associated with standard cAFM scans, we first discuss the observation of surprising conductance phenomena at charged head-to-head (h-t-h) and tail-to-tail (t-t-t) domain walls. We then use the neutral network autoencoder to disentangle different conductivity contributions, revealing the intrinsic electronic domain wall properties in (Er$_{0.99}$Zr$_{0.01}$)MnO$_3$.

3:45 PM MT07.02.06

Size Effects on the Structure and Properties of Relaxor Ferroelectric Thin Films

Jieun Kim$^1$, Yun-Long Tang$^{1,2,3}$, Hiroyuki Takenaka$^4$, Yubo Qi$^5$, Min-Jie Zou$^1$, Abel Fernandez$^1$, Lei Zhang$^1$, Margaret McCarter$^1$, Gabriel Velarde$^1$, Sahar Sarem$^1$, Yin-Lian Zhu$^1$, Xiu-Liang Ma$^3$, Andrew M. Rappe$^3$, Ramamoorthy Ramesh$^{1,2}$ and Lane W. Martin$^{1,2}$;

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The scaling behavior of ferroelectrics and related materials are of both fundamental and practical interest. In
particular, there has been significant progress in the understanding of scaling behavior for ferroelectrics over the past few decades. In stark contrast to ferroelectrics, understanding of size effects in relaxor ferroelectrics (relaxors), a special class of ferroelectrics, has been lacking, despite the close similarity between ferroelectrics and relaxors. In this work, we use a combination of thin-film epitaxy, X-ray diffuse scattering, scanning transmission electron microscopy, dielectric and ferroelectric characterization, and molecular-dynamics simulations to investigate the size-dependent evolution of structures and properties in the prototypical relaxor ferroelectric 0.68PbMg1/3Nb2/3O3-0.32PbTiO3. Here we demonstrate that reducing the size (i.e., thickness of the films), contrary to prior reports, first enhances relaxor behavior until a threshold thickness below which the critical temperatures that characterize various relaxor phases (i.e., dynamic, static, and frozen) collapse together, indicating destabilization of the relaxor state. Using temperature-dependent diffuse scattering, scanning transmission electron microscopy, and dielectric and ferroelectric measurements, we demonstrate that relaxors lose their defining characteristics below this threshold thickness. The mechanism for destabilization of relaxor behavior below the critical thickness is discussed in terms of faster dynamics of polarization fluctuations in ultrathin relaxor films.

4:00 PM MT07.02.07
In Situ Ferroelectric Domain Dynamics in PMN-PT Abinash Kumar1, Rohan Dhall2 and James M. LeBeau1; 1Massachusetts Institute of Technology, United States; 2Lawrence Berkeley National Laboratory, United States

Relaxor ferroelectrics are one of the most widely used functional materials as they exhibit low coercive field and giant piezoelectric coefficients [1]. These can be distinguished from classical ferroelectrics based on their diffuse phase transitions and dielectric properties. These properties are commonly associated with the existence of polar nanoregions in a non-polar matrix [2]. Recently, a model of slush-like response of a nanoscale multi-domain state is proposed to explain relaxor behavior, but these models are not are fully predictive [3]. In order to design relaxor ferroelectric materials, a fundamental understanding of their behavior under an applied electric field needs to be found-from the micro to atomic length scale. Recent advances in in situ microscopy and STEM detector technologies, such as 4D STEM and differential phase contrast (DPC) imaging [4], have allowed to reveal the structural information required to explain the origin of relaxor behavior.

We show that DPC provides robust imaging of the relaxor ferroelectric domain structure as a function of voltage bias. We apply the technique to Pb(Mg1/3Nb2/3)O3-28PbTiO3(PMN-PT) single crystals prepared using conventional polishing methods pair with photolithography to define the electrodes. First, influence of electron beam on the domain structure is studied by examining a series of DPC images without an applied field. The electron beam causes the domain walls to flicker in the time-resolved dataset, but large-scale changes are not observed at this field of view. A dramatic change in domains is observed at different applied electric fields. The domain structure at the start and end of a field cycle is explained in the context of remnant polarization. Effect of waveform shape on switching behavior is also determined. To quantify changes at the atomic scale, we demonstrate how in situ integrated differential phase contrast (iDPC) provides high signal-to-noise ratio imaging of oxygen atom columns, even in the presence of heavier atoms (Pb). Further, we demonstrate how the simultaneous acquisition of annular dark field (ADF) can be used to simplify the quantification and removal of drift and scan distortion from iDPC images [5]. From the drift-corrected iDPC images, the projected polarization is then quantified at different applied fields. It is observed that the polar nanoregions try to align to the electric field, but reside within a microscale ferroelectric domain that does not switch. With a combination of data across length scales for the same sample, we discuss how the resulting details provide new insights into the dynamics of relaxor ferroelectric domains.

References:

4:15 PM MT07.02.08
The Domain Switching in Rhombohedral PZT Observed by In Situ X-Ray Diffraction Study by Various Frequencies Takao Shimizu1, Yoshitaka Ehara2, Takanori Mimura1, Shintaro Yasui1, Tomoaki Yamada2, Yasuhiro Imai3, Yoshio Katsuya4, Osami Sakata1 and Hiroshi Funakubo1; 1Tokyo Institute of Technology, Japan; 2Nagoya

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Time resolved X-ray diffraction measurement was performed for rhombohedral lead zirconate titanate (PZT) with synchrotron X-ray source for various frequencies and pulse widths. The PZT is the most widely used ferroelectric and piezoelectric material due to its outstanding electric properties. In particular, their excellent electro-mechanical responses have been attracted a great deal of interest, because they enable us to produce the various applications, such as sensors and actuators. Because of the recent increase in the demand for these devices using micro-electro-mechanical-systems, it is required to understand the nature of the piezoelectric and dielectric properties of PZT more deeply. It is well recognized that non-180° domain switching plays essential roles for the piezoelectric responses in PZT. The frequency dispersion in piezoelectric and dielectric responses often become a problem to use PZT at high frequency. Because the dispersion is known to relate with the domain switching motions, the time-resolved measurement with broadband frequency is needed to understand the piezoelectric responses. In particular, remarkable frequency dispersion is reported for rhombohedral PZT.

The PZT films prepared by metal-organic chemical vapor deposition were used for the measurements. The in-situ X-ray diffraction was performed at SPring-8 BL15XU using the focused X-ray beam on area 2 × 3 μm² in width and height using a two-dimensional focusing refractive lens. To observe the domain switching for various frequencies and duty ratios, the pulse width and repetition frequency of the electric field, were varied. The domain switching was confirmed by applying electric field irrespective of the frequencies and duty ratios. We observed marked delay of the domain switching back when removing the electric field. The high frequency of 1 MHz electric field gave rise to a small amount of domain switching motion compared to low frequencies electric field. In addition, the larger duty ratio also smaller changes in domain fraction by the electric field even with the low frequency of 10 kHz. Interestingly, the domain fraction without electric field during electric cycling (i.e. in-situ measurement) is different from the original domain fraction before starting measurements if we used at high frequencies or large duty ratios. This means that the longer time required to recover original domain structure in rhombohedral PZT, which is quite different from tetragonal PZT responding to both applying and removing the electric field.

4:30 PM MT07.02.09
Investigating the Strain Governing the Dynamic and Charged Nature of Ferroelastic Boracite Domain Walls by 4DSTEM
Michele A. Conroy¹, Eileen Courtney¹, Steven Zeltmann², Benjamin Savitzky², Colin Ophus², Jim Ciston², Kalani Moore¹, Charlotte Cochard³, Joseph G. Guy³, Raymond G. McQuaid³, Roger Whatmore⁴, Alexei L. Gruverman⁵, Marty Gregg³ and Ursel Bangert¹; ¹University of Limerick, Ireland; ²Lawrence Berkeley National Laboratory, United States; ³Queens University Belfast, United Kingdom; ⁴Imperial College London, United Kingdom; ⁵University of Nebraska–Lincoln, United States

Conducting ferroelectric domain walls (DWs) are an emerging research focus in nano-electronics and potential quantum technologies [1,2]. DWs have their own unique electronic properties and most excitingly can be moved by an applied stimulus.[3] However, due to the high energetic cost of creating charged DWs in conventional ferroelectrics they are not stable long term. Improper ferroelectrics circumvent this issue as their driving force is not a polar instability, but instead is the symmetry-breaking non-polar primary mode. With this in mind there has been a recent surge in improper ferroelectric DW research. In this study boracite is the material we have chosen to focus on as it has already shown very promising results in terms of charged DW injection and movement. [5] Boracite is an improper ferroelectric material where the primary order parameter is the physical quantity spontaneous shear strain. As a ferroelastic material the conductivity of the charged DWs in boracite is governed by the shear strain direction of the neighbouring domains. Thus traditional atomic resolution Scanning Transmission Electron Microscopy (STEM) polarity mapping will not give the true picture of the ferroelectric properties. In order to understand the mechanism of the DW movement and the fundamental physics governing conducting DW formation strain analysis at the DW was completed by 4D-STEM [6] strain mapping. This strain analysis was then compared to the atomic resolution STEM imaging and polarity mapping. The dynamic nature of the DWs was investigated by utilising the applied electric field of the STEM probe itself, allowing for controlled angle of the incoming applied electric field and a corresponding STEM data set.

2. Ma, J., et al., Nature nanotechnology, 2018
The secondary nature of polarization in improper ferroelectrics promotes functional properties beyond those of conventional ferroelectrics. For example, in the hexagonal manganites, the non-ferroelectric distortive origin of electric polarization enables topologically protected ferroelectric vortex domain-patterns, conducting domain walls and multiferroicity. In technologically relevant ultrathin films, however, the improper ferroelectric behavior remains largely unexplored. Here, we probe the emergence of the coupled improper polarization and primary distortive order parameter in thin films of hexagonal YMnO₃. Combining state-of-the-art in-situ characterization techniques separately addressing the improper ferroelectric state and its distortive driving force, we reveal a pronounced thickness dependence of the improper polarization, which we show originates from the strong modification of the primary order at epitaxial interfaces. Nanoscale confinement effects on the primary order parameter reduce the temperature of the phase transition, which we exploit to visualize its order-disorder character with atomic resolution. Our results lay the foundation for understanding the evolution of improper ferroelectricity within the confinement of ultrathin films – essential for the successful implementation in nanoscale applications.

SESSION MT07.03: Space- and Time-Resolved Functional Characterization by Electron and Local Probe Microscopies
Session Chair: Marin Alexe
Thursday Morning, December 5, 2019
Hynes, Level 2, Room 205

9:00 AM MT07.03.01
In Situ Chemical Studies of Functional Materials via Combined AFM/ToF-SIMS Platform Anton V. Ievlev, Yongato Liu, Sergei Kalinin and Olga S. Ovchinnikova; Oak Ridge National Laboratory, United States

For the last several decades Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS) became a prime tool for chemical characterization of the materials at sub-micrometer and nanometer scales. However, most of the investigations published so far lacks information about physical properties of the studied samples and their time evolution. The solution can be found in combination of mass spectrometry with Atomic Force Microscopy (AFM). Such combined multimodal AFM/ToF-SIMS platform enables a nanoscale correlated studies of both chemical and physical properties of the sample. In this case, chemical phenomena characterized by the ToF-SIMS can be complemented with functional properties measured by the AFM. Furthermore, continuous data acquisition in both ToF-SIMS and AFM modes supplemented by multivariate statistical analysis allows characterization of time evolving processes. Here we utilize commercial AFM/ToF-SIMS platform to explore interplay of chemical and physical phenomena in ferroelectrics and photovoltaics. In particular, our research allowed to reveal chemical phenomena associated with polarization switching in ferroelectric thin films and study ion migration in hybrid organic-inorganic perovskites. Developed approach enables direct characterization of interplay between chemical and functional response in functional materials and aids in the development and optimization of novel functional devices. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility and using instrumentation within ORNL’s Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

9:15 AM MT07.03.02
Nanoscale Discharging Phenomena for Dielectric/Piezoelectric Multilayers Thomas Moran, Michael Martin, Jingfeng Song, Keigo Suzuki, Tadasu Hosokura, Nobuhiko Tanaka, Koji Murayama and Bryan D. Huey;
The ultimate dynamic electrical performance of functional ceramic devices depends on the nanoscale materials properties in 3-dimensions. Thickness effects and engineered heterogeneities are of particular interest, requiring advances in nanoscale functional measurements. Accordingly, emerging methods for micromachining and Tomographic AFM, along with Kelvin Probe Force Microscopy (KPFM), Piezo Force Microscopy (PFM), and Conductive AFM (cAFM), are used to study dielectric and ferroelectric heterostructures, including as a function of thickness. Dynamic charging and discharging processes are notably mapped with KPFM as a function of time and energy, providing novel insight into local dielectric behavior and especially the voltage dependencies of surface or grain boundary defect states. These are related to sub-surface features and thickness dependencies via tomographic PFM and cAFM, volumetrically revealing size effects, 3-dimensional heterogeneities, and charge dissipation pathways. By considering in-situ charging and discharging phenomena, the engineered performance for micro- and nano-scale electronic devices such as multi-layer-chip-capacitors can therefore be optimized.

9:30 AM *MT07.03.03
Correlated Microscopy Studies at Functional Ferroelectric Domain Walls Dennis Meier; Norwegian University of Science and Technology, Norway

Interfaces in oxide materials offer amazing opportunities for fundamental and applied research, giving a new dimension to functional properties, such as magnetism, multiferroicity and superconductivity. Ferroelectric domain walls recently emerged as a new type of interface, where the dynamic characteristics of ferroelectricity introduce the element of spatial mobility, allowing for the real-time adjustment of position, density and orientation of the walls. This mobility adds an additional degree of flexibility that enables domain walls to take an active role in future devices and hold great potential as functional 2D systems for electronics. For example, domain walls can readily be injected and deleted to control electric conductivity, enabling multi-level data storage. However, while this approach clearly achieves a step beyond conventional interfaces by utilizing the wall mobility, it does not break the mould of classical device architectures.

In this talk, I will present a conceptually different approach, utilizing ferroelectric domain walls to emulate key electronic components such as digital switches and diodes. In particular, I will discuss three experimental studies, showing how advanced microscopy strategies helped us to understand the complex nanoscale physics that give rise to the functional electronic domain wall properties. (i) The diode-like behavior that arises at electrode-wall junctions, for instance, became accessible due to innovative conductive atomic force microscopy (cAFM) studies performed under a.c. voltages in the kilo- to megahertz range [1]. (ii) By combining cAFM, transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS), we demonstrated and explained the gating of electronic currents at domain walls [2], and (iii) correlated cAFM, electrostatic force microscopy (EFM) and X-ray photoemission electron microscopy (PEEM) provided novel insight into their electrostatic properties [3]. Finally – going beyond just imaging (i-iii) – I will discuss the possibility to combine cAFM, focused ion beam (FIB) methodologies, and in-situ scanning electron microscopy (SEM) imaging to achieve domain walls with well-defined charge states. This possibility brings us an important step closer to electronic components based on individual domain walls, following the ultimate goal to achieve domain-wall based circuitry and networks.


10:00 AM BREAK

10:30 AM *MT07.03.04
Atomic Scale Structure and Dynamics of Domain Walls in Ferro-Electrics—Determination of the Configuration of Individual Dipoles Michele A. Conroy1, Kalani Moore1, Eoghan O'Connell1, Eileen Courtney1, Alan Harvey1, Joseph G. Guy2, Charlotte Cochard2, Raymond G. McQuaig2, Lewys Jones3, Clive Downing4, Roger Whatmore4, Marty Gregg5, Alexis L. Guverman6, Quentin Ramasse6 and Ursel Bangert1; 1University of Limerick, United Kingdom; 2Queens University, United Kingdom; 3Trinity College, Ireland; 4Imperial College London, United Kingdom; 5University of Nebraska–Lincoln, United States; 6SuperSTEM Laboratory, United Kingdom
Benefits of utilising the 2-D properties and the dynamic nature of ferro-electric domain walls are increasingly being explored. The combination of their sub-nm thickness and agility permits so far un-achieved applications in nano-electronic and -photonic devices, e.g., as ultrafast electrical switches, a.o., to pump for single photon emitters, or as mobile nano-mirrors in nano-scale lasers. To achieve this a fundamental understanding of these materials and their functionalities in terms of their physical, chemical and electronic structure down to the atomic level is required. Using atomic resolution transmission electron microscopy (TEM) methods, pico-meter shifts of individual atoms were observed (e.g., in boracite and lead titanate), resulting in the formation of electric dipoles. Comparison of the contrast of the atoms in (individual) dipoles to crystal models showed the relative shifts of cations with respect to anions, revealing the dipole orientation. Maps of atom shifts, signifying the formation orientation distributions of dipoles, were obtained over 1000 nm² areas, using the Atomap[1] program. Changes of dipole orientations along certain line directions then revealed domain boundaries and walls, as well as dipole (e.g., head-to-head or tail-to-tail) constellations and angles (e.g., 90°) along these walls. The shifts of atoms as well as the orientations of individual dipoles are revealed via high angle annular dark field (Z-contrast) and annular bright field imaging, the latter method depicting also the lighter atoms (e.g., O). Positions of all atoms together with their elemental nature are disclosed with sub-Å accuracy in areas on either side of domain walls and in the domain wall itself. These measurement are accompanied by differential phase contrast imaging to reveal the local electric field directions. The relative change in the distance of cations with respect to anions along the walls can furthermore give insight into whether these walls are expected to be conducting or insulating. Moreover, the movement of the walls and control over this movement are investigated and demonstrated via atomic-scale in-situ TEM.

11:00 AM MT07.03.05
Improvement of Time Domain Performance in Atomic Force Microscopy Feedback Controlled Electromagnetic Methods by Means of Image Reconstruction Stanislav Leesment1,2; 1NT-MDT Spectrum Instruments, Russian Federation; 2NT-MDT America Inc., United States

Atomic force microscopy (AFM) provides a wide range of methods which allow mapping of electrostatic (EFM, SCM, KPFM), piezoelectric (PFM) and magnetic (MFM) properties of samples with high spatial resolution. The performance of these methods is always a trade-off between signal to noise ratio, sensitivity, and speed. The latter is limited by the parameters of the probe sensor and the bandwidth of the feedback control system [1]. Scanning speed increment is an important direction for development of in-situ studies of dynamic properties at nanoscale.

The nature of tip-sample interaction forces detected by AFM is different for various techniques. But in all cases of feedback-driven methods, the major contribution in the final result is brought by the derivative of the tracked value: surface potential in KPFM, frequency shift in MFM, etc. In the assumption of linear disturbances and taking into account that errors in trace and retrace scanning directions have odd symmetry, the following transform can be applied to AFM data:

\[
\text{pr} \quad \text{and} \quad \text{pb} \quad \text{are trace and retrace profiles of tracked parameter and} \quad \text{pr} \quad \text{is a reconstructed profile.}
\]

The example of the described approach is shown in fig. 1 representing the map of surface potential (both trace) distribution over the charged line induced by the AFM tip on Si/SiO₂ surface. Scanning was done in two-pass AM-KPFM mode consequently at maximal speed which was fitting the KPFM feedback loop response and at an order higher rate (fig. 1 a and b). Fig. 1 c represents the reconstructed surface potential map. It is seen that the reconstruction result fits well with the image taken under appropriate conditions.

The proposed image reconstruction approach can be applied to images acquired by other feedback-driven AFM methods.

**Fig. 1** AM-KPFM images of charged line on Si/SiO₂ substrate. a and b correspond to scanning speeds of 10 and 140 μm/s. c – corrected image. d introduces corresponding scan profiles. Image size: 7,7×9,7 μm. Color scale: -2,3..-7,8 V

Image was acquired by means of Ntegra AFM system, NT-MDT Spectrum Instruments Co. The authors acknowledge funding from the European Union's Horizon 2020 research and innovation program, OYSTER under grant agreement No 76082

**References**


11:15 AM MT07.03.06
Time-Resolved Electrical Scanning Probe Microscopy for Studying the Effect of Grain Boundaries on Ion and Carrier Dynamics in Layered Perovskite Films Rajiv Giridharagopal and David S. Ginger; University of
Layered low-dimensional perovskites have emerged as a popular system for a wide range of optoelectronic applications due to their enhanced environmental stability and tunability relative to three-dimensional hybrid organic-inorganic perovskites. However, to date there have been few studies linking the photoinduced dynamics in these layered systems with their topographic features. Here, we use two complementary “big data” electrical scanning probe microscopy methods, fast free time-resolved electrostatic force microscopy (FF-trEFM) and general mode Kelvin probe force microscopy (G-KPFM), to probe light-induced dynamics in thin films comprising Ruddlesden-Popper phases of the layered 2D perovskite (C4H9NH3)2PbI4 (BAPI) as a function of position, time, and illumination. These scanning probe techniques capture the raw AFM cantilever motion and use advanced signal processing of the large (~50 GB) four-dimensional datasets (x, y, z, t) to extract microsecond-timescale dynamics. We use G-KPFM and unsupervised clustering to show that the photovoltage equilibrates over long timescales (hundreds of microseconds) that we attribute to ion motion. Surprisingly, this effect is actually slower at boundaries between adjacent grains as opposed to grain centers. With FF-trEFM, we extract faster dynamics at grain centers but with timescales consistent with electronic motion (70 - 100 μs). We therefore propose that the slower evolution at grain boundaries is due to a combination of ion migration occurring between PbI4 planes, as well as electronic carriers moving through traps at grain boundaries, thereby changing the time-dependent band unbending even within a micron-scale perovskite grain. Beyond perovskite optoelectronics, these experiments lay the groundwork for data-driven analysis of large microscopy datasets on other dynamic systems requiring sensitive detection of transient phenomena in scanning probe microscopy.

11:30 AM MT07.03.07
Unraveling the Relationship between Layer Stacking and Magnetic Order in Nb3X8 Systems via Controlled-Temperature Cryo-STEM
Elisabeth Bianco1, Ismail El Baggari1, Berit Goodge1, Christopher Pasco2, Tyrel McQueen2 and Lena Kourkoutis1; 1Cornell University, United States; 2Johns Hopkins University, United States

Nb3X8 (X=Cl or Br) are insulating, cluster-based, layered materials that exhibit an antiferromagnetic to non-magnetic transition [1]. In Nb3Cl8, the loss of magnetic order occurs at temperatures below 90 K and has been coupled to a symmetry-lowering crystallographic distortion and layer stacking change from a 2-layer (α-phase) to a 6-layer (β-phase) unit cell [2]. The transition temperature, however, depends strongly on composition with Nb3Br8 exhibiting the β-phase at 293 K. While tuning of the magnetic ordering temperature through composition is appealing for materials design, the mechanism by which the layer stacking reorganizes is not understood, and pinpointing the emergence of such structural changes and their relationship to magnetic order necessitates atomic-resolution imaging across the transition.

Atomic-resolution, cryogenic scanning transmission electron microscopy (cryo-STEM) has enabled precise mapping of structural responses related to underpinning low-temperature physics, such as periodic lattice displacements and associated charge density waves [3-5]. Most cryo-STEM, however, is performed at the absolute temperature of the holder, precluding access to intermediate temperatures, and thus limiting the ability to track structural transformations and the emergence of correlated phases over temperature. To overcome this, we have optimized a novel approach to cryo-STEM using a liquid-N2 specimen holder equipped with a 6-pin MEMS system for local heating [6]. This has expanded the realm of cryo-STEM to any desired temperature from ~95-500 K. Thus, we can use controlled-temperature cryo-STEM to explore the effects of temperature on the layer stacking of van der Waals Nb3Br8 and its relationship to magnetic order.

Employing controlled-temperature cryo-STEM we have observed a distinct structural phase transformation in Nb3Br8 with atomic-resolution. Plan-view imaging demonstrates a clear, reversible transformation from the α-phase to β-phase at ~250 K upon cooling and β-phase to α-phase at ~425 K upon heating through a series of apparent intermediate phases. Imaging of cross-sectional specimens, however, does not show a reorganization of layer stacking. Rather, persistent stacking faults are observed, some consisting of α-phase inclusions accompanying the β-phase unit cell. The lack of an observed transition in this geometry may indicate that the transition in thin, cross-sectional STEM samples is suppressed. Coupling the plan-view results with Multislice image simulations provides a clearer picture of the temperature-induced atomic scale changes in Nb3X8 systems. Developing controlled-temperature cryo-STEM has allowed investigation into the implications of composition and temperature on layer stacking in a single materials system. Understanding the mechanism of stacking changes and their effect on magnetic ordering will afford handles for new materials with tailored transition temperatures.
Electron Transport Cathode Luminescence Microscope for the Phase-Separated Transition Metal Oxides

Hidekazu Tanaka1, Azusa N. Hattori1, Masayoshi Ichimiya2, Rupali Rakshit1 and Masaaki Ashida1; 1Osaka University, Japan; 2The University of Shiga Prefecture, Japan

Phase transitions in transition metal oxides, such as metal-Insulator transition, ferromagnetic, ferroelectric materials, are useful phenomena to realize novel electrical/magnetic/thermal switching and sensing devices. The dynamical behavior of their nano- to micro-scale domain structures play an important role for phase transitions, and their scaling behavior would create superior functionally of steep changes in resistive switching magnetoresistance in VO2, magnetite [1] and so on.

Cathodoluminescence (CL) imaging technique realizes the multi-scale from nano to several hundred micro level observation for the spatial distribution of electronic properties via the optical excitation. So far, CL mapping was not applicable for the non-fluorescent samples. Electron transport cathode luminescence microscope (ETCLM) has been developed by the energy transfer (ET) ratio visualization in the dye-assist CL technique, where ET between luminescent dye and objective materials is applied in imaging for optical conductivity dispersion over the sample based on a conventional scanning electron microscope with a CL system. This ETCLM technique enables the simple and contractless image mapping to characterize the optical conductivity, i.e., metallic/insulating area distribution based on the contrast of the ETCL intensity image. The principle of visualization for optical conductivity dispersion is derived from the radiative/nonradiative emission reflecting ET coupling between the dye and objective materials. As a proof on the principle, the ETCL mapping for the prototype Au disk patterned SrTiO3 sample was attributed to the ET process substantiated by significant ETCL change of the dye. The capability of our technique for mapping metal/insulator property distribution is demonstrated for the observation of the phase separation during insulator-metal transition process in strongly-electron correlated VO2 and Magnetoresistive manganite. Temperature dependent ETCL images adequately capture the characteristic of metal/insulator electronic domain formation across the phase transition phenomena.

data with the results of micromagnetic simulations, we are able to gain a fuller understanding of the various energy terms that contribute to the behavior that we observe.

For example in artificial spin ices, we have explored the way in which aperiodicity leads to local variations in the energy landscape and to a difference in behavior with respect to periodic ASIs. We are able to calculate the energy at each vertex motif for each possible magnetic configuration from our simulations and thus determine which vertices play the most dominant role in influencing behavior in response to magnetic fields [1, 2] and to changes in temperature. Applied to magnetic skyrmions we used in situ LTEM to observe skyrmions in a Co/Pt multilayer film as a function of applied magnetic field, and by combining with simulations we were able to determine the strength of the Dzyaloshinskii-Moriya interaction [2].


2:00 PM MT07.04.02
Electronic Structures of MgO/Fe Interfaces Revealed by Hard X-Ray Photoemission with an Applied Magnetic Field Shigenori Ueda1, Masaki Mizuguchi2, Masahito Tsujikawa2 and Masafumi Shirai2; 1National Institute for Materials Science, Japan; 2Tohoku University, Japan

We have newly developed hard X-ray photoelectron spectroscopy (HAXPES) under an applied magnetic field of 1 kOe to study the electronic and magnetic states of the interface-induced perpendicular magnetic anisotropy (PMA), in particular for MgO/Fe interfaces [1]. In this work, we used MgO(2 nm)/Fe(1.5 and 20 nm)/MgO(001) structures to reveal the interface-induced electronic states of the Fe film. Perpendicular magnetization of the 1.5-nm-thick Fe film without extrinsic oxidation of the Fe film was detected by the Fe 2p core-level magnetic circular dichroism (MCD) in HAXPES under a magnetic field, and easy magnetization axis perpendicular to the film plane was confirmed by ex-situ magnetic hysteresis curve measurements. The valence-band HAXPES spectrum of the 1.5-nm-thick Fe film revealed that the Fe 3d electronic states were strongly modified from the thick Fe film and a reference bulk Fe sample due to the lifting of degeneracy in the Fe 3d states near the MgO/Fe interface. We found that the tetragonal distortion of the Fe film by the MgO substrate also contributes to the lifting of degeneracy in the Fe 3d states and PMA, as well as the Fe 3d-O 2p hybridization at the MgO/Fe interface, by comparing the valence-band spectrum with density functional theory calculations for MgO/Fe multilayer structures. Thus, we can conclude that the Fe 3d-O 2p hybridization and tetragonal distortion of the Fe film play important roles in PMA at the MgO/Fe interface. HAXPES with in-situ magnetization thus represents a powerful new method for studying spintronic structures. This is a first step for HAXPES under a coexistence of electrical and magnetic fields to understand the phenomena driven by electric and magnetic fields from the electronic structures.


2:15 PM MT07.04.03
Coherent Soft X-Rays as a Probe for Structure and Dynamics of Materials Exhibiting Magnetic and Electronic Phenomena Andi M. Barbour, Wen Hu, Stuart Wilkins and Claudio Mazzoli; Brookhaven National Laboratory, United States

The National Synchrotron Light Source II (NSLS-II) houses the world leading coherent soft x-ray (CSX) beamline, which was designed to exploit a high coherent x-ray flux (x10^13 photons s^-1) to study structure and dynamics of novel materials and model devices using resonance elastic x-ray scattering (REXS). By selecting incident energies of x-ray absorption edges (200 - 1800 eV), researchers use the in-vacuum diffractometer and liquid helium cryostat to investigate single crystals, thin films, and engineered nano-arrays. This energy range is particularly exploited by 3d transition metal oxides, but it is not limited to these materials. The variable setup of CSX offers scientists a variety of techniques including, but not limited to, nano-diffraction, ptychography, resonant reflectivity / diffraction, and x-ray photon correlation spectroscopy (XPCS). In particular, coherent diffraction produces a signal with x-ray speckles caused by domain boundaries and defects that act as phase objects, and XPCS uses speckles to characterize dynamics of electronic and magnetic ordering on the 10s of milliseconds to hours time scale. The x-ray speckles may also be used to study phenomena like return point memory or material degradation. Our main experimental-
station also has some limited in-situ capability with permanent magnets and 4-wire measurements. This is in addition to our new holography experimental-station that is outfitted with an electromagnet (0.8 Tesla maximum) with advanced application of current/voltage to samples. We will present these capabilities, some recent science from the first 4 years of operation, and our future plans.

2:30 PM MT07.04.04
Optical Investigation of Magneto-Elastic Coupling in van der Waals Ferromagnet CrBr₃ Vincent Plisson; Boston College, United States

Van der Waals materials give a unique ability to explore the physics in the effective 2D regime. Due to the possibility of using mechanical exfoliation, atomically thin samples can be prepared without much difficulty. Another advantage is that exfoliatable materials can be easily strained; this can be particularly useful in observing the effect of strain on magnetism as well as determining the role of magneto-elastic effects. A key parameter to maintaining magnetism in 2D is magnetic anisotropy, a spin configuration in which the spins align in a certain crystal direction called the easy axis. Previous experiments show CrBr₃ is a ferromagnet with out-of-plane ferromagnetic ordering with Ising anisotropy. Here we report on optical measurements (Raman Scattering) done on CrBr₃ to investigate the magneto-elastic coupling and the evolution of the Raman spectra in a full temperature dependent study.

2:45 PM BREAK

3:15 PM *MT07.04.05
Atomic Scale Characterization of Phase Transitions by Transmission Electron Microscopy Martial Duchamp¹, Kristina M. Holsgrove², Kamble Deepak¹, Miryam Arredondo², Laszlo Forro¹ and Raju V. Ramanujan¹; ¹Nanyang Technological University, Singapore; ²Queen’s University Belfast, United Kingdom; ³Ecole Polytechnique Fédérale de Lausanne, Switzerland

Here, we present in situ and operando in a transmission electron microscope (TEM) studies where the microstructure is characterized at atomic scale across phase transitions characterized by specific temperatures, i.e., Curie temperature, critical superconductive temperature (Tc). We use a dedicated low temperature double-tilt holder able of atomic-scale characterization in a 100 K to 1,000 K temperature range while applying electrical stimulus. We will present a few cases study where the combination of low temperature and atomic resolution imaging allow to get deeper understanding on the superconductor, ferroelectric and ferromagnetic materials properties. We will present the nano-confinement effect on the Curie temperature of the (MnNiSi)₁₋ₓ(Fe₂Ge)ₓ system for magneto-caloric applications with the aim to tune the ferromagnetic transition both by a control of the composition (x) and of the crystal size. The effect of the x, accounting for MnNiSi to Fe₂Ge phase ratio have been shown to control the Curie temperature by bulk characterization techniques but so far the size effects have not been investigated. The transition is monitored both by real-space imaging techniques inside a TEM combined with phase contrast techniques that allow the measurement of magnetic moments aligned perpendicularly to the electron beam propagation direction. We will also present our recent results on the imaging of high-temperature superconductor, Bi₂Sr₂Ca₂Cu₃O₁₀, around its critical temperature (~110 K). The use of scanning (S-)TEM techniques combined with multi-slice simulations at different collection angles allowed to follow how the micro-structure affects the superconducting mechanism. We measured operando the resistivity drop inside the TEM at micro-scale using standard IV characterization techniques and electron holography for local mapping of the electrostatic potential. Multiferroic, magnetoelectric, piezoelectric and lead-free – epitaxially strained bismuth ferrite (BFO) thin films exhibits both exciting physics and fascinating characteristics for tuning their functionality. Using SEM and FIB techniques, we identified pre-written AFM regions and milled cross-sectional lamellae across distinct regions which included an area of native polymorphs, an area which was electrically written into the pure T phase and an area which was transformed back into the mixed-phase via stress. We present direct measurements of the atomic and electronic structure of the native and post-external stimuli-written phases using nano-beam electron diffraction (NBED) and electron energy-loss spectroscopy (EELS) acquired using aberration-corrected STEM, accompanied by EEL spectra calculated using the program FEFF.

3:45 PM MT07.04.06
Large Polarization and Susceptibilities in Artificial Morphotropic Phase Boundary PbZr₅₋ₓTiₓO₃ Superlattices Eduardo Lupi¹ and Lane W. Martin¹; ¹University of California Berkeley, United States; ²Lawrence Berkeley National Laboratory, United States
Large susceptibilities in the PbZr$_{1-x}$Ti$_x$O$_3$ system have historically been attained by selecting materials in the compositional vicinity of the morphotropic phase boundary. This typically comes as a trade-off with saturation polarization, as polarization diminishes and susceptibility rises at the phase transition. Here, we take advantage of unit-cell precise growth to introduce ferroelectric-ferroelectric interfaces as an additional design parameter wherein the material response can be tuned by both composition and superlattice periodicity. We likewise focus on heterostructures with overall chemistry near this boundary, but built from compositions far from the phase boundary itself: rhombohedral PbZr$_{0.8}$Ti$_{0.2}$O$_3$ and tetragonal PbZr$_{0.4}$Ti$_{0.6}$O$_3$. Using reflection high-energy electron diffraction (RHEED)-assisted pulsed-laser deposition, we create atomically-precise (PbZr$_{0.8}$Ti$_{0.2}$O$_3$)$_n$(PbZr$_{0.4}$Ti$_{0.6}$O$_3$)$_{2n}$ ($n = 2, 4, 6, 8, \text{and} 16$ unit cells) superlattices with overall film chemistry PbZr$_{0.53}$Ti$_{0.47}$O$_3$. As compared to uniform films of the parent materials, the superlattice structures exhibit both large saturation polarization ($P_s = 64$ µC/cm$^2$) and dielectric susceptibility ($\varepsilon_r = 776$ at 10 kHz for $n = 4$ superlattices). AC field-dependent dielectric measurements suggest the presence of both phase-boundary- and parent-like switching events. First-order reversal curve studies reveal separate switching events for each of the parent layers in addition to an emergent phase-boundary-like interfacial layer. Ultimately, this reveals that artificial superlattices can be deterministically designed as an effective pathway for enhanced responses to external biases.

**Electric Field Induced Modification of Metal/Ferroelectric Oxide Interfaces in Composite Multiferroic Systems**

Andre R. Vantomme$^1$, Sebastien Couet$^1$, Manisha Bisht$^1$, Hiwa Modarresi$^1$, Maarten Trekels$^1$, Sergey Basov$^1$, Haraldar Pall Gunnlaugsson$^1$, Mariella Menghini$^1$, Jean-Pierre Loquet$^1$, Rudolf Rüffer$^2$, Michael Lorenz$^3$, Marius Grundmann$^3$, Vera Lazenka$^1$, Margriet J. Van Bael$^1$ and Kristiaan Temst$^1$; $^1$KU Leuven, Belgium; $^2$ESRF, France; $^3$Universität Leipzig, Germany

In composite multiferroics, magneto-electric (ME) coupling – e.g., altering the magnetic properties by applying an electric field and vice versa– can be achieved by creating an interface between a ferromagnetic and a ferroelectric compound. The induced magnetoelectric coupling originates from strain transfer and strongly depends on the structural and chemical features at the interface. In order to realize structurally stable metal/oxide interfaces for electronic device applications or to realize composite multiferroics with significant ME coupling, it is therefore important to understand the interface properties and to identify how the interface is modified in the presence of an external electric field.

In our work, we have studied the evolution of the magnetic spin structure and the Fe oxidation state at the interface using Fe/LNO (LiNbO$_3$) and Fe/BTO (BaTiO$_3$) as two model systems for ferromagnetic (FM)/ferroelectric (FE) interfaces. To this end, we relied on the isotope-sensitivity of Mössbauer spectroscopy and nuclear resonant scattering (NRS) of synchrotron radiation, which allows to isolate the signal of an approx. 1 nm thin Fe layer at (or near) the FM/FE interface. Doing so, the chemistry and magnetism at the interface can be in situ probed, while an electric field is applied.

The results show that application of a large enough electric field induces the formation of a thin magnetically dead layer at the interface between the metal and the FE oxide due to ion transport across the interface. Remarkably, the final interface state depends on the polarization history of the system. In turn, this magnetically dead layer results in an irreversible decrease of the magneto-electric coupling. With recent NRS measurements, we have identified the values of the critical field above which interface mixing occurs, for both Fe/BTO and Fe/LNO systems, to be of the order of 400 kV/m [1].

Based on our experimental findings, a model was proposed [1,2] for the effect of an applied electric field on the metal/FE oxide interface. Due to the work function difference between the metal and the oxide, a built-in electric field emerges at the interface during the growth of the metal layer onto the FE oxide. Depending on the direction of this built-in field (hence, depending on the sign of the work function difference), the direction of the applied electric field either favors ion transport across the interface or opposes it until the external field overcomes the built-in field.

We recently extended and validated this model by including a wider range of oxides. Therefore, we studied by Mössbauer spectroscopy the chemistry and magnetic state of the interfaces between an Fe layer and a number of complex oxides (with a wide range of permittivity values), before and after the application of external electric fields. Besides Fe/LNO and Fe/BTO, also Fe/BiFeO$_3$, Fe/SrTiO$_3$ and Fe/MgO were investigated. This allows us to compare
metal/ferroelectric interfaces with metal/non-ferroelectric oxide interfaces to identify the effect of the ferroelectric polarization charges on the electric field induced ion transport across the interface [3]. It is found that the nature of the oxide (ferroelectric or non-ferroelectric) determines if an external electric field will induce interfacial oxidation/reduction or not.

From our investigation, it is evident that for multiferroic studies, electric fields below the threshold values should be used to avoid significant interfacial changes due to ionic diffusion, which may deteriorate the magneto-electric coupling. These findings may have important implications not only for the further development of composite multiferroics, but also for complex oxide heterostructures in general.

References
[3] Manisha Bisht et al., to be published.

4:15 PM MT07.04.08
Scaling Effects in the Resistance-Temperature Characteristic of VO$_2$ on hBN Shingo Genchi$^1$, Mahito Yamamoto$^1$, Teruo Kanki$^1$, Kenji Watanabe$^2$, Takashi Taniguchi$^2$ and Hidekazu Tanaka$^1$; $^1$Institute of Scientific and Industrial Research, Osaka University, Japan; $^2$National Institute for Materials Science, Japan

Correlated oxide thin films often show spatial inhomogeneity in the phase states in the vicinity of the critical temperature, and consequently, the phase transitions become rather gradual. To extract the intrinsic phase transition properties of correlated oxides in device structures, therefore, spatial characterization of the phase domain sizes and the device scaling down to the domain size are necessary. Vanadium dioxide (VO$_2$) is an archetypal correlated oxide that shows a metal-insulator transition (MIT) around 340 K and of great interest for electronic device applications because the resistance changes by up-to 5 orders of magnitude across the MIT. Some studies have shown that VO$_2$ thin films consist of insulating and metallic phase domains near the critical temperature, whose sizes depend on the crystallinity determined by the growth substrates. Recently, we have demonstrated the growth of high-quality polycrystalline VO$_2$ thin films on hexagonal boron nitride (hBN) that is an insulating layered material. However, the phase domain sizes of VO$_2$/hBN have yet to be characterized. Here, we investigate the phase domain sizes and the scaling behavior of the resistance-temperature characteristics of VO$_2$/hBN. VO$_2$ thin films were grown on mechanically-exfoliated thin flakes of hBN by pulsed laser deposition. First, we employed temperature-dependent optical microscopy to characterize the domain sizes of VO$_2$/hBN, since insulating and metallic VO$_2$ are known to show different optical contrasts under visible light illumination. By optical microscopy, we found that the metallic phase domains were emerged near the critical temperature. The sizes of metallic domains were observed to range from several hundreds of nanometers up to a few micrometers, which are comparable to the grain sizes of VO$_2$/hBN measured by atomic force microscopy. Next, we measured the temperature-dependent resistances of VO$_2$/hBN of various sizes. We found that micrometer-scale VO$_2$/hBN showed a step-like behavior in the resistance-temperature characteristic, which reflects the MIT of individual domains in the thin film. The step-like resistance changes became more marked with scaling down to a few micrometers. Such step-like resistance changes can never be seen in a similar size of polycrystalline VO$_2$ on other substrates such as Al$_2$O$_3$ and is a unique feature of VO$_2$/hBN that consists of micrometer-scale domains.

4:30 PM *MT07.04.09
Quantifying Dynamic Processes in Ferroelectrics and Multiferroics—In Situ TEM Meets Data Science Mitra L. Taheri$^{1,2}$; $^1$Drexel University, United States; $^2$Johns Hopkins University, United States

Ferroelectric materials hold great potential for a wide range of technological advances and are an actively researched class of materials. Ferroelectric switching is governed by domain nucleation and domain wall motion. These dynamic processes are difficult to measure. Although fine-scale and local probes have provided much insight and understanding of the localized switching mechanisms, exploration on a global scale, taking into account both intrinsic and extrinsic effects on switching and interfacial phenomena, remains a challenge. This talk presents results from in-situ transmission electron microscopy (TEM) that allows for the visualization of ferroelectric domain switching at high spatial and temporal resolution. In-situ TEM allows for domain dynamics to be quantified in terms of factors such as local dislocation content, charge and point defect behavior, and strain enhanced phenomena. Many of these factors occur in one experiment, however, presenting difficulties for tracking their motion or measuring.
changes. Recent developments in direct electron detection for both imaging and spectroscopy allow for rapid acquisition of time-resolved spectral data and images at rates over 1000 frames per second. At these frame rates, signal to noise ratio is not necessarily optimal. Moreover, events that occur simultaneously can easily be “missed” with conventional image processing or data analysis tools. For these reasons, machine learning approaches are implemented to glean critical information that dictates ferroelectric and multiferroic behavior in datasets deemed too “noisy” for the naked eye. These advances present the possibility of understanding multiple factors in domain dynamics simultaneously, and thus the opportunity to tune these complex materials more predictively.

SESSION MT07.05: Poster Session: In Situ/Operando Studies of Dynamic Processes in Ferroelectric, Magnetic and Multiferroic Materials
Session Chairs: Michele Conroy, Marty Gregg, Alexei Gruverman and Sang Ho Oh
Thursday Afternoon, December 5, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

MT07.05.01
Impact of Ceramic-Target Crystallinity on Metal-to-Insulator Transitions in Epitaxial LaNiO3 Thin Films Grown by Pulsed Laser Deposition Choi Jin San1, Muhammad Sheeraz2, Jong-Seong Bae2, Jun Han Lee3, Joonyuk Lee4, Jongmin Lee5, Sanghan Lee5, Hyoungjeen Jeon5, Yoon Seok Oh3, Chang Won Ahn4 and Tae Heon Kim4; 1University of Ulsan, Korea (the Republic of); 2Korea Basic Science Institute, Korea (the Republic of); 3Ulsan National Institute of Science and Technology (UNIST), Korea (the Republic of); 4Pusan National University, Korea (the Republic of); 5Gwangju Institute of Science and Technology, Korea (the Republic of)

In complex oxide thin-film heterostructures, a pulsed laser deposition (PLD) technique has been widely employed for the epitaxial film growth. In PLD, we note that the plasma ions generated by the laser ablation of the ceramic target straightly move to the opposite side and then, adhere to the surface of a heated single-crystal substrate forming an epitaxial film layer eventually. Then, understanding such a dynamic process in PLD film growth is of practical interest in aspect of the high-crystalline thin-film fabrication. And, the physical properties of the as-grown films are significantly affected by the crystallinity of the initial ceramic target used for the PLD. However, the detailed studies on the relationship between the ceramic-target crystallinity and the linked physical properties have been rare. In this work, we demonstrate the effect of ceramic-target crystallinity on the metal-to-insulator transition in rare-earth nickelate thin films epitaxially grown by PLD. We first prepared two LaNiO3 ceramic targets with different crystallinity and then, visualized their surface morphology and the spatial distribution of local stoichiometry in these two LaNiO3 targets. Using various spectroscopic analyses, we microscopically examined how the target crystallinity directly affects the electrical transport properties in epitaxial LaNiO3 thin films. More details of our experimental results will be presented in conjunction with a discussion about the correlation between the observed metal-to-insulator transitions and the degree of disproportionation in the Ni charge valence state.

MT07.05.02
Structure and Electronic State of Misfit Strain Induced Morphotropic Phase Boundary Shift in Pb(Zr,Ti)O3 Epitaxial Thin Films on Various Substrate Takanori Kijuchi, Takumi Shimizu, Takahisa Shiraishi and Toyohiko J. Konno; Tohoku University, Japan

PbZr1-xTiO3 (PZT) is widely used for ferroelectric and piezoelectric applications like MEMS. PZT has a morphotropic phase boundary (MPB) where rhombohedral and tetragonal phases coexist. PZT of MPB composition leads to excellent dielectric and piezoelectric properties by free rotation of spontaneous polarization in structural gradient regions (SGR) at domain walls and phase boundaries1). The density of the SGR is expected to increase by controlling size and density of domains. We have previously elucidated that MPB compositional range of Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT) and PZT thin film deposited on SrTiO3(001) (STO) single crystal was extended in comparison with PMN-PT and PZT bulk crystals, and that nano-sized domains were formed due to residual strain induced by misfit dislocations3,4). This revealed that we could control the phase stability and domain structure by utilizing elastic field. The objective of this research is to elucidate the effect of elastic field on phase stability and domain structure in MPB composition of PZT thin films from the viewpoint of microstructure. The
target of this research is to elucidate the effect of the local strain around defects on the formation of the SGR and MPB compositional range, which leads to intensify the properties of the films. XRD 2θ-ω profiles and an electron diffraction patterns of PbZr0.3Ti0.7O3 (PZT30/70) on KTaO3 (KTO) thin films prepared by CSD method using MOD solutions with excessive 10 at% Pb indicated the cube-on-cube epitaxial relationship between the film and the substrate. The film involves only a perovskite phase with no pyrochlore phase. HAADF-STEM image and the strain map by geometric phase analysis of PZT30/70 on KTO. The interface between PZT30/70 and KTO interface is coherent without misfit dislocation owing to the little lattice mismatch of about 0.01 for the rhombohedral phase and about 0.005 for the a-axis of the tetragonal phase of the film. The volume dilatation map, which means the average of the normal strain both of the in- and out-of-plane directions, showed that two phases with different volume coexisted. The normal strain map in out-of-plane direction revealed that 90°domains of tetragonal phase were formed around the interface and that two-layer structure in out-of-plane direction. The tetragonal and the rhombohedral phases were dominant at the bottom region the upper region of the film, respectively. Then, MPB composition is around Zr/Ti=30/70. From our early studies on PMN-PT and PZT epitaxial films on STO, 90°domains of tetragonal phase nucleated at misfit dislocations in the semicoherent interface. However, the result on the PZT epitaxial films on KTO shows that the growth of 90°domains needs no misfit dislocation, which is corresponding to the PTO epitaxial films on STO with little lattice mismatch of 0.01 for a-axis. The strain map of normal strain in the in-plane direction shows that tetragonal phase grew in the out-of-plane direction from the edge of 90°domains. This result suggests that the edges of 90°domains also act as the nucleation sites of phase boundaries which plays the role of the SGR, indicating that the density of two kinds of SGR, i.e. phase boundaries and domain walls, can be extended by increasing 90°domain population.

Acknowledgements
This study was conducted with the support of JSPS KAKENHI Grant Numbers JP19H02421, JP19H04531, JP17K18970, JP17H05327 and Kato Foundation for Promotion of Science.

References
3) T. Kiguchi et al., 56, 10PB12 (2017).

MT07.05.03 In Situ and Ex Situ Studies on the Formation of Orthorhombic Phase in HfO2-Based Thin Films Takahisa Shiraishi, Takanori Kiguchi and Toyohiko J. Konno; Tohoku University, Japan

HfO2-based fluorite-type oxides are well-known as polymorphic materials (Monoclinic, Tetragonal, and Cubic phases). In recent years, ferroelectricity has been discovered in HfO2-based thin films containing a metastable orthorhombic phase (O-phase), and these materials have attracted much attention for future ferroelectrics. Since the O-phase is obtained by rapid thermal annealing of amorphous HfO2-based films deposited at room temperature, the crystallization and formation mechanisms of the film has been of great interest. In fact, the selection of crystalline phases depends on the condition of rapid thermal annealing due to polymorphism of HfO2-based oxide family. It is, hence, important to clarify the relationship between the annealing conditions and the resultant crystalline phase, including the O-phase. In this study, we investigated the influence of the annealing conditions on the crystalline phase(s) of HfO2-based thin films, with a particular emphasis on the formation of O-phase.

20 nm-thick (Hf,Ce)O2 films were deposited on (001) yttria-stabilized zirconia (YSZ) substrates by ion-beam sputtering. The deposition was carried out at room temperature in Ar atmosphere, then as-deposited films were annealed under various conditions (annealing time and temperature) in N2 atmosphere. The crystal structure of the deposited films was investigated by X-ray diffraction (XRD) and scanning transmission electron microscope (STEM).

XRD measurement confirmed that as-deposited films are amorphous, while in-situ XRD measurement showed that as-deposited films completely crystallized at a temperature above 600 °C. The lattice constants estimated from XRD 2θ-ω patterns changed discontinuously with decreasing temperature, suggesting that a phase transition has occurred. STEM observation for the annealed films revealed that the crystallization began at the film/substrate interface. We also found that the crystalline phase of the annealed films varied with annealing temperature, and most importantly, observed that the number of O-phase domains increased with increasing annealing time. The resulting (Hf,Ce)O2 films exhibited multidomain structures composed of the O-phase. We show that the optimum microstructure can be controlled by tuning the annealing condition.
This research was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI Grant No. 19K15282. In addition, this work was supported by the Murata Science Foundation and the Nippon Sheet Glass Foundation for Materials Science and Engineering.

MT07.05.04

Ferroelectric Domain Switching Behavior in the (110) Orientated BFO Film Yangyang Zhang¹², Myung-Geun Han², Nagarajan Valanoor¹ and Yimei Zhu²; ¹University of New South Wales, Australia; ²Brookhaven National Laboratory, United States

Investigation of reliable or non-volatile information storage has become an irresistible attraction in the field of modern electronic technology [1,2]. As ferroelectric domain walls are one to two orders of magnitude thinner than magnetic domain walls, exploration of switching properties and stabilization of ferroelectric domains can open a way from microelectronics to nanoelectronics, that is, it can help achieve higher information storage density [3]. Here, we focus on the (110) orientated BFO film, where the compression coming from the STO substrate can suppress certain ferroelastic switching. In order to observe the real-time domain evolution, in situ electrical biasing in transmission electron microscope (TEM) is applied. During the experiment, the switching processes including nucleation at the interface, propagation and growth has been captured. Moreover, using double-spherical aberration corrected TEM, the activation of domain switching near the antiphase boundary (APB) and the stabilization of 180° domain walls at the final state maintained by flux closure are also revealed down to atomic scale. Our study sheds light on switching performance of the BFO film grown on (110) orientated substrate and is expected to provide a potential pathway for future design of information storage devices.

References

MT07.05.05

Ferroelectricity and Temperature Dependent Dielectric Response in Rare Earth Doped Lead Zirconate Titanate Nano Crystalline Films Mohan K. Bhattarai, Karuna K. Mishra and Ram S. Katiyar; University of Puerto Rico, Rio Piedras, United States

Rare earth doped lead zirconate titanate (PZT) nano crystalline films have excellent dielectric, ferroelectric, and piezoelectric behavior and are useful for memory and energy storage devices. Herein we report rare earth La³⁺ and Sc³⁺ cation doped PZT thin films and studied their ferroelectric properties and energy storage capacity. The nano films of (1-y)[PbZr0.53Ti0.47] y[La₁₋ₓScₓ]O₃₋δ with y = 0.10 and 0 ≤ x ≤1, were fabricated by using pulse deposition method on La₀.₆₇Sr₀.₃₃MnO₃ (LSMO) coated MgO (100) substrates employing a KrF excimer laser of wavelength 248 nm. The thickness of the grown films, measured using profilometer, was ~ 350 nm. We observed (100) oriented thin films stabilized in tetragonal perovskite phase from analysis of x-ray diffraction data. The Raman spectra of these thin films at different temperatures suggest the nucleation and evolution of the polar nano-regions dispersed in a nano polar matrix attributed to their relaxor behavior. We observed the surface roughness of films between 3 - 10 nm from analysis of Atomic force microscopy. The film capacitors fabricated as LSMO/PLZTS/Pt were investigated for its dielectric and ferroelectric behavior. The temperature dependent (100-650 K) dielectric measurement in the frequency ranges 10²-10⁶ Hz, revealed dielectric constant ε' ~ 700-2000 with a comparatively low loss. Ferroelectricity of these thin films were evident well saturated hysteresis loops at room temperature recorded at several frequencies. The high dielectric constant, low losses and excellent ferroelectricity of nanostructured film capacitors suggest their potential application in electronic devices.

MT07.05.06

Tuning Two-Photon Absorption Effect in Magnetic Nanoparticles by Employing an External Magnetic Field—Ultrafast and Magnitude Measurements Eduardo S. Goncalves¹, Jonathas Siqueira¹, Wagner Wysses¹, Kinnari Parekh², Cleber Mendonca¹, Antônio M. Figueiredo Neto¹ and Leonardo de Boni¹; ¹University of São
Colloidal dispersions of magnetic nanoparticles (NP) were synthesized at the University of São Paulo, Brazil, and at Charotar University of Science and Technology, India, based on manganese-zinc ferrites, (Mn0.5Zn0.5Fe2O4). Solutions containing nanoparticles with spherical (MZS) and cubic (MZC) nanoparticles were studied by means of the Z-Scan technique in the open-aperture configuration, allowing the determination of the two-photon absorption cross-section ($\sigma_{2PA}$). Since the nanoparticles are in the superparamagnetic state and free to rotate within the liquid carrier, external magnetic fields, with magnitudes between 0 Oe and 3100 Oe, were applied in order to orient the nanoparticles in solution, aligning the axis of easy magnetization of each NP to the external field. These experiments were performed with the incident beam polarization in the same direction to the magnetic field lines, herein called parallel configuration, and in the case in which the polarization and the magnetic field directions were orthogonal, the perpendicular configuration. To better understand the nonlinear absorption, verified during the Z-Scan measurements, the electron dynamics were investigated by a spectrally resolved femtosecond transient absorption (without the presence of external magnetic field). Samples were pumped at 390 nm (region in which the samples present a large absorption) with different pulse energy and the relaxation dynamic was probed by using an ultrashort white-light continuum pulse (450 nm to 750 nm). In addition to these measurements, the pump beam was changed for 780 nm in order to check the dynamic induced by two-photon absorption. It is important to say that in the absence of magnetic field, linear absorptions of both samples are the same, as expected since the NPs have the same constituents. The magnetic field effects on the linear absorption was also evaluated and no changes were verified regardless the field presence, indicating that the nanoparticles are being oriented but not forming bigger structures that would scatter the light. The two-photon absorption cross-section in the absence of external magnetic field was measured as $\sigma_{2PA}^0$=18.0(6) GM for spherical nanoparticles and 17.0(7) GM for the cubes. The measured values are compatible with each other within the experimental errors. For both studied nanoparticles, the 2PA cross-section measured in the parallel configuration presented an increment in the value, while in the perpendicular configuration, the measured value decreased when compared to $H=0$. In the presence of magnetic fields, nanoparticles tend to align their magnetic momentum to the external field and, in consequence, there is an alignment of crystallographic planes of the material. Thus, these experiments put in evidence the optical anisotropy in the two-photon absorption of our ferrite nanoparticles, since in the parallel configuration components of the third-order nonlinear tensor was measured alongside the magnetic momentum direction, while in the perpendicular configuration, in the two dimensions perpendicular to that direction, that are equivalent. When there is not magnetic field applied, the nanoparticles are randomly oriented and the measurements correspond to an average over the three orthogonal directions. Femtosecond transient absorption measurements revealed an ultrafast relaxation process containing at least two separated dynamical processes, one shorter than 5 picoseconds, possible related to the hot electron relaxation or exciton-exciton annihilation, and a second one, much longer, may be related to the trapped electron on the conduction band. Also, the longer lifetime may be associated to the relaxation from the conduction to the valence band. Same behavior was observed by pumping the samples with 775 nm, indicating that the electronic states excited by two-photon absorption may be the same as the ones excited by one-photon absorption.

**MT07.05.07**

**Nanoparticle Shape Effect on the Determination of the First-Order Hyperpolarizability Anisotropy of Magnetic Colloids**

Eduardo S. Goncalves¹, Leandro Cozza², Wagner Wysses¹, Kinnari Parekh³, Cristiano Oliveira¹, Antônio M. Figueiredo Neto¹ and Leonardo de Boni²; ¹University of São Paulo, Brazil; ²University of São Paulo, Brazil; ³Charotar University of Science & Technology, India

Colloidal dispersions of magnetic nanoparticles were synthesized at the University of São Paulo, Brazil, and at Charotar University of Science and Technology, India, based on manganese-zinc ferrites, (Mn0.5Zn0.5Fe2O4). Solutions containing nanoparticles with distinct shapes (MZS, containing spherical nanoparticles, and MZC, composed of cubic NPs) were studied by means of the hyper-Rayleigh scattering (HRS) technique, allowing the determination of the optical second harmonic generation, defined as $\beta$. The size distribution and shape of nanoparticles were determined through small angle x-rays scattering (SAXS). Since the produced nanoparticles are free to rotate within the liquid carrier, an external magnetic field was applied in order to orient the particles in solution. Experiments with applied magnetic field were performed both in the parallel configuration (when the incident laser beam polarization was parallel to the magnetic field lines) and in the perpendicular case (where the polarization and the field directions were orthogonal). Furthermore, the linear attenuation spectrum was measured in the presence and absence of external magnetic field and it shows no changes regardless the field presence, indicating that the nanoparticles are being oriented but not forming bigger structures that would scatter the light. This is
supported by the SAXS data, also measured in the presence of magnetic field, that demonstrate the formation of small linear aggregates, composed by a few nanoparticles. In the absence of magnetic field the linear attenuation spectrum of both samples is the same, as expected since the NP's have the same constituents. In this case, the hyperpolarizability was measured, for spherical nanoparticles, as \( \beta^0 = 9.5(2) \times 10^{-28} \text{cm}^5/\text{esu} \), while for cubic ones, \( \beta^\square = 7.8(1) \times 10^{-28} \text{cm}^5/\text{esu} \). For both studied nanoparticles, optical second harmonic experiments were performed in the presence of external field in the parallel configuration. In this condition, an increase in the value was verified, that is, for spherical nanoparticles (MZS), \( \beta^0 \parallel = 10.1(2) \times 10^{-28} \text{cm}^5/\text{esu} \), and for MZC sample, \( \beta^\square \parallel = 8.1(2) \times 10^{-28} \text{cm}^5/\text{esu} \). On the other hand, a slight decrease on the hyperpolarizability value was measured for experiments performed on the perpendicular configuration, \( \beta_\perp = 9.3(3) \times 10^{-28} \text{cm}^5/\text{esu} \) for MZS and \( \beta^\square \perp = 7.4(2) \times 10^{-28} \text{cm}^5/\text{esu} \) for the cubes. For cubic nanoparticles the anisotropy in the first-order hyperpolarizability \( \delta \beta = (\beta_\parallel - \beta_\perp) / \beta_\parallel \) was 8.2 while for the spherical nanoparticles, 7.6%. In the presence of magnetic fields, nanoparticles tend to align their magnetic moment to the external field, in consequence, there is the alignment of crystallographic planes of the material. Therefore, in the parallel configuration the first-order hyperpolarizability was measured alongside the magnetic momentum direction, while in the perpendicular configuration, in the two dimensions perpendicular to that direction, that are equivalent. When there is not magnetic field applied, the nanoparticles are randomly oriented and the measured hyperpolarizability corresponds to an average over the three orthogonal directions. This can be verified calculating the weighted average of the hyperpolarizability in the presence of external field, that is, \( <\beta> = 1/3(\beta_\parallel + 2\beta_\perp) \), so \( <\beta^0> = 9.6(3) \times 10^{-28} \text{cm}^5/\text{esu} \) and \( <\beta^\square> = 7.7(2) \times 10^{-28} \text{cm}^5/\text{esu} \), in both cases compatible with the measured value for the system without magnetic field. This demonstrates the shape dependent anisotropy in the second-order nonlinear properties of ferrite NP's, opening the possibility of the development of optofluidic devices, associating magnetic nanoparticles in solution and optical elements as i.e. optical fibers, as optical magnetometers, that would allow the determination of the field magnitude and direction, as well as in information propagation since there are three possible states and light intensities for a system composed by magnetic NP and an external magnetic field.

MT07.05.08

Study of the Doping Effect of Yttrium on the Electrical Properties of BaTiO3 Synthesized by Spark Plasma Sintering Adl Alshoaibi; King Faisal University, Saudi Arabia

The effect of Y2O3 doping on the structure, transport, dielectric, and relaxation properties of BT ceramics will be investigated. The possibility of formation of an extensive range of solid solution regions and the formation of a polymorphism of Y-doped BaTiO3 Will be studied. In this study, coarse-grained and nano-sized grain BT ceramics will be synthesized by spark plasma sintering. Conventional sintering is expected to produce micro-sized grained ceramics, whereas spark plasma sintering of BT nanopowder could produce nanocermics/fine grained ceramics. The structure of the BT nanocermics will be investigated by X-ray diffraction, whereas FE-SEM, Raman, and AFM will determine the grain size and the chemical composition of the ceramics. The photocurrent characteristics of BT nanocermics will be studied by using Quantum efficiency and solar systems. The transport dielectric and relaxation properties will be studied by impedance spectroscopy measurements over wide ranges of temperatures and frequencies. Thermally stimulated depolarization current (TSDC) measurements are interesting and helpful technique that will be used to study the relaxation properties due to the defects in the studied ceramics. We will also perform investigations using theoretical calculations based on density functional theory (DFT) to study the role of cation substitution on structural and electronic properties in BaTiO3.

MT07.05.09

Optical Spectroscopy, Microscopy and Structural Characterization of Monodisperse Lanthanide Doped Titanium-Containing Perovskites for Optoelectronic, Piezoelectric and Ferroelectric Applications Benard Kavey; Central Michigan University, United States

Lanthanide doped-titanium-containing perovskite nanocrystals, \( \text{M}_{1-x} \text{Ln}_x \text{TiO}_3 \) (where \( \text{Ln} = \text{La}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Ti}^{3+}, \text{Yb}^{3+} \) and \( \text{M} = \text{Ba}^{2+}, \text{Sr}^{2+} \)), have have been synthesized via a solvothermal route at relatively low temperatures, \( T < 180 \degree \text{C} \). The versatility of the synthesis route has made it possible to synthesize similar sizes (20 nm) and shapes (cuboidal) for all Ln-dopant compositions and as such, trends in their electronic and optical properties can be explored. Without the need for high temperature annealing, X-ray diffraction patterns of the as-synthesized nanocubes such as \( \text{Ba}_{0.97} \text{Ti}_0.03 \text{O}_3 \), \( \text{Ba}_{0.97} \text{Er}_0.03 \text{Ti}_0.03 \) and \( \text{Ba}_{0.97} \text{Dy}_0.03 \text{Ti}_0.03 \) powders synthesized at 150 \degree \text{C} showed highly crystalline, single phase and pure nanocrystals. Transmission electron microscope coupled with an EDS-detector was used to map and quantify the actual composition and stoichiometric ratios of the lanthanide ions.
in the crystal lattice. Also, a fluorescence emission spectroscopy of the M1,χLnχTiO3 nanocubes colloidal solution showed interesting emission spectra such as an up-conversion of the excitation wavelength for some specific Ln-dopant compositions. Temperature dependent Raman spectroscopy was used to analyze the local structural distortions within the crystal lattice as well as the tetragonality of the ferroelectric phase. We observed that for certain compositions such as Ba0.95Yb0.05TiO3, the tetragonality increases with increasing temperature but decreases sharply after the transition temperature; 80 °C. Advanced microscopy techniques such as atomic force microscopy (AFM), piezoelectric force microscopy (PFM) and magnetic field PFM were used to study the electric and magnetic field response of the nanocrystals. With increasing percent compositions of the same Ln-dopant type, we observed a general trend in the ferroelectric and piezoelectric responses of the as-synthesized M1,χLnχTiO3 nanocubes. The general trend and values of piezoelectric displacement coefficient (d33) for all sample compositions has been measured at ambient and high temperature conditions.

MT07.05.10
Probing the Dynamics of Nanoscale Thermal Transport with Ultrafast Electron Diffraction Matthew Gorfien1, Xuan Wang2 and Jianming Cao1,3; 1Florida State University, United States; 2Institute of Physics, Chinese Academy of Sciences, China; 3Shanghai Jiao Tong University, China

The fabrication of smaller, denser, and higher frequency electronic devices has resulted in the need to completely understand and control thermal transport at the nanometer scale [1, 2]. At the nanoscale shorter than the heat diffusion length, thermal transport in semiconductor devices is dominated by phonon scattering across interfaces between the semiconductor heterojunctions and is quantified by the thermal boundary conductance (TBC). We investigated the kinetics of thermal transport across a GaAs/AlGaAs epitaxial interface using timeresolved Reflection High Energy Electron Diffraction (TR-RHEED). In the experiments, the temperature imbalance is created by ultrafast heating the top GaAs nanofilm selectively with 800-nm femtosecond optical pulses and monitored by tracing its temperature evolution with TR-RHEED. The thermal transport kinetics observed with TR-RHEED was also simulated using two separate models: a heat conduction and three-temperature model, providing a method of measuring and extracting the thermal boundary conductance in semiconductor heterostructures. The TBC was found to agree well with the Diffuse Mismatch Model at lower temperature imbalance across the interface, but start showing different behavior when the temperature of the top GaAs nanofilm is higher than the Debye temperature, opening up questions about the mechanisms governing interface heat transfer under highly non-equilibrium conditions.

References

SYMPOSIUM MS01
Extreme Mechanics
December 2 - December 6, 2019

Symposium Organizers
Basile Audoly, CNRS et Ecole polytechnique
Irene Beyerlein, University of California, Santa Barbara
Chiara Daraio, California Institute of Technology
Avinash Dongare, University of Connecticut
SESSION MS01.01: Session I
Session Chairs: Chiara Daraio, Lihua Jin and Claire Lestringant
Monday Morning, December 2, 2019
Hynes, Level 1, Room 109

8:00 AM *MS01.01.01
Modeling Shape Transforming Truss Metamaterials with a Geometrically Exact Beam Model Claire Lestringant and Dennis Kochmann; 1ETH Zurich, Switzerland; 2California Institute of Technology, United States

Slender beams undergo large deformations when subjected to moderate mechanical forces: they are therefore promising building blocks for the design of multistable, reconfigurable metamaterials. Combining these structures with active materials through advanced additive manufacturing techniques paves the way towards engineering truss metamaterials with properties tunable in time (so-called 4d-printing).

In this presentation, I use a discrete, geometrically exact beam formulation that can efficiently and accurately simulate the nonlinear deformation of slender beams featuring complex material behaviors, such as those found in the design of such metamaterials. I implement a numerical method that fully decouples the kinematics from the material behavior, and can handle finite rotations as well as a wide class of constitutive laws depending on the stretching, flexural and torsional strain and strain rates.

After presenting the underlying geometric description of framed curves, and the treatment of inelastic material models using variational constitutive updates, I will show examples covering different constitutive laws, including rate-dependent behaviors. These benchmark problems feature instabilities, nonlinear geometric couplings between bending and twist, as well as natural curvature. I will show that the convergence of the numerical method competes with classical nonlinear beam formulations.

Finally, I present an extension to beam assemblies and trusses with rigid joints, which I demonstrate on a set of examples including shape transforming structures, triggered by thermal and mechanical stimuli.

8:30 AM *MS01.01.02
Designing Nano-Architected Materials for Extreme Mechanical Properties Lorenzo Valdevit, Jens Bauer, Cameron Crook, Anna Guell Izard, Meng-Ting Hsieh, Yunfei Zhang and Marti Sala; University of California, Irvine, United States

Architected materials have long been explored for their ability to achieve extremal combinations of mechanical and functional properties. Optimal design of the topology has allowed numerous demonstrations of mechanical metamaterials with unique combinations of high stiffness, strength, energy dissipation, low density, and many other properties. More recently, progress in additive manufacturing has enabled fabrication of nano-architected materials, which can achieve far superior properties via combined optimization of their unit cell topology and base material micro/nano-structure. This presentation will cover recent progress in the design, manufacturing and characterization of ultralight nano-architected ceramic materials with unprecedented combinations of strength, energy absorption and high temperature stability. Lattice, plate and shell-based architected materials with nanoscale topological features are fabricated by two-photon polymerization Direct Laser Writing (DLW). The polymeric preforms are subsequently pyrolyzed in vacuum, resulting in a ceramic metamaterial (carbon or silicon oxycarbide, depending on the choice of resin). The effect of the processing parameters on the microstructure and mechanical properties (ultimate strength and strain to failure) of the resulting constituent materials is discussed first. Subsequently, we present ceramic mechanical metamaterials with various topologies and relative densities, and demonstrate extremal combinations of mechanical properties. In particular we show that with proper choice of topology, ceramic nano-architected materials can exhibit progressive failure, dissipating large amounts of energy. Finally, opportunities for scalability are discussed.

9:00 AM MS01.01.03
A Next Generation Auxetic Reinforced Self-Confining Concrete Metamaterial Simos Gerasimidis, Andrew
Among the major limitations of concrete as a building material is its brittle behavior, which provides little warning prior to failure. Lateral confinement of concrete, which involves applying pressure on the concrete element perpendicular to the direction of loading, is a well-known technique that is commonly used to improve the strength, ductility and other properties of reinforced concrete members. Until today, the techniques used for applying confinement pressure in concrete can be divided into two main types based on the method of applying the confinement pressure. Passive confinement employs internal transverse steel reinforcement, external steel jackets or fiber-reinforced jackets, with which the confining pressure is generated only as a direct result of the lateral dilation of concrete under loading. Active reinforcement on the other hand has been demonstrated as a much superior confinement technique mainly because in this case, the confinement pressure is applied on the concrete before loading and is more effective in delaying the dilation of concrete structures. However, all these techniques have not really altered the concrete material itself. The focus of this work is to build upon the work already accomplished in cellular auxetic architected metamaterials and harness their auxeticity to develop a next generation high-performance self-confining concrete metamaterial.

Fundamental mechanics work has led to the creation of groundbreaking families of lattice metamaterials with mechanical properties that are unachievable without the novel architectures that form the basis of such structures. New internally structured metamaterials have been developed in the last two decades which possess unusual properties such as a negative Poisson’s ratio. These internally structured materials have also been expanded to 3D metal lattice geometries with high stiffness and strength which can be used as reinforcement in the new concrete metamaterial. When encased in concrete, the auxetic reinforcement will apply confining pressure on the concrete as soon as compression is present and therefore the volumetric expansion of the two-phase material will be controlled. This mechanism dramatically increases the strength and ductility of reinforced concrete members. The new self-confining two-phase metamaterial is different to the passively confined reinforced concrete since the confinement in the new material is not a result of the concrete volumetric expansion but a direct result of the deformation of the reinforcement under axial loading. The main difference between the new material and active confinement techniques is that with the new material there is no need for confinement of concrete prior to axial loading. The presence of axial loading alone activates lateral confinement through the auxeticity of the reinforcement.

Shape-Morphing Shells with Programmed Temporal Behaviors

Smart materials have enabled self-directed deformations of initially flat geometries into 3D shapes. However, most self-morphing structures are not capable of time-dependent actuation paths. To achieve more complex target geometries and avoid self-collisions, it is critical to locally embed target curvatures and morphing rate information in shells prior to their deployment. While some structures with intrinsic actuation capabilities have incorporated temporal programming through the sequential folding of discrete hinges, these examples do not allow for changes in Gaussian curvature. Here, we demonstrate a method for encoding temporal morphing behaviors in architected bilayer shells that assume complex shapes and doubly curved geometries. Each shell layer is a tessellation of polymeric unit cells that soften in water at rates locally prescribed by a non-periodic mesostructure. The shells contract due to the effect of a pre-stretched elastic membrane, and stiffness differentials across each of their shell layers, inducing curvature changes. Morphing is locally finalized by rigid contacts between adjacent elements, locking shells in their target geometries. Mesoscales are encoded to perform specified behaviors through an inverse design tool that is based on a data-driven model of unit cells’ temporal responses.

Phase-Transforming Metamaterials

Mechanical metamaterials are materials with micro-architectures, which give rise to unusual mechanical properties that are difficult or impossible to achieve in homogeneous materials. In this work, new types of phase-transforming metamaterials are developed to demonstrate domain switching, shape-memory effects, and energy absorption. In the first design, a metamaterial composed of an elastomer with periodic holes can undergo a phase transformation when
subjected to a compressive load, yielding a large transformation strain. We show that such phase transformations can be broadly tuned by changing the geometric parameters of the metamaterial. Examples of domain switching and shape memory effects in such a metamaterial are demonstrated. In the second design, a metamaterial composed of a compliant elastomer and rigid granular particles is proposed as a reusable energy absorber. When the metamaterial is subjected to an external load, it undergoes phase transformations between the multistable states. Correspondingly, the input energy is partially trapped as elastic energy in the elastomer, and partially dissipated by friction between the granular particles, forming hysteresis between the loading and unloading force–displacement curves. Through tuning the structural design of the metamaterial, the pretension and stiffness of the elastomer, and the size of and friction between the particles, a vast design space is achieved to program the mechanical behavior of the metamaterial. Impact tests confirm the energy-absorbing capability of the proposed metamaterial.

10:00 AM BREAK

10:30 AM *MS01.01.06
Undulating Sheets are Shape-Switching Metamaterials with Memory Martin van Hecke; Leiden University & Amolf, Netherlands

We present thin, undulating sheets that switch rapidly and reversibly between flat, rolled, helixing and crumpled shapes under loading. While these complex states are stable when the undulations are big and the sheet is slim, switching back to the rest state is easy under external forcing: an ideal starting point for multi-shape materials.

We show that the sheets' reversible shape-switching is caused by the occurrence of many local, interacting, and hysteretic pop-through defects. We classify the various stable shapes into distinct shape families, and find a transition from rolled to helixing states depending on sheet aspect ratio. We also study how mechanically trained memory arises under repeated compression of the sheets. Our work provides a novel platform for designing multi-shape metamaterials with memory.

11:00 AM MS01.01.07
Stretchable Mechanical Metamaterial Fibers with Extreme Toughness Christopher B. Cooper and Michael Dickey; North Carolina State University, United States

This talk will discuss the use of core-shell structures to create tough mechanical “metamaterial-like” fibers that stretch to large tensile strains. Tough materials have large areas under a stress-strain curve. Thus, materials that require high stress to extend to large strains have high toughness. Metals require large stress in extension but fail at low strains. Elastomers require low stress yet can extend to high strains. Here, we combined these two properties using a metal (core) and elastomer (shell) fiber structure to achieve a tough material that requires high stress to extend to large strains. The core consists of gallium, which can be injected into the fibers and then solidified at room temperature. Extending these fibers causes the metal to fracture at high stress. Rather than experiencing catastrophic failure upon fracture of the metal, the elastomer shell holds the fibers together and additional strain, counterintuitively, causes additional fracturing of the metal. Polymer “bridges” (i.e. elastomeric shell with no metal core) form between the fractured metal segments, as the metal core segments continue to fracture into smaller pieces and dissipate energy. Stress is transferred from the elastomeric shell to the metal core segments via the core-shell interface. Although there are a variety of ways to create tough materials (including chemical and physical approaches), this approach is interesting because of its simplicity and the fact that the fibers are conductive and can self-heal. These types of tough materials have applications in stretchable electronics and soft robotics because of their ability to conduct electricity, sense touch, extend to large strains (500%), and provide toughness in a manner that is reminiscent of human skin. This talk will discuss this new approach to creating tough stretchable materials for future extreme materials design.

11:15 AM MS01.01.08
Experimental Realization of a New Zero Poisson’s Ratio Structure Vladimir Gaal1, Varlei Rodrigues1, Socrates O. Dantas2, Douglas S. Galvao3 and Alexandre F. Fonseca1; 1State University of Campinas, Brazil; 2Universidade Federal de Juiz de Fora, Brazil

A structural parameter proposed almost two centuries ago, the so-called Poisson’s ratio (PR), is still a very effective
way to characterize the mechanical behaviors of materials and structural models. PR is defined as the ratio of transverse strain to longitudinal extension strain along the direction of a stretching force. The vast majority of materials present positive PR, i.e. they laterally expand (shrink) when subjected to compressive (tensile) strains. Materials with negative (the so-called auxetic materials [1]) or zero PR can be found in nature and man-made and have many technological applications, such as sensors and actuators. In particular, null PR materials, i.e. the ones that neither contract nor expand laterally due to axial strains, have received much attention towards applications in different fields as medicine and aeronautics. The most common examples of zero PR materials are gases and cork [2]. Cork has inspired the development of semi-reentrant honeycomb-like structures [3], which have become the widely used paradigm for constructing zero PR structures. In this work, we have designed and experimentally realized a new type of topological model that presents null PR under compression. Our model is not based on either reentrant honeycomb or hexagonal structures. It is composed of arbitrary planar junctions of a given structural unit cell containing two main parts: two parallel rigid bars of smooth surfaces and a soft and elastic membrane or spring connecting the rigid bars. These unit cells or blocks were printed using a homemade 3D printer and randomly distributed on a surface to form sample arrays of \( m \) by \( n \) cells. Using a homemade vise, the arrays are compressed and the strains on both transversal and longitudinal measured, the obtained PR values were almost zero. These new and very simple proposed topological models present great potential for a new paradigm in creating zero or near-zero PR structures.


11:30 AM MS01.01.09
Tunable Strain Rate-Adaptive Impact Energy Dissipation via Liquid-Crystalline Elastomers Seung-Yeol Jeon1, Zeyu Zhu1, Lichen Fang1, Nicholas Traugutt2, Christopher Yakacki2, Thao Nguyen1 and Sung H. Kang1; 1Johns Hopkins University, United States; 2University of Colorado Denver, United States

Materials that can efficiently dissipate impact energy are attractive for various lightweight applications including aerospace, automotive, and personal protection. Liquid crystal elastomers (LCEs) can exhibit remarkable energy dissipation behaviors originating from the coupling of dynamics of LC molecules (Mesogens) and polymeric networks. Here, we investigated the extreme energy dissipative behavior of LCEs over a wide range of strain rates for a fundamental understanding of their strain-rate dependent energy dissipation behaviors. We synthesized main-chain LCEs based on a two-stage thiol–acrylate reaction to examine the effect of the ordering of mesogens and chain alignment on the rate-dependent dissipation behaviors. The impact energy dissipation capability was characterized through bistable structures consisting of LCE beams to have enough time for measuring the energy dissipation by reducing the peak values of acceleration even under high impact. We found that LCEs exhibited 1 to 3 orders of magnitudes higher energy dissipation compared to conventional elastomers (Polydimethylsiloxane (PDMS)) with an increase of the energy dissipation as a function of strain rate in the tested range of \( 10^{-3} \) to \( 10^{3} \) (1/s). Moreover, the strain-rate dependency was able to be controlled by the degree of alignment of mesogens within LCEs through simple control of the applied tensile strain during crosslinking. Then, we performed finite element analysis (FEA) to find the relationship between the arrangement of mesogens and strain-rate dependent energy dissipation based on Prony series parameters obtained from dynamic mechanical analysis. The results from FEA analysis showed good agreement with data from experiments at different strain rates. We envision that our findings can contribute to rationally designing and synthesizing LCE materials and structures with desired strain rate-adaptive energy dissipating capability, which will be useful for various applications including impact mitigation for aerospace, automotive, and personal protection materials and structures.

11:45 AM MS01.01.10
Graphene-Based Nanoscale Version of Da Vinci’s Reciprocal Structures Alexandre F. Fonseca and Douglas S. Galvao; State University of Campinas, Brazil

Structural reciprocity (SR) is a concept of self-supporting of load-bearing bars that together form larger mechanical resistant structures [1]. Dating back to the Neolithic, SR was found from native tepees and tents, to old bridges like the one over the Rhine that was built in the Roman Empire by Julius Caesar, and even in the drawings of Leonardo Da Vinci [2]. Commonly seen in floors or roofs, SR is also present in art, religious symbols and decorative objects. Although SR involves a mutual exchange of action and reaction between parts of the whole structure, it is also known to rely on a perfect symmetric relationship between them [1]. A structure having SR is called reciprocal
structure (RS). The main characteristics of a RS are, first, the role of supporting and being supported should not
occur in the same part of the structure, i.e., they must be separated, not overlapping like in truss bars. Second, each
element of a RS must, at the same time, support the others and being supported by the others. These two properties
make beams and two-dimensional materials very much appropriated to build RSs. Here, we propose a simple nano
version of a Da Vinci’s RS based on graphene nanoribbons. The stability and resistance against mechanical impacts
(ballistic projectile) were investigated through fully atomistic molecular dynamics (MD) simulations. We considered
different structures with three and four joins with and without RS topologies. Our MD results showed that structures
with RS topologies are more impact resistant than the ones without SR, despite the fact that the used graphene
nanoribbons are highly pliable. We discuss these results in terms of building self-sustained and resistant nano-domes
and nanocages and possible applications in nanoengineering.


SESSION MS01.02: Session II
Session Chairs: Chiara Daraio, Jonathan Hopkins and Dirk Mohr
Monday Afternoon, December 2, 2019
Hynes, Level 1, Room 109

1:30 PM *MS01.02.01
Mechanics of Optical-Tweezer Fabricated Micro-Granular Crystals Samira Chizari, Miles Lim, Michael Porter,
Sydney Austin and Jonathan Hopkins; University of California, Los Angeles, United States

The ability to engineer micro-granular crystals so that their constituent microspheres can be positioned within
lattices as desired would enable the control of extreme stress-wave propagation behavior due to the nonlinear
stiffness interactions between their microspheres. Whereas engineered granular media that consists of macro-sized
spheres (>1mm) support Hz-kHz stress waves for audible applications, engineered micro-granular crystals support
MHz-GHz stress-waves for more extreme high-energy applications. Such applications include armor that controls or
redirects the propagation of shock waves caused by explosions or high-speed impacts or acoustic lenses that
focus high-frequency phonons for underwater imaging, noninvasive surgery, and material damage detection
technologies.

Here we propose an approach that utilizes automated optical tweezers to simultaneously assemble many 1-10μm-
sized spheres at their intended locations within 3D micro-granular crystals. Unlike existing self-assembly, directed
self-assembly, or electrophoretic deposition approaches that can fabricate only a limited selection of ordered micro-
granular crystal lattices, the proposed optical tweezers approach possesses the flexibility to arrange microspheres of
different materials and sizes anywhere within a lattice to achieve high control over extreme stress-wave propagation
behavior. Moreover, the approach is automated to increase the placement accuracy and precision of the
microspheres and to dramatically increase the speed of assembly so that large test samples can be fabricated within
reasonable build-times. Once fabricated these samples, which can’t be made any other way, are tested to collected
data that is used to learn about the extreme mechanics that govern the behavior of these crystals.

We aim to present these results for both quasi-static compression tests and for dynamic laser-induced impulse force
tests conducted on differently packed micro-granular crystal lattices. The data collected is used to inform course-
grain molecular dynamic simulation models that when matched to accurately mimic the experimental results are
used to simulate numerous ‘what-if’ scenarios aimed to uncover what effects (e.g. sphere location, size, sphericity,
surface roughness, friction, electrostatic forces, adhesive forces, asperities, surface charges, and hydrodynamic
effects) govern the extreme mechanics of such crystals. This work sheds light on what mechanisms give rise to the
nonlinear stress-wave propagation behaviors of micro-granular crystals as well as those that explain how they
deform and ultimately fail.

2:00 PM MS01.02.02
Enhancing the Recoverability of Ceramic Nanolattices through Double Hollow Tube Architectures Marianna
Diamantopoulou, Thomas Tancogne-Dejean, Jeffrey Wheeler and Dirk Mohr; ETH Zurich, Switzerland

The design and fabrication of double hollow tube lattice architectures is pursued to enhance both the stiffness and recoverability of lattice materials. In essence, these structures correspond to the superposition of two truss lattices made from hollow tubes. Both trusses feature the same lattice parameters. As a result, the smaller diameter structure can be built inside a second structure of larger tube diameter. Design maps are developed through theoretical and computational analysis that express the stiffness of the proposed double hollow tube lattice as a function of the relative density and the outer-to-inner tube radius. Nanolattices with wall thicknesses ranging from 27 to 110 nm are fabricated from alumina through direct laser writing of a polymer scaffold, atomic layer deposition of alumina followed by removal of the polymer phase. In-situ compression experiments are performed on both single- and double tube configurations. While both configurations provide about the same stiffness of the same weight, a higher recoverability is observed for the new double hollow tube configurations.

2:15 PM MS01.02.03
Mechanical Behavior of Nonwoven Non-Crosslinked Fibrous Mats with Adhesion and Friction Vineet Negi and Catalin Picu; Rensselaer Polytechnic Institute, United States

Nonwoven fibrous mats are found in many applications such as cellulose nanofiber paper, electrospun polymeric fibrous scaffolds used in tissue engineering, filtration and insulation materials etc. In these materials, fibers are held together by adhesion and friction acting at inter-fiber contacts. We present a study of the mechanical behavior of random, non-crosslinked fibrous mats of nanofibers stabilized by inter-fiber adhesion. Fibers of various degrees of tortuosity, and of infinite and finite length are considered. The variation of structural parameters such as the mat thickness and the mean segment length between contacts with the strength of adhesion is determined. Mechanics in such systems has an energetic component, associated with stored strain energy in fibers, and a dissipative component, associated with friction. The dissipative component is dominant. The response to tensile loading of the mats has three regimes: a short elastic regime in which no sliding at contacts is observed, a well-defined sliding regime characterized by strain hardening, and a rapid stiffening regime at larger strains. Networks of finite length fibers loose stability during the second regime of deformation and do not exhibit stiffening. We relate the parameters that describe this behavior and the network strength to the structural network parameters. These results are relevant for the design of electrospun mats and other planar fibrous non-cross-linked networks.

2:30 PM *MS01.02.04
OPEN SLOT

3:00 PM BREAK

3:30 PM *MS01.02.05
Increasing the Structural Efficiency of Mechanical Metamaterials—Moving from Truss- to Plate-Lattice Architectures for Optimal Stiffness and Energy Absorption Thomas Tancogne-Dejean, Marianna Diamantopoulou, Colin Bonatti and Dirk Mohr; ETH Zürich, Switzerland

Beams, shells and plates are used as the basic building blocks of lattice materials. It is shown through combined theoretical and numerical analysis that the choice of the elementary building block strongly influences the mechanical performance of mechanical metamaterials. Increases in stiffness of up to 200% are observed when building isotropic lattices from plates instead of beams (while keeping the mass unchanged). Furthermore, it is shown that shell-lattices are ranked between truss- and plate-lattices as far as stiffness and yield strength is concerned. However, from the point of view of fatigue strength and impact energy absorption, shell-lattices might have a substantial advantage. In addition to deriving the effective yield surfaces through homogenization, the plastic anisotropy of elastically-isotropic metamaterials is analyzed in detail. All theoretical results are also validated through detailed finite element simulations. Selected metamaterials are additively fabricated from polymers using two-photon lithography and from stainless steel using selective laser melting. Static experiments are performed to confirm the theoretical modulus and yield stress estimates for uniaxial tension, compression and shear. Furthermore, dynamic experiments are performed on a Split Hopkinson Pressure Bar (SHPB) system to determine the effect of strain rate on the specific energy absorption response of mechanical metamaterials of 20% relative density.

4:00 PM MS01.02.06
Extraordinary Energy Absorption via High Rate Deformation of Multiwall Carbon Nanotube Mats

Edwin L. Thomas1, Jinho Hyon1, Owale Lawal2 and Ramathasan Thevamaran3; 1Rice University, United States; 2Eglin Air Force Base, United States; 3University of Wisconsin–Madison, United States

We present the ballistic energy absorption characteristics of thin (100-250 nm) mats comprised of an interconnected network of multiwall carbon nanotubes (MWCNT) investigated using a micro-projectile impact test with incident velocities from 300-900 m/s. The quasi-static properties of the MWCNT mats are quite modest but at the extreme strain rates and large strains of ballistic impact, a distinctive set of morphology dependent deformation mechanisms leads to extraordinary energy absorption. As the spherical projectile engages the film, the unoriented bundles of MWCNT tubes rotate, straighten, align and translate into the impact region, dissipating the kinetic energy of the projectile via frictional forces and elastic stretching energy of the principal tubes until axial fracture occurs. The specific energy absorption depends on impact velocity and film thickness and can range from 9-12 MJ/kg, much greater than any other material.

Elastocapillary Assembly of Cellular Structures

Shucong Li, Bolei Deng and Joanna Aizenberg; Harvard University, United States

Self-assembly is becoming increasingly important as a bottom-up method for building novel structures and controlling functions at length scales ranging from the nanometer to millimeter. Various driving forces for self-assembly have been studied at these length scales, including gravity, magnetic force, electrostatic interaction, entropy, and capillary interaction. Among these, capillary effects have received particular attention at the microscale because of their relatively significant magnitude, tunability, and simplicity, and a number of studies have demonstrated the formation of complex two- and three- dimensional structures by this method. However, such studies have been limited to isolated structures like pillars and posts where the neighboring units interact with each other only through capillary force, limiting the complexity of the assembly architectures can be achieved. In this project, we study the response of connected elastic lattices with the capillary force introduced via rapid evaporation of volatile organic solvents. Such micro lattices, different from micro-pillars, possess strong interaction between unit cells through capillary forces as well as the elastic coupling from the geometric compatibility of the underlying lattices, giving rise to programmable lattice transformations from the coalescence of the adjacent edges. Furthermore, as compared to micro-pillar systems, lattice structures are known to exhibit stronger mechanical strength and have a broader control space over the surface properties accompanied by lattice transformations.

Pulse-Driven Robot—Motion via Solitary Waves

Bolei Deng and Katia Bertoldi; Harvard University, United States

Soft robots have been shown to be able to perform a variety of tasks, including walking, grasping, crawling and swimming. However, to achieve all these functions their constituent actuators need to be inflated sequentially. In this work, we demonstrate a new generation of flexible machines that can be realized by harnessing propagation of non-linear elastic waves. To demonstrate this concept we focus on an iconic stretchable toy that has captivated children and adults all over the world: a Slinky. We show that by exploiting the propagation of nonlinear pulses this popular toy can be transformed into a robot capable of moving around without the need of legs.

From earthworms, snakes and caterpillars, to slugs and snails, many creatures successfully combine the flexibility of their body with the ability to locally manipulate frictional forces to move in complex environments without the need of legs. These limbless organisms have recently inspired the design of compliant robotic systems that take advantage of elastic deformation to crawl and maneuver through confined spaces. For example, snake-inspired robots with locomotive skills that surpass more conventional designs have been designed by incorporating anisotropic friction into soft elastomeric inflatable structures. Moreover, soft robots capable of worm-like motion have been realized by sequentially actuating contracting segments to induce peristalsis. However, these machines require multiple inputs to achieve the desired peristaltic motion, as each segment must be addressed independently according to a specific preprogrammed sequence.

Here, inspired by the retrograde peristaltic waves observed in earthworms, we show that the propagation of non-linear elastic waves in flexible structures provides opportunities for locomotion. To demonstrate the concept, we
focus on a Slinky -- an iconic stretchable toy that has captivated children and adults all over the world -- and use it to realize a pulse-driven robot capable of propelling itself. Our simple machine is built by connecting the Slinky to a linear actuator and using an electromagnet and a plate embedded between the loops to initiate nonlinear pulses that propagate from the front to the back. Notably, we find that the directionality of these pulses enables our simple robot to move forward. Moreover, our results indicate that the efficiency of such pulse-driven locomotion is optimal when the initiated waves are solitons - large amplitude (non-linear) pulses with stable shape and constant velocity along propagation. As such, our study expands the range of possible applications of solitary waves and demonstrate that they can also be exploited as simple underlying engines to make flexible machines move.

**4:45 PM MS01.02.09**

**Electrochemically Reconfigurable Architected Materials** Xiaoxing Xia¹,², Arman Afshar³, Heng Yang², Carlos M. Portela², Dennis Kochmann⁴,², Claudio V. Di Leo⁵ and Julia R. Greer²; ¹Lawrence Livermore National Laboratory, United States; ²California Institute of Technology, United States; ³Georgia Institute of Technology, United States; ⁴ETH Zurich, Switzerland

Architected materials represent an area of active research because they exhibit exotic properties such as negative Poisson’s ratios and negative refractive indices, and decouple historically correlated material properties such as strength vs. density and thermal conductivity vs. stiffness. Most architected materials reported to date are passive in the sense that they have a prescribed geometry fulfilling a single functionality. It was recently shown that architected materials can be reconfigured by mechanical deformation and instabilities, hydration-induced swelling, and magnetic actuation. Such smart, stimulus-responsive materials can make a long-lasting impact on adaptive, deployable, and dynamically tunable devices if they could overcome existing challenges of (1) requiring bulky external control, (2) toggling between “on” and “off” states, and (3) reverting to original configuration once external stimulus is removed. Most of these reconfigurable systems are small and idealized; scaling them up requires substantially increasing the number of repeating units that would inevitably introduce inhomogeneities similar to defects, gradients or grain boundaries that govern properties of classical materials.

Here we demonstrate a new mechanism to dynamically reconfigure architected materials by exploiting electrochemically driven alloying/dealloying reactions to induce continuous, non-volatile and reversible structural transformations. We used the alloying couple of silicon and lithium as a prototype system because Si is a high-capacity battery electrode material notorious for its ~300 % volumetric expansion after full lithiation. Buckling instabilities were observed in Si nanowires and etched honeycomb patterns during lithiation but they have not been systematically investigated as a design tool to achieve structural reconfiguration. Leveraging on Si’s mechanical resilience at small scales, we designed and fabricated Si-coated microlattices purposely structured to promote lateral in-plane buckling. *In situ* lithiation/delithiation observations revealed cooperative buckling among neighboring beams that reconfigures the tetragonal unit cells into curved ones with pairwise opposite concavity. Through experiments and finite element modeling, we discovered that the bistability of in-plane buckling leads to formation of multiple lateral domains separated by distorted domain boundaries, with domain sizes and distribution governed by defects and lithiation rate. We analyzed this phenomenon using a statistical mechanics approach analogous to the Ising model, and designed artificial defects to effectively program domain boundaries to emerge in prescribed patterns upon lithiation. Understanding and controlling defects provides a pathway to drive the dynamic response of architected materials along a particular trajectory. This new class of electrochemically reconfigurable architected materials has significant implications as it creates new vistas in designing dynamic mechanical metamaterials with novel stress-relief mechanisms and tunable phononic band gaps.

Reference:
8:15 AM MS01.03.01
A Viscoelastic Beam Theory of Polymer Jets with Application to Rotary Jet Spinning Qihan Liu¹² and Kevin Kit Parker¹²;¹Harvard University, United States;²Wyss Institute for Biologically Inspired Engineering, United States

Complex deformation of a polymer jet appears in many manufacturing processes, such as 3D printing, electrospinning, blow spinning, and rotary jet spinning. In these applications, a polymer melt or solution is first extruded through an orifice and forms a jet. The polymer jet is then dynamically deformed until the polymer solidifies. The final product is strongly affected by the deformation of the polymer jet. And the deformation is strongly affected by the viscoelasticity of the polymer. Here we develop a beam theory to incorporate both the nonlinear viscoelasticity and the bending/twisting stiffness of a polymer jet. As a demonstration, we study the formation of a polymer fiber under strong centrifugal force, a fiber manufacturing process known as rotary jet spinning.

8:30 AM *MS01.03.02
Extreme Mechanics of Epithelial Monolayers Marino Arroyo; Universitat Politècnica de Catalunya, Spain

Epithelial monolayers are very simple yet very important animal tissues with crucial mechanical functions. They consist of cohesive and highly organized cells that adhere to each other and often to an underlying matrix to form a barrier that lines internal and external organ surfaces, controls transport of gas or nutrients, protects us from pathogens or desiccation, and is involved in morphogenesis. Seen as materials, epithelial monolayers are truly remarkable. They can maintain barrier integrity while increasing their lateral area by 10-fold or while deforming into highly curved 3D shapes. In apparent contradiction, they can dynamically remodel by selectively disengaging cell-cell adhesions to heal wounds or to transport cellular materials through organized active flows during morphogenesis. This tunable mechanical behavior relies on a hierarchical organization. At a sub-cellular scale, structural proteins dynamically self-organize into cytoskeletal networks and adhesion complexes, which transduce chemical energy into mechanical work and determine cellular architecture and mechanics. In turn, groups of cells self-organize to form tissues and homeostatically maintain these tissues in a dynamical steady-state. A major question in mechanobiology is to understand the multi-scale self-organization of adaptable functional units at different scales and their integration to perform mechanical functions including morphogenesis, homeostasis, or motility. I will discuss our theoretical efforts to understand various aspects of cell and epithelial tissue mechanics and morphogenesis starting from sub-cellular models of the cytoskeleton and cellular adhesion. I will illustrate how subcellular dynamics, including molecular turnover and active force generation, determine mechanical properties at a tissue scale including solid-like or fluid-like rheology, active superelasticity, or pulsatile dynamics and ratcheting remodelling.

9:00 AM MS01.03.03
Domain Formations and Pattern Transitions via Instabilities in Soft Heterogeneous Materials Jian Li¹ and Stephan Rudykh²;¹Technion–Israel Institute of Technology, Israel;²University of Wisconsin – Madison, United States

We investigate instability-induced pattern transformations in soft particulate composites under large deformations [1]. The onset of instabilities are detected by numerical Bloch-Floquet techniques and experiments on 3D-printed specimens. We find that the system of stiff inclusions periodically distributed in a soft elastomeric matrix experiences dramatic microstructure changes upon the development of elastic instabilities. We observe experimentally the formation of microstructures with antisymmetric domains and their geometrically tailored evolution into a variety of patterns of cooperative particle rearrangements. In combination of numerical instability analyses and experiments, we find that the formation of domain occurs in macroscopic instability regime, while microscopic instability induces the cooperative new pattern of particles rearranged in a wavy chain. Our observation shows that these patterns can be tailored by tuning the initial microstructural periodicity and concentration of the inclusions. Thus, these fully determined new patterns can be achieved by fine tuning of the initial microstructure. Our findings open new ways for developing reconfigurable mechanical metamaterials that can find applications in a large variety of fields from acoustic metamaterials, actuators, and soft robotics to morphing devices remotely controlled by external fields for biomedical applications.
References

9:15 AM *MS01.03.05
The Wild Complexity Born from a Simple Nonlinearity and How to Tame It—A Reprise of the "Beam on an Elastic Foundation" Ryan S. Elliott, Timothy J. Healey, Nicolas Triantafyllidis, Shrinidhi Pandurangi and Ariel Ibarra Pino; 1University of Minnesota, United States; 2Cornell University, United States; 3Ecole Polytechnique, France

The problem of a beam on an elastic foundation has a long history in engineering mechanics. Its deformation and onset of buckling behavior have been employed as a surrogate for understanding an extensive list of technologically important applications, including sun-kinking of railroads, pipeline transportation engineering, and thin films on hard or soft substrates in microelectronic and biological applications. Despite this history, the global bifurcation behavior of the problem has not been fully explored. Indeed, the complexity of the equilibrium solution set will come as a surprise to many practicing and research engineers.

With an eye toward the study of creasing and deformation-localization problems in soft materials, this work studies the behavior of an inextensible infinite Euler-Bernoulli beam that is subjected to a compressive axial force and connected to a nonlinear (polynomial) elastic foundation. We seek global post-bifurcation equilibrium paths and their stability as a function of the applied force. All bifurcating paths (stable and unstable) are of interest due to the possibility of stable segments occurring on any path in the deep post-bifurcation regime of the global solution set. However, standard solution techniques (incremental Newton-Raphson coupled with strategically chosen imperfections) are foiled by the complexity of the problem's bifurcation behavior. Thus, it becomes necessary to employ sophisticated equivariant bifurcation theory and numerical methods, based on group theory, to tame the complexity and systematically obtain the desired results. These methods will be reviewed and their application to the problem at hand will be demonstrated as a typical example of their power to solve and bring order to an otherwise intractable set of equations. Finally, the results will be interpreted physically to explain the existence of localized-deformation and crease-like behavior. Parallels with phase transformation problems will also be drawn.

9:45 AM BREAK

10:15 AM *MS01.03.06
Extreme Mechanics of Soft Structures Katia Bertoldi; Harvard University, United States

Although the study of the effect of shape and geometry on the mechanical response of solid objects has a long history, the surge of modern techniques to fabricate structures of complex form paired with our ability to simulate and better understand their response has created new opportunities for the design of architected materials with novel functionalities (also referred to as metamaterials). Since the properties of architected materials are primarily governed by the geometry of the structure (as opposed to constitutive ingredients at the material level), I’ll show that their deformation and instabilities can be harnessed to achieve new modes of functionality, including motion, energy trapping and releasing, wave guiding and shape changes.

10:45 AM MS01.03.07
Snap-Shaping Origami Sheets Anne Meeussen and Martin van Hecke; 1AMOLF, Netherlands; 2Leiden University, Netherlands

Origami is not rigid; facets and hinges bend and stretch. This compliance enriches the physics of origami, leading to mechanical multistability, and opens up a rich design space to control shape-morphing in thin materials. We explore this new design space starting from an undulating "origami" sheet. This simple material switches reversibly between many stable shapes via snap-through instabilities. Its reshaping results from a hierarchical, geometry-mediated competition between different sources of compliance, which we demonstrate via experiments and minimal computational models.
Interplay of Origami Structure Properties in Fold Path Bifurcation Analysis

Andrew S. Gillman, Matthew Grasinger, and Phil Buskohl; Air Force Research Laboratory, United States

Origami structures are finding numerous technological applications including lightweight composites, soft robotics, metamaterial design, and deployable space structures, where their nonlinear deformations and instabilities are leveraged to form novel material behavior. The contrast in material (stiffness mismatch among deformation modes) and geometric (slender elements) properties in origami structures can lead to highly nonlinear mechanical behavior with unique macroscopic properties, such as multi-stability. We have recently integrated our nonlinear origami truss model with a robust continuation solver for bifurcation detection and branch tracking to map multistable energy landscape in order to characterize the role of discrete fold stiffness distributions. Towards the goal of developing more robust design tools to navigate this non-convex design space, involving energy landscapes with many bifurcations and stable equilibrium points, we investigate how changing stiffness distributions (stretching, folding, and facet bending stiffness) and non-zero fold reference angles shift the bifurcation and equilibrium points. These insights are leading to the development of a generalized design tool for origami structures exhibiting many stable configurations for deployability and lightweight material design.

Morphing and Shape Control—From Mechano-Biology to New Technologies

Antonio DeSimone; 1SISSA, Italy; 2Scuola Superiore Sant'Anna, Italy

Locomotion strategies employed by unicellular organism are a rich source of inspiration for studying mechanisms for shape control. The ones used by unicellular organisms are particularly interesting because they are invisible to the naked eye, and offer surprising new solutions to the question of how shape can be controlled, and for which function.

In recent years, we have studied locomotion and shape control in several biological systems using a broad range of tools ranging from theoretical and computational mechanics, to experiment and observations at the microscope, to manufacturing of prototypes.

A particularly interesting case study is provided by *Euglena gracilis*. This unicellular protist is particularly intriguing because it can adopt different motility strategies: swimming by flagellar propulsion, or crawling thanks to large amplitude shape changes of the whole body (a behavior known as “metaboly”, or “amoeboid motion”). The shape changes required for the two strategies are completely different and consist of bending waves along the flagellum in swimming motility, peristaltic expansion/contraction waves of the body in crawling motility. Interestingly, however, both the general morphing principle and its embodiment in the microscopic architecture of the active structural elements enforcing the shape changes are the same. Shape changes are achieved by Gaussian morphing, the paradigm by which curvature can be produced by differential in-plane stretches of the mid-surface (the tubular shell of the flagellum in one case, the body envelope in another). These stretches are in turn produced by molecular motors walking along microtubules, and causing the bending of microtubule bundles (flagellum) and the twisting of pellicle strips (cell envelope).

The behavior displayed by *Euglena* has been observed under the microscope, and reproduced quantitatively thanks to mathematical and computational models. The detailed understanding of the mechanics of the shape-shifting mechanism in terms of the body architecture provides the basis to design new engineering devices, based on bio-inspired, morphable structures.

We will survey our most recent findings obtained also in collaboration with M. Arroyo, G. Cicconofri, G. Noselli, within this stream of research which has been supported by ERC Advanced Grant 340685-MicroMotility.
Highly Fatigue-Resistant Stretchable Materials

Zhigang Suo; Harvard University, United States

Stretchable materials—elastomers, hydrogels, ionogels, and organogels, along with their hybrids—are under intense development to enable numerous and far-reaching applications. In developing a material for a load-bearing application, attention inevitably falls on the resistance of the material to the growth of a crack, characterized by toughness under monotonic load, and by threshold under cyclic load. Many methods have been discovered to enhance toughness, but they do not enhance threshold. Here we describe a principle of stretchable and fatigue-resistant materials. To illustrate the principle, we embed unidirectional fibers of a soft and stretchable material in a matrix of a much softer and much more stretchable material, and adhere the fibers and the matrix by sparse and covalent interlinks. When the composite is cut with a crack and subject to a load, the soft matrix shears readily and delocalizes the high stretch of a fiber over a long segment. The material achieves a fatigue threshold more than one order of magnitude higher than natural rubber. The principle of stretchable and fatigue-resistant materials is applicable to various materials, layouts, and methods of fabrication, opening an enormous design space for general applications.

2:00 PM MS01.04.02

Negative Creep Behaviour and Thermomechanical Alleviation in Titanium Alloys under Cyclic Loading

Yilun Xu and Fionn Dunne; Imperial College London, United Kingdom

Aero-engine titanium components endure extremes of loading which may be both mechanical and thermal, and which are known to give rise to the phenomenon of cold dwell fatigue [1]. This is argued to develop through combined effects of crystallography, localised slip due to plasticity and creep [2], and the redistribution of stress, often termed load shedding [3], which occurs during the stress hold stage of flight cycles. Evidence is emerging that a potentially important aspect of the deformation occurring is that due to negative creep. This is the activation of localised reversed time-dependent slip resulting from back stress development in titanium alloy (IMI834) and occurs interestingly on partial stress unloads (which are representative of in-flight loading cycles). The negative creep is potentially helpful in contributing to the thermal alleviation of the dwell fatigue phenomenon, and this is addressed in this paper.

A new thermo-mechanically coupled discrete dislocation plasticity (DDP) formulation is established, incorporating thermally activated dislocation escape and creep, which is integrated with experiments on polycrystalline IMI834. The experiments consider dwell fatigue cycling without and with a partial unload, as well as the inclusion of a thermal cycle [4], which are investigated with the DDP model.

The mechanistic basis of negative creep is shown to be the establishment of dislocation pileups and back stress development such that on partial unloading, reversed creep occurs by thermally-activated dislocation escape and reverse glide during secondary stress hold. Anomalous cyclic strain accumulation in both isothermal and anisothermal stress-loaded alloy IMI834 is thus explained by negative creep.

The magnitude of predicted macroscopic negative cyclic creep strain in dwell fatigue loading is found to be consistent with independent experimental literature. The inclusion of the thermal cycle including elevated temperature facilitates further negative creep by promoting dislocation escape via thermal activation. The experimentally observed ‘anomalous’ macroscopic cyclic strain accumulation in both isothermal and anisothermal loadings has been explained by negative creep at the dislocation scale. The latter also provides the underpinning explanation for the beneficial effect of elevated temperature excursions in diminishing cyclic creep accumulation and hence reducing dwell fatigue sensitivity in titanium alloys by thermal alleviation.

Keywords: Negative creep; Thermal alleviation; Discrete dislocation plasticity; Titanium alloys; Dwell fatigue

Reference
2:15 PM MS01.04.03
Atomistic Modeling of Cyclic Loading and Heat Treatment Processes for Tuning the Mechanical Properties of Amorphous Alloys Nikolai Priezjev; Wright State University, United States

The development of novel fabrication techniques for amorphous materials, including metallic glasses and high entropy alloys, is important for various structural and biomedical applications. The processing routes often involve mechanical and thermal treatments of disordered alloys that lead to changes in potential energy, microstructure as well as mechanical and physical properties. In this presentation, we discuss recent results of molecular dynamics simulations of three loading protocols: oscillatory deformation, flash annealing, and elastostatic loading of metallic glasses. In each case, the simulations are performed in a wide range of processing conditions and the optimum control parameters for the most relaxed and rejuvenated states are determined. The structural analysis is performed by identifying clusters of mobile atoms with relatively large nonaffine displacements. It is generally found that the most rejuvenated glasses are characterized by reduced elastic moduli and lower yield stress, thus leading to improved plasticity. These results are useful for the thermomechanical processing of metallic glasses with optimized mechanical properties.

2:30 PM MS01.04.04
Extreme Fatigue Life of Graphene Teng Cui1, Sankha Mukherjee1, Parambath M. Sudeep1, Guillaume Colas1, Farzin Najafi1, Jason Tam1, Pulickel Ajayan2, Chandra V. Singh1, Yu Sun1 and Tobin Filleter1; 1University of Toronto, Canada; 2Rice University, United States

Materials can fail when subjected to cyclic loading at stress levels much lower than the ultimate tensile strength or yielding limit, which is known as mechanical fatigue. Understanding the fatigue behavior is critical for any emerging material in order to evaluate its long-term dynamic reliability. Two-dimensional (2D) materials have been widely applied to mechanical and electronic applications, where they are commonly subjected to cyclic stress. However, the fatigue life and underlying damage mechanisms of these atomically thin, nearly defect-free, materials are unknown. Here we show the first fatigue study of freestanding 2D materials, in particular graphene and graphene oxide (GO). Monolayer and few layer graphene were found to exhibit ultrahigh fatigue life of more than one billion (10^9) cycles at large mean stress of 71 GPa. Such a remarkable fatigue life is higher than that of any material reported to date at similar stress levels. Monolayer graphene exhibits global and catastrophic fatigue failure without progressive damage, and the failure is attributed to bond reconfiguration near the defective site. The presence of functional groups on GO imparts a local and progressive fatigue damage mechanism. The fatigue life of GO was found to diminish significantly when the material is scaled up in thickness (10s of layers). This work not only provides new fundamental insights into the widely observed fatigue enhancement behavior of graphene-embedded nanocomposites, but also serves as a starting point for the mechanical dynamic reliability evaluation of other 2D materials.

2:45 PM MS01.04.05
Ultrahigh Temperature In Situ TEM Single Boundary Coble Creep Experiments Shen J. Dillon; University of Illinois at Urbana Champaign, United States

Measuring thermodynamics and kinetics for single grain boundaries has long been experimentally laborious and challenging. Developments in small scale experimentation present opportunities to develop new more efficient approaches to obtain this important data. This presentation will discuss ultahigh temperature in situ transmission electron microscopy based mechanical testing experiments designed to measure grain boundary diffusivity, surface diffusivity, surface energy, and grain boundary energy. The general approach, based on laser heating, is also demonstrated for more conventional stress-strain measurements. The approach is applied to zirconium oxide at temperatures between ≈1700 °C and ≈2500 °C.
Coupled Models for Polycrystalline Deformation—Creep and Deformation at High Strain Rates Javier Segurado\textsuperscript{1,2}, Marco Magri\textsuperscript{2}, Jifeng Li\textsuperscript{2} and Ignacio Romero\textsuperscript{3,2}; \textsuperscript{1}Technical University of Madrid (UPM), Spain; \textsuperscript{2}IMDEA-Materials Institute, Spain; \textsuperscript{3}Technical University of Madrid, Spain

Two continuum frameworks will be presented to simulate the deformation of polycrystals under different scenarios using coupled crystal plasticity finite element models.

The first one is a model to study polycrystals at elevated homologous temperatures under relatively small stresses, where deformation is controlled by the diffusion of vacancies to-and-from the crystal bulk to the grain boundaries as well as the diffusion within the grain boundary. This creep model is formulated as a coupled problem of diffusion and mechanical equilibrium. It is assumed that vacancy emission and absorption within grain boundaries is due to the climb of grain boundary dislocations, and therefore the creep kinetics is derived from physically-based mechanisms. The effect of grain size, applied stress, and grain boundary dislocations mobility will be presented.

The second framework is a fully coupled thermo-mechanical framework including thermal strains, temperature dependency of the crystal behavior and heat generation by dissipation due to plastic slip. The framework allows to bridge the plastic deformation and its rate with heat diffusion at the microscale. The model is used to simulate the machining process accounting for the effect of the microstructure heterogeneity, in this case the presence of soft and stiff grains.

4:00 PM MS01.04.07

Plasticity Effects in the Buckling of Supported Thin Films Junyu Yang, Sameer Damle, Spandan Maiti and Sachin Velankar; University of Pittsburgh, United States

The past decade has seen enormous development of buckled materials, materials in which one or more elements is in the form of a slender structure that buckles under compression. Such buckled materials are being considered for flexible electronics, as surfaces with tunable adhesion and friction, or materials with unusual mechanical properties such as a negative Possion ratio. In theoretical and experimental analyses, such situations are almost always treated within an elasticity framework, i.e. all materials are generally regarded as elastic, often linearly elastic. Here we examine plasticity effects in such buckled materials.

The situation considered is of a thin film of stiff plastic material (polyethylene) attached bonded to a softer elastomeric film. Upon stretching this bilayer composite, the plastic thin film stretches irreversibly, whereas the elastomer stretches reversibly, thus creating a “strain mismatch”. Upon releasing, the elastomer imposes compressive stress on the polyethylene film which then buckles. We explore the effects of film plasticity in this situation by experiment and numerical simulations. We show that plasticity has numerous effects beyond simply causing the “strain mismatch”: the film can yield in-plane during release; the film can buckle during release to form a strongly wrinkled surface; the film can yield and form plastic hinges during wrinkling. We show that plasticity can be exploited to achieve wrinkled surfaces with aspect ratios much higher than possible with analogous elastic systems. We also point out that the tendency of the plastic film to undergo necking sets a lower limit on the rubber yield stress necessary to achieve uniform wrinkling. Although these results are obtained for the specific case of a layered thin film geometry, the insights apply in general to all buckled materials in which a plastic material is combined with an elastic one.

4:15 PM MS01.04.08

Ductile-to-Brittle Transition of Micron-Sized Niobium at Cryogenic Temperature Gyuho Song and Seok-Woo Lee; University of Connecticut, United States

Thermal environment has been considered as one of the most important extreme conditions that affect mechanical properties of materials. Particularly, the mechanical properties at a low temperature has been extensively studied due to their importance in space exploration or marine engineering. The decrease in temperature usually causes the ductile-to-brittle transition (DBT) in body-centered-cubic (bcc) metals, which must be prevented to avoid the catastrophic failure of engineering devices working at a low temperature. Recently, extreme mechanics at the micrometer scale began to receive a great attention due to the strong interests in the development of micro-electro-mechanical system (MEMS) working under extreme conditions. If these devices operate at a low temperature, it is critical to prevent the DBT in micron-sized components. At the micrometer-scale, mechanical behaviors of single crystalline metals are remarkably differently from those at bulk scale due to the size effects. Source-controlled plasticity causes the size-affected strength as well as the intermittent plastic flow. In order to prevent the DBT at the
micrometer scale, it is critical to understand how the source-controlled plasticity is influenced by the decrease in temperature. For bcc metals, the lattice resistance, cross-slip of screw dislocation, the evolution of dislocation structure, and the presence of free surface should be critical factors to affect the DBT at the micrometer scale. In this work, therefore, we present our recent results on the DBT in a [0 0 1] bcc niobium (Nb) single crystal at the micrometer scale. The dog-bone shaped tensile samples with 2μm in width were fabricated via focused-ion beam milling and were tested at the nominal strain rate of 10^{-3} s^{-1} at 298, 100 and 56K using custom-built in-situ cryogenic micromechanical testing system. Stress-strain data showed the extensive ductility (~25%) at 298K but the limited ductility (~6%) at both 56 and 100K. Post-mortem scanning electron microscopy revealed that samples tested at 298K underwent uniform and homogeneous plastic deformation while samples tested at 56 and 100K underwent highly localized plastic deformation followed by brittle fracture that was initiated at slipped regions. Thus, micron-sized niobium single crystals indeed show the ductile-to-brittle transition. Post-mortem transmission electron microscopy showed the significantly high dislocation density in samples tested at 298K, but almost no dislocations in samples tested at 56K. These results imply the strong suppression of dislocation multiplication at a low temperature. The reduction of mobile dislocation, i.e., dislocation starvation, would induce the DBT in Nb at the micrometer scale. This DBT mechanism differs from that at bulk scale, which is caused by the decrease in mobility of screw dislocation. At the micrometer scale, all mobile dislocations seem to be annihilated at the free surface. Brittle fracture would occur due to the stress concentration at slipped region before dislocation nucleation occurs. Note that this presentation reports the first observation of DBT in bcc metals at the micrometer scale and in cryogenic environments. Our results will not only enable a deeper understanding of the combined effects of sample dimension and temperature on plasticity and fracture processes in bcc metals, but also guide a design of mechanically-robust materials used at the micrometer scale and at a low temperature.

4:30 PM MS01.04.09
High Heat and Particle Damage Effects on Tungsten and Tungsten Carbide Minsuk Seo¹, Vincent F. Cintron¹, Alec M. Cacheris², Sean R. Kosslow¹, John R. Echols¹ and Leigh Winfrey¹; ¹The Pennsylvania State University, United States; ²The University of Tennessee, Knoxville, United States; ³Oak Ridge National Laboratory, United States

One of the great concerns in fusion reactor operation is disruption events that deliver 10s to 100s of GW/m² of heat over microseconds to first wall materials, severely damaging plasma facing components, and therefore hamper their long-term durability. Specifically, the diverter region is one the most sensitive parts of the plasma facing portion of the reactor. In addition to causing damage to the vessel wall, disruption events can produce debris or lead to the diffusion of high Z material into the fusion plasma region. Tungsten based materials are promising as plasma for use in plasma facing components because of its high melting point, high thermal conductivity, and low tritium retention. However, it also has disadvantages such as radiation induced embrittlement and thermally driven high ductile to brittle transition. Most importantly, erosion by particle bombardment is great issues in off normal, i.e. disruption, events which gradually weaken the function of the vacuum vessel. To date, different types of tungsten, alloys, and ceramics have been proposed to minimize these challenges in first wall materials selection.

In this study, tungsten carbide was used because of having comparable characteristics that of tungsten thus could perform as a plasma facing material. At the same time, tungsten metal was used as a reference material to compare the emerging features from the macroscale to the microscale. HELIOS, the electrothermal plasma experiment was used to replicate the small angle, high heat and particle flux like conditions that these materials will experience in off normal events. As prepared tungsten (W) and tungsten carbide (WC) samples were subject to HELIOS device with the controlled variables such as heat flux, particle flux, sample temperature, types of ions and their energy, and duration. Scanning Electron Microscope was used to visualize the microstructure of sample both at the surface and depth. Similarly, Energy Dispersive Spectroscopy (EDS) was carried out to see the compositional profiles both at the surface and along the depth direction. To see the cross-sectional view, surface treatment including cut, mount and polishing is necessary to take advantage of Focused Ion Beam (FIB) technique. Atomic Forces Microscope (AFM) was conducted on the surfaces of the samples to see the emerged surface morphology due to plasma interaction. X-ray Diffraction (XRD) patterns were recorded to reveal the possible alteration of lattice structure after exposure. Nanoindentation was performed to see any deviations in microhardness to obtain the microscopic mechanical strength information. Collection of data were then connected to draw the plasma material interaction at the surface and bulk materials. Based on the concentration profiles along the depth dimension, it is available to quantify the penetrative behavior of tungsten carbide and tungsten in these environments. The overall damage on
tungsten and tungsten carbide are analyzed and correlated to materials characteristics.

4:45 PM MS01.04.10
Investigation of Indentation Cracking of 6H-SiC at Elevated Temperatures Using HR-EBSD and FIB Tomography
Bo-Shiuian Li, Anna Kareer, Junliang Liu, Phani Karamched, Angus J. Wilkinson and David Armstrong; University of Oxford, United Kingdom

Indentation cracking of 6H-SiC up to 700 °C were introduced via a high-temperature nanoindenter equipped with a Berkovich tip. Fracture toughness (Kc) for indents with radial cracks (<400 °C) were calculated based on the Ouchterlony-modified Laugier equation. However, this equation does not apply for indents above 400 °C, due to the more complicated crack morphology revealed by FIB tomography. Here, an alternative method for calculating fracture toughness based on nanoindentation and FIB tomography was proposed. Good agreement with literatures was found for RT but slightly overestimates for 700 °C, suggesting the dissipation of energy through plastic deformation. High-resolution electron diffraction (HR-EBSD) was also conducted to measure the residual stress/strain distribution and geometrically necessarily dislocations (GNDs) density around the nanoindents. The combined effort of FIB tomography and HR-EBSD will provide better understanding of the thermally-controlled deformation process.

SESSION MS01.05: Session V
Session Chairs: Michael Demkowicz, Nathan Mara, Amit Misra and Xin Wang
Wednesday Morning, December 4, 2019
Hynes, Level 1, Room 109

8:00 AM *MS01.05.01
Understanding Multicomponent Alloy Phenomena via Quantitative Imaging and Spectroscopy
Mitra L. Taheri1,2; 1Drexel University, United States; 2Johns Hopkins University, United States

Multicomponent alloys (MCAs) represent a new class of alloy that are composed of multiple principal elements, contrasted to conventional alloys that rely on a single principal element with additional alloying elements in relatively small abundance. Despite their nominal chemical disorder, several studies have reported short range order (SRO) in MCAs – i.e. preferential bonding, local elemental enrichment and/or clustering – and such SRO may have broad implications for MCA performance. To tackle this problem, a suite of spatially resolved, electron imaging, diffraction, and spectroscopy techniques is used to correlate coordination chemistry and local order with microstructural evolution and related dislocation phenomena. Specifically, microstructures of so-called medium entropy alloys and high entropy alloys subjected to a variety of deformation regimes are analyzed. The resulting microstructures are quantified using diffraction-based techniques, and ultimately compared to simulations of similar alloy families in order to determine the extent to which localized dislocation-based phenomena play a role in microstructural evolution, and how alloy chemistry plays a role in these determining factors. The techniques presented allow for the direct observation of the interplay between chemistry and microstructure, and thus, provides us with key tuning knobs for future MCA development, especially for use in extreme environments such as high strain rate deformation, corrosion, and irradiation conditions.

8:30 AM *MS01.05.02
Multiscale Investigation of the Microstructure-Mechanical Property-Processing Relationships in Mg and Mg Alloys
Xin Wang1, Lin Jiang1, Dalong Zhang1, Kehang Yu1, Timothy J. Rupert1, Irene J. Beyerlein2, Subhash Mahajan1, Enrique J. Lavernia1 and Julie M. Schoenung1; 1University of California, Irvine, United States; 2University of California, Santa Barbara, United States; 3University of California, Davis, United States

The hexagonal close packed (HCP) family of metals is of growing interest as it provides a potential solution to the ever-increasing variety of structural applications that require advanced materials with unprecedented combinations of mechanical properties. As an example, Mg and its alloys are promising candidates for light-weighted structural applications, e.g., aircraft, automobile, electronic, etc. Successful incorporation of Mg and Mg alloys into
engineering designs is however hindered by their limited plasticity compared to that of current structural metals, which can be attributed to the anisotropic dislocation slip and twinning behavior that is associated with the HCP structure. Higher critical resolved shear stresses (CRSS) are required to activate the non-basal slip systems on the prismatic and pyramidal planes to produce an arbitrary shape change.

Over the years, the scientific community has proposed various approaches to enhance the performance of HCP metals, including introducing pre-existing nano-scale growth or deformation twins and nano-particles/precipitates in a nanostructured matrix. While these strategies and many others have led to several 100% enhancements in strength, to simultaneously attain strength and strains-to-failure values that are comparable to those of other advanced metals requires important breakthroughs in fundamental science and innovative design and processing strategies. Recently, in-situ experimental techniques in TEM and HRTEM and multi-scale simulation tools have emerged as successful strategies to enhance our fundamental understanding of the deformation mechanisms in materials. In this presentation, results from our group on Mg and Mg alloys are discussed with particular emphasis on the following topics: recent findings on twin nucleation and its relationship to dislocation slip; the influence of slip-twin and twin-twin interactions on mechanical behavior; formation of twin-twin junctions in single crystal Mg at the nanoscale and synthesis of high densities of twin-twin junctions in polycrystalline Mg at the macroscopic scale; and rare earth element alloying effects on dislocation glide and twinning activity in Mg alloys. The fundamental deformation behavior and the underlying mechanisms in Mg and Mg alloys are discussed in an effort to facilitate the development of synthesis pathways to produce low-density, high strength, high toughness HCP materials that are suitable for advanced industrial applications.

9:00 AM MS01.05.03
Ultra-High Stress Mediated Lattice Disturbance and Twinning Nucleation Scott X. Mao; University of Pittsburgh, United States

It is well understood that strength of crystals goes up as specimen size goes down with defects in the crystals decrease. When the size is down to below 30–50 nanometer, stress for defects nucleation becomes extremely high for crystals with large lattice friction resistance such as W. In such extreme condition, high stress plasticity occurs with unique deformation mechanism. I will cover experimental molecular dynamics with the in-situ high resolution transmission electron microscope for observation on the ultra-high stress induced lattice disturbance, dislocation dipole nucleation, competition between slip and twinning, and twinning nucleation of nano-sized body center cubic metals pillar (30-50 nm diameter) with defects free condition under ultra high stress above 10 ~ 20 GPa compressive loading

9:15 AM *MS01.05.04
Healing of Nano-Cracks in Metals Due to Stresses Induced by Mechanically-Driven Grain Boundary Migration Ta Duong1, Abhilash Molkeri1, Christopher Barr2, Ankit Srivastava1, Khalid Hattar2, Brad Boyce2 and Michael J. Demkowicz1; 1Texas A&M University, United States; 2Sandia National Laboratory, United States

When external loads are applied to a material containing a crack, a characteristic stress field $s_{\text{rack}}$ builds up around the crack. If the material does not undergo any microstructure evolution during loading, the deflection of the crack faces depends on $s_{\text{rack}}$ alone. However, in polycrystalline metals, applied loads may cause the microstructure to evolve, e.g. through grain boundary migration, martensitic transformations, or differential distortion. This microstructural evolution generates complex stress fields $s_{\text{mstr}}$ of its own. The displacement of the crack faces then depends on the superposition of $s_{\text{rack}}$ and $s_{\text{mstr}}$, rather than on $s_{\text{rack}}$ alone. This coupling between mechanically-driven microstructure evolution and internal stresses gives rise to counterintuitive crack behavior, such as closure under applied mode I (tensile) loading. This talk will present atomistic and continuum-level simulations of stresses induced at a triple junction during mechanically-driven grain boundary migration and their effect on the behavior of a nearby nano-scale crack. The simulations will be compared with corresponding experiments on fatigue-induced nano-cracks in polycrystalline Pt.

9:45 AM MS01.05.05
Grain Boundary Engineering Leading to Enhanced Mechanical Properties of Superhard Boron Carbide Qi An1, Dezhou Guo1 and Madhav Reddy2; 1University of Nevada, Reno, United States; 2Shanghai Jiao Tong University, China
Boron carbide is superhard, but its extended engineering applications are prevented by the abnormal brittle failure arising from the high-density amorphous shear bands. To improve the mechanical properties of B₄C, we investigated how grain boundaries (GBs) determine the deformation and failure mechanism of B₄C. The deformation and failure mechanism of polycrystalline B₄C were studied using the reactive force field (ReaxFF) simulations. We found that the main deformation mechanism of nanocrystalline B₄C is grain boundary sliding, leading to a reverse Hall-Petch relationship. This GB sliding triggers the amorphous shear band formation at predistorted icosahedral GB regions with initiation of cavitation within the amorphous bands. Our simulation results are validated by the nanoindentation experiments in which an intergranular amorphous GB phase was observed due to GB sliding. Although most GB sliding events in our ReaxFF simulations lead to the intergranular amorphization, we do observe one intragranular amorphization initiates from grain boundaries (GBs) and propagates along the rhombohedral (011)[2-1-1] slip system. Combining density functional theory (DFT) and ReaxFF simulations, we found that the dislocation nucleation occurs along this particular slip system, accompanied with bond breaking of icosahedral-icosahedral bonds within B₁₁C cage. This leads to the amorphous shear band formation and intragranular amorphization. Our studies provide an atomistic explanation for the influence of GBs on the deformation behaviour of nanocrystalline ceramics, helping design strong and ductile superhard ceramics.

10:00 AM BREAK

10:30 AM *MS01.05.06
Interface-Microstructure-Enabled Mechanical Behavior of Metallic Nanocomposites Amit Misra; University of Michigan–Ann Arbor, United States

An overview of the mechanical behavior of metallic nanocomposites in terms of the interface-dominated microstructure will be presented. The interface microstructure will be characterized using parameters such as interface spacing, morphology, crystallographic orientation relationship, texture with respect to processing direction, interface defect structure and chemistry. A series of model Cu-X systems where X is BCC element such as Mo, Ta, Nb, V, Cr, Fe, etc will be used to highlight the novel mechanical behavior enabled by interface microstructures. The presentation will highlight the integration of theory and computational simulations across relevant length scales and in situ characterization of defect phenomena and mechanical behavior. In particular, examples from high strain rate testing and failure by shear band formation in ultra-high yield strength metallic nanocomposites will be highlighted.

11:00 AM MS01.05.07
Advanced Multimodal Studies of Microstructural Evolution under Shear Deformation Arun Devaraj¹, Bharat Gwalani¹, Tamas Varga¹, Changyong Park², Jorge D. Santos³, Tiffany Kaspar¹, Peter V. Sushko¹, Suveen N. Mathaudhu¹ and Cynthia Powell¹; ¹Pacific Northwest National Laboratory, United States; ²Argonne National Laboratory, United States; ³Helmholtz-Zentrum Geesthacht GmbH, Germany

Shear deformation of metallic alloys can induce deformation and microstructural changes which can be used to process materials in solid state, helping avoid melt processing and in achieving highly refined microstructures not achievable by conventional processing. In order to develop such solid phase processing methods for metallic alloys, we aim to better understand the fundamental atomic scale mechanisms of mass and energy transfer in materials under shear deformation. To achieve this aim, we employed synchrotron based in situ and ex situ high energy x-ray diffraction capabilities under high pressure with and without shear deformation, to enable real time investigation of microstructural evolution under such high deformation conditions. Such synchrotron based XRD results were correlated with detailed microstructural characterization before and after shear deformation using transmission electron microscopy and atom probe tomography, to develop a comprehensive understanding of the structural and compositional changes in the microstructure due to the shear deformation. Our results on structural and chemical modifications of several metallic alloys such as Al-Si, Cu-Nb and Cu-Ni provide new insights on the unique role of shear deformation in formation of metastable states as well as modifying the phase transformation pathways of these alloy systems. These new insights will be presented and compared with what is currently understood about role of shear deformation on generating super saturated solid solution states or self-organized nanolayers in metallic alloys.

11:15 AM MS01.05.08
Shear-Induced Deformation under a Microscope—Intermixing and Metastability in Heterolayers Peter V.
Understanding mechanistic pathways of far-from-equilibrium processes can help design materials with desired properties and control their behavior. Here we investigate how shear stress applied to nano-scale heterostructures of immiscible metals leads to the formation of metastable intermixed regions and establish the conditions for their stability. Heterostructures of Cr and Cu were grown using molecular beam epitaxy and subjected to linear shear by performing atomic force microscopy (AFM) scratch test. Controlling the force applied to the AFM tip and the ordering of the Cr and Cu layers allows us to control the tip penetration depth, the width of the wear track, and the amount of debris formed by the displaced material. Subsequent analysis performed using transmission electron microscopy and atom probe tomography reveals the character of the deformation field and the extent of shear induced intermixing under the wear track. Complementary molecular dynamics simulations provide additional insight into the mechanistic pathways of these off-equilibrium processes leading us to establish how the coupling between nano-structuring in the as-grown material and the shear loading determine the formation of mechanically-driven Cu-Cr intermixed regions.

The Influence of 3D Atomic-Level Interface Structure on the Mechanical Behavior of Nanocomposites

2-dimensional (2-D) sharp interfaces with distinct boundaries demarcating an abrupt discontinuity in material properties in nanolayered composites have been studied for almost twenty years and are responsible for enhanced behaviors such as strength, radiation damage tolerance, and deformability. However, 2-D interfaces have their limitations with respect to deformability and toughness. 3-D interfaces are defined as heterophase interfaces that extend out of plane into the two crystals on either side and are chemically, crystallographically, and/or topologically divergent, in three dimensions, from both crystals they join. Here, we present the synthesis, structure, thermal stability, and mechanical behavior of nanolayered Cu/Nb containing interfaces with 3-D character. By co-sputtering the bimaterial interfaces between the constituent pure phases, the resulting compositional gradient gives rise to new interphase boundary structures. Micropillar compression results show that the strength of Cu/Nb nanocomposites containing 3-D interfaces is significantly greater than those containing 2-D interfaces. Mechanical anisotropy, as well as shear banding is observed during pillar compression with retention of continuous layers across the shear band. We will present our recent results on deformation of such 3-D interfaces and structures, and describe their structural evolution mechanistically through the use of atomistic simulations.

Dynamic Response of High Energy Materials

Polymer bonded explosives consist of high energy particles in a polymeric binder. When these composites are subjected to heat, impact, or other stimulus they may undergo a rapid chemical change. This process is controlled by the formation of high temperature localized regions known as “hot spots”. The mechanisms of hot spot nucleation are controlled by the microstructure, for example in the same sample some particles ignite while others do not.

The sensitivity of the microstructure to initiation is studied with finite element simulations. The results help to identify the mechanisms of hot spot formation under a range of mechanical stimulus. The finite element model incorporates anisotropic plasticity and fracture and heat transport using a phase field approach. Microstructures with
different initial defects, including cracks, debonding and voids are analyzed. Furthermore, we analyze the relative importance of plastic dissipation and friction for different crystal orientations and grain sizes.

2:00 PM MS01.06.02
Nanosecond Resolved Temperatures of Shock Initiated Insensitive Energetic Materials  
Meysam Akhtar and Dana D. Dlott; University of Illinois at Urbana-Champaign, United States

We measured the hot spot and combustion temperatures of shocked insensitive high explosives in plastic-bonded explosive (PBX) formulations with nanosecond time resolution using optical pyrometry. The experiments used our shock compression microscope, which generates short-duration (4 ns) shocks using laser-launched flyer plates with velocities of 1-4.5 km/s. The microscope has, in addition to the optical pyrometer, a Photon Doppler Velocimeter (PDV) and high-speed imaging cameras.

The explosives were fabricated in the form of an array with 187 charges 1 mm in diameter and various thicknesses. The tiny charges were 80% explosive and 20% binder. The binder was polydimethylsiloxane (PDMS) and the explosives were triaminotrinitrobenzene (TATB), 1,1-diamino-2,2-dinitroethene (FOX-7), and 2,6-Diamino-3,5-Dinitropyrazine-1-Oxide (LLM-105). These explosives are particularly interesting because they are powerful but insensitive to accidental initiation.

The explosive temperatures were determined by measuring the spectral radiance in the visible region and fitting the radiance to a graybody model. However, since all these explosives are yellow, their absorption in the blue region gives apparent temperatures that are too cold. We measured the absorption spectrum in the PBX using diffuse reflectance spectroscopy. Knowing the absorption spectra, we have developed a modified graybody model that accounts for this absorption which allows us to measure the temperature more accurately.

2:15 PM MS01.06.03
Tracking Hot Spot Growth and Temperatures in a Model Plastic-Bonded Explosive Under Shock Compression  
Belinda P. Johnson, Hoya Ihara and Dana D. Dlott; University of Illinois at Urbana-Champaign, United States

The ability to probe the time-dependent microstructural response in explosives under shock compression is critical to understanding the initiation of explosives used in munitions and nuclear weapons. We have developed a tabletop apparatus that allows us to send initiating/detonation shocks to a sample and study the effects of microstructure on initiation. By using laser-driven impactors, we impart shocks lasting several nanoseconds and compress sample targets up to 10s of GPa. Using multi-frame fast photography with nanosecond temporal resolution we visually track thermal emission and its evolution over time. Additionally, we measure the time-dependent temperatures using a multichannel optical pyrometer coupled to a microscope objective that can resolve features down to 2 μm. The sample targets in this study consist of miniature arrays of explosive crystals embedded in various polymers, but sample targets can range from miniature, cylindrical explosive charges, thin films, and liquids. To date we have produced the first time-resolved images and simultaneous temperature measurements of shock-induced hot spots in a plastic-bonded explosive.

2:30 PM BREAK

3:30 PM *MS01.06.04
Novel Contributions to Deformation and Properties in Gradient Materials  
Suveen N. Mathaudhu 1,2; 1University of California, Riverside, United States; 2Pacific Northwest National Laboratory, United States

Metallic alloys with gradient microstructures have recently been shown to exhibit enhanced mechanical properties, namely increased strength with minimal loss in tensile ductility. One of the most common ways of engineering a gradient microstructure is via surface mechanical attrition treatment (SMAT) wherein hard balls are ultrasonically accelerated to impinge the surface and cause severe deformation and microstructural refinement. The improved properties are based on a number of proposed mechanisms, including dislocation cascading and mechanical incompatibility between layers, however less studied factors include the contributions of residual stress, texture, hardness and sample/process geometry. In this lecture, we will present research vignettes on each of these factors,
and deliberate on their overall roles in property enhancement. The results will be used to explain seemingly incongruent phenomena observed in many reports, and further unravel and decouple deformation mechanisms in gradient materials.

4:00 PM MS01.06.05
Distinct Driven Steady States Emerge from Diverse Initial Textures in Rolled Nanocomposites Ian Chesser1, Elizabeth A. Holm1 and Michael J. Demkowicz2; 1Carnegie Mellon University, United States; 2Texas A&M University, United States

Severe plastic deformation is a widespread method of making high-performance metallic materials. Single-phase polycrystalline metals undergoing severe plastic deformation develop steady-state textures that are characteristic of the mode of deformation. By contrast, we show that two-phase, Cu-Nb nano-laminate composites reach a variety of different steady-state textures under a single mode of deformation. Using molecular statics simulations and a novel algorithm for crystal rotation analysis, we observe that the final, steady state texture and interface character in these materials depends on the initial texture of the composite. This finding suggests that the range of bulk Cu-Nb nano-composite textures that may be made by severe plastic deformation is larger than previously demonstrated, with multiple plastically-driven steady states accessible, depending on initial texture. We propose a modification of accumulative roll bonding with highly textured seed layers as a means of accessing different driven steady states in layered composites.

4:15 PM *MS01.06.06
A Dynamic Look at MAX Phase Deformation and Damage Behavior Leslie Lamberson1, Xingyuan Zhao1, Hussien Badr2, Maxim Sokol2, Garritt Tucker1 and Michel Barsoum2; 1Colorado School of Mines, United States; 2Drexel University, United States

Layered solids are prevalent in both natural and synthetic systems from geological formations and ice, to microelectromechanical devices and traditional composites. MAX phases are a particular type of layered ternary transition metal carbide or nitride that essentially bridge the gap between ceramics and metals. They possess a unique deformation mechanism of atomistic buckling, termed ripplocations, which upon further load can lead to mesoscale nonlinear kink band formation (NKB). This mechanism is closely related to, but distinct from intrinsic rippling of 2D layered materials. Unlike dislocation motion, bulk ripplocations have no polarity or Burgers vector, allowing for a potentially useful energy absorbing intrinsic toughening mechanisms. On the bulk scale, MAX phases catastrophically fail in a nominally brittle manner due to the fact that critical resolved shear stresses have drastically reduced pathways for dislocation motion. As such, understanding the competition of ductile, pseudo-ductile and brittle deformation mechanisms across stress states and strain rates is imperative to moving toward tailoring the layered anisotropy for specific strength or stiffness performance metrics. Consequently, this talk presents orientation and strain rate investigations of randomly and highly-oriented MAX phase titanium silicon carbide (Ti3SiC2), among others. Specifically quasi-static and dynamic compression experiments both parallel and perpendicular to the c-axis (on highly-oriented MAX) and fracture investigations utilizing 2D digital image correlation with ultra high-speed imaging map surface kinematics, damage behavior and by extension, crack tip energetics through analysis. Ripplocation nucleation, self-assembly and propagation to the point of permanent kink banding, which is fundamental to the deformation of all layered solids, as well as the potential benefits of highly-textured MAX phases will be discussed. A model bulk experiment replicating ripple formation with associated nonlinear buckling analysis will also be presented.

4:45 PM MS01.06.07
High Strain Rate Compressive Behavior of Nanocrystalline Nickel Microlattices Rajaprakash Ramachandramoorothy1, Patrik Schürch1, Jakob Schwiedzik1, Thomas E. Edwards1, Damian Frey2, Jean-Marc Breguet2, Laetitia Philippe1 and Johann Michler1; 1Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland; 2Alemnis AG, Switzerland

Three-dimensional (3D) metallic printing of macroscale engineering structures is a well-established field that
promises precise spatial control and microstructure. The state-of-the-art metallic printer in the market that uses laser sintering has a minimum feature size of 20µm in thickness and 300µm in lateral direction. Thus the smallest structures that can be built are typically in the millimeter scale. On the other hand, micron scale metal architectures, with a simple extruded two dimensional shape such as micropillars and micro-cantilevers (with a length scale of ~2-30µm), can be fabricated only using focused ion beam (FIB) milling. Despite being widely used in the research communities, the use of FIB milling process in the industry is rather limited because of two key reasons: i) Defects are created in the milled structures due to gallium ion implantation and ii) it is an extremely time-consuming serial process, which severely limits the number of samples available for different studies. Thus, there is a critical need to develop a new method of 3D printing metals in the microscale (~1µm feature size) to create complex geometries (~10-100µm overall dimensions) such as microlattices, microsprings etc. Such a technology would enable us, for the first time, to design hierarchical microscale metallic structures with a unique combination of properties such as low density (<1000g/cc), high strength (>0.5GPa) and high ductility (>50% plastic strain). These full-metal microarchitectures can have profound applications in fabrication of freeform 3D metal microelectromechanical systems (MEMS) based devices and MEMS packaging for energy absorption/impact resistance.

In this presentation, for the first time, a new manufacturing technique for producing focused ion beam (FIB)-free templatable 3D metal microarchitectures such as microlattices, using a combination of two-photon lithography and electrodeposition will be described. The fabrication process which also involves a new electrodeposition overgrowth and inversion step, allowed the successful manufacture of full-metal 3D microlattices, with ~1µm feature size, to be made completely from nanocrystalline nickel, including the bottom substrate, the sample and a flat metal plate as the top-layer. Full-metal microlattices with such design are ideal for mechanical testing and for transfer to several applications/systems such as MEMS devices.

Subsequently, dynamic compressive properties of the full-metal nanocrystalline nickel microlattices, obtained using a state-of-the-art piezo-based \textit{in situ} micromechanical tester in a scanning electron microscope (SEM), will be presented as a function strain rate from 0.001/s to 200/s. Remarkably, the nickel microlattices with a density of ~1200g/cc (1/7th density of solid nickel) exhibit high yield strength of ~0.5GPa, due to the nanocrystalline nature of the electrodeposited metal. Also, the metal microlattices deform in an almost ideal plastic manner with a constant plateau-like crushing stress without initial stress peaks and are able to sustain significant strains up to 50% before densification. Further, given that the live monitoring of the high strain rate compression tests was not possible due to the low frame rates of the SEM (~35fps) finite element analysis (FEA) was used instead to understand the structural evolution of the nickel microlattices at high speeds. Thus the presentation will also report the results from FEA, including the determination of the constitutive laws using high strain rate nickel micropillar compression.

**SESSION MS01.07: Session VII**
**Session Chairs:** Curt Bronkhorst, Abigail Hunter and Jeffrey Lloyd  
**Thursday Morning, December 5, 2019**  
**Hynes, Level 1, Room 109**

**8:00 AM MS01.07.01**
**Hydrostatic Compression of the Portland Cement Clinker Minerals—Computational Modeling Investigations**
*Nirmalay Barua, Ingrid Espinosa and Ram V. Mohan; North Carolina A&T State University, United States*

Atomic level modeling is a highly effective and has been recently used tool to study complex multiphase cement composite systems. It can be used to predict the mechanical characteristics and associated constitutive material constants of the composite system, as well as an atomistic level understanding of how individual material phases affects the overall properties of the composite structure. Cement paste is a complex composite system that consists of both hydrated and unhydrated minerals and voids. Being the most popular construction material, cement materials are regularly subjected to high pressure under different loading conditions including those from underwater applications, impact, and shock loading. The overall mechanical behavior of cement composite paste under hydrostatic compression is a result of the mechanical deformation of each constituent phase of this composite material system. In this study, predictive molecular dynamics was used to model the atomistic deformation of the unhydrated phases under increasing pressure. A reactive forcefield was employed to capture the appropriate material chemistry changes in contrast to the classical forcefield that fails to capture the molecular reactions. Hydrostatic compression behavior of major clinker minerals were determined by the pressure-specific volume Birch-Murnaghan
equation of state (EoS) for Tricalcium aluminate (C₃A), Dicalcium silicate (C₂S), Tri-calcium silicate (C₃S) phases. Current modeling results indicate that calculated bulk moduli of the phases are in good agreement with previous experimental work reported for C₃A and C₂A. Among these three phases, C₃S was found to exhibit larger bulk modulus as well as isotropic compressibility, which can influence the behavior of cement composite of hydrated and unhydrated components.

8:15 AM MS01.07.02
Continuum Dislocation Dynamics-Based Grain Fragmentation Modeling Georges Ayoub¹, Ali Al-Hadi Kobaissy² and Mu'Tasem Shehadeh²; ¹University of Michigan, United States; ²American University of Beirut, Lebanon

This work proposes a grain fragmentation modeling approach that couples continuum dislocation dynamics analysis with a crystal-plasticity framework. The proposed model investigates the microstructural features of FCC metals subjected to severe plastic deformation. Several aspects of the deformation process were considered, including texture evolution, statistically stored dislocations and geometrically necessary dislocations (GNDs) densities evolution, and grains fragmentation and its effect on the overall mechanical response. The proposed model was applied to a reference volume element in which the grains are distributed and assigned an initial position. Each grain has the ability to split into 1024 new smaller grains, that was modeled by accounting for the grain-grain interaction, for which the concept of the GNDs is incorporated into the mean free path of the dislocations. The simulation results give reliable predictions of the crystallographic texture, the evolution of dislocation density, and the final grain size based on available experimental data.

8:30 AM *MS01.07.03
Scale Bridging Damage Model for Quasi-Brittle Metals Informed with Crack Evolution Statistics Kevin Larkin¹², Esteban Rougier², Viet Chau², Gowri Srinivasan², Abdessattar Abdelkefi¹ and Abigail Hunter²; ¹New Mexico State University, United States; ²Los Alamos National Laboratory, United States

Computationally efficient methods for bridging length scales, from highly resolved micro/meso-scale models that can explicitly model crack growth, to macro-scale continuum models that are more suitable for modeling large machine components, have been of interest to researchers for decades. In this work, a brittle damage model that includes the effects of material plasticity is presented for the simulation of dynamic fracture in continuum scale quasi-brittle metal components. Crack evolution statistics, including the number, length, and orientation of individual cracks, are extracted from high-fidelity, finite discrete element method (FDEM) simulations and are used to generate effective material moduli that reflect a material's damaged state over time. This strategy allows for the retention of small-scale physical behaviors such as crack growth and coalescence in continuum scale hydrodynamic simulations. A stress-based degradation criterion is introduced for the degradation of individual material zones. This allows for the development of a heterogeneous damage distribution within the bulk material. The effective moduli constitutive model is used to simulate beryllium flyer plate experiments. The results of these simulations are found to be in good agreement with numerical and experimental velocity interferometer data. Extrapolation of the effective moduli model to a higher rate flyer plate case shows promise for further reducing computational costs associated with crack statistics generation from high-fidelity simulations.

9:00 AM *MS01.07.04
Finite Amplitude Buried Blast Loading on Additively Manufactured Lattice Structures Jeffrey Lloyd¹, Christopher Cummins¹ and Eric Faierson²; ¹U.S. Army Research Laboratory, United States; ²Western Illinois University, United States

The objective of this work is to determine the utility of three architected lattice types for energy dissipation when a sandwich panel is subjected to buried blast loading. The load is imparted on a panel by detonating a scaled explosive charge underneath a layer of engineered soil and monitoring the top surface deflection. Each panel was additively manufactured out of Ti-6Al-4V using powder bed fusion and the density of each panel was varied by changing the characteristic thickness of the lattice struts within a unit cell. The three classes of lattices studied in this work are octet, auxetic, and continuous shell lattices. Large finite element simulations of the structure-blast interaction, employing direct numerical simulation, are used to determine how the structure dissipates energy and ultimately collapses when subjected to the blast loading event. Finite element predictions of performance, which is
characterized as maximum dynamic deflection of the top surface of the panel, are compared with in-situ measurements taken via Digital Image Correlation to rank order the structures. The key dissipation mechanisms of each lattice type are discussed in detail based on the finite element simulations, in-situ measurements, and post-mortem X-Ray CT scans of the tested structures.

9:30 AM MS01.07.05
Continuum Dislocation Dynamics for Finite Deformation Plasticity Kyle Starkey1, Anter El-Azab1 and Grethe Winther2; 1Purdue University, United States; 2Technical University of Denmark, Denmark

Continuum dislocation dynamics (CDD) is becoming an important approach for modelling metal plasticity at the mesoscale. CDD is a density-based approach for modeling dislocation evolution under the effect of the applied load and the dislocation short and long range interactions. The method is based on transport equations for dislocations for which the driving force comes from the stress in the crystal. Most CDD models were developed for small deformation. In order to capture lattice rotation effects, a finite deformation kinematics must be accounted for in CDD model development. We present a finite deformation formalism of CDD that distinguishes between the dislocation measures in various configurations of the deforming crystal, thus yielding both Eulerian and Lagrangian forms of the transport equations governing those measures. A strain driven homogenization scheme is used to solve the coupled dislocation transport and crystal mechanics equations at finite deformation under periodic boundary conditions. A numerical scheme based on a staggered solution of the transport and stress equilibrium problems has been implemented within a finite element framework. We present simulations of several test problems such as large angle grain boundary formation, known geometrically necessary boundaries, as well as twist boundaries forming under special loading modes. We also present preliminary predictions of the dislocation microstructural patterns and compare them with TEM data of the same. The lattice rotation effects of the forming patterns will be discussed.

9:45 AM MS01.07.06
On the Implementation of Dislocation Reactions in Continuum Dislocation Dynamics Models for Mesoscale Plasticity Vignesh Vivekanandan1, Peng Lin1, Grethe Winther2 and Anter El-Azab1; 1Purdue University, United States; 2Technical University of Denmark, Denmark

Continuum dislocation dynamics is becoming a popular framework for investigating the collective dislocation dynamics in single crystals undergoing plastic deformation. Continuum dislocation dynamics describes the spatiotemporal evolution of dislocations by transport-reaction equations that are coupled and solved concurrently with crystal mechanics, which is often formulated as eigenstrain problem. We present an approach to that facilitates an accurate implementation of dislocation reactions and cross slip in continuum dislocation dynamics. This approach seeks to rigorously enforce the dislocation line continuity from single slip system perspective in describing the reactions and cross slip. This is accomplished by adding virtual dislocation densities on each slip system to provide closure for all dislocation loops involved in cross slip or junction reactions, thus rigorously enabling the dislocation population on each slip system to satisfy the divergence free condition individually. We discuss the implementation of this approach and present results for the following: the stress-strain behavior of single crystals and the dislocation density evolution, the dislocation patterns, and the orientation dependence of the stress-strain response and the dislocation pattern. The later will be compared with experimental data for [001], [011] and [111] loading for FCC crystals.

10:00 AM BREAK

10:30 AM MS01.07.07
Structural Phase Transformation in Single Crystal Titanium During Dynamic Loading Curt A. Bronkhorst1, Biao Feng2, Benjamin Morrow3 and Ellen Cerreta3; 1University of Wisconsin - Madison, United States; 2Kimberly-Clark Corporation, United States; 3Los Alamos National Laboratory, United States

The mechanical loading of metallic materials to high pressures and over short time durations remains a technically challenging arena of research. These loading conditions typically preclude the availability of detailed experimental results for physics involving finite elasticity, plasticity mechanisms including slip and twinning processes, and structural phase transformation. Although wave dynamics study via free-surface velocity diagnostics is a long-standing discipline, much of what is believed about the response of materials to these loading conditions remains inferred from comparison to computational results. The pursuit of questions involving coupled physics and the
relationship between phase transformation and elastic and plastic deformation mechanisms is then best executed by integration of theory and experiment. We will present a study of structural phase transformation of high-purity titanium single crystals loaded by split-Hopkinson pressure bar (SHPB) and plate-impact conditions. Some sample material from these experiments was also soft-recovered and metallographically examined for structural evolution information. A thermodynamically consistent theory describing the finite elastic, dislocation slip, deformation twin, and phase transformation response of single crystals is presented. This theory presents physics coupling within both the energetic and structural components of the model for general high deformation rate loading conditions. The model performance is compared against the experimental results through numerical simulations of the experimental conditions. The SHPB and shock loading along the [0 0 01] and [1 0 -1 1] directions of single crystal high purity Ti is investigated computationally. Resonably good correspondence between simulation and experiment is obtained, which includes pole figures, volume fractions of components, free surface velocity, peak pressure, and phase transformation pressure. Multiple experimental phenomena are interpreted based upon the progression of dislocation slip, deformation twinning, and phase transformation. In compression with the [1 0 -1 1] crystal, a higher volume fraction in the primary twins but a lower secondary twin volume fraction in the [0 0 01] crystal in experiment was observed. The higher propensity for phase transformation occurs in the [0 0 01] crystal is reproduced. In addition to material texture, distributions of temperature, stresses, and plastic strains dependent on the impact loading directions are revealed.

11:00 AM MS01.07.08
Study of Pseudomorphically Transformed bcc Mg in Mg/Nb Multilayer Nanocomposite under Extreme Conditions
Manish Jain1, Marko Knezevic2, Johann Michler1, Nenad Velisavljevic4, Nathan Mara1, Irene J. Beyerlein1 and Sid Pathak1; 1University of Nevada, Reno, United States; 2University of New Hampshire, United States; 3Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; 4Los Alamos National Laboratory, United States; 5University of Minnesota, United States; 6University of California, Santa Barbara, United States

In recent years two-phase nanolayered composites with individual layer thicknesses varying from 200-300nm down to 1-2 nm have been the subject of intensive study because of their unusual physical, chemical and mechanical properties. For example, with decreasing layer thicknesses (down to nanometer length scales) the mechanical response of these nanocomposites becomes increasingly interface dominated, and they exhibit ultrahigh strengths approaching the theoretical limit for ideal crystals. Moreover if the constituent phases present large differences in strength, elastic modulus and ductility, these multilayers give rise to new possibilities for the deformation mechanisms and properties of the composite as a whole. In this work we explore the possibility of synthesizing multilayered composites where one constituent phase has a low ductility, with a final goal of enhancing both the strength and ductility of the system.

Using physical vapor deposition (PVD) techniques we synthesized a hexagonal close-packed (HCP) – body-centered cubic (BCC) Mg-Nb system (where twinning in Mg leads to its lack of ductility), over a range of layer thicknesses ranging from 5 nm to 200 nm. We investigated the structure of the hitherto-unknown bcc Mg phase in the Mg/Nb multilayer nanocomposite under high pressures in a diamond anvil cell experiment using synchrotron radiation x-ray diffraction (XRD). We utilize a suite of small scale testing techniques to evaluate the deformation mechanisms in these nanocomposites that involve both compressive loading scenarios such as (a) high throughput nanoindentation testing, to more-specialized FIB-fabricated (b) micro-pillar compression, and (c) micro-tensile tests. The mechanical data obtained from these tests are correlated with the structure information at complementary length scales using techniques such as XRD, SEM, and TEM. The use of such diverse testing technologies allows a detailed characterization of the structure-property correlations at each length scale of interest; ranging from the response of each individual interface within the laminate to properties of the ensemble.

The specialized testing techniques such as FIB-fabricated micro-pillar compression and micro-tensile experiments are used to characterize the anisotropic response of the nanolayered composite, with interfaces oriented either normal, parallel and oblique (45°) to the compression axis. Each of these configurations generate unique mechanical information: thus while compressions and tensions normal and parallel to the interface are important for a complete understanding of the anisotropy of properties and size-related effects, the tests with the interfaces loaded obliquely provide a measure of interfacial shear strength. Ductility and fracture toughness at the micrometer level are investigated using in-situ observations inside an SEM coupled with a micro-tensile geometry. Tests repeated as a function of layer thickness and interface orientations provide us with valuable information regarding the Mg-X
We have also extended our techniques to measuring the strain rate sensitivity (SRS) of the Mg-X nanocomposites using \textit{in situ} strain rate jump experiments conducted under both indentation and micro-compression/micro-tensile loading scenarios. Elevated temperature measurements are especially important, since the SRS for nano-(bcc)Mg is expected to differ from its nano-(hcp)Mg counterpart as a function of temperature from which activation energies/volumes for deformation mechanisms can be extracted. Results from these tests were analyzed in terms of the measured activation energies and activation volumes from sub-micrometer sized Mg/Nb multilayer nanocomposites. These findings reveal an alternative solution to obtaining lightweight metals critical needed for future energy efficiency and fuel savings.

\textbf{11:15 AM MS01.07.09}

\textbf{Shock-Induced Softening in Single Crystal Magnesium} \textit{Tyler J. Flanagan}\textsuperscript{1}, \textit{Sriram Vijayan}\textsuperscript{2}, \textit{Benjamin Bedard}\textsuperscript{1}, \textit{Cyril Williams}\textsuperscript{3}, \textit{Mark Aindow}\textsuperscript{2} and \textit{Seok-Woo Lee}\textsuperscript{1}; \textsuperscript{1}University of Connecticut, United States; \textsuperscript{2}The Ohio State University, United States; \textsuperscript{3}U.S. Army Research Laboratory, United States

The residual mechanical properties acquired from shock-compressed solids are often times dramatically different from those received under quasi-static conditions. This suggests that the deformation mechanisms present during shock compression may be significantly different than those seen under quasi-static conditions.

In this presentation, we will discuss shock-induced softening in single crystal magnesium. Single crystal magnesium samples were shock compressed to approximately 0.8 GPa and 1.7 GPa respectively along the \textit{<a>} and \textit{<c>} axes then released back to ambient conditions. Nanoindentation was performed on the shock recovered samples at regions free of deformation twins. We compared the nanoindentation hardness of these samples to those received from samples compressed under quasi-static conditions as well as those of pristine samples that did not undergo any plastic deformation. Our results show that quasi-static deformation increases the hardness due to conventional Taylor hardening. However, if only the deformed specimens are compared, the hardness decreased with increasing strain rate. The microstructure of the shocked samples showed a large number of deformation twins but there seems to be negligible storage of dislocations. Even pre-existing dislocations seem to be swept out. We hypothesize that due to the nature of the shock-compression experiments, although dislocations will be generated during deformation, they are able to glide through the sample unimpeded and emerge at the free-surfaces, whereas they would normally be constrained in conventional quasi-static compression. The stress-driven removal of dislocations could lead to abnormal softening in shock-compressed magnesium. Our observation counters the conventional belief that large numbers of dislocations are stored in samples subject to severe plastic deformation as usually seen in shock-compressed face-centered cubic metals. These results give an insight into the fundamental understanding of the residual mechanical response in shock-compressed materials.

\textbf{11:30 AM MS01.07.10}

\textbf{Spatially- and Temporally-Resolved Measurement of Pore Size Distribution of Granular Media under Dynamic Penetration} \textit{Andrew F. Leong}, \textit{Elaine Asare}, \textit{Vignesh Kannan}, \textit{Kaliat T. Ramesh} and \textit{Todd Hufnagel}; Johns Hopkins University, United States

The heterogeneous structure of granular materials makes their response to dynamic deformation quite complex. The size, shape, and orientation of the grains as well as the pore structure influence the distribution of forces and thus the constitutive behavior of the material. These structure-properties relationships have been actively investigated for quasi-static loading, where imaging (such as x-ray computed tomography) can provide detailed information about the evolving 3D structure of the material. But relationships determined for low loading rates may not carry over to dynamic loading, where inertial effects become important. Several groups have used high-speed x-ray imaging to study dynamic deformation of granular materials but the insights obtained have mostly been qualitative, because the information available is limited to 2D projections of complex 3D structures. This has limited the usefulness of such studies for the development and validation of models of dynamic behavior of granular materials.

In this talk, we present a robust algorithm with which we can measure the heterogeneous pore size distribution of a granular material from single projected x-ray phase contrast images. As a demonstration we apply our algorithm to sandstones undergoing dynamic wedge impact, using a sequence of images to track from their measured pore size
distribution the evolution of porosity, pore number density, and median pore size with micron-scale spatial resolution and sub-microsecond temporal resolution. We observe initial pore compaction close to the wedge tip to form an extended wedge that induces pore dilation downfield, leading to the development of intergranular cracks and failure. The insights available from these studies can provide a better understanding of how granular material response on the mesoscale influences macroscopic properties such as shear strength. This improved understanding may be beneficial for understanding complex dynamic loading problems, including planetary impacts and mine blasting.

11:45 AM MS01.07.11
*In Situ Synchrotron X-Ray and Neutron Studies of Metals under Extreme Conditions—High Temperature, Plastic Deformation, High Pressure and Shock Impact* Klaus-Dieter Liss1,2; 1Guangdong Technion - Israel Institute of Technology, China; 2Technion—Israel Institute of Technology, Israel

In-situ neutron and synchrotron X-ray diffraction deliver unique and complementary insight into the material’s response to high temperature, deformation and extreme conditions. Neutrons illuminate a larger bulk volume and reveal quantitative phase abundance, bulk texture, lattice parameter changes and other ensemble averaged quantities. In contrast, fine-bundled high-energy X-rays deliver reflections from a number of individual grains. For each constituting phase, their statistics and behavior in time reveal information about grain growth or refinement, subgrain formation, static and dynamic recovery and recrystallization, slip systems, twinning, etc. Examples will be presented on selected in-situ examinations on materials undergoing thermo-mechanical processing, high-pressure and response to shock.

1:30 PM *MS01.08.01*
Towards Predicting a Microstructure's Susceptibility to Spall Jie Chen1, Eric N. Hahn2, David Jones2, George T. Gray2 and Saryu Fensin2; 1University of Connecticut, United States; 2Los Alamos National Laboratory, United States

Understanding and predicting the response of materials under dynamic loading is a challenging problem due to complexities involved with the loading state and its interaction with various features in the microstructure. Previous experiments to study dynamic fracture in Tantalum (Ta) manufactured via Additive manufacturing (AM) has shown differences not only in the elastic plastic transition but also its spall properties. The goal of this work is to understand this difference in the dynamic response of AM vs. wrought Ta through the use of non-equilibrium molecular dynamics (MD) simulation. Both experiments and simulation data showed that altering the processing conditions also changed the number fraction of specific grain boundary types in the wrought and AM materials. To investigate if this change in boundary type distribution is the main cause of differences in the dynamic response of these materials, bi-crystal simulations were performed to quantify the effect of boundary type and structure on spall strength.

2:00 PM MS01.08.02
Effect of Microstructure on Spall Void Formation in Magnesium Hao Sheng1,1, Debjoy Mallick2,1,1, Suhas E. Prameela1,1, Timothy P. Weihs1,1, Kaliat T. Ramesh1,1,1 and Todd Hufnagel1,1; 1Johns Hopkins University, United States; 2U.S. Army Research Laboratory, United States

Magnesium is a potentially useful lightweight structural material for applications such as aerospace and defense, where materials can be subjected to extreme environments such as hypervelocity impact. In this study, we examine the effect of microstructure on spall void initiation during shock loading of pure magnesium. Using equal channel angular extrusion (ECAE), we processed pure Mg to produce an average grain size of 10 microns. Subsequent
Annealing increases the average grain size and influences the crystallographic texture of the material.

To study void initiation in these materials, we carried out spall experiments with a laser-driven micro-flyer apparatus capable strain rates exceeding $10^6 \text{s}^{-1}$, using photon Doppler velocimetry (PDV) of the back-surface velocity to determine the spall strength. We use x-ray computed tomography (CT) to characterize the incipient spall voids, and correlate this with the microstructure (texture and grain size) measured with backscattered electron diffraction (EBSD).

2:15 PM MS01.08.03

Shock, Spall and Melt—Measuring Dynamics with Pump-Probe Imaging and Interferometry of Extreme Mechanical Response of a Material from Ultrafast Laser Irradiation Abdul R. Ansari, Alex Sarracino, Ben Torralva and Steven M. Yalisove; University of Michigan, United States

Ultrafast laser-induced shock waves in metals can produce strain rates as high as 10^{11} (1/sec). The mechanical response to these extreme strain rates is important for ultrafast micro-machining, the study of extreme strain rate phenomena, de-orbiting space junk with ultrafast lasers, the response to biological systems as in eye surgery, and many emerging ultrafast materials applications. What is unique about our approach to studying these extreme conditions, which are on the order of ~10^{4} K and pressures up to 100 GPa, is that we are able to recover the material afterwards to study as well as use pump-probe methods to observe the dynamics on picosecond timescales. We deposit thin films (1 nm to 10 microns) on sapphire or glass substrates and irradiate the material through the transparent substrate. The fluence we use dictates which path the material will take through a temperature-density phase field. We are especially interested in studying materials in the vapor dome, the two-phase region where the liquid and gas phases are in equilibrium. Our work has demonstrated that we can force a material into the vapor dome 10-12 ps after the laser pulse ends [1]. Depending on the material and the irradiating fluence, we are able to keep the material in the vapor dome for up to 25 ps while maintaining its temperature to be, at most, 90% of that at the critical point[1]. We have demonstrated mixing of W and Ni to thermally stabilize the quenched nanograin material (~2 nm grain size). We have also shown that we can mix Ni and Ag layers at the higher temperatures in the vapor dome. These studies exploit the extreme quenching that can be observed—we are capable of quenching at 10^{10} to 10^{15} degrees per second.

This talk will focus on the dynamics of high strain rate shock loading and rapid heating. We will study Ni films of 200 to 300 nm thickness that are calculated to be capable of supporting a strong shock wave. Multiple deformation mechanisms are observed upon irradiation including delamination and deformation without fracture, fracture, spall, and melt. Results from 1-D plasma hydrodynamics codes (HYADES) with DOE equations of state show that internal mechanical spall from the large tensile component of the shock wave is possible. Our modeling results suggest that, with a 150 fs, 780 nm laser pulse, we are able to generate up to 23 GPa of tensile stress at the trailing edge of shocks using a fluence (0.9 J/cm^2) that is just below the melt threshold for Ni. The spall strength of Ni in static conditions is about 3 GPa. We will present results of ultrafast pump-probe imaging and interferometry of the back side to extract the dynamics and relative competition between heat flow and mechanical stress. This experimental and computational platform will be used to explore the limits of the phonon drag regime and the ultimate strength of materials. We will present the in-situ observations of the dynamics along with ex-situ microscopy of the recovered material. These will be discussed in the context of our computational results to show that material heating and loading at these extreme conditions lead to unique final states. Finally, we will show that this experimental approach is ideal for studying a large variety of other high-temperature and high-pressure phenomena.

References

2:30 PM MS01.08.04

Extreme Deformation and Failure of Materials by High Power Pulsed Laser-Driven Shock Compression and Tension Shiteng Zhao, Bruce Remington, Christopher Wehrenberg and Marc Meyers; 1University of California, Berkeley, United States; 2Lawrence Livermore National Laboratory, United States; 3University of California, San
Diego, United States

Pulsed lasers with power on the order of terawatts, once deposited on a target surface, will launch a strong stress pulse that propagates into the material. Owing to the ultrashort duration of the laser pulses, unprecedented extreme conditions which combine high pressures (and/or shear stresses), strain rates and temperatures can be generated in materials, yielding a yet unexplored regime of study: extreme mechanical metallurgy. During the talk, I will first summarize our efforts on laser shock compression of four covalently bonded materials, namely, silicon, germanium, boron carbide and silicon carbide (SiC). These materials are known to have high Peierls-Nabarro stress and negative Clapeyron slope. The profile of the shock waves was measured by a velocity interferometer system for any reflectors (VISAR). The shock deformation microstructure has been revealed by high-resolution scanning/transmission electron microscopy and all the materials exhibit shock-induced amorphization. This discovery indicates shock-induced amorphization as a generalized deformation mechanism under strong shock condition. Laser shock experiments can also be extended to the tensile regime when the compressive wave was reflected by the free surface. The tensile wave, once exceeds the ultimate tensile strength of the materials, will lead to a catastrophic failure. Our recent efforts on dynamic tensile fracture of tantalum with different grain size will be discussed. In addition to laser shock experiments, I will also talk about the dynamic behavior of CoNiCr-based high entropy alloy (HEA). These materials show strong resistance to shear localization under impact loading, which is mainly due to HEA's low stacking fault energy and therefore easy propensity to undergo twinning. Our results suggest that CoNiCr-based HEA may have good ballistic protection application.

2:45 PM MS01.08.05
Atomistic Simulations of Shock Compression of Single-Crystal and Core-Shell Cu@Ni Nanoporous Metals
Anupam Neogi, Lijie He, Niaz Abdolrahim and Ali Khourshaei Shargh; University of Rochester, United States

We have investigated the performance and applicability of a single-crystal and core-shell Cu@Ni nanoporous (NP) structure under shock-loading using atomistic simulations. Core-shell structure exhibits lesser volume compressibility than a single-crystal NP. Core-shell NP also demonstrates increased plastic deformation i.e., enhanced shock-energy absorption efficiency of around 10.5% larger than a single-crystal NP, albeit shock Hugoniots reflect a weak dependency on core-shelling of an NP structure. Shock-induced deformation behavior of NP-Cu with and without nano-coating of Ni has been studied. At $u_p < 0.15$ km/s, partial collapse of the pores are observed via direct crushing in both NP structures. At $0.15 \text{ km/s} < u_p < 0.55 \text{ km/s}$, single-crystal NP Cu shows complete collapse of pores through ordinary dislocation-mediated softening in the ligaments, while the core-shell Cu@Ni NP demonstrates increased strain-hardening in Cu/Ni interface. At $u_p = 0.75$ km/s, shock-induced deformed microstructure of both structures has been observed to be recovered through recrystallization.

3:00 PM BREAK

3:30 PM MS01.08.06
Micropillar Cyclic Compression Studies of an NiTi Thin-Walled Tube
Hyunmin Kim and Sharvan Kumar; Brown University, United States

A systematic examination of the cyclic compression response in three different orientations ($r, \theta$ and $z$) of micropillars obtained from a polycrystalline thin-walled NiTi tube (that is a precursor to laser machining of medical stents) was undertaken and correlated with texture measurements. The tube was textured with a strong $\{112\}-\{111\}$ duplex structure along the drawing direction ($z$), a strong $\{111\}-\{123\}$ along the $r$-direction and a near $\{011\}-\{012\}$ texture in the $\theta$-direction. Strain amplitudes examined included the entire transformation cycle as well as reduced amplitudes about targeted mean strains; the latter enables a comparison of the cyclic response of a predominantly austenitic microstructure with that of a predominantly martensitic microstructure. Further, single crystal micropillars were milled from an annealed NiTi sheet with 25-30 µm grain size with loading axis aligned in orientations corresponding to the tube texture and their cyclic response was compared to those obtained directly from the tube. Results from these studies will be presented and discussed.

3:45 PM MS01.08.07
Hierarchical Microstructure in Shear Bands of Pure Titanium
Dexin Zhao, Xiaolong Ma, Dinakar Sagapuram and Kelvin Y. Xie; Texas A&M University, United States
Shear bands in metallic systems are narrow regions of intense strained materials which could act as premature failure locations. A comprehensive understanding of shear band microstructure is the key to control the ductility of materials. However, large localized deformation usually develops within this thin region and nanoscale recrystallized grains are formed. Conventional characterization techniques such as EBSD and regular TEM imaging are inadequate to visualize the detailed microstructure inside these shear bands. For example, EBSD cannot provide high enough spatial resolution. TEM has the ability to determine the nanoscale grain size, but to elaborate the orientations of all grains is labor-intensive. Moreover, detailed orientation information cannot be obtained. In this work, we demonstrated that ASTAR (a technique that acquires the diffraction pattern of each pixel) could offer direct orientation information of microstructure feature down to 1 nm scale. Using the ASTAR results, we revealed the hierarchical structure including high-angle grain boundaries, low-angle grain boundaries, defect bundles in the shear bands.

4:00 PM MS01.08.08
Mechanical Properties of InP Nanowires—In Situ TEM Tests and Atomistic Simulations Zhilin Liu1,2, Ioannis Papadimitriou1, Miguel Castillo1, Gustavo Esteban-Manzanares1, Jon M. Molina-Aldareguía1 and Javier Llorca1,3,2, 1IMDEA Materials Institute, Spain; 2Central South University, China; 3Technical University of Madrid, Spain

The mechanical properties and fracture mechanisms of taper-free InP twinning superlattice (TSL) nanowires were ascertained by means of in situ uniaxial tensile tests in a transmission electron microscope. The nanowires were grown along the zinc-blende close-packed [111] direction and presented an average twin spacing of ~ 13 nm. The elastic modulus along the [111] orientation was 87 ± 17 GPa, while the fracture strain was 2.9 ± 0.3% close to the one reported in ZnO nanowires (~5%) but smaller than that of GaAs nanowires (10–11%). Fracture was brittle in all cases and occurred by the propagation of a crack along the twin boundary interface. No evidence of inelastic deformation mechanism was observed neither in the experimental stress-strain curve nor in the TEM images before fracture. MD simulations of the tensile deformation of untwinned and twinned InP nanowires of different diameters (12 to 30 nm) at 300 K were carried out to assess the experimental data. The elastic modulus obtained from the simulations (84 GPa) was fairly independent of the diameter and close to the experimental values. The failure strain and the tensile strength of the twinned nanowires in the MD simulations (~ 10% and ~ 6.7 GPa) were much higher than those observed experimentally but smaller than those simulated for untwinned nanowires, and these differences were attributed to the stress concentrations associated with the zig-zag waviness at the nanowire surface. Moreover, the simulations did not show any evidence of non-linear deformation mechanisms prior to fracture, that was triggered by the nucleation and propagation of a crack at the twin boundaries, in agreement with the experimental observations.

4:15 PM MS01.08.09
Extreme In Situ Mechanics of Ni-Based Superalloys: 800°C and Beyond Sanjit Bhowmick, Eric Hintsala and Asif Syed; Bruker Nano Surfaces, United States

High-strength structural materials such as Ni-based superalloys and diffusion bond coats are widely used in challenging environments and with exposure to mechanical fatigue, particle impact, and erosion at elevated temperatures. Diffusion aluminate bond coats are an example of compositionally and microstructurally graded coatings with significant variation in engineered mechanical properties across the cross-section. Nanoindentation and pillar compression, particularly in situ, can be considered as a well-suited technique for measuring the properties of such complex microstructural materials as the deformation volume can be carefully controlled to probe different precipitates and microstructural zones. In this study, an SEM nanomechanical instrument with an integrated high-temperature stage and an active tip heating was used to conduct pillar compression of aluminate bond coating and substrate at room temperature to well above 800degC. This is the first study of an in situ nanomechanical testing of any sample at such higher temperature with capturing deformation events in detail at that temperature inside an SEM. With combined analysis of chemistry and microstructural changes, the results were used to understand local mechanical properties variation as a function of temperature.

4:30 PM MS01.08.10
Recent Innovation in In Situ Extreme Mechanics at the Micro and Nanoscale Nicholas Randall1, Damian Frey1, Quentin Longchamp1, Jean-Marc Breguet1, Rajaprakash Ramachandramoorthy1, Jakob Schwiedrzik2 and Johann Michler2; 1Alemnis AG, Switzerland; 2EMPA, Switzerland
Nanomechanical tests are moving beyond the basic measurement of hardness and elastic modulus to encompass a host of different mechanical properties such as strain rate sensitivity, stress relaxation, creep, and fracture toughness by taking advantage of focused ion beam milled geometries. New developments, such as high cycle fatigue, are extending the range of properties which can be studied at the micro and nanoscale. However, such techniques are challenging due to low oscillation frequencies, long duration of tests and large thermal drift when attempted with standard indentation instruments. Novel piezo-based nanoindentation methods are now allowing access to extremely high strain rates (>10⁴ s⁻¹) and high oscillation frequencies (up to 10 kHz).

Until only recently, high strain rate testing of materials at strain rates from 100/s – 10000/s has only been possible using macroscale techniques, such as split Hopkinson bar, Kolsky bars and plate impact testers. At the microscale, strain rates have typically been limited to 0.1/s or less, owing to limitations in instrumentation and insufficient data acquisition rates.

This talk will focus on the most recent developments in instrumentation for in-situ extreme mechanics testing at the micro and nanoscales, with specific focus on a testing platform capable of strain rate testing over the range 0.0001/s up to 10’000/s (8 orders of magnitude) with simultaneous high speed actuation and sensing capabilities, with nanometer and micronewton resolution respectively.

Other recent innovations include cryogenic and high temperature tests covering the temperature envelope from -150 to 800 °C. The challenges in variable temperature tests and the associated technological and protocol advances will be discussed along with select case studies. The inherent advantages of using small volumes of sample material, e.g., small ion beam milled pillars, will be discussed together with the associated instrumentation, technique development, data analysis methodology and experimental protocols. Some examples of test data will be presented where a wide range of strain rate has been combined with variable temperature in order to investigate rate effects as a function of temperature. Finally, future research directions in this sub-field of micromechanics will be discussed.

SESSION MS01.09: Poster Session
Session Chair: Irene Beyerlein
Thursday Afternoon, December 5, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

MS01.09.01
High-Velocity Impact Induced Gradient-Nano-Grained Structure and Phase Transformation Claire Griesbach, Jizhe Cai and Ramathasan Thevamaran; University of Wisconsin--Madison, United States

We present a dynamically deformed material with a unique gradient-nano-grained (GNG) structure and martensitic phase transformation. GNG structures have been created through techniques such as surface mechanical attrition treatment [1], electroplating [2], surface rolling [3], and laser shock processing in germanium [4]. Studies show that nanograins provide increased strength while coarse grains retain ductility [1–3], simultaneously improving two mechanical properties that are often found to be mutually exclusive. However, a detailed structure-property relationship enabling predictions of material properties based on the gradient grain structure has not been developed yet. We investigate the process-structure-property relations in GNG metals through an experimental approach that allows us to tailor the grain structure and probe mechanical properties while observing microstructural changes. Using a laser induced projectile impact testing (LIPIT) apparatus, we impact single-crystal silver microcubes [5] onto a stiff target at ~400 m/s. The high-strain-rate deformation creates a gradient nano-grained structure with small ~10 nm grains near the impact plane and progressively larger grains farther from the impact region [6]. By varying impact parameters such as sample orientation and impact velocity, we produce different GNG structures with varying ranges of grain size and degree of gradient.

We show that a [100] impact orientation of the crystal initiates a phase transformation from a face-centered-cubic (fcc) to a hexagonal-close-packed (hcp) structure. Very rare naturally occurring hcp silver was found in north-eastern Russia in the 1970’s [7], and synthetic pathways have been developed recently [8]. A single-step method to dynamically induce such a phase transformation will allow for further tailoring of favorable material properties. We
also find that this phase transformation is orientation dependent as cubes impacted along the [100] direction undergo phase transformation while impact along the [110] direction does not yield a phase transformation. This is due to the varying stress states present in the sample during deformation and the favorable [100] loading geometry to create stacking faults on the {111} planes. We also show that over time small grains coalesce into larger grains due to recrystallization and results in a subsequent hcp-to-fcc phase transformation.

With an understanding of the process-structure relations, we investigate how these structures lead to improved mechanical properties of the material. Using a focused ion beam (FIB), we mill micropillars out of the impacted samples and perform micro-compression tests using an in situ SEM nanoindenter to measure strength and toughness. We also fabricate planar cross-sections of the sample using FIB and measure the hardness as a function of the gradient grain structure using the SEM nanoindentator. Developing detailed process-structure-property relations will enable the design of metals with optimal strength and toughness for a given engineering application.


MS01.09.02
Mechanical Properties of Micrometer-Size Cellular Foam-Like Auxetic Structures Ming Wang and David R. Harding; University of Rochester, United States

Two-photon polymerization (TPP) is a recently developed technique that was used in these experiments to “write” millimeter-size cellular structures (~0.2g/cm³) with micrometer-size resolution. This process is used to make auxetic structures, which are characterized by having a negative Poisson’s ratio. The purpose of this study is to develop a material that can dissipate energy from impacts or vibrations over a wide temperature range—from cryogenic to room-temperature conditions. Different auxetic structures were designed using finite element analysis methods to maximize the structural and plastic deformation that can occur at cryogenic temperatures without exceeding the strength properties of the material. These structures were then printed using a commercial laser writer (Nanoscribe GmbH) and tested at 23°C and 140 K using a thermal mechanical analyzer (Perkin Elmer) at loads ranging from 10⁶ to 10⁸ Pa and multiple cycles. The calculated energy (~32 J/kg) that is dissipated from a brief impulse (~17 ms) is compared to the measured energy dissipation. The robustness and performance of the structures is compared with the laser “writing” parameters used to make the structure, which requires full polymerization of the photosensitive material while avoiding embrittlement.

This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0003856, the University of Rochester, and the New York State Energy Research and Development Authority.


MS01.09.03
Designing a Mechanical Metamaterial Inspired from Crystalline Quartz Hye-in Na and In-Suk Choi; Seoul National University, Korea (the Republic of)

In this talk, we propose a design concept of architected mechanical metamaterials based on the crystalline quartz structure. Crystalline quartz is a repeating double helix structure of the SiO₄ tetrahedra with plenty of empty space that shows a zero-Poisson’s ratio. We mimic this crystalline alpha quartz structure to design a truss-based mechanical metamaterial. Both experiments and numerical analysis demonstrated that the inter-penetration of the
SiO₄ tetrahedra results in the zero-Poisson’s ratio similar to the crystalline quartz. Through dynamic analysis at various levels, it was possible to figure out several important features of this mechanical metamaterial.

MS01.09.04
High Temperature Mechanical Behavior of 3D Printed Inconel 718 Observed by In Situ Transmission Electron Microscopy
Supriya Koul, Le Zhou, Yongho Sohn and Akihiro Kushima; University of Central Florida, United States

Selective laser melting (SLM) refers to an additive manufacturing (AM) technique for metallic alloys, which uses a scanning laser to melt and fuse metallic powder bed layer-by-layer. It has advantages over traditional manufacturing methods in the design freedom and manufacturing flexibility. However, the SLM process with repeated melting and solidification leads to the unique microstructure that can include large columnar grains and periodic cracks. Moreover, the rapid solidification intrinsic to SLM can produce nanoscale structure different from traditional manufacturing processes. While post-heat-treatments are widely employed to improve the mechanical property of SLM-produced alloys, the unique, as-built microstructure can lead to varying response to traditionally defined heat treatment parameters. Therefore, the detailed understanding of the dynamic microstructure evolution as a function of temperature and its effect on the mechanical behavior is essential for optimizing the SLM and post-heat-treatment processes. Here, in-situ transmission electron microscopy (TEM) is a useful tool to observe nano-scale phenomena in real time. It provides direct observations of the deformation processes in nano-scale to study the deformation mechanism/procedures, and their relationships with the microstructural evolutions during heating. In this study, we designed a unique sample shape that enables tensile experiment of thin TEM lamellae without undesired off-plane deformations or bending.

We selected IN718 as representative SLM-produced alloy to discover the relationship between the microstructural evolution during heat treatment and the associated change in the mechanical behavior. The in-situ TEM captured a microstructural evolution of IN718 during exposure to a high temperature, with an emphasis on precipitation of spherical γ'/γ'' phases. Subsequent tensile experiment demonstrated brittle fracture in contrast to a ductile fracture of as-printed IN718 indicating a proper heat treatment (solutionizing and ageing) is necessary to improve the mechanical property. This study provides correlation among heat-treatment, microstructural evolution, and the mechanical behavior, which can be used to optimize the post-heat-treatment for SLM-produced alloy through microstructure control.

MS01.09.05
Revealing the Photo-Induced Non-Thermal Amorphization Mechanism of Phase Change Material
Subodh C. Tiwari¹, Aiichiro Nakano¹, Fuyuki Shimojo², Rajiv Kalia¹, Paulo Brancicio¹ and Priya Vashishta¹; ¹University of Southern California, United States; ²Kumamoto University, Japan

Phase-change materials (PCM) owing to their extreme electro-optical contrast between crystalline and amorphous states are used in optical data storage, flexible devices and neuromorphic computing. However, atomistic mechanisms governing photo-excitation induced non-thermal amorphization processes are still unknown. We perform excited-state dynamics within the framework of density functional theory to investigate the mechanism behind such crystalline to amorphous transition for Germanium Telluride (GeTe). Our study shows the GeTe non-thermal amorphization process is the key. Amorphous phase is characterized by computation of diffraction pattern in real time. Further analysis of bond-overlap analysis suggests a change in bonding behavior between Ge-Ge from anti-bonding to bonding state that leads to increase in Ge-Ge bonds and decrease in Ge-Te bonds. A rapid heat extraction during excited-state simulation does not lead to amorphous phase. Overall, our excited-state dynamics study demonstrates that the non-thermal amorphization in GeTe occurs due to antibonding character of excited electronic states. Since structural transformation limits the lifetime of PCM-based devices, a deeper understanding behind this mechanism may allow us to a new avenue in the design of future devices.

This work was supported as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC0014607

MS01.09.06
Stabilizing Laser Shock Peening Induced Compressive Residual Stresses for High Temperature Applications of Additively Manufactured Parts
Ali Beheshti¹, Kasra Momeni², Lloyd Hackl³, Keivan Davami⁴ and Michael Munther⁵; ¹George Mason University, United States; ²Louisiana Tech University, United States; ³Metal Improvement Company, Surface Technologies, Curtiss Wright, United States; ⁴The University of Alabama, United States; ⁵The University of Alabama, United States
States

Metal 3D printing is a versatile additive manufacturing (AM) process that produces parts from powders layer-by-layer directly from a digital model. Metal 3D printing allows for fabricating complex metallic components in an efficient and cost-effective manner compared to conventional manufacturing techniques. One significant roadblock for additively manufactured parts is that residual tensile stresses can be high in AM parts, which limits their applications, particularly for cyclic loading or at high temperatures. Post-processing methods to modify AM parts offer new opportunities for applications in extreme environments such as in turbines or nuclear reactors. Laser shock peening (LSP) is a technique that is used as a post-processing method to optimize the service life of critical components by inducing compressive residual stresses that increase the material’s resistance to surface-related failures such as creep, fatigue, stress corrosion cracking, etc. However, its application for ferrous materials has been limited to temperatures lower than ~400°C since the stresses are released at temperatures above that. A novel technique was developed to stabilize the LSP-induced compressive residual stresses at high temperatures (above 400°C). Nickel-based superalloy specimens (Inconel 718) were printed using a direct metal laser sintering (DMLS) technique. Various tests including X-ray diffraction spectroscopy, transmission electron microscopy, and nanoindentation were performed. Complementary molecular dynamics and phase field simulations were utilized to understand the underlying physical mechanisms governing the dislocation motion and their interaction with the microstructures to provide further insight to the effect of postprocesses on the final performance of printed parts, e.g. wear and fatigue. Nanoindentation hardness mapping showed that LSP increases the hardness of the top ~1.2 mm of the specimens, with a maximum hardness of ~6.6 GPa on the laser shock peened surface that gradually decreases with an increase in the distance from the surface and reaches 5.2 GPa. Electron microscopy proved that dislocation generation is the mechanism responsible for plastic deformation and hence hardening in laser shock peening. Specimens that were treated by our new technique, reserved more than 50% of the maximum magnitude of their compressive residual stresses, even after exposure to 700°C for 48 hours. The results will lead to AM materials with better performance at high temperatures, not only attributed to their inherent properties, but more importantly by optimizing microstructure, surface properties, and residual stresses.

MS01.09.07
Microstructure Evolution During Shear Banding in Compressed Nanocrystalline Ceramic Nanopillars Observed In Situ
Haw-Wen Hsiao, Shu Li, Karin Dahmen and Jian-Min Zuo; University of Illinois at Urbana-Champaign, United States

Shear banding is observed widely in a variety of materials and at different length scales. During shear banding, intense plastic shear is produced within a thin band, and shear localization strongly limits the material’s ductility, leading to catastrophic failure under stress. For these reasons, shear banding has attracted considerable research interest in uncovering the underlying mechanisms. However, connecting mechanical behaviors with microstructure evolution during shear banding is difficult, and the critical knowledge of structure-property relationship is still missing so far. In-situ observation during deformation is needed to uncover the origin of shear banding. Here, we report a direct observation of shear banding in nanocrystalline ZrN nanopillars. ZrN belongs to a class of materials, called nanocrystalline ceramics (NCCs), which are popular as protective coating because of their outstanding mechanical properties. The high strength of NCCs derives from the effect of nanograin size, following the well-known Hall-Petch relationship. A major drawback of NCCs, or nanocrystalline materials in general, is their low toughness due to the limited dislocation activities. However, when the grain size is reduced into the nanoscale regime, the effect of grain size begins to soften materials via the increased grain boundary activities. We show that plastic deformation in ZrN is carried out by intermittent granular activities in the NCC nanopillars without brittle fracture. Cooperative granular activities are found along the regions where shear bands form. Complementary cumulative distribution function (CCDF) of the associated stress drops suggests dislocation avalanches are suppressed by nanograin size.

Nanocrystalline ZrN was prepared in the form of thin film with an average grain size of 18 nm using unbalanced magnetron sputtering deposition. Nanopillars were fabricated in the plane view direction of the thin film. Compression tests of separate nanopillars were conducted in either bright-field imaging mode or nanobeam diffraction mode using Hysitron P195 picoindenter in JEOL 2010 LaB6 TEM. The experiments were simultaneously recorded as a video at the frame rate of 10 frames/s.

The study here demonstrates the secondary deformation mechanisms involving grain boundaries, in addition to the primary deformation mechanism operated by dislocations, and how together these mechanisms facilitate plastic deformation in nanocrystalline materials. The strong correlation of shear band formation and intermittent granular
activities are demonstrated, from which a shear banding model of NCC materials is proposed.

**MS01.09.08**

**Carbon Schwarzites Behavior Under Ballistic Impacts** Levi C. Felix¹, Cristiano F. Woellner² and Douglas S. Galvao¹; ¹State University of Campinas, Brazil; ²Federal University of Paraná, Brazil

Carbon Schwarzites are 3D porous crystalline pure carbon structures [1]. They contain rings with more than six atoms, which create negative Gaussian curvatures and the ‘flatness’ of these curvatures is dependent on the ratio of hexagon to non-hexagon rings. There are different Schwarzite families, such as primitive (P), gyroid (G), diamond (D), etc [2]. Previous studies suggested [3] that under compressive loadings, the mechanical properties of schwarzites is directly related to the local ‘flatness’ of each structure. Impact tests were performed on macroscopic 3D printed structures (cm size) [4], which showed that some qualitatively trends of the impact resistance and energy absorption are preserved from nano to macroscale. In this work we have investigated the Schwarzite behavior under ballistic impact. We considered four structures from two families (primitive (P688 and P8bal) and gyroid (G688 and G8bal)), which differ mainly by their local ‘flatness’. We used a spherical projectile with a diameter of 15 Angstroms and velocity range from 1 up to 3 km/s and with the same mass value of the target. We carried out fully atomistic molecular dynamics (MD) simulations using reactive force fields (AIREBO). Our MD results show that Schwarzites are very effective to absorb kinetic energy but their performance decreases as their ‘flatness’ increases. In P8bal and G8bal the projectile penetration is about four times deeper than in P688 and G688, with more extensive structural fractures. Considering that it was already demonstrated that macromodels of these materials can be 3D printed [4], our results open new perspectives to create new or to improve Schwarzite-based functional engineered materials.


**MS01.09.09**

**Role of Anisotropy in Swelling-Driven Fracture of Phase-Transforming Battery Materials** Ataollah Mesgarnejad and Alain Karma; Northeastern University, United States

Due to their high storing capacities, silicon and germanium have emerged as a promising anode material for high-capacity Li-ion batteries. Initial lithiation of both materials results in a crystalline to amorphous phase transformation accompanied by a large (300%) volume expansion that drives plastic flow and fracture above a critical particle size, which is several fold larger in Ge than Si. This difference is believed to be due to the fact that the motion of the atomically sharp crystalline-amorphous phase boundary is strongly anisotropic in Si but nearly isotropic in Ge. However, how this difference affects elastoplastic deformation and fracture remains poorly understood quantitatively. Here we exploit the phase-field approach to describe both the crystalline to amorphous phase transformation and stress-driven plastic deformation and fracture within a self-consistent mathematical framework to shed light on the role of anisotropy. We model the phase transformation using a modified Allen-Cahn model with anisotropic and isotropic mobilities, respectively. We model the mechanical response due to lithiation-driven swelling of the anode using neo-Hookean elasticity and finite J-2 plasticity. Finally, we model fracture using a variational phase-field formulation. Our model can describe both nucleation and propagation of cracks without interpenetration of crack surfaces under compression.

We use this multi-physics phase-field framework to investigate the lithiation of Si and Ge nanopillars as a function of yield strength and fracture energy. Using simulations without fracture, we first show that, for isotropic swelling, the tensile stresses driving fracture in the nanopillar remain capped by the yield strength. In contrast, for anisotropic swelling, tensile stresses become amplified severalfold by localization of plastic deformation near the particle surface. We relate this amplification to the existence of a critical yield strength below which plastic deformation occurs successively under compression and tension and above which it only occurs under compression. Next, using simulations with fracture, we show that this amplification of tensile stresses causes nanopillar to fracture at a smaller radius in Si than Ge as experimentally observed. Finally, we use our simulation results to obtain consistent estimates of elastic properties, yield strength, and fracture energy, which are compared to existing experimental data.
measurements.

**MS01.09.10**
**Microstructure and Tensile Behavior of Nanostructured Gradient TWIP Steel**  Jie Ding, Zhongxia Shang, Jin Li, Haiyan Wang and Xinghang Zhang; Purdue University, United States

Gradient nanostructured metallic materials have shown a combination of high strength and good ductility. A TWIP steel with large equiaxed grains was processed by surface mechanical grinding treatment, and the subsequent gradient structures formed near surface consist of surface nanolaminate layer, a mixed layer of deformation twins and shear bands, and a deformation twin layer. TEM studies reveal that detwinning occurs during microstructural evolution. Tensile studies show that the gradient structures increase the yield strength of TWIP steel prominently. The evolution of gradient microstructures and their influence on mechanical behaviors of the gradient TWIP steel are discussed.

**MS01.09.11**
**Low Temperature Compression of Glassy Carbon**  Dougal G. McCulloch¹, Sherman Wong¹, Thomas Shiell², Brenton Cook¹, Jodie Bradby³ and David McKenzie⁴; ¹RMIT University, Australia; ²Carnegie Institute of Washington, United States; ³The Australian National University, Australia; ⁴The University of Sydney, Australia

Diamonds are used in many industrial applications due to their extreme hardness, particularly for polishing, cutting, and pressure application. There has been an increasing interest in hexagonal diamond in recent years, largely due to its potential to be harder than diamond [1]. However, experimental hardness measurements for this technologically interesting material have yet to be reported due to the extreme temperature/pressure conditions required to form hexagonal diamond [2, 3] as well as the inability to form a phase-pure sample without cubic diamond inclusions [4]. Our recent study reports formation of pure hexagonal diamond at a record low temperature of 400°C that is proposed to be due to a shear-induced plastic flow [5]. This region of pure hexagonal diamond was observed in an annular region around the central region containing a graphite-like structure. In this work, the proposed shear-induced transformation pathway from this graphite-like structure to the phase-pure hexagonal diamond is explored and a pathway to further lower the required temperature is presented.

Transmission electron microscopy of lamellae containing both the graphite-like and diamond structures was examined to provide microstructural evidence for the shear-induced transformation mechanism. Within the graphitic regions, striations associated with plastic flow of graphitic sheets can be observed. The graphitic sheets are aligned along the flow direction, with the amount of orientation within these sheets increasing with increasing shear. At regions of higher shear, these flowing graphitic sheets were observed to progressively “lock-into” hexagonal diamond within a mixed region where both structures were present. The distribution of the hexagonal diamond is in good agreement with modelled shear-strain distributions. Density consistent with turbostratic graphite and hexagonal diamond are measured within their respective regions, with the density increasing linearly in the transition region. Graphitic inclusions within the hexagonal diamond and transition region were also found to have decreased interlayer spacing with increasing shear. The interlayer spacing of the inclusions within the hexagonal diamond region having a lower interlayer spacing than uncompressed graphite, making the transition to hexagonal diamond more energetically favourable. This is evidence for a step-wise transformation from the graphitic precursor to the hexagonal diamond structure due to a shear-induced flow mechanism.

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Engineering Impact Modification of Polypropylene for Energy Absorption under Extreme Loading Conditions Chinmay Saraf and Alan J. Lesser; University of Massachusetts Amherst, United States

This contribution focuses on how impact modified polypropylene (iPP) is engineered to absorb energy and fail in a ductile fashion under extreme loading conditions. Herein, we report the results from a systematic investigation on three different polypropylene systems modified using soft block copolymers SEBS (Styrene-ethylene/butylene-styrene), POE (Polyolefinic elastomer) and a combination of SEBS and POE. Comparisons are made between extreme conditions (high strain rate at -15°C and -30°C) and quasi-static fracture tests at 25°C. The mechanisms of energy dissipation and fracture are then investigated in these systems with regard to soft particle size, spacing, shape, and other morphological features that govern their energy absorption.

At 25°C and quasi-static loading rates, the formulation containing lower modulus SEBS shows the highest fracture energy release rate when compared to the other two formulations. At extreme loading rates, the SEBS formulation still shows the highest energy absorption, but its relative performance is not as contrasting. Morphological investigation using a scanning electron microscopy (SEM) indicates the formation of phase-separated soft-particle domains with a larger particle size of 1-2 um for SEBS containing formulation as compared to a 200-300 nm domains for the other two formulations. Detailed investigation of failure mechanism shows the formation of interconnected crazes and a significant particle-particle interaction for polypropylene formulation containing SEBS, whereas, POE containing formulations show isolated craze formation. Failure mechanism in these formulations suggests that dilatational strain is relieved by a craze formation rather than cavitation and shear band formation. Results indicate that soft particle domains larger than the critical particle size (about 1um) governs the energy absorption for polypropylene under extreme conditions.

Herein, we also investigate the effect that an additional reinforcement in the form of talc has on these polypropylene formulations. It is observed that talc acts as a nucleating agent and improves the dispersion of soft particle domains. Morphology of talc containing formulations indicates a significant decrease in particle size, most predominantly for SEBS. These phase-separated domains have a particle size of 150 nm, smaller than the critical particle size. Room temperature fracture toughness evaluation for talc containing formulations show that SEBS containing formulation has 35% higher fracture energy when compared to the other two formulations. Interestingly, low-temperature testing at -15°C and -30°C with an impact velocity of 4 m/s shows that polypropylene formulation containing SEBS and POE in the presence of talc has 20% higher impact energy absorption as compared to the other two formulations. As seen for the formulations not containing talc, the mechanism of energy dissipation did not change; Craze formation provides release of the hydrostatic stress and acts as a major energy dissipating mechanism. Room temperature testing on polypropylene system shows that the lower modulus SEBS has a higher fracture energy release rate, with or without talc reinforcement.

The Role of High-Temperature Annealing of Graphene Aerogels Martin Silhavik, Zahid Ali Zafar and Jiri Cervenka; Institute of Physics of the Czech Academy of Sciences, Czechia

Graphene aerogels (GAs) are a three-dimensional porous form of graphene with a high surface area. GAs have attracted a significant amount of interest in recent years due to their unique mechanical and electrical properties that show great potential for numerous applications in batteries, supercapacitors, electrochemical sensors and absorption of oil and organic pollutants. These unique properties are originating from a clever arrangement of two-dimensional graphene sheets in a three-dimensional porous monolith structure containing air-filled pores. Here, we investigate the mechanical and electrical properties of GA prepared via hydrothermal synthesis from graphene oxide without any stabilizing polymer. GAs prepared by this method are generally brittle materials because they contain a lot of defects and oxygen groups. However, the thermal annealing at temperatures over 1000 °C under inert gasses causes a significant improvement of the mechanical and electrical properties, resulting in highly flexible and electrically conductive GA materials. The high-temperature annealing causes healing or repair of defects, eliminating most of the oxygen from the structure, thereby enhancing the amount of π–π stacking between graphene sheets. The as-prepared GA exhibits superior compressive elasticity and structural integrity when subjected to the ultrahigh pressing (MPa).
High Rate Mechanical Characterization of Glassy Polymer Thin Films Using High-Rate Micro-Particle Impact Test
Shawn H. Chen, Amanda Souna, Edwin P. Chan, Christopher Soles and Stephan J. Stranick; National Institute of Standards and Technology, United States

Mechanical toughness of polymeric materials has long been understood to depend on the relaxations and interactions on the molecular level. Toughness arises as impact energy is dissipated through these molecular relaxations. However, the time and length scale of the molecular mechanisms are typically several orders of magnitude faster and more localized than the traditional experimental techniques used to characterize them. Here, we employ an all optical laser-induced projectile impact test (LIPIT) to study the dynamic deformation response of polycarbonate thin films for impact mitigation applications. Micro-projectiles deposited on a polymeric launch pad are accelerated via laser ablation of an absorbing layer. The deformation response of PC films of different MWs and thicknesses are investigated at high strain rates (10^5 to 10^7 s^-1). LIPIT measurements can help to elucidate the rate-dependent ductile-brittle transition of polycarbonates and the molecular relaxation mechanisms that contribute to the toughening/dynamic stiffening properties that are desirable for impact mitigation applications.

Limit of Temporal Resolution with Atomically-Engineered Probes while Preserving Picometer Range Spatial Resolution
Omur E. Dagdeviren; Yale University, United States

With recent advances in dynamic scanning probe microscopy techniques, it is now a routine to image the sub-molecular structure of molecules with atomically-engineered tips which are prepared via controlled modification of the tip termination and are chemically well-defined. The enhanced spatial resolution is possible as atomically-engineered tips can preserve their integrity in the repulsive interaction regime. Although the mechanism of improved spatial resolution has been investigated both experimentally and theoretically, the ultimate temporal resolution while preserving picometer scale spatial resolution still remains an open question. Here, we computationally analyze the temporal resolution of atomic force microscopy imaging with atomically-engineered tips using previously developed computational models [1-3]. Our computational results reveal that non-metal terminated tips, e.g. oxygen-terminated copper, are well-suited for enhanced temporal resolution up to video rate imaging velocities while preserving picometer range spatial resolution. Contrarily, the highest-attainable spatial resolution of atomically-engineered tips with low-stiffness, e.g. CO-terminated, deteriorate with increasing imaging velocity. Our results reveal that when atomically-engineered tips terminated with molecules are in use, imaging velocities in the order of nanometers per second at most are inevitable even for atomically flat surfaces to retain the atomic resolution and avoid slip-stick motion. In addition to shedding light on the temporal resolution of atomic force microscopy imaging with atomically-engineered tips, our numerical results provide an outlook to the scalability of atom-by-atom fabrication using scanning probe microscopy techniques.

References:

3D Helicoidally Architectured Thin-Film Composite for Tougher Bio-Inspired Material
Komal Agarwal¹, Sahay Rahul¹, Kento Yamagishi¹, Anbazhagan Subramani², Avinash Baji² and Arief S. Budiman¹; ¹Singapore University of Technology and Design, Singapore; ²La Trobe University, Australia

The helicoidal microstructures found in exoskeleton of mantis shrimp dactyl club, scarabaei, lobster provide them with remarkable toughness and high impact strength. During impact loading, these helicoidally arranged filaments tend to stretch, and twist along different planes and angles, absorbing energy, increasing the work of fracture and deflecting crack propagation. Such naturally occurring helicoidal architecture inspire us to develop bioinspired synthetic helicoidal structural materials to bolster toughness and impact resistance. Most existing studies employ conventional carbon epoxy or glass epoxy macroscopic prepregs to study the effect of helicoidal architecture in composites. We, however, use novel computer integrated near field solution electrospinning as an additive manufacturing method to fabricate 3D helicoidally arranged fiberous structures (micron/nano sized) using polyvinylidene fluoride. The aligned filament arrays are continuously collected one on top of the other with 45° angular offsets in polyvinyl alcohol bath to produce thin film composites (in range of 200 100 μm thick).
helicoidal arrangement of fibers in the matrix shows improvement in tensile behavior, crack propagation and toughness. These helicoidally oriented fiber composites show dramatical twisting and elongation of the fibers along the different directions, delaying the fracture events, as compared to its bulk counterparts. Further, surface treatment for interfiber and fibers-matrix adhesion shall be performed, and its influence on the mechanical characteristics of the helicoidal composite shall be studied.

**MS01.09.17**

**Carbon Nanotube Peapods under High-Strain Rate Conditions—A Molecular Dynamics Investigation**

José M. de Sousa¹, Cristiano F. Woellner², Leonardo D. Machado³, Pedro A. Autreto⁴ and Douglas S. Galvão⁵; ¹Instituto Federal do Piauí, Brazil; ²Federal University of Parana, Brazil; ³Federal University of Rio Grande do Norte, Brazil; ⁴Federal University of ABC, Brazil; ⁵University of Campinas, Brazil

Nanostructured systems under high-strain rate conditions, have been object of theoretical and experimental investigations in recent years. A recent joint theory-experiment study showed that carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs) under high-velocity impacts can be unzipped into nanoribbons [1]. However, the dynamics and fracture patterns of nanostructured systems under high-velocity impacts are not yet fully understood [2,3] and more studies are needed, especially involving hybrid systems, such as fullerenes encapsulated inside single wall carbon nanotubes (SWCNTs), the so-called CNT peapods [4]. In this work we have investigated C60 fullerene encapsulated inside SWCNTs (CNT-C60) under high-strain rate conditions. Our theoretical study was carried out through fully atomistic molecular dynamics simulations with the reactive force field ReaxFF. We have considered CNT-C60 shoot at high-kinetic energy (ultrasonic velocities values varying from 1 km/s up to 60 km/s) against a rigid substrate and into two different orientation relative to the target (lateral and vertical configurations). Our results show that for specific velocities and orientations, CNT-60 experience large deformations and are fractured at different configurations: i) just fullerene ejections; ii) tube fracture; iii) tube fracture with fullerene coalescence; and iv) under extreme conditions the formation of amorphous carbon structures. These results provide helpful insights in understanding the structural changes and fracture dynamics of nanostructures under high-rate conditions.


**MS01.09.18**

**Understanding Mechanical Behaviors of Auxetic Foams via Pore Structure Characterization Using X-Ray Tomography**

Lamei Du and Ye Xu; Beihang University, China

In this study, we aim to understand the connections between the negative Poisson's ratio and the pore structures of the auxetic polyurethane foam. The pore structure is visualized by X-ray tomography and key structure parameters were extracted. We found that the sphericity, tortuosity, bond angles are the most dominating structure parameters which determines the range and extent of the auxetic mechanical behaviors. In addition, the sensing performance of the CNT-coated polyurethane foams was also tested as a function of Poisson's ratio. The stronger the auxetic effect, the stronger the strain sensing capability.

**MS01.09.19**

**Characterization of Metal Strength and Toughness through Frictional Sliding Contact Mechanics**

Soheil Safari Loaliyan, Ryan Lacy, Parth Patel, Steven Palkovic and Simon Bellemare; Massachusetts Materials Technologies, United States

Contact mechanics provides a method of characterizing how a material responds to local deformation under controlled loading conditions. The most widely used implementation of contact mechanics is indentation hardness, where a hard stylus of known geometry is pressed into a softer material to measure the resistance to permanent deformation. In this research the mechanical properties of engineering metals are assessed using the concept of frictional sliding where a stylus is indented into a material and then slides across the surface leaving a permanent scratch or groove.
Frictional sliding with a spherical stylus on metals results in a ductile response that can be related to the elastic-plastic response of a power-law hardening material through equations developed with finite element analysis (FEA) simulations. Experiments performed on more than 20 steel and aluminum materials has shown that this approach can predict the material yield strength and ultimate tensile strength with close agreement to traditional laboratory tensile tests on the same sample. When a wedge-shaped stylus is used during frictional sliding tests, a chip of material separates from the substrate through fracture processes. If a small gap is included on the upstream face of the stylus then material in this region is subjected to increasing elongation as the separated chip flows up the wedge until a tensile fracture occurs. FEA simulations of crack propagation in elastic-plastic materials and frictional sliding experiments on steel have shown that the geometry of the fracture surface can be correlated to the material ductile fracture toughness ($J_c$). This concept can be extended to monitor fatigue behavior by applying cyclic loading at varying proportions of the steady state cutting force to determine the number of cycles required to propagate an existing crack. Overall, these examples show how contact mechanics can be used to correlate how a metal microstructure responds during frictional sliding to traditional mechanical properties of the substrate, including hardness, yield and tensile strength, fracture toughness, and fatigue.

**MS01.09.20**


Yin Liu and Changyong Cao; Michigan State University, United States

Magneto-active elastomers (MAEs) are soft polymeric materials embedded with magnetically responsive particles or carried with free currents, which respond to external magnetic fields by producing large deformations or varying mechanical properties. They have been increasingly used for many emerging applications such as soft robotics, printed untethered soft origami, magnetically anisotropic micro actuators, bistable switches and magnetoactive acoustic metamaterials. Thus, it is of interest and of paramount importance to develop a more rigorous continuum theory and numerical model to consider the strong field interaction in MAE analysis so as to have a deep understanding of the coupled mechano-magneto behavior of MAEs and facilitate the rational design of soft robotics with MAEs. In this paper, we present a continuum theory and finite element model to simulate the finite deformations of magneto-active elastomer (MAE) under applied magnetic fields or currents. The magnetic field is assumed to be measured in the background space with fixed spatial coordinates, rather than in the elastic MAE, leading to a concise and physically admissible continuum theory to describe coupled mechano-magnetic behaviors of MAE. Specifically, the magnetic field varies with prescribed free or localized currents and their spatial locations evolving with the motion of MAE, while the deformation of MAE is actuated by the surface or body forces applied by the external magnetic field or equivalent currents. A staggered finite element solution framework is developed to solve the strongly coupled governing equations in the two fields, and mesh distortion along the interfaces of MAE domain and free-space domain is resolved by considering concurrent deformation of the mesh in these two domains. Numerical examples are presented to demonstrate the validity and efficiency of the developed model for simulating the behaviors of MAE structures subjected to different sources of magnetic fields (e.g., free currents, magnetization or external magnetic field). This research offers a new method and mechano-magneto model for analyzing MAEs and will be useful for the rational design and analysis of MAE-based actuators and robotics in the future.

**MS01.09.21**

**Development of Energy Absorption Materials by Using the Fractal-Cut Concept**

Juhee Kim¹, Vivek A. Karupпасamy², Young-Joo Lee³, Jeong-Yun Sun¹, In-Suk Choi¹, Myoung-Gyu Lee¹ and Kijung Lee¹; ¹Seoul National University, Korea (the Republic of); ²Korea Institute of Science and Technology, Korea (the Republic of); ³University of Pennsylvania, United States

In this presentation, we will demonstrate an architected material for energy absorption based on the simple kirigami concept. We utilized our 2-dimensional hierarchical cut pattern named ‘fractal cut’ for an energy absorption structure. Both experimental and numerical analysis were carried out to systematically support the feasibility of our design concept. We found that the ‘Fractal cut’ structures can decrease the impulsive force of an incident object when implemented into soft materials because of high biaxial expandability. We were further able to optimize the effective design to dissipate the impulse energy through the dynamic analysis of fractal cut materials with various cut motifs and levels.

**MS01.09.22**

**Mechanical Property Changes of Tungsten Thin Films Due to Hydrogen or Helium Implantation**

Yoshiaki
Habu, Heun Tae Lee, Akira Nagakubo, Hirotugu Ogi, Kenzo Ibaro and Yoshio Ueda; Osaka University, Japan

Tungsten (W) plasma facing components in magnetic fusion devices experience extreme dynamical power (>10 MW/m²) and particle (>10²⁴ m⁻²s⁻¹) loads due to its interaction with the edge plasma [1]. The plasma-material interaction zone is a few nm deep, corresponding to the range of the implanted particles, leading to extreme concentration and thermal gradients. The large flux of implanted hydrogen or helium species, result in large near-surface strain fields due to their accumulation - driven by the low solubility of both hydrogen and helium in W. The resulting changes in the mechanical properties are critical to evaluate from the viewpoint of plasma operation and component lifetime issues. To date, the dynamical mechanical response of W under such non-equilibrium loading of hydrogen or helium far beyond its solubility limits is not well known due to: (1) the difficulty in probing the near surface properties, and (2) a lack of a suitable in-situ method that can be applied during plasma loading. This work focuses on overcoming the first problem, and we report on changes in the near-surface mechanical properties of W due to hydrogen or helium implantation using picosecond ultrasonics [2, 3]. W thin films (~40 nm) were implanted with deuterium (D) or helium using an ion or plasma beam, respectively. Ultrashort light pulses were used to excite and detect GHz-frequency elastic waves to determine the elastic modulus of the W thin films. It was found that the longitudinal elastic constant of the W thin film increased by up to 5 % following D implantation (1×10²³ m⁻²), while helium had a significantly larger effect. The results suggest picosecond ultrasonic method is a sensitive probe for characterizing the near surface changes in mechanical properties of plasma facing materials, opening the way towards in-situ applications.


Enhanced Damage Tolerance of Pre-Deformed Tungsten Microwires with High Dislocation Density Chaoqun Dang and Yang Lu; City University of Hong Kong, Hong Kong

Bulk tungsten is inherent room-temperature brittleness which limits its workability and performance in demanding applications. Pre-deformed tungsten microwires play a significant role in the strength, ductility, and damage tolerance of tungsten (W) fiber-reinforced metal matrix composites (MMCs) due to tungsten fiber’s ductile behavior and high tensile strength. Room-temperature fracture of extremely fibrous, pre-deformed tungsten wire does possess quite a different fracture in a ductile manner and substantial resistance to fracture at room temperature. It involves combinations of three fracture modes: cleavage, grain boundary delamination, and with individual grains necking to nearly 100% reduction in area. However, the difficulty of observing the action of individual tungsten fibers during plastic deformation has made it challenging to conclusively determine the mechanisms of a tungsten fiber-reinforced composite and presents a major bottleneck in the rational design of tungsten fiber-reinforced composites. Here, we conduct the in-situ tension of tungsten fibers as a promising platform to determine the precise role of individual tungsten fiber. It reveals that the continuous and massive dislocation nucleation and fast dislocation glide and escape by in situ TEM straining lead to the ultra-large elongation in nanoscale W fibers. This work could give insights for understanding pre-deformed tungsten wire at nanoscale and the design of pre-deformed tungsten wire based flexible devices and nanoscale tungsten fiber-reinforced composites.

Size Effects on Creep and Creep Fracture Mechanisms of Single-Crystal Metallic Nanomaterials Hiroyuki Hirakata, Takayuki Nagashima, Kotaro Yamaguchi and Takahiro Shimada; Kyoto University, Japan

It is well accepted that submicron- and nanometer-sized single-crystal metals demonstrate different mechanical properties from those of bulk counterparts; e.g. plastic resistance increases with decreasing specimen size. For the long time use of such nanomaterials, understanding of creep deformation and fracture is more important than plastic properties. It is significant to clarify whether small crystals can sustain high stress over a long period. The purpose of the study is to clarify the size effects on creep properties of submicron-sized single-crystal metals at room temperature and discuss the underlying mechanisms. We conducted long-term (up to 14 h) tensile creep experiments for submicron single crystal gold and aluminum under in situ field-emission scanning electron microscopy (FESEM) or transmission electron microscopy (TEM) observation. We directly measured the specimen elongation from the FESEM or TEM images to eliminate the measurement error in the displacement sensor owing to thermal drift and
evaluate the creep strain accurately. The creep behavior transitioned from continuous to discrete manner as the applied stress decreased, which was different from that of bulk metals. In the small stress region, although the creep strain increased with the passage of time, an arresting region appeared in which the creep deformation temporarily stopped. The in-situ TEM observation suggested that the appearance of the arresting region was due to the depletion of dislocations by recovery or the reduction of dislocations and activated dislocation sources. The smaller specimens required higher stress to reach a similar strain rate, indicating that the resistance to creep deformation increased with the decrease of specimen size. We discussed the mechanisms of the size effects based on the experimental results.

**MS01.09.25**

**Metal Doping Effects on the Sinterability and Mechanical Properties of Boron Carbide**

Toshiki Ota, Ryuichiro Koyama, Kouga Nakamura, Junya Watanabe and Satofumi Maruyama; Tokyo City University, Japan

Boron carbide materials possess attractive properties such as high hardness, lightweight and wear resistance, therefore it can apply various applications like cutting and grinding tools, ceramics bearing, etc. Boron carbide, so-called B<sub>4</sub>C, has a relatively wide range solid solution; B<sub>4.3</sub>C to B<sub>10.6</sub>C. However, boron carbide has a problem in sintering especially in boron-rich region in boron carbide because of the low self-diffusion coefficient in boron and boron carbide caused by the strong covalent bonding of boron. For example, boron carbide bulk materials are mainly sintered over 2273 K<sup>1</sup>,<sup>2</sup>. A few decades ago, Takagi et al proposed for new sintering method called “reaction boronizing sintering” for complex boride based hard materials<sup>3</sup>). In the reaction boronizing sintering, boronizing reaction is occurred by solid-state diffusion between metal and boron in first and the metal boride is generated. After the boronizing reaction, the eutectic liquid phase is appeared by the pseudo-binary eutectic reaction between boride and metal. In this method, the eutectic liquid phase has important roles for chemical reactions and the densification of the boride sintering body. In this study, we applied “reaction boronizing sintering” method to the sintering for boron carbide materials. 3d transition metals such as Mn, Fe, Co, Ni and etc. were adding to boron carbide to generate eutectic liquid phase between boron and metal element. Metal added boron carbides were synthesized by powder metallurgy method from metal powders, amorphous B powder, and C powder. To prevent the remain of free carbon in the sintering body and investigate the effect of molar ratios of B and C on the sinterability and mechanical properties, chemical compositions of boron carbide were B<sub>5.5</sub>C to B<sub>8.5</sub>C. Starting materials were mixed and sintered by Spark Plasma Sintering at 1973K. To refinement for the crystal structure and phase ratios, Rietveld analyses were carried out using Rietan-FP software. To investigate the microstructures and dispersion of the elements for the sintering body, SEM-EPMA measurements were performed. With the increase of the Mn contents, Vickers hardness was increasing and it reached more than 3000 HV2 for Mn 10mol% added B<sub>5.5</sub>C, which value was almost equal to standard boron carbide sintered body. According to the SEM images of Mn added B<sub>5.5</sub>C, observed pores in the fracture surface were decreasing with the increase of the Mn content. We will discuss about the effect of metal doping and chemical compositions of boron carbides on the microstructure and the mechanical properties for the boron carbide.

References

**MS01.09.26**

**Super Ductile Iron—Nano-Sized Structure and Fatigue Behavior**

Wentao Zhou, Kewen Dong and Cheng Liu; Yangzhou University, China

Ductile iron (DI) has attracted considerable interest in virtue of its good wear resistance, high strength together with good ductility, and high fatigue strength. A super DI with a multiphase structure was designed by a novel multi-step low-temperature austempering treatment. The influences of multiple microstructure on tensile strength and fatigue limit were examined applying tension and tensile-tensile fatigue tests. It showed that the tensile strength is over 1160MPa as well as an elongation of 3%, and fatigue life Nf exceeds 25,000 cycles in a high stress amplitude level of 600MPa, which were attributed to a synergistic strengthening and microcrack toughening from the super multiphase matrix comprising prior martensite (PM), bainitic ferrite (BF) and retained austenite (RA). It was found that the arrest and retardation of crack nuclei during either static stretching or dynamic deformation was controlled by a (BF+RA)<sub>nano</sub> structure, which was formed around the PM. The result can offer a great potential for super ductile iron in future critical application industry such as automotive
gears under heavily impact loads combined with wear.

**MS01.09.27**  
_In Situ_ Micromechanical Characterization of Metallic Glass Microwires under Torsional Loading  
Sufeng Fan and Yang Lu; City University of Hong Kong, Hong Kong

Small-scale metallic glasses have many applications in microelectromechanical systems (MEMS) and sensors which require good mechanical properties. Bending, tensile, compression properties of metallic glasses at micro/nano-scale have been investigated previously. Here, by developing a micro robotic system, we investigated the torsional behavior of Fe-Co based metallic glass microwires inside a scanning electron microscope (SEM). Benefiting from the _in situ_ SEM imaging capability, the fracture behavior of metallic glass microwires has been uncovered clearly. Large plastic strain is found under torsional loading at room temperature, which could be evidenced by the large torsion angle. Through the postmortem fractographic analysis, it can be revealed that both spiral stripes and shear bands contributed to the fracture mechanism of the microscale metallic glass. Plastic deformation of the microwires included both homogeneous and inhomogeneous plastic strain, which began with the liquidlike region, then a crack formed because of shear bands and propagated along the spiral direction. Moreover, three stages fracture mechanism of this metallic glass microwire was proposed. Although the metallic glass microwire broke in brittle mode, the shear strain was not lower than that of conventional metal wires. Moreover, we found an inverse relationship between the plastic strain and the loading rates.

**MS01.09.28**  
Non-Affine Deformation in the Flow of Metals and the Emergence of Roughness at Free Surfaces  
Wolfram G. Nöhring¹, Adam R. Hinkle¹,² and Lars Pastewka¹; ¹IMTEK, Germany; ²Sandia National Laboratories, United States

Almost all natural and man-made surfaces are rough, and this roughness controls many interesting phenomena, such as adhesion or friction between bodies, or transport across interfaces. The scaling of surface heights is often self-affine. This has been observed over many length scales, from atoms to mountains. However, the origin of self-affine roughness is not entirely understood. Here, plastic deformation is investigated as a possible generative mechanism for self-affine roughness in perfect crystals, High Entropy Alloys and metallic glasses. Bi-axial compression of initially flat samples is simulated using molecular dynamics. It is shown that the subsurface deformation field exhibits a fractal, self-affine geometry, independent of the atomic structure of the material. During deformation, the fractal structure of the subsurface displacement field is imprinted onto the free surface. Self-affine roughness is therefore a recording of the non-affine deformation process occurring in the bulk.

**MS01.09.29**  
Modeling and Simulation of Pore Migration in Tin Solders at High Homologous Temperatures Subjected to Large Electric Currents and Stress Gradients  
Zachary J. Morgan¹, Yongmei M. Jin¹, Vahid Attari² and Raymundo Arroyave²; ¹Michigan Technological University, United States; ²Texas A&M University, United States

Pore migration in solder joints driven by electric current and stress gradient is an important phenomenon that impacts the performance and reliability of electronic devices. It is a diffusional process at high homologous temperatures under large thermodynamic driving forces caused by applied electric fields and internal stress concentrations in complex microstructures. With the miniaturization of electronic devices, anisotropic properties of individual grains play increasingly important roles since a solder joint consists of only several grains. Tin-based solder alloys, the most common lead-free solder material, exhibit significant anisotropic characteristics in electrical conductivity, elastic modulus, and diffusivity. To investigate the effects of these anisotropic properties on pore migration, a phase field model is developed to simulate pore evolution in beta-tin polycrystals. In the model, mass diffusion describing pore migration is coupled with charge conduction and elastic deformation by solving microscopic Ohm’s law and microelasticity equations, respectively. The simulations reveal various anisotropy-caused pore migration behaviors including pore velocity and path, pore-pore interactions, and pore-grain boundary interactions. The results are analyzed in terms of internal electric and stress fields which relate the pore migration behaviors to the underlying grain structures.

**MS01.09.30**  
Fatigue Crack Growth Behavior of Multiferroic Concentric Composite Rings  
Ryan M. Stampfli and George Youssef; San Diego State University, United States
Multiferroic composites have been an area of recently increased research interest due to their potential in magnetoelectric coupling applications to increase efficiency and reduce component size when compared to traditional electromagnetic devices. Multiphase magnetoelectric composites exhibit coupling coefficients an order of magnitude larger than their single-phase counterparts by way of strain mediation of magnetic and electric energies. Concentric, toroidal ring structures are of a particular interest as they exhibit greater magnetoelectric couplings compared to similarly sized stacked laminated structures. In this study, a multiferroic ring composite consisting of lead zirconate titanate (PZT) piezoelectric ceramic concentrically bonded to Terfenol-D magnetostrictive alloy was investigated. To achieve their magnetoelectric coupling potential, these structures are typically operated at or near their resonant frequencies, hence a pre-existing crack at the interface propagates and degrades the strain mediation between the piezoelectric and magnetostrictive phases. Thus, a pre-defined crack was introduced at the interface, where the composite structure was subjected to an A/C electric field with near-resonant frequencies concurrently with a magnetic field corresponding to saturation. The crack behavior is reported along with its effect on the overall magnetoelectric performance of multiferroic composite ring structures.

MS01.09.31
Collective Motion of Quincke Rotating Bead

Etien Martinez Roman1, Tommy Fjelde Kristiansen1, Barbara Pacakova1, Jaako Timonen2, Paul Dommersnes1 and Jon O. Fossum1; 1Norwegian University of Science and Technology (NTNU), Norway; 2Aalto University, Finland

We present experimental results on collective dynamics and self-assembly in a suspension of Quincke electro-rotating granular particles (1). Depending of the value of the electric field or the concentration of the particles is it possible to find different active matter steady states such as gas or polar vortex structures. We perform Particle Image Velocimetry in order to compute the vorticity and velocity of the systems and also simple tracking procedure are performed as a complementary way of characterization (2,3). A striking new result is that the size of the vortices can be controlled with the electric field and also, that the shapes of the vortices are independent of the container’s shape. The results points to future applications in materials science to fabricate nano-/micro-structured surfaces with macroscopic functionalities including photonics, wetting, porosity and permeability.

(1) A. Bricard et al, Nature 503, 95 (2013)
(2) H. H. Wensink et al, PNAS 109,14308 (2012)
(3) A. Doostmohammadi et al., Nature Communications 7, 10557 (2016)

MS01.09.32
Role of Shock Wave Propagation and Twinning/Detwinning Behavior on Spall Failure of Cu-Ta Multilayered Structures at the Atomic Scales

Marco J. Echeverria, Avanish Mishra and Avinash M. Dongare; University of Connecticut, United States

The shock response of multiphase metallic microstructures comprising of immiscible fcc/bcc phases is determined by the shock wave propagation and reflection behavior that generates heterogeneities in the microstructure such as dislocation slip and deformation twinning, which can determine the dynamic strength, i.e. the spall failure, of the microstructure. For pure fcc-Cu and bcc-Ta microstructures, MD simulations indicate a contrasting role of twinning in the void nucleation stresses of both phases. An increment in the density of twin partials in Cu increases the dynamic strength, whereas in Ta it decreases as the twin volume fraction increases. However, the role of structure, the spacing of interfaces on the shock wave propagation, and the interplay between dislocation slip and deformation twinning have not been widely studied for these types of materials. Thus, large scale molecular dynamics simulations are carried out to investigate the role of deformation twinning in multiphase tri-layer microstructures comprising of Cu/Ta/Cu layers with interfaces perpendicular to the shock loading direction for layer thicknesses ranging from 100 nm to 500 nm. These MD simulations suggest that shock wave reflections at the Cu/Ta interfaces affect the twinning/de-twinning behavior in the bcc-Ta phase that can result in modifications in the spall strengths of the multiphase alloy. The links between twin volume fractions, dislocation densities and spall strengths in Cu-Ta multilayered structures will be presented.

MS01.09.33
Effect of Deformation Twinning and Phase Transformation on Spall Failure of Fe

Avanish Mishra and Avinash M. Dongare; University of Connecticut, United States
Due to the incomparable strength of alloyed Iron among metals, an immense interest has been generated to characterize the deformation/phase transition behavior of single-crystal Iron under shock loading conditions for its applicability in extreme environments. Shock compression of Fe-based microstructures shows an interplay between dislocation slip, deformation twinning, and phase transformation behavior. Ductile failure behavior under the dynamic loading conditions (spallation) is characterized by nucleation, growth and coalescence of voids. Such failure transpires due to the interaction of reflected waves; forming triaxial tensile stresses in a microstructure deformed during the shock compression. For single crystal microstructures, the mechanical behavior of the system strongly depends on the crystal orientation and shock-loading conditions that render variations in dislocation plasticity, deformation twinning, and phase transformation behavior. This emphasizes the need for an in-depth understanding of the microstructure evolution of material under shock loading, and the interaction of voids, slips, twinning, etc., mechanisms, which tailors the spall failure at the atomic scale. Molecular dynamics (MD) simulations are carried out to investigate the spallation behavior of single-crystal Fe systems-oriented along [110], [112], and [111] directions subjected to various impact velocities ranging from 750-2000 m/s. The MD snapshots are characterized to quantify the evolution of twin volume fractions, fractions of HCP phase, and damage (void sizes and fractions) for the range of pressures generated. The effect of crystal orientation and impact velocities on the deformation response and the spall strength will be presented.

SESSION MS01.10: Session IX
Session Chairs: Seok-Woo Lee and Benjamin Szajewski
Friday Morning, December 6, 2019
Hynes, Level 1, Room 109

8:30 AM MS01.10.01
Theory of Dislocation-Precipitate Bypass Benjamin Szajewski, Joshua C. Crone and Jaroslaw Knap; U.S. Army Research Laboratory, United States

The interaction between glissile dislocations and precipitates within a continuum is responsible for marked increases in material strength. Due to their desirable engineering features, dislocation-precipitate interactions have been the subject of study for decades. Towards enhancing our mechanistic understanding of the dislocation-precipitate bypass process, we present an analytic model of the Orowan bypass stress ($\tau_{\text{Orowan}}$) required for a dislocation to bypass an array of precipitates. We initially consider spherical precipitates described by a diameter ($D$) and inner precipitate spacing ($L$). Our model suggests a $\tau_{\text{Orowan}}$ scaling logarithmically with the precipitate diameter, $\tau_{\text{Orowan}} \sim \ln \frac{D}{L}$, which we validate against a well-established, yet empirical model. We also examine the influence of precipitate aspect ratio on $\tau_{\text{Orowan}}$. Finally, we demonstrate the application of our model towards predicting the scaling of $\tau_{\text{Orowan}}$ for an array of plate-like $\theta$ precipitates within an Al-Cu molecular statics materials system. Our analyses provide insight into relationships between precipitate size, shape, density, orientation and metallic strengthening mechanisms.

8:45 AM MS01.10.02
Microstructural Predictions of Thermo-Mechanical Fracture of H.C. P. Alloys Subjected to High Temperatures M.A. Zikry, T. Hasan and I. Mohammed; North Carolina State University, United States

A dislocation-density based multiple slip crystalline plasticity formulation and a new computational fracture approach have been used to investigate and predict thermo-mechanical fracture in hexagonal close packed (h.c.p.) materials with a focus on h.c.p. alloys with hydrides that have different crystalline structures than that of the matrix. This predictive framework has been used to understand and predict the interrelated effects of dislocation-density interactions, generation, and recovery on the competition between intergranular and transgranular crack nucleation and propagation. The validated predictions indicate that transgranular fracture is dominated by dislocation-density interactions with hydrides and intergranular fracture is dominated by GB misorientations. The proposed modeling framework can provide guidelines for a fundamental understanding of materials subjected to thermo-mechanical loading conditions, such that failure resistant material systems can be attained for extreme loading conditions and environments.
Orowan Alternating Slip and Intervoid Necking—Crack Growth Mechanisms in Moderate Purity Single-Phase Aluminum Grades 1100 and 1050

Diana E. Burden1, Brendan P. Croom1, Clifton H. Bumgardner1, Helena Jin2 and Xiaodong Li1; 1University of Virginia, United States; 2Sandia National Laboratories, United States

Comprehensive knowledge of crack growth mechanisms is vital to monitoring and predicting failure in ductile materials such as aluminum. Mechanical testing, microscopy, and tomography of single-phase aluminum grades 1100 and 1050 were applied to illustrate Al failure mechanisms and how those mechanisms changed with alloy composition. Al1100 and 1050 have been previously overlooked in favor of high purity or more specialized grades. Through low strain rate uniaxial tension testing, Al dogbone samples were strained to separation to reveal their fracture surfaces. The fracture surfaces exhibited smooth, void-free edge regions and dimpled centers with a smooth transition and were oriented perpendicular to the loading direction. The texture of the fracture surfaces supports the assumption that Orowan alternating slip (OAS) contributes to the fracture mechanism for dog Al1050 and Al1100 but the perpendicular fracture angle indicates that intervoid necking is another contributing mechanism. Center hole rectangular Al samples were strained under the same conditions as the dogbone samples but paused at key points to monitor crack formation and growth using computed tomography. Diamond-shaped cracks extended from the center hole towards the sample edge surrounded vertically and laterally by small voids with larger voids just beyond the crack tip. As strain increased, voids at the crack tip coalesced with the growing crack. The crack shape is indicative of OAS while the existence and coalescence of voids indicate intervoid necking. These mechanisms work together and describe Al1100 and 1050’s complicated growth behavior more effectively than a single mechanism would allow.

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Thermodynamic Theory of Crystal Plasticity—Formulation and Application to fcc Copper

Charles Lieou1 and Curt A. Bronkhorst2,1; 1Los Alamos National Laboratory, United States; 2University of Wisconsin–Madison, United States

We present a thermodynamic description of crystal plasticity. Our formulation is based on the Langer-Bouchbinder-Lookman (LBL) theory of dislocation motion, which asserts the fundamental importance of an effective temperature that describes the state of configurational disorder and therefore the dislocation density of the crystalline material. We extend the LBL description from isotropic plasticity to crystal plasticity with many slip systems. Finite-element simulations show favourable comparison with experiments on polycrystal fcc copper under uniaxial compression. The thermodynamic theory of crystal plasticity thus provides a thermodynamically consistent and physically rigorous description of dislocation motion in crystals. We also discuss new insights about the interaction of dislocations belonging to different slip systems.

Modelling Junction Reactions in a Continuum Dislocation Dynamics Framework

Peng Lin1, Vignesh Vivekanandan1, Grethe Winther2 and Anter El-Azab1; 1Purdue University, United States; 2Technical University of Denmark, Denmark

The performance of a crystal material depends on the evolution of underlying microstructures, e.g. dislocations. Continuum dislocation dynamics (CDD) is an effective tool to study the evolution of dislocations at microscale. In CDD, curved and connected dislocation lines are represented by density-like field variables. The evolution of dislocation systems are obtained by solving a set of transport equations. Here we discuss how the processes of dislocation reactions in which two interacting dislocations form junctions can be described within such a framework. The basic idea is that dislocation reactions are done by subtracting a dislocation density vector from each reacting slip system and adding to the corresponding junction density. This will result in an additional reaction term in
dislocation transport equations. Criteria including both Burgers vectors and dislocation line directions are established to determine whether reactions should happen. The model is solved within a 3D vector-density-based dislocation dynamics. Simple dislocation structures are tested for junction formation, followed by a loaded plastic deformation simulation. The results show that the model is able to capture the change of dislocation network due to reactions and the mechanical response is affected by dislocation reactions.

9:45 AM MS01.10.06
Effects of Microstructures on Superelasticity of CaFe2As2 Single Crystal Shuyang Xiao1, John T. Sypek1, Sriram Vijayan1, Paul Canfield2, Mark Aindow1 and Seok-Woo Lee1; 1University of Connecticut, United States; 2Ames Laboratory & Department of Physics and Astronomy, United States

Uniaxial micropillar compression tests on a CaFe2As2 single crystal have recently revealed the existence of extremely large elastic deformation, superelasticity, with an elastic limit up to 13%. The collapsed-tetragonal phase transition, which is the uni-axial process of making As-As bonding, is the main mechanism of superelasticity and differs entirely from the shear process of martensitic-austenitic phase transition in conventional shape memory alloys. Usually, superelasticity and its related structural transition are strongly affected by defect structures. In order to improve the superelastic performance of CaFe2As2, therefore, it is necessary to understand how defect structure influences the collapsed-tetragonal phase transition and the corresponding superelastic behavior.

In this study, therefore, we investigated the effects of microstructure on the superelasticity of [0 0 1]-oriented CaFe2As2 micropillar using the state-of-the-art in-situ micromechanical testing and transmission electron microscopy. Three different samples (Sn-solution grown, quenched FeAs-solution grown, and annealed FeAs-solution grown crystals) were prepared to produce different microstructures. Transmission electron microscopy showed that while a Sn-solution grown sample is nearly defect-free, a quenched FeAs-solution grown sample contains the extremely dense rectangular network of screw dislocations on a (0 0 1) plane. An annealed FeAs-solution grown sample contains nano-scale FeAs precipitates with coherent phase boundaries. Rectangular network of screw dislocations in a quenched FeAs-solution grown sample resembles the low angle twist boundary, and the corresponding lattice distortion would make the formation of As-As bonds more difficult, leading to the suppression of collapsed tetragonal phase transition as well as superelasticity. An annealed FeAs-solution grown sample showed the similar mechanical behavior with a defect-free Sn-solution grown sample, but fracture often occurred at a lower stress. The presence of nanoscale FeAs precipitates would act as a stress concentrator, which cause the early brittle fracture. In sum, superelasticity of CaFe2As2 is significantly influenced by defect structures, and our research outcomes will be generally useful to design the enhanced superelastic performance in other ThCr2Si2-type intermetallic compounds with the same crystal structure.

10:00 AM BREAK

10:30 AM MS01.10.07
Metal-Ion-Controlled Growth of Topologically complex Cu/Fe Thin-Film Morphologies for Enhanced Dynamic Mechanical Performance Benjamin K. Derby, Max Powers and Amit Misra; University of Michigan, United States

Interface morphology and other microstructural heterogeneities ultimately determine thin film performance under extreme conditions, especially high-strain rate deformation. Synthesizing novel and complex thin films with morphologies that go beyond single crystal and single-phase materials, is needed to understand the properties exhibited by multiphase materials under dynamic loading conditions. In this work we present a new PVD sputtering technique to process topologically complex and bicontinuous thin film microstructures that are dense with interfaces. Using the innovative High-power Impulse Magnetron Sputtering, or HiPIMS, technique to co-deposit immiscible Cu and Fe, the direction of phase separation with respect to a substrate can be manipulated via the deposition conditions and the introduction of metal ions during deposition that is unique to HiPIMS. This level of control -- which can be expanded to other FCC/BCC immiscible systems -- over phase separated morphologies allows for governable interface crystallography, chemistry, shape, and defect structure. All of these parameters will broaden understanding of the dynamic mechanical response of complex, multiphase materials.

10:45 AM MS01.10.08
SRO and Planar-Slip Assisted Deformation Twinning in a CrCoNi Medium-Entropy Alloy (MEA) Ruopeng
The emerging concept of multiple-principle element alloys have received tremendous interest in the last decade due to the unprecedented mechanical properties [1]. The CrCoNi-based, fcc single-phase alloy exhibits exceptional tensile ductility, fracture toughness and impact resistance thanks to its continuous work hardening rate, high frictional forces on dislocations and the tendency of nano-twin nucleation. The ability of maintaining the mechanical properties at very large plastic strain is especially attractive for potential structural applications.

Traditionally, the CrCoNi MEA is treated as a random solid solution, where atoms form a random distribution in the lattice. Nevertheless, it is reported that chemical short-range order could form in the alloy to lower the energy, thus, changing the stacking fault energy of the alloy and affecting the mechanical properties [2]. Such formation, along with the impact on the mechanical properties has been experimental observed in our previous study. The formation of SRO significantly increases the stacking fault energy and induces a wavy-to-planar slip transition.

In binary alloy systems, the formation of SRO usually leads to deformation localization and jeopardized ductility due to the glide plane softening effect and the subsequent planar dislocation slip [3, 4]. However, in the CrCoNi MEA, the ductility remains unaffected with the SRO and planar slip present. Microscopically, the formation of a nano-twin/planar slip network was observed despite the larger stacking fault energy. We speculate that the planar slip could reduce the local stacking fault energy by interrupting the SRO structure and provide nucleation sites for deformation twinning. A new twinning mechanism was proposed based on the TEM observation and theoretical calculations.


11:00 AM MS01.10.09
Nanoindentation Based Properties of Laser Peened Additively Manufactured Inconel 718 Superalloy
Tyler Palma1, Michael Munther1, Montu Sharma2, Lloyd Hackel2, Ali Beheshti3 and Keivan Davami1; 1The University of Alabama, United States; 2Metal Improvement Company, Surface Technologies, Curtiss Wright, United States; 3George Mason University, United States

Additive manufacturing (AM) is a novel technology that is transforming product design, manufacturing, and marketing. While the technique needs to be studied to address current challenges, a meticulous look into possible post-processing techniques for material property modifications seems necessary. Laser peening (LP) is a technique that is used as a post-processing method to optimize the service lives of critical components for various applications by inducing compressive residual stresses that increase the material’s resistance to surface-related failures, such as fatigue, fretting fatigue, corrosion-fatigue, and stress corrosion cracking. Herein, the effects of LP on the nanomechanical properties of additively manufactured Inconel 718 (IN718) are reported. AM cubic specimens peened without a protective overlay were evaluated under vigorous microscopy and nanomechanical studies. Depth sensing through hardness and modulus mapping was conducted to evaluate the plastic deformation and hardness enhancement introduced by the process. X-ray diffraction was used to measure the residual stresses to correlate hardness and residual stresses. The results showed that LP induces plastic strain in the surface and beneath the surface of the material that represents itself by a moderate increase in hardness (~20% to 30%). Slight changes in the elastic modulus were also recorded in LP specimens.

11:15 AM MS01.10.10
Structural Evolution and Mechanical Evaluation of In Situ Amorphous Steel Matrix Composites
Arash Yazdani1, Darren Dewitt1, Zezhou Li1, Haocheng Quan1, Wei Huang2, Günther W. Höhne3, Scott T. Misture4, Javier Garay1, David Kisailus1, Marc Meyers1 and Olivia Graeve1; 1University of California, San Diego, United States; 2University of California, Riverside, United States; 3University of Ulm, Germany; 4Alfred University, United States
SAM2×5 is an amorphous steel with a chemical composition of Fe₄₉.₇Cr₁₇.₇Mn₁.₉Mo₇.₄W₁.₆B₁₅.₂C₃.₈Si₂.₄. In this study, we have determined the crystallinity of the dense specimens of our bulk metallic glass using a novel differential scanning calorimetry technique. The dense specimens were prepared using the spark plasma sintering (SPS) technique at a heating rate of 500°C/min, a pressure of 100 MPa, and temperatures ranging from 615 to 675°C. Room and high temperature X-ray diffraction results showed that increasing the SPS temperature resulted in the devitrification of mainly carbide-based phases from the amorphous matrix. TEM observations showed that crystalline domains of less than 20 nm in size are uniformly distributed within the amorphous matrix. The average macro and micro compressive strength values of the specimens was between 1.7 and 2.2 GPa. Split Hopkinson Pressure Bar tests were carried out to measure the mechanical response of the sintered specimens under dynamic deformation, showing a yield strength of 2200 MPa under a strain rate of 900 s⁻¹.

11:30 AM MS01.10.11
Temperature Dependent Morphology of Immiscible Binary Alloys for Applications of High Strain Rate Deformation Max Powers, Benjamin K. Derby and Amit Misra; University of Michigan, United States

Cu-X alloys, where X is a BCC metal from group V or VI in the periodic table, are nearly completely immiscible through a wide range of compositions and processing temperatures under the melting temperature of Cu. Cu-X thin films produced via physical vapor deposition will self-assemble into phase separated regions during fabrication. These phase separated regions have atomically resolved interfaces that impede the movement of dislocations in the system, resulting in elevated mechanical performance compared to bulk samples. The extent of elevated mechanical performance will depend on the microstructure morphological geometries. Micron thick films of Cu-Ta were deposited via magnetron sputtering at four distinct temperatures: 25, 400, 600, and 800 °C. STEM and TEM characterization revealed the films deposited at room temperature to consist of nanocrystalline Cu-Ta matrix and films deposited at elevated temperatures as having interwoven bicontinuous structures with large Cu islands within a Cu-Ta matrix. Nanoinindentation has demonstrated a direct correlation between the morphologies and the observed mechanical properties of hardness and Young’s modulus. The distinct morphologies arise due to the highly disparate temperature-dependent mobilities of the constituent elements. The morphologies can be affiliated with applications in extreme mechanics as a bicontinuous structure adds a third dimensional component to the dislocation-interface interaction and the exact thickness of phase separated regions in the film will control the dominant yielding mechanism during deformation.

11:45 AM MS01.10.12
Effect of Cold Rolling on the Indentation Size Effect and Related Mechanisms in Zr₄₁.₂Ti₁₃.₈Cu₁₂.₅Ni₁₀Be₂₂.₅ Abhilash Gunti¹, Parijat P. Jana¹, Min Ha Lee² and Jayanta Das¹; ¹IIT Kharagpur, India; ²Korea Institute of Industrial Technology, Korea (the Republic of)

Zr₄₁.₂Ti₁₃.₈Cu₁₂.₅Ni₁₀Be₂₂.₅ (Vitrelloy-1) bulk metallic glass (BMG) has been cold rolled at room temperature up to 4.5%, 10%, 20% and 31% reductions. The glassy nature of the as-cast and cold rolled samples has been investigated by the differential scanning calorimeter (DSC) and x-ray diffraction (XRD). The indentation size effect (ISE) in Vitrelloy-1 BMG has been examined during nanoindentation at various maximum loads in the range of 50 mN- 500 mN before and after cold rolling. It has been observed that the size effect varies in differently cold rolled specimen. The nano-hardness and the reduced modulus of the as-cast and the cold rolled samples have been reduced with the increase of the indentation depth. Whereas, the hardness of the cold rolled samples increased in 4.5% and 31%, whereas decreased in 10% and 20% than the as-cast sample for all the maximum loads during nanoindentation. Such variation of the hardness and reduced modulus is linked with the free volume change in the glassy structure upon cold rolling. The observed ISE of as-cast and cold rolled samples has been correlated with the dynamic mechanical softening during nanoindentation and the friction between indenter and sample.
Phase Transitions in Strontium Oxalate at High-Pressure

Iskander G. Batyrev, Petrika Cifligu, Jennifer A. Ciezak-Jenkins and Michael Pravica

U.S. Army Research Laboratory, United States; University of Nevada, United States

We report theoretical and experimental investigations on the structure of strontium oxalate and Raman spectra at high-pressure. The system has shown progress in the generation of CO₂ and in the synthesis of high-energy polymeric carbon monoxide after X-ray irradiation facilitating reactions such as: SrC₂O₄ + hv -> SrCO₃ + CO₂ + poly-CO [1]. Density functional perturbation theory was used to calculate the zone center optical phonons and to identify the vibration modes in terms of atomic displacements. The simulations were compared to experimental Raman spectra and previous IR spectroscopic studies [1] in an effort to elucidate the details of phase transition between monoclinic and triclinic phases. Additional calculations of the phonon dispersion and density of states, as well as the electronic band structure and elastic moduli were performed to gain better insight into the phase behavior in strontium oxalate under high pressure.

References


Defect Formation in 4 nm Au Nanocrystals under High Pressure

Abhinav Parakh, Sangryun Lee, Lindsey Hanson, Mehrdad T. Kiani, David Doan, Martin Kunz, Andrew Doran, Seunghwa Ryu and Wendy Gu

Stanford University, United States; Korea Advanced Institute of Science and Technology, Korea (the Republic of); Trinity College, United States; Lawrence Berkeley National Laboratory, United States

Permanent, plastic deformation occurs in crystalline metals that are subjected to large strains. This is due to the irreversible interactions between dislocations, and between dislocations and microstructural features such as grain and twin boundaries. Recently, reversible deformation from large strains has been observed in a number of metallic nanostructures[1,2]. Rapid surface diffusion and reversible dislocation motion have been proposed as two possible mechanisms for this behavior,[1,3] but the correct mechanism has not been determined conclusively.

To resolve these issues, 3.9 nm Au nanocrystals were compressed under non-hydrostatic pressure in a diamond anvil cell (DAC) up to ~7 GPa. These nanocrystals were colloidally synthesized, and contained twins. Structural changes were observed using in-situ x-ray diffraction (XRD), optical absorbance spectroscopy and MD simulations. We observed that XRD peak position and LSPR peak position recovered completely with pressure cycle, which indicates that the elastic strain in the lattice and the shape of the nanocrystal were recoverable. The XRD peak width increased with pressure and remained at larger values even after unloading, which indicates that the defects like stacking faults and dislocations were nucleated in the nanocrystals and remained in the nanocrystal even after unloading. LSPR peak height also reduced with pressure cycle, which corroborates the XRD results and indicates that defects form in the nanocrystals.

MD simulations were used to compress nanocrystals of a similar size. Partial and full dislocations were nucleated at the surface of the nanocrystals. Some of the full dislocations interacted strongly with twin boundaries within the nanocrystals and were present in the nanocrystal even after unloading. XRD patterns were generated from the MD simulations, and found to be similar to the experimental XRD patterns. Hence, we conclude that the interaction of dislocations and twin boundaries is responsible for the permanent deformation observed in the nanocrystals. This dramatically changes our current understanding of dislocation nucleation and recovery in such small nanocrystals.

References


Heterostructured Metastable Aluminum-Magnesium System Processed by High-Pressure Torsion

Megumi Kawasaki, Jae-Kyung Han and Klaus-Dieter Liss

Oregon State University, United States; Guangdong University of Education, China

2:15 PM MS01.11.03

Heterostructured Metastable Aluminum-Magnesium System Processed by High-Pressure Torsion

Megumi Kawasaki, Jae-Kyung Han and Klaus-Dieter Liss

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2:15 PM MS01.11.03

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Megumi Kawasaki, Jae-Kyung Han and Klaus-Dieter Liss

Oregon State University, United States; Guangdong University of Education, China
Separate disks of Al and Mg were mechanically bonded through high-pressure torsion (HPT) processing for 100 turns under a compressive pressure of 6.0 GPa. The material after processing was followed by natural aging at room temperature for 60 days in order to evaluate the microstructural stability. The materials characterization revealed that such high straining through the HPT processing synthesized a bulk nanostructured metastable Al with grain sizes of 35-40 nm in a state of supersaturated solid solution with the measured maximum Mg solubility of ~38.5 at.%. A superhard Al solid solution with the maximum Vickers microhardness value of ~370 was observed consistently across the disk diameter and the high hardness was considered mainly due to grain refinement and solid solution strengthening. X-ray diffraction analysis was applied to quantitatively evaluate the supersaturated solubility of Mg in Al and the stability of metastability with computing microstrain and crystallite size of the aged material. Significantly high microstrain of 0.0202 was observed for the metastable Al and it was even enhanced to 0.0274 after natural aging. It was attributed solely to the high supersaturation of Mg solute in Al. Moreover, advanced analysis using high-energy synchrotron radiation was conducted to visualize the uncovered phase and texture heterogeneity in the metastable Al alloy. This study demonstrates one of the ultimate states of metals when they are diffusion bonded mechanically under severe plastic straining at ambient temperatures.

2:30 PM MS01.11.04

**The Transformation of Glassy Carbon to Diamond at High Pressure Using Pulse Laser Heating**

Brenton Cook, Thomas Shiell, Sherman Wong, David McKenzie, Matthew Field, Bianca Haberl, Reinhard Boehler, Jodie Bradby and Dougal G. McCulloch

RMIT University, Australia; The University of Sydney, Australia; Oak Ridge National Laboratory, United States; The Australian National University, Australia

The synthesis pathway to diamond from graphitic precursors using high pressures and temperatures has been studied and applied for many decade [1]. Industrial manufacturing methods require temperatures up to 1500 K, pressures between 5-6 GPa, and the use metallic catalysts [1]. Without these catalysts the pressure and temperature conditions required are far more extreme to overcome kinetic energy barriers. Recently, there has been considerable interest in the synthesis of pure, catalyst-free diamond and other novel forms of carbon from non-crystalline precursors, with the hope that the energy barrier impeding transformation will be reduced. For example, nanocrystalline diamond has been formed from carbon nanotubes following compression to 17 GPa at 2500 K [2]. The size of the nanocrystals were found to be similar to the diameter of the nanotubes, demonstrating that the type of precursor can influence the microstructure of the resulting diamond. Sumiya et al. observed the formation of nanocrystalline diamond (<10 nm in diameter) from a glassy carbon (GC) precursor when compressed for 10s at pressures of ~20 GPa and temperatures of ~3000 K [3]. When compressed for longer times, the nanocrystalline diamond evolved into larger crystals then exhibited a lamellar structure. Recently, it has been reported that it is possible to create an amorphous form of diamond has been synthesized from GC following compression to 50 GPa and laser heating to ~1800 K [4]. However, this previous work has only investigated the compression of non-crystalline graphitic precursors within a limited temperature range. There is a need for a more thorough experimental study at temperatures above 3000 K, in the region of the PT diagram encompassing the liquid-diamond phase boundary.

In this study, GC samples were loaded into diamond anvil cells with an Ar pressure medium and compressed to 16 GPa. A 1070 nm pulse laser was then used to heat the samples to temperatures ranging from 1900-4500 K. A total of 15 samples were made for *ex-situ* analysis using raman spectroscopy, scanning electron microscopy and transmission electron microscopy. At low temperatures (1900-2200 K), the GC was found to have transformed into an oriented graphitic material in which its graphene layers are preferentially aligned perpendicular to the compression axis. Nanodiamonds (~10-200 nm) begin to form near the surface of the GC at temperatures of ~2200 K. These nanodiamonds increase in size and density as the temperature increases up to 4500 K. Interestingly, above ~3500 K voids were observed in the microstructure, some of which contained Ar, which appears to have an epitaxial relationship with the surrounding diamond. This observation supports the proposition that at these high temperatures, the GC may have entered a liquid state prior to the formation of diamond crystallites.

The authors acknowledge the Australian Research Council for financial support (Discovery Project #DP170102087).

References:
2:45 PM MS01.11.05
Anomalies in Mechanical Response During Microscale Extrusion of Metals Bin Zhang and Wen Jin Meng; Louisiana State University, United States

Small scale metal forming, with characteristic forming dimensions ranging from millimeters down to micrometers, is of current interest in manufacturing of miniaturized components and devices. As compared to subtractive manufacturing techniques such as micro mechanical milling and micro electrical discharge machining, small scale metal forming offers the potential of high throughput, low cost, and dimensional repeatability. Metal forming operations typically involve deformation to large plastic strains [1]. Changes in the mechanical response of materials during forming as the characteristic forming dimension decreases to the meso/micro scale prevents straight forward adoption of macroscale forming practices to the small scales, such changes thus need to be better understood.

We report our recent results on characterizing the mechanical response and deformation characteristics of Cu in microscale axisymmetric reversion extrusion [2]. Specifically, the characteristic plastic strain for the extrusion process and the influence of the initial grain size of extruded material on the extrusion mechanical response and shape of extruded parts were examined through scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and transmission electron microscopy (TEM). We show that the mechanical response of extrusion exhibits deviations from continuum scaling behavior as the characteristic forming dimension becomes small as compared to the initial grain size. Materials based justification to the observations will be discussed.

References:

3:00 PM BREAK

3:30 PM MS01.11.06
Quasi-Plastic Zone Characterization of Regular and Si-Doped Boron Carbide Sisi Xiang and Kelvin Y. Xie; Texas A&M University, United States

Boron carbide (B4C) is a hard and lightweight material, which has many engineering applications. However, B4C loses its strength and toughness when subjected to high shear stresses. To improve its mechanical properties, the pervious computation work has suggested micro-alloying B4C with Si. Very limited understanding of the failure mechanism of boron carbide, both Si-free and Si-doped, under high shear stress conditions is due to the lack of direct experimental observation at the relevant length scale for damage zone. Here we investigate the local deformation microstructure of regular and Si-doped boron carbide under indents, using a novel precession electron diffraction technique and high-resolution transmission electron microscopy. We observed that Si-doped boron carbide displays dispersed micro-cracks, while Si-free boron carbide exhibits major local cracks and low interfaces.

3:45 PM MS01.11.07
Superior Energy Dissipation by Nanoscale Semi-Crystalline Polymer Films under High-Speed Micro-Projectile Impacts Jizhe Cai and Ramathasan Thevamaran; University of Wisconsin-Madison, United States

Developing revolutionary lightweight protective materials with superior specific energy dissipation and specific strength is critical for many impact mitigation applications—from ballistic protection of soldiers to foreign object damage prevention in air and spacecraft. Recent advancements in high strain rate experimental characterization
techniques have revealed the excellent properties of nanoscale polymer thin-films over conventional bulk polymers. For glassy polymer thin-films, decreasing the film thickness effectively modify the polymer chain morphology and mobility, therefore bringing additional energy dissipation mechanisms, such as crazing, yielding, and adiabatic heating, which increases the projectile’s kinetic energy required to perforate the film. Comparing to glassy amorphous polymer thin-films, semi-crystalline polymers exhibit more complex deformation mechanisms, being strongly related to their microstructure, including crystallinity and molecular conformation. In this work, we study the dynamic mechanical behavior of PVDF-TrFE polymer thin-films with thicknesses varied from 75 nm to 400 nm using a micro-ballistic testing apparatus with projectile speeds ranging from 200 m/s to 1000 m/s. We examine the size- and strain-rate-dependency of the specific penetration energy and the dynamic deformation mechanisms of the thin-films. The polymer films that are thinner than 100 nm exhibit superior protective properties, with specific penetration energy as high as 3.7 MJ/Kg for 1000 m/s impact, about 5 times larger than bulk steel plate from macroscopic experimental measurements. It is demonstrated that as the film thickness is decreased or impact projectile speed is increased, there is increase in the specific penetration energy and evident transition in failure mechanisms of the film. The microstructure of PVDF-TrFE thin-films is further modified by applying appropriate heat-treatment. We additionally study the relationship between intrinsic crystalline microstructure and dynamic mechanical properties in semi-crystalline polymer thin-films. Understanding those key structure-property relations in nanoscale semi-crystalline polymer thin-films will provide promising approaches for developing novel flexible and lightweight polymer-based protective materials.

4:00 PM MS01.11.08
Microstructural Instability of Polycrystalline Zirconia under High Temperature and Extreme Electrochemical Conditions Yanhao Dong¹, I-Wei Chen² and Ju Li¹; ¹Massachusetts Institute of Technology, United States; ²University of Pennsylvania, United States

Electroceramics are often subject to high temperature, reducing/oxidizing environment and/or applied electric field. Such is the case for stabilized zirconia during field-assisted processing and many applications in solid oxide fuel/electrolysis cells, thermal barrier coatings and others. Against the conventional wisdom that stoichiometry and microstructure of zirconia is insensitive to reduction because of its large bandgap of ~5 eV, we found hugely enhanced grain growth under severe electrochemical reduction, creating (i) a graded microstructure with 100 times grain size difference at the cathode and anode side and (ii) a sharp grain size transition halfway across the electrically loaded sample. Continuum-level transport theory and first-principles calculations were conducted to gain better mechanistic understandings, which bring out the hidden yet critical role of electronic defects (localized electrons on Zr⁴⁺, i.e. reduced cations; and localized holes on O²⁻, i.e. oxidized anions) on microstructural evolution in nominally ionic compounds under extreme conditions.

References

4:15 PM MS01.11.09
Suboptimal Toughness of Uniform Grain Boundary Distribution Edwin Chiu, Michael J. Demkowicz and Ankit Srivastava; Texas A&M University, United States

Fracture toughness of a material depends on the crack path, which in turn depends on the material microstructure. In a variety of technologically important structural materials, fracture involves preferential crack nucleation and growth along the grain boundaries particularly under extreme environmental loading conditions. For example, stress corrosion cracking, hydrogen embrittlement and low damage tolerance are all dominated by the grain boundaries. Over the past decades, our understanding of the relation between specific grain boundaries and their resistance to the aforementioned processes has increased along with the ability to choose processing routes leading to specific grain boundary character distributions, geometrical properties of the grains and chemical parameters. Recently, we have shown that the crack growth resistance of a crack propagating through a grain boundary network can be described by discrete unit events, and the final crack path in a specified grain boundary network is not necessarily the path of
least resistance. This raises an important question; if the crack path is not dictated by the path of least resistance then can we change the crack path through a grain boundary network by introducing heterogeneities such as weak grain boundaries. The extent to which an admixture of weak grain boundaries can enhance the fracture toughness of a grain boundary network and the corresponding toughening mechanism will be discussed.

4:30 PM MS01.11.10

Thermal Conductivity of Earth Minerals at Extreme Conditions Irina Chuvashova, Zachary Geballe and Alexander Goncharov; Carnegie Science, United States

Thermal transport properties of minerals and melts at high pressures and temperatures is of central importance to the evolution and dynamics of planets. The pressure of the Earth’s interior continuously increases with the depth from the surface of the Earth: several hundred MPa at the region of the crust, ∼20 GPa at the upper mantle and ∼130 GPa at the lower mantle. Precise data of thermal conductivity and/or thermal diffusivity for minerals at elevated pressure make it possible to estimate the heat budget in the Earth.

In the Earth’s core and mantle, thermal conductivity of minerals containing dominantly iron-bearing silicates and iron alloys defines the heat and energy flow as well as the geodynamo over the Earth’s history. Direct measurements of thermal conductivity of Earth minerals at extreme pressures and temperatures are very challenging; the available data are limited, inconclusive, and not corresponding to the theoretical calculations. Therefore, there is a lack of experimental data, which is currently substituted by extrapolations and estimations.

In the present work, we have studied the direct measurements of thermal conductivity of iron-bearing and non-iron-bearing minerals as well as iron alloys at different high pressure and temperature conditions up to 130 GPa using diamond anvil cells with continuous and pulse laser heating. Fast measurements allowed us to resolve the heating response through the sample and understand the tendency of minerals behavior within the mantle and core. The analysis of the obtained experimental data is currently in progress and the results will be reported at the conference.
Graphene, the prototypical 2D material, has attracted a considerable degree of attention for device applications since its discovery in 2004. The material is commonly synthesized via chemical vapor deposition (CVD) and can contain a variety of intrinsic and extrinsic defects. To enable applications that utilize the unique properties intrinsic to graphene, these defects will not only need to be controlled during synthesis, but will also need to be engineered to different degrees and patterns after synthesis. The current methods of defect engineering and patterning of graphene are either uncontrollable or result in deleterious side effects (i.e. dangling bonds) that reduce materials performance in fabricated devices.

In this work, we use electron-beam (e-beam) chemistry to engineer defects in CVD graphene by performing a highly controlled and tunable process that is ideal for photonic and electronic device fabrication without the use of photoresist. To enable e-beam chemistry on graphene, radiolysis products were produced by the interaction of the e-beam with water vapor inside a scanning electron microscope (SEM) [1]. These products reacted with the carbon atoms of the graphene at precise locations scanned by the e-beam. E-beam chemistry was performed on CVD graphene transferred using PMMA onto a Si/SiO2 substrate [1]. The effectiveness of this precise maskless, resistless process in creating defects at precise locations were verified using different characterization techniques. Raman spectroscopy in the defect engineered areas of graphene revealed the presence of large defect band signals at ~ 1350 cm\(^{-1}\) (D-band) and at ~ 1625 cm\(^{-1}\) (D'-band) with peak widths < 50 cm\(^{-1}\). To explore the degree of control in defect engineering exerted via e-beam chemistry, e-beam parameters (e.g. dwell-time, scan-rate, pressure etc.) were varied and their effect on intensity ratios (such as D/G ratio, where G-band corresponds to the graphitic peak at ~ 1590 cm\(^{-1}\), D/D' ratio, and G'/G ratio, where G' is the second order graphitic peak at ~ 2690 cm\(^{-1}\)), peak widths and average distance between defects (LD) were studied. Raman intensities were also theoretically calculated by considering scattering of incident photon by the phonons, electrons and holes in defect engineered graphene [2]. Comparison of experimental and theoretical analysis of Raman spectra revealed the presence of out-of-plane (sp\(^3\)-type; LD > 5 nm and IM/ID ~ 13) defects with no vacancies on the graphene lattice.

Our study also revealed the high resolution patterning via e-beam chemistry, as we observe negligible D-band intensity near the boundary of the defect engineered area. Atomic force microscopy images show higher phase contrast (as observed for oxidized graphene [1]) on the e-beam patterned regions compared to the non-patterned regions with ~ 100 nm spatial resolution. In addition, the e-beam engineered defects could be healed by annealing graphene at ~ 300 °C in air, which resulted in the complete removal of the D-band, thus demonstrating that the e-beam chemistry process is reversible and does not damage (or introduce vacancy in) the graphene lattice itself. E-beam chemistry thus enables us to employ a mask-less, resist-free process to directly engineer reconfigurable defects in graphene.

mechanical stretchability accompanying well-preserved electrical integrity and modulated transport properties. We employed a concept of strain engineering inspired by an ancient paper-cutting art, known as kirigami patterning, and developed 2D TMDs-based kirigami electrical conductors. Specifically, we directly integrated 2D platinum diselenide (2D PtSe$_2$) layers of controlled carrier transport characteristics on mechanically flexible polyimide (PI) substrates by taking advantage of their low synthesis temperature. The metallic 2D PtSe$_2$/PI kirigami patterns of optimized dimensions exhibit an extremely large stretchability of ~2000% without compromising their intrinsic electrical conductance. They also present strain-tunable and reversible photo-responsiveness when interfaced with semiconducting carbon nanotubes (CNTs) benefiting from the formation of 2D PtSe$_2$/CNT Schottky junctions. Moreover, kirigami field-effect-transistors (FETs) employing semiconducting 2D PtSe$_2$ layers exhibit tunable gate responses coupled with mechanical stretching upon electrolytes gating. The exclusive role of the kirigami pattern parameters on resulting mechano-electrical responses was also verified by finite-element modeling (FEM) simulation. These multifunctional 2D materials in unconventional yet tailored 3D forms are believed to offer vast opportunities for emerging electronics and optoelectronics.

9:00 AM MS02.01.03
The Role of Strain and Defects on the Electronic Properties of Atomically Thin Semiconductors Chitraleema Chakraborty$^1$, Christopher J. Ciccarino$^1$, Dirk Englund$^2$ and Prineha Narang$^1$; $^1$Harvard University, United States; $^2$Massachusetts Institute of Technology, United States

Atomically thin semiconductors have gained a lot of interest owing to their unique quantum optical and optoelectronic properties which are strongly dependent on inevitable structural distortions due to strain and defects in their lattice [1-2]. In this work, we study the modification of intrinsic electronic properties using first-principles methods due to the introduction of strain as well as defects in monolayer transition metal dichalcogenides (TMDCs). Our recent theoretical results predict the importance of spin-orbit and electron-phonon interaction on the studied dynamics [3-4]. Here we present the effect of biaxial strain on microscopic interactions in monolayer TMDCs. Our calculations predict a modulation of the spin-orbit splitting ($\approx$ 13 meV/%) at the K point of both band edges as a function of strain, where we also find a crossover from a direct to indirect band-gap. Carrier coupling with phonons is also modified with increased strain levels due to changes in intervalley energetics. The resulting dynamics from the static effect of strain were captured via calculation of the wavevector-resolved electron-electron and electron-phonon scattering rates. Along with strain, the formation of atomic defects is unavoidable in 2D materials with currently available growth techniques [1]. Nevertheless, there is a myriad of functionalities in modern optoelectronic and nanophotonic devices that leverage quantum defects including the recent demonstration of single photon emitters in 2D materials [2,5]. Therefore, we present theoretical calculations and analysis of the vibronic structure of a singly charged sulfur vacancy in monolayer TMDCs. Further, we show a pathway to strain and defect engineering for tailoring the valley properties in monolayer TMDCs and enabling sources of quantum emitters that would provide a physical implementation of a localized qubit.

References

9:15 AM MS02.01.04
How Does Strain Modify the Electron Mobility of 2D MX2 Semiconductor Yuanyue Liu; The University of Texas at Austin, United States

The strain has been widely used to engineer the electronic properties of 2D transition metal dichalcogenide (MX2) semiconductor. Although there are lots of studies about the strain effects on the band gap, effective mass, excitons etc, much less is known about the mobility. Here using Boltzmann transport theory with the scattering rates determined from first principles, which allows us to accurately calculate the intrinsic (phonon-limited) mobility, we will show how does the isotropic strain modify the electron mobility of 2D MX2 semiconductor. Particularly, we find two distinct behaviors in these materials, which can be explained by a simple physical factor.
Understanding the deformability, flexibility, and bending of two-dimensional (2D) materials is critical for the realization of next-generation electronics and nanomechanical devices. While the mechanics of few-layer graphene have been studied for more than a decade, there is still no consensus on bending stiffness and how it scales with thickness [1-3]. Electron microscopy provides a powerful platform for addressing these challenges by enabling measurements of the conformation and strain of 2D materials at atomic resolution. Using aberration-corrected scanning transmission electron microscopy (STEM), we show that bending in few-layer graphene is dominated by slip and shear between the atomic layers. These results, in combination with density functional theory (DFT) simulations, reveal an unusual, curvature-dependent bending stiffness in few-layer graphene. Unlike in conventional metals where bending produces dislocations which stiffen and embrittle the crystal, we find that slip between the atomic planes of 2D materials dramatically softens few-layer graphene by rendering the layers nearly frictionless when it is curved.

We explore how the bending stiffness of few-layer graphene varies with both thickness and bending angle by systematically examining its conformation over atomically-sharp hexagonal boron nitride (h-BN) steps. These geometries offer direct control over two key variables: number of graphene layers and h-BN step height. Using aberration-corrected STEM images, we extract the bending profiles of few layer graphene over the h-BN steps as a function of the graphene thickness and curvature, then use these values to calculate the bending stiffness of few layer graphene. We find the bending stiffness of few-layer graphene decreases sharply as a function of bending angle, tuning by almost 400% for tri-layer graphene. This softening results from shear, slip, and the onset of superlubricity between atomic layers and corresponds with a gradual change in scaling power of bending stiffness with thickness, from cubic to linear as it is curved. These behaviors are a direct result of changes in atomic registry between the atomic layers; as few-layer graphene is bent, its interlayer interactions transition between two limits: the strong coupling characteristic of Bernal-stacked graphite and the weak, superlubric interactions characteristic of multi-walled carbon nanotubes. Our results indicate that the bending stiffness of few layer graphene can be orders of magnitude smaller than previously thought and provide a new lower limit for the fabrication of ultra-soft, high mobility electronic nanodevices based on 2D materials.


A challenge and opportunity in nanotechnology is to understand and take advantage of the breakdown in continuum mechanics scaling laws as systems and devices approach atomic length scales. Such challenges are particularly evident in two-dimensional (2D) materials, which represent the ultimate limit of mechanical atomic membranes as well as molecular electronics. For example, after more than a decade of study, there is no consensus on the bending modulus of few-layer graphene, with measured and predicted values ranging over two orders of magnitude, and with different scaling laws[1–5]. However, comparing these studies is challenging because they probe very different and often fixed curvatures or magnitudes of deformation. To unravel the discrepancy, a systematic measurement of bending stiffness versus deformation is needed. The results have practical implications on predicting and designing the stiffness of many 2D mechanical systems like origami/kirigami nanomachines, stretchable electronics from 2D heterostructures, and resonant nanoelectromechanical systems. Moreover, many studies implicitly use the bending modulus to extract important parameters like the interfacial adhesion and friction or to predict the wavelength of 3D rippling in strained membranes.
In this study, we combine atomistic simulation and atomic scale imaging to theoretically and experimentally examine the bending behavior of few-layer graphene. First, we experimentally probe the nanoscale bending by laminating few-layer graphene over atomically sharp steps in boron nitride(h-BN) and imaging the cross-sectional profile using aberration-corrected STEM. Second, we use DFT simulations to examine the bending of few-layer graphene under compression. By measuring the nanoscale curvatures, we extract the simulated and experimental bending modulus while varying both the number of layers and the degree of nanoscale curvature. We further apply this framework to measure the bending stiffness of van der Waals heterostructures, by stacking graphene-MoS$_2$ heterostructure on the terraced h-BN. We find remarkable agreement between the theory and experiment and observe an unexpected curvature dependent bending stiffness of few-layer graphene that deviates from continuum scale bending mechanisms. We find that the bending stiffness of few-layer graphene versus curvature corresponds with a gradual change in scaling power with thickness from cubic to linear. We find that the transition in scaling behavior originates from a transition from shear, slip and the onset in superlubricity between the graphene layers at the van der Waals interface, verified by a simple Frenkel-Kontorova model. In contrast to few-layer graphene, the graphene-MoS$_2$ heterostructure shows an additive bending stiffness for stacking each layer. Thus we evaluate the impact of superlubricity at the van der Waals heterostructure interface under bending deformation. Our results provide a unified model for the bending of 2D materials and show that their multilayers can be orders of magnitude softer than previously thought, among the most flexible electronic materials currently known.

10:45 AM *MS02.01.07
2D Memory—An Application of Defects in Monolayers Saban Hus, Ruijing Ge, Xiohan Wu, Jack Lee and Deji Akinwande; The University of Texas at Austin, United States

This presentation focuses on the progress on 2D nanomaterials towards greater scientific understanding and advanced engineering applications. In particular the talk will highlight our pioneering work on monolayer memory (atomristors) that can enable various applications including zero-power devices, non-volatile RF switches, and memristors for neuromorphic computing. Non-volatile memory devices based on 2D materials are an application of defects and is a rapidly advancing field with rich physics that can be attributed to sulfur vacancies or metal diffusion. Recent studies based on atomistic modeling and imaging as identified point and cluster defects as primarily responsible for the non-volatile memory effect. Areas with defects typically exhibit memory effect while clean defect-free areas are absent of memory effect. Much work remains to be done to elucidate the underlying phenomenon and realize optimized devices for practical adoption.

11:15 AM MS02.01.08
Ultra-High Uniaxial Strain of Freestanding 2D Materials Jakob A. Genser, Maximilian G. Bartmann, Viktoria Ritter, Daniele Nazzari, Ole Bethge, Emmerich Bertagnolli and Alois Lugstein; TU Wien, Austria

Due to the ever-growing need of small-scale and high-performance semiconductor devices, two-dimensional (2D) materials have emerged as promising candidates for future device integration. Due to their exceptional mechanical properties, strain engineering is effectively used to exploit induced mechanical strain in order to tune the carrier mobility and optoelectronic properties of 2D materials. Although strain in 2D materials has been well studied in recent years, most straining methods rely on stretchable substrates to introduce strain and are thus limited to rather low strain values. Here, we present a novel straining approach enabling the application of ultra-high uniaxial strain on freestanding 2D materials and 2D heterostructures, while simultaneously allowing in-situ electrical and optical characterization.

The micromechanical straining devices patterned from SOI wafers enables ultra-high strain levels up to 15%. Mono and few layer 2D materials are transferred onto the straining device using state of the art mechanical exfoliation and dry viscoelastic stamping techniques minimizing unintentional contaminants. To enable reliable electrical contacts and to avoid slipping of the 2D materials they are pinned down by extended Ti/Au contacts. The applied strain was investigated by in-situ Raman measurements in a back-scattering geometry using a confocal μ-Raman setup. The Raman-active modes of graphene, hBN and MoS$_2$ are very sensitive to strain-induced shifts and are clearly observable during the experiments, thus proving the viability of this approach.

11:30 AM *MS02.01.09
Light Scattering and Emission from Coupled Layered Materials Andrea C. Ferrari; University of Cambridge, United Kingdom
Graphene is an ideal material for optoelectronic applications. Its photonic properties give several advantages and complementarities over Si photonics. I will show that graphene-based integrated photonics could enable ultrahigh spatial bandwidth density, low power consumption for next generation datacom and telecom applications.

Heterostructures based on coupled layers of atomic crystals have a number of properties often unique and very different from those of their individual constituents and of their three dimensional counterparts. I will show how these can be exploited in novel light emitting devices, such as single photon emitters, and tuneable light emitting diodes. The role of defects and strain and non-radiative recombination channels will be discussed.

SESSION MS02.02: Emergent Phenomena II
Session Chairs: Gwan-Hyong Lee and Michael Pettes
Monday Afternoon, December 2, 2019
Hynes, Level 1, Room 108

1:30 PM *MS02.02.01
Electrical Manipulation of Exciton Dynamics in Nanodevices Based on Atomically Thin Heterostructures
Luis A. Jauregui; University of California at Irvine, United States

Van der Waals heterostructures constructed of 2-dimensional (2-D) materials such as single layer transition metal dichalcogenides (TMDs) have sparked wide interest because of their large excitonic binding energy, allowing the exploration of novel quantum optical effects in a solid-state system and new opto-electronic devices. In this talk, I will discuss our results in van der Waals heterostructures formed by stacking together two different TMDs (forming a staggered heterojunction) encapsulated with hexagonal boron nitride (h-BN) with electrical contacts in each layer and a dual gate configuration. Interlayer excitons, with electrons and holes residing in spatially separated quantum wells, have long lifetimes (200nS, 5 orders of magnitude longer than intralayer exciton lifetimes). Because of their repulsive Coulomb interaction, they diffuse across the entire sample (20 mm long) driven by interaction, allowing their manipulation towards condensation. Also, we observed and manipulated long-lived charged interlayer excitons which can be used as carriers for quantum information. Interlayer excitons are important for novel opto-electronic devices such as high-temperature interlayer exciton condensates, valley-tronic devices, near-infrared tunable lasers and light emitting diodes. Our work opens a new frontier to explore novel low-dimensional opto-electronic devices and circuits.

2:00 PM MS02.02.02
Robotic Mechanical Exfoliation of Graphite and BSCCO
Young J. Shin1, Boyu Wang2, Minh H. Nguyen2, Kevin Yager1 and Charlse T. Black1; 1Brookhaven National Lab, United States; 2Stony Brook University, The State University of New York, United States

Van der Waals heterostructures are made of stacked atomically thin 2D materials, providing access to novel properties relevant to quantum information sciences. Despite the exciting promise of stacked 2D heterostructures, fabrication remains a laborious low-yield process requiring considerable human expertise and time. We present the development of an automatic robotic exfoliator, meant to automate the repetitive manual tasks of mechanically exfoliating thin flakes of such materials, as well as optically searching for flakes of desired characteristics. We provide statistical mappings between robotic exfoliation motion parameters and flake characteristics, such as thickness, in-plane size, and yield. We present preliminary results demonstrating the exfoliation of graphene, and BSCCO (Bi2Sr2CaCu2O8+y) flakes. In the near future, we will expand this methodology to a wider range of 2D materials.

2:15 PM MS02.02.03
Deep Learning Enabled Measurements of Single-Atom Defects in 2D Transition Metal Dichalcogenides with Sub-Picometer Precision
Chia-Hao Lee1, Chuqiao Shi1, Di Luo1, Abid Khan1, Nahl Sobh2, Blanka Janicek1, Sangmin Kang1, Wenjuan Zhu1, Bryan Clark1 and Pinshane Huang1; 1University of Illinois at Urbana-Champaign, United States; 2Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, United States
Defect and strain engineering of 2D materials is an emerging area of research, where homogeneous or heterogeneous alloying can stabilize exotic electronic phases such as Weyl semimetals or pattern the properties of 2D nanoelectronics and optoelectronics on the nanoscale. Aberration-corrected scanning transmission electron microscopy (STEM) is an important tool to study how atomic defects such as vacancies and substitutional dopants impact the structure and properties of 2D materials. Yet, high-precision characterization of defects in 2D materials remains challenging because they are irradiation sensitive, making it difficult to achieve high resolution and signal-to-noise ratio (SNR) measurements without modifying the intrinsic structure. Here, we apply deep learning techniques based on convolutional neural networks (CNNs) to process large volumes of atomic-resolution images of 2D transition metal dichalcogenides (TMDCs). CNNs have revolutionized image recognition in fields such as medical diagnosis, weather forecasting, and facial recognition; recently, they have been applied to detect defects in atomic-resolution STEM images [1]. In our work we utilize fully convolutional network (FCN), a variant of CNN, to identify defects in monolayer WSe₂₃Tex. Using the resulting data, we determine local picometer-scale strain fields to understand how single-atom defects interact with one another and the surrounding lattice.

In order to enable pm-scale structural measurements in 2D materials, we use an approach analogous to the single-particle reconstruction methods used in cryo-electron microscopy. First, we construct FCN models to identify and classify defects, including substitutions and single and divacancies. We then generate high quality class-averaged images of each defect type by rigid-registration [2] and averaging hundreds of nominally identical atomic defects. These methods result in final images with high SNR yet low dose acquisition, allowing us to extract the detailed atomic structure of defects such as single vacancies, which are highly sensitive to electron beam irradiation. Finally, we measure the locations of each atomic column using 2D Gaussian fitting and determine the local strain. We show that we are able to measure projected atom-atom separations with precisions of up to 0.38 pm, a 22-fold improvement over measurements using single images—representing the highest reported precisions for experimental strain measurements at single-atom defects. We find that two Te substitutions on top of each other in WSe₂₃Tex increase the projected W-W nearest neighbor distance by 4.1 pm, while single Se vacancies decrease the W-W distance by 16.3 pm. Picometer-scale precision also enables studies of long-range strain fields around single-atom defects, up to 1 nm away from the defect center. Our experimental strain maps quantitatively match simulations of continuum elastic theory using Eshelby’s inclusion approach [3]. In summary, we have developed measurement techniques using FCN to locate, classify, and measure the local structure of single-atom defects in 2D materials with sub-picometer precision for the first time.

References:

Acknowledgement:
This work was supported by the AFOSR under award number FA9550-7-1-0213 and carried out in part in the Materials Research Laboratory at UIUC. S.K. and W.Z. would like to acknowledge the support from ONR under grant NAVY N00014-17-1-2973.

2:30 PM BREAK

3:00 PM *MS02.02.04
Novel Quantum Light Sources in Layered Materials Mete Atature; University of Cambridge, United Kingdom

The attractiveness of single-photon sources in layered materials stems from their ability to operate at the fundamental limit of single-layer thickness, foreseeing high extraction efficiency and providing the potential to integrate into conventional and scalable high-speed optoelectronic device systems. In this talk, I will discuss recent progress on scalable and deterministic generation of quantum-emitter arrays in layered materials, charge and spin control, and progress towards confinement of interlayer excitons.

3:30 PM MS02.02.05
Stability, Scalability and Reproducibility—A Study of Emission Sites in CVD Grown Monolayer h-BN James
Defect-induced sub-bandgap emission from hexagonal boron nitride (hBN) is not only hugely interesting for quantum technology, opening a promising route for the design of next-generation single-photon sources [1], but equally offers a new high-throughput characterisation pathway for large-area h-BN films, an urgent requirement given the recent progress in synthesising h-BN; particularly by chemical vapour deposition (CVD) [2]. We present our latest data employing multidimensional super-resolution fluorescence microscopy and other techniques to simultaneously measure spatial position, intensity, and spectral properties of the emitters in h-BN [3,4]. We specifically focus on CVD grown mono-layer h-BN samples over cm areas, which readily offers scalable device integration routes. Our data reveals a correlation in blinking and spectral diffusion for single emitters in monolayer h-BN, closely reminiscent of the behaviour observed in quantum dots [3]. We explore a range of CVD growth, transfer [2, 5] and encapsulation methods warranting controlled, clean and direct emitting-monolayer interfacing, giving us the ability to vertically place emitters with high accuracy. We report on detailed emitter statistics dependant on process conditions and how surface interactions heavily influence the photodynamics. Drawing on quantum dot literature, we devise approaches to enhance and control h-BN emitter properties. We also compare this optical characterisation with a range of other h-BN characterisation techniques to develop a holistic understanding.


3:45 PM MS02.02.06
Manipulating Emission Characteristics of Quantum Defects in Few-Layered Hexagonal Boron Nitride Interfaced with a Phase Change Material Pankaj K. Jha, Yonghwi Kim, Hamidreza Akbari and Harry A. Atwater; California Institute of Technology, United States

Single-photon sources are elementary building blocks for photonic quantum networks, quantum information processing, and quantum metrology, where the photons are used as “flying” qubits [1]. In this work, we investigate the optical properties of quantum defects in few-layered hexagonal boron nitride interfaced with a phase change material, such as vanadium dioxide (VO₂) on a sapphire substrate. It is well known that VO₂ exhibits an insulator-to-metal phase transition when heated just above room temperature [2] which is accompanied with large change in its electrical and optical properties. By inducing this insulator-to-metal phase transition of VO₂ film of thickness ~100 nm, we control the emission characteristics of point-defects with emission centered (zero-phonon line) in the visible regime. We show that far-field radiation pattern and lifetime of the point-defects undergoes a sharp change around the phase transition temperature. Furthermore, we optimize the thickness of the VO₂ film to enhance the optical response of the defects in the vicinity of the phase transition temperature. Our simulations show a modulation of more than 50% in the lifetime of these defects when VO₂ undergoes the phase transition. Interfacing quantum emitters in atomically thin materials [3] with phase change materials opens new opportunity for manipulating single-photon sources near room temperature.

References:

4:00 PM MS02.02.07
Microsecond Lifetime of Defect-Bound Excitons in Single-Layer WSe₂ with Focused Ion Beam Irradiation Qingkai Qian1, Lintao Peng2, Nestor Perea1,1, Kazunori Fujisawa1,1, Kunyan Zhang1, Xiaotian Zhang1, Tanushree H. Choudhury1, Joan M. Redwing1,1, Mauricio Terrones1,1,1, Xuedan Ma2 and Shengxi Huang1; 1The Pennsylvania State University, United States; 2Argonne National Laboratory, United States

Transition-metal dichalcogenides (TMDCs) have been extensively studied for both fundamental science and optoelectronic applications owing to their unique properties, such as the atomic layer thickness, dangling-bond free
surface, strong light absorption, and layer-tuned direct/indirect bandgap [1]. Valley polarization of excitons can be realized in monolayer TMDCs by optical pumping [2]. However, valleytronics based on TMDCs typically relies on the delocalized excitons, which have an intrinsically fast recombination lifetime due to the large exciton oscillator strength. This short lifetime has placed a strict limitation on the pseudo-spin manipulation before the valley depolarization. Valley selectivity can be preserved for defect-bound excitons and the selective creation of defect-bound excitons with long lifetime could make significant breakthroughs for the practical valleytronics applications [3]. TMDCs are also promising platforms for solid state quantum light emissions, which have great flexibility in heterogeneous assembly and large extraction efficiency. Even though the position of quantum emitters can now be deterministically controlled by nanoscale strain engineering, the broad energy range of uncontrolled impurity- or defect-induced excitons brings a central obstacle to the development of single photon sources with high purity and indistinguishability based on TMDCs [4]. The lack of control over the presence and spatial distributions of defects in TMDs currently limits their utility for scalable devices.

Controlled defect engineering can be an important means for tailoring the electronic and optical properties of two-dimensional materials. In this work, defect densities ranging many orders of magnitude in single-layer WSe2 are controllably created by focused ion beam (FIB) irradiation. The influences of defects are systematically characterized by room-temperature Raman scattering/photoluminescence (PL), low-temperature PL and PL dynamics. Only when the FIB dose is higher than $10^{13}$ cm$^{-2}$ in WSe2, Raman spectroscopy can discern the defects at room temperature, which shows blue shifts for both $A_{1g}$ and $E_{2g1}$ peaks. Photoluminescence (PL) intensity of WSe2 drops with increased FIB doses, while the PL peak position and width show no significant changes for different FIB doses at room temperature. Low-temperature PL further reveals the peak of defect-bound excitons, which redshifts and broadens with increased FIB doses. Similar Raman shifts and PL intensity drops are observed for chemical vapor deposition (CVD) grown WSe2 after FIB irradiation. PL dynamics reveals a microsecond-long lifetime for these defect-bound excitons of single-layer WSe2, which is three orders of magnitude longer than that of the defect excitons without FIB treatment. This controllably generated ultra-long lifetime of defect-bound excitons in single-layer WSe2 can be useful for photo-catalytic reactions, valleytronics and quantum light emissions owing to the longer carrier separation/manipulation time.


4:15 PM MS02.02.08
Mechanics of Spontaneously Formed Nanoblisters Trapped by Transferred 2D Crystals Daniel Sanchez, Zhaohe Dai, Peng Wang, Andrei Dolocan, Arturo Cantu-Chavez, Christopher J. Brennan, Rui Huang and Nanshu Lu; The University of Texas at Austin, United States

Layered systems of two-dimensional (2D) crystals and heterostructures are widely explored for new physics and devices. In many cases, monolayer or few-layer 2D crystals are transferred to a target substrate including other 2D crystals, and nanometer-scale blisters form spontaneously between the 2D crystal and its substrate. Such nanoblisters are often recognized as an indicator of good adhesion but there is no consensus on the contents inside the blisters. While gas-filled blisters have been modeled and measured by bulge tests, applying such models to spontaneously formed nanoblisters yielded unrealistically low adhesion energy values between the 2D crystal and its substrate. Typically, gas-filled blisters are fully deflated within hours or days. In contrast, we found that the height of the spontaneously formed nanoblisters dropped only by 20%-30% after three months, indicating that liquid instead of gas is likely trapped in them. The blister contents are further analyzed using time-of-flight secondary ion mass spectrometry (ToF-SIMS) showing a mixture of water and organic matter at the 2D material-substrate interface. We therefore developed a simple scaling law and a rigorous theoretical model for liquid-filled nanoblisters, which predicts that the interfacial work of adhesion is related to the fourth power of the aspect ratio of the nanoblister and depends on the surface tension of the liquid. Our model was verified by molecular dynamics simulations, and the adhesion energy values obtained for the measured nanoblisters are in good agreement with those reported in the literature. This model can be applied to estimate the pressure inside the nanoblisters and the work of adhesion for a variety of 2D interfaces, which provides important implications for the fabrication and deformability of 2D heterostructures and devices.

4:30 PM *MS02.02.09
Quantum Calligraphy—Writing Single Photon Emitters in a Two-Dimensional Materials Platform  Matthew R. Rosenberger1, Chandriker Kavir Dass2,3, Hsun Jen Chuang1, Saujan V. Sivaram1, Kathleen McCreary1, Joshua Hendrickson2 and Berend T. Jonker1; 1U.S. Naval Research Laboratory, United States; 2Air Force Research Laboratory, United States; 3KBRwyle, United States

We present a paradigm for encoding strain into two dimensional materials (2DM) to create and deterministically place single photon emitters (SPEs) in arbitrary locations with nanometer-scale precision. Our material platform consists of a 2DM placed on top of a deformable polymer film. Upon application of sufficient mechanical stress using an atomic force microscope (AFM) tip, the polymer layer plastically deforms. While the AFM tip is in contact with the sample, the AFM tip forces the 2DM to deform with the polymer layer, resulting in tensile strain buildup in the 2DM. When the AFM tip is removed, the adhesive interaction between the polymer and the 2DM prevents the 2DM from relaxing back to its original, strain-free geometry, resulting in a permanent and highly localized strain field in the 2DM. We demonstrate control of indent size by modifying the applied load. Also, we show excellent repeatability of both indent shape and size. We show that SPEs are created and localized at nanoindents in a WSe2/PMMA structure, as confirmed by antibunching measurements. The SPEs exhibit single photon emission up to 60 K. This quantum calligraphy allows deterministic placement and real time design of arbitrary patterns of SPEs for facile coupling with photonic waveguides, cavities, and plasmonic structures. We further use the AFM to create trenches in the WSe2/PMMA structure, leading to nominally one-dimensional strain profiles. We find that the linear polarization orientation of SPEs in the trenches correlates with the orientation of the one-dimensional strain profile. This result holds for trenches made at different orientations relative to the WSe2 crystal orientation, suggesting that the polarization orientation of SPEs in WSe2 is determined by the strain profile alone. In addition to enabling versatile placement of SPEs, these results present a general methodology for imparting strain into 2DM with nanometer-scale precision, providing an invaluable tool for further investigations and future applications of strain engineering of 2DM and 2DM devices.

Reference:
MS02.03.02
Mutual Strain in MoS$_2$/WS$_2$ Heterobilayers  
Robert Waelder and Erik Einarsson; University at Buffalo, The State University of New York, United States

Lattice mismatch in heterostructures traditionally manifests as accumulation of strain in a thin film that has been grown on a bulk substrate. The strain persists until some critical thickness is reached, at which point the lattice relaxes and returns to its unstrained state. In short, only the deposited material bears the strain. Here we investigate the case in which both sides of a heterostructure are atomically thin transition metal dichalcogenide monolayers. We grew WS$_2$ on MoS$_2$ by chemical vapor deposition, and characterized the heterobilayer regions using photoluminescence (PL) spectroscopy. Density functional theory calculations predict a change in the optical bandgap of each monolayer under uniform, biaxial strain. The observed shifts in the A exciton peaks, determined from PL spectra, agree well with the numerical predictions. This suggests a mutual equilibrium is reached in which both materials bear some of the strain. Using the relation between strain and band gap, we calculated the strained in-plane lattice parameters based on the A exciton peak positions. Monolayer MoS$_2$ and WS$_2$ have in-plane lattice parameters of 3.16 Å and 3.19 Å, respectively, but both of these values become approximately 3.17 Å in the heterobilayer, differing by less than 0.4 pm. Our findings indicate that lattice matching occurs in 2D heterostructures, and should be taken into consideration when designing van der Waals solids for optoelectronic applications.

MS02.03.04
Strain-Induced Enhancement of Catechol Sensing Using 2D - WO$_3$ Nanofibers  
Sushmitha Veeralingam and Sushmee Badhulika; Indian Institute of Technology, Hyderabad, India

A low cost, flexible, sensing platform which can detect catechol in biological fluids and environment is of utmost importance in healthcare. In this work, we demonstrate a facile, low-cost approach to fabricate 2D-Tungsten (VI) oxide (WO$_3$) nanofiber-based strain induced highly sensitive and selective catechol sensor. 2D-WO$_3$ was synthesized using electrospinning technique followed by the drop casting of annealed nanofibers on to flexible PET substrates. X-Ray Diffraction (XRD) and Raman studies confirmed the formation of Hexagonal phase-WO$_3$ and O-W-O bending modes respectively while scanning electron microscopy (SEM) studies revealed the uniform distribution of WO$_3$ nanofibers on PET substrate. The sensor responded to a wide dynamic range of catechol concentrations from 1µM to 400µM, exhibited a sensitivity of 49.29 µA/µM cm$^2$ and a limit of detection of 0.52µM which were far more superior than previously reported catechol sensors fabricated using sophisticated fabrication techniques. The sensing response can be ascribed to the oxidation of catechol to benzoquinone in presence of n-type WO$_3$ nanofibers thus resulting in increased current flow through the device. Interestingly, when the sensor was subjected to compressive strain during catechol sensing, a remarkable increase in sensitivity of 86.34 µA/µM cm$^2$ was observed. The limit of detection also further reduced to 42 nM. Upon subjecting the sensor to a strain ranging from 3.14% to 47.6% an exceptional increase in current was observed. This strain induced increase in sensitivity can be attributed to the increase in the density of interconnected WO$_3$ nanofibers which enhances the potential active sites for catechol interaction. Furthermore, to explore the practical utility of the sensor, it was used to detect catechol in simulated blood samples for which it showed excellent selectivity towards catechol in presence of other interfering analytes like Ascorbic acid, Uric acid, Na+, Ca+, and glucose. The strategy outlined here can be used to fabricate wearable, chemiresistive platforms for detection of various biological analytes useful in point-of-care medical diagnostics.

MS02.03.05
Two-Phase State and Elastic Instability in Small Clamped Systems Undergoing Symmetry Changing Structural Phase Transitions  
Arkadi P. Levanyuk$^1$, Sergey Minyukov$^2$ and Ibrahim B. Misirlioglu$^3$; $^1$University of Washington, United States; $^2$Russian Academy of Sciences, Russian Federation; $^3$Sabanci University, Turkey

Understanding phase transitions in constrained crystalline systems such as in thin films on substrates has often been driven by the motivation to tailor the interesting physical properties coming about near the transition. Ferroelectric-paraelectric transitions in perovskites are an example. In all bulk perovskites these transitions are of the first order. There is no consensus in answering the question as to what happens with these transitions in thin films clamped on a substrate. The prevailing opinion is that a first order transition in bulk turns second order though it is in disagreement with results concerning first order transitions in large clamped systems. The apparent reason of this opinion is that in many reported cases the first-order transition in free crystal is relatively weak and would convert
into a second order in film form if the system remained homogeneous. In this talk, we report our theoretical analysis of this case both for laterally clamped slabs with free surfaces and for thin films on stiff substrates. The case of clamped objects allows a consistent analytical analysis in 1D case where the system is laterally finite but relatively large. For systems with small lateral sizes we perform numerical simulations. We observe formation of two-phase state that extend to a temperature range more than 10 degrees, likely smearing the transition anomalies. This temperature interval shrinks with diminishing of the lateral size and may disappear for very small sizes. For films on substrates no analytical theory of two-phase formation is possible though it is possible to analyze the loss of elastic stability of non-symmetrical phase when, at heating, the nucleation is inhibited and the homogeneous state conserves even in the region where the two-phase state is more energetically profitable. Although within a different approach this loss of elastic stability in large clamped systems has been predicted earlier but not for films on substrates. There exists a critical thickness for the stability loss and, seemingly, for the two-phase state formation which is fairly small for studied systems. We demonstrate our approach for an isotropic system that is possible to extend albeit rather cumbersome to experimentally studied perovskite systems where the elastic anisotropy might be important.

**MS02.03.06**

**Comparison of Characteristics of Sn:In$_2$O$_3$ Electrode with Different Sn Doping Concentration for Electrodes of Transparent Thin-Film Transistors**

Jin H. Park, Sang-Hwi Lim, Sung H. Jung, Hyung K. Cho and Han-Ki Kim; Sungkyunkwan University, Korea (the Republic of)

In this work, we studied the effect of tin doping concentration on the electrical, optical, morphological, and crystallographic characteristics of tin doped indium oxide (ITO) and comparison of interfacial characteristics between indium-gallium-zinc oxide (IGZO) and ITO with different tin doping concentration to improve the properties of ITO electrode which applied in transparent thin film transistors (TFTs). We deposited ITO films on the glass with 4 inch-sintered ceramic target with low (In:Sn=99:1) and high (In:Sn=90:10) concentration of tin doping by magnetron sputtering system at room temperature. To compare the characteristics of ITO films with high and low concentration of tin doping, Hall measurement, UV-vis spectroscopy, filed emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and ultra-violet photoelectron spectroscopy (UPS) were conducted. Both ITO films with high and low concentration of tin doping showed low electrical resistivity about 10$^{-4}$ ohm-cm and superior optical transmittance above 85 % in visible range. In detail, ITO film composed 1 wt% tin doping concentration showed lower sheet resistance and higher optical transmittance. As thickness of films increased, transmittance of both films shifted to red side. The highest figure of merit was obtained at the thickness of 150 and 125 nm in the case of low and high tin concentration ITO films, respectively. Through SEM image, both ITO films with high and low tin doping concentration showed crystalline microstructure. XRD results indicated both ITO films are bixbyite-In$_2$O$_3$ crystal structure. Therefore, we fabricated the top gate-transparent IGZO TFTs and circular transmission line method (CTLM) devices with ITO electrodes. Top gate-transparent IGZO TFTs consist of 100nm thick of ITO gate electrode, 80nm thick of Al$_2$O$_3$ gate insulator layer, 30nm thick of IGZO channel, and 100nm thick of ITO source/drain electrode. The transfer curve of both high and low tin doping concentration ITO electrode TFTs showed traditional n-type transistor characteristic and operated in depletion mode. And also, transistor parameters such as threshold voltage, field effect mobility, subthreshold swing, and on-off ratio were extracted. Saturation mobility and on-off current ratio in 1 wt% tin doped ITO TFT was higher than those in 10 wt% tin doped ITO TFT. In conclusion, we found that low doping level of tin in ITO is more proper to transparent TFT with room temperature process.

**MS02.03.07**

**Large Areal Coverage of MoS$_2$ Monolayer on Various Substrates and a Study of the Role of Interface Effects on Electrical Performance of Devices Based on these Monolayers**

Yan Jiang and Usha Philipose; University of North Texas, United States

A planar distribution of source material and a promoter enabled centimeter-scale growth coverage of molybdenum disulfide (MoS$_2$) monolayers by conventional ambient pressure chemical vapor deposition (APCVD). The molybdenum source and sodium chloride promoter were spin-coated on select planar substrates like silicon, sapphire and quartz. This technique was found to contribute to stable and consistent growth of MoS$_2$ monolayers. Results of Raman and photoluminescence spectroscopy attested to the high crystalline quality of the as-grown layers, while results of atomic force microscope verified the monolayer film thickness. The electronic quality of the films was found to depend on the growth substrate; the study enabled by fabrication of field effect transistors with MoS$_2$ monolayers functioning as the active layer. It was experimentally determined that MoS$_2$ monolayers grown on
sapphire substrates and contacted by two Cr/Au electrodes provides the most effective ohmic contact with very low
contact resistance. On the other hand, MoS$_2$ monolayers grown on silicon and contacted by identical metal contacts
yield high contact resistance, inadvertently affecting transport performance of devices with and without gate bias.
This work on the effective distribution of source and promotors on the growth substrate for the synthesis of high-
quality MoS$_2$ monolayers sheds light on the growth mechanism and the critical role of promotors on growth. The
correlation between electrical performance and growth substrates implicates the role of interface effects and its study
provides a path to improve device performance of MoS$_2$ monolayers.

**MS02.03.08**
Electronic Effects in Nanotribology by Using Few-Layer MoTe$_2$ under Semiconductor to Metal Transition
Shuyu Huang, Yongkang Wang, Lijian Zhan, Xiongyu Wu and Yunfei Chen; South East University, China

Friction is inherently a process of energy dissipation where electronic and phononic contributions are considered as
two primary channels of dissipative process. Mechanical strain has been demonstrated to be able to reversibly
control the phase transition of few-layer MoTe$_2$ semiconductor (2H) to metal phase (1T') at room temperature under
ambient conditions. Reversibly controlling of the phase transition enabling the monitor of electron concentration in a
same region in few-layer MoTe$_2$, which make it an ideal platform to study the electronic effects in nanotribology.
Herein, the nanoscale friction is measured in situ in few-layer metallic and semiconductor MoTe$_2$ by atomic force
microscopy (AFM) to extract the electronic effects, where the phase transition is controlled by mechanical strain.
First of all, mechanically exfoliated MoTe$_2$ thin film is transferred onto SiO$_2$/Si substrate pre-coated with 200 nm
gold by the wetting transfer method. Due to the intrinsic roughness of the thermal evaporation Au film, a tensile-
strain-modulated phase transition occurred when a certain amount of normal force is applied in MoTe$_2$. Both the
semiconductor and metal phase region existed, which has been confirmed by Raman spectra and conductive AFM
(CAFM). Then, we use AFM to characterize the nanoscale friction on the few-layer MoTe$_2$ while in situ record the
current by using CAFM to characterize the phase transition. Compared with the semiconductor region, the metal
region shows significantly higher current and greater friction. And the current between the metal phase MoTe$_2$ and
the tip is positively correlated with the friction force. Furthermore, we changed bias between conductive tip and
substrate, the results show that the friction in metal phase region increase with the increase of the external bias and
can be regulated by an external electric field. The experimental results reveal that much higher electron
concentration in 1T'-MoTe$_2$ cause a remarkable increase of friction force implying that friction energy can also be
dissipated through the electron channel.
Draw support from the few-layer phase transition material MoTe$_2$, we are able to extract the electronic contributions
in friction energy dissipation avoiding the effects of deformation, surface roughness, and changes in atomic
structure. This work facilitates an understanding of electronic effect in nanotribology and provide a new strategy to
study the electronic effects in nanotribology.

**SESSION MS02.04: Emergent Phenomena III**
Session Chairs: SungWoo Nam and Michael Pettes
Tuesday Morning, December 3, 2019
Hynes, Level 1, Room 108

**8:30 AM *MS02.04.01**
Nanoscale Strain Engineering of Giant Pseudo-Magnetic Fields, Valley Polarization and Topological
Channels in Monolayer Graphene
Nai-Chang Yeh, Chen-Chih Hsu, Marcus Teague and Jiaqing Wang; California
Institute of Technology, United States

The existence of nontrivial Berry phases associated with two inequivalent valleys in graphene can provide
interesting opportunities for investigating the valley-projected topological states. Examples of such studies include
observation of anomalous quantum Hall effect in monolayer graphene, demonstration of topological zero modes in
“molecular graphene” assembled by scanning tunneling microscopy, and detection of topological valley transport
either in graphene superlattices or at bilayer graphene domain walls. However, all aforementioned experiments
involved non-scalable approaches of either mechanically exfoliated flakes or atom-by-atom constructions. Here we
report a new approach to manipulating the topological states in monolayer graphene via nanoscale strain
By placing strain-free monolayer graphene on architected nanostructures to induce global inversion symmetry breaking, we demonstrate the development of giant pseudo-magnetic fields, global valley polarization, and periodic one-dimensional topological channels for protected propagation of chiral modes in strained graphene, thus paving a pathway towards realizing scalable graphene-based valleytronics and strain-induced superconductivity.

9:00 AM MS02.04.02
Zero-Dimensional Graphene and Its Behavior under Mechanochemical Activation with Zinc Ferrite Nanoparticles Monica Sorescu1, Matthew Knauss1, Alice Perrin2 and Michael McHenry2; 1Duquesne University, United States; 2Carnegie Mellon University, United States

Equimolar mixtures of zero-dimensional graphene (SkySpring Nanomaterials, 1-5 nm particle size) and zinc ferrite nanoparticles (Alfa Aesar, 50 nm particle size) were exposed to mechanochemical activation by high-energy ball milling for time intervals of 0-12 hours. Their structural and magnetic properties were analyzed by Mossbauer spectroscopy and magnetic measurements. The spectra of zinc ferrite milled without graphene were fitted with one quadrupole-split doublet (quadrupole splitting 0.5 mm/s, isomer shift 0.23 mm/s) and indicated that zinc ferrite was superparamagnetic. The line width of the doublet increased from 0.41 to 0.64 mm/s, which correlates with a reduction in particle size as effect of the ball milling processing performed. When graphene was added to the milling powders, the Mossbauer spectra showed the appearance of another quadrupole doublet, with a quadrupole splitting of 0.84 mm/s and an isomer shift of -0.38 mm/s. Its abundance to the spectrum remained constant to 4.48% while the milling time was increased. This second doublet could be related to carbon atoms occupying neighborhoods in the proximity of iron atoms. Hysteresis loops were recorded in an applied magnetic field of 5 T at a temperature of 5 K. A change in the approach to saturation of the loop was observed, with saturation being achieved for the sample milled for 12 hours with graphene. Zero-field-cooling-field-cooling (ZFC-FC) was performed on all samples between 5-300 K with an applied magnetic field of 200 Oe. Graphene was found to stabilize the magnetic properties of the milled system of powders to a blocking temperature of about 90 K.

NSF-DMR-1002627

9:15 AM MS02.04.03
Colossal Room-Temperature Magnetoresistances at Strongly-Coupled Graphene/Complex-Oxide Heterostructures J. Hu1,1, M. Yang2, J. Guo1,1, A.T.S. Wee1,1 and A. Ariando1; 1National University of Singapore, Singapore; 2Agency for Science, Technology and Research, Singapore

Magnetoresistance, the change in electrical resistance under an external magnetic field, has been widely used in magnetic sensing, recording and memory devices. Even though the mass production of single-layer graphene has entered the stage of commercialization, the magnetoresistance of single-layer graphene yielded limited success at room temperature, usually ranging from 60% to 775 % at 9 T which were achieved through various routes, such as decorating with gold nanoparticles, by fluorination and nitrogen doping, or through phonon-mediated effect. In this talk, we demonstrate a colossal magnetoresistance of single-layer graphene, nearly 5,000% at 9 T and 300 K, achieved by forming a graphene/perovskite-oxide heterostructure. For single-layer graphene fabricated on various perovskite oxides, we demonstrated a universal twentyfold enhancement in magnetoresistance compared to previous single-layer graphene devices at the same conditions. Combining scanning tunneling microscopy with theoretical calculations reveals that the colossal magnetoresistance stems from an inhomogeneous charge distribution due to the strong interfacial coupling between graphene and perovskite oxides, which creates a random resistor net-works in graphene. Our results suggest that the perovskite oxides can be an appealing substrate for high performance graphene-based magnetoelectronics.

9:30 AM BREAK

10:00 AM MS02.04.04
New Imaging Capabilities Enabled by the Electron Microscope Pixel Array Detector (EMPAD) for 2D Materials Kayla X. Nguyen; University of Illinois at Urbana-Champaign, United States

Scanning transmission electron microscopy (STEM) has been a ubiquitous characterization platform for reconstructing atomic-resolution images from highly scattered electrons or from the direct electron beam. These signals have become the standard for imaging in the electron microscope because of their ease of collection and
interpretability. Yet in these imaging modes, only a single contrast value is extracted at each scan position; all other information about the specimen encoded in the electron diffraction pattern is thrown away. Previous attempts to utilize the full electron scattering signal have been limited by electron detectors based on scintillators and charge-coupled devices which have slow acquisition speeds and limited dynamic ranges. Recently, a new generation of high-speed and high-dynamic range detectors have allowed for fast collection of the full electron diffraction pattern at each scan position from which information is no longer limited to conventional imaging techniques - but can extend beyond this to uncover quantitative measurements of thickness, strain, tilt, polarity, atomic fields and the long-range electromagnetic fields. Here, we highlight the electron microscope pixel array detector (EMPAD) whose previous demonstrations have shown broad, cross-disciplinary impact, this includes: (1) the development of the highest resolution electron microscope in the world, (2) quantitative imaging of fields from polarization vortices in ferroelectrics, and (3) strain and dislocation mapping of 2-dimensional (2D) materials with picometer accuracy.

Here, the high-dynamic range of the EMPAD is extremely advantageous when capturing the full scattering signature of 2D materials. In 2D materials, the incident electron beam tend to dominate the scattering signal such that intensities from diffracted spots are washed out by the incident beam. Using the high-dynamic range and high-speed of the EMPAD, we can map strain in 2D materials with high-precision at micrometers field of view; this method can be used to study lattice distortions to identify where lattice strain and dislocations most commonly occur. With the EMPAD, physical properties of 2D materials can be investigated and directly imaged to provide an interesting playground for exploration where new material physics can be recovered without the complications from multiple scattering.

1 Tate, MW. et al. Microscopy and Microanalysis 22, 237-249 (2016).

10:30 AM MS02.04.05
Crumpled MoS2-Graphene Photosensor with Enhanced Photoresponsivity Enabled by Exciton Drifting
Juyoung Leem1, Pilgyu Kang2,1, Jihun Mun3, Yeageun Lee1, Mohammad A. Hossain1, Arend M. van der Zande1, Sang-Woo Kang1 and SungWoo Nam1; 1University of Illinois at Urbana-Champaign, United States; 2George Mason University, United States; 3Korea Research Institute of Standards and Science, Korea (the Republic of)

Atomically-thin two-dimensional (2D) materials exhibit extraordinary optical, electronic, and mechanical properties, which make them promising material platforms for optoelectronic applications. Monolayer molybdenum disulfide (MoS2) is one of the widely used semiconducting 2D materials for photosensing owing to its direct bandgap. In addition to its intrinsic material properties, mechanical strain applied to the semiconducting material can modulate intrinsic electronic properties, such as bandgap. In this presentation, we report a mechanically self-assembled, crumpled MoS2 photosensor with graphene electrical contacts. Graphene was used as electrodes because it is mechanically robust and electrically conductive 2D material forming barrier-free electric contact with MoS2. Furthermore, by crumping monolayer MoS2, we introduced strain gradient over crumpled MoS2 structure, and such strain gradient enables nanoscale bandgap modulation, which induces exciton drift with light illumination. The exciton drift enables higher photoresponsivity in crumpled MoS2 photosensor, compared to photoresponsivity of flat MoS2 photosensor. We demonstrate power dependent photoresponsivity of our crumpled MoS2 photosensor as well as local photocurrent generation with photocurrent mapping. Our approach to mechanical self-assembly of atomically thin materials offers a simple but effective way to enhance photosensitivity and suggests a new way to engineer exciton funneling in 2D material system.

10:45 AM MS02.04.06
Electrical Actuation of Drum Type h-BN Nano-Mechanical Resonator Yusuke Morimoto, Kuni Takei, Takayuki Arie and Seiji Akita; Osaka Prefecture University, Japan

Nano-electro-mechanical resonators (NEMR) consisting of atomically thin two dimensional (2D) materials such as graphene are considered to be capable of highly accurate force measurements. The resonance properties of NEMR consisting of optically opaque 2D materials are highly affected by the light irradiation because of the photothermal effect. A hexagonal boron nitride (h-BN) is transparent in the visible light range. Thus, the photothermal effect on the h-BN NEMR would be suppressed. In addition, h-BN is an emergent material for single photon emitters that
are ultrabright and stable under ambient conditions. Very recently, theoretical prediction regarding quantum effects in a mechanically modulated single photon emitter composed of h-BN NEMR has been reported.[3] To discriminate the photothermal effect, the light induced effects on the resonance should be clarified. In this study, we investigate the photothermal effect on resonance properties of the electrically actuated drum type h-BN NEMR.

To compose the h-BN NEMR, a multilayered h-BN flake, which was prepared by mechanical exfoliation of bulk h-BN, was transferred using gel transfer method onto a predetermined pair of drum-shaped electrodes on a patterned n’Si / SiO$_2$ substrate. To form the h-BN NEMR suspended by metal electrodes, the SiO$_2$ layer underneath the h-BN drum (6 μm in diameter) was etched using buffered HF. The frequency resonance of the h-BN NEMR was measured in vacuum by optical detection method, where a laser with a wavelength of 520 nm was irradiated to the center of the h-BN drum as the probe. Additional laser with a wavelength of 685 nm was irradiated to investigate the photoinduced effect on the resonance.

The h-BN NEMR was successfully oscillated by applying the AC + DC bias voltage between the n’Si substrate and the Au electrode. The resonance frequency and Q factor were 26.48 MHz and 115, respectively. The oscillation amplitude increases linearly with increasing the AC or DC voltages. This behavior can be explained by the model based on the electrical actuation induced by the dielectric effect. Under additional light irradiation with a wavelength of 685 nm around the center of the drum, the linearity of the resonance properties were maintained under high intensity of 1 mW. Contrary, in the case of graphene drum resonator, which is optically opaque, the resonance property was affected even under the weak laser irradiation less than 10 mW because of the photothermal effect, which results in the modification of oscillation modes between linear and nonlinear.[1] Thus, the resonance mode of the h-BN NEMR is robust against the photothermal effect owing to the optical transparancy of h-BN.

References

11:00 AM MS02.04.07
Impacts of Stress and Dissipation in van der Waals Interfaces on 2D Material Nanoelectromechanical Systems

SunPhil Kim and Arend M. van der Zande; University of Illinois at Urbana-Champaign, United States

Two-dimensional materials such as graphene and MoS$_2$ represent the ultimate limit of both nanoelectronic and nanoelectromechanical systems due to their intrinsic molecular scale thickness.[1] While 2D materials exhibit many useful properties, many of the most exciting phenomena and applications arise at the van der Waals interface. Electrically, the van der Waals interface enables the constructing of heterostructures and molecular scale electronics. Mechanically, the van der Waals interface displays superlubricity[2] or solitons[3] depending on whether the interface is aligned. A fascinating question is how the van der Waals interface affects the mechanical properties of 2D membranes. Answering this question is important to incorporating 2D heterostructure electronics into diverse applications such as highly tunable nanoelectromechanical systems from suspended 2D membranes, stretchable electronics from crumpled 2D materials, and origami/kirigami nano-machines.

In this study, we explore the impact of the van der Waals interface by comparing mechanical resonance of electrostatically contacted circular drumhead resonators made from atomic membranes of monolayer graphene to commensurate (Bernal stacked) bilayers, incommensurate (twisted) bilayer, and graphene-MoS$_2$ heterostructures (2D bimorph).

For Bernal stacked bilayer, we observe the creation and destruction of individual solitons manifesting as stochastic jumps in the mechanical resonance frequency tuning. We find individual dislocation creation and destruction of single solitons lead to shifts in membrane stress of < 10 mN/m or an in-plane interlayer slip distance of < 1.42 Å. We observe similar jumps in the few-layer graphene and heterostructure, but not in the twisted bilayer. For twisted bilayer, amplitude dependent studies reveal that the resonators show a factor of 3 to 5 higher dissipation rate at room temperature. A further increase in amplitude leads to a large peak broadening rather than Duffing nonlinear behaviors observed in monolayer and Bernal stacked bilayer graphene resonators. In addition, the interface dissipation is strongly dependent on temperature, displaying tuning of nonlinear behaviors with a decrease in temperature.

These results show that van der Waals interfaces strongly affect stress and dissipation of many multilayer 2D atomic membranes; an important consideration in engineering 2D nanomechanical devices.
11:15 AM *MS02.04.08
Tuning Physicochemical Properties of MoS2 by Mechanical Strain Xiaolin Zheng and Sangwook Park; Stanford University, United States

Monolayers of 2D materials have ultrahigh mechanical strength, which enables the application of very large elastic strains (e.g., ~11% for MoS2 and 25% for graphene). The ability to sustain such large elastic strain offers unprecedented opportunities to engineer the physicochemical properties by applying mechanical strain. In this talk, I will present two examples on the effect of strain on the properties of MoS2 layer. The first example shows that elastic tensile strain reduces the bandgap of MoS2. When a gradient strain field is applied to MoS2 monolayer, the created bandgap gradient acts as an efficient funnel of photogenerated excitons that leads to enhanced photoluminescence. The second example shows that when elastic strain is applied to the sulfur vacancy on the basal planes of monolayer 2H-MoS2, the strain modifies the local electronic structure and catalytic activity. The proper combinations of S-vacancy and strain allow us to achieve higher intrinsic activity for hydrogen evolution reaction than the edge site of MoS2.

SESSION MS02.05: Emergent Phenomena IV
Session Chairs: SungWoo Nam and Michael Pettes
Tuesday Afternoon, December 3, 2019
Hynes, Level 1, Room 108

1:30 PM *MS02.05.01
Lattice Moire Characteristics and Electromechanical Properties of Multilayer Graphene Kyung-suk Kim; Brown University, United States

Lattice misalignments between the two layers of a bilayer graphene are found to provide peculiar electromechanical properties of the graphene. An example is the unconventional superconductivity in magic-angle graphene superlattices (Cao, et al. Nature, 556, 2018), and another the localization of electric polarization at the flexoelectric crinkle kinks (Kothari, et al. Roy Soc Proc, 474, 2018). The lattice misalignments are typically represented by the super-lattice moire-interference patterns for translational and rotational misalignments. Electronic force-field interactions, e.g. van der Waals and Coulomb interactions, between the atoms typically relax the super-lattice configuration from the geometrical moire interference pattern. In particular, non-uniform translational misalignments in translation lead to formation of van der Waals dislocations and flexoelectric crinkles. On the other hand, non-uniform misalignments in rotation generate in-plane disclinations and out-of-plane wrinklons. Here, we present studies of the dislocation, crinkle, disclination and wrinklon characteristics of a bilayer graphene. The characteristics could be investigated with an atomic-lattice interferometry (ALI), which is carried out with a dual-tip AFM interferometer (DT-AFMI). The optical coupling system of the DT-AFMI enables sensing differences between two simultaneous dual-tip scans of sample and reference graphene lattices, which in turn impart the moire fringes of the interference between the sample and reference lattices. The ALI moire fringes indeed reveal the relaxation of the super-lattice configuration. We compare the relaxations with those evaluated by density functional theory (DFT) calculations. Then, presented are correlations between the lattice moire patterns and the electromechanical properties of the bilayer graphene. Moreover, looked after are studies on stabilities of the van der Waals dislocations, the flexoelectric crinkles, the in-plane disclinations and the out-of-plane wrinklons in the bilayer.
Abstract: Two-dimensional materials constitute an exciting platform for investigation of both fundamental phenomena and electronic applications. However, many 2D materials are not air stable, making their studies and integration challenging. Here we discuss routes to stabilize such materials, using few-layer black phosphorus, a 2D semiconductor, and chromium triiodide, a 2D magnetic insulator, as examples. The chemical degradation pathways of both materials are accelerated by light. While simple encapsulation by Al₂O₃, PMMA and hexagonal BN (hBN) are sufficient to ensure air stability for few-layer black phosphorus devices, it only leads to modest reduction in degradation rate for CrI₃. We find that minimizing exposure of light markedly improves stability of CrI₃, and CrI₃ sheets sandwiched between hBN layers are air-stable for >10 days. By monitoring the transfer characteristics of CrI₃/graphene heterostructure over the course of degradation, we show that the aquachromium solution hole-dopes graphene. Finally, I will also discuss our latest results on transport measurements of twisted bilayer graphene devices that show both superconductivity and insulating behaviors.

2:30 PM BREAK

3:00 PM *MS02.05.03
Manipulating Valley Currents in Graphene Nanostructures Stephen Power; Trinity College Dublin, Ireland

Two-dimensional materials, such as graphene, are promising valleytronic candidates due to the K and K' valleys at the Dirac points. All-electronic control is particularly desirable for device applications. Many proposed setups exploit strain-induced pseudomagnetic fields which act oppositely in the K and K' valleys. This is illustrated for graphene nanobubbles, which can filter or split a charge current into its different valley components [1]. Experimental approaches in this direction are advancing, but the most promising signatures of valley-dependent phenomena have instead emerged from graphene/hexagonal boron nitride heterostructures. Large non-local resistance signals here have been interpreted in terms of a valley Hall effect (VHE) driven by a bulk Berry curvature [2], which in turn emerges from a gap-opening sublattice-asymmetric potential (mass term). A complete understanding of such measurements in terms of either bulk [3]- or edge-driven [4] mechanisms is very much an open question.

Here I demonstrate the emergence of a valley-splitting bulk transport mechanism in the absence of a global band gap [5]. This phenomenon requires instead the presence of local spatial regions (dots) with finite mass. An exact analytic solution to the scattering problem is derived for simple dots, which establishes a strong valley dependence for scattering at low energies. Tight-binding simulations confirm that this behaviour is robust for a wide range of mass distributions, and gives rise to a valley Hall conductivity in periodic systems.

Our findings provide an alternative mechanism for the generation of bulk valley currents and suggest that valley-dependent scattering may give rise to analogous effects to those expected for Berry-phase induced deflections. They also suggest more reliable guidelines for valley engineering, in contrast to proposals which require atomically precise edges or strain profiles.

References:

3:30 PM MS02.05.04
Controlling Rotation in 2D Material Flakes Harley T. Johnson¹, Shuze Zhu¹ and Pascal Pochet²; ¹University of
Interlayer rotation in van der Waals structures of 2D materials couples strongly to electronic properties and, therefore, has significant technological implications. Nevertheless, controlling the rotation of an individual 2D material flake remains a challenge in the development of rotation-tunable electronics. Here we reveal a general moiré-driven mechanism that governs interlayer rotation, relying on the concept of interlayer or van der Waals (vdW) dislocations. We present a theory to explain the connection between the moiré pattern and the arrangement of vdW dislocations, which can be understood to minimize the interfacial energy in the system. As a demonstration of this theory, we consider the arrangement of vdW dislocations due to growth or rotation of finite-sized MoS₂ flakes on larger crystalline substrates. We compare this to the classic critical thickness problem in thin film mechanics, and explain the small, stable rotation angles in finite 2D material flakes on crystalline substrates that are commonly observed experimentally. We show that by applying strain, and thereby controlling the moiré pattern, it is possible to select the amount of interlayer rotation between flake and substrate. The approach provides a powerful tool for the on-demand design of rotation-tunable electronics.

3:45 PM MS02.05.05
Exploiting Moiré Effects to Control Thermally-Activated Motion and Plasma Patterning in Twisted Bi-Layer Graphene Soumendu Bagchi, Harley T. Johnson and Huch Beng Chew; University of Illinois at Urbana-Champaign, United States

Recent studies have established synthesis protocols to enable twisting of bilayer graphene to change the stacking order, thereby controlling the resulting moiré pattern. Due to the moiré, electronic transport properties of the twisted bilayer graphene are found to be strongly-dependent on the twist angle, thus yielding a potential new class of low-dimensional carbon electronics. However, being driven by weak van der Waals interactions at the interfaces (~1/10th of room-temperature KT), these structures are susceptible to nontrivial thermal fluctuations which may severely affect their device level performance. Using large-scale molecular dynamics simulations, we uncover a size dependent thermal stability of Moiré patterns in free-standing twisted bi-layers. We show that small twisted graphene flakes on the order of 10nm in size can rapidly re-orient themselves into stable AB stackings at room temperature, while twisted graphene flakes on the order of 100nm and larger remain thermally-stable even at temperatures exceeding 1000° C. This size-effect on the thermal stability and kinetic behavior of twisted bilayer graphene is related to the incomplete moiré periodicity of the graphene flakes and is explained using a dislocation-based framework. For thermally-stable twisted graphene flakes, we show that the different stacking arrangements present in the moiré pattern can be used to bias the hydrogen-plasma etching rates. Specifically, the AA and SP regions in the bilayer graphene have much lower barrier energies, compared to the perfect AB stacking, for ion transmission through the top graphene layer for etching of the bottom layer. These results suggest that selective patterning of twisted graphene can be achieved, which is of significant importance in the top-down fabrication of porous graphene.

4:00 PM MS02.05.06
Ultrabright Trion Generated by Impact Ionization in High Quality Monolayer MoSe₂ Bumho Kim¹, Yue Luo², Daniel Rhodes¹, Yusong Bai¹, Song Liu¹, Jue Wang¹, Baili Huang¹, Zhaochen Li¹, Takashi Taniguchi², Kenji Watanabe³, Timothy Berkelbach¹, David Reichman¹, Stefan Strauf², Xiaoyang Zhu¹, Katayun Barmak¹ and James Hone¹; ¹Columbia University, United States; ²Stevens Institute of Technology, United States; ³National Institute for Materials Science, Japan

As atomically thin direct-gap semiconductors with strong light-matter interaction, monolayer transition metal dichalcogenides (TMDs) are promising for a broad range of optical and optoelectronic applications. In TMDs, strong electron-hole interactions due to quantum confinement and reduced dielectric screening produce strongly bound composite quasiparticles, including both neutral (e.g., excitons and biexcitons) and charged species (e.g., trions and charged-biexcitons). Of particular interest are trions, three-body charge-exciton bound states, which simultaneously carry charge and excitation energy, and inherit the robust valley polarization of the parent excitonic states. As charged quasiparticles, trions can be manipulated by electric fields. Furthermore, trions in monolayer TMDs have much stronger binding energy, compared to those in traditional semi-conducting materials of GaN, InN, and GaAs, an important factor to prevent dissociation under applied fields. These unique properties offer new opportunities to manipulate charge and excitonic energy in 2D TMDs, which can be exploited for optoelectronic applications including light emitting and photodetecting devices where directional energy or charge transport is
critical.
To date, the promising utilities of trions have been hindered by their short lifetime (∼15 ps), limiting drift length of trions under applied electric fields. The lifetime of trion in TMDs is governed by fast non-radiative decay processes such as trion-phonon interaction and defect-mediated non-radiative recombination. Also, the low trion quantum yield (QY) in monolayer TMDs is another obstacle to realization of trion-based optoelectronic devices. QY of monolayer TMDs is reported to be 0.1 - 8 %. The enhancement of the low QY has been demonstrated through the superacid treatment or the plasmonic cavity coupling techniques. However, the superacid treatment, which passivates charge sources, suppresses trion generation. Also, the cavity coupling approach enhances the spontaneous emission rate by the Purcell effect, thereby preventing the achievement of long trion lifetime. Therefore, the alternative approach to achieve both high trion quantum yield and long lifetime is to improve materials quality, since the low quantum yield and the short lifetime are attributed to the fast, non-radiative recombination rate of trion species in current TMD monolayers. In other words, the currently low QY and trion lifetime primarily arise from mediocre quality of TMDs with point defects concentrations on the order of 10^{12}-10^{13} cm^{-2}.
Here we report near-unity emission quantum yield, ∼89.2 %, by using monolayer MoSe₂ with a significantly lower defect density. Importantly, this produces the photoluminescence (PL) intensity which is mainly contributed to the trion species (>98%). The high trion PL quantum yield in the high-quality monolayer MoSe₂ is attributed to greatly suppressed non-radiative decay rate, leading to the long lifetime of trion (∼250 ps) approaching intrinsic radiative lifetime. Moreover, we propose that band-trap impact ionization in the high-quality monolayer MoSe₂ contributes to generation of ultrabright trion light emission over a wide range of doping concentrations. Our experimental results indicate that point defects as charge sources promote efficient trion generation in high quality MoSe₂. The high trion quantum yield and the long trion lifetime in the high-quality MoSe₂ provide the platform to explore new physics, including trion valley Hall effect and Moire excitons in heterostructures, demanding both high quantum yield and long lifetime. The superior optical properties of MoSe₂ are also expected to enhance the performance of the optoelectronic devices including light-emitters and photodetectors. Furthermore, the secondary carrier induced by band-trap impact ionization is expected to improve performance of optoelectronic devices, including solar cell and avalanche photodiodes.

4:15 PM MS02.05.07
Multiscale Nanostructures Enable Spatially-Defined Graphene Properties Shikai Deng¹, Dongjoon Rhee¹, Won-Kyu Lee¹, Songwei Che², Bijentimala Keisham², Vikas Berry² and Teri W. Odom¹;¹Northwestern University, United States; ²University of Illinois at Chicago, United States

Selectively functionalized graphene can realize spatially-defined properties that are highly desirable for atom-thin devices. Because curvature tunes the surface reactivity of graphene, patterning graphene into regions of different local curvatures can achieve domains with different levels of functionalization. Previous buckling methods were limited by the range of tunability over curvature and control of the orientation at the microscale. This presentation describes a scalable approach to achieve spatially selective graphene fluorination using multiscale wrinkles. Graphene wrinkles were formed by relieving the strain in thermoplastic polystyrene substrates conformally coated with fluoropolymer and graphene skin layers. Chemical reactivity of a fluorination process could be tuned by changing the local curvature of the graphene nanostructures. Patterned areas of graphene nanowrinkles and crumples followed by a single-process plasma reaction resulted in substrates with regions having different fluorination levels. We also demonstrated the conductivity of the functionalized graphene nanostructures could be locally tuned as a function of feature size without affecting the mechanical properties.

4:30 PM MS02.05.08
Computational Analysis of Tunability in the Electronic and Optical Response of Two-Dimensional Materials with Defects Ruth Pachter and Jie Jiang; Air Force Research Laboratory, United States

Defects play an important role in tuning the electronic and optical functionality of 2D materials that are useful for biosensing and nanoelectronics, or in providing the basis for single-photon emission for quantum information processing. We show that patterned graphene with vacancies may offer a route to bandgap generation, and potentially improvement of the I_{ON}/I_{OFF} ratio in a field effect transistor (FET) by nanohole passivation, e.g. through hydrogenation. FETs based on patterned graphene with small pores could have a high level of performance similar to graphene nanoribbons, however with the added benefit of no width confinement. In this context, we report on the theoretical characterization of Raman spectroscopy defect-induced intensities in graphene, which is difficult to achieve experimentally. Defective graphene oxide nanostructures are investigated in comparison to experiment,
where we find that the Raman $I(D)/I(D')$ intensity ratio decreases with increase in the nanohole size and the number of adsorbed oxygens, explaining the decrease of this characterization signature with increase of the exposure time to oxygen plasma. Predicted Raman spectroscopy intensity ratios are also confirmed by measurements for graphene oxide quantum dots. In addition, we discuss the optical spectra of monolayer transition metal dichalcogenides upon introduction of defects. The tunability in the optical response of mechanically deformed WSe$_2$ in comparison point defects is described. Finally, Raman intensity calculations demonstrate that a comparison between pristine and 2D WSe$_2$ with a single vacancy can provide a fingerprint for defect characterization.

SESSION MS02.06: Physico-Chemical Effects I
Session Chairs: SungWoo Nam and Michael Pettes
Wednesday Morning, December 4, 2019
Hynes, Level 1, Room 108

8:30 AM *MS02.06.01
Fracture and Strain Engineering of Two-Dimensional Materials Jun Lou; Rice University, United States

Two-dimensional (2D) materials, such as Graphene, hBN and MoS$_2$, are promising candidates in a number of advanced functional and structural applications, owing to their exceptional electrical, thermal and mechanical properties. Understanding mechanical properties of 2D materials is critically important for their reliable integration into future electronic, composite and energy storage applications. However, it has been a significant challenge to quantitatively measure mechanical responses of 2D materials, due to technical difficulties in the nanomechanical testing of atomically thin membranes. In this talk, we will report our recent effort to determine the engineering relevant fracture toughness of graphene with pre-existing defects, rather than the intrinsic strength that governs the uniform breaking of atomic bonds in perfect graphene. Our combined experiment and modeling verify the applicability of the classic Griffith theory of brittle fracture to graphene. In another example, we systematically characterize chemical vapour deposition-grown MoS$_2$ by photoluminescence spectroscopy and mapping and demonstrate non-uniform strain in single-crystalline monolayer MoS$_2$ and strain-induced bandgap engineering. Strategies on how to improve the fracture resistance in graphene, and the implications of the effects of defects and strain on mechanical and other functional properties of other 2D atomic layers will be discussed.

9:00 AM MS02.06.02
Bending of Multilayer van der Waals Materials Guorui Wang$^{1,2}$, Zhaohui Dai$^3$, Shizhe Feng$^4$, Luqi Liu$^1$, Zhiping Xu$^4$, Rui Huang$^1$ and Zhong Zhang$^1$; $^1$National Center for Nanoscience and Technology, China; $^2$University of Toronto, Canada; $^3$The University of Texas at Austin, United States; $^4$Tsinghua University, China

Out-of-plane deformation patterns, such as buckling, wrinkling, scrolling, and folding, formed by multilayer van der Waals materials have recently seen a surge of interest. One crucial parameter governing these deformations is bending rigidity, on which significant controversy still exists despite extensive research for more than a decade. Here, we report direct measurements of bending rigidity of multilayer graphene, molybdenum disulfide (MoS$_2$), and hexagonal boron nitride (hBN) based on pressurized bubbles. By controlling the sample thickness and bubbling deflection, we observe plate-like responses of the multilayers and extract both their Young's modulus and bending rigidity following a nonlinear plate theory. The measured Young's moduli show good agreement with those reported in literature ($E_{\text{graphene}}$ > $E_{\text{hBN}}$ > $E_{\text{MoS}_2}$), but the bending rigidity follows an opposite trend: ($D_{\text{graphene}}$ < $D_{\text{hBN}}$ < $D_{\text{MoS}_2}$) for multilayers with comparable thickness, in contrast to the classical plate theory, which is attributed to the interlayer shear effect in the van der Waals materials.

9:15 AM MS02.06.03
Study of Fracture Initiation Behavior of MXene with MD Modeling Congjie Wei and Chenglin Wu; Missouri University of Science and Technology, United States

Due to the directionality of Ti$_3$C$_2$T$_x$ and Ti$_2$CT, MXene, the fracture initiation property varies with loading directions. Understanding this rarely explored anisotropic fracture behavior of MXene is essential for material
design and engineering application. In this work, a series of molecular dynamics (MD) modeling is conducted on mono-layer Ti$_3$C$_2$ and Ti$_2$C MXene. Pre-cracks of both zigzag and armchair directions are created by removing atoms. For both cases, pre-cracked MXene is stretched to the crack initiation point and then energy minimization is conducted with canonical ensemble, where the stress distribution and J-integral are calculated and compared. Both mode-I and mixed mode scenarios with ranging loading directions are conducted to explore the combined effect of structural and loading directionality. Also, mode-I crack initiation scenario of graphene is conducted and compared with the Ti$_3$C$_2$Tx and Ti$_2$CTx MXene to explore the thickness effect. Results show that the thickness variation leads to difference of stress distribution around the crack tip, thus influences the crack initiation property.

9:30 AM BREAK

10:00 AM *MS02.06.04
Probing Anisotropic Thermal Conductivity of Transition Metal Dichalcogenides and Their Alloys Ronggui Yang$^1$, Puqing Jiang$^2$ and Xin Qian$^{1,3}$; $^1$University of Colorado at Boulder, United States; $^2$Huazhong University of Science & Technology, China; $^3$Massachusetts Institute of Technology, United States

Transition metal dichalcogenides (TMDs) and their alloys have attracted great interest in recent years due to their potential electronic, photonic and energy applications. However, due to the challenges on anisotropic thermal conductivity measurements, the thermal conductivities of layered TMDs and their alloys remain largely unexplored despite their critical roles in the reliability and functionality of TMD-enabled devices. Motivated by this perspective, we employed frequency-dependent time-domain thermoreflectance (TDTR) with variable spot sizes to systematically and accurately measure the anisotropic thermal conductivities of a series of TMD crystals, including MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$, and TMD alloys, WSe$_2$(1-x)Te$_2$x, in both the in-plane direction (parallel to the basal planes) and the cross-plane direction (along the c-axis). In both the TMD crystals and the WSe$_2$(1-x)Te$_2$x alloys, the cross-plane thermal conductivity was consistently observed to be dependent on the heating frequency (modulation frequency of the pump laser). A two-channel thermal model was used to analyze the experimental data and the frequency dependence was attributed to the non-equilibrium thermal resistance between different groups of phonons in the substrate. In WSe$_2$(1-x)Te$_2$x alloys, a clear discontinuity in both the cross-plane and the in-plane thermal conductivities is observed as x increases from 0.4 to 0.6, due to the phase transition from 2H to Td phase in the layered alloys. The temperature dependence of thermal conductivity for the TMD alloys was also found to be weaker compared to the pristine 2H WSe$_2$ and Td WTe$_2$ due to the atomic disorder. Our measurements serve as an important baseline to understand the thermal conductivity of TMDs and other layered materials.

10:30 AM MS02.06.05
Vibrational Energy Transport across Correlated Random Interfaces Taishan Zhu, Kiarash Gordiz, Arthur France-Lanord, Asegun Henry, Giuseppe Romano and Jeffrey C. Grossman; Massachusetts Institute of Technology, United States

Interfaces provide an effective opportunity to enable novel functionalities and avenues where intriguing physics occurs. While pristine interfaces have been mostly studied, random interfaces have thus far been less explored. In this work, we investigate the effects of correlated interfacial disorder on vibrational energy transport, using graphene-hexagonal boron nitride (G-hBN) interfaces as our model system. More than Poisson point process (white noise, uncorrelated) type of randomness, we studied different types of correlated disorder with varying correlation functionals. When disorder is present, in contrast to the conventional scattering theory (e.g. Rayleigh’s theory), our non-equilibrium Green’s function (NEGF) results show surprising enhancement of energy transmission for a wide spectrum of vibrational modes. To underpin the transport physics, we send probing wavepackets across the interfaces with (q, w) modal resolution. These wavepacket simulations demonstrate an identical frequency regime of transmission enhancement predicted by NEGF analysis, and reveal the effects of mode conversion absent for pristine interfaces due to structural disorder. Beyond the above single-particle picture, we calculate modal correlation matrix based on Green-Kubo modal analysis, and show the effects of interfacial disorder on modal correlation, as well as their contribution to overall interface conductance, both diagonal and off-diagonal. This work could help understand the physics of phonon transport across random interfaces, and would be interesting to practical interface designs, such as thermoelectric and acoustic applications.

10:45 AM MS02.06.06
Determination of Thermal Conductivity in Graphene and Related Materials Srinivasan Mahendran1, Jesús Carrete2, Georg Madsen2, Andreas Isacsson1 and Paul Erhart1; 1Chalmers University of Technology, Sweden; 2TU Wien, Austria

Graphene is viewed as a promising material with unique properties. Thanks to their excellent thermal conductivity, graphene and related materials can for example be used as composite filler materials. There is, however, a crucial lack of information regarding the connection between transport properties and materials morphology. For computing the thermal transport properties, traditional methods based on systematic enumeration of finite differences scale poorly with system size, especially in simulations with low symmetry and for systems with defects. Here, we combine advanced regression techniques for the extraction of force constants with the T-matrix approach [1] to systematically explore the impact of defects of varying dimensionality on the thermal conductivity. We employ the HIPHERGE [2] package for the extraction of force constants, which exploits crystal symmetries and advanced regression algorithms to dramatically reduces the number of reference calculations. As the latter are commonly carried out using computationally expensive first-principles methods, this reduces the computational effort by orders of magnitude.


11:00 AM MS02.06.07
Predicting Thermal Conductivity of Defective MoSe2 Using First-Principles and Modified Empirical Equations Zhequan Yan and Satish Kumar; Georgia Institute of Technology, United States

MoSe2 as one of the promising two-dimensional transition metal dichalcogenides (TMDCs) recently emerged as a promising alternative of graphene for nano-electronic and opto-electronic devices due to its unique transport properties. The inefficient heat removal due to the low thermal conductivity of monolayer MoSe2 can cause critical challenges for its devices. The defects due to the imperfection of growth processes, such as vacancies significantly reduced thermal conductivity and aggravate the thermal management challenges. Very few studies has focused on exploring the effect of defects on the thermal transport in monolayer MoSe2. In addition, a fully parameter-free defect model is needed to examine and estimate the thermal properties considering the influence of defects; this requires improvement in the existing empirical models. The first-principles Density Functional Theory (DFT) and the phonon Boltzmann transport equations based simulations are used to study the phonon transport properties of pristine and defective monolayer MoSe2 with Se vacancies. A model, which is fully parameter-free, is developed using first-principles approach. The impact of three different types of Se vacancies on the thermal conductivity of monolayer MoSe2 is studied. The findings indicate how the vacancy-induced phonon states and different phonon scatterings are influenced by different types of Se vacancies. The existing Se vacancies redistribute the phonon DOSs by lowering the frequency cutoff and generating defect-induced phonon states, which soften the phonon modes in the dispersion relations and result in a lower phonon group velocity. Furthermore, an empirical model to estimate the effect of Se vacancies is developed to compare with the DFT results. It’s found that the empirical defect model overestimates the influence of point vacancy at low temperature. Additional terms are introduced to the modified empirical model to consider defects providing a better match with the parameter-free DFT simulation. The results from this study will help us understand the mechanism of phonon transport under the influence of different types of point defects. This work provides insights and directions for validating and improving the empirical defect model, which can be used for estimating the material properties considering the influence of defects.

11:15 AM MS02.06.08
2D Heterostructures under Pressure—The Graphene/h-BN Case—From van der Waals to Covalent Ana Barboza1, Alan Souza2, Matheus Matos1, Juliana Brant2, Tiago Brabosa2, Helio Chacham2, Mario Mazzoni2 and Bernardo R. Neves2; 1UFOP, Brazil; 2University Federal-Minas Gerais, Brazil

Graphene atop (or sandwiched in) h-BN is, by far, the most investigated 2D material heterostructure. Their weak van der Waals interlayer interaction enables the investigation of exquisite physical properties. On a different path, the present work indicates a van der Waals-to-covalent interaction transition for such heterostructure under pressure. Insulating and conductive states appear depending on the number of graphene layers and pressure. While it benefits from weak van der Waals interaction for fabrication, the present study both induces and investigates the effects of strong interlayer interaction. As a consequence, it shows the emergence of different properties from their parent 2D materials with eventual intricate competing mechanisms. More specifically, scanning probe microscopy and ab initio
calculations reveal modifications on the electronic and structural properties of graphene/h-BN heterostructures induced by compression. Using AFM and EFM techniques, with charge injection being made in the heterostructures at different pressures, the charge injection efficiency monotonically decreases with increasing pressure for monolayer-graphene (MLG)+BN heterostructures, indicative of a conductor-insulator electronic modification. Bilayer-graphene (BLG)+BN and trilayer-graphene (TLG)+BN heterostructures show a non-monotonic behavior of charge injection versus pressure, indicative of competing electronic structure modifications. First-principle calculations of these systems indicate a pressure-induced van der Waals-to-covalent interlayer transition, where such interlayer covalent binding, in the presence of water molecules, results in a disordered insulating structure for the MLG+BN case, while it leads to an ordered conducting structure for both BLG+BN and TLG+BN heterostructures. Besides introducing a distinct perspective on the study of 2D materials and their van der Waals heterostructures, the present work stresses the importance of interlayer interaction in any device based on such heterostructures. For example, flexible optoelectronic devices are expected to suffer a significant strain variation, which may lead to different interlayer interaction regimes, ultimately affecting device performance. In other words, the present work shows that there is a strong role for interlayer interaction in the (initially) weakly-bound van der Waals heterostructures.

11:30 AM *MS02.06.09
Tuning Thermal Transport in van der Waals Solids under Extreme Strain Xianghai Meng¹, Tribhuwan Pandey², Abhishek K. Singh², Jung-Fu Lin¹ and Yaguo Wang¹; ¹University of Texas at Austin, United States; ²Indian Institute of Science, India

Strain is an effective tool to tune physical properties in a wide range of materials. In transition metal dichalcogenides (TMDs), a family of two-dimensional (2D) van der Waals (vdW) solids, strain can alter the interlayer distance, as well as bond strength, length and angle between the transition metal and chalcogen atoms, modifying the interatomic orbital coupling, interlayer wavefunction overlap and valence band splitting. In traditional mechanical bending/stretching experiments, the 2D materials sit on a flexible substrate and strain is determined by the elongation or radius of curvature of the substrate. Any slippage across the sample/substrate interface or imperfect strain transfer across layers can introduce large uncertainties. Moreover, strains generated in stretching/bending experiments are typically only less than 4%. Hydrostatic pressure created in a diamond anvil cell (DAC) can generate compressive strain as high as 30%, without introducing any damage to the samples. DACs have been extensively used in the geophysics field to simulate the high-pressure environment in planetary interiors. Pressure in a DAC is determined by monitoring the fluorescence peak of a ruby crystal placed adjacent to the sample, with an accuracy better than 1 GPa.

Previous studies demonstrated that with about 9% cross-plane compressive strain, molybdenum disulfide (MoS₂) exhibits a semiconductor to metal (S-M) transition, with an electrical conductivity enhancement from 0.03 S/m to 18 S/m. Extreme strain should also have a profound impact on phonon transport properties, which can affect the thermal transport in MoS₂. In this talk, I will present our recent work about tuning thermal transport of MoS₂ under extreme strain. A DAC device is integrated into our recently developed picosecond transient thermoreflectance (ps-TTR) system to measure the strain-tuned cross-plane thermal conductivity (κ) in bulk MoS₂ up to ~19 GPa (over 9% cross-plane strain). We observed roughly a 7x increase of κ, from 3.5 W m⁻¹K⁻¹ at ambient pressure to about 25 W m⁻¹K⁻¹ at 19 GPa. First-principles calculations and electrical conductivity measurements suggest that this drastic change arises mainly from the substantially strengthened interlayer force and heavily modified phonon dispersions along the cross plane direction. The group velocities of coherent longitudinal acoustic phonons (LAP), measured with coherent phonon spectroscopy (CPS), increase by a factor of 1.6 at 19 GPa due to phonon hardening, while their lifetimes decrease due to the phonon unbundling effect. These results suggest possible parallel tuning of structural, thermal and electrical properties of vdW solids with strain in multi-physics devices.
Strain and Defect Engineering in 2D Materials  
Ju Li; Massachusetts Institute of Technology, United States


2:00 PM *MS02.07.02
Revealing the Full Spectrum Layered Materials with Super-Human Predictive Abilities  
Evan J. Reed and Gowoon Cheon; Stanford University, United States

We have utilized data mining approaches to elucidate over 1000 2D materials and several hundred 3D materials consisting of van der Waals bonded 1D subcomponents, or molecular wires. We find that hundreds of these 2D materials have the potential to exhibit observable piezoelectric effects, representing a new class of piezoelectrics. A further class of layered materials consists of naturally occurring vertical hetero structures, i.e., bulk crystals that consist of stacks of chemically dissimilar van der Waals bonded layers like a 2-D super lattice. We further combine this data set with physics-based machine learning to discover the chemical composition of an additional 1000 materials that are likely to exhibit layered and two-dimensional phases but have yet to be synthesized. This includes two materials our calculations indicate can exist in distinct structures with different band gaps, expanding the short list of two-dimensional phase change materials. We find our model performs five times better than practitioners in the field at identifying layered materials and is comparable or better than professional solid-state chemists. Finally, we find that semi-supervised learning can offer benefits for materials design where labels for some of the materials are unknown.

2:30 PM BREAK

3:30 PM *MS02.07.03
Moire Quasiperiodicity in the van der Waals Heterojunctions  
Philip Kim; Harvard University, United States

Heterogeneous interfaces between two dissimilar materials are an essential building block for modern semiconductor devices. The 2-dimensional (2D) van der Waals (vdW) materials and their heterostructures provide a new opportunity to realize atomically sharp interfaces in the ultimate quantum limit for the electronic and optoelectronic processes. By assembling atomic layers of vdW materials, such as hexa boronitride, transition metal chalcogenide and graphene, we can construct atomically thin novel quantum structures. We demonstrate the enhanced electronic optoelectronic performances in the vdW heterostructures, suggesting that these a few atom thick interfaces may provide a fundamental platform to realize novel physical phenomena. In this presentation, we will discuss two topics associate with the commensuration and incommensuration between the vdW layers. Many exotic physical phenomena occur associated with the incommensurability of the moiré superstructures; the fractal energy spectrum of Hofstadter butterfly and recently discovered Mott insulating and unconventional superconducting behavior of the ‘magic’ twist angle bilayer graphene have demonstrated the wealth of the nontrivial topology of electronic band structures. We find that the vdW interaction energy that favors interlayer commensurability competes against the intralayer elastic lattice distortion to form a quasi-periodic domain structure, inducing profound changes in electronic structure. Particularly, we show quantitative analysis of the engineered atomic-scale reconstruction completely controlled by the twist angle between two graphene layers and anomalous electron transport occurring in the network of topologically protected propagation modes along the domain boundaries.

4:00 PM MS02.07.04
Crack-Free, Area-Specific Graphene Wrinkles with Switchable Orientation on Soft Skin Layers  
Dongjoon Rhee1, Jeffrey T. Paci2, Shikai Deng1, Won-Kyu Lee3, George Schatz1 and Teri W. Odom1; 1Northwestern University, United States; 2University of Victoria, Canada; 3Harvard University, United States

The buckling of graphene via strain relief of elastomeric substrates can engineer its physical properties such as
electrical conductivity and plasmon resonances without using lithographic processes. Because the wavelength and orientation of resulting crumples can change in response to applied strain, graphene functionalities can be dynamically modulated by stretching or bending the substrate. Graphene crumples, however, have been limited by crack formation under tensile strain, particularly in delaminated regions. Furthermore, area-specific tuning of structural parameters and hence properties is not possible because only textures with globally uniform wavelength and orientation can be produced. This presentation will describe a conformal wrinkling strategy that creates crack-free graphene nanostructures with locally different wavelengths on an elastomeric platform. By sandwiching fluoropolymer skin layers with spatially varying thicknesses between graphene and the substrate, we formed multiscale graphene wrinkles with predetermined wavelengths after strain relief. Because delamination was suppressed with the presence of the skin layer, the wrinkle orientation could be switched under cycles of stretching and releasing without significant cracking—even beyond the intrinsic fracture limit of graphene. Through mechanics modeling, we revealed that the fluoropolymer layer mediated structural evolution of the graphene wrinkles without cracking via conformal adhesion. With exquisite control over wrinkle topography, our crack-free, multiscale wrinkling strategy will be useful for optoelectronics and plasmonics based on graphene and other two-dimensional nanomaterials.

**4:30 PM TRAVEL TIME TO HYNES, LEVEL 3, ROOM 312 FOR KEYNOTE SESSION AT 4:30 PM IN FF01**

SESSION MS02.08/FF01.15/FF02.07: Keynote Session: Breakthroughs in Graphene and Beyond 2D Materials
Session Chairs: Zakaria Al Balushi and Chuanhua Duan
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Room 312

**4:30 PM *MS02.08.01/FF01.14.01/FF02.07.01**

**Keynote: Molecular Transport through Two-Dimensional Capillaries** Andre Geim; University of Manchester, United Kingdom

I will review our group’s work on the molecular transport properties of angstrom-scale channels fabricated by der Waals assembly of 2D crystals. These channels can be viewed as if individual atomic planes were extracted from a bulk crystal leaving behind two edge dislocations with an empty space in between. Gas, water, ion and proton transport have been studied in capillaries down to one atom in height.
applications will be also discussed.

9:00 AM *MS02.09.02
Defect-Mediated van der Waals Epitaxy of Transition Metal Dichalcogenides Xiaotian Zhang, Tanushree H. Choudhury, Benjamin Huet, Mikhail Chubarov and Joan M. Redwing; The Pennsylvania State University, United States

Direct growth of transition metal dichalcogenides (TMDs) such as WS\textsubscript{2} and WSe\textsubscript{2} on graphene and hexagonal boron nitride (hBN) is of interest for the fabrication of 2D heterostructures as an alternative to exfoliation and 2D layer stacking. Commensurability between the TMD lattice and graphene or hBN is favorable for epitaxy, however, it is difficult to control nucleation and wetting of the TMD on pristine van der Waals surfaces due to the low surface energy and lack of chemical bonding. In addition, mirror twins and inversion domains can form due to rotational symmetry which introduces grain boundaries in coalesced TMD films. However, the presence of defects in hBN and graphene can dramatically alter the energy landscape providing an alternative route to control nucleation and epitaxy.

Our recent studies have focused on the epitaxial growth of WSe\textsubscript{2}, WS\textsubscript{2} and related TMD monolayer films by gas source chemical vapor deposition (CVD) on hBN and graphene. The CVD process is carried out in a cold-wall reactor using metal hexacarbonyls and hydride chalcogen precursors in a hydrogen carrier gas. In the case of growth on epitaxial graphene on SiC, nucleation of WS\textsubscript{2} and WSe\textsubscript{2} occurs primarily at wrinkles and step edges resulting in different WS\textsubscript{2} rotational orientations. In the case of WSe\textsubscript{2} growth on hBN, however, single atom vacancies in the hBN were found to act as sites for metal atom trapping which facilitates the nucleation of WSe\textsubscript{2} domains on the surface. In this case, the TMD nucleation density can be controlled by manipulating the density of surface atom vacancies which can be achieved through plasma irradiation and annealing in NH\textsubscript{3}. In addition, the metal atoms break the surface symmetry which leads to a preferred orientation (~95%) for WSe\textsubscript{2} domains on hBN. Through careful control of nucleation and extended lateral growth time, fully coalesced WSe\textsubscript{2} monolayer films on hBN were achieved which exhibit optical and transport properties superior to comparable films grown on sapphire substrates. The results demonstrate the important role of defects in nucleation and epitaxial growth of 2D heterostructures.

9:30 AM BREAK

10:00 AM MS02.09.03
Controllably Strained Layered Transition Metal Dichalcogenides Grown on Single-Crystal Quartz Substrates via Chemical Vapor Deposition Fangze Liu, Oleg V. Kozlov, Vladimir Sayevich, Igor Fedin, Hsinhan Tsai, Wanyi Nie and Victor I. Klimov; Los Alamos National Laboratory, United States

Strain engineering is widely used for tuning the properties of materials and thereby realizing high performance electronic and optoelectronic devices. In bulk three-dimensional materials, the strain-controlled tunability is, however, limited by low values of ‘failure strain’ which triggers formation of lattice defects. On the other hand, two-dimensional (2D) materials such as graphene and layered transition metal dichalcogenides (TMDs) can tolerate much greater strain, and thus are perfect materials for practically implementing the ideas of strain engineering. [1] Among many different methods to introduce strain in TMDs, mismatch between coefficients of thermal expansion (CTE) of a growth substrate and a TMD layer is one of the most promising method mainly due to two reasons: (1) large-area strained TMDs can be directly prepared through bottom-up synthesis such as chemical vapor deposition (CVD) or molecular beam epitaxy (MBE); (2) the induced strain is maintained intrinsically without any external force or treatment since the as-grown TMD is anchored to the substrate at the fabrication stage. Previous reports on CTE mismatch of CVD-grown TMDs have been only able to achieve tensile strain or low compressive strain (<0.2%). [2] While tensile strain normally decreases the band gap of TMDs, compressive strain tends to increase the band gap. Moreover, recent theoretical and experimental studies [3, 4] have shown that a large compressive strain can be used to stabilize a nominally unstable 1T TMD phase, which is attractive for applications including hydrogen evolution and low-contact-resistance electronic devices. [5]

Here, we use single crystal quartz substrates, which have large CTE compared with MoS\textsubscript{2}, to achieve compressive strain up to 1%. The strong built-in strain is indicated by the increased photoluminescence and optical absorption energies as well as ‘stiffening’ of characteristic A\textsubscript{1g} and E\textsubscript{1g} Raman modes. Owing to the different CTE of single crystal quartz along the a- and c-axes, MoS\textsubscript{2} grown on different facets experiences different levels of strain.
Specifically, the layers grown on the c-plane exhibit higher strain compared to those prepared on the x-plane which is direct consequence of the higher CTE. Additionally, the MoS$_2$ layers grown on the AT-cut quartz are highly aligned due to the strongly anisotropic nature of the underlying quartz surface. [6]

The ability to tune electronic properties of TMD layers by engineered strain can be especially useful for controlling interfacial interactions in complex hetero-structures comprising TMD materials as electronically and/or optically active components. Presently, we are exploring this capability for manipulating charge and energy flows in multi-dimensional materials assembled from TMDs and colloidal quantum dots.


10:15 AM MS02.09.04
**Chemical Vapour Deposition Growth of Graphene from Petroleum Coke Feedstock upon Pre-Existing Graphitic Edges**
*Thomas P. Raine, Mark A. Bissett and Ian Kinloch; University of Manchester, United Kingdom*

Petroleum coke (PC), a cheap and readily available hydrocarbon feedstock has great potential as a starting material for synthesis of high value graphitic materials. Graphene produced by traditional graphitization of carbon materials at up to 3000 °C [1], and subsequent exfoliation, comes at a large energy cost. By utilising chemical vapour deposition (CVD), graphitic materials can be produced at far lower temperatures, thus providing a large cost and energy saving. Direct exfoliation of high quality coke (carbon content > 96 wt%) has been reported [2], however, lower quality coke requires modification prior to exfoliation.

In this work we present evidence for the synthesis of graphene directly from low quality PC powder by CVD growth from defective graphitic edges. Subsequent exfoliation of the coke materials after treatment allows for the isolation of high quality graphene flakes. We investigate low temperature plasma treatment of the coke powders in order to yield functionalised graphitic materials, with potentially useful properties. We examine the strain behaviour of the PC-derived graphene and their plasma functionalised analogues in order to understand the role of functional defects upon the properties of the graphene. Finally, we investigate the potential of PC for carbon nanotube (CNT) production by seeding coke powder with transition metal nanoparticles, thus synthesising graphene/CNT hybrid powders.


10:30 AM MS02.09.05
**Sweet Green Graphene—A Mechanochemical Synthesis**
*Ester Vazquez; UCLM, Spain*

Green Chemistry protocols have been recently applied to the design of nanomaterials, being the preparation of gold and silver nanoparticles successful examples of this trend. However, the preparation of graphene still offer challenging opportunities for the development of green technologies, involving the use of natural sources, safe solvents and energy efficient processes. Moreover, the implementation of the concept safe by design also applies to the preparation of nontoxic graphene products.

During this talk we will try to give answers to these questions: Can we design an aqueous soluble graphene material, suitable for being employed in biomedical studies, without changing graphene chemical characteristics? Can this design be optimized for Green Chemistry principles?
Following our previous experience in the preparation of graphene materials, we will describe the use of a mechanochemical treatment, in solvent-free conditions, using carbohydrates to exfoliate graphite in a simple and green approach. Among glucose, fructose and saccharose, the former shows the best behavior in terms of exfoliation, generating graphene materials with a relatively low number of defects. Once exfoliated, glucose can be washed and recovered, just by using water, and the final graphene material can be thoroughly characterized. Moreover, the addition of molar equivalents of water to the ball milling treatment, allows the formation of glucose-graphene cocrystals. Analogously to what happens with drugs, glucose-graphene cocrystals display higher performance in terms of stability in aqueous dispersions. In addition, we will show preliminary toxicological tests illustrating the safety of the designed material.

10:45 AM MS02.09.06
Mussel-Inspired Defect Engineering for High Performance of Graphene Liquid Crystalline Fibers  
Inho Kim, Taeyeong Yun and Sang Ouk Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Here, we present an effective fabrication method of graphene liquid crystalline fibers to attain high mechanical and electrical properties simultaneously inspired by mussel adhesive polydopamine (PDA). Two-step defect engineering was designed relying on bioinspired surface polymerization within GO dispersion and subsequent solution infiltration of PDA to improve the intrinsic limitation of graphene fibers arising from structural defects of graphene layers during wet-spinning process. For a straightforward understanding of the PDA-induced defect engineering mechanism, interfacial adhesion between GO flakes was carefully analyzed by AFM pull-off test. In addition, PDA could be converted into N-doped graphitic domain within the fiber structure by following pyrolysis resulting in mechanically strong fibers without scarifying electrical conductivity. This bioinspired graphene-based carbon fiber retains a great potential for a wide range of applications such as flexible electronics, multifunctional textiles, and wearable sensors.

11:00 AM MS02.09.07
The Effects of Graphene and Its Defects on Hydrogen Permeation in Cu  
Katherine T. Young1, Dale Hitchcock2, Colter Smith1, Tim Krentz2 and Eric M. Vogel1; 1Georgia Institute of Technology, United States; 2Savannah River National Lab, United States

Industrial processes such as natural gas separation, hydrogen production, etc. rely heavily on gas separation. For instance, hydrogen reforming from methane uses several techniques such as metallic, silica, zeolite, and polymer membranes for gas separation. The thickness of these membranes can range from tens of nanometers to microns. The efficiency of these membranes depends heavily on permeance through the membrane as well as gas selectivity. Ideally, a membrane would have pore sizes close to the kinetic diameter of the desired gas, while being as thin as possible to increase permeance. 2D materials with high impermeability, high aspect ratio, high strength, chemical inertness and atomic thickness may be able to fulfill this need.

Graphene has been shown to be an extremely impermeable barrier, largely due to its unique structure. Graphene is composed of C with sp² bonds in plane with π orbitals perpendicular to the surface, which form a delocalized cloud repelling other molecules. It was shown that mechanically exfoliated, pristine graphene is impermeable to He. Thus, any permeability must be induced by adding pores to the system. Adding uniformly distributed pores of a specific size has been a challenge, and has not yet been demonstrated with an adequate level of control. Other groups have focused on graphene synthesized by chemical vapor deposition (CVD) due to its scalability compared to mechanically cleaved graphene; however, transferred CVD graphene often has holes from the transfer process. These holes seriously degraded the selectivity of the graphene composite membrane so that it was only selective to molecules with diameters of > 1 nm, and smaller diameter gases were able to pass freely. Groups have tried to alter transfer methods, plug the induced holes, or stack graphene sheets, but these transfer-induced defects make it difficult to study the effects of intrinsic defects in CVD graphene, such as grain boundaries and point defects.

In this work, single layer graphene was synthesized by CVD on a Cu foil catalyst. H₂ is permeable in many metals, including Cu. Thus, the permeability of CVD grown graphene can be measured directly while still on the catalyst using a gas driven technique. The difference in permeability of the graphene-coated Cu from the bare Cu can be attributed to the permeability of the graphene. The graphene-coated samples consistently showed lower permeability compared to the bare Cu sample. Furthermore, since pristine graphene has already shown impermeability to gases, any permeability through the graphene should be through intrinsic defects like grain boundaries and point defects in
the graphene. Graphene grain sizes with varying orders of magnitude were synthesized, and the H₂ permeabilities measured. This work is able to systematically measure and model the effects of grain size by measuring gas permeation of graphene that is not transferred (so that cracks are not induced), and the only permeation must be through graphene defects. Thus, graphene with different grain sizes can be engineered to create membranes with different permeabilities to H₂, without needing to induce nanopores or fix transfer-induced cracks.

The project depicted is supported by the Savannah River National Lab (SRNL) Laboratory Directed Research and Development program (LDRD-2017-00028). SRNL is managed and operated by Savannah River Nuclear Solutions, LLC under contract no. DE-AC09-08SR22470 with the U. S. Government. This work was performed in part at the Georgia Tech Institute for Electronics and Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure, which is supported by the National Science Foundation (Grant ECCS-1542174).


11:15 AM MS02.09.08
Nanoscale Characterisation of Graphene to Determine the Level and Location of Functional Groups and the Effect on Mechanical Properties of Composites Barry Brennan1, Elizabeth J. Legge1,2, Keith Paton1, Magdalena Wywijas1, Rory Pemberton1, Naresh Kumar1, Greg McMahon1, Arun P. Raju1, Craig Dawson1, Andrew Strudwick1, James W. Bradley4, Vlad Stololjan2, Ravi Silva2, Stephen A. Hodge5 and Andrew Pollard1; 1NPL, United Kingdom; 2University of Surrey, United Kingdom; 3University of Manchester, United Kingdom; 4University of Liverpool, United Kingdom; 5Versarien Plc, United Kingdom

Graphene is a highly desirable material for a variety of applications due to its inherent material properties. However, realising the full potential of these properties has proved challenging due in part to difficulties in uniformly incorporating it within other media. One route towards tailoring the properties of graphene to allow better interaction with other materials and thereby improving the ultimate product performance is through functionalisation. For example, in nanocomposites the incorporation of functionalised graphene can lead to changes in tensile strength, optical transparency and electrical and thermal conductivity. However, often the resulting structure of the functionalised graphene material, and the location and level of the chemical species added via different functionalisation processes is not known or understood.

In this study we characterise a commercially available powder containing few-layer graphene (FLG) flakes, and the subsequent composite products, after both plasma and chemical functionalisation of the FLG with amine and -OH groups. Alongside confocal Raman spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) results, tip-enhanced Raman spectroscopy (TERS) and secondary ion mass spectrometry (ToF-SIMS and NanoSIMS) were used to show chemical changes in the FLG material at both the nanometre and micron scale and monitor the dispersion of the flakes within the composite for the various functionalisation processes. [1] These are the first reported TERS measurements on commercially available graphene materials and show the location of the defects associated with the attachment of functional groups to the FLG. Nanoscale TERS images of the D-peak intensity show changes within flakes [2] and variations between the different types of functionalisation, indicating that it is possible to discriminate between functionalisation taking place at the edge of the flakes or within the basal plane.

The plasma functionalisation process was observed to produce flakes with higher levels of functionalisation than chemical functionalisation. The amine functionalisation via plasma process created defects in the basal plane of the flakes, whereas the –OH functionalization appeared to have functional groups present predominantly at the edges of the flakes. ToF-SIMS depth-profiling results of nanocomposites subsequently produced with polyurethane suggested that the plasma –OH material agglomerated the least within the polymer matrix. However, the non-functionalised material produced the largest improvement in mechanical properties for the nanocomposite.


11:30 AM *MS02.09.09
Defect-Mediated Chemical Modification of Semiconducting 2D Metal Chalcogenides Qing Hua Wang; Arizona State University, United States

Metal chalcogenides that can be isolated as 2D semiconducting layers form a diverse family of materials with unique properties. Defects that are found or can be created in these materials are an important route for controlling their chemical reactivity. This talk will highlight our recent work on several defect-mediated chemical modifications of 2D metal chalcogenides. First, the covalent functionalization of the basal planes of the transition metal dichalcogenides (TMDCs) MoS2, MoSe2, WS2, WSe2, and the pnictogen chalcogenides (PCs) Bi2S3, and Sb2S3 using aryl diazonium salts occurs at initial point defect sites and edges, but propagates across the surface in a chain-like morphology. This functionalization scheme is studied in detail using density functional theory (DFT) and kinetic modeling for MoS2, and the diazonium salts can also be modified to enable tethering of proteins to the MoS2 surface. Second, MoO3 and WO3 nanoscrolls are formed by transformation from 2D MoS2 and WS2 nanosheets, respectively, via atmospheric plasma treatment which occurs due to the combination of different radicals in the plasma that simultaneously form defects and cracks in the 2D layers and oxidize them, so that the strain of the altered crystal structure is relieved by rolling into nanoscroll geometries. Finally, self-assembled monolayers of fullerene molecules on the surface of WSe2 are studied using atomic resolution scanning tunneling microscopy to show that the molecules exhibit a 2x2 rotational superstructure due to the interplay of molecule-molecule, molecule-substrate, van der Waals, and Coulomb interactions to form a charge redistribution network with long-range ordering.

SESSION MS02.10: Physico-Chemical Effects III
Session Chairs: SungWoo Nam and Michael Pettes
Thursday Afternoon, December 5, 2019
Hynes, Level 1, Room 108

1:30 PM MS02.10.01
Flexoelectricity Induced Electromechanical Response of Two-Dimensional Transition Metal Dichalcogenides Md Farhadul Haque1, Hyung Jong Bae1, Jin Myung Kim1, Chullhee Cho1, Michael C. Wang2 and SungWoo Nam1; 1University of Illinois at Urbana-Champaign, United States; 2University of South Florida, United States

Flexoelectricity is the strain gradient (direct effect) or electric field gradient (converse effect) induced electromechanical response in a dielectric material. Unlike piezoelectricity, flexoelectricity is ubiquitous in materials, not limited by inversion asymmetric crystal structure. However, flexoelectricity is limited in bulk material, because any significant amount of polarization would require large amount of strain gradient which is limited by mechanical fracture. Thanks to the atomically thin dimension, 2D materials can withstand large amount of strain gradient without mechanical failure. Therefore, flexoelectricity has enabled new opportunities in micro or nano electro-mechanical systems. However, a study of the mechanism of this universal yet underappreciated flexoelectricity in 2D materials has been limited. In this work, we investigated the converse flexoelectric response of 2D transitional metal dichalcogenides (TMDCs) by piezoresponse force microscopy (PFM). PFM is widely used technique to quantify effective piezoelectric coefficients, providing a direct correlation between applied electric field and resulting deformation in materials. Our results showed that the effective out-of-plane piezoelectric coefficient (d33) rises from mono-layer to bi-layer for MoS2 and WSe2, then saturates at a slightly reduced magnitude for tri-layer and quad-layer structures. We have correlated the d33 trend observed in our TMDC layers with materials adhesion to the substrate, flexural rigidity of the 2D materials and possible charge transfer between the substrate and the materials. We believe that the converse flexoelectric effect observed in 2D TMDCs arises from a combination of the effects of flexural rigidity of the atomically thin materials and charge transfer between the material and substrate. We further report that in-plane tensile strain reduced d33 by restricting the out-of-plane deformation. Our findings
can help understanding the fundamentals of flexoelectric behavior in 2D materials and pave the way for next generation actuators and energy harvesting devices.

1:45 PM MS02.10.02
Extreme Tensile Strain States in La_{0.7}Ca_{0.3}MnO_{3} Nanomembranes Seung Sae Hong1,2, Mingqiang Gu3, Manish Verma4, Di Lu2,1, Varun Harbola2,1, Arturas Vailionis1, Yasuyuki Hikita2, Rossitza Pentcheva1, James Rondinelli3 and Harold Y. Hwang1,2; 1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States; 3Northwestern University, United States; 4University of Duisburg-Essen, Germany

A defining feature of emergent phenomena in correlated systems is the competition and cooperation between ground states, which can be sensitively tuned by the lattice. This has been explored using hydrostatic pressure, epitaxial lattice-mismatch in films, and uniaxial strain. Manganites provide canonical examples where various metallic and insulating phases, and associated magnetic and orbital ordering, are delicately balanced. Extending the range of lattice control would enhance the ability to access and investigate new phases. Recent advances in the thin film epitaxy of a water-soluble layer enable the synthesis of many types of complex oxides and heterostructures as macroscale freestanding 2D nanomembranes [1] with considerable mechanical flexibility. Here we stabilize extreme tensile strain in nanoscale La_{0.7}Ca_{0.3}MnO_{3} membranes, exceeding 8% uniaxially and 5% biaxially [2], and study their magnetotransport properties down to cryogenic temperatures. These macroscopic strain states are found to correspond to microscopic lattice parameter changes, i.e. elastic deformation. The systematic control of biaxial strain reveals a rich phase diagram of competing phases, including a dramatic shift in the metal-to-insulator and magnetic transition, as well as a new insulating ground state that can be extinguished by magnetic field. Electronic structure calculations indicate that the insulator consists of charge-ordered Mn^{4+} and Mn^{3+} with staggered strain-enhanced Jahn-Teller distortions within the membrane plane. This highly-tunable strained membrane approach provides a broad opportunity to design and manipulate correlated states in 2D quantum materials.


2:00 PM MS02.10.03
Adhesion of Two-Dimensional Titanium Carbides (MXenes) to MXenes and Graphene Yanxiao Li, Shuohan Huang, Congjie Wei, Chenglin Wu and Vadym Mochalin; Missouri University of Science and Technology, United States

Two-dimensional (2D) transition metal carbides (MXenes) have attracted a great interest as a relatively new and large class of materials with unique electronic and optical properties. Among 20 different kinds of MXenes, Ti3C2Tx and Ti2CTx are most widely investigated. Understanding of adhesion between MXenes and MXenes or other 2D materials is critically important for 2D layered nanostructure composites fabrication, which are promising candidates for conducting high-performance energy conversion and environmental remediation. Herein, through atomic force microscopy (AFM) experiment on Ti3C2Tx-Ti3C2Tx, Ti3C2Tx-Ti2CTx, Ti3C2Tx-Ti2CTx-Ti3C2Tx, Ti3C2Tx-1-5 layer graphene interfaces using a Ti3C2Tx functionalized spherical tip, adhesion energy was measured respectively. To obtain adhesion energy more accurately, the Maugis-Dugdale theory which considers surface roughness was applied to convert the AFM measured adhesion force to adhesion energy. Our preliminary showed that the adhesion energy between Ti3C2Tx and Ti3C2Tx or Ti2CTx, MXenes are in the same level of the adhesion energy between Ti3C2Tx and graphene. In addition, no layer dependency was observed with the MXene adhesion measurements.

2:15 PM MS02.10.04
Ordered Buckling in 2D Single Layer Solids Guided by Self-Assembled Peptide Nanowires Hadi M. Zareie1, David Starkebaum1, Tyler D. Jorgenson1, Fadil Iyikanat2, Hasan Sahin2, Rene Overney1 and Mehmet Sarikaya1; 1University of Washington, United States; 2Izmir Yuksek Technology Institute, Turkey

Ubiquitous periodic structures formed at the nanometer scale on the surface of exfoliated graphite has been interpreted as ripples, stripe domains, 2D molecular patterns, corrugations, and wrinkled networks. The true origin for the formation of these periodic structures on single layer solids and the ways to control their formation and organization are fundamental to their potential utility in band gap engineering in graphene and single layer semiconductors such as MoS2 and WSe2 towards their utility, e.g., as strain sensors. Using both graphite and MoS2,
we show here that the nature of the buckling is indeed due to strain induced sub-nm scale periodic buckling and that its pattern can be controlled on atomically flat surfaces using the self-assembled solid-binding dodecapeptides that form 2D self-organized pattern in aqueous solutions forming ordered peptide nanowires commensurate and aligned with the underlying crystalline substrate. We attribute nanobuckling to be due to out-of-plane rippling effect caused by compressive strain within the top single layer introduced during mechanical exfoliation. The electronic behavior of the nanobuckled regions have been examined by scanning tunneling microscopy and spectroscopy show that the tunneling current varies with the peaks and valleys in the buckled region consistent with the tension and compressive stresses that we estimated by computational modeling using density functional theory. The phenomenon is observed both in graphite (semimetal) and MoS2 (semiconductor) may be a strong indication that nanobuckling is a universal phenomenon likely to be present also in other 2D layered solid systems. The results of the conductive atomic force microscopy (C-AFM) was also used to interrogate the electrical properties of the buckled samples of MoS2 showing changes in the gap energy that can be correlated with the compressed and expanded density of states in the top layer. While the study of new physical phenomena is enabled in the nanobuckling by the self-assembled peptides, they also facilitate controlled pattern formation in a wide range of 2D solids in designing new devices by controlling the local chemical and band-gap engineering by local strain. Periodic buckling patterns guided by self-organized peptides may pave a simplistic way for tailoring the surface nanostructures and electronic properties of single atomic layer solids towards designing new devices based on periodic local surface chemical potential and band gap by periodic surface-confined strain. The research is supported by NSF-DMREF program through the grant DMR-1629071 as part of the Materials Genome Initiative.

2:30 PM *MS02.10.05
Graphene Application for OLED Display Jong Hyun Park, Hoyoung Jeong, JiGon Kim, Shin-Bok Lee, Eunju Kim, Ju Young Bang, MoonBong Song, Harkjin Kim, Ji-Man Seo, Byungsam Yu, Sungpil Ryu, Hanshin Hwang and Soo-Young Yoon; LG Display Laboratory, Korea (the Republic of)

Graphene has been the promising material for flexible optoelectronic devices because of its outstanding material properties. Many research groups have shown potentials of graphene for various flexible devices such as touch-screen sensors, organic light-emitting diodes and organic photovoltaic devices. However, Graphene still faces some hindrances to overcome for the success of real commercialization. In this talk, from the commercial perspective, we'd like to share our opinion on most probable application fields of graphene for OLED displays. Specifically, we will highlight the application of graphene as a transparent electrode for OLED displays because of its extraordinary optical, mechanical and electrical material properties. In addition, we will also emphasize superior moisture barrier properties of graphene which have potentials for the application of OLED encapsulation. Graphene's unique mechanical flexibility combined with barrier property will be able to replace inorganic materials which have been widely used in OLED encapsulations. we will also briefly mention other possible application fields of graphene for OLED display.

For your information, we will also introduce the outline of LG display which has a global No.1 display market share. Finally, we will suggest some requirements and specifications to realize the commercialization of graphene for OLED displays. In my view, this presentation will be a chance to discuss the practical use of graphene for OLED displays.

**SYMPOSIUM MS03**

Mechanics of Nanocomposites and Hybrid Materials
December 2 - December 5, 2019

**Symposium Organizers**
Peter Fratzl, Max Planck Institute of Colloids and Interfaces
Wendy Gu, Stanford University
9:15 AM MS03.01.02
Dynamic Strain Ageing of ARB Cu/Nb Nanoscale Multilayers
Zhilin Liu1,2, Jeromy Snel1, Miguel A. Monclús1, Jon M. Molina-Aldareguía1 and Javier Llorca1,3; 1IMDEA Materials Institute, Spain; 2Central South University, China; 3Technical University of Madrid, Spain

Cu/Nb metallic multilayers with individual layer thicknesses in the range 7 nm to 63 nm were manufactured by accumulative roll bonding (ARB). Micropillars of square cross section of 5 x 5 µm² and an aspect ratio 2-3 were milled with a focused ion beam. The mechanical properties of the Cu/Nb multilayers were determined by means of in situ micropillar compression tests within a scanning electron microscope. Test were carried out at different strain rates (10⁻² to 10⁻⁴ s⁻¹) and temperatures (25°C to 400°C) and the yield strength, strain rate sensitivity and activation volume were determined from these tests for each multilayer as a function of temperature. In addition, the deformation and fracture mechanisms were ascertained from in situ observations during deformation and from transmission electron microscopy analysis of foils extracted from the deformed micropillars.

The strain rate sensitivity of all the multilayers at ambient temperature was in the range 0.015 s⁻¹ to 0.008 s⁻¹ and decreased slightly as the layer thickness increased. Mechanical tests at 400°C showed a large increase in the strain rate sensitivity, which ranged from 0.16 s⁻¹ for a layer thickness of 7 nm to 0.05 s⁻¹ for a layer thickness of 64 nm. Surprisingly, the strain rate sensitivity of the nanoscale multilayers with layer thickness below 34 nm dropped to 0 at 200°C while increased slightly with respect the ambient temperature value in the multilayer with 64 nm layer thickness [1]. In addition, serrations were observed in the stress-strain curves of the multilayers with small layer thickness tested at 200°C. From these experimental observations, it was hypothesized that the unexpected reduction in the strain rate sensitivity of the multilayers with small layer thickness at 200°C was due to dynamic strain ageing of the Nb layers due to the presence of oxygen in solid solution, following the results in the literature for dynamic strain ageing of Nb at this temperature [2]. The presence of oxygen in the Nb layers was confirmed by energy-dispersive X-ray microanalysis and atom probe tomography. The evidences for dynamic strain ageing of Cu/Nb nanoscale multilayers were discussed to the light of the experimental evidences and to the deformation mechanism map proposed for this system.


9:30 AM MS03.01.03
Nanoporous Tungsten—A Novel Low-Density and Ultra-Strong Nanocrystalline Material
Mingyue Zhao1, Inas Issa1, Michael Wurmshuber2, Manuel Pfeifenberger2 and Daniel Kiener1; 1University of Leoben, Austria; 2Erich Schmid Institute of Materials Science, Austria

Metallic nanofoams are a unique class of materials possessing low density, large surface area, excellent attributes and energy absorption ability, making them good candidates as future radiation shielding materials. Tungsten is ideally suited as the base material for such a foam, as it is commonly used as a shielding material in nuclear facilities, medical diagnosis systems and a number of other circumstances in order to protect personnel and sensitive equipment from radiation. Therefore, it is of great value and scientific interest to tailor such a novel nanoporous tungsten, which combines the beneficial properties of tungsten with the positive attributes of nanoporous foams and
has a great potential to satisfy the need for high performance materials that can endure harsh environments.

In this work, nanoporous tungsten was created on a bulk scale through a unique technique route involving the severe plastic deformation followed by reverse selective dissolution. Scanning electron microscopy and high-resolution transmission electron microscopy were utilized to characterize the microstructural evolution and analyze how the etching solutions affect the resulting nanoporous structures. The mechanical properties, which are an important consideration during many practical applications, were investigated by employing depth-sensing nanoindentation and other small-scale testing in situ in the SEM. Based on this, the elemental plasticity mechanisms governing the mechanical behavior were elucidated.

This work for the first time provides an innovative and adaptive approach to create nanoporous tungsten on a bulk scale. The developed reverse phase dissolution method is generally applicable and can be transferred to other refractory metals in the future. The promising mechanical results of nanoporous tungsten will serve as foundation for forthcoming related scientific studies and engineering applications.

9:45 AM MS03.01.04
**Toughening in Cu/Mo Hierarchical Nanocomposite Tested by In Situ Bending in SEM** Yuchi Cui¹, Benjamin K. Derby¹, Nan Li² and Amit Misra¹; ¹University of Michigan, Ann Arbor, United States; ²Los Alamos National Laboratory, United States

The fracture behavior of high-temperature co-sputtered Cu/Mo nanocomposites were investigated in this study through in situ bending test of pre-notched microbeams in SEM. The as-synthesized nanocomposites present hierarchical heterogeneous architectures that are composed of matrices of bicontinuous interpenetrating Cu/Mo with nanoscale ligaments and sub-micron scale Cu-rich islands containing Mo-rich nanoparticles. From previous nanopillar compression tests, the nanocomposites possess high strength over 2 GPa and good deformability without shear band formation. Our micro-scale bending test further shows that the hierarchical nanocomposite has higher toughness compared to Cu/Mo nano-multilayers and monolithic Cu-Mo nanocomposite, where only interpenetrating Cu/Mo with nano-scale ligaments presents. The Cu islands were observed to neck and bridge the crack surfaces, as well as blunt the crack tip, deterring crack propagation. As a result, crack formation in multiple directions was observed after the initial crack propagation during the bending test. From this study, our hierarchical nanocomposite presents a successful approach to break through the strength-toughness trade-off dilemma.

10:00 AM BREAK

10:30 AM *MS03.01.05
**On the Multifunctional Response of Bicontinuous Metal/Polymer Nanocomposites** Erica T. Lilleodden¹,², Murilo Hablitzel¹, Yijuan Wu¹, Kaixiong Hu³, Markus Ziehmer¹ and Jürgen Markmann¹,²; ¹Helmholtz-Zentrum Geesthacht, Germany; ²Technische Universität Hamburg-Harburg, Germany; ³Wuhan University of Technology, China

Composite materials bring together the structures and properties of two or more materials to create improved functionality. The chemistries, microstructures, and topologies of the phases dictate their individual constitutive response, while those characteristics combined with the properties of the associated interfaces dictate the composite behavior. Exploiting size effects and unconventional structural geometry is a clever approach to achieving novel materials that go beyond functions predicted by conventional models of composite response. In the case of nanoporous gold (NPG) - based composites, the strong size effects found in nanoscale gold structures lead to a strongly tailorable strength of the nanoporous gold phase, while the high surface area allows actuation and sensing functions when submerged in electrolyte. When infiltrated or coated with a polymer, the boundary conditions governing the behavior of the nanostructured gold are modified.

In this presentation we consider two NPG-based nanocomposites: NPG fully infiltrated with epoxy to improve strength and ductility, and PPy coated NPG which enhances the electro-chemo-mechanical coupling in an electrolytic environment. Using various micromechanical testing methods and the quantification of the 3D network structure, the novel functional response has been investigated. It was found that the dependence of the strength on the mean ligament diameter is much weaker in the NPG/epoxy composites compared to pure NPG, while no size effect in the nanoporous epoxy phase was found. The failure of the composite presented as in-plane “horse-shoe” shape delaminations between the gold and epoxy phases, which serves to dissipate energy while maintaining its load.
bearing capacity. In the case of NPG submersed in NaF electrolyte, electro-chemo-mechanical coupling resulted in a considerable increase of strength of pillars when surface adsorption occurred, i.e. under positive applied potential, and the stress response to potential jumps was found to be fast and reversible. Coating NPG with an electrically conductive polymer, PPy, allows additional strengthening and stiffening of the NPG while also exploiting the actuation and sensing capabilities of the high specific surface area NPG network structure under potential in the NaF electrolyte.

Results will be discussed in terms of the individual constitutive relations, topological characteristics, and interfacial chemistry and strength, and perspectives for further exploitation of this class of nanocomposites will be given.

11:00 AM MS03.01.06
Formation of Ultra-Fine Spheric Microstructure Consist of Dual Phase in Mg85Zn6Y9 Alloy Masafumi Matsushita1,1, Daiki Yamauchi1, Yuki Kawabata1, Toru Shinmei1, Hiroaki Ohfuji1, Michiaki Yamasaki2 and Yoshihito Kawamura2; 1Ehime University, Japan; 2Kumamoto University, Japan

High-pressure and high-temperature (HPHT) treatment can make fine and unique texture in materials. We have realized HPHT treatments on the Mg85Zn6Y9 alloy and then quenched and decompressed to ambient pressure. The alloy have a 18R-type long period stacking ordered structure synchronized with chemical concentration at ambient pressure, however it transform to duplex structure consist of “soft” hcp (α-Mg) phase and “hard” fcc-based superlattice (D03) phase at high-pressure condition (Matsushita, et al., Mater. trans. 56, 910, 2015, Mater. Let. 155, 11, 2015). The high-pressure phase can be recovered at ambient pressure. The recovered alloys after being treated at HPHT condition have ultra-fine and unique solidification pattern.

The alloy recovered after being treated at 10 GPa and 973 K have a lamella structure alternating layers of hcp and D03 phases with the layer thickness of 80~100 nm. On the other hand, the alloy recovered after being treated at 10 GPa and 1273 K takes spherulite with the diameter of 5~15μm. The term “spherulite” suggests a nearly spherical polycrystalline solidification pattern, which is rarely observed in solidification metals. As far as our knowledge, this is the first case the alloy takes spherulite of the volume percent above 80 %. The spherulite also contains duplex phase consist of hcp and D03. In the core part of spherulite, small grain considered as D03 in size below 50 nm distributed Mg matrix (Matsushita, et al. JALCOM, 784. 1284, 2019). Further fine column shape grains consist of D03 and hcp phases were spread from radially from the core. Similar unique spherical microstructure can be observed in the alloy treated at 5 GPa/1273 K and 15 GPa/1273 K.

The compression yield stress of the alloy consisted from spherulite structure is over 700 MPa, which much higher than that of lamella structure and the other magnesium alloys with similar composition made by severe plastic deformations. These results show the HPHT treatments and spherulite structure have great potential to develop the alloy with high strength.

11:15 AM MS03.01.07
Mechanical Response of Bicontinuous Copper-Molybdenum Nanocomposites Nathan J. Beets1, Yuchi Cui2, Diana Farkas1 and Amit Misra2; 1Virginia Polytechnic Institute and State University, United States; 2University of Michigan–Ann Arbor, United States

We present the results of a combined experimental and atomistic simulation study of the mechanical properties of a Co- Mo bicontinuous nanocomposites with varying ligament sizes. Simulations of bicontinuous nanocomposites under compression using atomistic molecular dynamics are compared to experimental results on in situ SEM and TEM microscale compression tests on co-sputtered Cu-Mo. The simulations allow the elucidation of the defect nucleation, glide and storage phenomena within individual Cu and Mo phases and Cu/Mo interfaces. The simulation results are also compared with the predictions of a dislocation theory based analytical model of glide of individual dislocations in nanoscale metallic phases confined by interphase boundaries that are strong barriers to slip transmission. The integrated simulation-experimental study shows that the bicontinuous intertwined morphology is effective in suppressing localized shear bands and promoting homogeneous distribution of plastic flow in metallic nanocomposites.

11:30 AM MS03.01.08
Alloyed and Layered Composite Nanofoams—A Multiscale Modeling and Experimental Validation Ioannis Mastorakos1, Hang Ke1, Andres Jimenez1 and David Bahr2; 1Clarkson University, United States; 2Purdue University, United States
Pure metal nanofoams in the form of interconnected networks of ligaments have shown strong potential over the last few years in areas of catalysts, batteries, and optics. However, they are often fragile and difficult to integrate into engineering applications. In order to mechanically strengthen them two new types of foams are studied in this work: alloyed and nanolayered. These materials will operate at the macroscale but they will maintain a nano or atomistic ordering requiring a multiscale approach for the study of their properties. For that purpose, in this work, we combined molecular dynamics and finite elements to study the mechanical behavior of these metallic structures made of copper and nickel and compared them to their pure metal counterparts. Furthermore, manufactured nanofoams were tested using nanoindentation and the findings are used to compare and validate the simulation results.

11:45 AM *MS03.01.09
Novel Stress-Assisted Structural Transformation and Plasticity Enhancement in Mo/Cu Bicontinuous Intertwined Composites Lijie He and Niaz Abdolrahim; University of Rochester, United States

Structural transition in Molybdenum has been reported to occur under large stresses in thin nanowires and tip of a crack. Here, we use Molecular Dynamics (MD) simulations to demonstrate that a uniform 3-step structural transformation of Molybdenum atoms can occur in Mo/Cu bicontinuous intertwined materials during tensile loading. The Mo atoms first transit from a <001>-oriented bcc structure to a <001>-oriented fcc structure via Bain transformation. The <001>-oriented fcc phase then transforms to a <110>-oriented bcc via Pitsh transformation. This novel homogenous transformation results into a stress-strain curve containing two elastic and two plastic regimes as well as enhanced plasticity with few dislocation slips and no twinning. Our results reveal that the driving force for such phase transformation is the high interfacial stress in the bicontinuous intertwined structure. This study suggests new strategies for improving the ductility of ultra-strong nanocomposite metals.

SESSION MS03.02: Metals and Metallic Nanocomposites
Session Chairs: Niaz Abdolrahim and Scott Mao
Monday Afternoon, December 2, 2019
Hynes, Level 1, Room 103

1:30 PM *MS03.02.01
High Speed Nanoindentation Testing—Indent Spacing and Analysis Tools Jennifer Hay, Phani Sudharshan and Warren C. Oliver; KLA, United States

The field of micro and nanomechanical testing has expanded dramatically. Many sample geometries and testing techniques have been developed to investigate a variety of mechanical material properties. Nanoindentation contact experiments with pyramid shaped indenters have led the way. The properties that one can determine using contact mechanics has expanded as well. In this talk we will focus on high speed indentation. This technique requires that dynamic mechanical effects must be considered to correctly to perform the experiments. The instruments must be carefully designed and characterized so that the dynamic effects of the instrument and sample on the combined results obtained can be separated and quantitatively understood. In addition, the spacing of the contact experiments must be sufficiently large to avoid interactions between the indentations. We will examine the question of how close they can be in detail. The results indicate that the indentations can be safely spaced twice as close as has been suggested in the literature. Once these experiments are performed several analysis techniques help make the data useful. In particular, data clustering algorithms can be used to separate phases in multiphase materials. We will show the results of such analysis on the technologically important example of bond layers in thermal barrier coatings on turbine blades.

2:00 PM MS03.02.02
In Situ TEM on Deformation and Fracture of Single Lattice Pillar Scott X. Mao; University of Pittsburgh, United States

Structural nanomaterials and nanocomposites have excellent mechanical performance, which can be tuned through
both structural architecture and material size effects. However, the behavior of individual component normally sized
at 5 - 50 nanometer in the structural nanomaterials is key important, has not been explored before. This talk will be
the in-situ mechanics for studying the mechanical behavior at atomic scale for 5 to 50 nanometer-sized pillars (so-
called lattice pillar) of metallic crystals. The experimental molecular dynamics with the in-situ high resolution
transmission electron microscope is going to open a new approach to directly characterize atomic-scaled
deformation with in-situ mechanics for such small sized pillar. I will cover the stress-strain behavior, high stress
induced lattice disturbance, dislocation dipole nucleation and competition between slip and twinning in the
deformation process, which potentially can be related to individual component of structural nanomaterials such as
nano-porous and nano-lattice materials.

2:15 PM MS03.02.03
Metastability and Hardness Variation of Metallic Nanocrystals under External Stimuli Zhitong Bai and Yue
Fan; University of Michigan–Ann Arbor, United States

Recent experiments show that metallic nanocrystalline materials can be rejuvenated under the stimuli of
femtosecond laser and the system’s hardness can be effectively tuned. However, a mechanistic understanding on
such phenomenon remains unclear. Here we investigate the responses of a group of <100> symmetric tilt grain
boundaries (STGBs) in a Cu modeling system under the driving of fast thermal cycling. A universal hysteresis
behavior is observed during such process, and the GB is driven to a higher energy state after the pulsive stimulus.
By employing an enhanced data-mining algorithm to analyze the annealing behavior of GBs at various thermal
conditions, we are able to construct a high-resolution pixel map for the GB’s energetic evolution and show that it
can be divided into an ageing regime and a rejuvenating regime over the broad energy—temperature parameter
space. We further demonstrate that the origin of ageing/rejuvenating is attributed to the energy imbalance along with
the elementary hopping processes in the GB’s underlying potential energy landscape (PEL). The hereby established
picture then allows us to develop a self-consistent kinetic equation to describe the GB’s energetic and mechanical
responses to external stimuli, which can qualitatively explain the recent femtosecond laser experiment. The present
study thus enables a deeper mechanistic understanding towards the non-equilibrium evolution of nanocrystalline
materials.

2:30 PM MS03.02.04
Programmable Nanoscale Origami Triggered by Electron Beam Irradiation Chunhui Dai1, Lianbi Li1,2, Daniel
Wratkowski1 and Jeong-Hyun Cho1; 1University of Minnesota, United States; 2Xi’an Polytechnic University, China

Origami inspired self-assembly of three-dimensional (3D) micro- and nanostructures shows diverse applications
across a broad range of areas, such as metamaterial and plasmonic devices, electronics, and biomedical devices.
Significant development of the assembly technique has been achieved based on various stimuli responsive materials.
However, precise bidirectional motion control with a desired sequence remains a challenge due to the limited
capability of delivering localized stimuli, resulting in constrained functions of origami. In this work, we report a
route to fully mimic the functions of origami including bidirectional curving, folding, stretching, and even knitting.
The mechanism involves electron irradiation triggered in situ crystallization in amorphous material, which results in
volume shrinkage, generating sufficient stress for assembly. The scanning electron microscopy (SEM) offers
capability of real time monitoring and fine focus, which enables precise stimuli delivery, leading to programmable
assembly. Prototypes including nano-machines, nanoscale test platforms, and advanced optical devices have been
demonstrated using this strategy, showing the possibility for innovation of next generation devices and smart
materials.

2:45 PM MS03.02.05
3D Periodic Tungsten–Silicon-Carbide Nanocomposites Designed for Mechanical Robustness Andreas Stein,
Zhao Wang, Kevin Schmalbach, David Poerschke, R. Lee Penn and Nathan Mara; University of Minnesota, United
States

Metal-ceramic nanocomposites exhibit exceptional mechanical properties with combinations of high strength,
toughness, and hardness not achievable in monolithic metals or ceramics, which make them valuable for
applications in fields, such as the aerospace and automotive industries. It has been shown that the interface between
components in a nanocomposite plays an important role in controlling these properties. Here we demonstrate the
preparation and mechanical properties of nanostructured tungsten–silicon-carbide composite materials, which
contain a ductile metal component and a brittle ceramic component interspersed at the submicron scale in periodic fashion. In these nanocomposites, the ratio of interfacial area to volume is systematically controlled through templating and nanocasting methods, permitting a systematic investigation of the brittle-to-ductile transition through nanoindentation and micropillar compression tests.

The material synthesis is enabled through colloidal crystal templating of three-dimensionally ordered macroporous (3DOM) materials as host structures to create nanocomposites with high interfacial area. 3DOM materials are porous solids that feature a highly ordered, fully interconnected, porous structure with pore sizes in the 200–500 nm range and struts that are tens of nanometers in diameter. The macropores can be infiltrated with a second phase in a nanocasting process to form periodic composite structures. The component ratio is controlled by the choice of the host and guest components and through processing, and the interface-to-volume ratio through the pore size. Here we investigate 3DOM W and 3DOM SiC materials infiltrated with SiC and W guests, respectively. Silicon carbide is a material with high hardness, high thermal conductivity, and high mechanical strength/oxidation resistance. However, it suffers from unwanted brittleness at elevated temperature. Introduction of tungsten can introduce the ductility of a metallic phase to modulate the composite strength and strain hardening behavior. Moreover, compared to other metals, tungsten has only a small mismatch in coefficient of thermal expansion with silicon carbide. Because tungsten and silicon carbide can react with each other to form tungsten carbide or tungsten silicide phases at different temperatures, we found that various interfacial compositions could be achieved by controlling the synthesis temperature. Nanoindentation and micropillar compression testing reveal enhanced strength, as well as significant deformation prior to fracture.

3:00 PM BREAK

3:30 PM *MS03.02.06
Mechanics of Architected Carbon: From Rubber-Like Deformation in Pyrolytic Nano-Carbon to Ultrastrong and Impact-Resistant Nano-Architected Glassy Carbon Julia R. Greer1, Bryce Edwards1, X. Zhang2, Andrey Vyatskikh1, D. Veysset3, Keith A. Nelson3, Huajian Gao4 and X. Li2; 1California Institute of Technology, United States; 2Tsinghua University, China; 3Massachusetts Institute of Technology, United States; 4Brown University, United States

Creating materials with a combination of high strength, substantial deformability and ductility, large elastic limit, and low density represents a long-standing challenge in materials science because these properties are typically mutually exclusive. Using a combination of two-photon lithography and high-temperature pyrolysis, we demonstrate micro-sized pyrolytic carbon with a tensile strength of 1.60+/-0.55 GPa, a compressive strength approaching the theoretical limit of ~13.7 GPa, a substantial elastic limit of 20–30%, and a low density of ~1.4 g cm⁻³. This corresponds to a specific compressive strength of 9.79 GPa cm³ g⁻¹, a value that surpasses that of nearly all existing structural materials. Glassy carbon samples with dimensions below 2.3 μm exhibit rubber-like behavior and sustain a compressive strain of ~50% without catastrophic failure; larger ones exhibit brittle fracture at a strain of ~20%. Large scale atomistic simulations reveal that this combination of beneficial mechanical properties is enabled by local deformation of 1 nm-long curled graphene fragments within the pyrolytic carbon microstructure, the interactions among neighboring fragments, and the presence of covalent carbon–carbon bonds. Building on these individual carbon nano-building blocks, we developed a process to create nano-architected glassy carbon that attains specific strength of up to one to three orders of magnitude above that of existing micro- and nanoarchitected materials. Experiments and simulations demonstrate that for densities higher than 0.95 g/cm³ the nanolattices become insensitive to fabrication-induced defects, allowing them to attain nearly theoretical strength of the constituent material. A key challenge in studying mechanics of nano-architected materials is their lack of a proper separation-of-scales between unit cell size and sample dimensions, which precludes proper impact testing when the impact time scale allows elastic waves to propagate information from the free boundaries back to the projectile. Another difficulty in dynamic testing of nanomaterials is the lack of reliable methods to achieve consistent loading conditions while capturing proper temporal and length scales. We developed a method to design, fabricate, and test nano-architected materials at supersonic impact speeds of up to 1 km/s that address these challenges by employing Laser Induced Particle Impact Test (LIPIT). In this method, a
pulsed laser accelerates a microscale impactor to velocities <1.2 km/s, and the impact is captured using frames from a high-speed camera within a microscope, allowing for nanosecond temporal and micrometer spatial resolution. We probed different impact regimes by selecting spherical SiO2 impactors of different diameters while varying impact velocity from 50 to 1,100 m/s. Post-mortem analysis of impacted samples via confocal and electron microscopy indicates that nanolattices with 26% relative density can withstand impact speeds that exceed 700 m/s, either absorbing or rebounding the projectile.

The combination of high specific strength, low density, impact resistance, and extensive deformability before failure lends such nano-architected pyrolytic carbon to being a particularly promising candidate for applications under harsh thermomechanical environments.

4:00 PM OPEN DISCUSSION

4:15 PM MS03.02.08
Improvement of an Electrocharging Assisted Fabrication Method for Nanocarbon-Aluminum Composites
Madeline Morales1,2, Xiaoxiao Ge1, Christopher Klingshirn1, Daniel Cole2 and Lourdes G. Salamanca-Riba3;
1University of Maryland, United States; 2U.S. Army Research Laboratory, United States

Carbon nanostructures represent a growing area of research due to their excellent mechanical, electrical and thermal properties. Research studying their synthesis has rapidly populated academic journals, but these procedures are difficult to implement in large-scale manufacturing due to their complexity and cost. In contrast, electrocharging assisted bulk processing of a novel class of materials, termed “covetics,” presents a practical option for macroscale production of nanocarbon-metal composites. Notably, this process facilitates incorporation of carbon on the order of a couple weight percent in metals where carbon solubility is normally in the low ppm range. A 40% increase in tensile strength and 40% increase in electrical conductivity has been measured in Al covetics; however, there is minimal understanding of the structure-process-property relationship and consequently there is high variability in measured properties among trials. To investigate the relationship between fabrication conditions and properties of the composite material, the parent alloy, Al 1350, is melted in a graphite crucible nestled within induction coils. Following the addition of activated carbon precursor, a DC current is applied to the molten mixture via a graphite electrode to initiate the electrocharging assisted conversion process. Raman spectroscopy is used to evaluate the structure and degree of crystallinity of carbon incorporated into the Al lattice via the Tuinstra-Koenig relation for graphitic carbon. XPS is used to measure the amount of carbon incorporated and determine the sp2/sp3 ratio. XRD is used to identify the formation of any secondary phases or carbides. Following structural characterization, four-point probe testing is performed to measure the bulk electrical conductivity of the covetic material. Atomic force microscopy techniques are used to measure the local electrical and mechanical behavior of the covetic by Kelvin probe force microscopy and nanoindentation, respectively. Results to date have found that the activated carbon precursor is converted to sp2 hybridized graphitic carbon with an increase in crystallite size as measured by Tuinstra-Koenig. From XRD and XPS, it has been determined that there is no measurable formation of carbide phases despite a couple weight percent of incorporated carbon. The electrical conductivity of the covetic material has also been shown to increase. The local electromechanical behavior of the covetic measured by AFM techniques will be used to develop a fundamental understanding of the improved properties measured in the composite and used to inform adjustments to the fabrication process accordingly.

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4:30 PM MS03.02.09
Hybrid Hierarchical Nanolattices with Porous Platinum Coating
Ehud Almog1, Amit Sharma1, Yuanshen Qi1, Julia R. Greer2 and Eugen Rabkin1; 1Technion - Israel Institute of Technology, Israel; 2California Institute of Technology, United States

Nanolattices exhibit wide range of unique properties and attract a growing interest in many scientific fields. The architected hierarchical structure allows tailoring the nanolattice properties to obtain objects of relatively large dimensions with nano-size features. In our work we fabricated a core-shell polymer-platinum nanolattice by combining several fabrication techniques. The polymeric nanolattice was designed by CAD, and fabricated by a two photon lithography technique to achieve the required architecture. The lattices were then coated with thin film of platinum using atomic layer deposition (ALD) method. The unique interaction of the gaseous ALD precursor with
the polymer surface resulted in a porous film with nano grains, providing a hierarchy ranging from the micrometer-size overall dimensions down to the microstructural features of a few nanometers. The microstructure evolution (i.e. grain size, pore size and defects) caused by annealing at elevated temperature was investigated, and correlated to the mechanical behavior of the lattices during in-situ compression inside a scanning electron microscope.

4:45 PM MS03.02.10
**Strengthening of Thin Metal Films Using Graphene Monolayer** Kaihao Zhang, Mitisha Surana and Sameh Tawfick; University of Illinois at Urbana-Champaign, United States

A practical route to exploiting graphene’s supreme properties for a variety of applications is to incorporate graphene layers in composite materials. Harnessing the high stiffness, intrinsic strength as well transport properties of graphene in its composites requires the combination of high-quality graphene having low defect density, and the precise control of the interfacial interactions between the graphene and the matrix. These requirements equally fold for polymer and metal matrices, and enable the use of graphene in applications ranging from tough thin films for flexible electronics to the design of advanced aerospace structures. In this study, to address the synthesis and control of these composites and their mechanical properties at the nano to the microscales, we propose a model system of ultrathin metal films coated with graphene monolayer via chemical vapor deposition (CVD) to study as-grown graphene’s contributions in graphene-metal nanocomposites.

However, several factors need to be considered to assure the stability of ultrathin catalysts at the elevated temperatures (1000-1100 C) for high quality graphene synthesis. We develop a highly dynamic CVD synthesis route (less than two minutes) to achieve high quality graphene monolayer growth on ultrathin (100-150 nm) Pd films while avoiding solid-state dewetting which easily takes place at the high temperatures. We study how the competition between temperature-driven segregation and precipitation of carbon atoms governs the graphene’s nucleation and growth kinetics on ultrathin Pd films. The result of the dynamic recipe is repeatable growth of graphene monolayers with over 2.5-fold faster graphene growth rate than that in typical Cu catalyzed synthesis, as well as very low defect density as confirmed in Raman spectroscopy.

Precise mechanical characterization of as-grown ultrathin graphene-Pd films is carried using micro bridge Nanoindentation. CVD grown graphene-metal composite thin films exhibit unusual increase in the elastic modulus, strength and toughness. For example, there is 35 % and 57 % increases in the Young’s modulus and tensile strength in graphene-Pd nanocomposites compared to those for a bare Pd film having a thickness of 66.4 nm. Notably, this enhancement is beyond the rule of mixtures limits, and exhibits scale effects, where the composite modulus increase varies with the thickness, and is highest for the thinnest metal thicknesses. This usual elastic modulus enhancement is attributed to the significant change in the surface stress of ultrathin films after coating with graphene. Raman spectroscopy and electron imaging of graphene-Pd surface reconstructions confirm the high interfacial stresses due to the combination of the lattice mismatch between the graphene and the underlying metals and the kinetics of CVD synthesis. We also observed significant increase in toughness and qualitatively different modes of crack propagation owing to the addition of the high stiffness graphene shield on the metal surface during synthesis. The findings of this study promote graphene-based thin film composites for flexible electronic devices, and enable fundamental studies of exploiting strain engineering at the graphene-metal interface for electronics, chemistry and mechanics.

SESSION MS03.03: Poster Session I: Metallic Nanocomposites
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

**MS03.03.01**
**Compressed Exponential Relaxation Originated Negative Strain Rate Dependency of Metallic Glass Flow Stress** Akio Ishii1, Tomoaki Niiyama2, Takahiro Hatano1, Tomotsugu Shimokawa1 and Shigenobu Ogata1; 1Osaka University, Japan; 2Kanazawa University, Japan

It is reported that negative or no strain rate dependency of the flow stress of metallic glasses appears at high strain
rate or low temperature condition [1][2]. We reveal that this curious strain rate dependency is strongly related to the rate of glass relaxation process from a rejuvenated glass state induced by activation of shear transformation. We use a constitutive model which estimates average residence time of thermal activation process and calculate the flow stress of metallic glass at certain strain rate and temperature [3]. In the model, we assume relaxation process recovers the activation energy of shear transformation of rejuvenated glass state and the relaxation is expressed as stretched or compressed exponential form. Interestingly, we find the negative or no strain rate dependency appears when the timescale of the activation of shear transformation approaches the characteristic timescale of glass relaxation process. Especially, the negative strain rate dependency only appears with the compressed exponential relaxation. The compressed exponential relaxation is always observed in the material with gel or colloid-like structure, and in this decade, it is observed in metallic glass too [4].


MS03.03.02
Mechanical Behavior of Metallic Thin Films Passivated by Ultra-Thin Layers Sunkin Choi, Yuhyun Park, Ho Jang Kim, Pragya Rani, Tae Soo Kim, Minsoo Kang, Kibum Kang and Gi-Dong Sim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Understanding the mechanical behavior of metal thin films at elevated temperature is essential for the design of reliable devices, which often operate above room temperature. So, from the past, several studies have been performed on the high-temperature behavior of freestanding metal thin films to understand their intrinsic properties. However, in real applications, there are very few cases where the thin films are placed as freestanding. Also, the mechanical behavior of metal thin films can be changed when they are layered with another thin materials due to the existence of interface. Therefore, understanding the performances of thin films with passivation layers at elevated temperature is important, but studies have been limited due to difficulties associated with sample handling, oxidation, temperature uniformity, and fabrication of multi-layers with passivation layers such as dielectric or 2D materials.

In this poster, we introduce an apparatus to perform micro-tensile tests at elevated temperatures inside a scanning electron microscope. The apparatus has a stroke of 250μm with a displacement resolution of 10nm and a load resolution of 9.7μN. Measurements at elevated temperatures are performed through use of two silicon-based micromachined heaters that support the sample. Each heater consists of a tungsten heating element that also serves as a temperature gauge. To demonstrate the testing capabilities, tensile tests were performed on submicron-thick freestanding metal thin films with and without the passivation layers from room temperature to elevated temperature. Ultra-thin dielectric (Si₃N₄) and 2D layers (e.g. MoS₂, graphene) were chosen as passivation layers, which are mainly used in electronic devices with metal thin films. Stress-strain curves show a significant decrease in yield strength and initial slope for the samples tested at elevated temperature, which we attributed to diffusion-facilitated grain boundary sliding and dislocation climb. However, when passivation layer is added on the film, the decrease of yield strength and necking of the metal thin films are expected to be inhibited and strain hardening may become significant due to dislocation pileups at the interface.

MS03.03.03
Mechanical Characterization of Sputter Deposited Nickel-Molybdenum-Tungsten Thin Films for High Temperature Metal MEMS Applications Yuhyun Park, Sunkin Choi, Hosun Jun, Won Seok Choi, Pyuck-Pa Choi and Gi-Dong Sim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Taking microelectromechanical systems (MEMS)-based devices such as sensor, actuator, micropower generator into the harsh environments (temperature greater than 200°C, power level above 100W) would greatly expand the applications ranging from miniature internal combustion engines, to high frequency switching, microheaters and high temperature sensors. However, the dominant structural material used in conventional MEMS devices are silicon, which can not be used in thermal environment due to its loss of mechanical properties at elevated temperatures. Therefore, the development of metallic MEMS alloys that possess enhanced mechanical and functional properties at intermediate to high temperature range, requisite dimensional stability, and the ability to be shaped on the microscale would provide the wider design space for novel MEMS applications. Metals and alloys are...
especially attractive in MEMS applications that require high density, electrical and thermal conductivity, strength, ductility and toughness.

Electrodeposited nanocrystalline LIGA Ni offers a route for microfabrication of metallic parts with high aspect ratios and have good room temperature yield strength, but temperatures as low as 200°C can result in grain growth and a significant loss of strength. Alloying elements with limited diffusivity can strongly suppress grain growth, in particular, Ni-W thin films prepared by magnetron sputtering are known to exhibit thermally stable nanocrystalline microstructures. Adding another solute element Molybdenum to the system can effectively improve dimensional stability by lowering the coefficient of thermal expansion over long temperature range while retaining mechanical integrity.

Here we report the mechanical behavior of sputter deposited Nickel (Ni)-Molybdenum (Mo)-Tungsten (W) ternary alloy thin films at various temperatures. The microstructure and chemical composition of deposited materials are characterized using transmission electron microscopy (TEM), scanning electron microscope (SEM), X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS). The as-deposited films go down as single-phase solid solutions and possess high nanoindentation hardness of approximately 9 GPa. Custom built micro-tensile tester which operates inside the SEM is used to perform comprehensive in-situ thermomechanical study on Ni-Mo-W thin.

First, the in-plane mechanical response of the as-deposited and heat-treated freestanding Ni-Mo-W thin films are investigated at room temperature. Then the mechanical properties of films annealed at 400°C are explored at elevated temperatures by Joule heating of two micromachined tungsten heater that support the tensile specimen.

MS03.03.04
Effect of Bonding Temperature on Thermal Residual Stress Near Edge of Interface on Ceramics to Metal Joint with Arbitrary Interface Conditions Shunsuke Muraoka1 and Masayoshi Tateno2; 1Kogakuin University Graduate School, Japan; 2Kogakuin University, Japan

This study provides that relationship between distributed thermal elastoplastic stresses near the edge of the interface and practical tensile strength of ceramics/metal joint system with arbitrary wedge angles. Interface wedge angles were defined as a configuration angle between interface and free surfaces of both materials. The wedge angles on ceramics and metal were described as $\phi_1$ and $\phi_2$ respectively. The wedge angles of the metal side $\phi_2$ were set over the range in $20^\circ < \phi_2 \leq 180^\circ$, as kept maintaining one of the ceramic side $\phi_1 = 90^\circ$.

Thermal elastoplastic FEM was carried out to clarify the distribution of the thermal residual stress near the edge of the interface each wedge condition using ceramics to metal joint FEM models bonded at high temperature ranges. The stress singularity was confirmed near the edge of the interface on the free surfaces of ceramic side each FEM model. The gradient of stress distribution was evaluated and compared in FEM elastoplastic analysis.

The numerical results were compared with the experimental results, which showed effects of the wedge angle on the practical tensile strength of silicon nitride to nickel joints specimens bonded at the same as numerical temperature conditions. Changing the wedge angle from a specific wedge angle improves the tensile bonding strength, since the residual stress was decreased by changing the wedge angle. This result corresponds with the FEM results as increasing $\phi_2$ from the right angle decreases the concentration intensity of the residual stress.

The dependency of the optimum interface condition on the bonding temperature was discussed based on both results of numerical and experimental in high bonding temperature ranges.

MS03.03.05
Metal or Alloy - Gr Composite Coatings via Electro- or Electroless Deposition for High Surface Performances Sishi Li, Gongsheng Song and Chunxu Pan; Wuhan University, China

In general, surface coating technology includes painting & organic coating, electro-& electroless deposition, physical vapour deposition, chemical vapour deposition and thermal spraying et al. Electro-deposition and electroless deposition are widely used in industry. Electro-deposition, is a kind of process that the metal ions in the electrolyte are reduced into metal with external electric assistance, and deposited on the surface of the substrate for forming a compact metal or alloy coating. Electroless deposition is a kind of process that the metal ions in the solution are reduced into metal under a strong and suitable reducing agent without external electric assistance, and deposited on the surface with catalytic active sites of the substrate for forming a compact metal coating.

As a new type of two-dimensional (2-D) carbon nanomaterial, graphene (Gr) is of many excellent properties, such as high strength, ductility, thermal conductivity, wear resistance, extremely large specific surface area, remarkable chemical inertness unless exposed to harsh reaction conditions, etc., and shows great application potential as an excellent reinforced phase in the field of composite materials. In recent years, our group engages in preparation of
the metal or alloy - Gr coatings via electro-deposition or electroless deposition for high surface performances, and explores their industrial applications.

1. **Zn-Gr composite coating via pulse reverse electro-deposition.**

In this work, the hydrophilic graphene oxide (GO), instead of the hydrophobic Gr, was chosen and added into the electrolyte bath. Due to the reduction of GO into Gr during deposition, a Zn-Gr composite coating was prepared successfully by using a pulse reverse electro-deposition method on the iron substrate. The experimental results reveal that: 1) The coating exhibits a strong adhesion with the substrate; 2) The Zn crystalline and morphologies change greatly due to the co-deposition of Gr, i.e., the main preferred orientations of (112) and (101) crystal planes in pure Zn coating gradually transform into the (103), (102) and (110) planes in the Zn-Gr composite coating. 3) There is an optimal GO adding amount in a range 0.3–0.5g/L in the electrolyte, at which the Zn-Gr coating exhibits the highest corrosion resistance and corrosion current density just be a hundredth comparing with that of pure Zn coating in simulated seawater environment.

2. **Alloy (Zn–Ni)-Gr composite coating via pulse reverse electro-deposition.**

The alloy (Zn–Ni)-Gr composite coating was prepared by using pulsed-reverse electrodeposition. It was found that: 1) the coating grain size became smaller after GO added into the electrolyte; 2) the presence of Gr could effectively inhibit the corrosion of the substrate; 3) comparing to regular Zn-Ni coating, the (Zn–Ni)-Gr coating's microhardness and elastic modulus were increased.

3. **Cu-Gr composite coating via electroless deposition**

In this work, the Cu-Gr composite coating was prepared successfully by using electroless plating with sodium hypophosphite (NaH2PO2) as the reducing agent. The experimental results reveal that: 1) Gr exhibits a significant effect on the microstructure of the coating, for example, the grain size of the composite coating varies from the concentration of the added GO, and the optimal value shows the smallest grain size and the highest compactness. 2) At the optimal GO concentration, the Cu-Gr coating also is of the highest mechanical properties. 3) Compared with regular pure Cu coating, the corrosion resistance of the Cu-Gr coating has a significant improvement, i.e. the $E_{\text{corr}}$, $i_{\text{corr}}$, corrosion rate and inhibition efficiency are also optimized at the optimal GO concentration. It is expected that the Cu-Gr coating will have broad application prospects in the fields of electronics industry, marine engineering and military industry.

**MS03.03.06**

**Micro-Mechanical Properties of Electrodeposited Au-TiO2 Composite Film**

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Electrodeposition is a widely applied method in fabrication of metal-based components in micro-electrical-mechanical systems (MEMS) devices. As an example, gold material, which has a high mass density of 19.3 x 10³ kg / m³ at 298K, is utilized as the proof mass in a MEMS accelerometer since performance of a MEMS accelerometer is highly related to overall mass of the proof mass. However, the relatively weak mechanical strength of gold limits the structure stability and reliability when used in movable micro-structures. Enhancing the mechanical strength is an important task to ensure high structure stability of movable structures in novel MEMS.

Co-deposition of metal matrix-oxide nanoparticles (NPs) composites is a simple and effective method to improve mechanical properties of the material. The NPs can be oxides such as Al₂O₃, TiO₂ and Cr₂O₃, carbides like SiC and TiC or graphitic materials like carbon nanofiber, carbon nanotube, and graphene oxide. A wide range of metals includes zinc, nickel, copper, nickel and silver has been used as matrix of the composite. In this study, TiO₂ NPs are introduced into the gold electrodeposition bath to enhance mechanical strengths of electrodeposited gold-based materials by forming TiO₂ NPs-reinforced gold matrix composites. Effects of the strengthening provided by the TiO₂ NPs are evaluated by micro Vickers hardness test and micro-compression test.

The Au-TiO₂ composite films were deposited on 1 cm² area copper plates. A common two electrode system was use for the electrodeposition with the copper plates as the working electrode, a platinum plate as the counter electrode, and a commercial non-cyanide sulfite-based gold bath containing various amounts of TiO₂ NP powder (AEROXIDE® TiO₂ P 25, Evonik) as the electrolyte. Temperature of the electrolyte was kept at 40°C. All the electrodeposition was carried out through galvanostatic method with a current density of 5 mA/cm² for 1.5 hours. A pure gold film was also deposited with the same electrodeposition parameters but without TiO₂ NP powder in the electrolyte for comparison. Composition and crystal structure of the composite films were characterized by energy dispersive X-ray spectrometry (EMAX, Horiba) equipped in an scanning electron microscope (SEM, S-4300SE, Hitachi) and an X-ray diffractometer (XRD, Ultima IV, Rigaku). Surface morphologies of the as-deposited films were observed with the SEM. Hardness of the films were evaluated by micro Vickers hardness measurement (HMV-
Micro-compression tests were conducted using micro-pillars fabricated by focus ion beam (FIB, FB-2100, Hitachi) from the composites films. Surface morphologies of the Au-TiO$_2$ composite films were found to be composed of particles through the observation of secondary electron images. A decrease in particle size was observed with an increase in content of TiO$_2$ NPs in the film from 1.45 to 2.72 wt%. XRD spectrum of electroplated gold, TiO$_2$ NPs, and Au-TiO$_2$ composite films were measured to confirm the crystal structure of composite films. The primary characteristic peak of P 25 TiO$_2$ NPs at $2\theta = 25.1^\circ$ (corresponding to characteristic peak of (101) plane, anatase phase) was also observed in spectrum of Au-TiO$_2$ composite films, which confirm the existence of TiO$_2$ NPs in the deposits. Broaden characteristic peaks of the Au-TiO$_2$ composite film indicated grain refinement caused by co-deposition with the TiO$_2$ NPs. Improvement of the mechanical properties was verified from the micro Vickers hardness measurement and micro-compression tests. The Vickers hardness increased from 135 HV (pure gold) to 207 HV (2.72 wt% TiO$_2$) and the Yield strength increase from 0.44 GPa (pure gold) to 0.84 GPa (2.72 wt% TiO$_2$). The results demonstrated the significant enhancement of mechanical strength by introducing TiO$_2$ NPs into the gold matrix.

TEM Investigation of Local Mechanical Behavior in Nanocarbon-Aluminum Composites Made by the Electrocharging Assisted Process

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Novel nanocarbon-metal composites called “covetics” have the potential to significantly improve upon the mechanical and electrical properties of established metals and alloys, including Al, Cu and Ag. When a stir-cast Al melt containing a C source is subjected to electric current above a threshold value, carbon atoms are ionized, causing nanoscale graphitic ribbons and chains to form and become incorporated within the resulting Al lattice. Greater understanding of the atomic-scale behavior of covetics is essential to improve desirable properties of Al alloys, and by extension their performance in aerospace, structural, and power transmission applications.

This work explores the relationship between the structure of nanocarbon-Al composites and their local mechanical and electrical properties. We characterize nanocarbon-Al interfaces in covetics using Raman spectroscopy, conductive AFM and nano-indentation, and TEM. AFM modulus mapping reveals areas of locally stiffer microstructure. All characterization is performed within a few µm of a chosen region of interest as guided by fiducial marks milled using a dual focused ion beam (FIB)/SEM. The FIB is also used to prepare TEM specimens from the region of interest for analysis of the dislocation structure. Dislocation densities on the order of $10^{10}$ cm$^{-2}$ are observed along with sub-grain misorientations of 2–3 degrees. Through close inspection of features identified by surface characterization techniques, we glean information about the role of nanocarbon phases on the mechanical and electrical performance of covetics.

Composition analysis is obtained by electron energy loss spectroscopy (EELS) in TEM as well as X-ray photoelectron spectroscopy (XPS). Raman and EELS spectrum images analyzed by nonlinear fitting and machine learning techniques reveal increased ordering of nanocrystalline carbon embedded within the Al lattice. The degree of ordering is found to depend on the applied electric current, with greater exposure corresponding to greater graphitic order as indicated by Raman G and D peak intensities and shifts. Further evidence of $sp^2$ carbon bonding and Al-C bonding is seen by EELS and XPS. Preliminary results indicate directionality in the microstructure potentially coordinated with applied current direction, which will be investigated for correlation with highly ordered graphitic features. The relationship between nanocarbon incorporation and grain growth behavior will also be explored.

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Multiphase Nano-Ductile Cast Iron with Super Wear Resistance

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Ductile cast iron (DCI) is becoming an increasingly important engineering material due to its remarkable strength, ductility, wear resistance and low production cost. However, the industrial heavy-loading components, like gears
and bearings, require a highly improved wear resistance of DCIs. A new austempering process is developed in a commercial unalloyed DCI, which comprises the following heat treatment cycle: austenitizing at 900 degrees Celsius for 30min, rapidly quenching into a patented water-based liquid at 60 degrees Celsius isothermally holding at 190 degrees Celsius (slightly lower than the starting temperature of martensite formation of DCI matrix) for 8h and air cooling. A multiphase matrix consisting of lenticular prior martensite (PM), bainitic ferrite (BF), retained austenite (RA) and a nano-scaled super bainite ((BF+RA) nano) is produced. It is shown from the pin-on-ring wear test that a super wear resistance under the load range from 20 to 500N during dry sliding is mainly due to the synergistic strengthening between multiple phases and nodular graphite. In the initial stage of wear, the main mechanism is adhesive due to the strip-off and breaking effect of graphite. In the later stage, the more martensite can be induced from (BF+RA) nano and RA through a TRIP effect with increasing the normal load, which is attributed to the higher wear resistance. The result shows a reasonable value of wear performance, which recommends the designed nanostructured multiphase DCI for more extensive application prospects.

MS03.03.09
Micromechanical Studies of Hypereutectic Al-20Si Alloy Heterogeneous Structure by Laser Surface Remelting
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Heterogeneous metallic materials with multimodal grain size distribution of constituent grains and phases show significant improvements in ductility at yield strength comparable to their nanocrystalline counterparts. However, the fundamental mechanisms for the increased plasticity were not well understood. Model system heterogeneous hypereutectic Al-20Si with µm-size Al coarse grains (CGs) embedded in nm-size Al-Si eutectic ultrafine grains (CGs) was fabricated by laser surface remelting (LSR). In this report, the mechanical properties of the LSR heterogeneous Al-20Si were studied. Hardness testing and micropillar compression reveal different mechanical properties for as-cast Al-12Si eutectic and LSR heterogeneous Al-20Si. In addition, the hardness increases as the fraction of nanoscale Al-Si eutectic UFGs increase. In-situ SEM and in-situ TEM further reveal the deformation behavior of micropillars and nanopillars. The different mechanical properties and in-situ observations of LSR heterogeneous Al-20Si may provide an explanation to the enhanced plasticity.

MS03.03.10
Structural and Mechanical Properties of Nanocomposites Formed by Deposition of Metals in Porous Silicon
Vitaly Bondarenko; Belarusian State University of Informatics and Radioelectronics, Belarus

Silicon is a main semiconductor material used for fabricating different devices and systems including but not limited to integrated circuits, microelectromechanical systems and various sensors. Physical properties of silicon are very well-studied and scientists have almost exhausted the possibilities of changing these properties by traditional methods based on implantation and diffusion of appropriate chemical elements in silicon. In this regard, there is a great interest in finding new methods for creating silicon-based composites exhibiting properties that silicon does not have. Such materials have been identified as a new solution for a significant expansion of the functional abilities of silicon.

This work is aimed at developing a simple and efficient method for the synthesis of nanocomposite materials that can be easily integrated with silicon wafers [1]. Our approach consists in formation of pore channels in a silicon wafer followed by deposition of different metals, which impart new functional properties to silicon. Research of mechanical properties of nanocomposites based on porous silicon is very important because these new materials (consisting of silicon skeleton and metals) are subjected to different chemical and thermal treatments at extreme conditions during fabrication of endpoint device or system.

Ferromagnetic metals (Ni, Co and Fe) were introduced into the pore channels to create new silicon-based materials demonstrating unique magnetic properties. To provide the luminescence, rare-earth metals and ZnO were deposited in porous silicon. Nanoparticles of noble metals were formed on the surface of silicon skeleton to ensure plasmonic properties.

Mechanical and structural characteristics of nanocomposite materials based on porous silicon and metals were investigated together with their magnetic and optical features. The most outstanding results are presented and discussed in this work.

**MS03.03.11**  
Characterization of Sn-Bi-Graphene Oxide Nanocrystalline Electrodeposited Coatings to Establish Microstructure-Property Correlation  
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Sn-Bi alloy provides a low melting, non-hazardous and feasible alternate to the conventional Sn-Pb solder alloys for circuit packaging and interconnects. In this work, Sn-Bi (Bi 27 wt.%) coating with varying concentrations of graphene oxide (GO) was electrodeposited over mild steel substrate. Microstructure-corrosion property correlation in SnBi-GO composite coatings was then investigated as a function of GO content. All the coatings exhibited compact and crack-free morphology with GO sheets embedded within the matrix. XRD analysis of SnBi-GO coatings revealed the formation of a two-phase matrix containing Sn-rich and Bi-rich phases. Tafel polarization measurements and electrochemical impedance spectroscopy (EIS) test results revealed that the corrosion rate of the coatings was sensitive to the amount of GO in the coating. The corrosion rate decreased with initial additions of GO to reach a minimum before increasing for higher GO additions. This indicated towards the presence of an optimum with respect to the amount of GO for achieving highest corrosion resistance performance. Microstructural characterization conducted using the electron back scatter diffraction (EBSD) technique correlated the observed corrosion behaviour with the relative fraction of the low and high angle grain boundaries present within the coating matrix. It was observed that the coating with highest corrosion resistance performance contained maximum fraction of low energy low angle grain boundaries. Transmission electron microscopy based analysis revealed that the addition of GO led to enrichment of Sn rich phase and dissolution of more Sn in Bi phase. TEM, EBSD and zeta potential studies were used to correlate the fraction of LAGBs with the amount and distribution of Bi in the matrix and the corrosion resistance performance of the Sn-Bi-GO coatings.

**MS03.03.12**  
Electrodeposition of Au-Cu Alloy Micro-Cantilevers and the Young’s Modulus by Resonance Frequency Method  
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Gold materials are commonly applied in electronic devices because of the superior corrosion resistance, electric conductivity, and chemical stability [1]. Recently, micro-electro-mechanical systems (MEMS) inertial sensors utilizing gold materials in the main components are reported to have 1000 times higher sensitivity than conventional MEMS inertial sensors [2,3], which is mostly because of the high mass density. For application of gold-based materials in next generation MEMS devices, further strengthening is needed to ensure high structure stability. Regarding strengthening of gold materials, grain boundary strengthening and solid solution strengthening mechanisms can be applied simultaneously by alloy electrodeposition process [4], which the yield stress reached 1.15 GPa when the grain size was refined to 5.3 nm with the copper concentration at 12.3 wt%. On the other hand, Young’s modulus of the high strength Au-Cu alloys is also needed in design of MEMS components, such as the micro-scale spring in MEMS inertial sensors. In this study, Young’s moduli of micro-cantilevers composed of the Au-Cu alloy are measured by a non-destructive resonance frequency method [5].

The Au-Cu alloy micro-cantilevers were fabricated by electrodeposition and lithography. The Ti adhesion layer and the Au seed layer were deposited by sputtering, and the layer thicknesses were both at 100 nm. The Au-Cu electrolyte used in this work was a commercially available electrolyte provided by MATEX Co. Japan, which contained 17.3 g/L of X3Au(SO3)2 (X = Na, K), 1.26 g/L of CuSO4, and EDTA as the additive with pH at 7.5. The electrodeposition was carried out at 50 °C, and the current density was varied from 0.5 to 2 mA/cm². A piece of Pt plate was used as the anode. Design-length of the micro-cantilever was varied from 50 ~ 1000 μm, and design-width of the micro-cantilever was ranged from 5 ~ 20 μm. Thickness of the Au-Cu alloy layer was from 2.6 ~ 4.0 μm. Composition of the films was characterized by energy dispersive x-ray equipped in a scanning electron microscope. Young’s moduli of the Au-Cu alloy micro-cantilevers were calculated from resonance frequencies of the micro-cantilevers. The resonance frequencies were experimentally obtained as shown in the following. First, a voltage pulse (amplitude: 10V, pulse width: 100μs) was applied between the cantilever and a fixed electrode to initiate free vibration mode. Next, a laser doppler vibrometer was used to measure displacements of tip of the cantilever. Finally, the resonant frequency was obtained from a FFT (fast Fourier transform) analyzer.

Surface conditions of Au-Cu alloy micro-cantilevers produced at a current density ranged from 0.5 to 2 mA/cm² were all uniform and smooth. The Cu content increased from 1.40 to 4.03 wt% as the current density increased from
0.5 to 2 mA/cm², which is because standard reduction potential of Cu is more negative than that of Au, and an increase in the current density leads to a more negative applied potential. Young’s modulus of a micro-cantilever composed of 98.3 % Au with the length at 700 μm, the width 20 μm, and the thickness at 3.95 μm was 80.9 GPa. The value is close to that of pure gold (79 GPa) and much lower than that of pure copper (117 GPa). On the other hand, no obvious trend was observed when the width changed from 10 to 20.

References

MS03.03.13
Fabrication of Multifunctional Nanostructured Superhydrophobic Surface on Aluminium Alloy by Simple Hot Water Treatment
Priya Mandal, Gopinath Perumal, Abhilash Shishodia, Harpreet Singh Arora, Sajal K. Ghosh and Harpreet S. Grewal; Shiv Nadar University, India

In this work, we have reported a very simple and facile route for the fabrication of multifunctional metal surface by simple hot water treatment (HWT). Micro-nano hierarchical structures were successfully fabricated on aluminium (Al) following a mechano-thermal synthesis. A self-assembled monolayer of low surface energy material 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FOETS) was also coated on the processed samples using a vapour deposition technique. The samples fabricated with process conditions exhibited a vivid range of wettability ranging from near 0° to 165°. Apart from high static and dynamic contact angles, the processed Al surface also showed extremely low contact angle hysteresis (CAH). The developed surfaces also showed extreme chemical stability while retaining the de-wetting behaviour as assessed by the immersion tests performed with salt water. The obtained results are explained on the basis of the ability of the processed surfaces to entrapped air resulting in the formation of the Cassie state. This entrapped air work as a protective layer and lowers the contact area with the corrosive media. These surfaces are thermally stable to a wide range of temperature from -25° to 200°C and exhibit excellent self-cleaning property. Our work introduces a simple strategy to fabricate multifunctional aluminium surface on a large scale which can be easily extended to other materials.

MS03.03.15
Effect of Post-Deformation Annealing on the Microstructure and Micro-Mechanical Behavior of Zn-Mg Hybrids Processed by High-Pressure Torsion
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Heterostructured metals have attracted increasing interest because of their unique capability to overcome the strength-ductility tradeoff typically observed in engineering materials. Here, a new strategy for synthesizing heterostructured Zn-Mg hybrids is proposed using quasi-constrained high-pressure torsion (HPT) under an applied pressure of 6 GPa and a rotational speed of 1 rpm up to 30 turns, followed by a post-deformation annealing (PDA) treatment at 200 °C for 1h. Experimental results indicate a transition from a relatively homogenous nanograined structure of ~ 100-200 nm with an even distribution of Mg₂Zn₁₁ and MgZn₂ nanoscale intermetallic precipitates after 30 turns HPT, to a heterogeneous microstructure consisting of a bimodal grain size distribution with the nanosized intermetallics segregated in Mg-rich grains upon subsequent PDA. The microstructural evolution during HPT and PDA was characterized through SEM, XRD and TEM/STEM. The resulting micro-mechanical behavior was investigated using Vickers hardness and nanoindentation testing, and it was concluded that PDA led to a simultaneous increase of hardness and strain rate sensitivity. Close inspection of the strain hardening capability revealed that Zn-Mg HPT-processed hybrids followed a three-regime behavior during plastic deformation. This mechanical response is suggested due to the activation of multiple strengthening mechanisms during HPT and subsequent PDA, including grain refinement, in-situ precipitation, and back-stress strengthening associated with geometrically necessary dislocations. Moreover, the synergistic effect of PDA in this strategy can be further extended to the fabrication of other metal hybrids, paving the way to the design of novel materials with attractive
properties for task-specific applications. In particular, the understanding gained on heterostructured Zn-Mg hybrids is intended to aid the development of Zn-based materials able to satisfy the demanding mechanical requirements of absorbable medical implant devices.

**MS03.03.16**

**Ultra-High Strength and Plasticity Mediated by Partial Dislocations and Defect Networks in Metallic Multilayers**

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Deformation mechanisms governing the strength of nanostructured metallic multilayers have been studied extensively for various applications. In general, size effect is the most effective way to tailor the mechanical strength of multilayers. Here we report that three Cu/Co multilayer systems with identical layer thickness but different types of layer interfaces exhibit drastically different mechanical behavior. *In situ* micropillar compression tests inside a scanning electron microscope show that coherent FCC (100) and (110) Cu/Co multilayer systems have low yield strength of about 600 MPa, and prominent shear instability. In contrast, the incoherent Cu/ HCP Co multilayers show much greater yield strength, exceeding 2.4 GPa, and significant plasticity manifested by a cap on the deformed pillar. Molecular dynamics simulations reveal an unexpected interplay between pre-existing twin boundaries in Cu, stacking faults in HCP Co, and incoherent layer interfaces, which leads to partial dislocation dominated high strength, and outstanding plasticity. This study provides fresh insights for the design of strong, deformable nanocomposites by using a defect network consisting of twin boundaries, stacking faults and layer interfaces.

**MS03.03.17**

**Bioinspired Metal-Coordinate Mineralization: Effective Metal-Binding Pathway for Mechanical Reinforcement of Organic-Inorganic Hybrid Materials and for Future Hard Tissue Engineering Application**

Sungjin Kim, Abigail Regitsky, Jake Song, Gareth McKinley and Niels Holten-Andersen; Massachusetts Institute of Technology, United States

Biology has evolved to recruit metal ions from surroundings to produce structural materials and enhance their mechanical properties in remarkably efficient manners. One such way is to reinforce the soft matrix with the strong metal-binding interaction utilizing metal-affinitive organic ligands (e.g., mussel holdfast, marine worm jaws) and another is to go through the biomineralization of the recruited metal ions to produce stiff bioinorganic components (e.g., chiton teeth, nacre, bones). Herein, using metal-binding chemistry inspired by mussels holdfast, we showcase the control and combination of both pathways - the macromolecular crosslinking and mineralization for reinforcing soft matter mechanics and for producing high-value organic-inorganic nanocomposite materials towards potential hard tissue engineering application. First, we introduce the highly efficient mechanical reinforcement of hydrogel network via *in situ* mineralization of the metals (with very small amount: < 0.1 vol %) localized at the monodisperse metal-coordinate crosslinking sites. As such, the viscoelastic behavior of the hydrogel could be dramatically tuned from liquid-like to solid-like with increased modulus and strength. Furthermore, we demonstrate that this metal-binding mechanism can work universally as a mineralization controller for inducing amorphous or metastable calcium carbonates and their effective transition to hydroxyapatite (i.e., bone minerals) nanocrystals. The ability of bioinspired metal-binding chemistry controlling the mineralization thus suggests the efficient material design/processing strategy for reinforcing materials and for applying to the practical biomedical technology.

**MS03.03.18**

**Quantitative Analysis of Retarded Sintering Behavior in Ni Alloy Thin Film for MLCC Internal Electrode**

Youngran Jung\(^1\), Wonhyo Joo\(^1\), Minjeong Choi\(^1\), Cheol Kim\(^1\), Kyungryul Lee\(^2\) and Young-chang Joo\(^1\); \(^1\)Seoul National University, Korea (the Republic of); \(^2\)Samsung Electro-Mechanics, Co., Korea (the Republic of)

Downsizing trend of Multi-Layer Ceramic Capacitor (MLCC) required the structure of alternating stacking layers of dielectric and electrode in MLCC to be as thin as possible to microscale. For a thinner layer, smaller nanoparticles for dielectric and Ni paste for electrode are used. One of the major issue caused by the smaller particle size is the enlarged sintering behavior difference between the ceramic and metal layer of MLCC during the high-temperature sintering process in the manufacturing process. Eventually, the difference in sintering behavior between the layers causes fracture of the device. Therefore, suggesting a Ni- alloy material for the electrode layer for sintering process delay and *in-situ* tool to analyze the sintering behavior of thin film is in demand. In this study, Ni alloy films were
fabricated and the sintering behaviors of Ni nanoparticles in thin films were quantitatively analyzed by optical laser stress analysis. First, several metal precursors were selected using the phase diagram and surface energy to delay the sintering. The Ni paste and metal precursors were mixed and fabricated to thin films by spin coating. Then, the fabricated films were heated in the closed chamber. During this process, in situ stress curve versus temperature graph was obtained using the optical laser system. The inflection points for Ni films were analyzed thoroughly. The microstructure analysis was carried out for the film samples quenched above and below the inflection point temperature. Therefore, specific inflection point resulted to be significantly related to the sintering process. In addition, retardation of sintering behavior was observed from the microstructure analysis of Ni alloy films. Lastly, for a deeper understanding of sintering behavior, crystal structure analysis for Ni alloy films was performed to identify delayed sintering mechanism. This study suggests an in-situ quantitative analysis method for sintering behavior and new material to reduce sintering behavior gap between the ceramic and metal layer of MLCC.

**MS03.03.19**

**Atomistic Simulation of the Strain Rate-Dependent Ductility in Metallic Glass Nanowires**  
Yanming Zhang\(^1\), Penghui Cao\(^2\), Liping Huang\(^1\) and Yunfeng Shi\(^1\); \(^1\)Rensselaer Polytechnic Institute, United States; \(^2\)University of California, Irvine, United States

Metallic glasses are very promising structural materials and their mechanical properties as well as deformation mechanism have been extensively investigated from both simulations and experiments. However, a complete understanding of the strain rate effect on mechanical response of metallic glasses is absent given the disparity in time scales between classical molecular dynamics simulations (MD) and experiments. Using accelerated MD simulations, we aim to, for the first time, report the mechanical properties of metallic glass nanowires ranging from 10^-8 s^-1 (classical MD simulations scale) to 10^-2 s^-1 (experimental scale). Specifically, embrittlement and reduction of failure strength is observed as the applied strain rate reduces, accompanied by a transition from shear fracture to cleavage. We suggest that the reduction of ductility in metallic glass nanowires as the applied strain rate decreases is due to the gradual relaxation of liquid-like structure. Finally, the metallic glasses quenched from more fragile liquids will be subjected to slow-rate mechanical tests, where the correlation between strain rate sensitivity of ductility and fragility will be established.

**MS03.03.20**

**Microstructure Design for Ductile Glass Composites Using Exclusively Brittle Metallic Glasses**  
Yanming Zhang\(^1\), Ying Zhang\(^1\), Binghui Deng\(^1\), Huijuan Zhao\(^2\), Mohammed Alnaggar\(^1\), Liping Huang\(^1\) and Yunfeng Shi\(^1\); \(^1\)Rensselaer Polytechnic Institute, United States; \(^2\)Clemson University, United States

Metallic glasses are promising structural materials owing to high strength, excellent wear and corrosion resistance. Brittleness of bulk metallic glass is the main drawback researchers have been trying to improve over the past decade. So far, compositing ductile crystalline phases is the major effective means of ductility enhancement in brittle metallic glass, which not only limits the materials selection for composites design but usually results in substantial decrease of strength in metallic glasses. Herein, using molecular dynamics simulations, we incorporated two brittle metallic phases with different stiffness and surprisingly obtained strong, ductile and work hardenable composites. Compared to monolithic metallic glasses (failure strain is ~7%), significantly enhanced ductility (over 80% in terms of failure strain) has been achieved for brittle-brittle composites. To understand the toughening mechanism, we have identified two figures of merits to characterize the flexibility of the strong glassy filament, and the propensity for crack deflection, respectively. Furthermore, we have constructed a ductility map using the above two figures of merits, which agrees with our MD simulation of over five hundred different composite designs. The composite design principles delineated here is likely to be applicable to other material systems beyond metallic glass system.

**MS03.03.22**

**The Advantages in Real-Time Imaging of Mechanical Tests (Including In Situ Nano-Mechanics)**  
Noa Lachman; Tel Aviv University, Israel

Composites are a large and versatile group, incorporating various materials such as metals, ceramics and polymers in multiple scales from the macro to the nano. As such, composites can be tailored to highly specialized applications such as biomed, sensors, energy storage and aerospace. Such tailoring requires understanding of the different
mechanisms dominant at different length-scales, as well as correlating the composite morphology and said mechanisms – correlation that can work both ways. This correlation calls for means of observation at the desired scale in real-time stimulation of the material – be it mechanical, electrical or other types of stimulation.

In this talk, the need for real-time imaging of mechanical tests will be explained using various length-scale case studies. These case studies will include digital image correlation (DIC) used to analyze standard tensile tests, micro-mechanics under scanning electron microscope (SEM), and nano-mechanics under transmission electron microscope (TEM). Discussion will include the additional data acquired from real-time imaging at such scales and its importance, as well as possible future applications for other nanoscale materials. The methods presented in these case-studies can therefore provide deeper understanding of composite materials behavior, which can be used to improve planning and designing of composites as multifunctional materials.

MS03.03.23
Fabrication and Properties of Selected High-Strength Composite Conductors Ke Han, Rongmei Niu and Vince Toplosky; Florida State Univ, United States

Nanostructured composites, which have been successfully used in high field magnets, reach their most desirable strength level when their interface spacing is below 100 nanometers. The usual fabrication methods for these composites are severe plastic deformation, which refines interface spacing and create anisotropy. The fabrication may also introduce shear-bands into the microstructure. Investigating both anisotropy and shear-bands helps to understand the deformation mechanisms of these composites under external force. The goal of our research is to relate microstructural anisotropy to the mechanical and physical properties of these composites in various geometries. Our current work is shedding new light on the detailed correlation between microstructure and properties. This presentation describes microstructure in different orientations, with emphasis on the impact of anisotropy and shear-band on properties.

This work was performed at the National High Magnetic Field Laboratory, which is supported by the National Science Foundation Cooperative Agreement No. DMR-1644779 and the State of Florida

MS03.03.24
The Role of Electron Beam Induced Heating During 3D Nanoprinting Eva Mutunga1,2, Robert Winkler3, Jurgen Sattelkow4, Philip Rack1,2, Harald Plank3,4 and Jason D. Fowlkes2,1; 1University of Tennessee, Knoxville, United States; 2Oak Ridge National Laboratory, United States; 3Graz University of Technology, Austria; 4Graz Centre for Electron Microscopy, Austria

Focused electron beam induced deposition (FEBID) is a direct-write technique where an electron beam dissociates surface bound precursor molecules at the focal point of the electron beam. FEBID has become a more viable 3D nanoprinting tool due to the sophisticated applications shown recently, such as FEBID simulation [1] that predicts and controls the growth of 3D nanostructures by modeling the dynamic interaction of the electron beam and the precursor molecules, and its accompanying 3D CAD program (3BID) [2]. The ability to fabricate functional deposits such as plasmonic 3D nanostructures [3] and, scaffolds for 3D magnetic nanowires [4] with high degrees of freedom and precision using 3D FEBID show it is a promising additive nanomanufacturing tool. Unfortunately, distortions such as deflections in overhang 3D nanowires where linear growth is prescribed limit the reproduction of 3D FEBID designs. The 3BID program offers a tool to correct the distortions, but these are empirical. A pattern generating algorithm [5] released recently adjusts for proximity effects and compensates for height-dependent precursor coverage. The results show quite good congruence between the prescribed and deposited 3D nanostructures. Here, however, we quantify the mechanism that causes these distortions, paving the way to a more quantitative correction strategy.

We will show a combination of experiments, models, and simulations that reveal beam-induced heating as the culprit that constrains the replication of 3D FEBID designs. The electron beam facilitating deposition during nanowire growth also causes Joule heating at the beam interaction region (BIR). The BIR temperature increases gradually during growth as nanowire elongation impedes heat flow. Heat transfer from extended surfaces is used to model the heat flow from the BIR, through the nanowire to the substrate. The temperature gradient in the deposit gives rise to an opposing precursor concentration gradient resulting in a deflected nanowire where otherwise a linear nanowire was specified. This vital role beam-induced heating plays in determining the final deposit shape will be discussed.
References:


**MS03.03.25**
**Additive Manufacturing of Metallic Materials—Mechanical Properties**

Prashanth Konda Gokuldoss; Tallinn University of Technology, Estonia

Laser-based powder bed fusion processes like the selective laser melting (SLM) is one of the additive manufacturing processes used to produce 3-D metal parts by selective melting of powders dictated by CAD data. Because of the high degree of freedom given by processing through additive manufacturing, it is possible to build parts with extremely complex geometries that would otherwise be difficult or impossible to produce using conventional manufacturing processes. However, until now, only conventional alloys like the AlSi10Mg, 316L, Ti6Al4V, etc. that either is developed for cast or wrought processes have been used for fabrication. Some of the alloys work well for the additive manufacturing process like the Al12Si, AlSi10Mg, because they have good fluidity and are readily weldable. Nevertheless, most of the materials fabricated by SLM show superior mechanical properties than their case counterparts. Even though superior mechanical properties were recorded, there are reports showing a premature failure of the materials (i.e.) the material fail before they achieve their maximum strength. Some of the reasons behind these premature failures will be discussed in detail.

**SESSION MS03.04: Nanocomposites I**

Session Chairs: Rainer Adelung and Horacio Espinosa

Tuesday Morning, December 3, 2019

Hynes, Level 1, Room 103

**8:30 AM *MS03.04.01**

**Hybrid Materials Based on Micro Mechanical Interlocking and Interpenetrating Composites**

Rainer Adelung; Kiel University, Germany

The demands on modern materials are highly challenging and partially contradictory. For example, materials should be strong like metals but chemically inert like soft low surface energy polymers. Another example is the need for extreme lightweight but fail-proof and high temperature stable materials. Furthermore, “intelligent” stimulus responsive materials and adaptive structures are requested. Those conflicts can be overcome by effectively combining disparate materials in composites that allow a fusing of the traditional material classes like ceramics, polymers and metals. For that purpose, in this presentation two basic concepts utilized in the functional nanomaterials group are introduced that might be employed to overcome such challenges. One is based on micromechanical interlocking at the interface, the other on interpenetrating composites with micro framework materials. In both cases, the chemistry and chemical compatibility of the materials play a negligible role, the selection of the constituents can be done by focussing exclusively on the material properties. This allows a targeted tuning of the micro-structure and enables the realization of atypical material properties like flexibility in ceramics. Furthermore, self reporting and actuating concepts can be added to create materials that replace complex micro-systems. Examples will be given including mechanical interlocking as universal material connection technology.
[1,2], a versatile template framework material [3], aero materials [4, 5], as well as sensor [6], and self reporting concepts [7].


9:00 AM MS03.04.02
Geologically-Inspired Ceramics—Shedding Light on Room-Temperature Cold Sintering Matthias Haug¹, Florian Bouville² and André R. Studart¹; ¹ETH Zurich, Switzerland; ²Imperial College London, United Kingdom

In the Earth’s upper crust, dense ceramic materials can be formed at mild pressures and nearly ambient temperature. This represents a tremendous reduction in energy used for densification compared to technical ceramic processing, in which temperatures above 1'000 °C are needed to produce dense structures. Inspired by this geological phenomenon, we demonstrated a new method called room-temperature cold sintering. In this process, small amounts of water and pressures up to 500 MPa are utilized to produce calcium carbonate compacts reaching 85 % relative density within only 30 min. While the densification process in geological carbonates is presumably based on dissolution – precipitation of the inorganic material and the diffusion through the thin water film present on the surface of the particles, the mechanisms underlying the densification of synthetic carbonate nanoparticles remain unknown. From the several compositions that have been proven to be compatible with cold sintering, carbonates are one of the very few classes of material that can be densified at room temperature. To better understand this unique process, we developed a methodology to probe the time-dependent structure of these carbonates at multiple length scales during water-assisted densification. We combined the observation of in-situ compaction behavior of calcium carbonate particles with high-energy X-Ray tomography to small-scale creep experiment using instrumented indentation. The synchrotron tomography experiments allowed us to directly observe the deformation of the particles in real-time and thus discriminate between mechanisms involving deformation or simple rearrangement of the particles. For a quantitative analysis, we used digital volume correlation to calculate local deformations and strains within the sample. Indentation was utilized to further probe the mechanical behavior of the sample from the micron to the nanometric length scale, allowing us to pin point the influence of the water on the room-temperature sintering process. Combined the tomography and indentation experiments provide a powerful multiscale temporal platform to shed light on the main factors that drives the room-temperature sintering of nanopowders under pressure.

9:15 AM MS03.04.03
Shape Memory Effect in Single-Crystalline Micro-Sized ZrHfO2-Based Ceramics Haolu Zhang¹, Justin Jetter², Hanlin Gu³, Xian Chen⁴, Manfred Wuttig⁵, Julia R. Greer¹, Richard D. James³ and Eckhard Quandt²; ¹California Institute of Technology, United States; ²University of Kiel, Germany; ³University of Minnesota, United States; ⁴The Hong Kong University of Science and Technology, China; ⁵University of Maryland, United States

Martensitic transformations, which give rise to the interesting properties of Shape Memory Alloys (SMA), have long been studied in metals and alloys, but understanding and emergence of their presence in metal oxides have been limited. Known for their transformation toughening mechanism, chemical composition of zirconia-based ceramics can be altered to increase the interphase compatibility between its high temperature phase (austenite) and low temperature phase (martensite), which suggests possible emergence of Shape Memory Effects (SME) in these ceramics. We synthesized samples with weight percentage \( x \) of ZrHfO₂ ranging from 0.6 to 0.9 by pressing and sintering oxide powders. Transmission Electron Microscopy (TEM) and Electron Backscattering Diffraction (EBSD) characterization of these synthesized ceramics reveal finely twinned microstructure within single 5µm grains, with no visible defects in the composition \( x=0.735 \), which aligns with theoretical prediction. We performed uniaxial compression experiments on single-crystalline cylindrical pillars with diameters of 200nm to 2µm that were carved out of individual 5um average grains using Focused Ion Beam (FIB). These nanomechanical experiments
revealed that the stress-strain response was elastic plastic with favored deformation mechanism through martensite rearrangement, and that the yield strengths follow a smaller is stronger power-law relationship, similar to the ubiquitously observed size effects in metals that deform by crystallographic slip. This prominent size effect can give insight into the role of deformation twinning in ceramic plasticity. We further demonstrate the one-way shape memory effect by heating the deformed samples to above their phase transformation temperatures to recover their original shape and reveal a strong dependence of shape recovery on chemical composition.

9:30 AM MS03.04.04
Flexible and Extremely Scratch-Resistant Hard Coating Materials from Molecular Necklace-Like Cross-Linkers
Jiae Seo, Sung Wook Moon, Byoung-ho Choi and Ji-Hun Seo; Korea University, Korea (the Republic of)

A flexible hard coating material displaying scratch resistance and flexibility was developed through the design of organic-inorganic hybrid coatings using alkoxysilyl-functionalized polyrotaxane cross-linkers (PRX_Si1). PRX_Si1 has a unique structure like a molecular necklace that can form organic-inorganic cross-linking points and can provide large molecular movement. Hybrid cross-linking points and dynamic molecular motion have been assumed to simultaneously increase scratch resistance and flexibility. To confirm this hypothesis, the crystalline structure and mechanical properties of PRX_Si1-based hard coating materials were analyzed by transmission electron microscopy, small angle X-ray diffraction, tensile, pencil hardness and scratch tests. Finally, the hard coating material based on PRX_Si1 was able to form homogeneously dispersed nanoscale siloxane crystalline domains, and the deformation at the breakpoint was three times higher than the commercial hard coating material so that even after 5,000 folding test runs, Did not occur. In addition, this material has very high pencil hardness (9H) and scratch resistance.

9:45 AM MS03.04.05
Electrochemically Switchable Elasticity of Hybrid Nanocomposites Based on Nanoporous Gold and Conductive Polymer
Jie Li1, Jürgen Markmann1,2, Jörg Weißmüller1,2 and Nadia Mameka1; 1Materials Mechanics, Helmholtz-Zentrum Geesthacht, Germany; 2Hamburg University of Technology, Germany

Dealloying derived nanoporous gold (NPG), a 3D bicontinuous network of nanoscaled ligaments and pores with large surface area, exhibits a plethora of mechanical and functional properties that can be precisely controlled by electric signals in electrolyte environments. Among them, actuation [1], switchable elastic modulus [2], Poisson’s ratio [3] and strength [4,5] are of special interest to understand interfacial phenomena at the nanoscale and to design novel materials with an adaptable mechanical behavior.

Recently, the actuation performance of NPG has been significantly improved by decorating the gold ligaments with a conducting polymer polypyrrole (PPy) film [6]. The enhanced length change of the gold skeleton was promoted by actuation of PPy upon ion exchanges in the polymer layer with surrounding electrolyte. The elastic modulus behavior of the NPG-PPy hybrid, which is also crucial for the functionality, has not been studied yet. In this work, a uniform PPy film with various thicknesses was formed on mm-size NPG by electropolymerization without blocking the original nanopores. The elastic moduli of the resulting NPG-PPy nanocomposites were monitored in situ during potential cycling in aqueous electrolytes in a dynamic mechanical analyzer (DMA). Remarkably, the in situ DMA experiments reveal a non-monotonic modulus response as a function of the potential during charging-discharging processes, as opposed to a nearly linear variation of the macroscopic length. Moreover, the modulus variation amplitude is enlarged for the thicker PPy films. In this contribution, we will discuss the origin of the stiffness behavior and elucidate a role of the Au/PPy interface in the unusual elastic modulus response of the hybrid material.


10:00 AM BREAK

10:30 AM *MS03.04.06
Bio-Inspired Polymer Toughening of Graphene Oxide
Horacio Espinosa, Hoang D. Nguyen, Xu Zhang, Lily Mao, Rafael Soler-Crespo, SonBinh Nguyen and Jiaxing Huang; Northwestern University, United States
Two-dimensional materials in mono- or few-layer forms have been used in the design of novel sensors, filtration membranes, and wearable electronic devices. In their multilayer form, nanocomposites are engineered to exhibit unprecedented combinations of specific stiffness and strength. However, the intrinsic brittle behavior of these atomically thin 2D materials, and their associated risk for catastrophic failure, has thus far precluded their adoption in practical applications requiring superior mechanical properties.

In the area of nanocomposites (structural materials), lightweight 2D materials are addressing high demand for safer and more energy efficient transportation systems, e.g., in automotive and aeronautical applications. Similarly, the next generation of protective body armor has inspired the search for lightweight materials with exceptional piercing resistance. Composites based on two-dimensional materials appear to be excellent candidates to address these societal needs. Unfortunately, the presence of “architectural defects” such as voids and wrinkles found in previously produced 2D materials, in thin film form, resulted in somewhat limited mechanical performance. This has precluded fundamental understanding of their full potential and their robust implementation in the aforementioned engineering applications.

A strategy to gain fundamental understanding of the potential of 2D materials, in their few layer or structural material forms, is to investigate 2D material specimens with tailored chemistries and controlled architectures in the form of a few layers. Here we present a combined experimental and computational approach, based on graphene oxide (GO) and poly-vinyl alcohol (PVA), as a model material system, to investigate surface chemistry effects and pathways for improved ductility and fracture of 2D materials. We will show that a larger-scale “extrinsic” toughening mechanism can be incorporated into GO monolayers through surface modification by an ultrathin strongly interacting polymer layer.

In this presentation, we will discuss nanoscale experiments that demonstrate such a crack-bridging and toughening behavior for GO-derived materials. We will show that by incorporating an atomically thin layer of a hydrogen bond-forming polymer, onto the surface of a GO nanosheet, the toughness of the resulting GO-Polymer nanolaminates is increased up to 300% that of GO monolayers, making them highly attractive as scalable building blocks for the next generation of engineered materials. Multiscale characterization reveals the presence of a hydrogen-bonding network on the surface of GO that can be exploited to reinforce its mechanical integrity via polymer adhesion to the oxidized domains in GO. This pairing results in a synergistic toughening mechanism in which the polymer chains effectively bridge a developing crack and allow the nanolaminate to exhibit superior piercing resistance, as verified by combined nanomechanical experimental and computational studies. As cracks develop, clusters of hydrogen bonds between GO and the polymer chains break and reform, which permits the polymer to act as a self-healing load-bearing element. Such a deformation mechanism provides key insight not only for the design of 2D materials-based nanocomposites but also for the engineering of more reliable sensors, filtration membranes, and wearable electronics devices.
A Three-Dimensional Unit Cell Model for the Analysis of Thermal Residual Stresses in Polymer Composites Reinforced with Wavy Carbon Nanotubes  

Yunfa Zhang, Andrew Johnston, Ali Yousefpour, Jingwen Guan, Benoit Simard and Christopher Kingston; National Research Council Canada, Canada

Similar to conventional carbon and glass fibre reinforced polymer composites, high temperature curing is mostly inevitable in the fabrication of polymer nanocomposites reinforced with carbon nanotubes. This paper presents a numerical approach to predict the thermal residual stresses in polymer nanocomposites reinforced with a periodic array of wavy carbon nanotubes. A novel unit cell model is established to accurately account for the waviness of the nanotubes. Periodic boundary conditions are rigorously determined for the three dimensional unit cell with a pair of curved surfaces. To validate the model, effective elastic constants of composites with compliant matrices are evaluated using the finite element method, and the results are compared with those in literature. Notably, orthotropic elastic constants are correctly predicted for the unit cell configuration which has only two planes of symmetry manifested explicitly in the model. By employing material properties of the two constituents, the thermal residual stresses induced by high temperature curing and cooling-down are examined for an epoxy/wavy-nanotube composite. In particular, temperature-dependent material properties are used for the matrix to better capture its response within the wide temperature range associated with the curing and cooling-down process. Numerical results show that the waviness has a significant influence on the distribution of the local residual stresses. Finally, it is demonstrated that the curing and cooling-down process tends to increase the waviness of the nanotube.

Embracing Instability—Hierarchical Nanoengineered Composites with Buckling-Densified Carbon Nanotube Arrays Reinforcement  

Xinchen Ni, Luiz Acauan and Brian L. Wardle; Massachusetts Institute of Technology, United States

Nanofiber (NF) arrays, such as aligned carbon nanotubes, with exceptional intrinsic and scale-dependent properties, along with their easy tunability, have enabled applications in diverse areas including aerospace, energy, and biomedicine. Here, we use photolithography-based patterning and mechanical buckling to form densified aligned NF arrays, which exhibit wavelike folding buckling shapes. Such hierarchical shapes are known to introduce multiscale and mixed-mode reinforcement mechanisms in nanocomposites, leading to composite strength and toughness enhancement. In this study, we introduce the buckling-densified aligned NF arrays into the resin-rich ply-ply interface of laminated carbon microfiber composites as a through-thickness reinforcement. Short-beam shear (SBS) and double-edge notched tension (DENT) tests are performed to assess the effect of buckling-densified aligned NF array reinforcement. The aligned NF-reinforced composites are found to have a 7% increase in SBS strength and a remarkable 25% increase in the in-plane DENT strength. Scanning electron microscope imaging and lab-based high-resolution micro-computed tomography scans of post mortem specimens reveal that the buckling-densified aligned NF arrays suppress delamination and drive the crack into the more desirable intralaminar region. The findings demonstrate great potential for harnessing instabilities to fabricate high-volume-fraction and shape-tunable NF arrays, opening avenues for uses that extend beyond composite mechanical reinforcement, such as supercapacitors, thermomechanical devices, and sensors. Future work includes developing a model that can fully predict the buckling response of aligned NF arrays as a function of pattern size, NF elastic properties, and NF/substrate adhesion, as well as conducting 4D in situ mechanical testing of the DENT configuration by using synchrotron-radiation computed-tomography to reveal the 3D progressive damage state.

Influence of Detailed Nanostructures of Organic-Inorganic Hybrid Aerogels on Their Unique Mechanical Behaviors  

Kazuki Nakanishi1,2, Kazuyoshi Kanamori1 and Ryota Ueoka1; 1Kyoto University, Japan; 2Nagoya University, Japan

SESSION MS03.05: Nanocomposites II  
Session Chairs: Peter Fratzl and Nicola Pugno  
Tuesday Afternoon, December 3, 2019  
Hynes, Level 1, Room 103

Influence of Detailed Nanostructures of Organic-Inorganic Hybrid Aerogels on Their Unique Mechanical Behaviors  

Kazuki Nakanishi1,2, Kazuyoshi Kanamori1 and Ryota Ueoka1; 1Kyoto University, Japan; 2Nagoya University, Japan
Organic-inorganic aerogels have extensively been studied to overcome the inherent poor mechanical strength (friability) of their inorganic counterparts which necessitate supercritical drying for their preparation processes. In order for the low-density wet gels to be evaporatively dried without fracture under ambient pressure conditions, the network should exhibit large reversible deformations, i.e. shrinkage and re-expansion, while enduring the stresses exerted by capillary force during the solvent removal process. So far, the authors’ group has been attempting to prepare such organic-inorganic hybrid networks with a broad spectrum of mechanical properties utilizing appropriate combinations of precursors, additives, solvents and catalysts. Approaches can be classified into three categories; (1) Methyl-modified silsesquioxane (MSQ) using tri-functional methyltrialkoxysilanes as presursor, (2) Organo-bridged siloxane networks from bis-type di- or tri-functional alkoxysilane precursors, and (3) Double-crosslinked networks by hydrolysis-polycondensation of oligomeric precursors containing pre-polymserized hydrocarbon chains connecting Si atoms in the monomeric precursor. For each system, preparation conditions have been specified for the product to give low density (0.1-0.2 g cm$^{-3}$) and transparency/translucency to visible light.

(1) Supercritically dried MSQ exhibited reversible deformation against uniaxial compression up to 80 % of the original height, suggesting the network is recoverable against isotropic deformations. The slow evaporation of nonpolar solvents such as hexane enabled one to remove the solvent under ambient pressure without causing serious cracks and fractures. A size recovery from ca. 70 % compressed (shrunk) state by the spring-back gave highly transparent, low-density xerogels in a monolithic form [1,2].

(2) Introduction of relatively short hydrocarbon chains between Si atoms resulted in the improvement of flexural strength evaluated by three-point bending tests without sacrificing other properties such as low-density and visible-light transparency. The decreased functionality of siloxane bridges further increased the range of flexural deformation reflecting in part the relaxation behavior of polymeric networks [3].

(3) Integration of longer organic crosslinks into di- or tri-functional siloxane resulted in the highest degree of dutility while minimizing brittle nature of inorganic aerogels. The ambient-dried gels could be easily cut into shapes with blade and was stable against the resorption of organic solvent into their hydrophobic pores. These unique mechanical behavior of hybrid aerogels are under analysis in more details using an electron microscope to characterize the morphological features of the network in relation to the chemical interaction among precursors, additives and solvents [4].

References

2:00 PM MS03.05.02
Behavior of Glass/Carbon Nanoengineered Hybrid Composites for Aerospace Applications under Mechanical Loading
Shashwata Chakraborty, Mohammad Uddin and Ajit D. Kelkar; North Carolina A and T State University, United States

Carbon fiber reinforced polymer composites are widely used in aerospace applications because of their high strength and stiffness properties. One of the disadvantages of using carbon fiber reinforced composites is lack of strength and stiffness in the transverse direction and that makes them vulnerable to out of plane loading situations like bird impact, lightning strikes, etc. To alleviate this problem, typically aircraft structures are designed with a sacrificial layer of fiberglass composite in conjunction with carbon fiber composites. Even though this type of hybridization has many advantages, still much research is needed to understand the interlaminar failure of glass/carbon interface under out of plane loadings. The present study investigates the effects of mechanical loading on glass/carbon hybrid nanoengineered fiber reinforced composites. Hybrid 9 layers composite laminates with a single layer of glass fiber lamina on the outer surface and 8 layers of carbon fibers lamina were fabricated using aerospace grade epoxy and vacuum assisted resin transfer molding (VARTM) technique. In-plane mechanical properties such as tensile,
flexural, impact and interlaminar shear strength (ILSS) characteristics were investigated. In addition, to improve interlaminar properties a layer of electrospun glass and carbon nanofibers are being used between glass fiber lamina and carbon fiber laminates.

2:15 PM MS03.05.03
High Volume Fraction Aligned Carbon Nanotube Carbon Matrix Nanocomposites for Next Generation Lightweight and Superhard Architectures Ashley L. Kaiser, Itai Y. Stein, Chloe Sackier and Brian L. Wardle; Massachusetts Institute of Technology, United States

Nanomaterials, such as polymer-derived pyrolytic carbons (PyCs), have great potential for next-generation lightweight structural materials due to their high mass-specific strength and stiffness. In particular, PyC matrices are most desirable for low density structural applications when they are reinforced with high strength nanowire arrays, such as aligned carbon nanotubes (A-CNTs) at high volume fractions ($V_f$), which addresses brittleness, enhances hardness, and allows tailoring of multifunctional properties. While modeling indicates that CNT-PyC nanocomposites at $V_f \sim 30\%$ could show $>300\%$ enhancements in hardness when compared to the neat PyC matrix, performing similarly to diamond and cubic boron nitride for superhard lightweight structures, it is unknown how CNT confinement at these packing densities influences the structural evolution of the PyC matrix. Therefore, a study of these effects on the formation, self-organization, and geometry evolution of the graphitic crystallites that comprise the PyC matrix of the nanocomposites is necessary. In this report, we synthesize CNT-PyC nanocomposites via the pyrolysis of CNT-phenol formaldehyde precursors to create superhard and lightweight aligned CNT-carbon matrix nanocomposites. In this study, the influence of CNT proximity interactions on the atomistic, nanoscale, and mesoscale structural evolution of PyC is determined experimentally as a function of CNT $V_f$ (up to 30%) using scanning electron microscopy, X-ray diffraction, Raman spectroscopy, and Fourier transform infrared spectroscopy to quantify the CNT-PyC matrix morphology, graphitic crystallite geometry, bonding character, and chemical structure evolution, respectively. This work identifies how high CNT confinement leads to modification of the graphitic nature of the PyC matrix, and it shows that the governing CNT-PyC interactions exist at the $< 10$ nm scale, thereby becoming increasingly significant as the inter-CNT spacing decreases below this value at $V_f \geq 20\%$. Using this approach, these results provide new insights to explain the predicted CNT-PyC hardness enhancements at high $V_f$ and enable the design and manufacture of next-generation superhard lightweight nanocomposites.

2:30 PM MS03.05.04
Sodium-Based Carbon Nanotube Synthesis for the through-Thickness Reinforcement of Advanced Filamentary Composites Richard Li, Erica F. Antunes, Andrew Liotta, Luiz Acauan, Estelle Kalfon-Cohen, Kehang Cui, Clementine Mitchell, Harden Cornwell and Brian L. Wardle; Massachusetts Institute of Technology, United States

The direct synthesis of carbon nanotube (CNT) on substrate surfaces and interfaces has been of great interest for enabling performance improvements of electronics, electrochemical energy systems, and advanced multifunctional composites among others. However, the extent of applications that may benefit from CNTs have been limited by the operational range of temperatures and substrates for traditional transition metal catalysts (Fe, Ni, and Co). Here, a new element has been discovered to catalyze CNT growth at temperatures below 400 °C using a thermal chemical vapor deposition technique: sodium. As the first alkali metal reported to catalyze CNTs, sodium enables direct and low temperature CNT growth across a wide array of substrates, including alumina fibers, polymer-coated fibers, silicon wafers, silicon nitride, titanium, and others. Aqueous solutions of common sodium-based compounds such as sodium hydroxide, sodium bicarbonate, sodium chloride, and sodium carbonate are all demonstrated to result in CNT growth on carbon fabrics using a single dipcoate step prior to CVD. Ex situ scanning electron microscopy and transmission electron microscopy analyses with energy dispersive x-ray spectroscopy as well as x-ray photoelectron spectroscopy performed on catalyst particles prior to growth and CNTs after growth confirm the identity of sodium as the active element for CNT catalysts. In addition, unlike transitional metal catalysts, Na exhibits a vanishing catalyst phenomenon in which catalyst-free CNTs can be formed during synthesis for applications that are sensitive to residual metal impurities, thus avoiding the need for post processing steps that may employ the use of harsh chemicals.

Moreover, as an exemplary application of Na-catalyzed growth, CNTs are circumferentially grown on carbon fibers
(CFs) to form “fuzzy” CFs that can be laminated into hierarchical nanoengineered polymer composites with the potential for interlaminar reinforcements and electrical conductivity increases. Previous efforts required harsh surface roughening techniques of carbon fibers to enable Fe catalyst adhesion and high temperature growths typically on the order of 800 °C, resulting in carbon fiber strength losses as much as 60%. Here, we demonstrate that carbon fibers dipcoated in NaOH solutions and subjected to CVD at 480 °C resulted in conformal CNT growth and retained microfiber strength as assessed through single fiber tests. These fuzzy CF fabrics were then infused with epoxy resin to form unidirectional fuzzy carbon fiber reinforced plastic (UD fuzzy CFRP) laminates that were trimmed into short-beam shear specimens for interlaminar shear strength (ILSS) enhancement characterization. Taken together, we present sodium as a facile and new low temperature versatile CNT growth catalyst with the potential to expand the range of substrates and applications that may benefit from direct CNT synthesis.

2:45 PM MS03.05.05
Tensile, Compressive and Tunable Large-Scale Strain Sensor Based on Carbon Nanotubes/Thermoset Foam Nanocomposites by Additive Manufacturing Chao Liu and Junjun Ding; New York State College of Ceramics at Alfred University, United States

Strain sensors are widely used as stretchable electronic, human motion detector, and health monitor due to their ability to convert large-scale mechanical deformation to the resistance change [1-3]. Forming the porous foam structure is a more promising method to build large-scale deformation strain sensor than forming the solid structure [4]. To quantitatively control the relationship between deformation and resistance change, carbon nanotubes (CNTs), with numerous surface area, are used as a component due to its good electrical conductivity [5]. Compared to traditional strain sensor manufacturing methods, material extrusion-based 3D printing (ME3DP) is a more suitable method to form viscous slurry into complex stacked models.

In this work, we fabricate a superelastic strain sensor based on CNTs/PDMS foam nanocomposites with controllable electrical properties by ME3DP. Low viscous PDMS Sylgard 184 and high viscous SE 1700 were mixed in the ratio of 3:2 for good moldability and printability of slurry. Sodium chloride (NaCl powder, 10-20 μm) was added into PDMS precursor as a sacrificial material to generate foam microstructures. Multi-walled CNTs (1 and 2 wt. % of PDMS) were added for adjustable electrical conductivity. ME3DP with a mechanically driven syringe extruder was used subsequently for the formation of 3D models. Both solid and hollow scaffolds were printed to investigate the influence of macro-voids on mechanical and electrical properties. NaCl microparticles were then removed by DI water bath for 24 hours to create porous open-celled microstructures. Based on our hypothesis, the interconnection rate of CNTs in micro-voids will affect the electrical conductivity when the structure is stretched or compressed, resulting in the different performance of the strain sensor. Further study will be focused on controlling density and size of micro-voids, the gap of macro-void scaffold structures, infill ratio of CNTs, and how these parameters affect stretchability, compressibility, and electrical conductivity.

Reference:

3:00 PM BREAK

3:30 PM *MS03.05.06
3D Printing Aerogels Marcus A. Worsley; Lawrence Livermore National Laboratory, United States

Graphene has shown the potential to significantly impact a number of different technologies. Properties such as high surface areas and electrical conductivity make it a promising material for hydrogen storage, battery, and ultra capacitor applications. One route to realizing the full potential of graphene in these energy storage applications is the assembly of three-dimensional macroscopic graphene networks that retain the properties of individual graphene sheets. However, given the low density and nanoporous structure of these graphene aerogels, they suffer from mass transport and mechanical fragility, both of which are detrimental. Here, we use additive manufacturing (AM) to 3D print graphene aerogels with improved mass transport and mechanical robustness. Using techniques such as direct
ink write and projection microstereolithography are shown as promising routes to improve the properties of graphene aerogels. The details of the synthesis and characterization of these 3D printed aerogels will be presented.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DEAC52-07NA27344.

4:00 PM MS03.05.07
Deformation Behavior of Nano-Composites with Hierarchical NP Organization Josef Jancar, Frantisek Ondreas, Petr Lepcio, Marek Zboncar and Klara Zarybnicka; Brno University of Technology, Czechia

Understanding the role of preparation protocol in morphogenesis of polymer nano-composites and developing theories quantitatively relating their nano-scale structural features and dynamics to the macro scale properties is vitally important. Here, we report on the effects of kinetic variables on the spatial organization of nanoparticles with strong and weak interfacial attraction to the polymer matrix. While individually dispersed NPs provide the largest elastic moduli and strength, chain bridged NP clusters endow the largest ductility. Hierarchical systems combining both chain bridged NP clusters and individually dispersed NPs exhibit simultaneous enhancement of stiffness, strength and ductility with its extent tunable by the cluster content. Our results provide an experimental insight into the role of processing and kinetic traps on the structure development in real polymer nano-composites which can enable their broader exploitation as building blocks of lightweight dynamic engineering structures.

4:15 PM MS03.05.08
Bulk Supercrystalline Ceramic-Organic Nanocomposites—New Processing Routines and Insights on the Mechanical Behavior Diletta Giuntini, Berta Domenech, Buesra Bor, Alexander Plunkett and Gerold A. Schneider; Hamburg University of Technology (TUHH), Germany

In the strive to produce nature-inspired hierarchical materials with an enhanced combination of mechanical properties, supercrystalline ceramic-organic nanocomposites have been produced in bulk form and characterized from a variety of perspectives. Through an interdisciplinary collaboration at the crossroad between materials science, chemistry and mechanical engineering, a bottom-up approach has been designed. It consists of a sequence of self-assembly, pressing and heat treatment, and it leads to macroscopic poly-supercrystalline materials with exceptional mechanical properties and behavior. The crosslinking of the organic phase induced by the heat treatment does not only increase the materials’ stiffness, hardness and strength (elastic modulus up to 70 GPa, hardness up to 5 GPa and bending strength up to 630 MPa), but alters also their constitutive response. Fracture toughness values higher than theoretical predictions have emerged, implying the presence of extrinsic toughening mechanisms, such as the crack-path deviation observed at indents’ corners. Ex-situ nanoindentation and in-situ SAXS/microcompression studies also suggest the possibility for supercrystalline materials to accommodate compressibility and plastic-like deformation. Defects analogous to the ones typically observed in crystalline lattices, such as stacking faults, dislocations and slip bands, are detected at the superlattice scale (even if one order of magnitude larger than the atomic one, and with interactions among the nano-building blocks controlled by the organic phase). Correlations between defects, processing and mechanical properties have been drawn by adapting the classic theories of mechanical behavior of materials. These same materials are additionally being used as bricks for the development of novel hierarchical composites, via additive manufacturing or fluidized bed techniques.

4:30 PM MS03.05.09
Enhancing Water-Based Coating Corrosion Resistance with Boron Nitride Nanotube Additives Yu Ren Zhou, Ju Li, Michael P. Short and Bilge Yildiz; Massachusetts Institute of Technology, United States

Water-based anti-corrosion coatings have great potential as environmentally-friendly alternatives to solvent-based coatings due to lower volatile organic compound (VOC) emission during drying. However, state-of-the-art water-based coatings exhibit inferior corrosion resistance in marine and oceanside environments. Careful in-situ observations of acrylic-TiO2 composite water-based coatings on carbon steel substrates aged by the ASTM B117 salt spray test, simulating a marine environment, suggest that these coatings fail by loss of substrate adhesion, crack propagation and corrosive chemical species (e.g. H2O, O2, NaCl) penetration. Boron nitride nanotubes (BNNTs) hold great promise as corrosion resistance-enhancing additives since they potentially bridge surfaces of crack tips and raise crack propagation energy, and potentially form an inter-coating scaffold offering tortuous diffusion paths for corrosive species. Furthermore, the electrically insulating nature of BNNTs prevents the formation of galvanic
couples with the steel substrate (as observed with conductive nanomaterials such as graphene), thereby avoiding accelerated anodic dissolution of the substrate. Water-based acrylic-TiO$_2$ coatings infused with 0.1 wt.% BNNTs will be fabricated by ball mill mixing of aqueous BNNT dispersion with water-based paint, followed by drawdown bar application of BNNT-infused paint onto carbon steel substrates. In-situ observations of unmodified and BNNT-infused coatings on carbon steel during salt spray aging will be compared to confirm superior corrosion resistance of BNNT-infused coatings. Enhanced crack propagation resistance of BNNT-infused coatings will be determined by in-situ scanning electron microscope (SEM) observation of a crack tip while the free-standing coating is subject to a tensile stress test. Solubility and diffusivity of H$_2$O, O$_2$ and aqueous Na$^+$ and Cl$^-$ ions in unmodified and BNNT-infused coatings will be measured using various permeation tests, and differences in these values will be correlated to high-resolution observations of unmodified and BNNT-infused coating structure. To understand the kinetic processes leading to the dried coating morphologies, the 3D structural evolution of unmodified and BNNT-infused coatings during the coating drying process will be tracked in-situ with nanoscale computed tomography (nano-CT) at the National Synchrotron Light Source-II (NSLS-II) at the Brookhaven National Laboratory (BNL).

4:45 PM MS03.05.10
Mechanical Dissipation in Polymer-Grafted Nanoparticle Assemblies—Design of Ultra-High-Rate-Impact-Resistant Thin Films
Allen B. Schantz$^1$, Florian Käfer$^2$, Jason Streit$^1$, Jinho Hyon$^3$, Christopher Ober$^2$, Edwin L. Thomas$^3$, Lawrence Drummy$^1$ and Richard A. Vaia$^1$; $^1$Air Force Research Laboratory, United States; $^2$Cornell University, United States; $^3$Rice University, United States

Assemblies of canopy-entangled, polymer-grafted nanoparticles (PGNs) provide a method to avoid nanoparticle aggregation common in polymer-nanoparticle blends, and have enabled mechanically robust designs for a variety of structural, electronic, and optical applications. Recent studies have elucidated the relationship between PGN design (graft density ($\Sigma$), graft length ($N$), and nanoparticle size ($r_0$)) and the plasticity of the assembly below $T_g$, and identified the key design parameters for PGN assemblies to retain polymer-like plasticity (i.e. crazing). Herein, we discuss the extension of PGN mechanical robustness to ultra-high strain rates ($>10^6$ s$^{-1}$) examined with Laser Induced Projectile Impact Testing (LIPIT). Assemblies of polystyrene-grafted silica and Fe$_3$O$_4$ nanoparticles exhibit unexpected deformation mechanisms at these extreme deformation rates, resulting in unprecedented energy absorption, and kinetic energy dissipation of the micro-projectile. Mechanistically, instantaneous plastic deformation of the nanocomposite glass adiabatically heats the impact site, triggering cumulative energy dissipation processes, such as melt-draw. Linear polystyrene exhibits similar behavior, and successful PGN design should fulfill the requirements for both instantaneous and cumulative mechanical dissipation processes, i.e. retention of polymeric-like plasticity, such as crazing, and optimization of elongational viscosity to maximize energy dissipation while avoiding premature melt-rupture. PGNs with high-molecular-weight, entangled canopies ($N/N_c > 5$, $2 < r_0\Sigma^{0.5} < 10$) exhibit specific penetration energy ($E_{p*}$) >30% more than prior record-setting reports of comparable polystyrene thin films. Understanding the impact of PGN design on melt viscosity and elongational flow provides a framework to maximize the high-rate impact performance of PGNs through cumulative dissipation processes, and to guide gram-scale synthesis of next-generation PGNs via a novel mini-monomer encapsulated ARGET ATRP emulsion polymerization process.

SEENION MS03.06: Poster Session II: Nanocomposites
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

MS03.06.01
Grain Size Effect on Mechanical Properties of Polycrystalline Graphene
Sangil Hyun, Youngho Park and Myoungpyo Chun; Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of)

Characteristics of nanocrystalline materials are known substantially dependent on the microstructure such as grain size, crystal orientation, and grain boundary. Thus it is desired to have systematic characterization methods on the various nanomaterials with complex geometries, especially in low dimensional nature. One of the interested nanomaterials would be a pure two-dimensional material, graphene, with superior mechanical, thermal, and
electrical properties. In this study, mechanical properties of “polycrystalline” graphene were numerically investigated by molecular dynamics simulations. Subdomains with various sizes would be generated in the polycrystalline graphene during the fabrication such as chemical vapor deposition process. The atomic models of polycrystalline graphene were generated using Voronoi tessellation method. Stress strain curves for tensile deformation were obtained for various grain sizes (5–40 nm) and their mechanical properties were determined. It was found that, as the grain size increases, Young’s modulus increases showing the reverse Hall-Petch effect. However, the fracture strain decreases in the same region, while the ultimate tensile strength (UTS) rather shows slight increasing behavior. We found that the polycrystalline graphene shows the reverse Hall-Petch effect over the simulated domain of grain size (< 40 nm).

MS03.06.02
Fabrication of Graphene Grafted with Nylon 6,6 Grafted Multi-Walled Carbon Nanotubes for Mechanical Reinforcement of Nylon 6,6 Muhyeon Kim, Dong Eun Kim, Seung Youn Lee and Chang Keun Kim; Chugang University, Korea (the Republic of)

Reduced graphene oxide grafted with multi-walled carbon nanotubes (MWCNT-RGO) was prepared to reinforce mechanical properties of the nylon 6,6 (PA66). Aminopyrene (AP) and 1-pyrenebutyric chloride (PBC) were attached on the MWCNT (MWCNT-PBC) and RGO (RGO-AP) by physisorption, respectively, followed by reacting acyl chloride groups in the MWCNT-PBC with amine groups in the RGO-AP to graft MWCNT on the RGO. The resulting MWCNT-RGO was melt mixed with PA66 with an expectation of reaction between acyl chloride groups remained on the MWCNT-RGO and PA66. As a result, PA66 grafted MWCNT-RGO (PA66-g-MWCNT-RGO) was fabricated. Formation and properties of MWCNT-RGO were confirmed by several analyses including FE-SEM, XPS, TGA and its interfacial adhesion behavior with PA66. The interfacial adhesion energy of the composites was characterized by using drop-on-fiber method, and PA66 composite containing MWCNT-RGO exhibited enhanced interfacial adhesion energy compared with PA66 composite containing pristine MWCNT and RGO. The PA66/MWCNT-RGO composite showed better filler dispersion than the PA66/MWCNT/RGO composite owing to improved interfacial affinity. For fixed filler content in the composite, the tensile strength and fatigue life of the PA66/MWCNT-RGO composite were the highest among the composites examined.

MS03.06.03
Liquid Collecting 3D Surface Decorated with Hierarchically-Structured TiO2–Al Flake Inspired from the Mimosa Leaf Microstructure Sun Mi Yoon1,2, Hyebin Lee1, Sahn Nahm2 and Myoung-Moon Moon1; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Korea University, Korea (the Republic of)

The surface functions of living organisms have drawn attention because of their unique properties caused by their intrinsic topological structures as well as chemistry for various applications such as self-cleaning surfaces, water harvesting, and nano-micro robotics. Among the plants or animals having functional surfaces or structures, Mimosa pudica is well known as a sensitive plant that can react in response to environmental changes like mechanical touches of even small pressure by raindrops. Furthermore, for maintaining its pressure sensitivity, the leaf surface shows the extreme wettability of a strong superhydrophobicity as well as robust self-cleaning against water drops, which is attributed by the well-distributed microscale clusters made of nanoscale wax flake.

In this work, we present a hierarchical hybrid nanocomposite of TiO2 nanoparticle encapsulated Aluminum (Al) flake clusters by mimicking the hierarchically grown flake clusters on the leaf of Mimosa pudica. These flake clusters formed by the aluminum hydrolysis process with TiO2 nanofluid could be fabricated not only on a flat substrate but also on the curved structures of a 3D printed leaf surface. When Al was immersed in heated TiO2 nanofluid with the 3D substrate, the Al source reacts with hydroxyl ion decomposed water in nanofluid to form flake-like AlOOH nanostructure during which TiO2 nanoparticles functions as the nucleus of a single AlOOH flake structure and the hierarchical flake cluster structures. The TiO2-Al based flake has long-term stability (more than two month) in superhydrophilicity due to dual scale roughness by AlOOH flake clusters as well as TiO2 effect while the Al base substrate showed mild hydrophilic but not lasted for a longer duration. Hierarchical structures with long-lasting superwetting properties were applied for the liquid collecting system by the 3D printed structures with fluid transport path, which were also mimicked from the leaf vein structure of Mimosa pudica.

MS03.06.04
Mechanical Response of Segmented Copolymer Coatings to the Growing Tin Whiskers under Harsh Environments Preeth Sivakumar1, John Daye2, Imani Ballard2, Surbhi Du2 and Junghyun Cho1,1; 1State University
Polymer conformal coating over the whisker-prone tin (Sn) surface significantly reduces the risk of electrical short circuits caused by tin whiskers. The choice of coating material and possible degradation with time/environmental exposure can impact the effectiveness of the coating. The conformal coating should be strong enough to buckle a metal whisker without being punctured through the coating but also sufficiently tough to avoid the cracking ahead of the tin whisker growth. In addition, the adhesion of the conformal coating should be high to avoid itself from being peeled from the tin surface during the vertical growth of the whiskers and nodules. In this study, polyurethane-based conformal coatings, which consist of the hard and soft segments, were prepared at various curing conditions to control the aggregation of the hard segments that result in the brittleness of the coating. In an effort to restore the toughness, a toughening agent was also added to the polymer to form the phase-separated domains. Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to examine the degree of curing and its impact on the microstructure developments of the coating. Mechanical deformation of the microstructure-engineered coatings was evaluated by universal testing machine and indentation techniques that mimic the growing whisker. In particular, the contact mechanics between the growing tin whiskers and the protective polymer coating surface will be highlighted. Further, the effect of long-term high temperature and high humidity exposure on the adhesion of the coating and tin whisker mitigation behavior will be presented. This study provides a potential source of developing the effective copolymer microstructure and optimal mechanical properties that can well entrap the growth of tin whiskers and nodules beneath its coating.

**MS03.06.05**

**Interface Strengthened Carbon Fiber-Graphene Fiber Reinforced Polymer Hybrid Composite** Mingxin Li and Jie Lian; Rensselaer Polytechnic Institute, United States

Thanks to its superior specific strength to weight ratio, carbon fibers have been extensively used to reinforce polymers in composites for aerospace, automotive and construction uses since the 1970s. However, the atomic cross-linking that allows for the incredible strength of PAN-based carbon fibers comes at the price of increasing phonon scattering points, thus sacrificing thermal conductivity. Here, we report a new polymer composite reinforced with both PAN-based carbon fibers and highly thermal conductive (up to 1290 Wm⁻¹K⁻¹) graphene fibers. Heavily oxygenated graphene oxide is chemically grafted to the fibers to improve interfacial properties by increasing fiber-matrix contact area and introducing large amounts of hydrogen bonds between the carboxyl functional groups on the heavily oxygenated graphene oxide and the epoxide groups within the epoxy-based polymer matrix. Such a configuration provides ample mechanical strength and thermal conductivity for a comprehensive range of applications in the aerospace industry.

**MS03.06.06**

**Mechanical Behavior of Epoxy Composites in the Presence of Graphene-Based Core-Shell Nanoparticles as Toughening Agents** Radhika Wazalwar and Ashok M. Raichur; IISc, India

Aircraft grade tetra-functional epoxy, which is inherently strong but highly brittle, was reinforced with polystyrene-graphene oxide (PS-GO) core-shell nanoparticles to improve its mechanical properties with a focus on fracture toughness. PS-GO core-shell particles were synthesized by in situ emulsion polymerization of styrene in the presence of an aqueous dispersion of GO. The size of the core-shell particles was in the range of 300-600 nm. Scanning electron microscopy (SEM) images of the core-shell particles showed wrinkled spheres which indicated that the PS spheres have been well coated by the GO sheets. Epoxy composites were synthesized by adding 0.1, 0.5 and 1.0 wt.% of the core-shell nanoparticles to neat epoxy resin. The cured composites were tested for fracture toughness and compressive strength and maximum improvements of 25% and 21% respectively for the 0.5 wt.% and 0.1 wt.% PS-GO epoxy composites respectively were observed. At 1.0 wt.% loading, the mechanical properties were on the decline due to the plausible agglomeration of the nano-filler in the matrix. SEM images of the fractured surface showed that the modified epoxy samples had a rough surface while virgin epoxy had a smooth surface. Toughening occurred due to filler matrix debonding causing crack arrest. The thermal behavior of the composites was tested using dynamic mechanical and thermal analysis (DMTA). It was observed that there was a ≤ 2% change in the storage and tan modulus of the modified epoxy as compared to the unmodified epoxy. Hence, the desired improvement in fracture toughness and compressive strength of tetra-functional epoxy was achieved by reinforcement with PS-GO nanoparticles without compromising the thermal properties.
MS03.06.07
Tribological and Mechanical Behaviour of Cr$_3$C$_2$ Reinforced Tribaloy-T400 Hybrid Suspension-Powder Plasma Sprayed Coating
Moumita Mistri$^1$, Shrikant Joshi$^2$, Kamal K. Kar$^{1,1}$, and Kantesh Balani$^1$; $^1$Indian Institute of Technology Kanpur, India; $^2$University West, Sweden

Co superalloy Tribaloy T400 (CoCrMoSi: 8.5% Cr, 28.5% Mo, 2.6% Si, and Co as balance weight) is considered as a potential candidate in impeding the wear-assisted surface material loss from engineering modules such as combustion chamber gas engines, bearings, valves, etc. operating at a temperature as high as 800 °C. A hybrid suspension-powder plasma spray technique has been employed to deposit T400 (average powder size = ~10-45 µm) reinforced with Cr$_3$C$_2$ ($d_{50}$ = 3.8 µm) of high hardness (600-1200 HV) and adequate tribo-corrosion protection for such application. A uniform and adherent T400-Cr$_3$C$_2$ coating of thickness ~100 micrometer with 34.4% reduced 2D theoretical inter-lamellar porosity (ImageJ Pro) with respect to T400 revealed in microstructural analysis infer a favorable higher densification characteristic to suspension plasma spray. Dendritic laves' CoMoSi/Co$_3$Mo$_2$Si and hard intermetallic Co$_7$Mo$_6$/Co$_2$Mo$_7$ phases of T400 along with the corresponding Cr$_3$C$_2$ phases are confirmed in T400-Cr$_3$C$_2$ phase analysis. Synergistic reinforcement of Cr$_3$C$_2$ has further elicited an enhancement in elastic modulus (of ~188.5 GPa) by ~39.4%, and Vickers hardness (of ~10.6 GPa) by ~68.2% in comparison to that of T400 (~135.2 GPa, and ~6.3 GPa respectively); which unambiguously elucidates the consequent increase in plasticity index by ~15.7%, and a drop in maximum displacement amplitude ($h_{\text{max}}$) by ~21.2% in T400-Cr$_3$C$_2$. Correspondingly, an enhancement in COF from 0.37 to 0.43 at 40,000 fretting wear cycles with a 65% reduced experimental specific wear rate in fretting estimated from Hertzian contact theory is obtained for T400-Cr$_3$C$_2$. In conclusion, Cr$_3$C$_2$ reinforcement in T400 can cater heavy-duty load bearing application by providing substantially improved micro-hardness via retaining the smaller grain size, and a subsequent fretting wear augmentation through carbide phase strengthening.

MS03.06.08
Mechanical Properties and Failure Behavior of Layered Heterostructures of Two-Dimensional Nanomaterials
Govind Mallick; Army Research Laboratory, United States

2D nanomaterials have shown many unique and attractive properties of which mechanical properties play very significant roles in manufacturing, performance, coating, and integration in the development of their potential applications. In this work we study the mechanical properties of combinations of multi-layered heterostructures of 2D nanomaterials, including graphene and hexagonal boron nitride (hBN) by performing nano-indentation through atomistic molecular dynamic simulations. Different stacking order of the free-standing 2D films are chosen and simulated indentation analogous to indentation via atomic force microscopy (AFM) are performed. Elastic properties and intrinsic breaking strengths including Young's modulus, bending modulus, ultimate tensile strength, and fracture strain are measured through nanoindentation simulation and compared to monolayer and bilayer 2D nanostructures. Our results suggest the heterostructures are comparatively more robust than their mono- and bi-layer counterparts. However, the indented area of hBN is much smoother than graphene which had comparatively rough fractured area. The magnitude of strength and fracture strain of monolayer and bilayer graphene is marginally greater than their respective hBN layers whereas that of three layered heterostructures are substantially stronger than their counterpart homostructures. The computed results will be compared with the experimental results during the presentation.

MS03.06.09
Role of Grain Boundaries in Plasticity and Fracture of Nanocrystalline MgAl$_2$O$_4$
Jessica M. Maita$^1$, James Wollershausen$^2$, Edward Gorzkowski$^2$, Boris Feigelson$^2$ and Seok-Woo Lee$^1$; $^1$University of Connecticut, United States; $^2$U.S. Naval Research Laboratory, United States

Transparent materials are used extensively in vehicles, cameras, sensors, and displays due to their ability to transmit light and provide physical protection from external chemical and mechanical interactions. Currently, glass is the most commonly used transparent material, but its protection capability is inferior to metals or alloys due to its low toughness. Recently, transparent nanocrystalline ceramic, MgAl$_2$O$_4$, has been developed through environmentally controlled pressure-assisted sintering of ceramic nanopowders with grain sizes ranging from 3.7 nm to 80 nm, the smallest grain sizes currently reported. This nanocrystalline ceramic is regarded as an excellent candidate for transparent armor in military applications because mechanical properties of ceramics are usually better than those of
glasses. Due to the small size of sintered ceramics, however, the determination of its mechanical properties has not been thoroughly investigated. The nanocrystalline structure contains a high density of grain boundaries, so it is critical to understand how grain boundaries influence plasticity and fracture behavior.

In this study, therefore, we performed nanoindentation and in-situ micromechanical tests on nanocrystalline MgAl₂O₄ to elucidate the role of grain boundaries in plasticity and fracture. For nanoindentation, the Hall-Petch (H-P) relation was observed up to 10.5 nm grain size with a peak hardness of 25.7 GPa, after which an inverse H-P relation was observed with decreasing hardness. These results imply that under the confined deformation mode of nanoindentation, the plasticity mechanism resembles that of nanocrystalline metals, where the grain boundary sliding occurs below the Hall-Petch limit. However, micropillar compression showed entirely different results. In-situ uni-axial micropillar compression showed brittle fracture without any noticeable plasticity. The fracture strength increases monotonically as the grain size decreases. Thus, the inverse H-P relation does not appear in fracture strength. The larger and sharper grain boundaries of 80 nm grain size samples could act as stronger stress concentrators which result in a lower yield strength based on the Griffith criterion. Thus, the grain boundary plays completely different roles; as fracture initiators in uniaxial compressions and plasticity barrier (H-P) or plasticity carrier (inverse H-P) in nanoindentation. High-resolution transmission electron microscopy analysis will also be presented to describe the unique amorphous-crystalline hybrid structure along grain boundaries, which could also be the critical factor controlling both plasticity and fracture processes. These results help provide a better understanding of the mechanical behavior of nanocrystalline MgAl₂O₄ and eventually lead to an improved design of transparent armor with the superior protection capability.

MS03.06.10
**Effect of Nanoparticle Surface Modification on Magnetic and Mechanical Properties of Iron Oxide–Poly(ethylene oxide) Nanocomposites**

Donovan Weiblen¹,¹, Grace Gionta¹,¹, Deniz Rende¹, Pinar Akcora² and Rahmi Ozisik¹,¹; ¹Rensselaer Polytechnic Institute, United States; ²Stevens Institute of Technology, United States

Magnetically susceptible nanoparticles have shown promise in diverse application areas such as shape memory polymers, membrane technology, and drug delivery. In the current work, the impact of surface coating of iron oxide nanoparticles on the bulk magnetization properties of poly(ethylene oxide), PEO, nanocomposites as well as the structure of the nanocomposites were explored. PEO was chosen as the matrix polymer due to its wide use in the healthcare industry. Two coatings were investigated in addition to bare nanoparticles: poly(ethylene glycol), PEG, coated and amine coated 10–nm–diameter iron oxide nanoparticles. Nanoparticles were dispersed in concentrations varying from 0.010–0.750% by weight in PEO. A significant increase in temperature was observed in all samples when PEO/Fe₃O₄ nanocomposites were exposed to an alternating magnetic field. Analysis of magnetization curves revealed an unusual result. The uncoated nanoparticles showed a stronger magnetization than the PEG coated nanoparticles even though the PEG coated nanoparticle containing PEO/Fe₃O₄ nanocomposites showed a much more significant and rapid magnetic heating response. Shape retention properties of samples were also investigated as a function of alternating magnetic field process parameters and iron oxide surface chemistry.

*This material is based upon work supported by the National Science Foundation under Grant No. CMMI-1825254.

MS03.06.11
**In Silico Nanoindentation of Calcium-Silicate-Hydrates**

Yuan Chiang and Shu-Wei Chang; National Taiwan University, Taiwan

Although cement as a durable and affordable building material that has been widely used in construction environments, it still remains unclear on how their microstructures and chemical compositions at the molecular level affect the mechanical properties and time-dependent behaviors. The multiscale heterogeneities in the cementitious materials hinder the scientist from comprehensively understanding the mechanisms of the macroscopic phenomenon. With various hydration extent, irregular porous void and impurities like ettringite, portlandite and sulfate hydrates in the OPC (Ordinary Portland Cement), the study of the cement paste structure with accurate morphology from the molecular level to macroscale becomes challenging. In the light of recently proposed reactive modeling techniques of Calcium-Silicate-Hydrate (C-S-H), the elastic modulus of cement paste at the atomic scale as well as the effect of random nanopores on strength and toughness performance has been explored. However, fast and massive production of the full atomistic model is constrained by speed and size in that the reactive model using ReaxFF is computational intensive. In this study, we focus on straightforward modeling approach based on NMR experiments to study how defects at the nanoscale, for example, the intrinsic defective attribute of calcium silicate...
chains, including the mean chain length and the calcium-to-silicon ratio (Ca/Si), could strongly affect the mechanical properties of cement paste at macroscale. The combinations of calcium silicate hydrates with various Ca/Si ratios ranging from 1.2 to 2.1 are established and analyzed. From the bottom-up perspective, molecular dynamics simulations are carried out to simulate nanoindentation. By analyzing atomic structures and response under different loading, we reveal the relationships between the mechanical properties and the atomistic structure of C-S-H. This method helps us to bridge the atomistic structures with the material properties of C-S-H at larger scale level.

**MS03.06.12**

Multifunctional Hybrid Sol-Gel Coatings for Marine Renewable Energy Applications—Synthesis, Characterization and Comparative Analysis with Organically Modified Silicon Precursor Coatings

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Aluminium (Al) based marine equipment go through a natural degradation when exposed to corrosive and erosive conditions. The reliability and maintenance of these marine based objects is found to be a major problem due to cavitation erosion. In addition, marine biofouling which is caused due to the presence of hydrogen sulphide in the microbes leads to Microbially Induced Corrosion (MIC) in objects in the marine environment. Together, the synergistic effect of erosion, corrosion and fouling leads to reduced lifespan of the structural and operational components in the marine renewable industry. Given the sheer scale of the marine renewable industry which is estimated to reach around €9 billion by 2030, the effects of cavitation erosion, corrosion and biofouling can cause large losses to the industry which will further increase the significant costs in the operation of such offshore technology. Numerous approaches have been developed to withstand the corrosion of the Al metals. Due to environmental concerns with regard to hexavalent chromium, chromate based coatings are being phased out and the present focus is on the advancement of chromate free coating systems. Conventionally, biocides were used in the antifouling coatings to stop the accumulation of fouling organisms like bacteria, fungi, barnacles etc. Nevertheless, these biocides were found to be toxic to the environment. This is the main driver behind developing eco-friendly multi-functional sol-gel coatings for marine renewable applications. The sol-gel process has the capability to develop coatings with low temperatures and provides uniform coatings with consistence thicknesses and also suitable in developing low fouling surfaces.

The main aim of this work is to develop hybrid sol-gel coatings which act as protective layers for the Al metal. Baseline coatings were synthesized using organically modified silicon precursor 3-methacryloxypropyltrimethoxysilane (MAPTMS) mixed with zirconium (IV) propoxide. The newly synthesized hybrid coating formulations will be compared with the developed baseline coating in terms of their corrosion and cavitation erosion resistance properties. The hybrid coatings were synthesized with a zirconium/alkoxide precursor which were then deposited by dip coating on Al panels. Characterization of the developed coatings included evaluation of properties such as surface finish, chemical composition, morphology, wettability and anti-corrosion properties. The structural and functional, thermal and electrochemical properties of the coatings were evaluated using ATR-FTIR, Differential Scanning Calorimetry (DSC), Open Circuit Potential (OCP) and Potentiodynamic polarization techniques. Furthermore, other properties such as cross-cut adhesion, hardness and Water contact angle (WCA) were determined. The baseline coating were shown to have hydrophobicity with the water contact angle (WCA) of 82°. Thermal analysis revealed that the baseline coatings were stable up to 220°C. Open circuit potential and potentiodynamic polarization measurements indicated a considerable improvement in the corrosion resistance of the coated substrates. Cavitation erosion and abrasion tests were completed on all coatings and rankings of these were produced. Mass loss measurements and surface roughness were used to compare and evaluate the relative degradation of the coatings. The tested coatings will be developed further to improve their cavitation erosion, abrasion and anti-contamination properties.

**MS03.06.13**

Anodized Aluminum Oxide/Polydimethylsiloxane Hybrid Mold with Improved Mechanical Properties for Roll-to-Roll Nanoimprinting

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Two types (hard and soft) of the molds have been used in nanoimprint lithography (NIL) for a high throughput in a large area, and high-resolution parallel patterning. Although hard molds have proven excellent resolutions and high temperature strength, cracks of mold often occur, and high pressure is needed. On the other hand, although soft
molds can operate at lower pressure without cracks, it has poor pattern resolution. Here, we introduced a novel hybrid mold of anodized aluminum oxide (AAO) template chemically connected with polydimethylsiloxane (PDMS) layer. Due to the flexible nature of PDMS, we could obtain various nanostructured polymers on not only flat substrate but also curved substrate under relatively lower pressure. Furthermore, the hybrid mold is successfully used for roll-to-roll imprinting for the fabrication of high density array of various nanostructured polymers in a large area.

MS03.06.14
Controlling the Meso-Scale Assembly of CNTs/PBI Interlayers for Toughening of Thermoplastic Composites
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Thermoplastic resin-based laminated composites with remodeling/reshaping ability, recyclability, and multifunctionality, if combined with reinforcement agents, have drawn attention in the composite industry. However, incorporation problems of reinforcement agents such as carbon nanotubes (CNTs) into highly viscous thermoplastic matrices have been challenging due to the difficulties in processability at elevated temperatures and poor dispersion which leads to weak interfacial bonding with the polymer matrix. Utilizing the grown CNTs on nanofibers having high surface area provides an ability to tailor mechanical, electrical and thermal performance in various applications such as lithium-sulfur batteries, laminated composites, and supercapacitors. Hence, to effectively produce CNT-reinforced interleaves with a high CNT quality, it is required to propose an alternative method to overcome these implementation problems.

In this study, growth of radially aligned CNTs on curved polymeric nanofibrous substrates has been conducted for the first time to address one step CNTs synthesis on polybenzimidazole (PBI) nanofibers at high temperatures, which benefits from the synergetic effect of the nanofiber network and stiff and conductive CNTs. Additionally, direct synthesis of CNTs on polymeric nanofibers has the potential of being used as interleaves without tarnishing the quality of the CNTs, as delamination, collection, dispersion, and distribution steps would have been avoided, achieving a single-step approach. The growth of radially oriented CNTs on PBI nanofibrous substrates has successfully been achieved by chemical vapor deposition method (CVD) and these interleavers are used for toughening in CF/PEEK laminated composites.

PBI nanofibers were produced by firstly dissolving PBI solution (PBI Products, 26.2 wt.%) in N-dimethylacetamide (DMAc) solvent to prepare a 20 wt.% solution, followed by an electrospinning process (Argeteknolab). 10 mM catalyst solution (Fe(NO3)3,9H2O (404.0 g/molar, Emir Kimya) and iso-proponal (Sigma Aldrich)) were prepared to deposit Fe3+ ions onto nanofibers which acted as a catalyst for CNT growth. Then, nanofibers were kept at 50 °C for 5 hours in an oven. The growth of CNTs onto PBI nanofiber was achieved at 600 °C with 15 min. nucleation and 10 min. growth times. The morphology of the produced CNT/PBI nanocarpet was investigated by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

After the production of CNT/PBI nanocarpet, compression molding was utilized to lay up CNT/PBI nanocarpets and Polylethersulphone (PES) films (GoodFellow, thickness 0.5 mm) with different sequences where CF/PEEK prepregs (Mir AR-GE) were used as top and bottom layers. The main reason for the integration of PES films into composites was to provide compatibility between the CF/PEEK prepregs and the CNT/PBI nanocarpet. Following the compression molding process, the samples were hot-pressed for 30 minutes at 320 °C under a pressure of 10 bars. The thickness of the final composite structures was measured to be 1.5±0.03 mm.

The mechanical performance of PES/PBI/PES and PES/CNT-PBI/PES integrated CF/PEEK composite samples under flexural loadings was investigated by a universal test machine (UTM, Shimadzu AG-X Plus) according to ASTM D790-18 standard. The initial results showed that the flexural strength of the neat PBI nanofiber integrated CF/PEEK laminated composite was 103.5±8 GPa, while CNT/PBI nanocarpet integrated laminated composite was around 144.3±10 GPa. In the final paper, to further investigate the effect of the CNT integration on the overall composite structure, a dynamic mechanical analyzer (DMA) (TA Instrument, Q850) will be used to determine storage and loss moduli and to evaluate their variation with frequency and temperature using a three-point bending fixture.

MS03.06.15
Large Scale Growth of SWCNT Forests for Advanced Structural Nanocomposites
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In this era of advanced manufacturing, a plethora of materials and methods have been developed to produce lightweight materials with unique mechanical properties. Record high strength/modulus to density ratios, flaw tolerance, flexibility of ceramic materials, and combination of seemingly conflicting properties (e.g. stiffness and damping) show the promise of nanoscale material architectures. Vertically-aligned single-walled carbon nanotube (SWCNT) forests is one of the best platforms to build these materials from, by the virtue of aligned, a-few-nanometer diameter, and long length (> 1 mm) struts with exceptional mechanical properties arising from strong C-C sp² hybridized bonds. However, mass production of SWCNT forests needed for their wider adoption is hampered by a poor understanding of how to scale CNT growth recipes from small benchtop reactors to larger scale systems. We sought to address the SWCNT forest growth scalability by gaining a deeper understanding of the CNT growth process. We first identify the limiting step in the SWCNT growth rate and determine the dependence of the reaction kinetics on chamber pressure, gas composition and flowrates. We then employ this knowledge in translating the CNT forest growth to successively larger areas, ranging from 1 × 1 cm² pieces to 6-in. wafers. We demonstrate synthesis of high-density (> 10¹² CNTs/cm²), small-diameter (~ 2 nm) SWCNT forests with structural characteristics and growth kinetics that are uniform over large areas, up to 4-in. diameter. Achieved carbon conversion efficiency far exceeds typical benchtop reactor processes and is on par with the best values reported in the literature. We also demonstrate that the carbon conversion efficiency increases with substrate area and decreases with total flow rate. This trend can be rationalized by accounting for the reactant gas flows in the showerhead CVD reactor, as shown by computational fluid dynamics simulations. We finally demonstrate that, by varying the gas mixture, flowrates, and chamber pressure, we can tune CNT growth kinetics as desired without affecting the forests’ structural properties. These results and insights gained from them will prove to be a valuable guideline for future scale up efforts of SWCNT forests for advanced mechanical/structural nanocomposites.


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MS03.06.16
Controlling Mechanical Behavior in Nanocrystal Films—How Layer and Substrate Properties Play a Role
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Cutting-edge technology such as flexible electronics and displays, biocompatible health monitoring systems, novel photovoltaic devices, and functional coatings rely on novel behavior of thin-film materials such as nanocrystal layers. While the optoelectronic properties of semiconductor nanocrystals are well-studied, deploying these materials in flexible/stretchable devices requires an understanding of the mechanical behavior of the nanocrystal layers, which can be challenging to investigate in-situ. Nanoindentation experiments and other probe-based techniques can be used to evaluate single-nanocrystal elastic/plastic deformation – but are more difficult to employ as in-situ methods for layers of nanocrystals on elastomeric substrates. Recently, our group created a novel in-situ framework for evaluating the mechanical properties of thin layers of luminescent silicon nanocrystals (SiNCs) by measuring the onset of instabilities in the SiNC layers on polydimethylsiloxane (PDMS) under finite bending deformation. Our work revealed a neo-Hookean coefficient (µ, analogous to shear modulus at low stress/strain) of a 4.5 µm-thick SiNC film to be 345 ± 23 kPa, which is several orders of magnitude smaller than the shear modulus of a single SiNC. While we hypothesize that the reason for this property difference is due to the porosity of the SiNC layer, there are many other parameters that could influence the mechanical behavior of the SiNC layers including layer thickness, SiNC size and surface functionality, and mechanical properties of the PDMS substrate. Here we investigate these important parameters regarding their influence over the mechanical properties of SiNC layers on PDMS. We prepare the PDMS in-house using a Sylgard 184 elastomer kit. Next, we synthesize SiNCs using a low-pressure nonthermal plasma and then inertially impact them into thin layers onto the PDMS through a slit-shaped orifice. We control the SiNC size, surface functionality, and layer porosity using the gas flowrate, pressure, gas composition, and deposition stage parameters. The PDMS properties depend on the prepolymer/catalyst ratio and curing conditions during PDMS preparation. Our results indicate that the layer and PDMS parameters exert competing influences on the mechanical properties of the SiNC layer. For example, we found that reducing the stiffness (reducing µ) for PDMS leads to a decrease in µ for the SiNC layer. This change occurs simultaneously with a microstructural densification of the SiNC layer, although the relationship is not monotonic. Unraveling the interconnectedness of these parameters on the physical, mechanical, and optoelectronic
properties of the SiNCs will allow for predictive engineering of nanocrystal films for flexible devices and thin-film technology going forwards. While we use SiNCs on PDMS as our testing system, our discoveries are applicable across material types and realize a non-destructive, \textit{in-situ} approach for evaluating the mechanical properties of other multilayered architectures of elastomers and nanocrystals.

\textbf{MS03.06.17}
\textbf{Fabrication of Ductile Ceramic Foams by Anodization and Proton Irradiation} Jung Woo Kim, Heonyong Jeong, Naeun Lee and Sung Oh Cho; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Zirconia is a representative example of ceramic materials that demonstrate outstanding strength and relatively high fracture toughness and is utilized engineering application. In addition to fields requiring physical and chemical stability, it has been considered a candidate fuel matrix and cladding material in the nuclear power sector because of its radiation tolerance when its crystal grain is reduced to the nano-scale level. Moreover, tetragonal stabilized zirconia has a crack-resistant mechanism so-called transformation toughening. This reversible phase transition is involved volume expansions (4-5\%) of tetragonal \textit{ZrO\textsubscript{2}} to monoclinic \textit{ZrO\textsubscript{2}} phases, and has been widely studied to apply to composite materials. However, despite its advantages, zirconia has a brittle nature that can easily be broken by external impacts. Ceramics perform high strength and stiffness compared to other metals and polymers. On the other hand, the lack of plasticity and sensitivity to flaws are actually weak in terms of structural stability and thus limited in its use. In brittle ceramic materials, it is generally accepted that pores are considered as a detrimental flaw because of serving an occurring point that higher stress is locally concentrated. On the other hand, an insight for suppressing brittle fracture has been proposed recently by applying uniform porous and hollow structures on the nano-scale level. In order to improve the mechanical properties of the ceramic material, not only the morphological aspects, a thoughtful microstructure design is also required in terms of constituent atomic arrangements.

In this study, through the anodization technique, the zirconia layer with nanoporous structure was fabricated. It is aimed to examine the mechanical responses of nanoporous ceramics when manipulated in atomic arrangements. The annealing treatment and proton beam process were utilized as an effective tool inducing the crystallization to the amorphous ceramic oxide layer. To observe the mechanical properties of the zirconia ceramic with nanoporous structures, the micro-pillars were prepared and uniaxially compressed. The deformed morphology of the compressed pillars was also characterized to analyze the mechanical behaviors of each condition.

The zirconium oxide layer with a honeycomb-like structure was fabricated by optimized anodization technique. The microstructure of zirconium oxide layer can be manipulated by utilizing the annealing and ion beam treatment. It was observed that as-fabricated nanoporous oxide layer with amorphous structure was experienced to be fully or locally crystallized. Through micro-compression tests, the plasticity without generating cracks was exhibited in both as-anodized and irradiated pillars with amorphous structure. This fracture tolerant response with large plasticity could be caused by that the compressed pillar has an amorphous structure. The mechanical properties of conventional ceramics manifest in the case of annealed pillar, implying that crystalline structure brings out the brittle feature. In proton irradiated condition, the increased free volume induced by ion bombardments made the ceramic layer more plastically responded. From the results of the mechanical behaviors, the occurrence of plasticity without brittle failure of the ceramic material implies the great potentials that the nanoporous oxide layer can be utilized for various engineering applications by securing the material stability. Especially in ion beam process, it is expected that the ideal characteristics for high strength with remarkable plasticity can be designed by controlling the degree of crystallization with varying the dose of the beam irradiation.

\textbf{MS03.06.18}
\textbf{Fabrication and Mechanical Properties of Functionalized Boron Nitride Nanoplatelets Reinforced Epoxy Matrix Nanocomposites} Joon Hui Kim, Sung Chan Yoo, Ho Jin Ryu and Soon Hyung Hong; Korea Institute of Science and Technology, Korea (the Republic of)

After publication of first 2D material, Graphene, numerous journals treating with 2D nanomaterials were published. Boron nitride (BN) is a synthetic material made from boric acid or boron trioxide and consists of the same number of boron (B) and nitrogen (N) atoms. BN has an isoelectronic structure similar to that of a carbon lattice and shares the same number of electrons between adjacent atoms. The mechanical properties of BNNPs are comparable to those of graphene. The elastic modulus of BNNPs ranges from \textasciitilde 800–850 GPa, depending on the degree of chirality. Like graphene, the mechanical properties and thermal conductivity of BN nanostructures make them attractive as nanofillers in composite materials.
The major applications of BNNP is the polymer nanocomposite. Unlike other polymer composites, polymer nanocomposites show superb property despite of low volume percent of reinforcement material. In addition, polymer nanocomposite is easier to fabricate than conventional consolidation process. The major fabrication factor of polymer nanocomposite is dispersibility of reinforcement material in polymer matrix. However, BNNP agglomerates among themselves due to van der Waals force, so this problem needs to be solved.

To solve agglomeration and dispersion problem, we adopted functionalization process to give BNNP proper dispersibility in solvent. BNNP was covalently functionalized using hydroxide-assisted ball-milling processes, which both induce chemical exfoliation and apply strong mechanical shear forces. This covalent functionalization resulted in more stable dispersion than was attainable with non-covalent functionalization.

In this research we functionalized BNNP to prevent agglomeration and increase own properties by using hydroxide functional group. This functionalization process exfoliates BNNPs via the synergetic effect of chemical peeling and mechanical shear forces to overcome the limitations of the previous approaches. After functionalization of BNNP, functionalized BNNP/Epoxy (BNNP/Epoxy) composite were fabricated by solvent mixing. Mechanical properties of BNNP/Epoxy composites were characterized by using Microforce testing machine.

Mechanical properties of BNNP/Epoxy composites showed 1.8 times enhanced elastic modulus and 2.7 times enhanced fracture toughness, compared to pure epoxy. These results could be explained by hydroxides stacked on surface of BNNP flakes, which hindered agglomeration among BNNP flakes. Furthermore, hydroxides on BNNP improved interfacial bonding with epoxy matrices. This result leads to homogeneous dispersion of BNNP in Epoxy and successfully optimized mechanical properties of nanocomposites. Our team wish that these results could provide useful property criteria of Boron nitride Nanoplatelet for structural materials as industrial applications.

MS03.06.19
Fabrication of High Recovery Ultralight Materials Using Carbon Nanotube and Low Molecular Weight Carboxymethylcellulose Kazuki Matsushima, Naoto Shioura, Tomonaga Ueno and Takahiro Segi; Nagoya University, Japan

Ultralight materials are expected to be applied to structural materials, heat insulating materials, and filters, etc. Various composite materials such as carbon nanotubes, graphene, and polymers have been proposed for the improvement of mechanical properties for ultralight materials. Recently, ultralight materials have been proposed which have high recovery rates for compression. Since carboxymethylcellulose (CMC) acts as a dispersant for carbon nanotubes, an ultralight material consisting of carbon nanotubes (CNT) and CMC has been reported, but a high recovery rate against compression at low density was not observed. In this study, we fabricated the ultralight materials with the apparent density of 1.25 mg/cm³ consisting of CNT and CMC, and showed that the material has a high compression recovery rate. In this case, the low molecular weight CMC is necessary for the ultralight material to show a high compression recovery rate.

In this study, single-walled CNT (SWCNT) with diameter of 2nm was used. Then, two kinds of CMC with different molecular weights were prepared. The viscosity of low molecular weight CMC (l-CMC) and high molecular weight CMC (h-CMC) solutions at 1 wt% was 50 mPa s and 1734 mPa s, respectively. SWCNT was added to an aqueous solution in which CMC was dissolved, and subjected to ultrasonic treatment to prepare a CNT dispersion. The CNT dispersion was frozen while controlling the temperature with a heat insulating material, and freeze-drying was performed to produce a CNT/CMC ultralight material. The upper surface is controlled to −80 ° C, and the bottom surface is thermally insulated by a heat insulating material, whereby the hexagonal ice crystal structure formed on the upper surface reaches the lower portion, and vertical gaps are arranged. Structural observation was performed by a scanning electron microscope, and mechanical properties were evaluated by a compression test.

Samples were made with an apparent density of 5 mg/cm³, 2.5 mg/cm³ and 1.25 mg/cm³ as the target. No recovery after compression was observed in the composite materials with an apparent density of 5 mg/cm³, 2.5 mg/cm³, and 1.25 mg/cm³ regardless of the two kinds of CMC. However, in the density of 1.25 mg/cm³, the clear difference of mechanical properties was observed between h-CMC and l-CMC. In CNT/h-CMC, no recovery was observed. On the other hand, in the CNT/l-CMC ultralight material, the drastic recovery was observed. The recovery rate was 60% against 80% compression. Then, it has low compressive stress even in high strain range. The compressive stress was 0.0014 MPa for 80% strain. Moreover, the compression recovery rate was kept when the compression test was repeated.

In high density of CNT/CMC materials over 2.5 mg/cm³, hydrogen bonds are formed between adjacent CMC. In this range, the recovery rate is lowered because the hydrogen bond force is greater than the resilience by CNT. The low density of CNT/l-CMC materials shows a higher recovery rate than the other samples because the resilience by CNT was greater than the attraction of hydrogen bonds between CMC molecules.
**MS03.06.20**

**Improvement of Mechanical Properties of Porous Silica Insulator by Nano Fiber Addition**

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Effective use of heat by heat insulation attracts attention from the aspect of energy saving. Insulating materials are used widely in homes, automobiles, and space transport aircraft. In recent years, development of silica aerogel has been promoted as an ultimate heat insulating material. Silica aerogel is a porous silica body that has both a high porosity (90% or more) and a pore structure with an average diameter of 20 to 40 nm. Heat transfer is generated by three mechanisms of convective heat transfer of gas, heat transfer of solid, and radiative heat transfer. Silica aerogel with low density and fine void structure can greatly suppress convective heat transfer of gas and heat conduction of solid, and achieve extremely low thermal conductivity of 0.02 W / (m K) or less at room temperature. However, the low mechanical properties due to the low density, and the need for high pressure processes such as supercritical drying are problems. In this study, we focused on porous silica. Porous silica is an aggregate of silica particles, and has fine voids of several nm to several tens of nm, which is a powder material. Porous silica has very high thermal insulation performance due to its bulky, fine void structure. Furthermore, since porous silica is a powder, if it can be aligned sparsely in the material as much as possible, it has lower density than silica aerogel and high heat insulation performance is expected. However, as in the case of the silica aerogel, the low mechanical properties, and the poor formability due to the powder are problems. Therefore, we attempted to improve mechanical properties and formability by combining carbon nanotube (CNT), for which high mechanical properties are reported, with porous silica. The high thermal conductivity of CNT may increase the thermal conductivity of the heat insulating material, but in this study, this was suppressed by the coating of CNT with a polymer. Furthermore, since CNT are nanomaterials having a diameter of several nm to several tens of nm, there are extremely many interfaces and interface contact points. As a result, the thermal conductivity of the bulked actual material becomes significantly lower than the theoretical value due to the thermal resistance of the interface. Porous silica has a high transmittance in the infrared region and radiation heat transfer is not suppressed. The carbon material has a high absorption rate of radiation, and the addition of CNT is also expected to shield the radiation. Using Carboxymethyl cellulose (CMC) as a dispersing agent, CNT was dispersed in water by ultrasonication. This liquid was mixed with porous silica and freeze-dried to obtain a CNT / CMC / SiO2 composite material. The structure of the material was observed by an optical microscope and a scanning electron microscope (SEM). The mechanical properties were measured by uniaxial compression test and three-point bending test. Thermal conductivity was measured as a measurement of adiabatic performance.

In the case where no CNT was added, the material was largely shrunk by freeze drying, and it was not possible to form a compact. However, the addition of CNT made it possible to produce a high porosity (90% or more) CNT / CMC / SiO2 composite material with almost no shrinkage. This material is composed of voids of several tens of μm derived from ice crystals upon freeze drying, and these fine voids are expected to suppress the convection of gas. In addition, the mechanical property was improved by the increase of the added amount of CNT. By increasing the amount of CNT added from 0.5 mg / cm³ to 2 mg / cm³, the bending strength is from 0.01 MPa to 0.02 MPa, and the strain until the material breaks is increased 4.1% to 8.5%. The increase of CNTs confirmed the improvement of the flexibility of the material.


**MS03.06.21**

**Understanding Self-Healing in Nanocomposite Materials**

Christopher B. Cooper, Jiheong Kang and Zhenan Bao; Stanford University, United States

Self-healing materials offer a promising mechanism to create wearable electronics and soft robotics with high stretchability and durability, due to their intrinsic ability to recover after damage. Embedding different self-healing materials with distinct nanomaterials can impart different functionalities (e.g., conductors, semiconductors, insulators) to a self-healing polymer. Recently, researchers have designed composite systems in which healing restores not only the mechanical integrity of the device but also its electrical functionality. However, the mechanism for the self-healing of nanocomposites is not well understood, and a variety of factors including size, shape, and chemical interactions of the embedded particles can influence the rate of healing in a composite self-heaving device. In this poster, we present different examples of self-healing composite systems and discuss how the self-healing
properties of the composite change based both on the polymer matrix and the embedded nanomaterials. This work highlights potential insights into the design of self-healing composites with improved properties and their potential to be integrated into robust wearable electronics.

**MS03.06.22**

**Manufacture of Al₂O₃-Composites by the Combination of RBAO and SPS Processes** Enrique Rocha-Rangel¹, Jose A. Rodriguez-García¹, Ruth P. Alvarez-Carrizal¹ and Yoshikazu Todaka²; ¹Universidad Politecnica de Victoria, Mexico; ²Toyohashi University of Technology, Japan

In this work, the effect of additions of silver or titanium nanoparticles on the microstructure and mechanical properties of Al₂O₃-based composites was studied. The processing method for the manufacturing of alumina-based composites was a combination of RBAO and SPS processes. After milling stage, carried out in a high energy mill, we have that approximately 90% of the powders have a particle size less than 0.5 μm. After SPS process well densified bodies with almost full density were obtained. The microstructure observed by OM, shows that the reinforcement metal (silver or titanium) occupies intergranular positions and the grain size is very fine and homogenous. On the other hand, with respect to mechanical properties, addition of metals on alumina increases significantly its fracture toughness, being more significant the effect of silver, because K<sub>IC</sub> rises from 3.2 MPam<sup>0.5</sup> for monolithic Al₂O₃ to 6.9 MPam<sup>0.5</sup> for Al₂O₃/1wt%Ag composite, whereas, for the Al₂O₃/1wt%Ti composite, the value of K<sub>IC</sub> was of 5.7 MPam<sup>0.5</sup>.

**MS03.06.23**

**Bio-Inspired High Tough Carbon Nanotube Yarn** Hyunsoo Kim and Seon Jeong Kim; Hanyang Univ, Korea (the Republic of)

A carbon nanotube (CNT) yarn is attracting as strong and lightweight yarn because of impressive mechanical properties. Especially, among their yarns, tough performance, which is the ability to absorb mechanical energy before fracture, is considered an important mechanical property for the protection of damage to external force. We described high tough carbon nanotube yarn by inspired a muscle structure of nature, which called myofibrils. The muscle inspired CNT yarn is dramatically improved both tensile strength and strain, and yarn provides a high-energy absorption, which is higher than spider dragline silk (165 J/g) and Kevlar (78 J/g). Additionally, not only demonstrates high tough performance in the wetting and high temperature conditions but also shows ease in shape change by using water. This sewable, wearable, and shape controllable tough yarn has a potential for various applications such as bulletproof material, wearable device, stretchable electrode, aerospace industry, and artificial muscle.

**MS03.06.24**

**Development of “Paper Actuator” Using Carbon-Nanotube-Composite Papers** Takahiro Ampo and Takahide Oya; Yokohama National University, Japan

In this study, we propose a unique actuator based on a polymer type actuator and carbon-nanotube (CNT)-composite papers. The polymer actuators have different features from existing actuators. These are low voltage operation, light weight, flexible and molecular level movement. For the above reasons, energy saving is possible and more complex operation can be realized. In addition, other actuators using bucky gel that consists of CNTs and ionic liquid have been also developed.

CNTs are substance consisting of carbon and have many excellent properties such as high electrical conductivity, light weight, high strength and flexibility. Since CNTs have these properties, CNTs are expected to be used for various things. In contrast, CNTs are nanoscale powdery substance. Therefore, we may contrive to use it or develop the way for applications such as combining with other materials. Thus, we focus on “papers” as the material which is able to change shape easily and is a familiar material of our daily life. We made a paper mixed with CNTs. This material had many excellent properties based on CNTs. We have called this material “CNT-composite papers”.

Recently, development of a lightweight and flexible polymer actuator has been required for medical use, interior design, and so on. Here, the paper can be cut and pasted. So, if the polymer actuator made of CNT-composite papers can be developed, it can be used in various situations. And more complex movements can be performed than existing mechanical actuators. For the above reasons, we aim to develop the “paper actuator” using CNT-composite papers.
One of the polymer actuators contains ions and harnesses the force generated by the movement of ions for operation. We here focused on this type of the actuator in this time. This actuator composes of two types of layers, i.e., the electrode layer and the electrolyte layer. The electrolyte layer is sandwiched between the electrode layers and generally contains ionic liquids. Both the electrode layers and electrolyte layer contain the electrolyte. And the electrode layer contains CNTs. When a voltage is applied to the actuator, cations are attracted to the cathode and anions are attracted to the anode. In ionic liquids, there is a difference in the size of the cations and anions. If cations are bigger than anions, the cathode will be extended and the anode will be shrunk. From this process this device operates as an actuator.

Here our device has a three-layer structure, we designed. The outer layers consist of the CNT-composite papers as the electrode. And the inner layer bases on an ordinary paper containing no CNTs as the electrolyte layer. The ionic liquid was included in this device as the electrolyte.

The production method of the CNT-composite papers is based on Japanese washi papermaking method. First, we prepare the pulp dispersion by stirring pulp fibers in water and prepare the CNT dispersion by mixing CNTs and dispersants with ultrasonication in water. Next, we mix the pulp dispersion and the CNT dispersion. And then, we pour the mixture dispersion in the mold on the net, and scoop up the mixture by the net and dry it by heat pressing. Then, we can fabricate CNT-composite papers by this process. Then an ordinary paper containing no CNTs is sandwiched between CNT-composite papers. We layer the papers by heat pressing in this state. After that, we drip the ionic liquid. When voltage was applied this sample, we confirmed that our sample showed the operation as the actuator, as a result.

We believe our CNT-composite paper will be used as actuators in near future.

MS03.06.25
Mechanical Durability of Slippery Liquid-Infused Porous Surface with Silica Aerosol Dispersed PDMS
Youngeok Kim1, Jin Hwan Kim2 and Byungsu Lee2; 1Korea Electronics Technology Institute, Korea (the Republic of); 2Kangnam Jevisco Co., LTD, Korea (the Republic of)

Slippery liquid-infused porous surface (SLIPS) technology provides unique capabilities that are unmatched by any other surface technologies. SLIPS comprises a smooth and slippery lubricating surface, where lubricant is trapped within the pores of a solid material to repel various substances, such as water and ice. Thanks to their ultralow ice adhesion strength, SLIPS materials have actively investigated in the field of icephobic coatings where the ice accreted on the coating is passively detached by ice’s own weight. The SLIPS coatings however are still far from being employed in the real environment because of limited durability of the slippery liquid that can be removed together with the detached ice.

Here, we investigate icephobicity of a SLIPS coating based on oil-infused polydimethylsiloxane (PDMS). In order to improve the durability, porous silica aerogel (specific surface area of 600 ~ 800 m²/g, porosity above 90%) is used as the oil container. The different viscous oils (viscosity of 6, 100, and 350cst)-infused aerogel and PDMS are mixed and bar-coated, and the hardened films are followed by additional swelling of the oils.

We setup the reliable measuring instrument for icephobicity and characterize oil content, surface topography, ice adhesion strength during repeated icing/deicing cycles of the SLIPS films with different aerogel content. Finally, the inclusion of aerogel container is confirmed to increase the total oil content of the film, which results in more durable icephobicity.

MS03.06.26
Experimental Mechanics of Pure MXenes (Ti3C2Tx) and MXene (Ti3C2Tx) /Polymer Nanocomposites
Shreyas Srivatsa1, Krzysztof Grabowski1, Leon Mishnaevsky2 and Tadeusz Uhl1; 1AGH University of Science and Technology, Poland; 2Technical University of Denmark, Denmark

Titanium Carbide (Ti3C2 - MXene) with surface termination (Ti3C2Tx; Tx: -F, -OH, -O) have created a lot of interest for applications in electro-mechanical engineering domain apart from material science investigations. This interest is primarily due to unique conductivity and hydrophilic behavior exhibited by MXenes which are useful for fabricating nanocomposites for multifunctional sensing applications. The investigation of mechanical properties of a single layer (flake) or few-layer pure (free-standing) Ti3C2Tx and Ti3C2Tx nanocomposites reported in the literature are limited to the estimation of elastic properties like Young’s modulus and tensile strength. Experimental identification of structural parameters of pure MXenes and MXene/Polymer nanocomposites from the point of view of mechanics is necessary for the design and development of smart structures for Structural Health Monitoring (SHM).

The focus of this paper is on the modeling of pure MXenes (Ti3C2Tx) and MXene nanocomposites. Characterization
of Ti$_3$C$_2$Tx and Ti$_3$C$_2$Tx nanocomposites along with experimental validation of the models are performed. The characterization tests discussed in this paper are conducted with Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and X-ray Diffraction (XRD). MXene flakes are modeled as thin plates in microscale while the macroscale samples subjected to testing are modeled as one-dimensional and two-dimensional structures. These models help in studying the mechanics of the samples and determining the mechanical tests to be performed. Nanocomposites with MXenes as fillers in polymer matrices like epoxy, polydimethylsiloxane (PDMS) and polyvinyl alcohol (PVA) are fabricated and subjected to mechanical loads. The flexible films formed by PDMS and PVA and rigid films formed by epoxy are subjected to tensile and bending tests. Results of these tests are compiled and discussed. The paper concludes with the discussion on the possibility of using MXenes for smart structure and smart coating for SHM.

MS03.06.27
Microstructure-Electrochemical Behaviour Correlation for NiCo-MWCNTs and NiCo-Graphene Oxide Composite Coatings Sweety Arora and Chandan Srivastava; Indian Institute of Science, India

The magnetic behaviour of NiCo coatings along with high hardness, corrosion resistance and excellent wear resistance makes them a suitable candidate for applications in sensors, actuators and protective coatings. Addition of foreign particles into NiCo matrix is known to promote grain refinement and randomization leading to enhanced corrosion resistance behaviour. In the present work, varying amount of multi-walled carbon nanotubes (MWCNTs) and graphene oxide (GO) was incorporated separately into the NiCo coating matrix which was electrodeposited over mild steel substrate. The formed composite coatings were characterized using scanning electron microscopy (SEM), x-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDS) techniques for morphology, phase identification and composition of the coatings respectively. Electrochemical impedance spectroscopy and potentiodynamic polarization studies in 3.5 wt.% NaCl solution revealed that the corrosion behaviour of the coatings was sensitive to the amount of graphene oxide and CNTs present in the coatings. With the continued addition of CNTs and GO the corrosion rate of the composite coatings first decreased to the lowest corrosion rate value and then increased to values higher than that of pristine NiCo coatings. This indicated towards the existence of optimum concentration of CNT or GO for achieving highest corrosion resistance performance. Addition of optimum CNT concentration provided hydrophobicity to the coatings and promoted growth along low energy (111) direction. Electron backscatter diffraction (EBSD) analysis of the coating cross-section prepared using SEM-FIB revealed that samples exhibiting maximum corrosion resistance (for optimum CNT/GO concentrations) also had the highest fraction of low angle grain boundaries (LAGBs) with no additional strain in the matrix.

MS03.06.28
Brittle to Ductile Transition via Ultrastructural Design of Single Crystalline Silicon Nitride Nanoporous Membrane Ali Khourshaei Shargh and Niaz Abdolrahim; University of Rochester, United States

In this work we use molecular dynamics simulations to investigate mechanical behavior of silicon nitride nanoporous membranes upon tensile loading. We show that pore arrangement pattern, pore size, as well as pore separation distance play an important role in mechanical behavior of the nanostructure with hexagonal pore shape. A brittle to ductile fracture mechanism criterion is successfully developed for hexagonal pore pattern via introducing a new ultrastructure based parameter. For ductile fracture, it was found that von-Mises shear strain is localized into a network of narrow bands within the ligaments that connect the pores. In consequence, a compressive stress is produced within the nodes that connect ligaments and cause suppression of crack propagation and enhances the ductility. In contrast, the accumulation of tensile stress in nodes leads to brittle fracture.

MS03.06.29
Mechanical Properties of Diamond Schwarzites—From Atomistic Models to 3D-Printed Structures Levi C. Felix$^1$, Vladimir Gaal$^1$, Cristiano F. Woellner$^2$, Varlei Rodrigues$^1$ and Douglas S. Galvão$^1$; $^1$State University of Campinas, Brazil; $^2$Federal University of Paraná, Brazil

In the recent years, 3D printing has been employed as an effective tool to study hierarchical structures that are difficult or elusive to be synthesized on atomic scale, such as the Schwarzites [1]. Schwarzites [2,3] are 3D carbon nanostructures with their shapes resembling triply periodic minimal surfaces (TPMS), which are porous structures possessing negative Gaussian curvature. In this work we investigated the mechanical properties of diamond Schwarzites through fully atomistic molecular dynamics (MD) and 3D printing techniques. The geometrically
optimized atomic models were used to create macroscale models that were then 3D printed (cm size) in home-made device using PLA (polyactic acid) and ABS (acrylonitrile butadiene styrene) polymers. Interestingly, as it was also observed for other Schwarzite families (gyroid and primitive) [1], some qualitative trends of the mechanical behavior (in particular with relation to compressive/tensile deformations and energy absorption/dissipation mechanisms) are present at nano and macroscale. This is especially evident when the ratio between the number of octagons to hexagons (‘flatness’) increases. Another interesting feature is that they exhibit negative (auxetic) [4] and zero Poisson’s ratio regimes. Considering that our multiscale approach is completely general (to use atomic models to create macro models that can be 3D printed), it can be very useful to create new or to improve Schwarzite-based engineering functional materials.


MS03.06.30
Improved Mechanical Properties of Graphene/Carbon Fibre/Epoxy Hybrid Composites through Silanization
Xudan Yao, Mark A. Bissett and Ian Kinloch; The University of Manchester, United Kingdom

Carbon fibre reinforced polymer (CFRP) composites have been widely used owing to their superior specific strength and modulus. Meanwhile, graphene-based composites have drawn much attention since it’s discovered with exceptional mechanical, electrical and thermal properties. More recently, interest in hybrid composites combining continuous fibres with nanomaterials has grown for achieving ideal properties. For these hybrid composites, the nanomaterial dispersion as well as the interfacial bonding raise the challenges.

In this work, graphene/carbon fibre/epoxy hybrid composites were investigated. The graphene was achieved through in lab electrochemical exfoliation, followed by filtration, washing and drying. The obtained graphene has adequate in-situ oxygen groups, i.e. hydroxyl and carboxyl groups, which makes the dispersion easier as it could stay stable in either water or ethanol. On the other hand, in order to improve the interfacial bonding, silanization was introduced with the 3-Aminopropyl)triethoxysilane (APTES) as the coupling agent. The APTES could react with both oxygen groups of the graphene and amine groups of the hardener, thus build the bridge between them. After the surface modification, the graphene was dispersed in ethanol then sprayed on to carbon fibres, followed with vacuum assisted resin infusion to manufacture the composites. During the mechanical testing, compared with the sample without functionalization, the delamination was largely removed after the silanization. As a result, the mechanical properties, especially for the tensile and flexural strength, improved by more than 60%.

MS03.06.31
Rapid and Energy-Efficient 3D Printing of Continuous Carbon Fiber/Thermosetting Composites Kun Fu; University of Delaware, United States

Additive manufacturing of continuous carbon fiber composites using thermosetting polymers is a challenge and so far very few work has been reported. Recently, we developed a novel 3D printing system allowing one-step manufacturing of continuous carbon fiber/thermosetting composites in a rapid and energy-efficient way. Our 3D printing system has good compatibility with commercial carbon tow and bundles, and most of epoxy resins. Our 3D printed composites exhibit high fiber volume fraction (>60%) and high tensile strength (>800 MPa). In this oral presentation, I will talk about our 3D printing technology, including the fundamentals and applications. In addition to carbon fiber, our 3D printing technology can also be extended to other high performance fiber composite manufacturing, including kevlar/thermosetting, and glass fiber/thermosetting.

MS03.06.32
Synergistic Effect of Cellulose Nanocrystals and Carbon Nanotubes on Interfacial Properties of Carbon Fiber Epoxy Composite Ozge Kaynan and Amir Asadi; Texas A&M University, United States

Load bearing capability and lifetime of the epoxy composites can be enhanced by improving interfacial adhesion fiber and epoxy. In this paper, we aim to elucidate the mechanisms that create the interface of cellulose nanocrystals
(CNCs)-bonded carbon nanotubes (CNTs)- carbon fiber reinforced polymer (CFRP) composites. Particularly, we will articulate the CNTs/CNCs’ synergistic effect on the interfacial strength of carbon fiber epoxy composite. To date, several approaches have been proposed to improve interfacial bonding of epoxy composites including sizing of reinforcing fiber [1], nanofiller coating [2, 3] and nanoparticle growth on the surface of fibers [4]. Among these, coating of fibers as a thin layer of polymeric components or nanoparticles is a widely adopted strategy for interfacial enhancement. However, the main challenge is still to develop scalable techniques to incorporate well-dispersed nanoparticle in polymer matrix composites to create a strong bonding between the matrix and reinforcing fiber to enhance interfacial properties. We have introduced a novel processing technique in which CNCs are exploited to control the dispersion and deposition of pristine CNTs onto carbon fibers. CNCs are spindle-shaped nanocrystals having 3-5 nm width and 5-500 nm length [2] with high mechanical properties (130 GPa modulus and 7 GPa strength). Our results show that the integrating 0.2 wt % CNC and 0.2 wt % synergistically increase the flexural and interlaminar properties of CFRP composites by 44%. The CNC-CNT suspension was prepared by sonication in deionized water and the suspension was used to coat the carbon fabrics prior to infusion of resin in a vacuum assisted resin transfer molding (VaRTM) process. To investigate the interfacial properties of CNC-CNT coated carbon fiber/epoxy, in-situ single fiber fragmentation test under an optical microscope is performed. Furthermore, AFM-nano-IR characterization will be used to correlate the chemical composition (with 200 nm resolution) and surface topology of the interphase to its mechanical properties such as strength and modulus.

References

MS03.06.33
Interfacial Analysis on Functionalization Exfoliated Graphene in Polyamide 66 Under Novel High Shear Elongational Flow Justin W. Hendrix1,2, Thomas Nosker1, Thomas Emge1 and Jennifer Lynch-Branzoi1; 1Rutgers, The State University of New Jersey, United States; 2Naval Surface Warfare Center, United States

Graphene is publicized as the game changing material of this millennium. As research continues to expand our knowledge of this 2D semimetal, interfacial properties are increasingly becoming an important characteristic for an idealized graphene integrated composites system. Our research suggest translating graphene’s properties at the nanoscale to the macroscale is best achieved by forming primary or secondary chemical bonds from the matrix to a graphene flake. In our previous work, we have invented a method of creating a graphene reinforced polymer matrix composite (G-PMC) from flake mineral graphite and PA66 in-situ, using high shear elongational flow. Due to our process, we were able to identify chemical bonding at graphene’s surface and edge by XPS and Raman Spectroscopy. By electron microscopy, our results shed light on the mechanism to the formation of graphene functionalities and the creation of unique modified nanostructured morphologies. This work highlights a method to green chemical routes for manufacturing scalable graphene composites.

MS03.06.34
Highly Compressible, Porous Ethylenediamine-Reduced Graphene Oxide Aerogels with Enhanced Structural and Restorative Properties Benjamin Zimmerli and Junjun Ding; New York State College of Ceramics at Alfred University, United States

Graphene oxide (GO) and reduced graphene oxide (rGO) aerogels have been studied intensively over the past decade for their immense potential speculated by the highly desirable mechanical, electrical, and physiochemical properties. Herein, we report the fabrication of an ethylenediamine (EDA)-reduced GO aerogel via lyophilization freeze-drying method from prepared rGO/EDA hydrogels. EDA is added to the GO solution to act as a partial reducing agent, in addition to serving as a crosslinker during the formation of the hydrogel. The resulting structures exhibited extremely high compressibility and structural stability, while additionally exhibiting significant compressive elasticity. Aerogel samples were reported to hold up to 3000x the sample mass, while simultaneously
compressing less than 40% of the total volume. In addition, fabricated aerogel samples were measured to exhibit extremely little, even negligible fatigue over several testing cycles, which further describes the extent of the aerogel’s structural integrity. This gives rise to the potential of EDA/rGO aerogels towards mechanical applications such as shock absorbance or impact resistance.

**MS03.06.35**

**Modification of Interlaminar Fracture Toughness and Through-Thickness Conductivity in PANI-GNP Reinforced CFRP**
Dilli Dhakal, Pralhad Lamichhane, Kunal Mishra and Ranji Vaidyanathan; Oklahoma State University, United States

Carbon fiber-reinforced polymer (CFRP) are lightweight composites and have massive potential towards aerospace and automobile component application. However, the delamination cracks of CFRP are still a challenging topic for the researcher. Numerous works have been done by adding nano-fillers to modify the polymer and improve the mechanical, electrical, and thermal properties. Understanding and minimizing the delamination cracks in CFRP are extremely valuable to reduce the failure in aerospace and automobile parts. Also, CFRP has very low through-thickness conductivity in comparison to conductivity in the fiber direction due to limited the fiber contact surface. The study of through-thickness conductivity is essential because delamination activity in CFRP can be monitored with a change in electrical resistance in through-thickness direction. Investigation and improvement in through-thickness conductivity of CFRP will lead to understanding and reducing the delamination of CFRP during the catastrophic event like lightning strike.

In this present investigation, Polyaniline (PANI) doped graphene nanosheets (GNS) are used as nano-filler, and its effect on fracture toughness and through-thickness conductivity has been studied. The impact of variation in GNS (0, 0.2, 0.5, and one wt %) with respect to PANI is investigated. A double cantilever beam (ASTM D5528) experiment is carried out to characterize the interlaminar fracture toughness. Through-thickness conductivity is measured by impedance spectroscopy. Scanning Electron Microscopy (SEM) is used to study the cross-section of the laminate. Also, viscoelastic properties have been studied in DMA.

**MS03.06.36**

**In Situ Growth of Si$_3$N$_4$ Nanofibers on BN Surface to Enhance the Thermal Conductivity of the Polymer Composites**
Tong Yao, Ke Chen, Yigang Yang and Ying Yang; Tsinghua University, China

Thermally conductive but electrically insulating materials become more and more important for the thermal management. However, the traditional high filler loading to build a thermally conductive network usually leads to significant increase in the viscosity of the precursor mixtures and mechanical deterioration of the polymer composites. Therefore, it is necessary to increase the thermal conductivity of the composites with as little filler as possible. In this work, the surface of BN was firstly coated by SiO$_2$ via hydrolysis and condensation reactions with tetraethyloxyorthosilicate (TEOS). Then, atomic layer deposition (ALD) technique was used to coat alumina (Al$_2$O$_3$), which would play a catalytic role in the subsequent reaction, on the surface of BN coated by SiO$_2$ (BN@SiO$_2$). After that, the BN@SiO$_2$ treated by ALD (BN@SiO$_2$-Al$_2$O$_3$) was mixed with a certain proportion of super P. Si$_3$N$_4$ nanofibers grown in situ on BN can be obtained through reduction and nitridation heat treatment in a nitrogen (N$_2$) atmosphere. In this structure, which Si$_3$N$_4$ nanofibers grown on the surface of BN (BN/Si$_3$N$_4$), BN can form the main thermally conductive paths and the Si$_3$N$_4$ nanofibers can connect the neighboring BN like “bridges” to construct phonon transmission pathways. This special structure can be used to enhance the thermal conductivity of the polymer composites.
Diego, United States

Photoactive deformable polymers have drawn a significant amount of attention due to their distinct advantages such as fast responsiveness, local and wireless control, and environmentally-friendly actuation. Photo-responsive polymers (PRPs) can convert the light energy into the mechanical work. Accordingly, these functional soft materials have been utilized as the bio-mimetic devices and light-responsive soft robots. Among them, the liquid crystalline polymer (LCP) doped with the azobenzene molecules exhibits large and reversible mechanical deformation in response to the UV/visible light irradiation. When the 365 nm-light ray is illuminated, the rod-like trans-moieties are excited and then, isomerized into bent cis-molecules. The photo-chemical reaction induces the collapse of the initial symmetry of the LCP network, which results in the macroscopic deformation. In order to analyze and design the deformation of the PRPs, the multiscale simulation framework, which integrates the mesoscopic light-triggered response and macroscopic mechanical behavior, is systematically developed. Especially, we consider the effects of the diverse design parameters such as the initial LC phase, morphology of the polymer network, and geometry of the specimen to carry out multiscale simulation-based design of the photo-mechanical deformations. First, the coarse-grained molecular dynamics (CG MD) simulation is performed to investigate the changes in properties of the macromolecular network in response to the photo-isomerization reaction. The mesoscale photo-switching potential is firstly developed by using the iterative Boltzmann inversion (IBI) technique to reflect the light-induced molecular shape change and LC phase transition. As a result, we successfully reproduced the light-activated transition between 3 phases (Smectic A (Sm A) – Nematic (N) – Isotropic (I)) and corresponding mesoscale deformations. The light-induced polymeric shape change and softening effect on the elastic properties are parameterized by the photo-isomerization ratio, which represents the extent of the photo-chemical reactions. Then, the mesoscale parameters are upscaled to the continuum scale stress-strain relationship, which is derived from the neo-classical elastic free energy of the LCPs. In order to efficiently reflect the light-induced rotation of the LC mesogens and geometric nonlinearity, a co-rotational formulation is implemented to the finite element (FE) shell model. The presented multiscale analysis efficiently realizes the exotic 3D deformations as well as the simple bending behavior. In addition to these deformation prediction capability, the instability of the snap-through deformations are systematically investigated in terms of the material parameters. We expect that the present scale-bridging computational study can help to practically design the deformed topographies of the photo-responsive mechanical actuators and light-stimuli soft robot components.

Acknowledgements

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9:00 AM MS03.07.02
Rational Design of Polymer Nanocomposites to Advance Their Thermomechanical Performance via Predictive Multiscale Modeling Wenjie Xia; North Dakota State University, United States

Understanding and predicting the thermomechanical behaviors of polymer nanocomposites are challenging as they are greatly influenced by many factors, such as interfacial energy and filler volume fraction, giving rise to the presence of nanoscale interfaces. To better design of polymer nanocomposites, we have recently developed a predictive multiscale modeling approach, namely the energy-renormalization method, to examine how the nanoscale interfaces and molecular characteristics influence the mechanical and glass transition properties of polymer nanocomposites. Taking nanofiller reinforced glassy polymer as a model system, I will present a multiscale modeling framework based on coarse-grained modeling, in conjunction with machine learning, to achieve improved and tunable performance of nanocomposites.

9:15 AM MS03.07.03
Peeling of Composite Membranes Daniele Liprandi1, Federico Bosia2 and Nicola M. Pugno1,3,4; 1Università degli Studi di Trento, Italy; 2Università degli Studi di Torino, Italy; 3Queen Mary University, United Kingdom; 4KET Lab, Italy

Biological and bio-inspired materials are an example of composite materials with superior mechanical properties. Nature can provide inspiration for mechanical optimization of artificial matrix-reinforcement systems, often involving high tunability and synergetic properties. One of the emerging topics of interest in this respect is the study
of the mechanical behaviour of composite adhesive structures. This involves the full characterization of the interaction between complex surfaces, a problem that remains to be fully understood in three-dimensional cases, with adhesive and frictional properties emerging from effects from the nano- to the macro-scale. Indeed, unless specific symmetries or simplifying conditions are considered, it is almost impossible to exactly predict the interaction between generic composite surfaces, due to the large number of parameters involved, including geometrical features, mechanical properties of the materials, substrate properties and the adhesive potentials determining the contact properties. If composite materials are considered, the complexity of the mechanics involved is further increased. To tackle this problem, we have developed a theoretical-numerical approach to simulate the behaviour of a heterogeneous composite adhesive membrane-like structure interacting with a rigid substrate. The model is based the framework method to discretise continuous bodies using structured spring lattices. An in-house developed C++ code has been developed, which allows the model to have a great portability and versatility. As an example, the model is applied to simulate the peeling behaviour of a composite spider disc attachment, composed by a stiff tread fused with a softer silk plaque. The adhesive interface is described using a 3D cohesive law, validating the solutions with analytically predictions for symmetrical problems. Results show how the geometrical properties of the membrane determine the maximal pull-off force and extensibility of the system, and how tearing phenomena and the heterogeneity of the structure change the overall behaviour of the spider disc attachment. Numerical predictions are compared with experimental results from collaborating groups.

9:30 AM  MS03.07.04
Mechanics of Cellulose Nanomaterials Using a Coarse-Grained Modeling Scheme  Upamanyu Ray, Zhenqian Pang and Teng Li; University of Maryland College Park, United States

The quest for alternative biodegradable materials such as cellulose to replace plastics is attracting tremendous attention among the materials science community in addition to being directly aligned with the public interest. Most cellulose nanomaterials comprise of a combination of small (~nm) but strong nanofibers and long (~ μm) but weak microfibers. We investigate the role of interactions of such fibers, spanning across different length-scales, in improving the mechanical properties of the nanocomposite. To qualitatively understand the interface mechanics in the composite material, we devise a three-tier multi-scale coarse-grained (CG) modeling scheme. The levels of the CG scheme are as described: (a) Cellulose molecular chain level (~ Å); (b) Elementary fibril level (~ nm); and (c) fiber level (~μm). We characterize the length and diameter of the fibers using Atomic Force Microscopy and thereby choose the 2nd and the 3rd level of the CG scheme to model the nano and the microfibers respectively to reproduce analogous experimental conditions. We construct hybrid models by mixing the nano and microfiber models. Changing the mass % of the separate nanofibers help explore the fundamental reason behind why the hybrid show greater strength and toughness than the material separately fabricated using only nano or microfibers. From the quantitative aspect, we obtain that the fracture resistance enhances efficiently by around 57 times when the nanofiber content is about 85.7%. Independent molecular simulations of inter-fiber sliding in the nano-, micro- and hybrid fibers elucidate the formation and breaking of hydrogen bonds and clearly explain the role of hydrogen bonding across their interfaces which directly imparts superior mechanistic properties in the hybrids. Implementing the above CG scheme, we also study the interaction between two neighboring fibers (nano & micro) shedding fundamental insight on the mechanical response of cellulose nanomaterials under various representative loads. Such multi-scale modeling investigations, in addition to being very timely, can also be extended to other fundamental building blocks and directly influence the material design of novel hybrid materials having tunable interfacial properties.

9:45 AM  MS03.07.05
Three-Dimensional Transformation of Membrane-Type Electronics Based on Plastic Framework and Plasticization Heungcho Ko; Gwangju Institute of Science and Technology, Korea (the Republic of)

Recent technology of developing membrane-type electronic devices which can deform without losing electrical performance enables stick-and-play system. Because thinner structure is more bendable, a number of researchers tend to make tremendous efforts to develop printable electric devices thinnest possible and transfer printing process. Most efforts work well by thin structure directly when the target applications require mechanically high flexibility but confront some problems of the lack of rigidity to realize three dimensional (3D) electronics devices such as omnidirectional sensory or display system. Here, we report the reliable strategy of handling membrane-type electronic devices, which can deform easily but cannot maintain the shapes by themselves. The method uses linear thermal plastic frameworks that can mechanically support the thin device and also undergo transition from glassy
state to rubbery state, in which their Young’s moduli generally decrease from several GPa to several MPa and migration of polymer chains are also possible. We carried out solvent- or heat-assisted plasticization to allow traveling into the rubbery state temporarily for controlled transformation. The strong advantage of this method is the possibility for positioning membrane-type electronics not only neutral mechanical plane but the top or bottom of the plastic frameworks, which is not available without plasticization. Using this method, we successfully developed bezel-less tetrahedral image sensors or curvilinear arrays of IGZO transistors with nonzero Gaussian curvature from planar forms.

10:00 AM BREAK

10:30 AM *MS03.07.06
Materials by Design Using Artificial Intelligence Markus J. Buehler; Massachusetts Institute of Technology, United States

What if we could design materials that integrate powerful concepts of living organisms – self-organization, the ability to self-heal, and an amazing flexibility to create astounding material properties from abundant and inexpensive raw materials? This talk will present a review of bottom-up analysis and design of materials for various purposes – as structural materials such as bone in our body or for lightweight, strong and resilient composites, for applications as coatings, and as multifunctional sensors to measure small changes in humidity, temperature or stress. These new materials are designed from the bottom up and through a close coupling of experiment and powerful computation as we assemble structures, atom by atom. Materiomics investigates the material properties of natural and synthetic materials by examining fundamental links between processes, structures and properties at multiple scales, from nano to macro, by using systematic experimental, theoretical and computational methods. We review case studies of joint experimental-computational work of biomimetic materials design, manufacturing and testing for the development of strong, tough and mutable materials for applications as protective coatings, cables and structural materials. We outline challenges and opportunities for technological innovation for materials and beyond, exploiting the use of artificial intelligence as a way to complement conventional physics-based modeling and simulation methods. Altogether, the use of a new paradigm to design materials from the bottom up plays a critical role in advanced manufacturing, providing flexibility, tailorability and efficiency.

11:00 AM MS03.07.07
Using Machine Learning Techniques to Predict Mechanical Properties of Composites beyond the Elastic Limit Youngsoo Kim1, Charles Yang2, Yongtae Kim1, Grace Gu2 and Seunghwa Ryu1; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2University of California, Berkeley, United States

Composites with superior mechanical properties are widely used in advanced engineering applications. In the hopes of designing high-performance composites, various analytical, numerical, and experimental methods are used to predict the mechanical properties of composites in terms of reinforcement arrangement and external shape. However, the vast design space of composites, limited accuracy of analytical and numerical approaches in fracture, and time-consuming nature of experimental methods make the rational optimization of composite properties almost infeasible, especially when considering the entire failure mechanism. In this presentation, we introduce two representative works on composite design problems where we utilize machine learning techniques to predict material properties and use the trained models for optimization. First, we use convolutional neural network (CNN) to predict and optimize the stiffness, strength, and toughness of a model composite system consisting of two different linear elastic-perfectly brittle materials, with a reasonable amount of training data (full stress-strain curves of 100,000 random configurations obtained by crack phase field simulation). Despite the astronomically larger combinatorial design space, CNN’s fast inference speed enables the prediction and the optimization of composite design with acceptable accuracy. Second, we leverage Gaussian process regression (GPR) for the design of bio-inspired composites with relatively periodic and regular arrangements with a small training set (full stress-strain curves of 3D-printed samples with 50 different configurations obtained by experiments). The GPR-based design strategy provides a route for strength and toughness optimization when analytical or numerical approach is limited due to the nonlinearity of constituent materials and the uncertainty in manufacturing processes. Our studies demonstrate the potential for machine learning techniques to accelerate the composite design optimization process considering inelastic properties.

11:15 AM MS03.07.08
"In Situ, Multiparametric Nanocharacterization of Composite Materials Using Combined AFM/SEM/FIB"

Georg E. Fantner\textsuperscript{1}, Santiago Andany\textsuperscript{1} and Jason Killgore\textsuperscript{2}; \textsuperscript{1}École Polytechnique Fédérale de Lausanne, Switzerland; \textsuperscript{2}National Institute of Standards and Technology, United States

The complexity of nanocomposites poses tremendous challenges for the quantitative characterization of the properties of the individual components within the composite. The need for multifaceted characterization of the nanocomposite (mechanically, chemically, electrically, magnetically, etc) requires a multitude of nanoscale characterization methods to be applied to a single sample. While a myriad of excellent techniques exist that can provide information about specific aspects of the material, combining these individual techniques sequentially is particularly difficult for nanoscale composites for reasons of colocalization, contamination, and the hierarchical structures that can span several length scales (from nm to mm).

Combining multiple measurement techniques into one in-situ nanocharacterization instrument can solve these issues to enable multiparametric analysis of nanocomposites. For this purpose, we have developed a combined AFM/SEM/FIB instrument that combines the broad range of physical nanocharacterization methods of atomic force microscopy (mechanical, electrical, magnetic) with the chemical characterization capability of scanning electron microscopy and the micromachining capabilities of focused ion beam milling. Of particular interest for nanocomposites is the correlation of chemical composition, with structure and mechanical properties mapping. The vast differences in Young’s moduli between the individual components in many nanocomposites makes nanomechanical characterization particularly challenging. We therefore use advanced AFM based mechanical property measurement techniques (off resonance tapping in combination with contact resonance) to span three orders of magnitude in Young’s moduli.

In this presentation we will discuss examples of this in-situ nanocharacterization for 2D and 3D study of polymer blends, biological nanocomposites and high-performance self-healing synthetic materials.

11:30 AM MS03.07.09

Mapping Storage and Loss Modulus of Polymer Composites across Time and Temperature with AFM-Based Nano-DMA

Bede Pittenger, Sergey Osechinskiy, John Thornton, Sophie Loire and Thomas Mueller; Bruker Nano Surfaces, United States

For heterogeneous polymer samples like polymer composites and thin films, it is often of interest to understand the mechanical properties of microscopic domains within the material and near the boundaries between one component and another. Atomic Force Microscopy (AFM) has the nanometer level resolution and sensitivity needed to investigate these domains, but established AFM measurement modes do not yield results that allow direct comparison to established rheological techniques like Dynamic Mechanical Analysis (DMA). Contact resonance [1] provides mechanical property maps at well-defined frequencies, but cantilever resonances are many orders of magnitude higher than DMA, making comparisons indirect at best. Intermittent contact methods like TappingMode[2], force volume, and PeakForce Tapping [3, 4] face challenges in calculating intrinsic mechanical properties like storage and loss modulus (or tan delta) due to the non-linear process of making and breaking contact [5].

AFM based nano-DMA (AFM-nDMA) provides viscoelastic results that can be directly compared with bulk DMA. Like bulk DMA, it provides spectra of storage and loss modulus across frequency and temperature allowing construction of master curves through Time Temperature Superposition (TTS) [6]. In addition, it allows high resolution measurements of the microstructure of heterogeneous samples to allow better understanding of their properties and behavior. This presentation will examine the capabilities of this new mode with examples in a wide range of polymers and composites.

Coupled Electrical Resistance Measurement and IR Thermography Monitoring for Analysis of Damage Development and Fatigue Strength of Composite Materials  
Kundo Park¹, Seunghwa Ryu¹ and Flavia Libonati²;  
¹KAIST, Korea (the Republic of); ²Politecnico di Milano, Italy

Rooted from its heterogeneous microstructure, composite materials possess high strength to weight ratio and, therefore, they are applied in a wide range of industry. However, their complicated microstructure makes it difficult to predict the failure mechanism and residual material life. The in-situ health monitoring system has received much attention in recent years as one of the promising solutions for the aforementioned limitations of composite material. In this research, electrical resistance measurement and IR thermography is utilized simultaneously as a unified non-destructive testing system to monitor the initiation and evolution of damage inside the composite materials. Through the experiment where we combined our coupled NDT system and a uniaxial tensile test of GFRP, the deformation and failure timeline of GFRP under tensile test could be subdivided into three different levels and finally enabled us to identify a characteristic stress value called ‘Damage stress($\sigma_D$)’. In this research, we suggest that the Damage stress value, characterized by our coupled NDT system, can be a reasonable estimation of the fatigue strength of the studied material. In contrast with the conventional fatigue tests that requires tens of thousands of loading cycles, application of our coupled NDT system can effectively characterize the fatigue strength of composite materials in a single uniaxial tensile test. Series of analysis on the experiment result were carried out to understand how the damage stress value can be equivalent to the actual fatigue strength of the studied material. Furthermore, the correlation between the thermal, electrical and mechanical behavior of composite materials was thoroughly understood through multiphysics modeling study.

Bioinspired Fabrication of Complex Vascular Architectures in Polymers and Composites  
Nancy R. Sottos, Mayank Garg and Jeffrey Moore; University of Illinois at Urbana-Champaign, United States

The introduction of vasculature to polymers and composites enables adaptive and environmentally responsive materials with properties like self-healing, self-cooling, and electromagnetic reconfigurability. Previously, we demonstrated thermal degradation of sacrificial poly (lactic acid) (PLA) templates embedded in thermoset matrices to create multifunctional composites with interconnected vascular networks [1]. However, this vascularization method is a two-step process that requires significant energy input and time to first polymerize the thermoset matrix and then to depolymerize the PLA into volatile products at elevated temperatures (ca. 200 °C for 12 hours). Here, we introduce a biologically inspired, simultaneous depolymerization of sacrificial templates during frontal polymerization of the surrounding matrix [2]. As the reaction front propagates to polymerize the matrix, the released heat is sufficient to concurrently degrade and volatilize the sacrificial template. We explore sacrificial materials such as cyclic poly(phthalaldehyde) (cPPA) and poly(propylene carbonate) (PPC), which depolymerize at relatively low temperatures (~100°C). This new manufacturing process enables freeform fabrication of complex, porous vascular networks with potential for highly functionalized interfaces.


Uniaxial Extension of Ultra-Thin Freestanding Polymer Film

R K. Bay and Alfred J. Crosby; University of Massachusetts Amherst, United States

Recently, we developed a method for quantifying the complete uniaxial stress-strain relationship for ultra-thin polymer films. The key to this method is the use of liquids to help support ultra-thin, often fragile, films. Although this method has provided new insights into mechanical properties and deformation mechanisms for dimensionally-confined polymer systems, for some polymers the presence of a liquid may influence the ultra-thin properties. Here, we introduce a new method, freestanding tensile tester to directly measure the uniaxial stress-strain response of freestanding polymer thin films. Using polystyrene thin films, with thickness 15 nm-100 nm, we observe and quantify large strain deformation mechanisms, as well as yield stress and elastic moduli, and compare these results to the liquid supported measurements. We find that the liquid acts as a craze stabilizer for polystyrene thin films which leads to lower strains in the freestanding method compared to the liquid supported method. These results provide new fundamental insights into how the surface interactions can alter polymer behavior in thin confined polymer films.

Characterization of the Carbon Fiber/Matrix Interface in Frontally Polymerized Composites

Douglas Ivanoff, Clément Viers, Jaeuk Sung and Nancy R. Sottos; University of Illinois Urbana-Champaign, United States

Current manufacturing of carbon fiber reinforced polymers (CFRPs) consumes a significant amount of energy due to high temperature and pressure cure cycle requirements. Frontal ring opening metathesis polymerization (FROMP) reduces the total energy cost of manufacturing CFRPs by orders of magnitude while reducing the fabrication time. Using a resin system comprising of a ring-strained dicyclopentadiene (DCPD) monomer and a latent second-generation Grubbs catalyst, site-heating generates a self-propagating polymerization front that consumes the monomer and creates rigid, tough thermosets and composites with greater than 50% fiber volume fraction. pDCPD composites currently display suboptimal mechanical properties attributed to weak adhesion of the hydrocarbon matrix to the carbon fibers with commercially available surface chemistries. In this work, several olefinic sizing agents are synthesized and applied to carbon fibers to covalently bond the matrix and reinforcement for increased interfacial shear strength (IFSS). The IFSS, debond length, and fiber slippage at the interface are all characterized in single fiber fragmentation tests under cross-polarized light. Sizing agents applied to the carbon fiber increase the amount of norbornene moieties on the surface, resulting in a reduced critical fiber length. This improved surface functionality increases the IFSS by over 50% from the epoxy-sized fibers. Due to the high fracture toughness of the pDCPD matrix, fiber debonding along the weak interface occurs preferentially to matrix cracking. In addition, we investigate the impact of the unique thermal processing history during FROMP on interfacial properties and compare to conventionally cured samples.

New Deformation Modes in Three-Dimensional Liquid Crystal Elastomer Microstructures

Joanna Aizenberg; Harvard University, United States

Adaptive, responsive and self-regulated 2D and 3D materials hold promise for a variety of applications – from energy-efficient transducers and energy harvesting to autonomously moving devices and homeostatic systems. From a wide variety of designs that have been utilized to engineer such materials, a hybrid bioinspired system comprised of high-aspect-ratio skeletal elements embedded in a responsive gel “muscle” has proven very versatile. One limitation of this system is its reliance on the responsiveness of the gel, in order to achieve the macroscopic deformations provided by the movement of the skeletal elements. We will present several active temperature- and light-responsive systems where microstructures made of liquid crystal elastomers (LCEs) are themselves the responsive elements. By varying the molecular structure of the LCE precursors and cross-linkers and by predetermining nematic ordering of the resulting elastomers through choosing the orientation of the prepolymer samples in the external director – magnetic field – we have realized a wide range of systems capable of temperature- and light-induced deformations, many of which are unattainable in traditional gel-skeletal element responsive designs or in well-known cellular structures. We will demonstrate predetermined and self-regulated deformations in these LCEs, as well as designs capable of chirality generation and switch, and unprecedented nonmonotonic
responses to monotonic stimuli. We foresee that this platform can be widely applied in switchable adhesion, information encryption, autonomous antennae, energy harvesting, soft robotics, and smart buildings.

4:00 PM MS03.08.05
Size Effect of Freestanding Ultrathin Polymer Films Guorui Wang and Tobin Filleter; University of Toronto, Canada

The mechanical properties of thin polymer films are of scientific and technological interest to diverse communities of researchers. This interest is mainly driven by the development of flexible and stretchable electronics with a wide range of applications in flexible, wearable, and implantable devices. While the moduli of thin polymer films are known to deviate dramatically from their bulk values, the nature of such size effect still remains debatable. Specially, indentation technique gives rise to contradicting results from both buckling experiments and molecular dynamics calculations, which is claimed to result from the substrate effect. Herein, freestanding ultrathin polymethyl methacrylate (PMMA) films with thickness ranging from 6 nm to 129 nm were measured by atomic force microscope (AFM) based nanoindentation. Obvious plate-to-membrane transition is observed in the deformation characteristics with decreasing thickness. Combined with the classical plate theory and contact mechanics model, we demonstrate the great enhancement in both Young's moduli and yield strength even in the absence of substrate, which is further evidenced and interpreted by molecular dynamics (MD) simulations. Additionally, the broadening of the elastic strain range allows higher stretchability, which is anticipated to further advance the development of flexible and stretchable electronics.

4:15 PM MS03.08.06
High-Strain-Rate Plasticity of Block Copolymer Microspheres Correlating with Microphase Separation Ara Kim and Jae-Hwang Lee; UMASS Amherst, United States

In the use of advanced manufacturing, targeting certain mechanical performances by tailoring inherent material properties is a success factor, and material diversities are emphasized as the application area expands to non-metallic materials and mixed composites. Multi-phase polymers or phase-separated block copolymers (BCPs) consist of two or more mechanically distinctive nanoscale phases. The diverse nanostructures of BCPs, which can be tailored through thermal annealing process, cause obvious changes in mechanical properties. Moreover, the high-strain-rate deformation characteristics are generated and controlled by impact tests with different collision conditions. Polymers are emerging materials in additive manufacturing such as the cold spray technique, however, mechanical behaviors including extreme plastic deformations resulting from collisions have not been demonstrated thoroughly. In order to obtain insight into the novel phenomena of BCP’s mechanical behaviors with anisotropic nanostructures, single-particle impact experiments of polystyrene-block-polydimethylsiloxane (PS-b-PDMS) block copolymer (BCP) microparticles with different nanostructures were performed to demonstrate the effects of nanostructures of BCP microparticles before and after impact against rigid substrates. BCP particles with different volume fractions of PS and PDMS were annealed at diverse conditions to obtain different degrees of ordered nanostructures in two phases, such as cylinders and lamellae. Both annealed and non-annealed BCP particles were tested by using the laser-induced projectile impact test (LIPIT) method. A single BCP micro-particle was accelerated to a high velocity (70 – 600 m/s) and impacted onto a rigid substrate, and the collision was monitored with an ultrafast imaging system using femtosecond illumination pulses. Coefficients of restitution, critical velocity, acceleration-force-induced inelastic deformation and collision-induced extreme plastic deformation features of the BCP particles were investigated for different nanostructures and impact conditions. Electron microscopy and focused ion beam milling were used to demonstrate ordered nanostructures and impact-induced morphological changes of the BCPs before and after the collisions. Acceleration-force-induced inelastic deformation was investigated by analyzing dimension changes during acceleration and until the moment of impact. As critical velocities and coefficients of restitution of BCPs were changed depending on the status of the nanostructures, the morphologies of nanostructures were important factors in deciding the mechanical characteristics of BCP before and after impact. One of the most critical findings of this study was that nanoscale structural changes of BCP microparticles cause microscale changes in mechanical behaviors, and it furthers research into how BCPs can be tailored to satisfy target performances in additive manufacturing.

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4:30 PM MS03.08.07
Complex-Shaped Cellulose Composites Made by Wet Densification of 3D Printed Scaffolds

Michael Hausmann\textsuperscript{1,2}, Gilberto Siqueira\textsuperscript{1,2}, Dimitri Kokkinis\textsuperscript{2}, Antonia Neels\textsuperscript{3}, Tanja Zimmermann\textsuperscript{1}, Rafael Libanori\textsuperscript{2} and André R. Studart\textsuperscript{2}; \textsuperscript{1}Swiss Federal Laboratories for Materials Science and Technology, Switzerland; \textsuperscript{2}ETH Zürich, Switzerland; \textsuperscript{3}Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Cellulose is an attractive material resource for the fabrication of sustainable functional products, but its processing into structures with complex architecture and high cellulose content remains challenging. Such limitation has prevented cellulose-based synthetic materials from reaching the level of structural control and mechanical properties observed in their biological counterparts, such as wood and plant tissues. To address this issue, we report a simple approach to manufacture complex-shaped cellulose-based composites, in which the shaping capabilities of 3D printing technologies are combined with a wet densification process that increases the concentration of cellulose in the final printed material. Complex-shaped composites with cellulose concentration up to 27.35 vol % can be created through the wet densification of 3D printed scaffolds. The densification process involves the exchange of the aqueous phase of the printed wet scaffold by a liquid mixture that works as a poor solvent for the cellulose particles. Because of their high cellulose concentration, composites obtained via infiltration of wet densified scaffolds with an organic phase show significantly higher fracture strength and stiffness compared to state-of-the-art 3D printed cellulose-based materials. This strengthening effect arises from the very high concentration of cellulose achieved in the final composite and is also partly affected by the strong alignment of the cellulose particles along the extrusion direction during the printing process. The high level of structural complexity and control achieved with this combined process opens the way to the fabrication of cellulose-based materials that capture some of the design principles of biological structures like wood and morphing plant structures. Since mechanical stability and high cellulose content are key to achieve long-term durability and to fully benefit from the sustainable nature of this material resource, the proposed manufacturing workflow is also expected to have a major impact in future cellulose-based structural, biomedical and energy-related products.

SESSION MS03.09: Poster Session III: Polymer Nanocomposites

Wednesday Afternoon, December 4, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

MS03.09.01

Direct Observation of Chain Adsorption Processes on to a Solid Surface

Yuma Morimitsu, Hisao Matsuno and Keiji Tanaka; Kyushu University, Japan

Polymer/inorganic filler composites have attracted a great deal of attention as a light-weight structural material with excellent mechanical properties. So far, it has been widely accepted that the interface between a polymer and a filler is a key to control the material performance. However, it is still open how the interfacial layer composed of adsorbed chains is formed. In this study, the direct observation of the formation processes for the interfacial adsorbed layer was performed by atomic force microscopy (AFM). As a model polymer, deoxyribonucleic acid (DNA) was selected because of its relatively-large molecular size, leading to observation with relative ease. Lambda phage DNA with 48.5k base pairs, hereafter referred to as DNA, was used. Basically, DNA molecules used take a random coil conformation in a solution state. The radius of gyration ($R_g$) and the persistence length determined by small-angle X-ray scattering measurement were 284 nm and 29.3 nm, respectively. DNA solutions at various concentrations were prepared by diluting a stock solution of DNA with 40 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer solution containing 5 mM NiCl$_2$ (5Ni). Mica disks were incubated with the diluted DNA solutions for a given time and then washed with 40 mM HEPES containing 10 mM NiCl$_2$ (10Ni). To study the morphology of single chains, AFM observations for the sample incubated in 0.1 mg/mL DNA solution with 5 Ni for 2 min were carried out. A single chain of DNA adsorbed on a mica surface was clearly captured. It took a two-dimensional (2D) extended coil conformation. The radius of gyration estimated from the AFM image, defined as $R_{g,2D}$, was approximately 630 nm. This value was twice larger than the corresponding value in a solution state determined by SAXS. For statistical analyses, the wide AFM images, containing two or three DNA chains, were acquired. The $R_{g,2D}$ and the persistence length evaluated by fast Fourier transform (FFT) analysis were 796 nm and 362 nm, respectively, meaning that DNA chains were more extended onto the mica surface than in the solution. This is
probably due to create greater contact points between DNA and mica surface. To discuss the adsorption processes of DNA chains, AFM observations for the samples incubated in a 0.1 mg/mL DNA solution with 5 Ni for 5 - 45 min were carried out. With increasing incubation time, the amount of adsorbed DNA chains increased. Interestingly, DNA chains were inhomogeneously adsorbed, although there were a lot of empty sites on the mica surface. To obtain a better understanding of this finding, we focused on the distance between adsorbed DNA chains. First, the AFM-FFT analysis was made for the sample incubated for 2 min. Since DNA chains were highly isolated for one another, the power spectrum as a function of spatial frequency ($L^{-1}$) so obtained corresponds to the form factor spectrum. Then, the structure factor spectra for the samples incubated for several hours were obtained from each FFT spectrum after dividing it by the form factor spectrum. In these spectra, a peak corresponding to the distance between adsorbed DNA chains was observed at $L^{-1}$ of approximately $6 \times 10^{-4}$ nm$^{-1}$, namely 1.5 μm, which was slightly smaller than twice $R_g$ described above. This peak position was not dependent on the incubation time. This result means that DNA chains were inhomogeneously adsorbed since the earlier stage of adsorption process. Also, entanglements between two DNA chains were clearly observed. Taking into account that the concentration of the solution here used was much lower than the overlapping concentration of DNA, the results indicate that the entanglements between precedingly adsorbed chains and free chains occurred on the mica substrate, called “cooperative adsorption”. In our presentation, effects of molecular weight of DNA and ionic strength of DNA solutions on the adsorption process will be also discussed.

**MS03.09.02**  
*Influence of Graft Density on Dynamically Coupled Polymer Grafted Nanocomposites*  
Andrew Ehlers¹, Pinar Akcora² and Rahmi Ozisik¹; ¹Rensselaer Polytechnic Institute, United States; ²Stevens Institute of Technology, United States

The viscoelastic behavior of polymer grafted nanocomposites (PGNs) with significantly different glass transition temperatures ($T_g$) between the graft and matrix polymers is investigated with molecular dynamics simulations. These types of PGNs have been shown to have reversible and repeatable stiffening behavior upon heating (Senses, E.; Isherwood, A.; Akcora, P. *ACS Appl. Mater. Interfaces* 2015, 7, 14682). This unique thermal stiffening behavior was attributed to the dynamic coupling of the high-$T_g$ adsorbed chains and low-$T_g$ matrix chains. The PGN studied in the current work consists of a nanoparticle with grafted high-$T_g$ polymer chains in a low $T_g$ polymer matrix. The effect of the dynamic coupling of the grafted and matrix polymer chains is studied by molecular dynamics simulations. The influence of the graft density on viscoelastic properties is investigated to identify the mechanism of the observed stiffening in these types of PGNs.

**MS03.09.03**  
*Water-Triggered Evaporation of Fragrance Oil from Porous Particles Coated with Hydrophilic Polymers*  
Hesson Chung¹, Young Sim Song² and Jeongae Lee¹; ¹KIST, Korea (the Republic of); ²Cleani Co., Korea (the Republic of)

Fragrance oils were encapsulated in a variety of porous particles by preparing emulsion of fragrance oil/hydrophilic polymer and by kneading the emulsion with porous particles. Depending on the hydrophilic polymers, the evaporation rate was slowed down and was controlled by the addition of water. Corn starch, polyvinylalcohol, chitosan, carboxymethyl cellulose were effective because the evaporation rate of fragrance oil was low (lower than 20 %) in air and was high (higher than 80%) in water when the particles were stored at room temperature for 2 hours. The evaporation rate was similar in air and in water in case of sodium alginate, xanthan gum and carboxpol. Among the porous particles including activated carbon, powdered charcoal, zeolite, porous silica and magnesium aluminum metasilicate, powdered charcoal had the lowest evaporation rate of fragrance oils. However, the water-triggered evaporation was not observed since fragrance oil did not evaporate even in the presence of water. Choice of fragrance oils was also important in controlling the evaporation rate. In air, more than 50 % of limonene, citronella and peppermint oils evaporated when the particles were stored at room temperature for 2 hours. Only less than 20 % of lavender, tea tree and ylang-ylang oils were evaporated under the same experimental condition. When water was added to the magnesium aluminum metasilicate particles containing corn starch, 80 % of the lavender oil evaporated in 2 hours while 50 % was evaporate in 24 hours in air. The water absorbent particles retained absorbent power after the emulsion containing the fragrance oil and hydrophilic polymer. The prepared particles were mixed with superabsorbent polymers to be used in manufacturing the pet pads. The particles and the superabsorbent polymers had different densities and therefore had to be shaken from time to time to ensure the mixing.
Water-absorbent particles such as Syloids and Neusilins were effective in controlling the water-triggered evaporation of fragrance oils because the particles deprive water from the hydrophilic polymers and help form the outer protective polymer layer. When the particles were used with the superabsorbent polymers the urine odor was eliminated by absorbing the chemicals in the urine, by odor-masking of the evaporated fragrance oil, and by the antimicrobial activity of the fragrance oil.

**MS03.09.04**

**Hybrid Heat-Hydration Triple Shape Memory in Electrospun Polymer Blends** Emily Sharp, Michelle Pham, Melodie Lawton and Patrick T. Mather; Bucknell University, United States

Contemporary research based on electrospinning fabrication has continued to grow as this technique has proven to be an efficient and highly reproducible method for nanofiber production. Electrospinning is the process of forming nanofibers from viscous polymer solutions exposed to electrostatic forces that drive continuous jet formation as solvent is removed and the jet is stretched. The use of dual-electrospinning, involving a two-solution delivery system, in reducing fabrication time and fabricating composite fibrous mats has continued the advancement of electrospinning-based research. This study aims to utilize such advancements to demonstrate triple shape memory via two distinct stimuli that is possible in dual-electrospun poly(vinyl acetate) (PVAc) and poly(ε-caprolactone) (PCL) films.

The term shape memory (SM) refers to the ability of a material to form and recover from a secondary shape to its permanent shape through the application of an external stimuli. We have reported that isotropic PVAc:PCL blends prepared by electrospinning exhibit dual and triple SM, meaning that they can form two distinct temporary shapes. Hydration of the composite films was found to reduce the PVAc glass transition to a subambient level as water molecules disrupt intramolecular bonding and mobilize the network chains. This reduction produces a rubbery material that has a well-separated glass transition temperature (of PVAc) and melt temperature (of PCL), thus allowing this material to exhibit triple SM using two different external stimuli: heat and water.

We report on hybrid shape memory behavior involving both heat and mass transport for PVAc/PCL blends. Heating blends above the melting point of PCL, deforming the sample, and cooling will result in one temporary shape. Deforming the sample again in a water bath, followed by drying, forms a second temporary shape. Rehydration of the composite returns the sample to the first temporary shape and reheating the sample returns it to the original shape. Variables considered include the concentration of PCL, the overall sample geometry and thickness, and the extent of the shapes formed. This hybrid SM is quantified using a Dynamic Mechanical Analyzer (DMA) in conjunction with uniaxial tensile testing with a water immersion bath to separately quantify the SM response to heat and the response to water, respectively. Qualitative analysis is performed through image processing with visual confirmation through video documentation. This provides valuable information on a hybrid process of two well-defined and well understood phenomena, aiding in future research and product concepts that have the potential to revolutionize multiple different fields ranging from textiles to medicine.

**MS03.09.05**

**Melt Extrusion of Novel Nanocomposites with Thermal Stiffening Behavior** Chen Gong1,1, Pinar Akcora2 and Rahmi Ozisik1,1; 1Rensselaer Polytechnic Institute, United States; 2Stevens Institute of Technology, United States

A class of polymer-absorbed silica nanoparticle reinforced polymer nanocomposites were found to have a peculiar thermal stiffening response with increasing temperature that not only provides a new method to manipulate mechanical properties as a function of temperature but also offers the opportunity to develop new products based on thermal stiffening. The next step towards mass production requires testing these new class of materials’ processability via traditional polymer processing techniques such as extrusion. In the current work, a laboratory mixing extruder was used to evaluate the processability and the effect of processing conditions on thermal stiffening behavior. Polymers with different rigidities were absorbed on to silica nanoparticles before they were dispersed in a poly(ethylene oxide), PEO, matrix. Then these nanocomposites were melt extruded under various extrusion conditions. The resultant extrudates were characterized using Fourier-transform infrared spectroscopy (FTIR) and electron microscopy. Thermal stiffening behavior of the extrudates was characterized using a parallel plate rheometer. Systems with highly rigid adsorbed polymers, the storage modulus values dropped drastically after extrusion. Systems with less rigid adsorbed polymers recovered and even experienced a slight reinforcement in storage modulus after extrusion. The current work probes the processability of a novel nanocomposite system and also provides new insights towards its dynamics under complex deformation conditions.
Damage-Free and Selective Transfer of Ultra-Thin Films by Solvent-Assisted Adhesion Control

Sumin Kang, Boo Soo Ma, Taeshik Yoon, Min Sun Cho and Taek-Soo Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Interfacial adhesion has been regarded as a key factor for mechanical peeling and transfer of ultra-thin films which are necessary to fabricate next-generation electronics. Ultra-thin films have strong adhesion because their extreme flexibility enables conformal contact to the topography of a substrate. Whereas, strong interfacial adhesion between a film and a substrate causes both structural damage to the film during delamination process and difficulty of interfacial crack initiation. To reduce adhesion energy and structural damage, solvent assisted transfer methods have been developed by using water and ethanol recently. However, quantitative control of adhesion and its application to damage-free, selective transfer have not been demonstrated yet.

In this work, we show damage-free and selective transfer of ultra-thin films by solvent-assisted interfacial adhesion control. Double cantilever beam fracture testing is performed in various solvent environments including water, ethanol, diiodomethane to measure quantitative adhesion energy of graphene-Cu and Au-Si interfaces. Moreover, two-component surface energy analysis and Owen-Wendt method are exploited to calculate work of adhesion, which is required energy to separate an interface and create new surfaces. Various solvents introduce dramatic change of the interfacial adhesion energy owing to the surface energy difference in the crack-tip environments, and the variation is corresponded to the calculated work of adhesion. Accordingly, the interfacial adhesion can be controlled by modulating surface energy of solvents, and it can be estimated by work of adhesion.

Solvent-assisted adhesion control enables structural damage-free and selective transfer of ultra-thin films. Degree of structural damage in transferred graphene and Au nanofilm is investigated by Raman area mapping and optical images. The solvent environments allow effective mitigation of structural damage in the transferred films by reducing interfacial adhesion energy, and the transferred graphene electrodes with less damage have outstanding mechanical reliability due to uniform stress distribution. Furthermore, novel method for selective transfer of patterned thin films is developed by modulating wettability of thin films and utilizing surface tension of a solvent. Diverse patterns of Au nanofilm such as serpentine electrodes, thin film spiral inductors, and characters are achieved, and the patterned thin films are transferred onto a flexible substrate. We expect that this study will provide an advanced transfer technology to integrate a patterned ultra-thin film without damage onto an arbitrary substrate.

Developing Advanced Manufactured Composite Polymer Filaments for Extreme Environments

Zachary Brounstein1,2, Jianchao Zhao1, Joseph H. Dumont1, Samantha J. Talley1, Eamonn C. Murphy1, Kwan-Soo Lee1 and Andrea Labouriau1; 1Los Alamos National Laboratory, United States; 2The University of New Mexico, United States

Extreme environments comprised of elevated temperatures, harsh chemical species such as acids and bases, mechanical stresses, and ionizing radiation are of serious concern in every industry relying on materials retaining their inherent properties throughout their lifetime. Furthermore, some industries or uses require these materials to protect its workers and instrumentation from such aggressive conditions. In the current aerospace, defense, and nuclear industries, commercial products are readily used as protective barriers, but there are circumstances when these are less than ideal at providing optimal shielding against extreme conditions, especially neutrons and gamma rays[1][2]. In addition, these non-optimized materials may not possess desired properties such as ideal topology and geometry and thus mechanical behavior. As innovations to aerospace, defense, and nuclear technologies continue to progress, developing new engineered materials and composites for extreme environments grows in importance and need.

In the present work, we used an advanced manufacturing (AM) technique known as Fused Filament Fabrication (FFF) to create novel feedstock composite materials for 3D printing. FFF is a layered AM process whereby thermoplastic filaments are heated up to their melting point and extruded into cross-sections of the end product[3][4]. Because FFF has the capability to create prototypes and end-use parts with fine resolution details and excellent strength-to-weight ratios, the technology is ubiquitous across many enterprises requiring enhanced manufacturability and unique features.

Difficulties in creating composite filaments for FFF arise from fabricating a homogenous wire that has uniform thickness and a smooth surface. If a filament does not have these initial properties, then either the FFF process will
not work or the end product will not be as desired. Creating a homogenous wire proves more difficult when different base and filler materials are used in the fabrication process, however, this can be solved if the organic materials are solvated in a liquid solution and then mixed with the inorganic phase. Creating a wire of uniform thickness relies heavily on the extrusion process, whereby the temperature and extrusion speed are controlled.

In this study, we have prepared homogenous composite filaments for AM from a variety of polymer bases and incorporated a high weight percent loading of metal fillers. Thermal, mechanical, chemical, and radiative properties were evaluated to determine the efficacy of this process of creating AM feedstock material for FFF technologies.

References


**MS03.09.08**

**Electrospun Nanofibrous Bilayer Fabrication Technique Based on Electrolyte-Assisted Electrical Discharge**

Hyeonseok Han¹, Sang Min Park¹,², Hyeonjun Hong¹ and Dong Sung Kim¹; ¹POSTECH, Korea (the Republic of); ²Pusan National University, Korea (the Republic of)

Due to the advantages of electrospinning process including facility, versatility, cost-efficiency, it has been widely used to fabricate a polymeric nanofiber mat in the engineering field. Especially, a wide range of material selectivity, high surface area to volume ratio and porosity of electrospun nanofibers have contributed to remarkable developments in tissue engineering by recapitulating the hierarchical architecture of the extracellular matrix (ECM).

Significant development of electrospun nanofibrous scaffold in tissue engineering has been associated with the alignment of electrospun nanofiber with respect to topographical effects on cellular activity of cell proliferation, migration, and differentiation. More specifically, the aligned nanofiber mat has been demonstrated to promote the regeneration or repair of various in vivo tissues (e.g. skin, cardiac muscle, and peripheral nerve) and to be used for medical applications.

To produce aligned nanofibers, a number of approaches including electric field-controlled technique (e.g. parallel ground electrodes) and mechanical technique (e.g. high speed rotation of mandrel) have been proposed previously. Among them, the electric field-controlled method can easily produce an aligned nanofiber mat without an additional motion control system of the mechanical method. Moreover, diverse configuration of the alignment, like uniaxial and radial alignments, could be achieved by arranging the ground electrodes. However, the aligned nanofiber mat fabricated by the electric field-controlled method is too mechanically weak to handle. In addition, the charge retention of as-spun nanofibers, which cause unstable electric field and repulsive force near the aligned nanofiber mat, impedes the fabrication of thick aligned nanofiber mat in the process. In order to resolve the limitations of mechanical weaknesses, electrospun nanofibrous bilayer which is composed of the aligned nanofiber layer (functional layer) and the random nanofiber layer (supporting layer) was introduced in previous studies. Though several methods such as transfer method and charge retention-based method have been suggested to generate the electrospun nanofibrous bilayer, the disadvantages (e.g. additional transferring process, misalignment, time-consuming, non-uniformity etc) of each method have not been improved.

In this study, overcoming the aforementioned disadvantages, we have developed a novel electrospinning process for the fabrication of electrospun nanofibrous bilayer based on electrolyte-assisted electrical discharge. Interestingly, the newly suggested electrospinning process enabled in situ fabrication of aligned and random nanofiber multilayer (e.g. triple, quadruple layer) by sequentially changing ground electrode from arranged metal electrodes to electrolyte with a simple liquid filling system and without additional transferring process to induce misalignment of the nanofiber. The adoption of the electrolyte was found to provide a stable electric field by an electrical discharge from the deposited nanofibers and allowed the focused electric field on upper surface area of electrolyte. Consequently, the fabrication time was reduced by 2.5 times compared to conventional method. In addition, more homogeneous
morphology of the deposited nanofibers was shown. The improved elastic modulus of 4.5 MPa due to the compactly deposited random nanofiber layer demonstrated the sufficient mechanical properties for handling compared with the elastic modulus of 2 MPa of conventional method. To examine its possible utilization in the field of regenerative medicine, biological \textit{in vitro} wound healing assay was proceeded with NIH3T3 fibroblasts. The accelerated fibroblasts on the aligned nanofibers suggest the potential of the electrospun nanofibrous bilayer as a wound healing patch and indicated the wound closed faster than the control.

**MS03.09.09**

An Investigation on Finding an Optimal Pore Structure in Porous Materials Using Finite Element Simulation

Dongmyung Jung and Yongwoo Kwon; Hongik University, Korea (the Republic of)

Effective properties of a porous material comprising solid and pore phases can be varied between upper and lower bounds at a given porosity by varying its pore structure. However, achieving low thermal conductivity and high Young’s modulus at the same time is difficult because there is a trade-off. Nevertheless, there must be an optimal pore structure. In this work, we try to find the optimal structure for a porous metal using finite element simulation. Relations between structural parameters and properties are characterized for several pore structures with porosity of 50%. The structural parameters are local curvatures of interfaces (morphology) and Euler characteristics (topology). Then, some rules will be extracted and applied to design an optimal structure.

**MS03.09.10**

Molecular Dynamics Simulations of Thermal Nanoimprint Lithography for Polymeric Materials

Jahlani I. Odujole and Salil Desai; North Carolina A&T State University, United States

Nanoimprint lithography (NIL) is a low-cost, high-throughput method used to manufacture products at the nanoscale. The benefits of nanoscale research are the improved physical characteristics of materials at smaller scales. Two of the most prominent methods of NIL are thermal (T-NIL) and UV. In general, T-NIL processes utilize a pre-fabricated rigid mold to imprint a pattern onto a substrate coated with a thermoplastic resist. This research focuses on the molecular dynamics (MD) simulations of T-NIL for four candidate polymers as resist materials: poly methyl methacrylate (PMMA), polyacrylic acid (PAA), polyethylene terephthalate (PET), and polycryliconitrile (PAN). This is a novel method that considers more than two polymers as possible resists. In order to make inferences about the effect of temperature, force, and pressure on the quality of T-NIL results, the polymers are operated upon using MD. The specific force field applied to this system is a modified version of the consistent valence force field (cvff). It is shown that PMMA yields the most consistent imprints given a certain set of simulation parameters. The simulation parameters were modified to produce changes in: penetration depth, imprint depth, and recovery behavior. The ability to manipulate multiple polymer materials for T-NIL processes is demonstrated by this research.

**MS03.09.11**

Amplified Photo-Actuation Performance in Azobenzene Incorporated Heterogeneous Polymer Network via Sequential Thiol-ene Reactions and Isomer Self-Interconnection

Chenzhe Li, Hyunsu Kim and M. Cho; Seoul National University, Korea (the Republic of)

Photo-actuation is of great interest because the light stimuli are capable of transferring remote controlling signals and high energy density power supply spontaneously with great spatial selectivity. Azobenzene, as one of the molecular scale photo-strain generator, offers direct light-mechanical responses with high energy conversion efficiency and fast responding kinetics. The direct utilization of this molecular-level photo-strain phenomenon is challenging. Conventionally, azobenzene monomers are homogeneously copolymerized with other host materials (such as liquid crystalline polymers), therefore by disturbing the local polymer network structure, the molecular-level photo-generated strain could be translated to mechanically applicable macro-scale actuation. While this strategy offers great optical efficiency, material selection feasibility and programmability, the translation of the molecular-level strain to mechanically applicable macro-scale is inefficient. In this study, we describe a versatile heterogeneous polymer fabrication strategy to achieve significant enhancement in the translation process, resulting in amplified the photo-actuation responses in azobenzene incorporated polymers. The strategy employs a facial two-step polymerization process based on the sequential orthogonal thiol-ene Michael addition (thiol-acryloyl) and free-radical (thiol-allyl) reactions. In the first step, a combination of di-acryloyl and AB-type allyl/acryloyl functionalized azobenzene moieties undergo thiol-acryloyl addition reaction in the presence...
of the catalyst. This step offers accurate size control of azobenzene interconnected oligomers with a wide molecular weight range (from 2,300 to 23,000 Da). In the second step, free radical polymerization was carried out for the embedment of the azobenzene oligomers with the host polymer matrix, which provides free-standing actuators with heterogeneous polymer networks. Because of the great chemoselectivity between thiol-acryloyl and thiol-ene reactions, one-pot synthesis scheme is implemented. To better understand the contribution of isomer interconnectivity for photo-actuation performances, free-standing polymer films with different azobenzene interconnectivity (2,300, 5,000, 7,000, 9,000 and 23,000 Da) are tested under various working conditions (irradiation parameters, external loadings, and strains). The power output limits are also measured and fairly compared with the homogenous cases. Results of our study show significant photo-actuation performance enhancement in the isomer-interconnected heterogeneous network comparing to the homogenous cases. In extreme cases (23,000 Da), the maximum power output performances enhancement is up to 500%. Studies within different azobenzene interconnectivity also suggest that the increase of the interconnectivity of isomer significantly benefit the photo-actuation performances. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2012R1A3A2048841).

MS03.09.12
Toughening in Epoxy Nanocomposites by Nanoparticle Debonding and Cavitation Mithil Kamble, Nikhil Koratkar and Catalin Picu; Rensselaer Poly Institute, United States

In this study we investigate a toughening mechanism in epoxy filled with silica based on nanoparticle debonding and subsequent cavitation. The fractographic analysis suggests that such processes take place in the crack tip region due to the high localized hydrostatic stress, and support enhanced dissipation and enhanced toughness. We study the toughening mechanism using models of composites with stochastic microstructure, aiming to identify the distribution of nanofillers which produces the largest toughness enhancement. To this end, we consider composite microstructures with spatial fluctuations of porosity/nanofiller concentration and of elastic moduli, and explore the design space defined by the amplitude and spatial correlations of these stochastic parameters. Based on this combination of experimental and modeling results, we develop design rules for nanocomposites with non-uniform distributions of fillers.

MS03.09.13
Mechanical Characterization and Impact Behavior of Single Polymer Composite Made through Hybrid Yarn Technology Ashraf N. Khan, Ramasamy Alagirusamy, Apurba Das and Puneet Mahajan; Indian Institute of Technology Delhi, India

With the advancement in the technology, Composite materials are picking up paramountcy in its expansive overall application from Automobile structural material to Aerospace application, from Household to Marine application and several others like biotechnology, and so forth. Everywhere composite materials are finding its place by superseding conventional materials like metal, ceramic, etc. Low weight and high specific mechanical property make a composite material attractive for developing high load bearing-bridge, bulletproof armor, and high energy efficient process, etc.

In the present work, Composites have been fabricated with the same matrix and reinforcement material (i.e single polymer composite) having different molecular mass and degree of crystallinity. Purpose of choosing the same reinforcement and matrix material is to enhance its interface strength by increasing fiber and matrix compatibility because the same material has high affinity to make strong bonding in comparison to a different material (that is an increase in adhesive/cohesive force). Here, Composite material is chosen which is completely recyclable which makes it environment-friendly.

In this work, the main objective is to optimize mechanical and impact property of different composite flat-panel prepared by using the same matrix and reinforced material. So, By changing the internal architecture of reinforced material through different geometrical weaving like uni-directional and bi-directional fabric reinforcement structure. For the comparison purpose, the composites are produced having the same fiber/volume fraction. Composite’s mechanical and impact behavior keeps on changing as the fiber alignment changes. Mechanical strength and modulus have been calculated through prescribed ASTM standard.

Due to the high viscosity of thermoplastic material, it is difficult to obtain a uniform flow of a matrix during production time throughout the composite which leads to low load transfer from a matrix to the reinforcement material. To sort out this problem, Composite preform is prepared in such a way that melt flown distance of matrix is reduced to very small(through Hybrid yarn technology) which lead to a uniform flow of the matrix material which
in turn gave excellent quality (High interlaminar/intralaminar strength) of a composite. Detailed study of the specimens has been done after mechanical and impact testing. Mechanical testing has been performed using DIC software (Digital image correlation) and mechanical strain gauge. CT (computed tomography) scan has been performed for a thorough analysis of damage to different composites occurred during testing. XRD (X-Ray Diffraction) analysis has been performed to study the crystal structure of fiber to check the temperature sensitiveness on a crystal structure. SEM (Scanning electron microscope) images of the cross-section of different composites have been taken to view the interface between fiber and matrix and quality of the composites. Numerical Simulation has been performed through ANSYS software to validate the experimental results.

MS03.09.14
Characterization of a Nanocomposite of Polyurethane Reinforced with Fiberglass Additivated with TiO2
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The increase in the consumption of plastic materials is currently one of the major environmental concerns worldwide. To minimize this environmental impact generated by the plastics has been developing polymers from plant sources. Among these biodegradable polymers, the development of polyurethane (PU) using renewable raw material is growing every year, since PU is one of the most versatile polymers in the world today [1]. Despite the advantages that biodegradable plastics can bring to the environment it is necessary that these plastics have adequate durability in their final application especially when exposed in outdoor environments. For this, it is necessary to use stabilizing additives of UV light [2]. In this context, the objective of this work was to synthesize and evaluate the structural, morphological and mechanical properties of a nanocomposite of plant origin PU reinforced with fiberglass (FG) and additivated with Titanium Dioxide (TiO2) nanoparticles. For the nanocomposite formulations, the micronized rutile TiO2 was used, whose particles are in the range of 10 to 25 nm, which ensures that these micropigments reflect the UV rays without reflecting any visible light. The rutile form is considered the crystalline form more photo-stable, besides having a refractive index greater than the anatase [2]. The synthesis of PU/FG/TiO2 specimens was performed by adding 0, 5 and 10% of TiO2 and 50% of FG to a certain amount of polyol and disocyanate in the ratio 1:1 stirring until completely homogeneous. The mixture was then placed in molds which were placed for 48 hours in a pressure vessel. The characterization of the nanocomposite was done by Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and Tensile Tests, which were performed followed the ASTM D3039/D3039M 14 standard [3]. DSC analyses showed that, regardless of the amount of nanocarga used, there was an increase in the melting temperatures of the TiO2 materials compared to PU containing only FG, indicating that the doped materials appeared to have a higher thermal resistance. SEM images showed that the PU/FG samples containing TiO2 presented a surface with small agglomerates of small spherical particles which is indicative of the presence of TiO2. According to tensile tests, the TiO2 decreases the mechanical properties, like tensile strength and ultimate strain, of the composite.


MS03.09.15
Highly Stretchable, Self-Healable Radiation Shielding Hydrogel Composites Jinwoo Park and Jeong-Yun Sun; Seoul National University, Korea (the Republic of)

Radiation poisoning causes serious problems such as sterility, leukemia and death. Recently, radiation shield research has been in great need to prevent the danger of radiation exposure danger in various fields such space engineering, nuclear generation, and environmental engineering. Radiation shield is typically composed of metals, such as lead, tungsten, and tin which are high atomic numbers and densities to block the transmission rate of radiation. However, such heavy metals are too heavy, rigid and bulky to be used commercially. In this study, we fabricated a highly stretchable hydrogel shield which was fabricated from acrylamide polymer with PbO2 metal particles and crosslinked by clay. By utilizing metal nanoparticles and incorporating them into
hydrogels, the hydrogel nanocomposite exhibit attenuation coefficient (0.1343 cm\(^{-1}\)) and was stretched to 1400%. Furthermore, because hydrogel composite is physically crosslinked by clay, it has a self-healing property with a maximum self-healing efficiency value of 96.55% at 55°C for 2 hours. However, self-healing efficiency tended to decrease at high radiation dose. Accordingly, XRD, rheometer, GPC were used to investigate these tendency.

MS03.09.16
Mechanoactive Camouflage Systems with Main-Chain Chiral Liquid Crystalline Elastomers
Se-Um Kim, Young-Joo Lee, Dae Seok Kim, Rui Yin, Jiaqi Liu, Randall Kamien and Shu Yang; University of Pennsylvania, United States

Inspired by a variety of camouflage mechanisms in nature, much effort has been made to develop rapid and reversible color changing systems for smart windows, displays, sensors and biomimetic devices. However, current technologies largely depend on modulating the periodicity of photonic structures, thereby the degree of deformation, the magnitude of the spectrum shift, and the color-tuning range are innately restricted. Here we demonstrate a novel type of main-chain chiral liquid crystalline elastomers (MCLCEs) that exhibit outstanding color changing capabilities under mechanical strain. When subjected to a tensile strain perpendicular to the helical axis, MCLCEs contract along the helical axis with a Poisson's ratio greater than 1, causing the Bragg wavelength significantly moves across infrared, visible, and UV spectra. A camouflage system is assembled using an array of patterned MCLCE films that can be actuated by pneumatic inflation. This device applies a bi-axial transverse strain to lead a highly efficient change of structural colors in accordance with the background pattern. Our research will provide new insights for designing smart windows and camouflage systems based on CLCEs.

MS03.09.17
Finding the Ultimate Shape of Adhesive Fibril by Using Machine Learning Techniques
Yongtae Kim\(^1\), Youngsoo Kim\(^1\), Charles Yang\(^2\), Grace Gu\(^2\) and Seunghwa Ryu\(^1\); \(^1\)Korea Advanced Institute of Science and Technology, Korea (the Republic of); \(^2\)University of California, Berkeley, United States

Over the last decade, a significant attention has been paid to design the adhesive fibril with excellent adhesive properties, by searching for the geometry which give rise to flattened stress distribution because the detachment initiates at a location with high stress concentration. However, the previously optimized fibril geometries were obtained from a limited design space, and the stress distributions were significantly dissimilar with the optimal flat stress distribution. In this study, we introduce the ultimate adhesive fibril shape covering extensive design space by using machine learning technique, kernel support vector machine (SVM) and random forest repressor (RFR). To explore the vast design space, first, we conducted numerical simulation to obtain the stress distribution with 200,000 different fibril shapes defined on the grid. Using the numerical results as a training set, we trained kernel SVM to classify and exclude the geometry with stress singularity at the edge of adhered interface. We then define a score function that represents the similarity with the optimal flat stress distribution, and adapted RFR to predict the score of a given geometry. After establishing the machine learning model, we combine the genetic algorithm and the greedy algorithm to search for the optimized adhesive fibril shape with vast design space. The optimization is repeated until it converges, and the optimized results are compared with the optimized adhesive-fibril in previous studies. Our study demonstrates that the stress distribution at the adhered interface is highly sensitive to the subtle change of the shape, and provides a new strategy of optimizing the adhesive fibril geometry.

MS03.09.18
Dissipative Particle Dynamics Simulation of Poly(Urethane-Urea)-Based Nanocomposites—Microstructure and Mechanical Properties
Yelena Sliozberg, Jeffrey Gair, Alex Hsieh and Asha Hall; Combat Capabilities Development Command Army Research Laboratory, United States

Hierarchical polymer composite materials are used in numerous applications that require high stiffness and high specific strength. Poly(urethane urea) polymers are high performance segmented polyurethanes and polyureas elastomers, particularly attractive as matrix materials because of their versatile properties and high tailorability achieved by tuning their microstructure. To further enhance the properties of PUUs, nano-scale fillers such as carbon nanotubes (CNT) are incorporated into PUUs, which form polymer nanocomposites (PNCs). The mechanical properties of these materials are controlled by their complex morphology caused by association of the hard segments (urea segments), which serve as physical cross-link sites due to the inter-chain joining that reinforce the soft matrix (urethane segments). Morphology of PNCs also depends on the nanofiller loading and orientation. Supplementary to
experimental efforts, modeling approach provides a powerful means to investigate a broad range of parameters, which is challenging to explore experimentally. We employed dissipative particle dynamics simulations to systematically study impact of chemical and compositional variables on structural and mechanical properties of PUU-based composites. The effect of soft to hard blocks ratio, chemistry and molecular weight as well as CNT concentration and orientation were studied. Our results demonstrated that inclusion of nanofillers is able to alter morphology of PNCs from mixed-phase to interface-mediated microphase separation states, which alter the mechanical response of these materials. Our simulation results are in agreement with recent experimental data.

**MS03.09.19**

**Influence of Composition and Uni/Biaxial Stretching on the Evolution of Structure and Dielectric Properties of PBT/PEI and PET/PEI Blends**

Zeynep Mutlu and Mukerrem Cakmak; Purdue University, United States

Capacitors are two terminal devices for energy storage. Polymers like polyethylene (PE), biaxially oriented polypropylene (BOPP), polystyrene (PS), polyethylene terephthalate (PET) are widely used in capacitor applications because of their good film forming properties such as low cost, high dielectric strength and low loss. State of art of polymeric dielectric films are biaxially oriented polypropylene with breakdown strength of 600-700 V/µm (for 10 µm thickness) and with dielectric constant of ~2.21,2. Various strategies have been used to increase the dielectric constant and the dielectric strength of polymeric dielectrics. One of them is to orient crystalline domains of polymers to make a torturous path, by applying mechanical deformation in semi-molten state. However, it is challenging to understand the polymer responses under deformation. One way to characterize the microstructural morphology is to measure the birefringence during deformation. By also looking WAXS and SAXS patterns these findings can be supported.

In this research, two different blends are investigated; PBT (polyethylene terephthalate/PEI (polyether imide) and PET/PEI. PBT and PET which are semi crystalline thermoplastic polymers, blended with different ratios of PEI which is an amorphous thermoplastic polymer with Tg ~220°C for high temperature applications. By doing so, processability of PBT also increased. It is found that up to 30/70 (PBT/PEI) blend can still crystallize on the other hand for PET/PEI above 30 % PEI the blend disappears. In the absence of orientation, the increase of PEI fraction leads to decrease of crystallizability as expected from the dilution effect that spatially prevents the crystallizable polymer chains from coming together. Blends with high PBT & PET amount can be stretched more and during stretching in blends, amorphous orientation takes place rapidly, followed by crystallization. Stress optical behavior which exhibits a multi stage behavior that depends on process conditions is also investigated3. At low stretching temperatures and high rates the stress optical behavior was found to start with an initial glassy photoelastic behavior.


**MS03.09.21**

**High Throughput Quantification of Plasticity and Failure in Pixelated Polymer Nanocomposite Thin Films**

Anesia D. Auguste¹, Allen B. Schantz¹, Andrew S. Gillman¹, Andrew Tibbits¹,², Phil Buskohl¹ and Richard A. Vaia¹; ¹Air Force Research Laboratory, United States; ²UES, Inc., United States

Nanoscale thin films with improved toughness, stiffness, and fracture resistance are crucial to numerous technologies, ranging from devices for human-machine interfaces to soft robotics, medicine, energy storage, and smart separation membranes. However, techniques that rapidly quantify the plasticity and failure mechanisms of these thin films, especially in relevant environments, are limited; and thus, hinder development of structure-composition-processing-performance relationships. In this work, we will discuss a high throughput concept to measure the elastic moduli, plasticity and failure strain of thin polymer and nanocomposite films. Building from the Wrinkling-Crack method, we design and additively manufacture compliant lattices to replace the traditional elastomeric support. The geometry of the lattice transduces macroscopic, uniform, in-plane deformation into a wide range of local deformation fields at each lattice cell via differing Poisson’s ratios. By placing a thin film on top of the lattice structure, each cell acts as a unique deformation stage, allowing simultaneous mapping of the yield and...
fracture envelope. Combining this with optical techniques, automated image processing, and pixelated films with varying composition, thickness, or process history, enables statistically robust analysis of many different parameters in parallel. The use of polystyrene and associated nanocomposite thin films facilitate the identification of opportunities and challenges for this concept.

**MS03.09.22**

Investigating Interlayer Bonding Strength of FDM 3D-Printed PEEK through Design of Experiment (DOE) and Three-Point Flexural Test  
Chya-Yan Liaw, Andrew House and Murat Guvendiren; New Jersey Institute of Technology, United States

Poly-Ether-Ether Ketone (PEEK) is a high-performance thermoplastic with excellent chemical resistance and mechanical performance under high-temperature and high-pressure environments. Therefore, PEEK has been commonly used in severe conditions such as aerospace, automotive, oil and gas field. In addition, PEEK has good biocompatibility and is easy to sterilize, which makes it become an important group of biomaterials for medical applications and a strong candidate as an alternative to replace metal and ceramic implants [1]. In recent years, FDM (fused deposition modeling) 3D printing has offered a new manufacturing technology which is able to fabricate complex and customized PEEK products that are either impossible or too expensive with conventional methods. Despite the widespread use of FDM technology, very few studies have investigated the effect of process parameters on the interlayer bonding of PEEK printed objects [2], where the interlayer bonding is a critical factor in order to create strong functional parts.

To address this problem, we adopted a DOE (Design of Experiment) approach to investigate printing parameters on the interlayer bonding using a three-point bending test and the crystallinity in the polymers. In this research, the aim is to identify significant main effects among four independent factors, including nozzle temperature, layer height, print speed, and layer time for the 3D printed PEEK. A $2^{4-1}$ design (resolution IV) was chosen which include fewer runs than a full factorial design but is efficient enough for identifying key factors. The samples were printed in an upright position, and were loaded in the weakest direction (layers are perpendicular to the tensile stress in the convex side of the specimen) in the three-point bending fixture. Flexure strength, modulus, and strain at break were evaluated.

The results show that the nozzle temperature is the most important factor which affects the flexure strength, strain at break and crystallinity of the PEEK part greatly, but has very little effect on modulus. The flexure modulus mainly depends on layer height. In addition, wait time and layer height had a significant effect on the flexure strength and crystallinity respectively. The examination of fracture surface through scanning electronic microscopy (SEM) shows different fracture types for specimens printed under different conditions. Overall, the combination of DOE and three-point bending test offers a systematic and efficient paradigm to investigate the effect of printing parameters on the interlayer strength of 3D printed PEEK.


**MS03.09.23**

A Multiscale Investigation of Polydopamine and Polytetrafluoroethylene Adhesion and Wear Mechanisms  
Mathew Brownell and Arun K. Nair; University of Arkansas, United States

Polydopamine (PDA) is used as a surface modifier for a wide variety of applications. Many experimental and computational studies have investigated the use of PDA and its adhesive properties, and it is believed that hydrogen bonding and van der Waals forces contribute to the adhesion of polydopamine. The application of PDA between a substrate and a surface coating has dramatically increased the wear resistance of thin film coatings, specifically polytetrafluoroethylene (PTFE). PTFE has been studied as a low friction surface coating since its discovery; using an intermediate layer of PDA between stainless steel and PTFE produces an incredible improvement in wear rate of the PTFE film. While experiments have shown that PTFE and PDA adhere quite strongly, the adhesive mechanisms between the two polymers remains relatively unknown. In this study we investigate the adhesive properties of PDA.
and PTFE via density functional theory and molecular dynamics. Various PDA oligomers are used to investigate the adhesive forces between PDA and PDA, and PDA and PTFE. Indentation and scratch tests are then performed on PDA/PTFE models and the deformation and wear mechanisms are studied between the interfaces. This study will elucidate the cause of tenacious adhesion between PDA and PTFE, as well as observe the influence of PDA molecules on the friction and mechanical properties of PTFE thin films.

**MS03.09.24**

**Investigation of Polytetrafluoroethylene Microscale Deformation Mechanisms** Mathew Brownell and Arun K. Nair; University of Arkansas, United States

Polytetrafluoroethylene (PTFE) has a low coefficient of friction but also a high wear rate. Numerous experimental and computational studies have investigated wear and the deformation mechanisms of PTFE films, however, severe limitations exists which prevent the modeling of PTFE on length scales which experimentalists are able to investigate. In this work, a coarse-grained model is developed to enable the computational modeling of PTFE particles at the microscale. The coarse-grained potential parameters are derived from first principle based ReaxFF force field simulations, while the PTFE particles are modeled after experimental observations. Indentation and scratch tests are performed using the newly developed coarse-grained models; it was found that the indentation force is dependent on the density of PTFE, and a smooth surface topography decreased the coefficient of friction of the particle. The development and use of the coarse-grained model of PTFE will enable numerical modeling of PTFE on length scales similar to experimental PTFE thin films, thus allowing for a deeper understanding of the deformation, wear, and failure mechanisms of microscale PTFE particles and films.

**MS03.09.25**

**Improved Viscoelastic Analysis of GY70/339 Composite Materials Using an Enhanced First-Order Shear Deformation Theory in Laplace Domain** Jang-Woo Han¹, Jun-Sik Kim² and M. Cho³; ¹Korea Institute of Industrial Technology, Korea (the Republic of); ²Kumoh National Institute of Technology, Korea (the Republic of); ³Seoul National University, Korea (the Republic of)

Recently, advanced composite structures have been widely used in various engineering applications due to their light-weight and high-stiffness characteristics. With increasing utilization of laminated composite structures, there are many theories developed to accurately predict their elastic responses, such as the well-known conventional theories (FSDT; first-order shear deformation theory) and many other refined shear deformation theories (EHOPT; efficient higher order plate theory, EFSDT; enhanced first-order shear deformation theory).

Meanwhile, composite structures have viscoelastic characteristics such as creep strain, stress relaxation and time-dependent failure because composite material is composed of elastic fibers and viscoelastic matrix. Thus, viscoelastic effects of the laminated composite structures should be considered for the reliable analysis. This brings us to develop a new type of enhanced first-order shear deformation theory (EFSDT) by employing the concepts of the strain energy relationship and Laplace transformation. This will allow us to analyze accurately the viscoelastic behavior of laminated composite plates under mechanical loading and to investigate viscoelastic effects such as creep strain and stress relaxation.

In this paper, viscoelastic finite element implementation based on the EFSDT will be performed, and the results of the present theory will be compared to those reported in the open literature. The process of strain energy transformation in Laplace domain and finite element formulation will be described in detail.

**MS03.09.26**

**Engineered ‘Organic-Inorganic’ Nanocomposites Properties through Embedding of Smaller Nanoparticles in a Thermoset Polymer Matrix: Structure and Property Characterization** Sanju Gupta and Alex Henson; Western Kentucky University, United States

Organic and inorganic nanoparticle reinforcements have garnered widespread attention for polymer nanocomposites to yield properties enhancement useful for wide ranging modern and future technologies including photovoltaics, catalysis, optics, and renewable energy. Recent experiments and computational simulations revealed the macroscopic properties are governed by mesoscale structure and interfacial layer dynamics due to the interactions between the polymer matrix (host) and nanoparticle reinforcements (guest). However, a clear fundamental understanding of the role of size, shape, loading (volume fraction) in controlling the structure and dynamics of
polymer-nanoparticle interfacial layer is limited. Moreover, ‘forward’ engineered polymer-nanoparticle composites often require higher volumetric density and better dispersions remains a challenging task. We report on developing polymer nanocomposites engineered to minimize dielectric losses and investigating structure and dynamics of interfacial layer to predict macroscale properties. The nanocomposites consist of poly(2-vinylpyridine) (P2VP) polymer matrix with (1) spherical silsesquioxane molecule clusters (~2-5 nm diameter) and silica nanoparticles (~10-20 nm diameter) and (2) planar nitrogenated graphene nanoribbons (~20 nm wide), having dimensions comparable to polymer matrix characteristic length i.e. gyration radius (Rg ~5 nm). This approach will enable improved nanocomposites properties due to enhanced interfacial interactions and identify key molecular parameters governing non-linear dielectric loss mechanisms while studying structure and dynamics using broadband dielectric spectroscopy and small-angle X-ray scattering. The transmission electron microscopy will reveal microscopic structure and the lattice bonding, interfacial stress transfer and conjugation length will be determined from micro-Raman spectroscopy. The exact loading and glass transition temperature, Tg, will be obtained using thermogravimetric analysis and differential scanning calorimetry, respectively. We will gain fundamental insights into the interfacial layer and diffusion dynamics above and below Tg and establish quantitative microscopic structure-property correlations, while predicting macro-scale properties. KY NSF EPSCoR and KY NASA EPSCoR subaward Grants.

MS03.09.27
A Ferroconcrete-Like All-Organic Nanocomposite Exhibiting Improved Mechanical Property and High Breakdown Strength
Zhenkang Dan and Yang Shen; Tsinghua University, China

Polymer based nanocomposites with excellent mechanical property and high energy density are crucial enablers for numerous applications in modern electronic and electrical industry. The energy density of parallel plate capacitors is determined by breakdown strength and dielectric permittivity of the inner dielectrics. Poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)), with the highest permittivity among all the dielectric polymers, is promising candidate for high energy density capacitors. However, its poor mechanical property and relatively low breakdown strength restrict the applications. In this work, we propose a novel method combining combinatorial-electrospinning and hot-pressing to fabricate P(VDF-TrFE-CFE) based all-organic dielectrics with ferroconcrete-like structure. In this structure, continuous fibers of polysulfone (PSF) with high Young's modulus act as tough scaffold to improve the mechanical properties of nanocomposites, and an over 750% enhancement of Young's modulus is obtained. The enhanced mechanical properties bring about significant improvement in Weibull breakdown strength to 485 MV/m, more than 50% higher than neat terpolymer. Besides, the suppressed leakage current and conduction loss thus improved discharge energy efficiency under moderate electric field are achieved due to the high insulation of PSF and interface regions restricting the mobility of space charges.

MS03.09.28
Mechanical Performance of Polymer-Derived Ceramic Nanocomposites
Patel Tulsi, Dayton Street, Lisa Rueschoff, Robert Wheeler, Joe Bowen, Michael Cinibulk and Matthew B. Dickerson; Air Force Research Laboratory, United States

Structural ceramics provide exceptional mechanical properties at elevated temperatures. The inherent drawback of ceramics is its brittle nature, which paves way for catastrophic failure and is therefore, undesired for practical applications. However, at the nanoscale, materials properties have the capability to be enhanced through careful control of structure and morphology. This talk will precisely focus on nanocomposites based on polymer-derived ceramic reinforcement with tailored architectures for improved mechanical strength. Various polymer/ceramic and ceramic/ceramic systems will be considered and its corresponding structural and mechanical properties will be discussed. Ultimately, these structure/processing/property relationships will provide key insight in the design and development of structural, aerospace components that experience extreme conditions, such as in hypersonic flight.
Supramolecular Engineering to Guide Biomolecules into Functional Hierarchical Biomaterials Alvaro Mata; Queen Mary University of London, United Kingdom

There is great interest to develop materials with properties that resemble those of biological systems such as hierarchical organization, high stiffness, and the capacity to grow or self-heal. While supramolecular chemistry offers an exciting opportunity to grow materials with nanoscale precision, the ability to transform molecular design into functional devices with enhanced utility at the macroscale remains a challenge.

To tackle this problem, our group is developing supramolecular fabrication tools that combine self-assembly with engineering principles to enable the design of materials with innovative properties. These approaches take advantage of phenomena such as the interplay between protein order and disorder, compartmentalization, diffusion-reaction processes, and host-guest interactions to guide assembly of multiple types of building blocks hierarchically and with molecular and supramolecular control. Some of these building blocks include ions, peptides, proteins, and other components such as graphene oxide.

The resulting materials exhibit properties such as hierarchical organization, the capacity to grow, tuneable mechanical properties, and anisotropic bioactivity and are being used for the regeneration of tissues such as enamel, bone, and blood vessels as well as the fabrication of more biologically relevant in vitro models.

References

Tissue-Like Hydrogels by Design Shaoting Lin and Xuanhe Zhao; Massachusetts Institute of Technology, United States

The majority of natural tissues in human body are elegantly structured to bear a range of functional loads in diverse conditions. Cartilage, ligament, tendon, and muscle, to name a few, possess a set of combinational mechanical properties, including high strength (~1 MPa), superior compliance (~100 kPa) and high toughness (~1000 J/m²), which are unmatched by their engineering counterparts (i.e., synthetic hydrogels). These unprecedented mechanical properties, particularly fatigue resistance, are highly desirable for emerging applications of synthetic hydrogels as diverse as tissue adhesives, gastro-retentive devices, hydrogel electronics, hydrogel robots, and optical fibers. The study of mechanics and design of tissue-like hydrogels are both scientifically interesting and technologically important.

This talk particularly focuses on one extreme property, i.e., fatigue resistance, which is rarely achieved in synthetic hydrogels. The reported fatigue threshold (i.e., the minimal fracture energy that crack does not propagate) for synthetic hydrogels is on the order of 1 to 100 J/m². We propose a general principle that introduction of high-energy nanostructures in hydrogels can substantially enhance their anti-fatigue-fracture properties by fracturing beyond amorphous chains. We demonstrate that the controlled introduction of crystalline domains (1) and/or aligned nanofibrils (2) can substantially enhance hydrogels’ fatigue threshold as high as 1000 J/m². We further show that the principle can be readily employed to achieve fatigue-resistant adhesion by bonding ordered nanocrystalline domains of synthetic hydrogels on engineering materials, which gives a world record high interfacial fatigue threshold of 800 J/m². The principle for achieving anti-fatigue-fracture properties in synthetic hydrogels can evoke a number of applications including ingestible gastro-retentive hydrogel devices (3), fatigue-resistant hydrogel coatings, and robust hydrogel robots (4).

References

**9:15 AM MS03.10.03**

**Bioinspired Routes to Damage Tolerant Materials—Unique Microstructure and Fracture Properties of Enamel in the Mammal-Like Grinding Dentition of the Hadrosaurid Dinosaur**

Sid Pathak, Brandon A. Krick, and Gregory M. Erickson; 1University of Nevada, Reno, United States; 2Lehigh University, United States; 3Florida State University, United States

The *enamel* of grazing animals represents one of Nature’s most remarkable biological materials — a ceramic-like composite showing exceptional strength, toughness, wear-resistance and controlled-crack propagation. In this work, we study these multi-functional, damage-tolerant biomaterial composites that preserve and ensure life-long reliability for survival (feeding). The goal of our interdisciplinary research is to understand the biomechanical form, function and performance of aprismatic wavy enamel present in hadrosauroid dinosaurs. We test the hypothesis that these wavy enamel structures in hadrosaurid dinosaurs served the same function as those of current grazing mammals through comparative fracture experimentation. Preservation of fracture properties in fossil enamels, many of which are not found in living animals, allows exploration of past form and function and provides a novel source for biomimetically inspired next-generation ceramics.

Hadrosaurid (duck-billed) dinosaurs are the only the only animals known that independently evolved a grinding dentition in the absence of prismatic enamel. Unlike mammals (such as grazing horses and bovids (mammals from cattle family)) hadrosaurids with grinding dentitions utilized undulating wavy enamel (= folded layers of parallel hydroxyapatite crystallites separated by thin layers of loosely aggregated inter-layer matrix), the most complex enamel known in any reptilian taxon.

Wavy enamel has a highly complex hierarchical internal structure and is a particularly challenging material to characterize mechanically, especially at the micron length scales where the mineral and voids once occupied by collagen components are closely intertwined and the available testing methods are limited. We utilized a suite of small scale testing techniques for this work, which involve (a) high throughput nanoindentation testing, to more-specialized FIB-fabricated (b) micro-pillar compression, and (c) micro-tensile loading scenarios. The mechanical data obtained from these tests is correlated with the structure information at complementary length scales using techniques such as BSE-SEM and Raman Spectroscopy.

Our indentation results show that the trends of both the elastic (indentation modulus) and plastic (yield strength) properties are highly complementary to each other and closely reflect the 2D optical profilometry map of the harder and softer enamel tissue layers. The structure-property maps reflect the unique morphology of the wavy enamel layering, where the periodic variations in properties between the layers, combined with the enamel layer undulations, is postulated to promote the remarkable fracture resistance, localized damage and strategically controlled crack directionality of this structure. More-specialized micro-pillar compression testing of the wavy enamel tissue shows clear differences between the fracture behavior under compression of the harder (higher compressive yield and fracture strength) vs. softer tissue layers in hadrosaurid wavy enamel. Intriguingly, the harder tissue layers show initiation of multiple cracks before fracture, suggesting another level of hierarchy where this layer could be composed of weaker interfaces and subsequent sub-layers.

Such insights are crucial for effective approaches to bio-mimetic designs originating from the wavy enamel structure. We utilize the knowledge gained from this work to incorporate the undulating architecture of the hadrosaurid wavy enamel on to a Cu-TiN multilayered nanolaminate structure, synthesized using physical vapor deposition techniques. Our initial results show that, similar to the enamel layer undulations in hadrosaurids, the addition of the waviness to the layering of the metal-ceramic multilayer is instrumental in undulating the crack propagation, thus robbing the crack tip of the required strain energy and controlling its propagation through the laminate.

**9:30 AM MS03.10.04**

**Characterization of a Cartilage-Like Hydrogel-Nanofiber Composite**

Jacob M. Ludwick and Michelle L. Oyen; East Carolina University, United States

Articular cartilage plays an important role in synovial joint function, but this function is diminished when cartilage breaks down in osteoarthritis. Tissue engineering is a promising approach for replacing failed cartilage, which has no blood supply or intrinsic capacity to heal. Here, a biomimetic composite scaffold is developed, composed of a
composite poly (vinyl alcohol) (PVA) and poly (acrylic acid) (PAA) hydrogel, reinforced with gelatin nanofibers. The PVA-PAA hydrogel is cross-linked by repeated freeze-thaw cycles and contains pH-activated charges, which increases the compressive stiffness of the hydrogel. The gelatin nanofibers provide reinforcement against tensile loads, mimicking the function of collagen fibrils in cartilage. Mechanical characterization of the novel composite includes indentation tests, tensile tests and trouser tear fracture tests to measure stiffness, time-dependent behavior, strength and toughness of the composite. Properties approach those of natural cartilage and exceed values obtained for single component hydrogels. By combining biomimicry and composite engineering practices, a better solution for osteoarthritis can be developed.

9:45 AM MS03.10.05
Modelling Self-Healing Behaviour in Biological Materials and Bioinspired Composites Federico Bosia¹, Gianluca Costagliola¹ and Nicola M. Pugno²³⁴; ¹University of Torino, Italy; ²University of Trento, Italy; ³Queen Mary University London, United Kingdom; ⁴Ket Lab, Edoardo Amaldi Foundation, Italy

Self-healing is a characteristic property of many biological materials, leading to enhanced mechanical strength and toughness. Various efforts have been devoted to emulating this property in composite materials for applications in structural engineering. Modelling approaches are essential for this goal, helping to understand how failure processes and global mechanical properties can be modified by self-healing processes and their parameters. We present various approaches developed recently using lattice spring or random fuse models with the addition of self-healing characteristics. We highlight how these influence the scaling of mechanical properties of the corresponding composites, identifying some characteristic signatures from a statistical mechanics point of view, focusing on observables like avalanche distributions, maximum strength and crack roughness. We show how some of these observables can be exploited as indicators of imminent failure and discuss the influence of self-healing parameters on the time evolution of damage in composites, e.g. in determining a transition from a more ductile to a more brittle fracture.

10:00 AM BREAK

10:30 AM *MS03.10.06
Negative Poisson’s Ratio of a Natural Nanocomposite Discovered by In Situ TEM Mechanical Testing Jin-Kyung Kim¹, Jinsol Seo¹, Jiwon Jeong¹, Jeehun Jeong¹, Zhen Wang¹, Yue Liu², Huajian Gao² and Sang Ho Oh¹; ¹Sungkyunkwan University, Korea (the Republic of); ²Brown University, United States

The teeth of limpets are reported to be the strongest natural material, with tensile strength values ranging from 3 to 6.5 GPa. However, the origin of ultrahigh strength of limpet teeth is still unknown. Limpets use conveyor belt-like radula to scrape rocks and extract algae during feeding. These processes require extremely strong teeth. Limpet teeth show characteristic composite nanostructures consisting of high volume fraction of reinforcing goethite crystals and softer amorphous hydrated silica matrix. The volume fraction and morphology of goethite crystals are heterogeneous at different locations of the tooth, which leads to site-specifically heterogeneous mechanical properties. The present work reports on the relationship between microstructures and deformation mechanisms of limpet teeth, using transmission electron microscopy (TEM) and in-situ TEM deformation. At the leading part of a limpet tooth, goethite crystals are mainly aligned along the principal direction of a tooth. The goethite crystals are rod-shaped, with approximately 30 nm in diameter and 300 nm in length. The volume fraction of the goethite crystals is approximately 50 %. TEM characterization of a longitudinal section at the tip of a limpet tooth shows both normally and laterally aligned goethite crystals, with some clusters of the normally aligned crystals. In addition, transition areas at the interfaces between goethite crystals and amorphous matrix are frequently observed. Atomic scale scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) analyses show that the transition areas have different atomic structures and chemical composition from the original goethite crystals. The trailing part of a limpet tooth shows larger goethite crystals, with lower volume fraction than the leading part. To understand deformation behavior of limpet teeth, in-situ TEM deformation experiments were conducted using the samples taken from the tip of a limpet tooth. Upon tension, the sample shows both positive tensile and transverse strain, which indicates negative Poisson’s’s ratio. Through a digital image correlation (DIC) analysis, the rotation of laterally-aligned goethite crystals appears to result in the observed negative Poisson’s ratio. Inspired by the observation on its structure and deformation pattern, we constructed a conceptual finite element model to mimic its behavior, which can be extended into the framework of micropolar elasticity. When the sample fractures, a crack propagates very fast right after its initiation. The ultrahigh strength of limpet teeth is expected to
delay initiation of cracks. The present work will discuss the relationship among microstructures, deformation/fracture behavior and mechanical properties of limpet teeth. This could provide an insight into design of bioinspired engineering composite materials with superior strength and toughness.

11:00 AM MS03.10.07
The Leonardo da Vinci's Legacy, 500 Years After His Death  Nicola M. Pugno; University of Trento, Italy

The Italian artist, inventor and scientist Leonardo da Vinci (1452–1519) can probably be considered the father of bio-inspired mechanical design, as illustrated by his artificial wings and flying machines, based on bird observation and dissection. Today, 500 years from his death, bioinspiration is attracting widespread attention worldwide, both in academia and industry. This lecture provides a short overview of my group's research activity at the University of Trento, Italy, in line with the Leonardo's legacy on bio-inspired nanomechanics, including nano (i) and bio-inspired materials (ii), as well as their natural evolution towards what we have defined as "bionocomposites" (iii).

11:15 AM MS03.10.08
Bio-Inspired Polymeric Heart Valves Exhibiting Valve-Like Mechanical and Hemodynamic Behavior Xing Zhang1,2, Feng Guo1,2, Rizheng Han1,2 and Yun Bai1,2; 1Institute of Metal Research, Chinese Academy of Sciences, China; 2University of Science and Technology of China, China

Heart valve disease with major symptoms of stenosis and regurgitation is prevalent worldwide. Surgical replacement of diseased heart valves at the end-stages has been widely performed with mechanical valves (MVs) or bioprosthetic heart valves (BHVs). All these current devices have significant limitations with risks of further morbidity and mortality. For example, MVs may cause hemorrhage and thromboembolism, and require anticoagulation for the lifetime of the patients. BHVs show better hemodynamic behavior due to the composition and structural similarity to native heart valves when compared to MVs, however, they do show limited durability because of calcification and progressive degeneration [1]. Thus, polymeric heart valve (PHV) prostheses combining the advantages of MVs and BHVs with long-term durability and no necessity for permanent anticoagulation are of great interest and also show potential applications in advanced transcatheter devices.

In this study, two types of silk fibroin (SF) fiber membranes with anisotropic (ASF) and isotropic (ISF) properties were prepared by electrospinning methods, and were further combined with poly(ethylene glycol) diacrylate (PEGDA) hydrogels to serve as polymeric heart valve (PHV) substitutes (PEGDA-ASF and PEGDA-ISF). The uniaxial tensile tests showed obvious anisotropy of PEGDA-ASF composites with elastic moduli of 10.95 ± 1.09 MPa and 3.55 ± 0.32 MPa, respectively, along the direction parallel and perpendicular to the fiber alignment, close to those of native aortic valve leaflets, while PEGDA-ISF processed isotropic property with elastic moduli of 4.54 ± 0.43 MPa. These novel PHVs consisted of polymeric fibers to mimic the fibrous networks in the fibrosa and ventricularis layers for stress bearing, as well as PEGDA hydrogels to improve anti-fouling function [2,3]. Furthermore, the presence of PEGDA hydrogels in the composites improved the resistance to progressive calcification of the embedded fibers in vitro, likely due to prevention of large-size hydrated ions to pass through by the polymeric networks of the hydrogels [3]. The non-fouling PEGDA hydrogels encapsulated the surfaces of the composites and prevented contact between platelets and the underlying fibers [4]. Pulse duplicator tests presented good hydrodynamic characteristics of these PHVs from PEGDA-ASF and PEGDA-ISF composites according to the ISO 5840-3 standard. Finite element analysis (FEA) revealed the PEGD-ISF valve with anisotropic property showed a lower peak maximum principle stress value (2.20 MPa) in commissures during diastole compared to that from the isotropic PEGD-ISF valve (2.37 MPa). In systole, the bending area of the PEGDA-ISF valve was close to free edges, however, which appeared in the belly portion and near the attachment line for the PEGDA-ASF valve. Hence, our results revealed that anisotropic properties played important roles not only in mechanical properties, but also in hydrodynamic performance of these artificial PHVs. These novel PHVs with good biocompatibility and hemodynamic property can likely be used for heart valve replacement in future.

References
SESSION MS03.11: Poster Session IV: Biocomposites
Thursday Afternoon, December 5, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

MS03.11.01
Biomimetic Boron Nitride/Gelatin Artificial Nacre for Biomedical Applications
Sung Chan Yoo, Joon Hui Kim, Ho Jin Ryu and Soon Hyung Hong; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Atomic thin hexagonal boron nitride (h-BN) nanosheet (BNNS), a structural analogue of graphene, has received great attention due to its remarkable properties, which includes which include superior mechanical, thermal conducting and electrical insulating properties, high surface area, excellent chemical stability, high oxidation resistance, and potential biocompatibility.

Regardless of the development of facile and scalable BNNS fabrication processes, the impressive properties of BNNSs have not been exploited at the industrial scale because of the challenges associated with assembling the 2D crystals into macroscopic materials that can leverage the excellent properties of the nanoscale building blocks. On other hand, in nature, nacre exhibits surprisingly high mechanical properties with elegant simplicity in structure consisting of a brick-and-mortar assembly of inorganic and organic constituents. Furthermore, recent developments in nanomaterials and bioinspired materials revealed that excellent mechanical and functional properties can be simultaneously achieved by assembling the nanomaterials into brick-and-mortar (B&M) structure from the nanocrystals. Herein, artificial nacre-like materials were fabricated using hyperbranched polyglycerol (HPG)-functionalized BNNS and gelatin through a vacuum filtration-induced self-assembly technique. The electrostatic interaction-induced self-assembly of BNNSs and gelatin resulted in the formation of a layered B&M nanocomposite structure resembling that of natural nacre. In contrast to previously reported traditional polymer nanocomposite materials, BNNSs constitute a major load bearing hard component in the nanocomposite material, similar to the brick phases in the nacre structure, while the soft gelatin phases bind the hard brick phases together. Alignment of the BNNSs into a B&M structure was achieved by linking interlayer bridges through electrostatic interactions between anionic hydroxyl functional groups on the BNNSs and cationic amine functional groups on gelatin. The resulting nacre-like nanocomposite exhibited a controllable nanoscale alignment and mechanical properties similar to those of human cortical bones; these properties could be tuned by changing the amount of BNNSs, and by using a functionalization process. Moreover, biological characterization of the nacre-like nanocomposite revealed excellent biocompatibility with signs of negligible cytotoxicity and cell differentiation induction. Furthermore, we believe that various drugs and bioactive molecules could adhere to the surface of BNNSs via a functionalization process to improve biological functionality. The excellent mechanical properties and high biocompatibility of the nacre-like BNNS/gelatin nanocomposite suggests biomedical applications, including in bone implants, bone fillers, and biocompatible biomaterial coatings.

MS03.11.02
Plant-Derived Nanocellulose as Structural and Mechanical Reinforcement of Freeze-Cast Chitosan Scaffolds for Biomedical Applications
Kaiyang Yin, Prajan Divakar and Ulrike G. Wegst; Dartmouth College, United States

Despite considerable recent interest in micro- and nanofibrillated cellulose as constituents of lightweight structures and scaffolds for applications that range from thermal insulation to filtration, few systematic studies have been reported to date on structure-property-processing correlations in freeze-cast nanocellulose-based composite scaffolds, in general, and their application in tissue regeneration, in particular. Reported in this study are the effects of the addition of plant-derived nanocellulose fibrils (CNF), crystals (CNC) or a blend of the two (CNB) to the biopolymer chitosan on structure and properties of the resulting composites. Nanocellulose-chitosan composite scaffolds were freeze cast at 10°C/min and 1°C/min, and their microstructures were quantified in both the dry and fully-hydrated states using scanning electron and confocal microscopy, respectively. The modulus, yield strength,
Anisotropic Freeze-Cast Collagen Scaffolds for Tissue Regeneration—How Processing Conditions Affect Structure and Properties in the Dry and Fully Hydrated States

Prajan Divakar, Kaiyang Yin and Ulrike G. Wegst; Dartmouth College, United States

Few systematic structure-property-processing correlations for directionally freeze-cast biopolymer scaffolds are reported. Such correlations are critical to enable scaffold design with attractive structural and mechanical cues in vivo. This study focuses on freeze-cast collagen scaffolds with three different applied cooling rates (10, 1, and 0.1 °C/min) and two freezing directions (longitudinal and radial). A semi-automated approach for the structural characterization of fully hydrated scaffolds by confocal microscopy is developed to facilitate an objective quantification and comparison of structural features. Additionally, scanning electron microscopy and compression testing are performed longitudinally and transversely. Structural and mechanical properties are determined on dry and fully hydrated scaffolds. Longitudinally frozen scaffolds have aligned and regular pores while those in radially frozen ones exhibit greater variations in pore geometry and alignment. Lamellar spacing, pore area, and cell wall thickness increase with decreasing cooling rate. Both longitudinally and radially frozen scaffolds possess higher mechanical property values, when loaded parallel rather than perpendicular to the ice-crystal growth direction. Systematic trends and correlations become useful, when they allow predictions of performance and thus, the custom-design of new materials and structures. Traditionally, in the freeze-casting community, structural features, such as the lamellar spacing, λ (which in our case is equivalent to the short pore axis), are correlated with the freezing front velocity, v, during processing. Since the accurate measurement of the freezing front velocity for a given mold design and freezing setup is an elaborate undertaking that either requires specialized molds or cryo-X-ray tomography, it is more practical and useful to obtain correlations between structural features and the applied cooling rate. This is what we propose and report, here, for the case of longitudinal solidification, which results in a particularly reproducible and regular pore architecture. Correlations between the short axis of the pore, the pore area, and the applied cooling rate, ċ, are presented as well as correlations between cell wall thickness, modulus and yield strength. Collated, these correlations enable the custom-design of freeze-cast collagen scaffolds, which are ideally suited for a large variety of tissue regeneration applications.

Overcoming the Disadvantages of Applying Bio-Inspired Wettability Controlled Surfaces Underwater Using Electrochemical Water Splitting

Yongjae Jeung and Kijung Yong; POSTECH, Korea (the Republic of)

The fouling and drag force are major issues in fluid transport systems because they cause additional costs for cleaning and fuel consumption, respectively. However, the biggest problem is drag force and anti-fouling ability have conflicting relations so it is difficult to find the surface which satisfies both. For example, a superhydrophobic surface shows drag-reducing effect due to the formation of air layer underwater but this empty air layer could easily collapse by air diffusion and hydraulic pressure. On the other hand, a superhydrophilic surface shows outstanding anti-oil fouling ability due to its high affinity to water but this causes the drag-enhancing effect. To overcome this conflicting relation, we suggest a unique method which is employing electrochemical gas generation system to both bio-inspired wettability controlled surfaces. A superhydrophilic surface has a great advantage for electrochemical water splitting (EWS) due to its large surface area and superaerophobicity underwater. Because of superaerophobicity underwater, a superhydrophilic surface generates the small air bubbles (~ 30 μm sizes) on the surface which form an air layer. This air bubble layer lowers the near surface fluid density which induces an almost
26.5% drag reduction efficiency compared to the flat surface. This value is comparable to the superhydrophobic surface which is the well-known drag reduction surface for fluid transport. In the case of superhydrophobic surface, when the air layer is collapsed the nanostructure could contact with water which means EWS could occur on the surface. Thus, the air bubble is generated on the surface which induces regeneration of the air layer. This study presents an idea that combines the bio-inspired wettability surfaces with EWS bubble generation system for drag-reduced superhydrophilic surface and long-term stability superhydrophobic surface which is useful for an application on the fluid transport system.

MS03.11.05
Dynamic Compressive Strength of Hydrated Lamellar Bone at the Microscale
Cinzia Peruzzi1, Johann Michler1, Edoardo Mazza2 and Jakob Schwiedrzik1; 1Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; 2ETH Zürich, Switzerland

Bone is a hierarchically structured composite tissue spanning several length scales. It consists of collagen molecules, calcium phosphate minerals and water. Mineralized collagen fibrils (MCF) are embedded into an extracellular matrix and form lamellar bone. Lamellae are 3 to 7 µm thick layers of MCF’s arrays and constitute the majority of cortical bone. To better understand the mechanical properties of bone, it is necessary to characterize the material over several length scales, as well as under conditions resembling a physiological environment [1]. It is important to note that not only are bones subjected to various strain rates on a daily basis, but especially so upon impact, e.g. falling [2]. Therefore, we investigated the strain rate dependency of bone at the length scale of a single lamella via micropillar compressions under hydrated conditions. The micropillars were produced in ovine bone using focused-ion beam (FIB) in axial and transverse orientations, using a well-established procedure [3]. The pillars had diameters of 5.493 +/-0.158 µm and heights of 10.557 +/- 0.744µm. Compression experiments were performed under ambient pressure with a relative humidity of over 90% using a customized nanoindenter setup. Compression tests were carried out under displacement control at different strain rates, varying from 10^-3 to 10^2 1/s, to cover the mechanical response of bone over 6 orders of magnitude in strain rate. Within this range, the change in yield stress, as well as post-yield characteristics were assessed. The anisotropy of the strain rate sensitivity was investigated and post-test HRSEM analysis was performed to image the deformation and failure mechanisms and correlate them to the measured mechanical behaviour.

These experiments highlight the importance of physiological condition testing and the influence of strain rate dependency on bone yield stress and ductility. The generated data may enhance existing micro-finite element models for the clinical evaluation of fracture risk in osteoporotic patients in the future.


MS03.11.06
Optimization of Bacterial Nanocellulose Fermentation Using Lignocellulosic Residues and Development of Novel BNC-Starch Composites
Francisco G. Silva1, Ricardo Carvalho1, Fernando Dourado1, Eugénio C. Ferreira1, Fátima Poças2 and Miguel Gama1; 1University of Minho, Portugal; 2Centre for Biotechnology and Fine Chemistry, Portugal

In the papermaking industry, a significant fraction of fibres that cannot be re-utilized is wasted, which raise economic and environmental concerns. On the other hand, the development of renewable polymeric materials became a priority for the sustainability of several industries. Bacterial nanocellulose (BNC), a biopolymer extruded by Gluconacetobacter xylinus as a 3D nanofibrillar network, provide interesting properties as high porosity, high water retention, biocompatibility, non-toxicity and biodegradability. These properties have sustained promising applications in the biomedical field, pulp & paper, composites and foods. However, large-scale BNC production remains a challenge, due to the low productivities, ineffective fermentation systems and high operating costs. Therefore, the production of BNC through lignocellulosic residues has been studied. Recycled paper sludge (RPS) composed of small fibres with 40% of carbohydrates were hydrolysed and used as a carbon source in culture media formulation. Then, a Response Surface Methodology (RSM) optimization with RPS was assessed in order to maximize BNC production, through static fermentation with K. hansenii ATCC 53582. Overall, the results suggest that RPS had the potential to be an alternative carbon source for BNC production with a maximum BNC yield of 5 g/L. BNC produced as described above was then used for the development of novel green thermoplastic
nanocomposites, combined with starch. When mixed with water and glycerol (with heat and shear), starch undergoes spontaneous destructuring, forming thermoplastic starch (TPS). In particular to food packaging applications, BNC has remained unexploited in spite of being considered to have enormous potential. In this work, two approaches for composite production were assessed. Firstly, BNC 3D membrane was filled with biodegradable bio-based thermoplastic starch (TPS), where the production was achieved in a two-step process: impregnation of TPS in the BNC membrane, followed by drying. Different thicknesses of BNC membrane were studied (1-5 mm) as two impregnation time (24h;72h). The second approach consisted on the use of glycerol-TPS as a matrix, where different concentrations (0.05 -0.5% w/v) of cellulose (Plant (PC) and BNC) was added. TPS-BNC and TPS-PC films were prepared by solution casting method. All nanocomposites manufactured were then characterized in terms of mechanical properties, morphology and permeability to water vapour (WVT). Overall, enhanced mechanical and barrier properties were obtained with composites composed by BNC membrane filled with TPS. In comparison to TPS-BNC and TPS-PC films, higher young modulus and tensile strength were obtained with the BNC membrane filled with TPS. Being longer and thinner, the BNC fibres offer greater mechanical resistance than the ordinary TPS-cellulose composites. In addition, the elasticity remains similar to the TPS-cellulose composites, despite having a lower concentration of starch/glycerol. The authors gratefully thank funding through the project Multi-biorefinery PAC (SAICTPAC/0040/2015) and SkinShip with reference PTDC/BBB-BIO/1889/2014 (financiado pelo Fundo Europeu de Desenvolvimento Regional (FEDER) através do Programa Operacional Competitividade e Internacionalização - COMPETE 2020, do Programa Operacional Regional de Lisboa e por Fundos Nacionais através da FCT - Fundação para a Ciência e a Tecnologia no âmbito do projeto POCI-01-0145-FEDER-016595).

MS03.11.07
New Bioplastic Composites of Polycoumarate Copolymers with Polybutylene Succinate Maninder Singh and Tatsuo Kaneko; JAIST, Japan

Fabrication of environment-friendly polymers are in great demand as they are derived from naturally occurring molecules which degrade easily into the environment without causing any harm and can be useful for solving environmental problems. One such environmentally benign, high performance polymer poly(4HCA-co-DHCA) was synthesized using phenolic monomers (4-hydroxycinnamic acid (4HCA) and dihydroxycinnamic acid (DHCA)) has high thermal and mechanical strength than usual aliphatic polyesters such as poly(lactic acid) which makes the resulting polymer highly rigid in nature. Also, these polymers show liquid crystalline behavior which sometimes dramatically increases the mechanical strength. Because of the high rigidity, these polymers cannot be used in applications which require flexible polymers. Poly(4HCA-co-DHCA) is brownish in color and look alike wood but it is very rigid in nature. This polymer can be a good candidate to be explored further to obtain a flexible polymer. To increase the flexibility of poly(4HCA-co-DHCA), some aliphatic chain such as polybutylene succinate (PBS) can be introduced. PBS is also derived from biobased monomers and it is biodegradable as well. In this report, we will present the synthetic protocol for copolymerization of rigid poly(4HCA-co-DHCA) with PBS. Flexibility and toughness of composite can be controlled by changing the wt.% of the PBS chain. The results will be discussed using various characterization techniques using NMR, GPC, TGA and tensile measurements.

MS03.11.09
Biodegradable PCL-PLGA-Brushite Scaffolds for Bone Tissue Engineering Aneela Anwar1,2 and Xiaojun Yu1; 1Stevens Institute of Technology, United States; 2University of Engineering and Technology, Pakistan

Introduction: Every year more than 2.2 million bone graft procedures are performed to treat the bone defects worldwide, which costs approximately $2.5 billion. Recent approaches for segmental bone defect reconstruction are limited to autografts, which are considered as gold standard due to their osteoconductivity, osteogenicity and osteoinductivity properties. However, there are some restrictions and concerns of this procedure results in donor site morbidity, secondary infection, restricted availability, and surgical limitations. In this context, synthetic scaffolds have proved to be a potential candidate for the bone grafts due to their unlimited supply. However, the major challenge to repair the segmental bone defect is the development of synthetic porous scaffold using biodegradable biomaterial for proper cell adhesion and proliferation in abundance in order to get required porosity and better mechanical properties. A variety of techniques and scaffolds are being made for this engineering. The choice of material, mechanical properties, and porosity of the scaffold can affect the cell progression after implantation [1]. Therefore, we have developed a novel biodegradable biocomposite scaffold based on polycaprolactone-poly lactic-co-glycolic acid (PCL-PLGA)-Brushite by using compression molding methods. Its structural and biological properties have been assessed. Importantly, faster degradation of PLGA than PCL led to the creation of in situ pores
in the matrix of PCL, which can help in the neovascularization.

**Materials and Methods:** The biocomposite scaffolds were prepared by heating the mixture of PCL, PLGA and brushite at 150 °C in a PTFE mold, followed by compression. X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were used for the phase analysis and surface characterization of the as-sintered samples. The energy dispersive spectroscopy (EDS) was used for the analysis of brushite distribution in the PCL-PLGA matrix. The percentage porosity and density were measured by using liquid displacement method. For the mechanical testing, cylindrical samples of 6 mm diameter and 12 mm height were tested at a speed of 1.3 mm/min using the universal testing machine. Furthermore, the samples were tested for its degradation behaviour in 1×PBS at 37 °C for 2, 4, 6, 8, 16, 24, and 48 weeks.

**Results and Discussion:**
As-sintered cylindrical-shaped scaffolds were characterized by a dense structure with density ~1.07 g/cm³, which is comparable to the cancellous bone (0.1–1.0 g/cm³). The SEM carried out in the secondary electron mode revealed a micro-rough surface. This rough surface is expected to play an important role in cell adhesion and proliferation. A comparison of XRD results confirmed the presence of the amorphous phase of PLGA and crystalline phases of PCL as well as brushite. The mechanical testing of scaffolds showed a significant effect of PCL and PLGA ratio on the yield strength and young’s modulus. Furthermore, the detailed SEM-EDS mapping confirmed the uniform distribution of brushite (Ca, P, and O). The mechanical testing of scaffolds showed a significant effect of PCL and PLGA ratio on the yield strength and young’s modulus.

**Conclusions:**
In this study, we have prepared a novel biodegradable scaffold composed of PCL, PLGA and brushite and investigated its structural and biological properties. Based on our findings, we believe that this biomimetic scaffolds are suitable for bone tissue engineering applications and could be used a promising material for future endeavors.

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**MS03.11.10**

**Bioinspired Fatigue-Resistant Adhesion of Hydrogels** Ji Liu¹², Xinyue Liu¹, Shaiting Lin¹, Zhao Qin¹ and Xuanhe Zhao¹; ¹Massachusetts Institute of Technology, United States; ²Southern University of Science and Technology, China

The adhesion of soft connective tissues (tendons, ligaments, and cartilages) on bones in many animals can maintain high toughness (~ 800 J m-2) over millions of cycles of mechanical loads. Such fatigue-resistant adhesion has not been achieved between synthetic hydrogels and engineering materials, but is highly desirable for diverse applications such as artificial cartilages and tendons, robust antifouling coatings, and hydrogel robots. Inspired by the nanostructured interfaces between tendon/ligament/cartilage and bones, we report that bonding ordered nanocrystalline domains of synthetic hydrogels on engineering materials can give an extremely fatigue-resistant adhesion with a record-high interfacial fatigue threshold of 800 J m-2, since the fatigue-crack propagation at the interface requires a much higher energy to fracture the ordered nanostructures than amorphous polymer chains. Our method enables fatigue-resistant hydrogel coatings on diverse engineering materials with complex geometries. We further demonstrate that fatigue-resistant hydrogel coatings on metallic joint replacements can give lower friction and better wear-resistance against natural cartilages than the commonly used polyethylene coatings.

**MS03.11.11**

**Exploratory Study of Composite Materials with Diatoms Fillers** Izabela B. Zglobicka¹, Jürgen Gluch², Cathy Kilroy³, Ehrenfried Zschech² and Krzysztof Kurzydlowski¹; ¹Bialystok University of Technology, Faculty of Mechanical Engineering, Poland; ²Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany; ³National Institute of Water & Atmospheric Research Ltd., New Zealand

Diatoms constitute the largest and the ecologically most significant group of organisms on Earth. The unique silicified cell structure as well as intricate morphology of these microorganisms attract scientists attention for over 100 years. The details of their structure and the functionalities are still under debate and applications of diatom shells are in progress.
One of the widely spread diatom species is a freshwater diatom - *Didymosphenia geminata*, composed of siliceous cells and extracellular polymeric fibrous stalks. The present paper [1] concerns the possibilities of using frustules of this diatoms as a novel filler in epoxy composites. Preliminary results of the research aiming at achieving this goal have been presented in [1,2].

The current study, extends earlier investigations on the possibility of using the diatom frustules in innovative composite materials with metallic matrix. The results are presented of the exploratory research on the properties of the composite, which show a great potential for the development of bio-based metallic matrix composites.


**MS03.11.12**
Hierarchically Cellulose Nanofiber/Titanium Dioxide Nanowire Film with Morphological Matching for Reusable Organic Pollutant Photodegradation

Ting-Han Lin, Yu-Han Liao, Yin-Hsuan Chang, Ying-Han Liao and Ming-Chung Wu; Chang Gung University, Taiwan

Cellulose is the most abundant natural polymer on earth and exists numerously in wood, crop, and cotton. It shows potential to be a candidate for the sustainable material in next generation due to its bio-compatibility, bio-degradation, chemical stability, non-toxicity, and renewable ability. Cellulose nanofiber (CNF) extracted from plants has been reported that it exhibits the unique optical properties, good mechanical strength, and high aspect ratio. TEMPO-oxidation is an effective way to separate the CNF in cellulose microfibril bundles due to the formation of the regioselective repulsive force between each nanofibrils by modification of C6 carboxylate. For extending the application, combining the photocatalysts might provide multi-functional properties with solvent-resistance and degradation capability of pollution. One-dimensional TiO$_2$ nanomaterials can achieve the network structure easily that provides an efficient charge transport path to inhibit the recombination of electron-hole pairs. Moreover, nanofiber-shaped materials can be probably combined with CNF to form the dense, flexible, and freestanding composite film because of the accordance size between each other. In this study, we proposed a simple way to prepare the TiO$_2$ NFs/CNF nanocomposite film with flexibility, solvent resistance, and photocatalytic performance. The relationship between the chemical, physical properties of the TiO$_2$/CNF film and the morphological-matching were discussed. CNF is fabricated by TEMPO-oxidation method and post-reduction by NaBH$_4$. Various TiO$_2$ based materials with different dimension and morphologies, such as P25 nanoparticles, anatase TiO$_2$ nanowires, microparticles, and Ag:TiO$_2$ nanowires were incorporated with cellulose nanofibers. To obtain the uniform and freestanding TiO$_2$/CNF film, the well-dispersion TiO$_2$/CNF mixture solution was activated by UV-ozone treatment to improve the TiO$_2$ hydrophilicity. After the drop-casting and drying, various TiO$_2$/CNF films with 10 mm-thickness were obtained. With the various TiO$_2$, the surface on two sides of film was totally different, which is caused by the TiO$_2$ distribution and dimension in CNF. From the cross-sectional FESEM images and EDS mapping, 1-D TiO$_2$ were entangled with CNF near the edge of film, but P25-TiO$_2$ NPs and TiO$_2$ MPs were embedded and assembled in the CNF hierarchical structure. The distribution of TiO$_2$ in the CNF matrix directly rearranged the CNF ordering stack. We also investigated the crystal structure as well as grazing-incidence wide-angle X-ray scattering (GIWAXS) for the detailed preferred orientation of cellulose nanofiber film. In particular, the TiO$_2$ nanowires entangled with CNF improved the hierarchical stack due to the similar morphology and stacking orientation. Therefore, the mechanical properties including tensile strength and young’s modulus can be improved and higher than that of TiO$_2$ particles/CNF. In the testing of solvent resistance for 30 days, these various TiO$_2$/CNF film showed the outstanding resistance and stable in the acetone and dimethylformamide (DMF). For the better photocatalytic activity, Ag:TiO$_2$ nanowires were employed. In the photodegradation of 1.0 ppm methyl orange in ethanol, Ag:TiO$_2$ NWs/CNF film presented the high degradation efficiency of 87% and showed the excellent stability of morphology and activity after 3 cycles. In addition, Ag:TiO$_2$ NWs/CNF film presented remarkable degradation behavior and stability toward the VOCs including methanol, n-butanol, and DMF with 5,000 ppm.

**MS03.11.13**
Clay Hybrid Nano-Layer Assembly, Structure and Mechanics at the Air-Water Interface

Paulo H. Michels Brito, Antônio Gasperini, Lina Mayr, Ximena Puentes-Martinez, Romulo Tenorio, Leide P. Cavalcanti, Koiti
We present a study on the structural organization and mechanical proprieties of clay colloidal particle films at the air-liquid interface. The film self-assembly and stability is monitored employing the Langmuir Trough (LT) method. Both pure clays and modified clays are studied in an LT using synchrotron X-ray Grazing Incidence techniques (GID and GIXOS). The Langmuir film thickness and in-plane organization are monitored in order to investigate mechanisms for control of adsorption on different interfaces. These results are important for particle coating studies and for the development of new routes for assembling clay colloidal particles on liquid surfaces/interfaces. Surface properties are particularly important in relation to Pickering emulsions where particle coatings on droplets effectively prevent droplet coalescence and produce mechanically very stable surfactant-free emulsions. The adsorption of colloidal particles at the surface of liquid droplets [1] has applications in several areas such as the food-, cosmetics-, pharmaceutics-, and the petroleum sector. [2]. Here we demonstrate how the ordering of clay nanoparticles on a confined two-dimensional aqueous surface can be investigated in detail. In particular, we recreate the process of Janus clay-platelets exfoliation and clay platelet re-assembly, using synthetic Fluorohectorite clays [3], in the interfacial confined environment provided by the LT.


MS03.11.14
Fracturing of the Polycrystalline MoS2 Nanofilms Marianna Sledzinska1, Gil Jumbert1,2, Marcel Placidi3, Alois Arrighi1,2, Peng Xiao1,2, Francesc Alzina1 and Clivia M. Sotomayor Torres1,4; 1ICN2, Spain; 2Universidad Autonoma de Barcelona, Spain; 3IREC, Spain; 4ICREA, Spain

In the recent years we have observed a fast increase in the demand for personal flexible and wearable devices, for sensing, health monitoring and leisure. With the raise of 2D materials, the pursuit of high-performance flexible devices seems even closer to realisation. 2D materials seem perfect candidates for flexible nanotechnology because of their unique physical and mechanical properties. One of the issues innately related to flexible electronics is the ability of the active components to handle reasonably high strain. Therefore over the years it has been crucial to exploit the properties of 2D materials for the proper function of the flexible devices. But, while single crystals of 2D materials possess outstanding elastic properties, point and line defects will play an important role in potential technological applications of large-area samples grown, for example, by chemical vapour deposition.

In this work we investigate the crack propagation on micro- and nanoscale in polycrystalline MoS2 films in a very small grain limit. The study is performed on two types of MoS2 samples differing in the grain orientation with respect to the film plane, i.e., horizontal (in plane)-vertical (out of plane) and purely horizontal, with thickness of 17 nm and 3 nm, respectively. Using electron microscopy techniques we determine critical uniaxial strain as approximately 5%, independently of the sample morphology and thickness. We also study the nanoscale crack propagation under the transmission electron microscope and show that they propagate along the grain boundaries as well as through the grains preferentially along van der Waals bonding. Our results provide an insight on the fracture of polycrystalline 2D materials as well as new means for tailoring the critical strain and nanofabrication of ultra-thin MoS2 devices, by using well-developed tools and of great interest of flexible electronics industry.

MS03.11.15
Synthesis of a Novel Flame-Retardant Hydrogel for Skin Protection Using Xanthan Gum and Resorcinol Bis(diphenyl phosphate)-Coated Starch Yuan Xue1, Mingkang Li2, Bole Pan3, Lisa Quinto1, Jalaj Mehta4, Lauren Stiefel1 and Miriam Rafailovich1; 1Stony Brook University, United States; 2Shanghai Star-river Bilingual School, China; 3Guangzhou Tianhe Foreign Language School, China; 4Hauppauge High School, United States; 5Yeshiva University High School for Girls, United States

Firefighters continually endanger their lives in order to rescue others. This can leave them with severe burns; in
2017 alone, 2,835 U.S. firefighters suffered from burn-related injuries. In this research, a flame retardant hydrogel was synthesized using biodegradable, non-toxic materials: xanthan gum (XG) and resorcinol bis(diphenyl phosphate) (RDP) and starch. RDP was first coated onto the xanthan gum and starch surface. Fourier-transform Infrared Spectroscopy confirmed the hydrogen bonding between RDP and XG/starch. To evaluate the protection of FR hydrogel, sheepskin was embedded in aluminum pans, covered with hydrogel, and burned continuously for 150s. Temperature change of the sheepskin was recorded during burning test. Results showed the formation of a uniform char layer from the FR hydrogel which protects the underlying gel layer and skin. The FR hydrogel sample outperformed its pure XG gel control sample by 29% in terms of the final temperature. The FR hydrogel helped to remain the skin temperature below 45 °C for over 50 seconds and below 55 °C for 114 seconds upon direct burning with a propane torch. TGA tests showed that the FR hydrogel had more residue after test which is in agreement to the char formation during the burning test. Data from the viscosity tests revealed that all samples displayed shear-thinning behavior. Thermal protective performance (TPP) tests were also done to evaluate heat transmission through the FR hydrogel when exposed to a continuous heat source, and result compared to the Stoll Curve which represent the heat level for causing second-degree burn. The TPP test result showed that the FR hydrogel provided a prolonged protection time comparing to the control sample.

**MS03.11.16**

**Mechanical Behavior and Applications of Nanocomposite Fibers and Scaffolds**

Panagiota Gkertsiou, Spyridon Kassavetis, Zoe Dardani, Christoforos Gravalidis, Stelios Karamanidis, Varvara Karagkiozaki and S. Logothetidis; Aristotle University of Thessaloniki, Greece

Nanocomposite fibers in the form of scaffolds are candidate materials for several applications such as tissue engineering, regenerative medicine, controlled drug release and multifunctional surfaces. The performance and service life of such scaffolds is significantly affected by the mechanical properties of the nanocomposite fibers and the adhesion to the surface of their substrate material. Thus the understanding of the mechanical behavior of the fibers and scaffolds is critical for potential applications.

In this work, we focus on the fabrication of nanocomposite polycaprolactone (PCL) fibers and scaffolds via electrospinning and on their structural and mechanical characterization using X-Rays Diffractions (XRD), Atomic Force Microscopy (AFM) and depth-sensing Nanoindentation (NI), respectively. The scope is to correlate the structure of the nanocomposite fibers and scaffolds with their mechanical behavior and their antibacterial properties in terms of cell / bacteria adhesion and colonization.

For the Electrospinning of the nanocomposite PCL fibers we used: a) ZnO nanoparticles (NPs) with 15 nm average diameter, developed by precipitation method using Zinc Acetate Dehydrate, Sodium Hydroxide and Polyvinylpyrrolidone (PVP) as a surfactant and b) drugs such as Curcumin and Vancomycin. X-ray diffraction characterization showed the addition of 1% w/v ZnO NPs results to more crystalline PCL fibers. The NI testing, using a Berkovich type indenter and penetration depth up to 1/10 (~ 100 nm) of the fibers thickness (> 1 μm), and analysis of the NI Load-Displacement curves showed that the Elastic Modulus values of the PCL:ZnO(NPs) nanocomposite fiber increases from 1.2 GPa (pristine PCL) to 1.7 GPa, whereas the Hardness values remains almost the same (0.7 GPa). In addition, the tip of the AFM cantilever was used to deform the nanocomposite fibers and to estimate the critical load (Pc) for the onset of the elastic/plastic deformation and the formation of a clear imprint on the PCL:ZnO(NPs) fibers surface. It was found that Pc decreases from 1.25 μN to 1.07 μN, after the addition of the ZnO NPs.

The adhesion of the nanocomposite PCL:ZnO(NPs) fibers to glass substrate was also tested by AFM and it was found that although the fibers are subjected to plastic deformation and cutting, they remained adhered to the glass substrate. In conclusion, the incorporation of ZnO NPs into PCL fibers was found to affect both the crystallinity and the mechanical behavior of the nanocomposite scaffolds and fibers.

**MS03.11.17**

**Evaporation-Driven 3D Scaffolds of Carbon Nanotubes for Composite Reinforcement**

Asaf Nissenbaum, Israel Greenfeld and H. Daniel Wagner; Weizmann Institute of Science, Israel

Many biological composites (e.g., bone, tendons, seashells) possess superior mechanical properties (e.g., strength, toughness) mostly due to their hierarchical organization. These structures grow through unique self-assembly processes, via a ‘bottom-up’ approach. Such an approach may inspire the synthesis of novel man-made multiscale composites, with enhanced mechanical properties. A key material for ‘bottom-up’ construction of multiscale composites is carbon nanotubes (CNT). However, up until today, the methods for assembling CNTs into hierarchical
structures have not led to sufficient improvement of the mechanical properties with respect to conventional composite materials. Here we introduce a method termed Evaporation Driven Self Assembly (EDSA) patterning, assisted by high surfactant concentration. This technique enables the deposition of thick, oriented CNT layers onto quartz fibers, which are then used as a reinforcing component in polymer-based composites. We describe a series of experiments that are intended to characterize the composites microstructure and assess the interfacial adhesion of the CNT-coated quartz fiber to the surrounding matrix. These experiments include visual analysis by light and electron microscopy, as well as μCT scanning, and fragmentation testing to evaluate the interfacial shear strength. The results reveal that, although the nanoscale deposition is random (i.e. single nanotubes do not show any preferred orientation), the composite microstructure exhibits a ribbon-like, thick coating (thicker by an order of magnitude compared to the quartz fiber) that is approximately oriented parallel to the fiber long axis. The mechanical tests reveal that when this layer is impregnated by epoxy, it adopts a 'fibrous' behavior, namely the layer undergoes sequential fragmentation much like classic single-filament composites. A modified Cottrell-Kelly-Tyson (CKT) model is used to assess the interfacial shear stress and the results exhibit a threefold increase in composite strength. This type of multiscale composites could further realize the high potential of CNT mechanical properties, mainly due to the EDSA deposition that solves, to some extent, fundamental issues such as CNTs dispersion and low volume fraction.

MS03.11.18
Reactive Molecular Dynamics Modeling of the Compression of Two-Phase Composites of Cement Paste at the Nanoscale
Ingrid M. Padilla Espinosa and Ram V. Mohan; North Carolina A&T State University, United States

A complete understanding of materials at nanoscale facilitates the possibility of nanomanipulation to improve the materials macroscale properties. Although cement paste is widely used and studied, due to its complexity as a hierarchical random composite, there are still several unknowns related to the effects of molecular features on its macroscopic behavior. Molecular dynamics modeling with a reactive force field was used to study one of these unknown features: the effect of cement paste phases interactions at molecular level on the response to loading conditions at macroscale. Tricalcium silicate (C₃S) and amorphous calcium silicate hydrate (CHS) are modeled as minerals nanolayers. Under compression, the calcium atoms in the C₃S interact with water molecules from the CHS at the interface. Also, the water in the CHS favors the displacement of silicate chains and the breaking of Ca-O bonds, therefore, the CHS phase is more compressible than the C₃S phase in the composite.

MS03.11.19
Engineering Ductile Acrylic Blends Using Biodegradable Copolymers
Robert Wong, Stephanie Silva, Nora Ruth, Ryan Davis and Miriam Rafailovich; Stony Brook University, United States

The goal of this study is to develop and characterize a polymer blend consisting of polymethyl methacrylate (PMMA) and polybutylene adipate terephthalate (PBAT) using graphene as a compatibilizer. A polymer blend of this nature has the potential to be utilized in many aspects of the medical field, including antimicrobial bone implants and provisional dental crowns, while offering the ease of customizable manufacturing through 3D printing. PMMA is a nonconductive material with low impact toughness and high modulus, while PBAT is biodegradable, ductile, and has antibacterial properties; so by blending the polymers we aim to form a high-modulus, ductile material that can easily decompose in the environment. It is, however, difficult to form such a blend due to PMMA and PBAT being immiscible with each other. To overcome this problem, graphene is added as a compatibilizer to decrease interfacial tension and increase polymer–polymer adhesion. Graphene is expected to work well as a compatibilizer due to it having a high aspect ratio, and its work function with PBAT and PMMA is higher than that of PMMA with PBAT, indicating that the graphene will, critically, align along the polymer interfaces. Furthermore, graphene has high electrical, tensile, and antibacterial properties, which are desirable traits for the bulk blend. Based on previous studies working with similar polymer blends, we will start with a 70/30 mixture of PBAT/PMMA that will be tested with varying concentrations of graphene. Thermal, mechanical, and electrical properties will be examined with an objective to find optimal polymer concentrations to maximize these traits. In addition, to determine enhanced properties of the composite for biological applications, we will be testing antibacterial efficacy.
using E. coli and S. aureus and biocompatibility by testing cell viability of dental pulp cells. This novel blend of common low cost polymer gives a unique edge in fulfilling applications held traditionally by PMMA while also being more environmentally conscientious.


SYMPOSIUM MS04

High-Entropy Alloys and Other Novel High-Temperature Structural Alloys
December 2 - December 5, 2019

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SESSION MS04.01: Thermodynamics and Properties of High-Entropy Materials
Session Chairs: Shou-Yi Chang and Junping Du
Monday Morning, December 2, 2019
Hynes, Level 1, Room 110

8:30 AM *MS04.01.01
Metastable High Entropy Alloys—Effects of Bulk and Low Dimensional Thermodynamics on Mechanical Properties Dierk R. Raabe, Z. Ming Li, Wenjun Lu, Christian Liebscher, Gerhard Dehm, Fritz Körmann, Blazej Grabowski and Jörg Neugebauer; Max Planck Institute for Iron Research, Germany

Most alloys are thermodynamically metastable during some stages of synthesis and service. Here we discuss scenarios where metastable phases are not coincidentally inherited from processing, but rather are engineered. Specifically, we present approaches to compositional (partitioning), thermal (kinetics), and microstructure (size effects and confinement) tuning of metastable phases so that they form stacking faults together with planar slip and can trigger athermal transformation effects such as TWIP and TRIP when mechanically or thermally loaded. Such concepts work both at the bulk scale and also at a spatially confined microstructure scale, such as at decorated lattice defects. In the latter case, local stability tuning works primarily through elemental partitioning to dislocation cores, stacking faults, interfaces, and precipitates. Depending on stability, spatial confinement, misfit, and dispersion, both bulk and local load-driven athermal transformations can equip metastable medium- and high-entropy alloys with substantial gain in strength, ductility, and damage tolerance. We explore and demonstrate these effects along three specific thermodynamic questions: First we study the roles of magnetic and vibrational entropy contributions for understanding bulk metastability. Second, grand-canonical effects arising from spatial confinement will be discussed. Third, we present alloy cases with extreme metastability, forming self-organized two-phase
Understanding the thermodynamics of multi-principal-element alloys (MPEA), also known as high entropy alloys (HEA) is crucial to addressing their synthesis, properties, stability, materials compatibility and technological applications. While the thermodynamics of binary and ternary alloys have been relatively well investigated both experimentally and theoretically over the last five decades, this is not the case for multicomponent (>4 element) alloys. The classical calorimetric methods (e.g., liquid metal bath, direct reaction, and flux calorimeter) used for binary and ternary alloys will often encounter difficulties for alloys with more than three elements. Thus, a more flexible and general calorimetric approach is needed.

The present work introduces a new methodology for measuring the enthalpy of formation and mixing of metals based on high temperature oxidative calorimetry. This technique is based on the well-developed oxide melt solution calorimetry (OMSC). Using this method, the heats of formation of four binary (AlNi, AlFe, AlCo, and AlFe₃), one quaternary CrFeCoNi and one quinary Al₀.₁₄Ti₀.₁₈V₀.₁₈Nb₀.₂₆Ta₀.₂₃ alloys were obtained. The values in kJ/(mol atom) are: AlNi, -60.11 ± 3.94; AlFe, -23.46 ± 2.39; AlCo, -51.80 ± 1.89; AlFe₃, -13.72 ± 2.39; CrFeCoNi, -3.24 ± 2.39; Al₀.₁₄Ti₀.₁₈V₀.₁₈Nb₀.₂₆Ta₀.₂₃ -11.93 ± 4.80. The results are compared with predicted values from the Miedema model and with available experimental data. The methodology is thus established to be generally useful for determining the thermodynamic properties of MPEA.

Al₀.₇₅CoCrFeNi high entropy alloys received excessive scientific attention due to their promising mechanical and corrosion resistance properties. These alloys may contain a mixture of FCC and BCC phases were the latest has an important role in its hardening. It was demonstrated that increasing the Al fraction in Al₀.₇₅CoCrFeNi alloy will lead to an increase in the volume fraction of the BCC phase in the alloy. This BCC phase is usually a mixture of a disordered BCC Fe-Cr rich (A2) and an ordered BCC (primitive cubic, B2) Al-Ni rich phases. Moreover, heat treatment history has a major impact on the microstructure and properties as well.

In the present talk, the metallurgy behavior of Al₀.₇₅CoCrFeNi will be discussed. The experimental results suggested that sluggish diffusion and high activation energy for precipitation of A2 phase (disordered BCC) from B2 (ordered simple cubic) phase play major rule on the alloy phase composition. Moreover, the morphology of A2 phase found to be sensitive to cooling rate and the soaking temperate during heat treatment. It was concluded that the lattice distortion dominates microstructure and composition of phases.

The plastic deformation behavior of single crystals of the FCC equiatomic CrMnFeCoNi high-entropy alloy and its derivative equiatomic quaternary and ternary medium-entropy alloys has been investigated in a temperature range of 10-1273 K, paying special attention to possible variations in mechanical properties with heat-treatment that may cause different short-range ordering of the constituent elements. Deformation occurs via slip of
the \{111\}\{<110>\} system exclusively in the whole temperature range for all alloys investigated. The CRSS values increase with decreasing temperature, especially below room temperature, so that the concept of ‘stress equivalence’ is obeyed for all alloys investigated. This is a clear indication that the strength of these alloys should be described by a mechanism based on solid-solution hardening. Dislocations are smoothly curved in the slip plane without any preferred line orientation, indicating no significant anisotropy in the mobility of edge and screw segments. Planar \(\frac{\sqrt{2}}{2}\{<110>\}\{111\}\) dislocations dissociate widely into Shockley partials for all alloys investigated, indicating their low stacking fault energies; 30 ± 5 and 11 ± 3 mJ/m² for CrMnFeCoNi and CrCoNi, respectively. The CRSS values extrapolated to 0 K for polycrystals of equiatomic quinary, quaternary and ternary alloys are reported to be well scaled with the mean-square atomic displacement from the regular FCC lattice points (calculated based on density-functional theory). This seems also the case for the CRSS values at 10 K for single crystals of the present three alloys, although some modifications are definitely needed. Deformation twinning occurs on the conjugate system in the form of the Lüders type deformation in the later stage of deformation at low temperatures in all of the three alloys. The variation of the CRSS values, twinning stress and the stacking-fault energy upon heat-treatment and its inter-correlation will be discussed.

11:00 AM MS04.01.06
**Enthalpic an Entropic Contribution to the Stability of High Entropy Alloys—An Ab Initio Perspective**

George Bokas¹, Wei Chen¹, Stéphane Gorse² and Geoffroy Hautier¹; ¹Université Catholique de Louvain, Belgium; ²Institut de Chimie de la Matière Condensée de Bordeaux, France

High entropy alloys (HEA) have attracted a lot of attention in the last decades mainly due to their good mechanical, and thermal properties. HEA includes five or more alloying elements forming random solid solution phases. Based on the existing phase diagrams, multicomponent alloys would expect to contain many different phases. However, it is assumed the high value of the configurational entropy promotes the formation of simple solid solution phases inside the multicomponent alloys. It is crucial to understand why some multicomponent alloys can be formed as a single phase whereas some others cannot. In order to answer this question, several methods using atomic descriptors, empirical rules, and thermodynamic modeling have been proposed. These approaches suffer however from insufficient experimental data. Therefore, the prediction of alloys that can form random solid solution phases remains a challenge hindering the discovery of novel HEA and the understanding of what is driving their phase stability. In this work, we use DFT calculations to shed light in the relative thermodynamic stability of BCC and FCC random solid solutions. Using a regular solution model fitted on DFT computation, we created a database of almost 80,000 FCC and BCC alloys up to the quinary. We will report on the technical challenges in building this database and on the understanding of what is driving phase stability in HEA that one can extract from such a large data set. A special focus will be given to how entropy and enthalpy competition behave as the number of components increase in alloys.

11:15 AM MS04.01.07
**Phase Stability, Microstructure and Mechanical Properties of Nanoeutectic CoCrFeNiTa\(_x\) (0.2 < \(x\) < 0.5) High Entropy Alloy**

Barnasree Chanda and Jayanta Das; Indian Institute of Technology Kharagpur, India

High entropy alloys are a new class of alloys which consists of five or more major element in the range of 5-35 at.%. The ever increasing demands for new structural applications, high entropy alloys (HEA) are transpire as a new paradigm shift in material society. Nano-eutectic HEAs exhibit superior mechanical properties over the single-phase high entropy alloys. The optimum combination of strength and ductility are the key features of eutectic HEAs. In this work, the novel CoCrFeNiTa\(_x\) (0.2 ≤ \(x\) ≤ 0.5) HEAs with eutectic microstructure were designed and cast by arc melting. The phase composition, mechanical properties and stability of these alloys were investigated. The evolved microstructure in all the HEAs consist of eutectic lamellae with alternating α (γ-Ni)-FCC phase and β (Co,Ta)-type Laves phase. It was observed that \(x=0.2\), and 0.5 alloys contains eutectic microstructure along with proeutectic phase and at \(x=0.4\) homogenous eutectic microstructure was obtained. The CoCrFeNiTa\(_{0.4}\) HEA with the eutectic microstructure exhibited a relatively high combination of yield strength (∼1820 MPa) and ductility (∼21 %). Further, analysis regarding the eutectic phase stability in terms of different thermodynamic and electronic parameters considering the synergistic effect atomic size difference (\(\delta_0\)), mixing enthalpy (\(\Delta H_{mix}\)) and valence electron concentration (VEC) were carried out. Also, from literature EHEAs comprising of FCC /BCC solid solution phases and intermetallic compound/topologically closed packed (TCP) phases have been surveyed thoroughly. The assessment predict the existence of stable eutectic/near eutectic phases in all surveyed and present EHEAs when \(-18 ≤ \Delta H_{mix} ≤ -6\), \(6 ≤ VEC ≤ 8.5\) and \(\delta_0 > 3\%\).
11:30 AM MS04.01.08  
**Dual-TRIP Effect in Metastable High-Entropy Alloys** Shaolou Wei, Jinwoo Kim and Cem Tasan; Massachusetts Institute of Technology, United States

Microstructural metastability engineering, especially transformation-induced plasticity (TRIP) effect, is one of the most effective strategies to enhance strain hardenability in exploring advanced high-entropy alloys (HEAs). While appreciable effort including both compositional and microstructural optimization has been accomplished to modulate the TRIP effect, the resultant transformation product, martensite, still seriously impedes the property advancement: its extensive defect density and limited hardenability inevitably lead to local embrittlement and thereby failure. Here in this presentation, we will demonstrate that by manipulating the mechanical stability of the parent FCC phase in an Fe-Mn-rich HEA, the strain induced HCP-martensite can become further transformable, activating an FCC→HCP→FCC dual-TRIP effect. With the aid of in-situ synchrotron X-ray diffraction, SEM/EBSD, and microstructural-based strain mapping techniques we reveal the corresponding transformation kinetic, kinematic, and global-local strain evolution characteristics. We will show that this sort of dual-TRIP mechanism exhibits a desirable potential to overcome the inherent property improvement threshold of classical TRIP effect.

11:45 AM MS04.01.09  
**Origin of Antiferromagnetism in Entropy-Stabilized Oxides** Zsolt Rak and Donald Brenner; North Carolina State University, United States

The origin of antiferromagnetism in the entropy-stabilized oxide Mg$_{0.2}$Co$_{0.2}$Ni$_{0.2}$Cu$_{0.2}$Zn$_{0.2}$O has been investigated using first principles electronic structure calculations within the DFT. To characterize the magnetic structure of the entropic oxide, the total energy in the ferromagnetic (FM) as well as in the type-I and type-II antiferromagnetic (AFM) configurations are calculated. In agreement with the experimental findings, the most stable configuration corresponds to the type-II AFM order, where the ferromagnetically coupled (111) planes are stacked antiferromagnetically along the [111] direction. To characterize the magnetic interactions between the nearest neighbor (NN) and next nearest neighbor (NNN) magnetic ions (Co, Ni, and Cu), the calculated total energies are mapped onto the Heisenberg spin hamiltonian and the exchange coupling constants, $J_1$ and $J_2$, are evaluated. The strong antiferromagnetic NNN coupling and the weaker ferromagnetic NN coupling is consistent with the type-II AFM magnetic configuration. The relative strengths and the signs of the exchange coupling constants are analyzed in terms of the calculated electronic structure. The results are compared to recent experimental investigations of long-range magnetic ordering in high entropy oxides.

This work is supported by the U.S. Office of Naval Research MURI program (grant No. N00014-15- 1-2863).

1:30 PM *MS04.02.01  
**Short-Range Order and the Mechanical Properties of Medium/High-Entropy Alloys** Robert O. Ritchie$^{1,2}$, Andrew M. Minor$^{1,2}$, Mark Asta$^{1,2}$, Jun Ding$^2$, Ruopeng Zhang$^2$,$^1$, Shiteng Zhou$^{2,1}$ and Qin Yu$^2$; $^1$University of California, Berkeley, United States; $^2$Lawrence Berkeley National Laboratory, United States

CrCoNi-based medium/high-entropy alloys can display exceptional combinations of strength (~1 GPa), ductility (~60-90%) and toughness (>200 MPa√m), properties which are further enhanced at cryogenic temperatures. *In situ* TEM observations identify multiple deformation mechanisms, associated with their high friction stress yet low stacking-fault energy, that act synergistically to generate damage-tolerance. For example, studies on CrCoNi reveal a hierarchical twin network that generates substantial 3-D barriers to dislocation motion with marked strain hardening, while simultaneously providing pathways for easy dislocation motion. Here we focus on the effect of local chemical ordering which appears to be an important factor governing the exceptional mechanical properties of...
these alloys. Our DFT-based Monte-Carlo simulations on CrCoNi show that variations in local chemical order have a profound effect on the stacking-fault and twin-boundary energies, the TRIP effect, and the formation energy of point defects, all features that influence mechanical properties; these predictions have recently been further confirmed by MD calculations. Despite the clear evidence from atomistic simulation, the existence of such short-range order in medium/high-entropy alloys has lacked direct experimental confirmation, having only been indirectly detected using x-rays. Here using energy-filtered TEM techniques, we provide direct experimental evidence for the presence of short-range order in the CrCoNi MEA, and comment on its significant effect on elastic and plastic deformation properties. These results highlight the possibility of “tuning order in disorder” in the form of a science-based atomistic tailoring of multiple-principal-element alloys to achieve specifically desired macroscale mechanical performance.

2:00 PM MS04.02.02
Understanding Short-Range Ordering in Refractory High-Entropy Alloys Wei Chen1, George Kim1, Chanho Lee2 and Peter K. Liaw2; 1Illinois Institute of Technology, United States; 2The University of Tennessee, Knoxville, United States

The material-design strategy of combining multiple elements in near-equimolar ratios has spearheaded the emergence of high-entropy alloys (HEAs), an exciting class of materials with exceptional engineering properties. While random mixing has been widely assumed in multi-principal element solid solutions, both experimental and computational evidence suggests short-range ordering (SRO) exists in many solid-solution HEAs. We employed an integrated first-principles and experimental approach to understanding the thermodynamic effects of SRO in the refractory NbTaTiV and NbTaTiVZr HEA systems. Results are compared with predictions from Special Quasi-random Structures (SQS). The existence of SRO produces distinct lattice distortion features in these HEAs and affects their mechanical properties.

2:15 PM MS04.02.03
Revealing the Short-Range Order and Its Effects in the CrCoNi Medium Entropy Alloy Shiteng Zhao1, Ruopeng Zhang1, Jun Ding2, Mark Asta1,2, Robert O. Ritchie1,2 and Andrew M. Minor1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

The equiatomic ternary CrCoNi medium entropy alloy (MEA) exhibits an exceptional combination of high strength, ductility as well as fracture toughness. Although usually considered as a random solid solution, it has been suspected that short-range order (SRO), i.e. atomic scale correlation of elemental distribution, exists in this alloy, which may significantly affect the mechanical behavior. However, up to date, the direct observation of SRO by electron microscopy has not been possible due to their intrinsically small scale and lack of contrast. In this investigation, we confirm the existence of SRO in a thermal-mechanically treated MEA by deploying an in-column, energy-filtered transmission electron microscope. The inelastically scattered electrons can be effectively eliminated by the energy filter, dramatically increasing the signal-to-noise ratio, enabling the detection of SRO diffraction pattern. Using energy filtered dark field imaging, we show that these SRO domains are as small as several angstroms and distribute uniformly across the sample. The influence of the SRO on the mechanical behaviors of the MEA are evaluated by nanoindentation, bulk tensile testing as well as pulse-echo ultrasonic measurement. The deformation microstructure, especially the dislocation configuration is examined by diffraction-contrast STEM imaging. It was shown that SRO promotes the planarity of the dislocation slip and increases the stacking fault energy of the MEA; It also slightly improves both nanoindentation hardness and yield strength without sacrificing the ductility. These discoveries corroborate with DFT-based Monte-Carlo computation, suggesting that the degree of SRO is an intrinsic materials parameter that can be tuned to tailor the structure-property relationship. Strategies of obtaining different degrees of SRO by thermal-mechanical treatment will also be touched base in this talk.

2:30 PM MS04.02.04
Investigation of Defects in High Entropy Alloy HfNbTaTiZr by Positron Anihilation Spectroscopy Petr Hruska1, Jakub Cizek1, František Lukac1,2, Radek Musalek2, Oksana Melikhova1, Jan Kuriplach1, Miloslav Janecek1, Jiri Zyka1 and Jaroslav Malek3; 1Charles University, Faculty of Mathematics and Physics, Czechia; 2Institute of Plasma Physics of the Czech Academy of Sciences, Czechia; 3UJP PRAHA, Czechia

High entropy alloys (HEA) exhibit various combinations of interesting physical properties due to the formation of
solid solution stabilized by a high configurational entropy. HEAs with high melting point are promising candidates for low density refractory metals, e.g. HfNbTaTiZr alloy. Since conventional preparation by arc melting results in a dendritic structure of bcc phases, long term and high temperature annealing is necessary for homogenization of the structure [1]. On the contrary, powder metallurgy is a fast way of producing fine grained alloys. The HfNbTaTiZr powder prepared by gas atomization was processed by spark plasma sintering (SPS) at various sintering temperatures. By characterization of its microstructure, lattice defects and mechanical properties [2] the sintering conditions were optimized in order to obtain a fully dense single-phase material. Defects formed during the process of SPS were characterized by positron lifetime spectroscopy (LT). LT is a well established non-destructive experimental technique with high sensitivity to open-volume defects (e.g. vacancies and vacancy clusters, dislocations, grain and phase boundaries). Moreover, the experimental LT data can be directly compared with ab-initio theoretical calculations. Analysis of measured LT spectra enables both identification of the type of defects in the material as well as evaluation of their concentration. Since the concept of HEAs is inherently related to severe lattice distortions which affect also open volumes, any information on the defects in the bulk solid solution phases is invaluable. LT may be used also for monitoring of the remaining porosity at the very atomic level in alloys prepared by SPS.


2:45 PM BREAK

3:15 PM *MS04.02.05
Modeling Co-Cr-Fe-Ni-Mo High Entropy Alloys—Structural and Mechanical Properties Michael Gao1,2, Zongrui Pei1,3, Jeffrey Hawk1 and David Alman1; 1National Energy Technology Laboratory, United States; 2Leidos Research Support Team, United States; 3ORISE, United States

It is well known that addition of molybdenum to steels and nickel-base alloys can increase the mechanical strength and the resistance to pitting corrosion. However, it is less known how Mo addition may impact the atomic structure and hence the intrinsic physical and mechanical properties of the alloys as a function of temperature and composition. In present work, the evolution of the atomic structure (including short range order, atomic occupations, or local lattice distortion) of Co-Cr-Fe-Ni-Mo high entropy alloys in liquid, in solid, and during solidification is first studied using density functional theory (DFT) methods, ab initio molecular dynamics, and Monte Carlo simulations. This information gives implications for the mechanical properties from a thermodynamic perspective. As the next step, the elastic constants and stacking fault energies of the model alloys are calculated using DFT, which further improve our understanding of the impact of Mo on the yield stresses.

3:45 PM MS04.02.06
Microstructure Simulations of Complex Concentrated Alloy HfNbTaTiZr Jan Kuriplach1, Jakub Cizek1, Oksana Melikhova1, Frantisek Lukac1,2, Jiri Zyka2 and Jaroslav Malek1; 1Charles University, Czechia; 2Institute of Plasma Physics, Czechia; 3UJP Praha a.s., Czechia

The HfNbTaTiZr refractory alloy is intended for high temperature applications and crystallizes in the bcc structure at high temperatures. The microstructure of this alloy is studied by means of the density functional theory using the supercell approach. It is first explained why HfNbTaTiZr is not a true high entropy alloy. The tendency of the alloy to short range ordering is then demonstrated for several partially ordered structures based on the bcc lattice. Next, the Metropolis Monte Carlo algorithm is employed in order to simulate the short range order in the HfNbTaTiZr alloy. The tendency to short range ordering increases with the decreasing temperature. This indicates that a phase separation could occur at lower temperatures, which is indeed detected experimentally. The question why the alloy could not have an hcp structure at lower temperatures is also addressed. Finally, the structure of a $\Sigma_5$ grain boundary in the HfNbTaTiZr alloy is investigated. Such a grain boundary exhibits quite low grain boundary energy and the segregation of Ti is detected. The results of the simulations are compared with other experimental data available.

4:00 PM MS04.02.07
Microstructure Evolution of Refractory Alloys During Powder-Based Dealloying Alyssa Chuang and Jonah Erlebacher; Johns Hopkins University, United States

A key consideration in designing high-performance materials with exceptional strength and toughness is tuning the
microstructure. Dealloying is a processing method for producing metallic materials with a unique bicontinuous microstructure, which has been shown to exhibit size-dependent improvements in mechanical properties. Previously, dealloying was limited to electrochemical systems, but the emergence of liquid metal dealloying and solid state dealloying has expanded the capabilities of this technique to include refractory alloys.

Powder-based dealloying is a novel approach to creating bulk quantities of refractory metal composites with a complex, interconnected network of ligaments. By mixing and pressing together powders of the parent alloy with powders of the metallic solvent into a bulk sample, we can create a material in which dealloying occurs uniformly throughout the bulk of the material, not just at the geometric surface. These experiments offer insight into the microstructural evolution of dealloyed refractory metal composites as a function of time, temperature, and composition. Here we present an assessment of the mechanical properties of these materials, in addition to a study of the dealloying kinetics between pressed powders. Studying the fundamental kinetics of powder-based processing is the first step to developing the high-temperature processing techniques necessary to apply dealloying to additive manufacturing of refractory alloy composites.

4:15 PM MS04.02.08
Microdistortions Correlate with Misfit Volumes in High Entropy Alloys Wolfram G. Nöhring\textsuperscript{1,2} and William A. Curtin\textsuperscript{1}; \textsuperscript{1}École Polytechnique Fédérale de Lausanne, Switzerland; \textsuperscript{2}University of Freiburg, Germany

The yield strengths of High Entropy Alloys (HEA) have been shown to correlate with picometer-scale lattice distortions. Therefore, distortion measurements could be used to estimate strengths. Alternatively, a predictive model of HEA strength based on solute misfit volumes is available. Here, the connection between lattice distortions and misfit volumes is examined for two model ternary alloy families, fcc Cr-Fe-Ni and bcc Nb-Mo-V. The root mean square lattice distortion is nearly proportional to the misfit volume parameter over a wide composition range. The reported correlation of yield strength with lattice distortion is thus a consequence of the correlation between lattice distortion and misfit parameter and the derived dependence of yield strength on the misfit parameter.

4:30 PM OPEN DISCUSSION

4:45 PM MS04.02.10
Microstructure Evolution and Orientation Relationships of CoCrFeNi Thin Films Grown on (0001) α-Al\textsubscript{2}O\textsubscript{3} Younes Addab\textsuperscript{1}, Maya Katapadi Kini\textsuperscript{2}, Blandine Courtois\textsuperscript{1}, Alan Savan\textsuperscript{3}, Alfred Ludwig\textsuperscript{3}, Nathalie Bozzolo\textsuperscript{4}, Christina Scheu\textsuperscript{2}, Gerhard Dehm\textsuperscript{2} and Dominique Chatain\textsuperscript{1}; \textsuperscript{1}Aix-Marseille Univ, CNRS, CINAM, France; \textsuperscript{2}Max-Planck-Institut für Eisenforschung GmbH, Germany; \textsuperscript{3}Ruhr University Bochum, Germany; \textsuperscript{4}MINES ParisTech, PSL, France

The study of HEA in the form of thin films aims at providing missing data on HEA phase stability. Indeed, the small bulk volume of a film, combined with the presence of grain boundaries and interfaces, helps in achieving thermodynamic equilibration of these complex alloys. In addition, polycrystalline films can be used to test the role of grain boundaries on the mechanical properties of HEAs. Here we present a study of the stability of polycrystalline CoCrFeNi thin films, grown on (0001) α-Al\textsubscript{2}O\textsubscript{3} (c-sapphire), with respect to annealing treatments. It has been found that extremely large grains can grow in the film depending on their orientation relationship to the c-sapphire substrate. Despite their complex chemistry, the grains in the 200 - 670 nm thick CoCrFeNi FCC films investigated, adopt the same orientation relationships as those of pure FCC metal films on c-sapphire. However, the grains in CoCrFeNi grow much larger at homologous annealing temperatures.

The films have been synthesized at room temperature, using magnetron sputtering from four pure element targets in a chamber with UHV base vacuum. They consist of 30-100 nm wide columnar FCC grains with a <111> texture. Upon annealing for 1 hour in the range 973 K to 1423 K under an Ar-H\textsubscript{2} atmosphere, grain growth and grain boundary grooving compete to either stabilize or break-up the film. The microstructure evolves into larger grains and/or islands, of four different orientation relationships: OR1 (Me(111)[1-10]//α-Al\textsubscript{2}O\textsubscript{3}(0001)[1-100] and OR2 (Me(111)[1-10]//α-Al\textsubscript{2}O\textsubscript{3}(0001)[1-10] and their twins (OR1t and OR2t). Thinner films and higher temperatures favor the dewetting of the film to form single-crystalline islands. Dewetting initiates from holes which nucleate at grain boundary triple junction grooves, and which have deepened sufficiently to reach the substrate. At the highest temperatures, the OR2 and OR2t grains grow to sizes exceeding 1000 times the film thickness. The migration of the grain boundaries of these grains is fast enough to overcome both grooving and the nucleation of dewetting holes.
An alternative route toward production of high entropy alloy nanoparticles (HEA-NPs) is demonstrated using metal carburization and subsequent precipitation of graphite inside carbon nanotubes. Nanoparticles exhibit barely seen structures, including coexistence of different crystal structures and multiple phases. Magnetic hardening is also observed with saturation magnetization much greater than ferromagnetic particles consisting of single and/or binary components. Calculations support experiments and further reveal carbide mediated HEA-NP formation to be thermodynamic favorable.

Effect of Deposition Power on the Microstructural Properties of Sputtered AlCoCrCu0.5FeNi High Entropy Alloy (HEA) Thin Films Naveed Aziz Khan, Behnam Akhavan, Marcela M. M. Bilek and Zongwen Liu; The University of Sydney, Australia

High entropy alloy (HEA) thin films are immensely studied in recent times due to their excellent mechanical and physical properties having high hardness, superior corrosion resistance, and high electrical resistivity. This study reports the findings of radio frequency (RF) magnetron sputtered HEA thin films of AlCoCrCu0.5FeNi from a single stoichiometric target on Si (100) substrate in presence of argon with a substrate heating of 250 °C at three different powers of 200 W, 250 W, and 300 W. The argon flowrate was maintained at 15 sccm with a deposition pressure of 10 mTorr for all the films grown at three different powers. The characterization results reveal that the increase in deposition power from 200 to 300 W increases the average grain size roughly from 27 to 80 nm as well as the surface roughness of the films from 2.64 to 25.2 nm observed from the Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) micrographs, respectively. X-ray diffraction (XRD) indicates that all the films are polycrystalline in nature with a mixture of FCC and BCC having a lattice parameter of 3.61 Å and 2.87 Å, respectively. The surface chemistry analysis from the X-ray Photoelectron Spectroscopy (XPS) confirms the presence of Al2O3 and Cr2O3 on the surface of all the HEA thin films grown at different deposition powers, acting as surface protective layers for superior oxidation and corrosion resistance. Energy Dispersive Spectroscopy (EDS) mapping confirms the homogeneous distribution of all the elements throughout the films grown at three different powers. The hardness data measured from the nanoindentation test shows a significant decrease in hardness from 15.95 GPa (200 W) to 4.84 GPa (300 W) with the increase in deposition power. The HEA films grown at various deposition powers were quite resistive and the highest resistivity of 945.13 µΩ·cm was obtained for the film grown at 250 W measured using the four-point probe method. The above characterization results show that the variation in deposition power is an important parameter to tune the microstructural properties of AlCoCrCu0.5FeNi HEA thin films during the sputtering process which intern governs the chemical and physical properties of the sputtered HEA thin films having potential applications as hard and protective coatings suitable for the energy and aerospace industry.

Predicting Properties of High Entropy Carbides from Their Respective Binaries Mina Lim1, Pranab Sarker2, Christina Rost3 and Donald Brenner1; 1North Carolina State University, United States; 2Duke University, United States; 3University of Virginia, United States

Recently, High Entropy Carbides (HECs) have been predicted the selection of candidate compositions with the phase stability from an entropy-forming-ability (EFA) descriptor from first principle. The predicted compositions are applied to disordered refractory five metal carbides, experimentally synthesized as rocksalt structure and
measured their mechanical properties. We report in this work the results of DFT calculations that were carried out to explore the degree to which properties of high entropy carbides containing different five-atom combinations from the elements Nb, Ta, Mo, W, Ti, Zr, Hf and V can be related to the properties of their respective binary compounds. Cohesive energy, bulk modulus and lattice constants from the Density Functional Theory (DFT) calculations were studied and compared between HECs composition and averaging the values from the binaries. These properties from the binary averages are either matched or slightly under-over estimated the DFT results. For the carbon vacancy formation energy (CVFE), the majority of HECs are distributed roughly within defined upper and lower limit CVFEs of the constituent binary carbides. Mixing multiple metal compositions in HECs still introduces the similar properties from the respective binaries and indicates more energetically stable in structures.

We also investigate the effect of carbon stoichiometry on thermal conductivity of high entropy carbide and its influence on the electrical contribution to thermal conductivity using DFT calculations together with semi-classical Boltzmann transport theory. The energy and electrical conductivity of the fully stoichiometric system, as well as systems containing carbon vacancies and interstitials were calculated. Both the vacancy and interstitial formation energies are positive, however, the energy for creating interstitial carbon is considerably larger than that for creating a vacancy such that the formation of a second carbon phase is highly favorable when excess carbon is introduced into the system. These results are consistent with experiment, where carbon indicative of a second phase is measured for high methane flow rates.

MS04.03.04

In Situ TEM Characterization of Segregation Kinetics of Quinary Solutes V-Nb-Mo-Ta-W in Cu(V,Nb,Mo,Ta,W) Alloy Yu-Ting Hsiao and Shou-Yi Chang; National Tsing Hua University, Taiwan

A robust ultrathin diffusion barrier layer is demanded for the Cu interconnects of integrated circuits to inhibit the rapid diffusion of Cu atoms and to prevent Si devices from failure. In recent years, based on the large positive mixing enthalpy between Cu and refractory metals and the thermodynamically-driven solute segregation, a “self-forming” technique was developed to generate a thin layer of refractory metal from a Cu alloy film doped with refractory solutes, for use as a diffusion barrier. Accordingly and additionally attributed to the high mixing entropy of multiple components, for the first time in our recent study, an ultrathin solid-solution layer of quinary V-Nb-Mo-Ta-W refractory alloy was self-formed from a Cu(V,Nb,Mo,Ta,W) alloy film. As confirmed by high-resolution TEM observations and elemental mappings, the doped solutes segregated to the Cu/Si interface and formed a continuous quinary alloy layer of only 1.5 nm thick. Because of the sluggish diffusion in high-entropy alloys, the quinary alloy layer was found to resist the interdiffusion of Cu and Si at 700 degree C, higher than the resisting temperature (< 600 degree C) of unitary metal layer. In-situ TEM characterization of the segregation of the quinary solutes V-Nb-Mo-Ta-W in a Cu(V,Nb,Mo,Ta,W) alloy foil was further conducted, and the diffusion kinetics of the solute elements in Cu were estimated. Elemental mappings indicated the entropy-stabilized incorporative diffusion of the five solute elements at an average rate of about 50 nm/h at 400 degree C. Mo and W segregated at a higher rate owing to the higher mixing enthalpies with Cu for 19 and 22 kJ/mol, respectively, while V, Nb and Ta segregated at a lower rate due to the lower enthalpies for only 2 to 5 kJ/mol.

MS04.03.05

Lattice Distortion Effect on Elastic Anisotropy of High Entropy Alloys Chao-Chun Yen1, Guan-Rong Huang2, Yun-Cheng Tan3, Han-Wen Yeh1, Shou-Yi Chang2 and Yu-Chieh Lo3; 1National Tsing Hua University, Taiwan; 2National Center for Theoretical Sciences, Taiwan; 3National Chiao Tung University, Taiwan

High-entropy alloys (HEAs) are at the hot topics of metallic materials research because of their outstanding mechanical properties, e.g. high fracture toughness in extreme temperature conditions. Currently, most researches focus on examining their plasticity instead of the elasticity. Compared with conventional alloys, HEAs may perform superior elastic properties because of the uneven local lattice strain. It is difficult for experimentalists to clarify the effect of severe lattice distortion on their mechanical properties. In order to investigate the elastic anisotropy, we conducted molecular dynamic simulations, composed of 1 ~ 5 atomic types containing Ni, Ni60W20, Ni60W40, FeCrNi, and CoCrFeMnNi under the Lennard-Jones potential, embedded-atom method (EAM) potential, and modified EAM potential. We analyzed Young's modulus E (h k l) and Poisson's ratio ν (h k l,θ) along [100], [110], and [111] loading direction for FCC crystals, and explored the performance of the elastic properties for each element type in HEAs. Our results suggest that electron density inconsistency among atomic elements dominates the elastic anisotropy of HEAs rather than the atomic radius difference.
Investigation of Laser Shock Peening Effect on Mechanical Behavior in CrMnFeCoNi High Entropy Alloy
Yanghoo Kim, Hyo Jae Jeong, Jae Hyang Lee and Jiyong Park; Korea Institute of Industrial Technology, Korea (the Republic of)

Laser shock peening process is a well-developed surface enhancement method which enhance fatigue life and damage tolerance of metallic materials by introducing a beneficial residual compressive stress. In this study, the laser shock peening effect on microstructure and mechanical behavior in face centered cubic CrMnFeCoNi high entropy alloy, known as Cantor alloy, was investigated. Three specimens with different thermomechanical condition, or recrystallized, cold rolled and laser shock peened after recrystallization, were subjected to hardness and sliding wear test to quantify the laser peening effect. Clear improvement of hardness and wear resistance was confirmed with comparable level to the rolled condition as well as residual stress reached several hundred MPa near the surface.

SESSION MS04.04: Kinetics and Properties of High Entropy Materials
Session Chairs: Shu-Wei Chang and Arun Devaraj
Tuesday Morning, December 3, 2019
Hynes, Level 1, Room 110

8:45 AM *MS04.04.01
Efficient Mass Transport Calculations Using a Variational Principle Dallas R. Trinkle; University of Illinois at Urbana-Champaign, United States

While first-principles methods can compute activated state energies using the nudged-elastic band method, upscaling to mesoscale mobilities requires the solution of the master equation. The general solution for mass transport coefficients involves the inversion of rate matrix: the Green function. However, while the rate matrix is typically sparse, its inverse is not; moreover, numerical algorithms for the Green function are currently only available for cases of dilute defect concentration. By recasting the calculation of transport coefficients as a variational problem, we can compute transport coefficients from thermal average quantities instead of trajectory-based calculations. The variational principle also ensures that our diffusivity calculations are upper bounds of the true diffusivities. Replacing kinetic Monte Carlo calculations with Monte Carlo averages, or approximations for thermal averages, also increases the efficiency of mass transport calculations. We showcase this approach for random multicomponent systems.

9:15 AM MS04.04.02
Computational Modelling of Interdiffusion in CoCrFeMnNi High Entropy Alloys Mohammad Afikuzzaman, Irina Belova and Graeme Murch; Newcastle University, Australia

High-entropy alloy (HEAs) are a class of multicomponent alloy made with equal or near equal quantities of five or more principal elements. In this study, the problem of interdiffusion in HEAs is addressed. Detailed studying of the diffusion composition profiles in several interdiffusion couples in CoCrFeMnNi is performed. A constant as well as a composition dependent interdiffusion matrix was used for investigating the diffusion behaviour in CoCrFeMnNi HEAs. These composition dependent interdiffusion matrices are calculated according to the Darken and the Manning formalisms. MATLAB programing language is used as the main tool for generating composition profiles using an explicit finite difference method (EFDM). The simulated composition profiles are found to be in a very good agreement with the available experimental results [1, 2]. The ultimate purpose of this modelling is to systematically investigate interdiffusion in CoCrFeMnNi alloys in diffusion couples with substantial changes in composition.

Keywords: Interdiffusion, High entropy alloy (HEAs), Manning approach, Darken approach

High-entropy alloys, or complex concentrated alloys, are currently of significant attention in materials science owing to their exceptional mechanical properties that include the considerable cryogenic ductility of FCC-type alloys and the superior elevated-temperature strength of BCC-type alloys. It has been proposed that, in single-phase high-entropy alloys, the intrinsic atomic-level complexity causes a severe lattice distortion and an atomic-level pressure variation, which further affects the dynamic behavior of crystalline defects. However, the atomic-level formation mechanism of crystalline defects and the interaction of these defects with the intrinsic distorted and heterogeneous environment in high-entropy alloys remain unclear. In our previous in-situ microscopic experiments of micro- and nano-pillar compression in several crystalline systems of high-entropy alloys, the gum-like uniform barrel-deformation accompanied with the abundant nucleation sites of plastic regions was clearly observed. With the aid of atomistic simulations, the soft spots identified by the spatial distributions of low-frequency vibration modes have been further found to serve as the precursors of atomic-level rearrangement in solid-solution alloys. In high-entropy alloys, the successive defect growth exhibits a chain-like manner which relies on the coupling of local shear transformations and vortex-like atomic motion. This formation and growth mechanism resembles the reported nucleation mechanism of shear transformation zone in metallic glasses, which is different from the dislocation slip-induced planer fault growth in dilute solution alloys. In addition, the extremely short correlation length of mechanical heterogeneity in high-entropy alloys suppresses the synchronized motions of dislocation line, which impedes the long-range dislocation slip and contributes toward a strong strain hardenability. The critical defect formation mechanism at the atomic level provides the theoretical description of various-signature mechanical properties of high-entropy alloys.

High entropy alloy (HEA, also known as compositionally complex alloy) refers to simple-phase solid solution alloy that contains multiple principal components in equimolar or near-equimolar ratios. To computationally address the complexities of this type of high-order alloy systems, we have performed atomistic simulations to predicte the solid-solution stability as well as the short-range ordering in CoCrFeNi and AlCoCrFeNi bulk alloys and CoNiRuRh nanoparticles. In our simulations, the interatomic interactions were described using a set of modified embedded atom method (MEAM) interatomic potentials for these alloy systems. First, we used atomistic simulation methods to examine solid-solution phase formation rules for CoCrFeNi high entropy alloy. Using the Monte Carlo (MC) simulations based on the developed MEAM potentials, we sampled the thermodynamically equilibrium structures of the CoCrFeNi alloy and further predicted that the CoCrFeNi alloy could form a solid solution phase with high configurational entropy of 1.329R at 1373 K. Then, we examined the stability of this solid solution phase of the CoCrFeNi alloy against the well-recognized solid-solution phase formation rules by varying the MEAM potentials and thus tuning the atom size and mixing enthalpy in the alloy. Our simulation results revealed that it required atom size difference effect and mixing enthalpy effect -10 kJ/mol < ΔH < 0 kJ/mol for the modeled CoCrFeNi alloy to remain a single solid solution phase. Furthermore, we studied the stability of solid-solution phase of AlxCoCrFeNi HEAs using the developed MEAM potentials and the atomistic MC simulation method. In our MC simulations, different constituent elements were allowed to exchange their positions and thus the modelled HEAs were relaxed to their thermodynamic equilibrium states after several millions MC steps at 1300 K. The mixing Gibbs free energy of the HEAs was calculated using adiabatic switching thermodynamic integration method. We predicted that the AlxCoCrFeNi HEAs would form a single fcc solid-solution phase when x<0.21, a single bcc solid solution phase when x>1.08, whereas a mixture of fcc and bcc phases when 0.21<x<1.08. Our theoretical results are quite consistent with experimental observation. Moreover, we investigated the formation of solid solution phase in Co_{0.12}Ni_{0.14}Ru_{0.43}Rh_{0.30} nanoparticles with size ranging from 2 to 5 nm through a combined molecular dynamics (MD) and MC approach. Our simulation results indicated that the local severe lattice distortion could block the diffusion of atoms and hence lead to a stable solid solution phase during a carbothermal shock synthesis procedure. Consequently, we have demonstrated that atomistic simulation techniques as useful methods for understanding the composition-structure-property relation of novel high entropy alloys.
Correlated Multimodal In Situ Analysis of Oxidation of High Temperature Alloys

Arun Devaraj1, Bharat Gwalani1, Elizabeth J. Kautz1, Sten Lambeets2, Libor Kovarik2, Daniel Perea2, Daniel Schreiber1, Swapup Chena2, Yi-Sheng Liu3 and Sutharampillai Thevuthasan2; 1Pacific Northwest National Laboratory, United States; 2Env Molecular Science, United States; 3Lawrence Berkeley National Laboratory, United States

Metallic alloy surface oxidation process at high temperature remains inadequately understood. The early stages of this complex process involve structural and chemical transformations that require to be observed and described at the atomic scale. When it comes to high temperature alloys with complex composition such as high entropy alloys, the possibility of multiple oxide product phases further complicates the oxidation mechanisms. Hence, we employed in situ transmission electron microscopy, an environmental reaction chamber attached to an atom probe tomography and synchrotron based x-ray absorption near edge spectroscopy, in order to reveal the structural, compositional and chemical state transformations occurring during early stages of metallic alloy oxidation at high temperatures. This multimodal approach was used to analyze oxidation of selected model and commercial Zirconium alloys, Titanium alloys and high entropy alloys at high temperatures. We demonstrate the atomic scale changes to the composition of oxide layers, formation of polycrystalline structure of oxides, and presence of metastable phases in the early stages of oxidation. The time dependent variation of structure, composition and chemical state of the oxide layers can be correlated to corresponding alloys mechanical properties and thus can guide the development of accurate predictive mechanistic models.

Calculating Thermal Conductivity from the Electron and Phonon Subsystems in High Entropy Alloys

Michael J. Abere, Christopher B. Saltonstall, Nicolas Argibay and Andrew B. Kustas; Sandia National Laboratories, United States

The thermal conductivity of high entropy alloys does not follow typical trends in metals. Not only are they an order of magnitude less conductive than what rule of mixtures would predict, but their conductivities are also known to increase with temperature between 300-550K. Here, transport is calculated in an analytical model as the sum of contributions from the electron and phonon subsystems. For the lattice subsystem, conductivity is treated with the Leibfried and Schlömann formulation with perturbations for both electron-phonon interactions and point defect scattering. The electron subsystem is dominated by alloy scattering, which is calculated based on a virtual crystal approximation derived from each constituent’s Lennard-Jones potential. The model predictions are then compared to time domain thermoreflectance measurements in the Al0.5CoCrFeNiCu as well as previously published measurements of the Al0.37CoCrFeNi alloy.

This work was supported by the Sandia National Laboratory Directed Research and Development (LDRD) program. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under Contract No. DE-NA0003525. This work describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the U.S. Government.

Utilizing AI Algorithms for High Speed, High Temperature, Correlative Characterization of AlxFeCrNiMn (x=0, 0.3, 1) Alloys

Eric Hintsala1, Youxing Chen2, Bernard Becker1, Nan Li3, Nathan Mara4 and Douglas D. Stauffer1; 1Bruker Nano Surfaces, United States; 2University of North Carolina at Charlotte, United States; 3Los Alamos National Laboratory, United States; 4University of Minnesota Twin Cities, United States

Development of new structural materials for service under extreme conditions is slowed by the lack of high-throughput test protocols for investigating properties under relevant operating conditions. Here we demonstrate a method that integrates high-throughput nanoindentation mapping with precise temperature control under vacuum atmosphere. AlxFeCrNiMn (x=0, 0.3, 1) high entropy alloys (HEAs), which may possess the strength and stability...
required for high-temperature structural materials for nuclear applications, are investigated here. These alloys have distinct microstructural morphologies, and nanoindentation mapping reveals the mechanical behavior of the distinct phases as a function of temperature up to 400°C. The complexity of the microstructure, investigated under correlative conditions, allows the determination of specific phase properties. The FeCrNiMn consists of a FCC matrix with BCC precipitates exhibits significant softening in both phases at elevated temperature. In contrast, both the FCC phase and FCC-BCC phases present in Al_{0.3}FeCrNiMn show approximately 90% retention of the room temperature hardness at 400°C, and AlFeCrNiMn with BCC and B2 structures show a similar, 85%, retention of hardness.

Artificial intelligence algorithms, e.g. clustering, allow the for the relatively fast binning of structure and property into statistical forms without losing the location information required for the reproduction of maps. Experimental techniques and a brief discussion of what is required to validate the AI clustering is presented.

11:15 AM MS04.04.09
Mechanical Performance of Irradiated Refractory High Entropy Alloys at Elevated Temperatures Bo-Shiuan Li, Anna Kareer, Angus J. Wilkinson and David Armstrong; University of Oxford, United Kingdom

Refractory high-entropy alloys (RHEAs) are an alternative type of HEAs that possess BCC matrix and superior high-temperature strength compared to their FCC predecessors, making them ideal structural materials for extreme nuclear environment. The mechanical properties of a single-phase quaternary TiVCrTa alloy were investigated after ion-irradiation, using advanced micromechanical tests and high-resolution electron microscopy (HR-EBSD, TEM). Nanoindentation results of the as-cast sample irradiated to 3.5 dpa showed no irradiation hardening and TEM confirms negligible defect accumulation. Deformation mapping around the nanoindents via HR-EBSD were also carried out to provide mechanistic understanding of the irradiation resistance in term of change in strain localisation and GND density. Future experiments will apply high-temperature nanoindentation on the irradiated samples so the mechanical performance under relevant reactor operating conditions can be measured.

11:30 AM MS04.04.10
A Molecular Dynamics Approach after Burnup and Its Integrity in the Interim of Irradiation Willie Ahli¹, Zhao Hongtao² and Li Zhongyu³; ¹Harbin Engineering University (HEU), China; ²Harbin Engineering Uni, China

High Burnups can cause major structural changes in the edge of the fuel rod and a general degradation of the thermal conductivity. In irradiated oxide fuels of UO₂ and PuO₂, several fission products (FP) are produced and they take various chemical states depending on the conditions of the fuel. This work, based on the energy of the specified metallic fuels predominantly has some passive safety features during core off-normal events. During the structural and mechanical property changes, dissolved fission gases as well as thermal expansion cause the fuel to expand and swell to the cladding, where the fuel at the interface will transform to the molten phase, reducing reactivity in the reactor and helping to prevent the core from going supercritical. Uranium in particular has a low melting point; however, by alloying to metals that are also in BCC phase at high temperatures, the melting point can be increased. Lattice parameter, Burnups and the thermal conductivity were calculated for specified UO₂ and PuO₂. This calculations relate the degradation of thermal conductivity with a number of pores and increasing temperature. Finally, the migration energy barrier and the recovery energies of the obstruction type defects were calculated by molecular dynamics and molecular statics simulation.

SESSION MS04.05: Novel Alloys and Compounds Other than HEAs
Session Chairs: Qi An and Yong-Jie Hu
Tuesday Afternoon, December 3, 2019
Hynes, Level 1, Room 110

1:30 PM *MS04.05.01
Crack Propagation in Metallic Glass TEM Samples Xilei Bian, Gang Wang, Haijian Chu and Tong-Yi Zhang; Shanghai University, China
The present presentation reports experimental observations of crack propagation in both tough and brittle metallic glasses (MGs) via in situ high-resolution transmission electron microscopy (HRTEM) tensile tests, illustrating the cracking behavior of MGs is governed by an intrinsic cavitation mechanism ahead of the crack tip. Based on the experimental results, we proposed a model of surface diffusion induced cavitation in the strained region ahead of a crack tip and conducted numerical simulations to verify the proposed model. The simulation results catch the main and essential features of the cavitation mediated cracking behavior observed in situ HRTEM tensile tests. In addition, we also observed in situ HRTEM tensile tests that introducing nanocrystals in the front of the crack can effectively blunt the crack tips and retard the crack propagation. The in situ HRTEM observations and numerical simulations validate the proposed model of surface diffusion induced cavitation and cracking in MGs, thereby offering new insights into the deformation and cracking mechanism and paving a novel way for the design of MGs with high toughness.

2:00 PM MS04.05.02
3D Characterization of Nano-Scale Precipitates in Shape-Memory Alloys Dexin Zhao, Tejas Umale, Jobin Joy, Dimitris Lagoudas, Ibrahim Karaman and Kelvin Y. Xie; Texas A&M University, United States

Shape-memory alloys (SMAs) have wide aerospace and biomedical applications due to the capability to recover from large deformations via solid-to-solid transformations from martensitic to austenitic phases. Recently, Ni-Ti-Hf SMAs have attracted tremendous research interests because their phase transformation temperature is higher than that of traditional Ni-Ti counterparts. This expands their applications in high-temperature environments. Our previous research has indicated that the presence of nano-scale precipitates could further improve the cyclic transformation response in the Ni-Ti-Hf system. However, there lacks a detailed understanding of these precipitates, including crystal structure, chemistry, size, distribution and volume fraction. Moreover, the precipitate evolution as a function of heat treatment temperature and time is also not well understood. In this work, we combine STEM with TEM tomography to construct 3D models for these nano-scale precipitates to characterize and understand why nano-scale precipitates in SMAs could lead to even more consistent actuation responses in Ni-Ti-Hf SMAs.

2:15 PM *MS04.05.03
Role of Advanced Characterization in Novel Alloys Design Yufeng Zheng¹, Stoichko Antonov², Qiang Feng² and Hamish L. Fraser³; ¹University of Nevada, United States; ²University of Science and Technology Beijing, China; ³The Ohio State University, United States

In order to reduce the fossil fuel consumption and greenhouse gas emissions, there is a continued demand for the new generation high temperature materials and lightweight materials for better performance. Integrated Computational Materials Engineering (ICME) has the capability to replace the time-consuming and labor-intensive traditional trial-and-error approach to expedite the design of novel materials and predict the microstructure and performance of materials produced by advanced manufacturing. However, the physics-based or data-based models in ICME highly rely on the accurate understanding of microstructure in materials during processing and service. For example, in order to produce shaped products that possess consistent and high-quality property performance using additive manufacturing, it requires the provision of solutions to problems, such as coarse columnar microstructures, porosity and residual stresses, which requires rapid and reliable microstructure determination using multi-scale ex-situ and in-situ characterization techniques. This presentation is mainly focused on the use of analytical microscopy techniques to explore the fundamental mechanisms in the development of novel metallic materials. Two studies about designing high temperature used Ni based superalloys and high strength lightweight titanium alloys for aerospace application via microstructure engineering utilizing advanced characterization will be introduced. The effect of Re on the long-term creep behavior and microstructural evolution in Ni-based single crystal superalloys have been systemically studied via multiscale electron microscopy, atom probe tomography and synchrotron XRD. The results show that Re is an effective creep strengthening element for Ni-based single crystal superalloys and long-term creep life of the alloys can be significantly improved by the addition of small amount of Re. Ultra-high strength metastable beta titanium alloys, via precipitation strengthening through the omega phase assisted alpha precipitation mechanism, have been realized by coupling the atomic resolution aberration-corrected S/TEM with phase field modeling. The pre-formed nano-scaled omega phase particles can alter the local structure and composition in the parent phase matrix and therefore provide additional driving force and nucleation sites for the formation of super-refined scale alpha phase precipitates.

2:45 PM MS04.05.04
Solute-Dislocation Interactions in bcc Refractory Alloys and Resulting Effects on Mechanical Properties
Yong-Jie Hu1,2, Michael Fellinger3, Brady Butler4, Laszlo Kecskes5, Dallas R. Trinkle3, Liang Qi2 and Zi-Kui Liu1;
1The Pennsylvania State University, United States; 2University of Michigan, United States; 3University of Illinois at Urbana-Champaign, United States; 4U.S. Army Research Office—Materials Science Division, United States; 5Johns Hopkins University, United States

The solute-induced softening and hardening effects in bcc W for twenty-one substitutional alloying elements (Al, Co, Cr, Fe, Hf, Ir, Mn, Mo, Nb, Ni, Os, Pd, Pt, Re, Rh, Ru, Ta, Tc, Ti, V and Zr) are examined to search for a similar softening effect as that observed with Re. The changes in energy barriers of dislocation motion caused by solute-dislocation interactions are directly computed via a first-principles approach with flexible boundary conditions. The effect of solutes on the critical resolved shear stress of the $\frac{1}{2} <111>$ screw dislocation in bcc W at room temperature is quantitatively predicted, as a function of alloy concentration, via a mesoscopic solid-solution model using the first-principles results as input. Al and Mn are proposed to be promising substitutes for Re as these two elements introduce similar softening effects as Re in bcc W. In addition, the trends of the solute-dislocation interactions, and their correlations to the dislocation core structure geometries are discussed.

3:00 PM BREAK

3:30 PM *MS04.05.05
Thermal Processes and Mechanisms in Refractory Nanomultilayers Andrea M. Hodge; University of Southern California, United States

The potential of nanomultilayers (NMMs) as a route to synthesize nanostructures is explored by examining the microstructural evolution of refractory Mo-Au, Hf-Ti and Ta-Hf NMMs through differential scanning calorimetry (DSC) and heat-treatments at different temperatures. Transitions occurring between room temperature and 1000°C are identified using DSC scans. The microstructural evolution of these materials and the nanostructures that develop after annealing are not well understood but can provide insight of active thermal processes and stabilization mechanisms. A wide range of characterization techniques including TEM and APT were utilized to examine compositional changes and gain insight into thermally activated events such as layer roughening, solute grain boundary segregation and phase separation. Understanding the evolution of these NMMs will allow tailoring nanomaterials with enhanced thermal stability.

4:00 PM OPEN SLOT

4:15 PM MS04.05.07
Enhancing High Temperature Performance of Titanium Matrix Composites by Constructing Network Microstructure Lujun Huang; Harbin Institute of Technology, China

The improvement of mechanical properties must be achieved by designing and constructing more suitable microstructure, such as hierarchical microstructure and nano microstructure. In order to significantly enhance the creep resistance of titanium alloys, one two-level hierarchical microstructure with micro-TiB whiskers (TiBw) and nano Ti5Si3 reinforcements were constructed to form the modified composites by powder metallurgy combining with in-situ synthesis and precipitation. The micro TiBw reinforcement were in-situ synthesized around titanium matrix particles, which formed the first scale network microstructure. The nano Ti5Si3 particle were precipitated and distributed in the beta phase around alpha phase which formed the second network microstructure. The results showed that the high temperature strength has been significantly enhanced. The tensile strength at 550oC for Ti6Al4V matrix composites is increased to 1050MPa. Moreover, the creep rate of the modified Ti6Al4V matrix composites was remarkably reduced by an order of magnitude compared with the conventional Ti6Al4V alloys at 550 oC, 600 oC, 650 oC under the stresses between 100 MPa and 350 MPa. Moreover, the rupture time of the composites increased by 20 times, compared with Ti6Al4V alloys at 550 oC/300 MPa. The superior creep resistance can be attributed to the two-level hierarchical microstructures and the two-scale reinforcements. The micro-TiBw reinforcement in the first network boundary contributed to creep resistance primarily by blocking grain boundary sliding, while the nano-Ti5Si3 particles in the second network boundary mainly by hindering phase boundary sliding. In addition, the nano-Ti5Si3 particles were dissolved to smaller-sized Ti5Si3 particles during creep deformation due to high temperature and external stress, which can further continually enhance the creep resistance. Finally, the creep rate during steady-state stage was unprecedentedly decreased, not stable or increased, which
manifested superior creep resistance of the composites. The calculated results indicated that the dislocation climb is the dominant mechanism for the composites tested at 550 oC/(250-350) MPa and 650 oC/(100-250) MPa.

4:30 PM MS04.05.08
First Principles High-Throughput Screening to Enhance the Ductility of Lightweight Magnesium Alloys Qi An, Yidi Shen, Hongwei Wang and Bin Li; University of Nevada, Reno, United States

Magnesium (Mg) and its alloys are the lightest structural metals, but the low ductility at low temperature prevents them from massive manufacture process and extended engineering applications. Therefore, it is urgent to improve the ductility of Mg. Here, to provide guidelines of accelerating this improvement, we proposed a hierarchical high-throughput screening (HHTS) approach for alloy design that is based on full general stacking fault (GSF) energy surface (γ-surface) derived from density functional theory. We simplify the HHTS approach by examining only the unstable stacking fault energy (γus) on γ-surface. We applied this approach to determine the promising dopant elements in Mg-X binary alloys which may activate the pyramidal dislocations by decreasing GSF energy and thus improve the ductility of Mg. From our HHTS approach we sifted out ten promising elements, including Hg, Tl, Sn, Sb, Bi, Te, As, Pb, In and Ca. Particularly, Mg-Te alloy has the lowest γus of 156 mJ/m² among all binary alloys, which is 25% lower than that of Mg (209 mJ/m²), suggesting that it is the most promising alloy to enhance the ductility of Mg.

4:45 PM MS04.05.09
Role of Five-Fold Symmetry in Undercooling of Aluminium Based Alloys Noel Jakse; Grenoble institute of Technology, France

Understanding evolutions of transport properties in undercooled liquids and their interplay with their structural features represents an important issue for solidification processes of metallic alloys, such as crystallization and formation of quasi-crystalline or amorphous phases [1–4]. In the present work, we focus on various classes of Aluminum alloys such as Al-Ni [5], Al-Cu [6], Al-Cr [7] and Al-Zn-Cr [8] that are important for many automotive and aeronautic applications due to their light weight, good forgeability, high thermal conductivity, and low corrosion. Using ab initio molecular dynamics, we simulate the undercooling process of these alloys during which we monitor the structural and atomic transport properties. We find that diffusion, viscosity and structural relaxation time undergo a crossover between an Arrhenius and non-Arrhenius behavior at a temperature T_X during the slowing down, which corresponds to an onset of dynamic heterogeneities (DHs) that develop. The structural features display characteristics compatible with the occurrence of the icosahedral short-range order (ISRO) as well as the development of a medium range order (MRO) upon cooling. The interplay between the ISRO and MRO and the dynamic heterogeneities is examined. The differences and similarities between these alloys is also discussed.


SESSION MS04.06: Poster Session II: Novel Alloys and Compounds Other than HEAs
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

MS04.06.01
Investigation of Stacking Fault and Antiphase Boundary Segregation in Ni-Based Superalloys Using Density
**Functional Theory** Brian S. Good and Timothy M. Smith; NASA Glenn Research Center, United States

Ni-base superalloys have a long history of use in jet turbine engines, and efforts to improve their performance in that application are ongoing. It is known that the precipitation of the Ni$_3$Al gamma prime phase within the disordered FCC gamma phase strengthens the overall material. However, in the high-temperature environment found inside a turbine engine, creep can cause the gamma prime phase to transform to different, weaker phases along stacking faults, which leads to a deterioration of performance. In the gamma prime phase, one mode of creep deformation is the formation of stacking fault ribbons, which consist of intrinsic stacking faults further shearing into antiphase boundaries (APBs). It is also known that certain alloying additions exhibit segregation to gamma prime stacking faults. If elements that segregate to the intrinsic stacking fault but not to the APB could be identified, the inclusion of such elements could lead to improved creep strength in these alloys.

To investigate this possibility, a density functional investigation was performed on the segregation of W, Mo and Cr to both a superlattice intrinsic stacking fault (SISF) and an APB. It was found that W, Mo and Cr all exhibit segregation to the SISF. In contrast, for the APB, Cr was either energy-neutral or segregated, depending on the presence of additional nearby Cr or on the specific lattice site on which it was placed. However, Mo and W did not segregate to the APB. Due to the segregation of W and Mo to the SISF but not to the APB, the inclusion of these elements could provide a degree of protection against creep-related deterioration.

**MS04.06.02**

**On the Segregation of Re at Defects in the γ’ Phase of Ni-Based Single Crystal Superalloys** Xiaoxiang Wu$^1$, Surendra Kumar Makineni$^1$, Jaber Rezaei Mianroodi$^{1,2}$, Pratheek Shanthraj$^{1,3}$, Bob Svendsen$^{1,2}$, Christian Liebscher$^1$, Gerhard Dehm$^1$, Paraskevas Kontis$^1$, Dierk Raabe$^1$, Baptiste Gault$^{1,4}$ and Gunther Eggeler$^1$; 1Max-Planck-Institut für Eisenforschung GmbH, Germany; 2RWTH Aachen University, Germany; 3The University of Manchester, United Kingdom; 4Imperial College London, United Kingdom; 5Ruhr-Universität Bochum, Germany

Single crystal Ni-based superalloys are an essential material for application in gas turbines in aero engines and power plants due to their outstanding high temperature creep, fatigue and oxidation resistance. These properties originate from their typical γ/γ’ microstructure, and by manipulating different alloying elements, the γ/γ’ morphology, misfit and corresponding properties will change significantly. A turning point was the addition of 3 wt.% Re in the 2nd generation of single crystal Ni-based superalloys, which doubled its creep life. Despite the significance of this improvement, the reasons for the so-called ‘Re effect’ continue to be debated in the field of superalloys. It is of great scientific and economic interest to understand the role of Re in extending the lifetime of single crystal Ni-based superalloys, and for the development of new superalloys. Here, we show direct evidence of Re, as well as Cr and Co, segregating to crystalline defects (dislocations and stacking faults) formed during creep deformation inside γ’, using combined transmission electron microscopy and atom probe tomography. Phase field modelling is employed to support our interpretation of the effect of Re on dislocations and stacking faults. The new observations and understanding regarding the ‘Re effect’ will help design future Ni-based and Co-based superalloys.

**MS04.06.03**

**The Effect of Solutionizing and Ageing Temperature on the Microstructural Evolution and the Mechanical Properties of Allvac 718Plus** Geeta Kumari$^{1,2}$, Carl Boehlert$^1$, M Sundararaman$^2$ and S Sankaran$^2$; 1Michigan State University, United States; 2Indian Institute of Technology Madras, India

Alloy Allvac 718Plus is a relatively new superalloy developed to improve the properties of the widely-used superalloy Inconel 718 (IN 718). The strength of IN 718 significantly decreases at temperatures of 650°C and above due to the transformation of the metastable, γ” (tetragonal, D022 structure) phase into the δ phase (orthorhombic, D0a structure). Allvac 718Plus, which was designed to address this issue, exhibits service temperature up to 704°C (55°C more than that for IN 718 and close to Waspaloy) and its formability is similar to IN 718 and better than that for Waspaloy. The major changes in chemistry for Allvac 718Plus include a three times increase in aluminum (Al) content and the substitution of 18wt.% iron (Fe) with 9wt.% cobalt (Co) and 10wt.% Fe. The change in the (Al+Ti)/Nb ratio favors the formation of the γ’ as the major strengthening phase in Allvac 718Plus. Another significant phase in Allvac 718Plus is the Nb-rich phase δ, which preferentially forms at grain boundaries. The δ phase plays a major role in controlling the grain growth during processing and fabrication. The volume fraction of the γ’ and the δ phase can be controlled by solutionizing followed by aging. In the present work, the effect of
solutionizing and aging on the resulting microstructure and the corresponding mechanical strength of Allvac718Plus was examined. Samples were solutionized at two different temperatures, 1000°C and 954°C, and then aged. To study the effect of aging temperature on solutionized samples, three different aging treatments were performed as follows: 1) one-step aging at 788°C for 16 h followed by faster cooling, 2) one-step aging at 704°C for 16 h followed by faster cooling, 3) Two-step aging at 788°C for 8 h followed by cooling to 704°C for 8 h then air cooling. Metallographic samples of the as-received and heat-treated samples were prepared to identify different phases using optical microscopy and scanning electron microscopy. Electron backscatter diffraction and energy dispersive spectroscopy was performed to investigate the composition of the various phases. Room temperature and elevated-temperature tensile and hardness testing will be performed on the aged samples to investigate the effect of the microstructure on the strength. The data obtained will be compared with the existing data and will help in understanding the dependency of time and temperature on the microstructural changes and mechanical properties.

MS04.06.04
Estimation of High-Temperature Properties of Structure Alloy by Molecular Dynamics Simulation Kenso Ueno and Yasushi Shibuta; The University of Tokyo, Japan

We proposed new methodology for estimation of high-temperature properties of structure alloy by molecular dynamics simulation. Using this method, solid-liquid interfacial properties of Fe-Cr alloy are investigated with an EAM potential (Bonny et al., Philo. Mag. 91 (2011) 1724). After estimating melting points of pure Fe and Cr of the EAM potential, solidus and liquidus compositions with respect to temperature were estimated as follows. The solid-liquid coexisting system with the same concentration (X_S = X_L) as the initial state was relaxed under the constant pressure and temperature (NPT) condition. Calculations were carried out until the propagation of the solid-liquid interface due to solidification and solute partition did not proceed. It is considered that converged concentrations in solid and liquid phases correspond to the equilibrium concentration at the set temperature. Therefore, the same calculations were performed for various temperatures. By connecting solidus and liquidus concentrations with respect to temperature, the phase diagram for the Fe-Cr alloy for the EAM potential was successfully derived.

Next, a solid-liquid coexisting system with equilibrium concentrations in the obtained phase diagram are relaxed at equilibrium temperatures to investigate the temperature dependence of the solid-liquid interfacial energy. The capillary fluctuation method (Hoyt et al., Phys. Rev. Lett. 86 (2001) 5530) is employed to estimate the solid-liquid interfacial energy including its anisotropy. The solid-liquid interfacial energy increases with increasing equilibrium temperature. On the other hand, regarding the anisotropy effect, the interfacial energy of solid-liquid interface with (100) orientation is larger than those of (110) and (111) orientations at all temperatures. In summary, the methodology proposed in this study can be easily applied to other novel high-temperature structural alloys including refractory alloys and Co-based superalloys.

MS04.06.05
Dislocation Mobility in BCC Multicomponent Solid Solution Alloys Han-Wen Yeh1, Chao-Chun Yen2,1 and Yu-Chieh Lo1; 1National Chiao Tung University, Taiwan; 2National Tsing Hua University, Taiwan

Multicomponent solid solution alloys (e.g., high entropy alloys) are at the cutting edge of metals research due to their outstanding mechanical properties such as the refractory characteristic in BCC HfNbTaTiZr alloys. At high temperature, the major deformation mechanism of BCC is dislocation creep, and it is directly related to the dislocation mobility. However, until now, studies have been most devoted to kink-pair nucleation and kink migration mechanism in multicomponent BCC alloys, and seldom discussed the dislocation mobility in them. Therefore, we conducted large scale molecular dynamics to study dislocation mobility in multicomponent BCC alloys including AlCoNiFe and AlCoNiFeTi by applying embedded-atom method (EAM) potential. To look into the dislocation mobility, we measured the dislocation velocities of multicomponent BCC alloys under different stresses, components, and temperatures. By this work, we could figure out the influence to the dislocation mobility and further affect the creep.
8:45 AM *MS04.07.01
Modeling and Simulation of Defect and Defect Behavior in High Entropy Alloys Shigenobu Ogata¹², Junping Du¹, Peijun Yu¹, Shuhei Shinzato¹, Tomohito Tsuru¹, Tomotsugu Shimokawa³, Koretaka Yuge², Yoshiteru Aoyagi² and Momoji Kubo⁵; ¹Osaka University, Japan; ²Kyoto University, Japan; ³City University of Hong Kong, Hong Kong; ⁴Japan Atomic Energy Agency, Japan; ⁵Kanazawa University, Japan; ⁶Tohoku University, Japan

High-entropy alloys (HEAs), are multi-component random solid solution alloys with nearly an equiatomic composition, have been receiving tremendous attention due to the excellent cryogenic temperature ductility, superior mechanical strength and good wear resistance, exceptional damage tolerance. These excellent and distinguishing mechanical properties originates the curious properties of the lattice defects, such as vacancy, dislocation, twin, grain boundary, and so on, owing to the characteristic non-equilibrium quasi-random / short-range ordered atomic arrangement. To reveal the fundamentals of the mechanical properties, we studied the relation between the local atomic arrangement and the defect behavior and properties, such as vacancy diffusion, dislocation motion, deformation twinning and phase transformation, and grain boundary stability, using first-principles, molecular dynamics and Monte Carlo methods. We show that the local atomic arrangement, which is specified by the short-range order parameter and the local atomic strain, strongly correlated with the defect behavior in HEA.

9:15 AM MS04.07.02
Effect of Atom Propotions to Co-Cr-Mn-Fe-Ni High-Entropy Alloys Mechanical Behaviors—Molecular Dynamics Investigation Satoshi Takemori and Toshihiro Kameda; University of Tsukuba, Japan

High entropy alloys (HEAs) are solid solution materials composed of a large number of components (five and more) available in equiatomic or nearly equiatomic proportions. HEAs are considered to show “high entropy effect, severe lattice distortion effect, sluggish diffusion effect and cocktail effect”(B.S. Murty (2014), M.C. Gao(2016)). Since the proportion of each elements in HEAs changes those mechanical behavior, the most suitable assortment can be chosen for each objectives as a structural material by investigation.

Molecular dynamics(MD) simulation is the powerful tool to investigate those atomic effects and the influence of proportion because proportions of each atoms are easily decided for comparison of mechanical behaviors. The second nearest neighbour(2NN) modified embedded atom method(MEAM) potential is used to our MD simulation. Each parameters of 2NN-MEAM potentials of five elements Co, Cr, Fe, Mn and Ni pure and binary systems are taken from published literature.

In this study, influences of Cr proportion for mechanical behaviors at non-equiatomic Co-Cr-Fe-Mn-Ni high-entropy alloy were observed. Models are monocrystals and fcc structures. Six models with different Cr proportions were set to 5, 10, 15, 20, 25, and 30 percents as Co, Fe and Mn proportions were set to 20 percents. As a result, increase of Cr proportion rised monocrystal young module at each models. Moreover, Seven models with different Cr proportions were set to 5, 10, 15, 20, 25, 30 and 35 percents as Co, Ni and Mn proportions were set to 20 percents. Increase of Cr proportion rises young module at models less than Cr 25 percents. Increase of Cr proportion also rised ultimate tensile strength at models less than 25 Cr percents. The highest value of ultimate tensile strength is 20.6 GPa at the equiatomic model. At models more than 20 Cr percents, decrease of Cr proportion brought down each young moduli and each ultimate tensile strengths. In the future work, influences of other components for mechanical behaviors will be revealed as well as Cr. We are also planning to invstigate relationship between atomic proportions and dislocation activities.

9:30 AM MS04.07.04
Nanomechanical Behavior of Body-Centered Cubic VNbTaMoW Alloy Hicham Zaid, Jacob Stremfel, Koichi Tanaka, Angel Aleman, Jenn-Ming Yang and Suneel Kodambabka; University of California, Los Angeles, United States

We report on microstructural and mechanical characterization of a commercially-available V₀.2Nb₀.2Mo₀.2Ta₀.2W₀.2 bulk alloy. w-2θ X-ray diffraction spectra revealed multiple reflections corresponding to a single-phase, body-centered cubic polycrystal with a lattice constant of 0.319 ± 0.001 nm composed of nanoscale grains. Spatially-resolved energy dispersive X-ray spectra acquired from the sample indicated that the alloy is compositionally homogeneous (heterogeneous) elemental composition at millimeter (micrometer) length scales. Nanoindentation tests carried out using Berkovich diamond indenter yielded hardness and elastic modulus values of 9 ± 1.4 GPa and
207 ± 19 GPa, respectively. In situ scanning electron microscopy based uniaxial compression tests conducted at room-temperature on cylindrical pillars of sizes \( d \) between 0.3 µm and 1 µm revealed that all the pillars undergo plastic deformation. From the load-displacement data, we find that the yield strengths of the pillars increase with decreasing \( d \) from 3.3 GPa at \( d = 1 \) µm to 9.0 GPa at \( d = 0.3 \) µm. Work hardening exponents increase over two-fold with increasing \( d \) from ~0.3 at \( d = 0.3 \) µm to ~0.8 at \( d = 1 \) µm. We attribute the observed behavior to size-dependent variations in displacement burst frequency and slip events. We expect that our results provide new insights into the nanomechanical response of body-centered cubic alloys.

9:45 AM BREAK

10:15 AM *MS04.07.05
Theory for Yield Strength of BCC HEAs William A. Curtin and Francesco Maresca; 1Ecole Polytechnique Federale Lausanne, Switzerland, Switzerland; 2University of Groningen, Netherlands

BCC High Entropy Alloys (HEAs) consist of many elements distributed at random on the BCC lattice. The collective fluctuations in solute/dislocation interaction energies, even in dilute binary BCC alloys, lead to the spontaneous energy-lowering formation of a kinked/wavy structure for both screw and edge dislocations, respectively, over characteristic lengths \( \zeta_{\text{screw}} \) and \( \zeta_{\text{edge}} \). Dislocation motion starting from the kinked/wavy structure is determined by the energetics at scale \( \zeta \). New general theories for both screw and edge motion in BCC alloys starting from this basic phenomenon are presented. The screw theory is sketched briefly, and shown to accurately predict strength versus composition and temperature in Nb-Mo and Nb-W binary alloys. As for BCC elements, the necessary inputs are difficult to establish, especially in more complex alloys. Key comparisons to simulations help demonstrate major features of the theory. More importantly, the edge theory shows that edge strengthening can be sufficient to compete with screw strengthening. Moreover, edges can control strengthening, especially at high temperatures, in some BCC HEAs. The edge theory, for which all inputs can be computed easily, explains (i) the exceptional retention of strength measured in MoNbTaW and MoNbTaVW at temperatures up to 1900K, and (ii) why the V-containing alloy is stronger. The edge theory can be reduced to a simplified analytic form that enables efficient computationally-guided design of new alloy compositions predicted to have high retained strengths and strength-to-weight ratios. Several new compositions are proposed. The combination of both screw and edge theories enables assessment of strengthening versus composition and temperature across the entire domain of Cr-Mo-Nb-Ta-V-W-Hf-Ti-Zr BCC HEAs.

10:45 AM MS04.07.06
From First-Principles toward Atomistic Understanding of Mechanical Properties and Strength in High-Entropy Alloys Peter A. Schultz, Julien Tranchida, Michael Chandross and Aidan P. Thompson; Sandia National Laboratories, United States

Refractory high-entropy alloys (HEA) show great potential for high-temperature structural applications, particularly involving additive manufacturing. It is important to gain improved understanding of their mechanical properties. Valuable insights and predictions can be gleaned from atomistic simulations, but these are hampered by both the physical complexity of HEA (mandating numerous simulations with large models) and computational cost (driven by the need for accurate quantum-based density functional theory (DFT) to obtain reasonable accuracy). Using a simplified Al-Nb-Ti equi-composition metal alloy (bcc) as our examplar, we present a systematic approach to investigate mechanical strength, beginning with DFT to compute converged elastic properties in random composition alloys, and then using DFT data and machine-learning methods to generate SNAP (Spectral Neighbor Analysis Potentials) interatomic potentials for accurate finite-temperature molecular dynamics simulations of hardness and tensile strength of complex multi-component systems. We refine and assess DFT supercell-based approaches, using the SeqQuest code and PBE functional. The Al-Nb-Ti alloy proves to be physically different than its constituent species, and numerically more robust in calculations than elemental or crystalline (B2) alloys. For instance, the AlNbTi random bcc alloy is much stiffer in shear compared to crystalline sub-alloys. Computed properties of the equi-composition alloy are well converged with small (54-atom) random occupancy cells, are insensitive to the particular assignment of elements to sites in the cells, are robust to modest deviations from equi-composition, and (notably the shear moduli) converge much more rapidly against crucial aspects such as k-point sampling. This advantageous numerical behavior makes these modest supercell models ideal for generating the large training database needed for SNAP potential development. Each DFT model takes just a couple minutes to compute,
and collectively encompass an accurate converged description of shear behavior crucial to predictive atomistic simulations of strength. — Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

11:00 AM *MS04.07.07
Atomic-Scale Deformation Mechanisms in FCC High-Entropy Alloys Maryam Ghazisaeidi and Carlyn LaRosa; Ohio State University, United States

We present a phase transformation strengthening mechanism in CrCoNi, a ternary derivative of the CrMnFeCoNi high entropy alloy. CrCoNi alloy exhibits a remarkable combination of strength and plastic deformation, even superior to the CrMnFeCoNi high-entropy alloy. We connect the magnetic and mechanical properties of CrCoNi, via a magnetically tunable phase transformation. While both alloys crystallize as single-phase face-centered-cubic (fcc) solid solutions, we find a distinctly lower-energy phase in CrCoNi alloy with a hexagonal close-packed (hcp) structure. Comparing the magnetic configurations of CrCoNi with those of other equiatomic ternary derivatives of CrMnFeCoNi confirms that magnetically frustrated Mn eliminates the fcc- hcp energy difference. This highlights the unique combination of chemistry and magnetic properties in CrCoNi, leading to a fcc-hcp phase transformation that occurs only in this alloy, and is triggered by dislocation slip and interaction with internal boundaries. In addition, we discuss the importance of average stacking fault energies (SFE) on deformation mechanisms in alloys of various compositions. The average SFE will be compared against the change in local bonding environment and the implication on competing deformation mechanisms will be discussed.

11:30 AM MS04.07.08
Exploring Solid Solution Strengthening of High and Medium Entropy Alloys through Experiments and Modelling Mathilde Laurent-Brocq1, Guillaume Bracq1, Céline Varvenne2, Loïc Perrière1, Jean-Marc Joubert1 and Ivan Guillot1; 1Université Paris Est, ICMPE (UMR 7182), CNRS, UPEC, France; 2CINaM, UMR 7325, Aix-Marseille Univ., CNRS, France

In 2004, the face-centered-cubic (fcc) single-phased CoCrFeMnNi was discovered and very promising mechanical properties were demonstrated. Since then, new interesting compositions of high and medium entropy alloys (HEA and MEA) were tested, some of them having superior mechanical properties compared to the CoCrFeMnNi alloy such as CoCrNi but also similar or even lower properties. Through thermodynamic calculations, it was shown that the fcc solid solution is stable for a large range of compositions in the quinary Co-Cr-Fe-Mn-Ni system [1]. These studies motivate a more systematic and comprehensive exploration of this multi-component system. This remains complex because the composition domain to explore is very large and because the mechanical properties are due to several strengthening mechanisms (e.g. : due to solute or Hall&Petch effect), which are difficult to separate.

In this context, the objective of this study is both to explore the mechanical properties due to solid solution strengthening (SSS) within the fcc domain of Co-Cr-Fe-Mn-Ni system, and to provide physical understanding of their evolution with alloy composition. To do so, based on thermodynamic simulations, 24 compositions were selected within the fcc domain to cover as much as possible the quinary system and subsequently processed with a simplified and reproducible metallurgical route. The lattice parameter was measured by X-ray diffraction and nanoindentation was selected as an efficient tool to measure only the SSS. Then, using a recently developed model for SSS in HEA [2], yield strength predictions were performed using as inputs only experimental data, including the lattice parameters measured here. The sensitivity of the predictions to the inputs will be exposed. Afterwards, experimental nanohardness and predicted yield strength will be compared. Then, the trends of evolution of SSS with composition will be connected to physical quantities such as elastic constants and lattice misfit. Finally, the different strategies for exploring solid solution strengthening of HEA will be discussed.

References:
1:30 PM *MS04.08.01
Mesoscopic Dislocation Dynamics and Its Structural Origin in High Entropy Alloys Jian-Min Zuo\(^1,2\), Hu Yang\(^1\), Yu-Tsun Shao\(^1\), Haw-Wen Hsiao\(^1\) and Qun Yang\(^2\); \(^1\)University of Illinois at Urbana-Champaign, United States; \(^2\)ShanghaiTech University, China

High entropy alloys (HEAs) are composed of five or more elements of a near-equal molar percentage in solid solutions. This contrasts with most metallic alloys that are designed based on the addition of a small amount of impurities, or alloying elements, to improve the properties of pure metals. A major character of HEAs is severe lattice distortion. The elements that make up the HEAs have different atomic sizes. These size differences inevitably lead to distortion of the lattice. Lattice distortions contribute to the free energy and impede dislocation movements and lead to pronounced solid solution strengthening.

Here we show that the impedance of dislocation motion by lattice distortion in the HEAs lead to mesoscopic dislocation interactions inside nanopillars of hundreds nm in diameter. The manifestation of mesoscopic dislocation dynamics enables their observation by transmission electron microscopy (TEM), and thus provide an unprecedented opportunity for studying dislocations and dislocation dynamics. To demonstrate the above effect, we investigated the nature of lattice distortions in both fcc and bcc HEAs, and we performed correlation studies of dislocation dynamics with mesoscopic mechanical properties of the HEA nanopillars.

An example of correlative structure-property study is the observation of dislocation avalanches inside nanopillars of a HEA, Al\(_{0.1}\)CoCrFeNi. Our results show that the avalanches start with dislocation accumulations and the formation of dislocation bands in the HEA. Dislocation pileups form in front of the dislocation bands, whose giveaway triggs the avalanche. The experimental technique employed for the study is based on electron imaging, while a nanoindenter is used to exact the applied force and pillar displacement. Using this approach, we have observed and determined the conditions for the multiplication of dislocations, dislocation pinning, as well as a broad range of dislocation motions from nm/s to mm/s.[1]

To determine the nature of lattice distortions, we used electron nanodiffraction. Information about crystal symmetry, lattice strain and atomic distortion are data-mined and mapped from many (~10\(^4\)) diffraction patterns. Application to the HEA reveals two embodiments of distortion, nm-sized mosaic blocks of paracrystals and strained nano-clusters. Their interaction gives rise to fractal strain field across nanoscopic to mesoscopic scales.[2][3]

References:
[3] The work is supported by DOE BES (Grant No. DEFG02-01ER45923). RLY is supported by SRC.

2:00 PM MS04.08.02
Real-Time Insight into the Cyclic Deformation Behavior of a High-Entropy Alloy Rui Feng\(^1\), Xie Xie\(^1\), Dunji Yu\(^2\), Yan Chen\(^2\), Ke An\(^2\), Tamas Ungar\(^3,4\) and Peter K. Liaw\(^1\); \(^1\)The University of Tennessee, Knoxville, United States; \(^2\)Oak Ridge National Laboratory, United States; \(^3\)E"otv"os University, Hungary; \(^4\)The University of Manchester, United Kingdom

Recently, high-entropy alloys (HEAs) attract worldwide attention due to their outstanding properties, showing a huge potential as engineering structural materials. In practical engineering applications, materials are usually subjected to cyclic loading during service, leading to fatigue fracture. However, few low-cycle fatigue (LCF) studies have been reported on HEAs so far. In this study, the LCF behavior of a multiphase HEA, are systematically studied
by integrated experiments and fatigue-life prediction models. Real-time in-situ neutron diffraction was employed to dynamically monitor the cyclic-deformation behavior of this HEA. Advanced microscopy techniques, such as transmission-electron microscopy (TEM), electron-backscattered diffraction (EBSD), and scanning-electron microscopy (SEM), were used to characterize the microstructural evolution during LCF. The in-situ real-time insight into the cyclic-deformation behavior of this HEA will pave the way to design innovative HEAs with outstanding fatigue resistance.

2:15 PM MS04.08.03
Fatigue Behavior of Equimolar HfNbTaTiZr Refractory High-Entropy Alloy at Room Temperature
Benjamin Guennec1, Vasuki Kentheswaran2, Loïc Perrière3, Akira Ueno4, Norio Horikawa1, Ivan Guillot5, Jean-Philippe Couzinié3 and Guy Dirras2; 1Toyama Prefectural University, Japan; 2Université Paris 13, France; 3Université Paris-Est, France; 4Ritsumeikan University, Japan

Concentrated complex alloys (CCAs), also usually referred as high-entropy alloys (HEAs) emerges as a deep paradigm shift in conventional metallurgy. Such solid solution phases are based on multi-element combination, instead of the regular one accepting a unique base element. Recent investigations have recently emphasized promising mechanical such as high yield stress, excellent resistance to wear, corrosion or creep. Among this new family of metallic materials, the refractory HEAs are focusing a lot of interest due to its good ability to retained high strength at elevated temperature, making potential unprecedented structural applications accessible. Nevertheless, the viability of HEAs as structural material requires to assess their mechanical properties under typical loading, such as fatigue one.

In the present work, the fatigue resistance of equimolar HfNbTaTiZr HEA is investigated in air and at room temperature. An outstanding fatigue strength is obtained under four-point bending fatigue, such as fatigue limit at $10^7$ cycles exceeding the uniaxial yield stress is found. Further investigations are also carried out in axial loading. An intergranular fatigue crack initiation and transgranular crystallographic crack propagation mechanisms occur. Analysis of the crack path in terms of crystallographic planes is also included, revealing that the crack spreads along both {011} and {112} slip planes. This particularity implies singularities in the crack propagation phenomenon in comparison with other metallic materials prone to similar crystallographic crack propagation.

2:30 PM BREAK

3:30 PM *MS04.08.04
In Situ Transmission Electron Microscopy on Twinning vs Dislocation Hardening Process in High Entropy Alloys Scott X. Mao1, Qian Yu2, Easo P. George3 and Robert O. Ritchie4; 1University of Pittsburgh, United States; 2Zhejiang University, China; 3Oak Ridge National Laboratory and the University of Tennessee, United States; 4University of California, Berkeley, United States

In situ transmission electron microscopy is carried out to investigate deformation mechanisms in the medium- and high entropy alloys (CrCoNi and CrMnFeCoNi), which exhibit very high hardening behavior after plastic yielding, leading to high strength and toughness. With the deformation of CrCoNi, we find that a three-dimensional (3D) hierarchical twin network forms from the activation of three twinning systems. This serves a dual function: conventional twin-boundary (TB) strengthening from the interaction of dislocations impinging on TBs, coupled with the 3D twin network which offers pathways for dislocation glide along, and cross-slip between, intersecting TB-matrix interfaces. The stable twin architecture is not disrupted by interfacial dislocation glide. While, for CrMnFeCoNi, we found attacking faults and full dislocation process are dominating the plastic deformation, which serves the hardening process for the alloy.

4:00 PM MS04.08.05
Plasticity in the Precious Metal Based High-Entropy Alloy AuCuNiPdPt Felix Thiel1,2, David Geissler1, Dirk Seifert1, Kornelius Nielsch1,2, Alexander Kauffmann1, Sascha Seils3, Martin Heilmaier3 and Jens Freudenberg1,4; 1Leibniz Institute for Solid State and Materials Research Dresden, Germany; 2Technische Universität Dresden, Germany; 3Karlsruhe Institute of Technology–Institute for Applied Materials, Germany; 4Technische Universität Bergakademie Freiberg, Germany

High-Entropy Alloys (HEA) show outstanding mechanical and physical properties, which would not have been expected regarding their simple crystal structure and the fact that they are single phased. Despite, there are already
many systems known exhibiting this behavior, the mechanisms, responsible for their exceptional properties, were not completely clarified yet. In this study we report on the novel precious metal based HEA: AuCuNiPdPt, which crystallizes in the Cu-type face-centered cubic structure (fcc) and is single phase without chemical ordering after homogenization and recrystallization treatments. This alloy can be cold worked up to a logarithmic deformation degree of $\phi=2.4$ applying rotary swaging. During compression tests it further deforms homogeneously up to an engineering strain of $\varepsilon=30\%$. The yield strength ranges from 820 MPa in the recrystallized state to 1170 MPa when prior strain hardened by cold work with a logarithmic deformation degree of $\phi>0.6$. The texture with almost random orientation distribution in the recrystallized state develops towards a mixture of $<111>/ <001>$ fiber components during cold work. This is a similar behavior like what has been seen for conventional fcc alloys, such as Cu-based alloys or austenitic steels. Further, AuCuNiPdPt shows localized dislocation slip in the majority of all grains at low strains, leading to pronounced stacking faults and slip bands. In grains with a (near-) $<111>$ orientation, extended stacking faults develop towards deformation twins even with higher order causing significant grain refinement and finally to the aforementioned work hardening behavior. The results from mechanical testing are verifiably correlated to the microstructure by means of APT, SEM (EBSD, EDX), TEM as well as XRD analysis.

4:15 PM MS04.08.06
Generalized Planar Fault Energies and Twinning in BCC High Entropy Alloys—A First-Principles Study
Abu Anand and Chandra V. Singh; University of Toronto, Canada

High entropy alloys (HEAs) is a relatively recently identified class of metallic alloys [1] which, in contrast to its conventional counterparts, have four or more elements mixed in near-equimolar composition to form a single-phase alloy [2]. High entropy alloys of refractory elements like Nb, Ni, Zr, Ta, Cr, Ti have reported exhibiting superior mechanical properties while having low-density [3]. In this work, we investigate the generalized fault energies of the BCC High Entropy Alloy system NbMoTaW using Density Functional Theory and compare the competing deformation mechanisms of slipping and twinning. A 23 layered (1-21) type plane structure was generated and systematically sheared along the [111] direction to get stacking faults and twins. Energy landscapes for twinning (Generalised Planar Fault Energy curve) and for slipping (Generalised Stacking Fault Energy curve) was calculated for NbMoTaW and compared with the component elements. These energy landscapes include parameters like unstable stacking fault energy for slipping and twinning, stable stacking fault energies, twin boundary migration energy, etc. It has been found that the stacking fault and planar fault energy values for the HEA are lower than that of all component elements. Twinnability, the ratio between Twin Boundary Migration energy and the difference in unstable stacking fault energies ($\gamma_{TBM}/\Delta\gamma_{us}$), of the HEA system was calculated from the simulated energy landscapes to investigate the competition between formation of full dislocation and emission of partial dislocations from subsequent atomic layers. This ratio was found to be 0.13 suggesting extensive deformation twinning can happen in the HEA system. Origin of low fault energies in NbMoTaW was investigated using Integrated Crystal Orbit Hamilton Population (ICOHP) which is the molecular bond order analog in solid state. For each pair of interactions in the HEA system, bond weighted Density of States was computed, integrated up to the Fermi level and then compared with the interactions (Nb-Nb, Mo-Mo, Ta-Ta, W-W) in pure component elements. Among the component element interactions, Nb-Nb has the highest ICOHP energy (weakest interaction) and lowest Stacking Fault Energy. W-W interaction is the strongest and it in-turn has the highest stacking fault energy. Except for W-Mo, W-Ta, interactions in NbMoTaW was found to be as weak as the Nb-Nb interactions which explain the reduced fault energies. As the interactions involving Tungsten are stronger than the other interactions, stacking fault and twin formation is less likely to happen near Tungsten rich regions of the alloy. Since deformation twinning is preferred as suggested by the twinnability parameter, the twins formed are likely to be Tungsten deficient due to these strong interactions.

References

4:30 PM DISCUSSION TIME

4:45 PM MS04.08.08
Microstructure and Mechanical Properties of AlCoCuFeNi0.8 High Entropy Alloys Zhongwei Chen;
Northwestern Polytechnical University, China

Compared with traditional alloys, high entropy alloys have excellent properties such as simple phase composition, higher strength, higher hardness, better wear resistance, better corrosion resistance, and unique electromagnetism as a novel alloy. In this work, Effects of Al and Cu content on the microstructure and properties in AlxCoCu1-xFeNi0.8 alloys were investigated by XRD, SEM, EDS, TEM, microhardness testing, tensile and compression testing. In AlxCoCu1-xFeNi0.8 (x=0.25, 0.3, 0.4, 0.5, 0.75) high-entropy alloys, the phase composition of alloys gradually changes from a single face-centered cubic (FCC) structure to a body centered cubic (BCC) structure and a little amount of FCC structure with the increase of Al content and the decrease of Cu content. Microstructure of the as-cast AlxCoCu1-xFeNi0.8 (x=0.25, 0.3, 0.4, 0.5) alloys presents the typical dendritic morphology, and microstructure of as-cast Al0.75CoCu0.25FeNi0.8 alloy presents the cellular crystal structure and the dendritic morphology. EDS results show that Cu element tends to be segregated in the inter-dendrites. Al0.75CoCu0.25FeNi0.8 alloy has the best comprehensive mechanical properties. The compressive yield strength and compressive strength are 1585MPa and 2049MPa, respectively. The fracture strain is 16.4%, and the hardness is 619.4HV. The heat treatment of AlxCoCu1-xFeNi0.8 (x=0.25, 0.3, 0.4, 0.5) alloys at 800°C for 0.5h, 6h, 12h were investigated, too. The inter-dendritic phase was obtained by eutectic reaction and grain boundary generated spinodal decomposition after heat treatment, forming a net structure. After 0.5h of heat treatment, the nano-sized precipitate phase is generated. With the increasing of heat treatment time, the nano-meter precipitate phase is dissolved, and the spinodal decomposition occurs in Al0.25CoCu0.75FeNi0.8 alloy. The highest yield strength is obtained at 0.5h heat treatment, and BCC phase is still the main phase of Al0.75CoCu0.25FeNi0.8 alloy. After heat treatment for 6h, the yield strength of Al0.75CoCu0.25FeNi0.8 alloy is as high as 1719MPa.

SESSION MS04.09: Design and Synthesis of High-Entropy Materials I
Session Chairs: Guan-Rong Huang and Liang Qi
Thursday Morning, December 5, 2019
Hynes, Level 1, Room 110

8:45 AM *MS04.09.01
Combinatorial Screening and Identification of Non-Equiatomic High Entropy Alloys for Improved Mechanical Properties John Balk; University of Kentucky, United States

The largely unexplored phase space of high entropy alloys (HEAs) offers potential for transformative enhancement of metallic material properties, but the breadth of this phase space also invites an approach for high-throughput evaluation of candidate alloys. One possibility is combinatorial thin film screening. Different combinations of CrMnFeCoNiCu and VNbMoTaW thin film samples were prepared by simultaneous magnetron sputtering of the elements (all 6, or subsets of 5) onto silicon wafer substrates, to identify potential FCC and BCC HEAs, respectively. Due to the arrangement of the sputtering targets, a wide chemical composition gradient was achieved in the films. The various areas of these films exhibited different phases, some of which were non-equiatomic single-phase regions. In order to screen the crystal structure and chemical composition of these potential HEAs, multiple characterization techniques were used: scanning electron microscopy, energy dispersive x-ray spectroscopy, X-ray diffraction and electron backscattered diffraction analysis. Based on the results of this combinatorial method, potential single-phase HEAs were identified and successfully produced in bulk form via arc-melting followed by thermomechanical processing. A second possibility for high-throughput evaluation of candidate alloys is slow cooling from the melt, which allows the alloy system to find its stable composition(s). Equiatomic CrMnFeCoNiCu was melted and then cooled at a slow, controlled rate, resulting in a multiphase microstructure consisting of Cr-rich needles inside a matrix that was itself an HEA. This matrix was used as the basis for fabricating new alloys with similar composition. These approaches yielded bulk alloys that exhibited improved mechanical properties in comparison to their equiatomic counterparts. This presentation will describe the identification of candidate HEAs with desired microstructure (stable single-phase alloy), their fabrication in bulk form, thermomechanical processing, and mechanical testing with a focus on tensile properties.

9:15 AM MS04.09.02
Quinary TWIP-TRIP High-Entropy Alloys—Design, Microstructure, Mechanical Behaviour and Magnetism
Xiaoxiang Wu1, Zhiming Li1,2, Yuji Ikeda1, Biswanath Dutta1, Fritz Körmann1,3, Jörg Neugebauer1 and Dierk Raabe1; 1Max-Planck-Institut für Eisenforschung, Germany; 2Central South University, China; 3Delft University of Technology, Netherlands

The effect of magnetic ordering on stacking fault energy (SFE) is of great interest and significance for designing high entropy alloys (HEA) with targeted mechanical properties. To reveal the influence of magnetic ordering on SFE and correspondingly its influence on the deformation mechanisms and mechanical properties, we designed a class of novel non-equiatomic quinary HEAs by a combination of ab initio simulation and experimental validation. A wide compositional space of Cr20MnxFe10Co20Ni2 (x + y + z = 60, at. %) was probed by density functional theory (DFT) calculations to search for potential alloys displaying the TWIP (twinning induced plasticity) /TRIP (transformation induced plasticity) effects. Several representative HEA compositions with low computed SFEs were metallurgically synthesized, processed, and probed for microstructure, deformation mechanism and mechanical property evaluation. It is found that the Mn content plays a key role in the stabilization of antiferromagnetic configurations which strongly contribute to the SFEs and eventually lead to the prevalent deformation behaviour observed. The impact of valence electron concentration (VEC) on TWIP/TRIP behaviour in Mn-containing HEAs is also probed and discussed.

9:30 AM MS04.09.04
High-Entropy Ceramic Thin Films Synthesized by Magnetron Sputtering Alexander Kirnbauer and Paul H. Mayrhofer; TU Wien, Thin Film Materials Science Division, Austria

The demand on materials for various applications is growing continuously, especially in the field of ceramic coatings used to protect various components or tools for hard-to-machine materials. The development of materials that can withstand high thermal and mechanical loads is therefore in focus of many materials science activities. In this respective, a relatively new class of materials, so-called high-entropy materials, gained enormous attraction. These alloys consist of multiple principal elements (more than 5), which lead to a high configurational entropy (> 1.5R, R being the universal gas constant) if single-phased. Typically, these high-entropy materials exhibit four core effects: 1) The high-entropy effect, which significantly reduces the overall Gibbs free-energy (especially with increasing temperature); 2) the severe lattice distortion, stemming from the different atom radii forming the solid solution; 3) the sluggish diffusion, due to the increased activation energy for diffusion as the individual atomic neighbourhood is different; and 4) the so-called cocktail effect, allowing to combine the individual properties. More recently as for metallic bulk materials, this concept was also introduced to ceramics and especially hard coatings and ceramic thin films.

Here we show the beneficial effect of the high-entropy concept applied to several thin film material systems including nitrides, borides, and oxides. The study focuses on their preparation with physical vapor deposition, their (non)sensitivity to deposition parameters, their thermal stability and mechanical properties. All coatings investigated exhibit outstanding thermal stability and significantly decelerated decomposition and softening processes, outperforming their commonly-used binary or ternary constituents.

9:45 AM BREAK

10:15 AM MS04.09.05
OPEN SLOT

10:45 AM MS04.09.06
Development of High-Entropy Aluminum Alloys (HEA-Al) Mohammad Asadikiya, Libo Wang, Diran Apelian and Yu Zhong; Worcester Polytechnic Institute, United States

High entropy alloys (HEAs) have been investigated in recent years due to their superior properties such as high strength, high hardness, and high temperature softening resistance. Meanwhile, the traditional aluminum alloys possess attractive properties including light weight, high corrosion resistance, and high thermal conductivity. In this project, the ICME approach (Integrated Computational Materials Engineering) is applied to design a new alloy by combining high-entropy alloys and traditional aluminum alloys. In other words, the “high entropy” concept will be utilized in this new alloy with the aluminum FCC matrix. Combining the “high entropy” concept borrowed from HEAs and aluminum FCC matrix shows a totally new composition region, which has higher entropy of mixing.
comparing with the traditional aluminum alloys. After manufacturing the samples based on the simulation guidance and experimental characterizations, it was found that the designed alloys show promising ultimate tensile strength and elongation.

11:00 AM *MS04.09.07
Equiatomic and Non-Equiatomic Refractory High Entropy Alloys That Exhibit Tensile Ductility Cem Tasan¹, Shaolou Wei¹, SangJun Kim², Eun Soo Park², Yongjie Zhang³ and Tadashi Furuhara³; ¹Massachusetts Institute of Technology, United States; ²Seoul National University, Korea (the Republic of); ³Tohoku University, Japan

After the recognition that conventional superalloys have reached their limits in high-temperature applications, there has been growing interest in developing alternative metallic-based structural alloys. Owing to their unique characteristics such as high melting point and excellent softening resistance, refractory metals have attracted significant focus in high-entropy alloys (HEAs) design. However, the investigation of novel refractory HEAs is largely retarded by the traditional trial-and-error alloy design framework, particularly within the non-equiaxial composition regime. To this end, here we present that by making use of the natural thermodynamic mixing characteristics, a series of non-equiaxial refractory HEAs can be developed. We show that these non-equiaxial HEAs exhibit desirable strength-ductility synergy and promising high-temperature performances.

11:30 AM MS04.09.08
The International Space Station U.S. National Laboratory—Opportunities for Improved High-Entropy Alloys via Microgravity Solidification Ryan D. Reeves, Etop Esen and Michael S. Roberts; International Space Station U.S. National Laboratory, United States

High-entropy alloys exhibit many desirable mechanical properties, including high fracture toughness, wear resistance, and crack resistance. However, the large atomic mass differential between constituent elements can lead to undesired compositional segregation and inhomogeneity. Gravitational effects (e.g., convection and sedimentation) during the melt cause density-driven phase segregation leading to inhomogeneity in the composition of the alloy. This causes reduced mechanical strength and toughness.

The International Space Station (ISS) U.S. National Laboratory offers a unique environment of persistent microgravity and, if desired, exposure to the harsh space environment in low Earth orbit. Microgravity mitigates gravitational phenomena such as buoyancy-driven convection, density-driven sedimentation and segregation, and heterogeneous nucleation at surface interfaces. Early studies of the solidification of high-entropy alloys in microgravity have demonstrated a higher degree of compositional homogeneity compared with terrestrial solidification. In addition, microgravity provides the opportunity to decouple the effects of Stokes sedimentation from Marangoni flow in order to better understand the heat and mass transfer dynamics in the melt and during solidification.

We will introduce the underlying phenomena directing the physics of the high-entropy alloy melt in persistent microgravity and will present the roles of Stokes sedimentation, Marangoni flow, and buoyancy-driven convection during the melt and solidification of high-entropy alloys. Additionally, we will present case studies of high-entropy alloy solidification in microgravity and compare the results with terrestrial experiments. We will also discuss translational lessons learned from microgravity experiments that inform and direct terrestrial research and manufacturing. Finally, we will present opportunities for future microgravity experiments and access to ISS facilities through the ISS National Laboratory.

11:45 AM MS04.09.09
Strengthen Mechanical Property of a Novel FeMnCoCrNiSi Medium Entropy Alloy by Deformation Induced FCC To HCP Phase Transformation Kaifan Lin, Shih-Che Chen, Hung-Wei Yen and Hsin-Chih Lin; National Taiwan University, Taiwan

High entropy alloy (HEA) or Medium entropy alloy (MEA) have attracted extraordinary attention since the single faced-center-cubic (FCC) Cantor alloy with excellent mechanical properties in a cryogenic environment was observed. Based on the cantor alloy, equal-atomic CoCrFeMnNi, nemours Cantor-like alloy systems have been widely studied in the past decade. Adding external elements and adjusting operational element contents, all of the alloy design strategies were to enhance the mechanical performance through different strengthen mechanism. In this work, a FeMnSi-based MEA containing 10% Cobalt, 12.5% Chromium and 5% Nickel (at atomic%) was achieved to be a single FCC crystal structure through vacuum argon melting furnace, and it is realized the improvement in the
mechanical properties through tensile test comparing with those of Cantor alloy. By reduction of valuable contents, such as cobalt and nickel, the cost of the novel MEA has been cheapened, and the addition of Silicon into this system has diminished the stacking fault energy (SFE) in order to trigger the deform-induced ε martensite phase transformation over a tensile test. Under the transmission electron micrograph (TEM) observation, various hexagonal close-packed (HCP) martensite phases were investigated among the deformed microstructure. The result from cryogenic tensile under the liquid nitrogen environment illustrated two series of interwoven ε martensite phases that behave both slat-shaped and needle-shaped sizes, which contribute the ultimate tensile strength (UTS) to a value over 1.2GPa. To further study the effect of microstructure evolution on the mechanical property among the elongation process, X-ray diffraction (XRD), electron backscatter diffraction (EBSD) technique have applied in this work.

SESSION MS04.10: Design and Synthesis of High-Entropy Materials II
Session Chair: Yu-Chieh Lo
Thursday Afternoon, December 5, 2019
Hynes, Level 1, Room 110

1:30 PM *MS04.10.01
Thermal Shock Synthesis of High-Entropy-Alloy Nanoparticles Liangbing Hu; University of Maryland, United States

The controllable incorporation of multiple immiscible elements into a single nanoparticle merits untold scientific and technological potential, yet remains a challenge using conventional synthetic techniques. We present a general route for alloying up to eight dissimilar elements into single-phase solid-solution nanoparticles, referred to as high-entropy-alloy nanoparticles (HEA-NPs), by thermally shocking precursor metal salt mixtures loaded onto carbon supports [temperature ~2000 kelvin (K), 55-millisecond duration]. We synthesized a wide range of multicomponent nanoparticles with a desired chemistry (composition), size, and phase (solid solution, phase-separated) by controlling the thermal shock parameters (substrate, temperature, shock duration, and heating/cooling rate). To prove utility, we synthesized quinary HEA-NPs as ammonia oxidation catalysts with ~100% conversion and >99% nitrogen oxide selectivity over prolonged operations. The unique shock synthesis enables high-entropy mixing and non-equilibrium processing to create HEA-NPs, and shows generality, tunability, and potential scalability. The successful synthesis of HEA-NPs opens a new research area for materials discovery and optimization, where the elemental composition and mixing entropy of nanoparticles can be carefully designed and controlled.

2:00 PM MS04.10.02
The Synthesis of Bi-Sr-Fe-Zr-Y-O High Entropy Oxide Cheng-Hao Lin and Jyh Ming Wu; National Tsing Hua University, Taiwan

High entropy oxide composed of Bi, Sr, Fe, Zr, and Y is synthesized by sol-gel method. Using nitrate-based compound including 4Bi(NO3)(OH)2-Bi(OH), Sr(NO3)2, Fe(NO3)3-9H2O, N2O7Zr-xH2O and Y(NO3)3-6H2O to synthesize the Bi-Sr-Fe-Zr-Y-O. First, all compounds are poured in a beaker with water and stir it for 1 hour. Then, adding the citric acid to as the chelating agent that catches all metal atoms rotates for half an hour. Next, the solution is adjusted to PH=7 by adding ammonia solution and put it into the oven that is at 90 degree Celsius for 48 hours. After that, it is sintered at 900 degree Celsius for 12 hours in the furnace. Finally, the High Entropy Oxide, Bi-Sr-Fe-Zr-Y-O is formed as nanoparticle.

2:15 PM MS04.10.03
Softening by Room Temperature Aging in High Entropy Alloys Norihiko L. Okamoto1, Tokujiro Yamamoto2, Martin Luckbauer1, Hiromu Watanabe1, Kouichi Hayashi1, Hidemi Kato1 and Tetsu Ichitsubo1; 1Tohoku University, Japan; 2Utsunomiya University, Japan; 3Twente University, Netherlands; 4Nagoya Institute of Technology, Japan

Although solid-solution strengthening (SSS) is one of the most important mechanisms that dominate the mechanical strength of high entropy alloys (HEAs), the classical theories of SSS, which were established mostly for dilute
binary solid solutions, cannot be applied to HEAs, because the definition of “solvent” or “solute” in HEAs is difficult and also because the “solute” concentration is as high as ~20 at.%. It has recently been proposed, however, that the mean-square atomic displacement (MSAD) averaged over the constituent elements can be a good scaling parameter to predict the degree of SSS in HEAs [1]; the MSAD is a measure of the local lattice strain that acts as obstacles for moving dislocations. In the course of investigating atomic environment of each of the constituent species in the Al$_{0.3}$CrFeCoNi HEA by X-ray fluorescence holography (XFH), some of the authors (TY & KH) have found that the holograms and reconstructed atomic images drastically change after room-temperature (RT) aging for 18 months, which invokes that certain diffusionless structural relaxation occurs at room temperature in the HEA. The RT structural relaxation will have an impact on the MSAD value, resulting in change in strength/hardness. In the present study, we have investigated the resonant frequencies, internal friction, Vickers hardness, and MSAD value in Al$_{0.3}$CrFeCoNi as a function of RT-aging time after casting, in order to elucidate what kind of structural relaxation occurs during RT aging. The resonant frequencies/internal friction measured by electromagnetic acoustic resonant spectroscopy monotonically increase/decreases with the aging time whereas the Vickers hardness decreases by approximately 5%. These phenomena can be understood by considering a situation where atoms located at unfavorable (metastable) positions just after casting, which are largely displaced from the average lattice points (ALPs), are shifted to more stable positions closer to ALPs with the aid of thermal energy during RT aging. In other words, just after casting the atoms are somewhat loosely bonded to each other with large MSAD, consequently, to exhibit a relatively low elastic modulus (low resonant frequencies) and high hardness, but they become more tightly and regularly arranged with small MSAD during RT aging, resultingly exhibiting higher elastic stiffness (higher resonant frequencies) and lower hardness. The decrease in the MSAD value after RT aging has been exemplified by single crystal X-ray diffraction analysis. This softening behavior observed in the hardness is opposite to the age hardening observed in some aluminum alloys and should be taken into consideration for the practical usage of HEAs as structural materials.

Reference

2:30 PM MS04.10.04
Atypical Phase Separations in High-Entropy, Lanthanide Oxides Kuo-Pin Tseng$^{1,2}$, Ming-Hung Tsai$^2$, Qun Yang$^2$ and Waltraud M. Kriven$^1$; $^1$University of Illinois at Urbana-Champaign, United States; $^2$Pacific Northwest National Laboratory, United States; $^3$National Chung Hsing University, Taiwan; $^4$ShanghaiTech University, China

The increase of temperature typically facilitates the mixing of materials because it enhances the effect of entropy. However, a series of high-entropy, lanthanide oxides, with nine different five-component high-entropy oxides involved, has shown the opposite behavior. Those nine candidates exhibit single-phase, high-entropy crystal structures below 1100 °C, but experience phase separations as well as multiple phase transformations at high temperature, up to 2200 °C. In this study, in-situ, high temperature synchrotron data of this high-entropy lanthanide system was collected. Atomic resolution, high angle annular dark-field (HAADF) imaging and energy-dispersive X-ray mapping (STEM-EDS) were performed on our candidates before and after phase separations. Another five-component, high-entropy, lanthanide oxides system, with similar cation radii differences ($\delta$) compared to the prior system, has been studied. Those candidates remained structurally stable without phase transformation from room temperature to melt. By comparing these two systems, a hypothesis has been made based on their crystal structures, oxidation states and difference in constituent cation radii. This research introduces that the single-phase oxide could possibly be transformed to multi-phases under thermal treatments. Therefore, the possible structural transformation(s) of the constituent mono-cation ceramic (e.g. oxide) need to be considered in the design of high-entropy ceramics.

2:45 PM MS04.10.05
Single Crystal High Entropy Perovskite Oxides—Functional Properties Beyond Structural Purposes Yogesh Sharma$^{1,2}$, Alessandro Mazza$^1$, Aiping Chen$^2$ and T. Zac Ward$^1$; $^1$Oak Ridge National Laboratory, United States; $^2$Los Alamos National Laboratory, United States

High-entropy alloys (HEAs) have proven to exhibit remarkable mechanical and structural properties. Beyond HEAs, the high entropy oxides (HEOs) have been proposed as a promising material system, where configurational disorder due to the random distribution of constituent elements into the cation sublattice can act as a driving force to tailor physical properties as well as stabilize new material phases and functionalities. In this talk, we will present on
growth and functional properties of single-crystal epitaxial thin films of extremely configurationally disordered ABO$_3$ perovskites; Ba(Zr$_{0.2}$Sn$_{0.2}$Ti$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$)O$_3$, La(Cr$_{0.2}$Mn$_{0.2}$Fe$_{0.2}$Co$_{0.2}$Ni$_{0.2}$)O$_3$ and (La$_{0.2}$Nd$_{0.2}$Sm$_{0.2}$Gd$_{0.2}$Y$_{0.2}$)(Cr$_{0.2}$Mn$_{0.2}$Fe$_{0.2}$Co$_{0.2}$Ni$_{0.2}$)O$_3$. These new materials conform to standard tolerance factor considerations where multicomponent on A or B-site can be simply being treated as the average ionic radii value. A first investigation on the crystal, magnetic, relaxor-ferroelectric, and thermal properties of these high-entropy perovskite oxide thin films grown by pulsed laser epitaxy will be presented. X-ray diffraction and scanning transmission electron microscopy show single phase growth of these films with excellent crystallinity and atomically abrupt interfaces to the underlying substrates. Atomically resolved chemical mapping confirms a uniform and random distribution of all B-site cations. We will close by discussing how “Entropy-Stabilization” approach provides an ideal opportunity to design materials from a much broader combinatorial cation pallet for fundamental studies in strongly correlated materials where local disorder can play a critical role in determining macroscopic properties.

This work was supported by the U. S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division.

3:00 PM BREAK

3:30 PM *MS04.10.06
OPEN SLOT

4:00 PM MS04.10.07
Can Thin Films be Used to Study High-Temperature Oxidation of Refractory High-Entropy Alloys? A Study of the Effect of Film Thickness on Oxygen Penetration Howie Joress$^1$, Daniel B. Miracle$^2$, Todd M. Butler$^2$ and Jason R. Hattrick-Simpers$^1$; $^1$National Institute of Standards and Technology, United States; $^2$Air Force Research Laboratory, United States

The large composition-processing space for high-entropy alloys (HEAs) makes study of them using high-throughput screening methodologies advantageous. The most common method of rapid synthesis is to create combinatorial thin film libraries. For refractory HEAs, an important and necessary property is high-temperature oxidation resistance. Currently it is unknown if high-temperature oxidation in HEAs can be studied in thin films as there is some question as to whether the finite thickness of the film, on the scale of a couple of microns, will affect the ability to measure oxygen penetration and oxide thickness compared to semi-infinite bulk samples. An answer to such question is necessary to justify the translation of thin-film high-throughput refractory HEA oxidation resistance to bulk alloys. In this work we create NbTiTa thin films with a range of thicknesses and subject them to oxidation at varying times and temperatures. As a function of thickness, we look at oxygen penetration depth and oxide thickness to determine the limits of time and temperature at which the thin film becomes bulk-like and no longer exhibits finite size effects.

4:15 PM MS04.10.08
Development of CoCrFeMnNi-0.18Ti High Entropy Alloy via Mixed Powders and Electron Beam Melting Mehmet Cagirici$^{1,2}$, Pan Wang$^1$, Mui Ling Sharon Nai$^1$, Chun Yee Aaron Ong$^2$, Jun Ding$^2$ and Jun Wei$^1$; $^1$Singapore Institute of Manufacturing Technology, Singapore; $^2$National University of Singapore, Singapore

High entropy alloys (HEAs) have great potential to combine numerous properties for structural applications. Here, mechanical mixing of pre-alloyed CoCrFeMnNi and pure Ti powders are employed to reduce the complexity of powder fabrication and the cost of synthesizing high-purity pre-alloyed powder. The CoCrFeMnNi-0.18Ti HEA is successfully fabricated with homogenous chemical compositions via electron beam melting (EBM), which is one of popular powder bed fusion additive manufacturing technologies. It is revealed that EBM is a promising method to develop new alloy using mixed powder. A detailed investigation on microstructural evolutions through the building direction is conducted by a transmission electron microscope, a scanning electron microscope with energy dispersive spectroscopy and electron backscattered diffraction. Besides of FCC phase, three precipitates, Cr-rich γ, Ni-rich D0$_{22}$, and σ (CrFe) are identified. The formation of these precipitates and their evolution are discussed based on the rapid cooling and subsequence in situ heat treatment during the EBM process. In addition, the tensile and compressive mechanical properties are also revealed based on the size and distribution of the precipitate.

4:30 PM MS04.10.09
Exceptional Mechanical Properties of BCC Structured Zr-Based Medium Entropy Alloys Designed by High-Throughput Screening Xuehui Yan and Yong Zhang; University of Science and Technology Beijing, China

Zr-based alloys are considered as the most promising materials in the biomedical application fields because of its excellent in vivo performance, acceptable mechanical properties, and great corrosion resistance. However, due to the complexity of composition and nonlinear relationship between the performance and mixing-entropy, efficienctive screening of Zr-based alloy with ideal phase structure and properties is a huge challenge.

In this work, a high-throughput method combining co-sputtering and physical mask, was used to prepare the compositional gradient films, which will be used to screen in Zr-based medium entropy alloys with BCC structure. Based on the screening results, the formation, structure and mechanical properties of bulk Zr-based medium entropy alloys were further discussed in detail. This work not only offers novel BCC structured Zr-based medium entropy alloys with prominent properties for practical applications, but also shed light on development of high-throughput preparation technology in general.

4:45 PM MS04.10.10
Development of Novel High Entropy Alloys of AlCoCrFeTi0.5Ni x with Enhanced Strength and Plasticity Lin Liu; Huazhong University of Science and Technology, China

Abstract
The improvement in plasticity is usually compensated by the reduction of strength in structural materials, which is a long-standing conflict referred as the strength- plasticity trade-off. In recent years, a new type of structural materials of high-entropy alloys (HEAs) with equiatomic or near-equatomic concentrations has attracted increasing attention due to their unique mechanical properties. However, HEAs with BCC structure normally exhibit high strength but low plasticity, while the HEAs with FCC structure show inversely high plasticity and low strength. The formation of the mixing structures (i.e, FCC+BCC) is an approach to solve the problem. In this work, a BCC-based AlCoCrFeTi0.5 high-entropy alloy (HEA) was modified by the addition of Ni to improve the plasticity. The new HEAs have the composition of AlCoCrFeTi0.5Ni x (x=0~3 mol%), which were prepared by arc melting following by copper mold casting. The effect of Ni concentration on the microstructures and mechanical properties of AlCoCrFeTi0.5Ni x alloys were systematically studied. It was found that the phase transformation follows the following sequences with the increase of Ni concentration: BCC1 (disordered)→BCC1+BCC2 (ordered)→BCC1+BCC2(ordered) +FCC(ordered). FCC phase appeared at Ni=1.5 mol% and then increased in amount with further increase of Ni content. Consequently, the mechanical properties changed drastically due to the phase transformations. A good combination of strength and plasticity was achieved at Ni=2.5 mol%, in which the proportion of FCC phase and BCC phases (BCC1+BCC2) are nearly equivalent. This high entropy alloy exhibits yield strength of 1.41 GPa, compressive plastic strain of 31.8% and fracture toughness Kq of 64.3MPa *m^1/2. The toughening mechanism of the HEAs are discussed on the basis of the microstructure evolutions associated with Ni addition.
**SESSION SB01.01: Multifunctional Materials**
Session Chairs: Ximin He and Andreas Lendlein
Monday Morning, December 2, 2019
Hynes, Level 3, Ballroom A

8:15 AM SB01.01.01
**Braiding Nanoscale and Microscale Fibers Using Repulsive Capillary Forces** Cheng Zeng, John M. Faaborg, Ming Xiao, Yohai B. Sinai, Martin Falk, Rozhin Hajian, Michael P. Brenner and Vinothan N. Manoharan; Harvard University, United States

Braids have been used for centuries to enhance the material properties of fibers. However, although nanoscale and microscale braids are expected to show interesting mechanical and electric properties, braiding them remains challenging. Such thin fibers suffer from easy breakage when handled by mechanical braiding machines. Moreover, the complexity of braid topologies makes it extremely difficult to self-assemble braids. Here we demonstrate a gentle yet robust method to programmatically assemble nanoscale and microscale fibers into arbitrary braid topologies. This method relies on repulsive capillary forces to effectively trap and move small floating objects (“floats”) at the air/water interface inside designated channels of our devices. We designed the channels to change shape along the vertical axis. As a result, when a device is moved through the air/water interface, the shape of the meniscus and thus the capillary forces change. This change in force causes lateral motions of floats at the interface. Thus, we can steer the floats around simply by moving the device into or out of water. To braid wires, we attach them to the floats and operate the device such that the floats switch positions in a desired order to drive braid formation. Capillary forces are gentle enough to ensure wires don’t break during braiding. We show that it’s possible to translate, rotate, switch, and separate floats with capillary forces. We also demonstrate methods based on geometry or contact line pinning to repeatedly braid fibers without disassembly. Lastly, we show that any arbitrary braid can be fabricated with our method.

8:30 AM SB01.01.02
**Rational Design Strategies for Tough Self-Healing Materials** Christopher B. Cooper, Jiheong Kang and Zhenan Bao; Stanford University, United States

The design of robust wearable technologies (e.g. e-skin) and soft robotics requires a combination of highly conformal mechanical properties and long-term durability to withstand repeated damage from daily use. Self-healing materials offer a promising solution as they continuously and autonomously heal after experiencing damage, however improving self-healing abilities often results in materials with low toughness or large hysteresis. While a range of self-healing materials have been reported in the literature, limited understanding exists on the specific structure-function relationships between molecular design of the polymer and optimizing its resulting macroscopic properties such as toughness, elasticity, and self-healing speed and efficiency.

Here, we present our work to address this gap in knowledge and allow for the more intelligent design of self-healing materials. Using a model system with precise, tunable properties, we simultaneously study the effects of molecular design on the temporal characteristics and spatial morphology of the polymers and relate these changes to their macroscopic properties. Using small-angle x-ray scattering (SAXS), we examine how the molecular design of the polymers affects their resulting microstructure. In addition, through in-situ monitoring via SAXS under dynamic mechanical loading, we investigate how these microstructures evolve via distinct mechanisms after strain and over time as the networks relax. By combining the insights from these analyses and other characterization methods, we propose new rational strategies for the molecular design of self-healing materials, which will be highlighted in this talk. This work aims to provide a better understanding of the underlying molecular mechanisms driving the observed macroscopic properties of self-healing materials and is essential for more efficient design and integration of these
materials into advanced multifunctional materials and adaptive structures.

8:45 AM SB01.01.03
Biomimetic Fully Autonomous Self-Reporting and Self-Healing Strategies with In Situ Generated Ferromagnetic Particles
Ying Zhao and Jinglei Yang; Hong Kong University of Science & Technology, Hong Kong

Polymer materials are susceptible to small damages at micron level during service life, which is difficult to detect and further repair, yet can significantly propagate into larger one and subsequently compromise the integrity and functionality of the polymeric materials if left unattended at the early stage. Previously, efforts put on this issue have demonstrated some smart systems, like incorporation of AIEgens, pH indicators, or dyes. However, most of them either needed human intervention, like UV irradiation, or could only tackle the visual detection matter whereas the repairing solution still needed to be dealt with. To develop materials with in-situ autonomous visual indication and simultaneous repair functionalities towards the mechanical damages is a promising yet challenging task, due to difficulties in integrating different functional elements for packaging and lack of suitable vehicles to carry multirole triggers with high reactivity.

Herein, inspired by biomimetic external wound healing and internal bone fracture healing process, a genuinely fully autonomous smart composite material capable of self-reporting and self-healing was designed via simply incorporating the triple microcapsules containing Fe-ion solution, strong basic hardener and isocyanate/epoxy, respectively, as prepared by the versatile interfacial or in-situ polymerization methods. Microcapsule concentration and relative ratios were optimized.

Damage-triggered visualization, magnetization and healing can be accomplished by the delivery of core healants that precipitate magnetic nanoparticles and form new polymer networks upon mixing. Both ‘subcutaneous’ damage and macroscopic surface damage can be warned by the sharp color change from light yellow to conspicuous black, not only rapidly upon occurrence but also permanently even after repaired. Despite of black color visible to naked eyes, the magnetism of the precipitated ferromagnetic particles allows multiple methods for further detecting the damage shape, like magnetic sensor, and thermal imagery. Assisted with the Fe-ion/-OH/isocyanate combinations, the coating showed superior anti-corrosion and sealing performance. Also, a sharp color contrast occurred exactly where the crack is. Interestingly, by applying an alternating magnetic field, the ferromagnetic particles answered with heating effect, which could be utilized for thermal imagery, or as heat source (up to 60 degrees Celsius) intrinsic self-healing of thermal plastics coatings, while avoiding heating the non-damaged regions. On the other hand, the combination of Fe-ion/-OH/epoxy showed high healing efficiency up to 100% for both fracture toughness and dynamic impact strength. The magnetic detection and thermal imagery here enabled a detailed understanding of the damage shape and scale, which is beneficial for evaluation of the damages and consideration for further solutions.

9:00 AM SB01.01.04
One-Step Polymerization Induced Self-Assembly of Synthetic Biomimetic Vesicles with Photo/Chemo-Responsive Permeability
Gong Cheng and Juan Perez-Mercader; Harvard University, United States

The design and self-assembly of membrane-bounded cell-like artificial vesicles not only offers new inspiration for technology and applications in many fields, but also has the potential to help uncover the mechanisms for compartmentation that may have occurred in the origin of life. In natural cells, the out-of-equilibrium self-assembly of their membrane is a critical process that eventually results in the control of cell behaviors such as vesicular transport, cell motion or division. An intriguing aspect of the cell membrane in extant living systems is their dynamic permeability. It is selectively permeable to small molecules but blocks the passage of certain macromolecules, and, at the end of their lifetime, it would be disassembled by the degradation of the lipid amphiphiles to lead to burst release of all cellular contents. Despite the advance in the assembly of various vesicular structures (e.g. liposomes, fatty-acid vesicles, colloidosomes, polymersomes), to date, little progress has been made in the construction of biomimetic vesicles with such a similar dynamic membrane and application potential to many areas in chemistry and engineering.

To address this challenge, we designed and synthesized biomimetic vesicles with a photo/chemo programmable synthetic membrane using a one-step polymerization induced self-assembly (PISA) strategy. These polymeric vesicles can realize either release of small molecules only by light-induced selective permeability, or burst release of all contents from their lumen by chemo-induced degradation of the amphiphiles and the vesicular structure. Notably, the cell-like dynamic permeability is realized by installing a single azobenzene to bridge the hydrophilic block and
hydrophobic blocks of the amphiphiles. Specifically, light-induced isomerization of the azobenzene module in the membrane enables the full system to direct dissipative energy into functional pathways as a form of dynamic membrane permeability. Our work not only exemplifies a new strategy and easily implementable at the laboratory and industrial scales for the construction of cell-like active vesicular structures, but also opens new avenues to engineer synthetic material structures with spatially controllable functionalities.

9:15 AM SB01.01.05
Liquid-Free, Non-Faradaic and Stretchable Ionoelastomer Devices for Electro-Adhesion and Electro-Mechanical Transduction
Hyeong Jun Kim¹, Baohong Chen², Zhigang Suo² and Ryan Hayward¹; ¹UMass Amherst, United States; ²Harvard University, United States

Soft solids capable of conducting ions offer promise for the design of entirely new classes of highly deformable and bio-inspired devices. While resistive and capacitive ionic circuit elements are well established, next generation ionotronics will require advanced elements that can control and switch ion flow. Here, we introduce ‘ionoelastomers’—soft polymer networks capable of selectively conducting either anions or cations—to demonstrate liquid-free, elastic, and stretchable ionic diodes and transistors that operate entirely via non-Faradaic processes. We show that the junction of two oppositely charged ionoelastomers yields an ‘ionic double layer’, analogous to the depletion layer in a semiconducting p-n junction. This enables the design of ionic devices for rectifying and switching non-Faradaic ionic currents. Further, soft and stretchable ionoelastomer junctions provide fundamentally new functionalities including: 1) low voltage reversible electro-adhesion and 2) electro-mechanical transduction, i.e., the conversion of mechanical deformation into electrical signals. Our studies provide new fundamental insight on the interface between two oppositely charged ionoelastomers and open opportunities for the application of these soft ion-conducting devices.

9:30 AM *SB01.01.06
Self-Organization of Electrostatically and Sterically Stabilized Colloidal Nanocrystals—The Roles of Topology, Image Charges and Non-Classical Nucleation
Dmitri V. Talapin, Igor Coropceanu, Erik Janke and Michael A. Boles; University of Chicago, United States

Colloidal nanocrystals offer a route toward engineering new classes of materials by acting as discrete units that can be assembled to construct composite solids. The self-assembly of two sizes of spherical nanocrystals has revealed a surprisingly diverse library of structures. To date, at least fifteen distinct binary nanocrystal superlattice (BNSL) structures have been documented. BNSLs naturally represent a powerful platform for practical implementations of multifunctional materials. However, the stability of the observed binary phases cannot be fully explained using the traditional conceptual framework treating the assembly process as entropy-driven crystallization of rigid spherical particles. We evaluate new theoretical models treating the co-crystallization of deformable spheres and to formulate new hypotheses about the factors affecting the nucleation and growth of the binary superlattices. The deviation from hard sphere behavior can be explained by specific topological textures developed within deformable layers of surface ligands. Our results also suggest that the relative abundance of BNSL phases is determined not only by their thermodynamic phase stability but also by a postulated pre-ordering of the binary fluid into local structures with icosahedral or polytetrahedral structures prior to nucleation.

Strong electronic coupling between individual nanocrystals within a superlattice is an important prerequisite for the emergence of non-additive physical properties. However, a simultaneous realization of strong electronic coupling and dense ordered packing of nanocrystal solids has remained elusive. We report a method for growing all-inorganic highly ordered solids of electrostatically-stabilized nanocrystals with the interstitial space filled with a glassy metal chalcogenide matrix which, combined with the short separation between particles leads to very strong electronic coupling. Temperature-dependent conductivity measurements show metallic transport across our supercrystals. The formation of strongly-coupled all-inorganic nanocrystal assemblies represents an important step toward the bottom-up design of functional nanostructured composites.

10:00 AM BREAK

10:30 AM *SB01.01.07
Nanoscale Magneto-electric Nanostructures for Cell Trapping Applications
Christopher Lynch¹,², Auni Kundu² and Yu-Ching Hsiao²; ¹University of California Riverside, United States; ²University of California, Los Angeles,
Magnetoelectric cell sorting offers the potential to sort large numbers of cells quickly. Cells can be tagged with fluorescent markers that identify cell type. They can also be tagged with magnetic micron or smaller magnetic beads. These beads experience a translational force in the presence of a magnetic field gradient. Macro scale cell sorting magnetically tags cells that are to be captured, making it possible to hold those cells and remove the unwanted cells. Magnetoelectric devices offer the ability to control magnetism at the sub-micron scale. There are multiple challenges faced when applying magnetoelectric devices to cell sorting. In an envisioned device, the magnetically tagged cell is in a fluid bath that flows across a nanomagnet. The magnet traps the cell. Ideally, when voltage is applied, the cell is released. Some of the challenges include: the design of nanomagnets to produce the right force to trap and hold a cell in a flow field, and the ability to alter the magnetization in a way that enables releasing the cell. Ideally, an applied voltage would turn the magnetization off completely. The approach taken to developing a voltage-controlled magnet was to produce magnetostrictive structures on a piezoelectric substrate. At small length scales this approach can be used to produce single domain magnets with the magnetization in-plane. In certain systems like a NiCo layered structure, when the layers are thin enough, interface effects dominate and the magnetization shifts to an out-of-plane orientation. The work that will be presented describes the design of the nanomagnets to produce the desired capture force, the fabrication and characterization of an array of nanomagnets under an applied magnetic field to produce M-H curves, and the effect of strain on those M-H curves. Although the ability to switch these magnetic structures from a state of perpendicular magnetic anisotropy to an in-plane magnetic state has not yet been demonstrated, sufficient progress has been made to suggest that the approach may ultimately be successful.

11:00 AM SB01.01.08
Ferromagnetic Soft Continuum Robots—Towards Next-Generation Medical Robots Yoonho Kim and Xuanhe Zhao, Massachusetts Institute of Technology, United States

Enabling access to hard-to-reach areas in a remotely controllable manner, small-scale soft continuum robots capable of active steering and navigation through complex and constrained environments hold great promise for medical applications in diverse areas across the human body. Several concepts of continuum robots have been commercialized so far, offering a range of new therapeutic and diagnostic procedures that are safer for patients owing to their minimally invasive nature. However, existing continuum robots are often limited to relatively large scale due to miniaturization challenges inherent in their conventional actuation mechanisms such as pulling mechanical wires. Such miniaturization challenges have rendered even the most advanced form of commercialized continuum robots, mostly used for cardiac interventions, substantially unsuited for neuro-surgical applications due to the considerably small and tortuous vascular structures.

Recently, burgeoning efforts have been made to utilize fully soft-bodied robots in medical applications with great expectations that their inherent compliance would lead to enhanced safety. Despite the purported advantage, the field of soft robots is still faced with a set of key challenges. First, existing soft robots based on pneumatic or hydraulic actuations are mostly heavily tethered, which limits their use in realistic medical applications that typically require tether-free actuation. Second, most soft robots are difficult to accurately control based on quantitative models, largely because their actuation mechanisms often rely on highly nonlinear deformation or instabilities. Third, conventional soft robots are difficult to miniaturize below millimeter scales, because their actuation mechanisms and associated fabrication methods are often unfavorable to such small size.

Here we present a submillimeter-scale, self-lubricating soft continuum robot with omnidirectional steering and navigating capabilities based on magnetic actuation, which are enabled by programming ferromagnetic domains in its soft body while growing hydrogel skin on its surface. The robot’s body composed of soft polymer matrices with embedded ferromagnetic microparticles can be miniaturized below a few hundreds of microns in diameter. To cope with the significant friction experienced by the robot while navigating through highly unstructured environments, we grow hydrogel skin, a thin layer of hydrated crosslinked polymers, onto the robot’s surface. This hydrogel skin substantially decreases the surface friction due to its high water content.

Elaborating on our recent progress in magnetic soft materials towards untethered soft machines and robots, we present novel material systems and fabrication schemes to realize ferromagnetic soft continuum robots at submillimeter scale. We also present our model-based material design strategies to optimize the actuation parameters.
performance of our soft continuum robots. Combining all these features, we demonstrate the capability of navigating through complex and constrained environments with close relevance to clinical challenges, such as tortuous phantom neurovasculature with cerebral aneurysms, which are difficult to navigate with bulky robotic catheters or manually controlled passive instruments. Incorporating a functional core, such as an optical fiber, in the robot’s body, we further demonstrate additional functionalities such as steerable laser delivery for potential clinical applications in laser atherectomy. Given their compact, self-contained actuation and intuitive manipulation, our ferromagnetic soft continuum robots may open new avenues to minimally invasive robotic surgery for previously inaccessible lesions, thereby addressing challenges and unmet needs in healthcare.

11:15 AM SB01.01.09
Designing Magnetorheological Fluids for Soft Robotics Abigail L. Rendos, Kevin McDonald, Tommaso Ranzani and Keith A. Brown; Boston University, United States

Smart fluids are suspensions of functional particles in which an applied field drastically changes the fluid’s properties. For example, ferromagnetic microparticles in solution form magnetorheological (MR) fluids in which an applied magnetic field causes the liquid to solidify through the formation of rigid columns of particles. This field-driven transition enables the fluid to change reversibly from a viscous state to an elastic state that can be described as a Bingham plastic. As a result of this unique property, MR fluids have been widely used in a variety of systems such as brakes, dampers, and clutches. We propose to leverage MR fluids to realize novel classes of soft robotic systems in which magnetic fields interact with fluid flow to actuate systems in novel ways. However, there are two major barriers to this vision, (1) new architectures of actuation need to be developed and (2) more generally, sedimentation of the magnetic particles is a common issue hindering the use of MR fluids. We address the sedimentation challenge through the detailed exploration of MR fluid performance with different thixotropic agents in novel water-based MR fluid formulations. Controlling the formulation allows us to realize low sedimentation, low off-state viscosity, and high on-state viscosity. By mapping their response to magnetic fields, we ensure a predictable, variable resistance caused by increased thickening of the fluid enabling users to design a variety of systems from one MR fluid recipe. These materials innovations allow us to explore novel soft actuation architectures based upon MR fluids.

11:30 AM SB01.01.10
Tunable Silver Nanofilament Formation Dynamics in Polymer-Ionic Liquid Electrolyte Composites by Direct-Write Zhongmou Chao and Susan Fullerton; University of Pittsburgh, United States

Direct-write is a bottom-up fabrication approach where material is added to a substrate in well-defined locations. With the advent of 3D printing and the need for inexpensive, printable and flexible electronics, direct-write patterning is attracting more attention for its ease to use for fewer processing steps. In this work we demonstrated a direct-write, electrochemical approach to the formation and dissolution of silver filaments through a new type of multifunction polymer electrolyte consisting of a UV-crosslinkable polymer, polyethylene glycol diacrylate (PEGDA), and an ionic liquid (IL), 1-butyl-3-methylimadazolium hexafluorophosphate ([BMIM]PF₆). A conductive atomic force microscope (C-AFM) is used to form and dissolve the filaments at pre-programmed locations using a custom script. Filament formation and dissolution kinetics are measured at various IL compositions and formation biases. The IL strongly impacts filament formation kinetics by controlling the local PEGDA structure. For example, in a highly crystalline PEGDA film with a low IL concentration (10 wt%), silver filament formation kinetics vary significantly with XY location and exhibit highly asymmetric formation time distribution; in contrast, when the IL concentration is increased to 30 wt%, PEGDA crystallization is suppressed and the filament formation times exhibit a normal (Gaussian) distribution with respect to XY location. In addition, we show that a competition between electric double layer (EDL) screening, ion transport, and electrochemical reactions gives rise to a non-monotonic dependence of formation time on applied voltage. Time-dependent analysis of formation current along with scanning electron microscope (SEM) characterizations suggest that filament structure is directly related to the magnitude of formation voltage, which can be tuned to improve the filament switching capability. Our results provide deeper understanding of the kinetics of filament formation through a crosslinkable polymer electrolyte, which is potentially useful for multiple material functionalities including the development of new metamaterials with reconfigurable optical properties, and non-volatile, on-board resistive random-access memory (ReRAM) for printable and flexible electronics.

11:45 AM SB01.01.11
Photocontrol of Structural Colors in Self-Organized Helical Superstructures Lang Qin and Yanlei Yu; Fudan University, China

Light-driven cholesteric liquid crystals (CLCs) exhibit unique selective reflection, originating from their inherent self-organized helical superstructures, and dynamic reflection tuning in response to light, which has unique advantages for remote, temporal, local, and spatial manipulation. Such elegant systems may represent ideal candidates for use as “photonic inks” to realize changeable information in color reflective displays, especially those providing paperlike viewability in sunlight where backlit devices perform poorly. To this end, phototunable reflection across the visible spectrum has been demonstrated for CLCs and was induced by photoresponsive chiral motors and switches with tetrahedral, axial, or planar chiralities. These triggers undergo photoisomerization, giving rise to both the variations in helical twisting power (HTP) and the color change.

In this report, we demonstrate several new strategies for manipulating the structural colors of CLCs. We design a tristable chiral switch by incorporating two different azobenzenes into one chiral structure. Three stable configurations of the chiral switch endow the CLC with two continuous and adjacent tuning periods of the reflection, covering not only entire visible spectrum, but also one more wide period within near-infrared region. The resultant CLCs are capable of creating images of RGB colors with a black background, which is realized based on piecewise reflection tuning. In addition, we proposed a novel tuning mechanism based on a partial photochemical phase transition to enable continuous patterning of photostationary RGB colors in a CLC system, which contains nonresponsive chiral dopants and o-fluoroazobenzenes (Fazo) to serve as the photoswitch. Distinct isomer ratios of Fazo result in precise light-directed RGB colors for the photostationary states, and, thus, a fixed relationship is established between the light stimulus and the reflection color. Accordingly, the RGB color patterns can be continuously erased and rewritten under light irradiation with different wavelengths.


SESSION SB01.02: Responsive Materials and Drug Delivery
Session Chairs: Pablo Valdivia y Alvarado and Christian Wischke
Monday Afternoon, December 2, 2019
Hynes, Level 3, Ballroom A

1:30 PM *SB01.02.01
Biomimetic Glucose-Responsive Smart Insulin Delivery Zhen Gu; University of California, Los Angeles, United States

Closed-loop drug delivery strategies have proven to be a practical tool for homeostatic regulation, by tuning drug release as a function of biosignals relevant to physiological and pathological processes. Among them, a glucose-responsive “closed-loop” insulin delivery system mimicking the function of pancreatic cells holds great promise to improve quality of life and health in people with diabetes. In this talk, I will introduce our ongoing efforts in developing formulations and related devices for glucose-responsive insulin delivery. I will first discuss the transdermal microneedle patches integrated with glucose-sensitive components for self-regulated insulin delivery tested on both mice and pigs. I will further introduce integration of beta cells and microneedle patch loaded with the synthetic “glucose-signal amplifier” for releasing insulin with a glucose-responsive manner. In addition, synthetic beta cells with vesicle fusion-mediated mechanism for glucose control will also be presented.

2:00 PM SB01.02.02
Instant Strong Adhesion of Wet Tissues and Devices for Biomedical Applications Hyunwoo Yuk and Xuanhe Zhao; Massachusetts Institute of Technology, United States
Two dry surfaces can be instantly adhered upon contact with each other by intermolecular forces such as hydrogen bonds, electrostatic and van der Waals interactions. However, it is extremely challenging to form such instant adhesion between wet surfaces such as biological tissues, because water separates molecules from the two surfaces to form instant interactions. Existing tissue adhesives, mostly in the form of liquids or gels, rely on diffusion of their molecules into the polymer networks of the tissues for bonding, which can take significant time and give weak adhesion. Consequently, these limitations have severely hampered the scope of applications of existing tissue adhesives and their efficacy in practice. In this talk, we introduce a new mechanism to realize instant strong adhesion of a broad range of wet tissues and devices, implemented in various form factors including double-sided tapes, tissue-mimicking patches, and injectable pastes. Our new tissue adhesives boast unprecedented capability of forming instant adhesion less than 5 s with superior adhesion performance over 1,000 J m$^{-2}$ interfacial toughness, 120 kPa shear and tensile strength, surpassing commercially-available solutions. This work not only reveals a new paradigm in wet adhesion but also provides new opportunities and solutions in applications as diverse as tissue adhesives and sealants, bioscaffolds, drug delivery, and wearable and implantable devices.

2:15 PM SB01.02.03
Supramolecular Hydrogels for Sustained Release and Enhanced Thermal Stability of Biotherapeutics
Catherine Meis, Anthony C. Yu, Anton A. Smith, Caitlin L. Maikawa and Eric A. Appel; Stanford University, United States

The emerging generation of drugs is dominated by biotherapeutics, such as antibodies, hormones, and other proteins, for critical treatment applications ranging from cancer to autoimmune diseases to vaccine development. However, many of these drugs suffer from short half-lives in vivo, leading to the need for frequent administrations in order to maintain their concentrations at therapeutic levels in the body. In addition, these large complex-structured macromolecules are inherently unstable in formulation, requiring cold-chain transportation and storage and limiting their long-term viability in in vivo depots. To address these challenges, we have developed a multifunctional, injectable delivery system utilizing supramolecular hydrogels that can sustain the release of these drugs over an extended period of time while simultaneously maintaining their stability, even at high loading concentrations. This work will focus on assessing the ability of these supramolecular polymer-nanoparticle hydrogels to improve the thermal stability of biotherapeutics. In vitro plate assays conducted under accelerated aging conditions are used to investigate how the hydrogel formulation influences the biostability of various model protein drugs, including hormones, enzymes, and antibodies. In addition, correlation between hydrogel mechanical properties and their ability to act as a stabilizing agent is explored. We demonstrate that these hydrogels are capable of extending the thermal stability of sensitive biotherapeutics at even at high concentrations, potentially enabling new drug formulation strategies.

2:30 PM SB01.02.04
Micromotor-Enabled Active Drug Delivery to Treat Gastrointestinal Diseases
Jinxing Li1,2, Liangfang Zhang2 and Joseph Wang2; 1Stanford University, United States; 2University of California, San Diego, United States

Advances in bioinspired design principles and nanomaterials have led to tremendous progress in autonomously moving synthetic nano/micromotors with diverse functionalities in different environments. However, a significant gap remains in moving nano/micromotors from test tubes to living organisms for treating diseases with high efficacy. Here we present the first, to our knowledge, in vivo therapeutic micromotors application for active drug delivery to treat gastric bacterial infection in a mouse model using clarithromycin as a model antibiotic and Helicobacter pylori infection as a model disease. The propulsion of drug-loaded magnesium micromotors in gastric media enables effective antibiotic delivery, leading to significant bacteria burden reduction in the mouse stomach compared with passive drug carriers, with no apparent toxicity. Moreover, while the drug-loaded micromotors reach similar therapeutic efficacy as the positive control of free drug plus proton pump inhibitor, the micromotors can function without proton pump inhibitors because of their built-in proton depletion function associated with their locomotion.

2:45 PM SB01.02.05
Novel Drug Eluting Soy Protein-Based Films
Lior M. Matsliah1, Daniella Goder1, Ariel Furier2 and Meital Zilberman1; 1Tel Aviv University, Israel; 2Israel Defense Forces, Israel

Bioresorbable structures can be used as drug eluting platforms in various biomedical applications. Soy protein is a
new natural material in the medical field with very promising properties. It has been used in our lab as basic material for wound dressings designed for pre-hospital treatment, mainly of burn injuries. Our dressing design consists two layers: a porous layer in contact with the skin, which allows better water permeability and accommodates newly developed tissue, and a top, dense layer, preventing pathogen penetration. In the current study the porous layer was loaded with the hemostatic agent tranexamic acid for bleeding control, and the dense layer was loaded with both an antibiotic drug (Cloxacillin) for infection prevention and with an analgesic drug (Bupivacaine). The whole soy protein structure was crosslinked by glyoxal and plasticized by glycerol.

A film containing higher crosslinking density achieved better strength and modulus, while a film with lower crosslinking density and higher plasticizer concentration exhibited a higher maximal strain. The water vapor permeability, the most important property of burn dressings, was also affected by the film’s formulation: increasing the crosslinking agent resulted in a lower water vapor transmission rate. The swelling ratio and weight loss were higher for the less crosslinked film as well.

A cytotoxicity test was performed with samples containing 3% Cloxacillin (w/w of dense layer). No significant difference was found between the drug loaded film and the neat film without drug. Both did not show any cytotoxic effect.

In conclusion, our novel wound dressing holds a promise to be a most effective measure for casualty pre-hospital treatment, as multi-drug releasing platform, which may also support tissue regeneration.

3:00 PM BREAK

3:30 PM *SB01.02.06
Chemical Reactions as Active Elements in Multi-Responsive Materials and Devices Stephen Craig; Duke Univ, United States

The materials chosen for use in soft devices tend to be compliant elastomers whose function is to deform in a way that meets the mechanical requirements of the application. In recent years, a new idea has emerged: namely, that the strains that naturally occur during device function can be harvested to drive chemical changes and add function to the devices. One strategy toward capturing strain is to use tension in polymer molecules to trigger the covalent response of an embedded mechanophore. This talk will discuss structure-activity relationships in mechanophore design and their application in multi-responsive materials and devices.

4:00 PM SB01.02.07
Soft Magnetically Responsive Materials for the Manipulation of Stiffness, Friction and Adhesion Alexander Bennett1, Elise Corbin2, Brianna Messam1, Alexia Vite1, Kenneth Margulies1 and Kevin T. Turner1; 1University of Pennsylvania, United States; 2University of Delaware, United States

Smart materials with tunable properties have opened new avenues for studying the fundamental, dynamic behavior of cellular systems. The behavior of biological cells is strongly dependent on their mechanical micro-environment. To date, efforts to study this dependency have relied on the use of mechanically static materials with stiffness that can be changed through preparation. This approach provides only half the story though as cells and tissues are dynamic in nature. We have developed a composite extracellular matrix platform with dynamically tunable mechanical properties and have used it to assess the response of cardiomyocytes and fibroblasts to dynamic changes of their mechanical environment. The key material in this platform is a magnetorheological elastomers (MRE) that is composed of an elastomer (polydimethylsiloxane) and ferritic particles. This MRE is a soft (E~10-100 kPa) active material with mechanical properties that can be manipulated through the application of a magnetic field. We have characterized the change in modulus, friction, adhesion, and surface roughness of these MREs that occur due to an applied magnetic field. The effect of the magnitude of the field, the material composition, and material synthesis method on the response were characterized. The stiffness, friction, and adhesion changes were characterized via indentation and sliding tests at the millimeter scale. The results show that the magnetic-induced changes in viscoelastic modulus (up to ~5x) lead to changes in the tribological behavior (friction and adhesion) of the materials. Surface roughness and geometry changes resulting from the strong magnetostrictive response of these MREs to weak fields was also characterized. Finally, the severity, spatial uniformity, repeatability, and time-dependency of the MR effect were also examined. The knowledge gained through indentation and tribology experiments as well as through roughness characterization of these MREs will lead to the design of new stimuli responsive materials that enable more accurate study of dynamic, biological systems.
4:15 PM SB01.02.08
Twisted Shape Memory Nanocomposite Fibers Jinkai Yuan1, Wilfrid Neri1, Cécile Zakri1, Pascal Merzeau1, Karl Kratz2, Andreas Lendlein2,3 and Philippe Poulin1; 1Ctr de Recherch Paul Pascal, France; 2Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Germany; 3University of Potsdam, Germany

Macroscopic rotating engines powered by electricity or fuel are very common devices that are generally used to produce mechanical energies. However, it is very difficult, to integrate them into microdevices. Making high-speed and strong miniaturized engines with simplicity, robustness and low cost is always very challenging. Up to now, the strongest rotary motors ever reported are based on the concept of twisted fibers. [1] The concept of twisted fiber can actually be used to develop rotary motors by involving several mechanisms, such as entropic elasticity of polymer chains, [2] solvent swelling in CNT yarns,[3] or the expansion/contraction of GO via water adsorption and desorption.[4] Here, we study the shape memory effect by twisting polymer fibers and explore their application for strong engines.

To make strong microengines, it is necessary to reinforce the torsional properties of polymer fibers by inclusion of nanoparticles. We prepared carbon nanotube (CNT)- or graphene oxide (GO)-doped polyvinyl alcohol (PVA) fibers by using wet-spinning method. As compared to pure PVA fiber, CNT and GO nanosheets have nearly the same reinforcement efficiency on the tensile properties. However, GO nanosheets have more significant effect on the improvement of torsional properties because of its unique two-dimension nanostructure. We used such strong GO fiber to prepare torsional motors. By measuring the recovered angle against an applied constant torque, we achieved a maximum generated energy density as high as 2800 J/kg. To our knowledge, this is actually the first report of the use of graphene to reinforce torsional properties of polymer composites and the greatest energy density observed in rotary motors.


4:30 PM SB01.02.09
Density Functional Theory Calculation Study of Two-Dimensional Electromechanical Actuation Materials
Zhe (Jefferson) Liu; The University of Melbourne, Australia

Miniaturization of electromechanical devices will bring a revolution to humanity in the coming decades synonymous with the effects of miniaturizing electronic devices in those previous [1]. They promise and deliver a myriad of applications within industry, including those within the automotive, electronics, aerospace, environmental, and defence. An electromechanical actuator — a device that converts electrical energy to mechanical deformation or motion — is the core component of many such devices. Consequently, research interrogating mili-, micro-, and nano-actuation has, and will continue to become increasingly essential.

In this talk, I will first present a quick overview of my team's density functional theory based computational materials design for high-performance two-dimension (2D) actuation materials [1-5]. 2D materials have a combination of several desirable properties for actuation at a small scale, e.g., atomistic thickness, excellent mechanical strength and flexibility, superior electronic properties, and excellent tunability [6,7]. Various actuation mechanisms are explored in our studies, such as piezoelectricity, electroactive, quantum mechanical effect, and shape memory effect. We will use several material systems to demonstrate these different actuation mechanisms briefly.

My presentation will focus on the shape memory effect (SME) of 2D materials [2-3]. Shape memory materials (SMM) have a unique feature of programmability. This stimulates novel device design concept, so-called material-as-machine, in which SMM can be programmed for actuation/motion following a pre-determined sequence, just like machines but with higher intelligence and flexibility whereby the materials can sense and react accordingly. This concept is particularly appealing at small length scale. However, the conventional shape memory alloy will lose its reversible martensitic phase transformation (origin of the shape memory effect) below a critical size (4 – 60 nm).
Our recent study discovered a set of promising 2D shape memory materials. The physical mechanisms of their SME are fundamentally different from conventional SMMs. The external stimuli to trigger the shape memory behaviour are also different from conventional SMMs, i.e., electric field, charge doping, and mechanical force, versus the thermal field. These new stimuli will enable quick response (up to GHz) and precise control (down to nm), which are highly desirable for actuation devices at small length scale.

References

4:45 PM SB01.02.10
Monolayer Studies on the Interplay between Cross-Linking and the Degradation Kinetics of Biomaterials
Rainhard Machatschek1, Burkhard Schulz1,2 and Andreas Lendlein1,2; 1Helmholtz Zentrum Geesthacht, Germany; 2University of Potsdam, Germany

Improving the state of the art of treatments in regenerative medicine demands for materials that are capable of accomplishing multiple tasks, e.g. providing mechanical support while releasing a drug and then vanishing from the body. Such highly multifunctional materials require distinct properties which are achieved by tailored molecular architectures. Mechanical properties and thermal transitions are adjusted by e.g. joining different building blocks. Cell recognition motifs can be provided by grafting functional side chains or modifying chain-ends, drug loading capability enhanced by strategically placing functional groups to optimize the binding energy between drug and matrix. Cross-linking is a common approach to create polymer networks capable of forming hydrogels or to obtain rubber-like materials. However, while the material properties are a result of the synthesis and the processing of the material, functionalities arise from its interaction with the environment. For example, a hydrogel requires the presence of water and a cell binding motif is useless without cells. Quite often, the different functions are also not orthogonal in a sense that one environmental interaction can trigger multiple functionalities. For example, the swelling of a material in water triggers both drug release and degradation. Ensuring that all material functions are executed as intended therefore requires an understanding and a holistic prediction of the material behavior when responding to a stimulus. Especially predicting material degradation, which has a drastic impact on all material properties and therefore also functions, remains a great challenge. Without such a prediction, designing a biodegradable multifunctional material with a specified lifetime is only possible on an empirical basis.

To support the predictive design of multifunctional materials, a theoretical model for the interplay of cross-linking and molecular degradation kinetics is presented. It is elaborated how the degree of crosslinking affects the degradation kinetics of macromolecules. This model also predicts the decrease of the degree of cross-linking with proceeding degradation in dependence on the molecular fragmentation mechanism, which could be e.g. a random fragmentation or a preferential cleavage of certain bonds. Using the established theories of rubber elasticity, the evolution of the material’s mechanical properties can be deduced from the degradation models. Such an analytical model provides a qualitative understanding for the impact of cross-linking related molecular parameters on the material behavior during degradation. Taking into account the inhomogeneous microstructure of processed, real-world materials and the complex geometries of medical implants, a lifetime prediction of multifunctional medical devices will require multiscale computational simulations. Moreover, all models rely on
input parameters such as reaction rate constants, which have to be determined experimentally. The Langmuir monolayer degradation technique is an established way to determine these parameters for materials degrading in aqueous environments in experiments that take only a few hours\(^1\). Here, it is presented how the technique was used to verify the analytical models and to determine the kinetic parameters for poly(ε-caprolactone) based networks which were prepared \textit{in-situ} on the Langmuir trough. In such a system, the cross-linking density can be varied by compressing the layer, and the decrease of the cross-linking density during degradation is registered as a decrease of the storage modulus by means of interfacial rheology.

**Literature**


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**SB01.03.01**

A Dual-Function Collagen-Based Scaffold with On-Demand Drug Delivery for Diabetic Wound Healing

Tauseef Ahmad\(^1\), Ronaldo do Amaral\(^{1,2}\), Renuka Sitram\(^1\), Brenton Cavanagh\(^1\), Fergal J. O’Brien\(^1,2,3\) and Cathal J. Kearney\(^1,3\); \(^1\)Royal College of Surgeons in Ireland, Ireland; \(^2\)National University of Ireland Galway, Ireland; \(^3\)Trinity College Dublin, Ireland

About 20% of the over 400 million diabetic patients will develop diabetic foot ulcers (DFUs) in their lifetimes. DFUs are associated with high incidences of morbidity and mortality that includes higher lower-limb amputations rates, and worse post-amputation survival rates than breast and prostate cancers. A reason for the recalcitrant nature of these wounds is that sequential physiological healing is absent in DFUs. By restoring the normal temporal healing profile using signalling factors, we aim to reinstate co-ordination of biological processes to drive enhanced healing. To achieve this, we are developing a tissue engineering device with dual functionality: (1) ultrasound-responsive alginate microparticles for on-demand delivery and (2) a collagen-glycosaminoglycan (CG) scaffold that houses these particles and acts as a regenerative template for the cells. This device would be capable of delivering bioactive agents on-demand and by mimicking nature’s temporal profile for angiogenesis (e.g., sustained vascular endothelial growth factor (VEGF) and delayed platelet-derived growth factor (PDGF) signalling), we hypothesise that sequential healing of DFUs can be effectively driven.

To develop the system, PEGylated gold nanoparticles (PEG-AuNP) were incorporated into combinations of high (~250kDa; 0 – 1%) and low (~70kDa; 0 – 1.5%) molecular weight alginate. Alginate microparticles were generated by electrospaying (11kV) and ionically crosslinking using CaCl\(_2\) (30mins, 100mM). A CG slurry was blended using type I bovine collagen (5 mg/ml) and chondroitin-6-sulfate (0.44 mg/ml) in 0.05 M acetic acid solution. The microparticles (20% final volume) were mixed with the CG slurry and cast in steel trays for freeze-drying. SEM images revealed local disruption of pore structure neighbouring the microparticles but an open interconnected porous structure in the remainder of the scaffold. Scaffolds were crosslinked (by UV, dehydrothermally or by carbodiimide chemistry). Ultrasound was applied (0 – 35% amplitude) to trigger AuNP release. Up to 50% AuNPs was released in <5 min using ultrasound; baseline release of AuNPs was negligible. With the proof-of-concept confirmed using model nanoparticles, we next tested a bioactive nanoparticle in the device. PDGF conjugated PEG-AuNPs were developed and their bioactivity confirmed using a mesenchymal stem cell (MSC) and fibroblast proliferation assay. PDGF-AuNPs enhanced cell proliferation by 30%. Optimum PDGF dose and timing was assessed using a suite of \textit{in vitro} vascularisation assays (e.g., vessel formation in the CG scaffolds). When added at delayed time-points, 25ng/ml PDGF stabilised vessels in CG scaffolds; however, vessels regressed when PDGF was not added or when added at earlier time-point. Finally, PDGF-PEG-AuNP doped CG scaffolds were fabricated and subjected to ultrasound. PDGF functionalised AuNPs could be successfully released from within the scaffolds and retained their bioactivity (cell proliferation assay). To protect the structural integrity and regenerative potential of the CG scaffolds from ultrasound, a bilayered system was fabricated with alginate-PDGF-AuNPs doped into a
sacrificial CG scaffold annealed to a main regenerative CG scaffold. These results demonstrate the ability of this alginate-doped collagen-GAG scaffold to facilitate cell seeding and to locally deliver drugs on-demand. Future work will demonstrate the devices’ full potential to coordinate angiogenesis and direct healing.

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SB01.03.03
Personal Thermal Management via Engineered Optical and Evaporation Phenomena 
Matteo Alberghini¹, Matteo Fasano¹, Yi Huang², Luis M. Lozano², Francesco Signorato¹, Eliodoro Chiavazzo¹, Gang Chen², Pietro Asinari¹ and Svetlana V. Boriskina²; ¹Politecnico di Torino, Italy; ²Massachusetts Institute of Technology, United States

The increasing energy demand worldwide must be addressed with sustainable technologies to mitigate further climate change. In particular, the energy employed for heating and cooling covers 79% of the total energy consumed in the European households. Both reducing the cooling demand and improving the efficiency of the energy conversion processes could limit the environmental impact of building cooling. On the one hand, novel materials for personal thermal management can be adopted to shift upwards by few degrees the set-point of room temperature, therefore reducing the cooling load at fixed thermal comfort. On the other hand, the energy consumption of traditional vapour-compression systems can be significantly reduced by achieving sub-ambient temperatures in the condenser thanks to passive coolers.

Recent developments in materials science allowed to reinvent two long-standing passive cooling technologies, namely radiative and evaporative cooling, thus increasing their performances and expanding their application field. We combine the complementary evaporative and radiative cooling features to overcome the intrinsic limitations of conventional polymeric textiles for personal thermal management. Polymeric films and fabrics with tailored optical properties have already been proposed for daytime radiative cooling, reaching a specific cooling capacity up to 100 W m⁻² and acceptable wearability. These composite organic-inorganic nanoparticle-filled polymer materials combine strong spectral selectivity of nano-particles with unique lateral heat-spreading capability of semi-crystalline polyethylene films and textiles. However, their radiative cooling potential is strongly limited by the ambient humidity; additionally, these textiles are not yet optimised to favour the typical skin cooling by sweat evaporation.

We optimize the material, sizes and plot of the fabric to enhance both radiative and evaporative cooling performance via multi-physical modelling, which considers water wicking and evaporation, vapour permeation and spectrally selective optical properties. The optimized multi-functional textiles, including dual-mode, reversible or ambient-responsive materials, could be employed for more effective personal thermal management, thus allowing a substantial reduction of the economic costs and environmental footprint of building cooling.

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SB01.03.04
Hierarchical Mushroom-Like Re-Entrant Arrays for Superomniphobic Surfaces
Joon Hyung An, Jiseong Choi and Seongmin Kang; Chungnam National University, Korea (the Republic of)

In this work, we present a robust hierarchical mushroom-like structured surfaces by using novel and low-expertise fabrication method. The microscale re-entrant mushroom-shaped structures were fabricated on a substrate by a replica molding technique using a polydimethylsiloxane (PDMS) and an ultraviolet (UV)-curable polyurethane acrylate (PUA) containing inorganic nanoparticles. The tiny inorganic particles were used to make nanoroughness on the top of the re-entrant structures by using plasma polymer etching process. Finally, we have successfully obtained hierarchical mushroom-shaped structures without any structural failure, and the nano/micro multiscale re-entrant features demonstrated remarkable superomniphobic properties repelling water and oil. It is expected that the hierarchical structures are to be applied in a wide range of applications requiring self-cleaning and antifouling surfaces.

SB01.03.05
Multifunctional Ultra-Thin Crosslinked PEDOT:PSS Films for EMI Shielding and Organic Electronics
Pritom J. Bora, Amith G. Anil, Praveen C. Ramamurthy and Sankaran Subramanian; Indian Institute of Science,
PEDOT:PSS conducting polymer films have found numerous application in organic electronic systems, as sensors, hole transport materials, transparent conducting electrodes, flexible electronics, thermoelectric systems etc. However, stability of the thin films against moisture remains a bottleneck for extending their application potential. Researchers have adopted crosslinking as one of the strategies to improve moisture stability and mechanical strength, although in many cases this adversely affects the conductivity of the obtained films. Recently, a crosslinking method was reported to make moisture stable PEDOT:PSS films wherein the crosslinker also acts as a dopant, improving the electronic properties of the film. In this work, a similar system with simpler composition is reported to produce highly flexible, free standing, water resistant, ultra-thin (12 \pm 1 \, \mu m) films of PEDOT:PSS exhibiting a superior electrical conductivity of 59300 \, S\, m^{-1} compared to pristine PEDOT:PSS film(18 \, S\, m^{-1}) . These films also displayed excellent electromagnetic interference (EMI) shielding behaviour as opposed to pristine PEDOT:PSS films. A 12\pm 1 \, \mu m thick crosslinked PEDOT:PSS film exhibited an average EMI shielding efficiency (SE) of 40 \, dB which is adequate for commercial applications. On the contrary, EMI shielding efficiency of pristine PEDOT:PSS films is only 20 \, dB. The absolute SE of crosslinked PEDOT:PSS film is calculated to be 51480 \, dB\, \text{cm}^2\, \text{g}^{-1}, highest ever reported for an all polymer EMI shielding system. The absorption predominant SE originates from the coarser morphology and interpenetrating layers generated by cross-linking. Tensile strength testing with a micro UTM revealed that crosslinked films could bear double the amount of stress compared to pristine films. The outstanding moisture stability combined with high electrical conductivity of the crosslinked films makes them potential candidates for encapsulant and back electrode of organic photovoltaic systems. Moisture stability and transmission characteristics of these films are currently being investigated. In addition, their higher electrical conductivity also makes them suitable for active electrode materials in sensor applications for environmental monitoring, wherein their stability in water also plays a crucial role. Application potential of the films in these avenues are currently under scrutiny.

**SB01.03.06**

**Non-Destructive Investigation of Dispersion, Bonding and Thermal Properties of Emerging Polymer Nanocomposites Using Close-Up Lens Assisted Infrared Thermography**

Ali Ashraf, Nikhil Jani, Francis Farmer and Jennifer Lynch-Branzoi; Rutgers, The State University of New Jersey, United States

Polymer nanocomposites possess unique sets of properties that make them suitable for applications, including structural materials, aerospace, flame retardant material, electromagnetic wave reflector, strain/solvent sensor, thin film transistor, flexible display, and many more.\(^1\) The properties of these nanocomposite are dependent on nanofiller dispersion and bonding with polymer matrix (i.e. particle-matrix interaction). Thermal imaging is a non-destructive method that may be used to gain insight into dispersion and particle-matrix interaction.\(^2\) Infrared (IR) radiation emitted from these nanomaterial polymer composite depends on the emissivity of the individual components. In addition, during flash heating and cooling, thermal conductivity of components in the nanocomposite can influence IR radiation being emitted. Moreover, during in-situ incorporation of filler with polymer and during curing of thermostet nanocomposites, exothermic and endothermic reactions representing bond formation can be investigated with IR camera\(^3\). Even for nanoscale phenomenon as electron transport and energy dissipation, nanomaterials like graphene can be characterized by IR imaging\(^4\). We have used an economical mid wavelength IR camera Fluke RSE600 equipped with a close up macro lens and algorithm based on MATLAB image processing toolbox to analyze dispersion, voids, thermal diffusivity and energy dissipation of patented graphene polymer nanocomposite materials (G-PMC)\(^5\) in micron scale. These G-PMCs can act as a standard material to determine the potential of our IR thermography technique due to their homogeneity and lack of impurity due to unique fabrication process. Thermal diffusivity and dispersion of nanoparticles in our G-PMCs was estimated after irradiation with a xenon flash lamp by spatially mapping transient IR radiations with time from different G-PMCs using a Fluke RSE600 thermal imager. Our thermography technique was used to study nanomaterial agglomeration, energy dissipation or thermal transport during sensing application of G-PMCs. Interpretation of the thermal image will be verified by performing scanning electron microscope (SEM), Rheometry, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). We believe this low cost, fast, non-destructive technique will provide valuable insight into functional polymer nanocomposite fabrication and corresponding mechanical, electrical, and thermal properties.

**SB01.03.07**

**Effective Thermal/Electrical Conductivities of Three-Dimensional Cellular Architectures Based on Triply Periodic Minimal Surfaces**

Juveiriah M. Ashraf, Dong-Wook Lee, Oraib Al-Ketan, Aliaa Abou-Ali, Kin Liao and
Cellular structures based on Triply Periodic Minimal Surfaces (TPMS) are structures in three-dimensional (3D) space with a locally net zero curvature and a unique architecture that locally minimizes the surface area. They can be divided into two main categories; solid and sheet networks. The special morphology of TPMS, along with their low density and yet high surface area has led them to demonstrate enhanced electrical, thermal, and mechanical properties. The objective of this paper is to computationally evaluate the effective electrical and thermal conductivity of three cubically symmetric TPMS cellular structures – namely Gyroid, IWP and Diamond over a range of relative densities and morphological parameters using the Finite Element Method (FEM). Particularly, it compares the solid cellular structures with each other and investigates the inter-relation between the solid and sheet networks. Results show the effective conductivity to vary linearly with increasing relative density for the three shapes, with the sheet networks demonstrating higher conductivities than the solid networks at all relative densities. The IWP and Gyroid exhibit similar trends while the Diamond shows a lower conductivity for the same values of relative density. Among all the structures, the IWP presented the highest value of 0.17 for the sheet networks and 0.13 for the solid networks, both at a relative density of 25%. The second parameter that is investigated in this study is varying the morphological parameter c-value, which changes the ratio of the two volumes divided by the minimal surface, and at a critical value, alters the geometry such that TPMS-based tube-networks are formed. As observed for the Gyroid, at the same relative density, increasing the c parameter decreases the effective conductivity of the structures due to a decreased surface area available for heat transfer. The effect of varying the c value for the Diamond and IWP tube-networks show similar trends to the Gyroid. The findings of this work are to be used as a validation for measuring the thermal and electrical conductivities of TPMS-based graphene 3D lattices synthesized experimentally where the minimal surfaces of polymer material will be fabricated using additive manufacturing, coated with graphene oxide and subsequently etched via thermal methods to obtain pure 3D graphene architectures.
engineering due to the possibility of allying, through the appropriate choice of a polymer matrix and inorganic filler, biocompatibility, bioabsorption and mechanical resistance properties to be compatible with bone structures. The rapid prototyping technique (3D printing), via fused deposition modelling, enables the fabrication of bone implant structures with complex shapes at a suitable scale. The aim of this work was to obtain nanocomposites filaments, composed by PLA (poly (lactic acid) and nanohydroxyapatite (nHA). PLA is a polymer of low density, great biocompatibility and biodegradability, compatible to be applied for bone reconstruction strategies. nHA is toxicless, non-inflammatory ceramic, with high osteointegration capacity due to the Ca-P composition, similar to bones. PLA2003D (NatureWorks) were cryogenically ground and mixed with powder nanohydroxyapatite (Sigma-Aldrich) at proportion PLA:HA 70:30. The powder mix were extruded at 180°C to obtain filaments with 1.75 mm diameter. A Clever CL1 printer was used for fused deposition modeling (FDM) of samples at 175°C. Compression strength samples geometry were settled at H:20 W:10 and T:10 mm and for Scanning Electron Microscopy (JEOL microscope running at 15 kV) the geometry were 4 mm of diameter and H:1mm, which was cryogenically fractured. The hydroxyapatite was distributed homogeneously with effective interaction between the polymer matrix and ceramic material. The compression behavior was similar to those reported in the literature on bionanocomposites. However, the bionanocomposite demonstrated higher mechanical properties in comparison with pure PLA.

SB01.03.10
Titanium Aluminide (MAX Phase) Thin Films for Optoelectronic Applications Abhijit Biswas, Sachin Kumar Singh, Swati Parmar, Arundhati Sengupta and Satishchandra B. Ogale; IISER Pune, India

Recently, research in layered ternary carbides has attracted immense interest as the materials show both ceramic and metallic properties. Here, we have grown hexagonal layered Ti₃AlC₂ (MAX) thin films on structurally compatible c-Al₂O₃ substrates by pulsed laser deposition (PLD) and studied their physical properties and potential applicability. Structural and morphological characterizations by x-ray diffraction (XRD), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy confirm the high crystallinity with low surface roughness of < 1 nm. We have elucidated the strain in the films as a function of layer thickness using Raman spectroscopy. Resistivity (ρ) of bulk 80 nm film is found to be ~50 µΩ-cm at T = 300 K, which increases only to a bit higher value of ~60 µΩ-cm at T = 5 K. The incredibly low temperature coefficient of resistance (TCR) indicates that the electronic transport in this unique system is marginal between metallic and semiconducting modes of transport. Moreover, the bulk film is nonmagnetic with a positive magnetoresistance (MR) ∝ B², attributed to the Lorentz contribution. Surprisingly, with reducing the film thickness, even the ultrathin 2 nm film shows sheet resistance (Rₛ) only of ~700 Ω/square sheet at T = 300 K. Importantly, this highly conducting ultrathin 2 nm film transmits ~75% light in the visible wavelength range, making it suitable as an excellent transparent conducting bottom electrode for several optoelectronic applications. Furthermore, when tested for Triboelectric Nano-generator (TENG) device application, the bulk Ti₃AlC₂ films show an open circuit voltage (Vₒc) ~30 V when grown on c-Al₂O₃ and ~80 V, when grown on flexible Kapton substrate.

SB01.03.11
Programmable Soft Matter—From Active Membranes to Self-Replication Alexander Boeker; Fraunhofer Institute for Applied Polymer Research - IAP, Germany

This contribution discusses various approaches to create programmable soft matter either by directly incorporating functional biomolecules into polymeric materials or by transferring concepts conceived by nature to fully artificial materials.

The first approach involves the synthesis of polymer-protein conjugates and their self-assembly to form biofunctional membranes [1-3]. We introduce a new strategy using engineered natural protein channels decorated with polymer chains followed by self-assembly at a fluid interface to form ultrathin, permeable and highly selective membranes. A similar strategy can be used to incorporate sensitive enzymes into a fluid-like polymer membrane environment, thus allowing to almost completely retaining their initial activity after immobilization and even boosting their temperature stability.

The second example is aiming towards creating artificial materials systems that are able to self-replicate. To achieve this, an indispensable prerequisite is the multi-directional control of interactions between the building blocks of materials. Thus, we aim to create a new class of multi-patch colloidal particles via an advanced micro-contact printing technique yielding patches of different chemical or physical functionalities. The new production process
allows precise control over the patch location and chemistry and thus also gives particles that go well beyond known ABA- or ABC-type Janus particles [4-7].


**SB01.03.12**

**Comparison of Experimental and Modeled EMI Shielding Properties of Periodic Porous Composites** Avi Bregman; University of Michigan, United States

With the advent of massive telecommunications networks and the expansive development of wireless electronics operating in the gigahertz range, “electromagnetic pollution” has risen to unprecedented levels. To mitigate the effects of electromagnetic interference (EMI) from spurious radiation, improved EMI shields are needed. Shields composed of solid metals or metal-based coatings oftentimes exhibit high shielding efficiency (SE) but have issues such as poor wear and corrosion resistance and high rigidity. Foaming of these materials has demonstrated higher broadband EMI absorption as compared to the non-foamed material due to minimization of the air-to-shield impedance mismatch. However, the pore morphology inside the foam is highly dependent on the specific foaming conditions and materials involved. The final pore morphology can drastically affect EMI shielding efficiency resulting in significant resources being spent on optimization of the foaming process. Herein we present an approach that relies on the introduction of periodically placed air-filled pores into conducting polymer composites in order to reduce material requirements and maximize microwave absorption. The presented research will demonstrate experimental validation of a novel route for the development of highly efficient EMI shields based on a magnetically functionalized graphene composite material. First, constitutive electromagnetic properties of bulk composite material are retrieved from scattering parameter measurements. The constitutive properties are manipulated through variable addition of magnetoelectric filler material. Second, electromagnetic properties are utilized in finite element method-based optimization to establish optimal periodic geometry that have high EMI shielding for a desired range of frequencies and incidence angles. Finally, optimized geometries are realized via compression molding. We demonstrate the validity of this approach using two different polymer systems, one of which includes a segregated conductive network.
In Vitro Antitumoral Activity of the Black-Tailed Rattlesnake (*Crotalus molossus*) Encapsulated in Chitosan-TPP-Alginate Nanoparticles
Alexel J. Burgara-Estrella, Jorge Jimenez-Canale, Jose A. Sarabia-Sainz, Daniel Fernandez-Quiroz and Martin R. Pedroza-Montero; Universidad de Sonora, Mexico

Cancer is one of the first causes of death within developed countries, and still on the rise. Nanomedicine offers novel tools to treat these types of diseases by implementing nanocarriers that diminish secondary noxious effects and enhance therapeutic properties. Herein, we prepared biocompatible and biodegradable polymeric nanoparticles (NPs) through the ionotropic gelation process in order to encapsulate crude venom from the Mexican Black-Tailed rattlesnake (*Crotalus molossus*). Low molecular weight (LMW) Chitosan (Cs) was used and Tripolyphosphate (TPP) alongside LMW sodium alginate (ALG) were utilized as crosslinking agents. Cs-TPP-Venom-ALG and Cs-NaCl-TPP-Venom-ALG NPs presented a size distribution of 1284 ± 80.23 nm and 504.7 ± 22.3 nm, with a surface charge of 61.6 ± 2.48 mV and 41.0 ± 1.66 mV, respectively. NPs Surface membrane interaction with T-47D breast cancer cells was demonstrated by fluorescence microscopy. T-47D treated with NPs without venom had no significant cytotoxicity effect, while cells treated with NPs with venom showed lower cell viability. This justifies pursuing the strategy of nanoencapsulating venom toxins, in order to follow new therapeutic strategies against various malignant cells.

Anti-Biofouling Coating for Orthopedic Implants through Lubricating Micro-Nano Structured Surface
Kyomin Chae1, Woo Young Jang2, Kijun Park1, Yeontaek Lee1, Jin Hyeok Lee2, C. K. Lee2 and Jungmok Seo1; 1Yonsei University, Korea (the Republic of); 2Korea University, Korea (the Republic of)

Orthopedic implants are widely used for diverse orthopedic treatments to sustain the broken bone and substitute for the worn joint. However, conventional implant materials are vulnerable to bio-contamination, which might cause the bacterial invasion into the wounded area and even lead to postoperative infection after the treatments. Inspired by the slippery surface of the Nepenthes pitcher plant, we have developed a durable anti-biofouling surface on the orthopedic implant [1]. To fabricate the anti-biofouling surface, we first etched the implant material in HF and HNO3 solutions to form the micro/nano roughness on the surface [2]. After that, perfluorocarbon-based self-assembly monolayer (SAM) coating was applied to the etched surface, which allows the surface to hold the thin film of medical-grade perfluorocarbon-based lubricant. The developed surface exhibited extreme liquid-repellency against diverse liquids from low surface tension liquids like alcohols to viscous liquids like blood. We further demonstrated that the developed surface prevented the formation of biofilm, and the attachment of biochemical substances and calcium on the implant in vitro. The developed surface shows less than 1% attachment of bacteria and all biochemicals in comparison to the untreated surface. In addition, we confirmed that the property of anti-biofouling is maintained even after repeated physical damages applied in a surgical operation. Moreover, even though bacteria exposed implant was used in orthopedic treatments in vivo, we confirmed that the developed surface showed no tendency to infection over 4 weeks experiment. However, treatments using the bare and superhydrophobic treated implant caused severe infection even delaying bone regeneration rates to less than 20% compared to the developed implant. We envision that the developed surfaces with extreme anti-biofouling property and mechanical durability can be applied to infection-free orthopedic treatments.

Acknowledgement
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References

Liposome-Based Nanosensors for Biological Sensing
Rona Chandrawati; University of New South Wales (UNSW Sydney), Australia

The detection of target biological molecules in a specific and sensitive manner is critical for the development of
diagnostic devices. Nanoparticle biosensors have the potential to enhance or supersede current analytical techniques, and their introduction could have a great impact in clinical practice.\(^1\) Lipid assemblies in the form of spherical liposomes have played a key role in the design of biosensing assays.\(^2\) Liposomes offer advantageous physical and chemical properties as biosensors; they have a large internal cavity for encapsulation of signal markers and a high surface area for conjugation of recognition elements that allows for the detection of a wide variety of biomolecular analytes. This talk will describe a number of examples of liposomes used for biosensing applications. We recently developed an assay for the selective and sensitive detection of cancer biomarkers,\(^3\) influenza biomarkers (miRNA),\(^4\) and food spoilage indicator.\(^5\) This system does not require washing, amplification or separation steps, and present a unique sensing mechanism inspired by nature. By tuning the recognition elements, this platform may be used for sensing other biological targets, including proteins, drugs, and cells.

References:

SB01.03.16
Scalable Fabrication of Resonant Sensors and Applications in Wireless Reporting of Soft Material Deformation Sadaf Charkhabi, Yee Jher Chan, Doh Gyu Hwang, Sean T. Frey, Michael D. Bartlett and Nigel F. Reuel; Iowa State University, United States

This work focuses on the development of kirigami-patterned, passive resonant sensors that operate in the short-wave radio frequency range (1-150 MHz) to wirelessly monitor the deformation of materials in closed systems. At first, the sensors are rapidly prototyped out of Pyralux\textsuperscript{©}, a copper-coated polyimide substrate. The Archimedean spiral design is masked by drawing on the copper with an indelible marker (using a craft XY plotter) and the unwanted copper is etched away with hydrochloric acid and hydrogen peroxide. The samples are then rinsed with acetone to release the mask, coated with polydimethylsiloxane (PDMS), and laser-cut to add the kirigami-inspired pattern to the sensor. The onion ring-shaped resonant sensor is wirelessly coupled to external, two-loop reader antennas to report the extent of material deformation. The reader antennas are connected to a benchtop vector network analyzer (VNA) which can capture both the reflection and transmission scattering parameter signals. We have defined the sensor response as the resonant frequency, which is the minimum of the sigmoidal feature in the transmission scattering signal (\(S_{21}\)). The resonant frequency of the sensor is modulated by changing the physical parameters of the resonator such as coil length and spiral pitch. The resonant frequency of the sensors are tracked over an extension range of 0-22 cm and a major shift in the resonant frequency is observed. For instance, a 90 MHz shift in the sensor response is observed by stretching the sensor to 10 cm. Moreover, the effect of the pitch size of the resonator on the sensor’s linear span and gain value (MHz cm\(^{-1}\)), which is defined as the linear slope of the resonant frequency-stretch curve, is studied. In order to confirm the repeatability of the gain of kirigami resonant sensor, a 96 cycle hysteresis experiment is conducted for sensors with different pitch sizes. Furthermore, the coated sensors are placed in a pipe to test the ability of kirigami resonators to wirelessly report different flow rates. The sensor with 1 mm PDMS coating exhibits the highest flow gain value (0.17 MHz.s mL\(^{-1}\)) and largest linear span (10–100 mL s\(^{-1}\)). Finally, since Pyralux\textsuperscript{©} is a relatively expensive substrate and the etching process produces unwanted waste, we demonstrate scalable, sustainable fabrication of resonant sensors with screen printing using conductive silver paste. The resonators are characterized in terms of their electrical and magnetic properties (e.g. resistance, quality factor) as well as their physical properties (using microscopy). Also, the quality of screen-printed resonators is compared to copper-etched and ink-jet printed resonators. We will also discuss current work to print on soft, compliant materials such as Tegaderm\textsuperscript{™} (3M product). In conclusion, flexible, passive, kirigami-patterned resonant sensors can be fabricated for many proposed applications in healthcare, motion and deformation tracking, virtual reality, and soft robotics.

SB01.03.17

Magnetic Field Driven Buckling in Architected Magnetoelastomers

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Magneto-Active Elastomers (MAEs) are an important class of soft, shape-recoverable materials that exhibits a stiffness increase in response to an applied magnetic field. Using magnetic field to tune material stiffness is advantageous due to the fast, remote and reversible switching, which is relevant for applications in areas of soft actuators, adaptive vibration dampers and acoustic filters. 1D and 2D architected MAE composites, such as laminates and periodic inclusions, have been predicted to possess novel mechanical instabilities, due the spatial distribution of stiffness mismatch and the ability to dynamically tune the mismatch with magnetic field. We fabricated MAE composites using a commercial silicone as the non-responsive soft matrix and a silicone loaded with iron microparticles for the stiff, magnetoactive regions to experimentally demonstrate these concepts. The silicone matrix formulation was modified to increase the stiffness contrast between the soft encapsulating matrix and the stiff MAE regions, including tuning of the crosslinker to polymer ratio, and addition of silicone oil to further reduce crosslinking. 3D printed templates were used as molds to construct laminates and 2D periodic MAE architectures. Magnetic field induced stiffening was characterized using a custom compression test jig that was designed and 3D printed to systematically load the specimen within a 2 Tesla electromagnet. The study provides experimental feedback on the sensitivity of the buckling strain to experimental specimen sizing/edge effects and provides broader insight on the practical integration of MAE instabilities into functional devices.

SB01.03.18

Stretchable Solid-State Electrolytes Based on Butyl Rubber -Poly(ethylene oxide) Graft Copolymers

Yiting Chen1, John Trant1, Elizabeth Gillies2, R. Stephen Carmichael1 and Tricia B. Carmichael1; 1University of Windsor, Canada; 2Western University, Canada

The emergence of stretchable and wearable electronics raises a strong demand for stretchable electrolyte materials. Compared to the traditional liquid electrolyte, solid-state electrolytes (SSEs) are non-flammable and have improved mechanical and thermal stability, making them promising for applications in advanced stretchable electronics such as lithium batteries, supercapacitors, and light-emitting electrochemical cells (LEECs). Current research activities in SSEs have focused on improving the electrochemical stability and ionic conductivity of ceramic, polymeric or composite materials to replace flammable liquid electrolytes. Although ceramic electrolytes exhibit high ionic conductivities of the order of ~ 10-3 S/cm, they fracture easily and typically exhibit a high interfacial resistance. Polymeric electrolytes are often complexes of lithium salts and high-molecular-weight polymers such as polyethylene oxide (PEO). However, these polymers typically have low conductivities at room temperature, typically ~ 10-5 S/cm.1,2 Although adding plasticizers or liquid electrolyte into polymer electrolytes improves the ionic conductivity at room temperature, these composite electrolytes generally exhibit poor mechanical stretchability. For advanced stretchable electronics, mechanical performance becomes a critical performance consideration since SSEs need to tolerate repeated volume change during cycling and survive external forces during use. Thus, it remains challenging to fabricate SSE materials that have robust mechanical properties without sacrificing ionic conductivity. Here, we present a new stretchable SSE that shows both high mechanical performance and high ionic conductivity at room temperature using a mixture of an elastic graft copolymer and lithium triflate salt. This elastic graft copolymer has a butyl rubber backbone that provides mechanical flexibility, with PEO sides chains that complex lithium salts to provide ionic conductivity. The resulting SSE provides a superb stretchability of >100% with an ionic conductivity of 1.33 x 10-5 S/cm, which is comparable to that of PEO based SSEs. We demonstrate the application of this new stretchable SSE in iridium complex-based LEECs. LEECs fabricated using a composite blend of iridium complex and the SSE showed one order of magnitude faster light emission response to applied voltage compared to LEECs fabricated using the pristine iridium complex alone, highlighting the higher ionic conductivity of the composite. In addition, the high mechanical stretchability of the SSE provides stretchable and durable LEECs that exhibit a negligibly changed peak radiance under repetitive strain. This new copolymer SSE, with outstanding mechanical properties and ionic conductivity similar to state-of-the-art polymer-based
electrolytes, opens up a new opportunity in high-performance stretchable electronics.

**SB01.03.19**

**Design and Characterization of Zwitterionic Materials to Address Long-Standing Challenges at Biointerfaces**

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Material-associated biofilm, blood coagulation, foreign body response, and biofouling have significant impacts on a variety of applications, including biomedical devices, biosensing, marine industry, etc. To fill the needs of a broad spectrum of applications, materials with superior antifouling property and tunable properties, such as anti-microbial, conducting, mechanical, optical properties, are urgently needed. Countless efforts have been devoted to developing materials that can effectively address these long-lasting challenges. Among these emerging materials, zwitterionic materials have demonstrated superior anti-fouling properties resisting proteins, mammalian cells, and microbes, and better biocompatibility compared to other anti-fouling materials. Although existing zwitterionic polymers exhibit unseen antifouling property at the interface, current zwitterionic materials cannot provide all desired properties, such as electron conducting, antimicrobial, pH-responsive and mechanical properties, for biomedical applications. For example, zwitterionic materials lack electronic conductivity and suffer from weak mechanical properties and lack of elastic property to function as the structural materials. Over the past ten years, we conducted a set of studies to understand the structure-function relationships of zwitterionic polymers. In this presentation, I will show you how we use the design criteria that we learned from structure-property studies to design high-performance zwitterionic materials with superior antifouling/antibiofilm, tunable mechanical, conductive and degradation properties to address the unsolved complications at biointerfaces.

**SB01.03.20**

**Facile Electrochemical Routes for the Conformal Coating of PEDOT/Au Nanoparticles on Inverse Opals as Highly-Sensitive Biosensors**

Pei-Sung Hung, Guang-Ren Wang, Tze-Ting Chiang, Tsung-Eong Hsieh and Pu-Wei Wu; National Chiao Tung University, Taiwan

Conducting polymers have received considerable attention in various fields, including electronic devices, sensors, energy materials, anti-corrosion coatings, and biomedical applications. Not only through their tunable electronic properties, but also the soft organic material nature and facile functionalization process render these materials as versatile platforms. Via the hybridization with inorganic compounds, such as metal nanoparticles (NPs), a further enhanced electrochemical properties as well as synergistic effects, could be realized. With these improvements, they can be utilized in the rapid identification of certain biomarkers for early detection of various diseases. In this work, we report a single-step fabrication route, which exploiting the simple electrosynthesis process of conducting polymers, to construct composite sensors with metal NPs incorporation. In addition to their deposition on the planar electrodes, both the deposition bath recipe and processing parameters are explored and optimized for the conformal coating on metal-based inverse opals with flexible substrates support. The composite coating on such bio-inspired 3-D nano-scaffold as the sensing layer could fully utilize the increased specific surface area and improved mass transport brought by the intriguing honeycomb structure. Meanwhile, the enclosed metal inverse opal is employed as the current collector to ensure a highly conductive pathway for signal transduction. The sensing performance for these 3-D sensors is evaluated by the selective detection of ascorbic acid (AA), uric acid (UA), and dopamine (DA). Relevant structural and compositional characterizations are conducted by SEM, EDX, XPS, and Raman spectroscopy.

**SB01.03.21**

**Electrochemical and Thermal Properties of Polymer Gel Electrolytes Based on Ionic Liquid and Organic Solvents**

Dae Hyun Cho, Keun Hyung Lee and Jeonghui Kim; Inha University, Korea (the Republic of)

Ionic liquids (ILs), or room temperature molten salts, composed entirely of low molecular weight cations and anions, have attracted great attention in a broad range of electrochemical devices owing to their physicochemical and electrochemical properties such as non-flammability, non-volatility, high ionic conductivity, and large electrochemical stability windows. The use of highly viscous ILs in electrochemical devices often limits the performance of the IL-based devices due to slow ion transport. To enhance the mechanical integrity of the liquid electrolyte, structuring polymers are often blended to form a chemically or physically cross-linked network, resulting in solid polymer electrolytes known as ion gels. However, the addition of a polymer network in ILs even
lower the ionic motion, which leads to slow response of the ion-gel-based devices to an external signal. Mixing organic solvents with ILs is an effective strategy to alleviate the issue mentioned above. In this work, we blended the four different kinds of organic solvents with the ion gels and investigated the effect of the blend composition on the electrical and thermal properties of the solid electrolytes. The electrical properties depended on the viscosity and dielectric constant of the organic solvent, whereas the thermal properties depended on the vapor pressure of the component materials. When these mixed ion gels were applied in electrochemical thin-film device, the mixed ion gel-based devices showed superior performance to the pure ion gel without organic solvents owing to the enhanced ionic motion.

SB01.03.22
Stretchable Synesthetic Sound-in-Display Electronics Based on Strain-Insensitive Silver Nanowire Electrodes
Seungse Cho, Donghee Kang, Hyejin Lee and Hyunhyub Ko; Ulsan National Institute of Science and Technology, Korea (the Republic of)

With increasing importance of human-machine interface along with the rapid growth of Internet of Things (IoT), integration of sound generation and visual display in a stretchable form of single sound-in-display device has attracted great attention to connect human with machines via a visualization of auditory system. Herein, synesthetic bimodal senses of sound and color is demonstrated by stretchable sound-in-display devices consisting of strain-insensitive silver nanowire electrodes and field-induced inorganic electroluminescent (EL) phosphor emissive layers. While sound-in-display devices embedding EL phosphors in a dielectric elastomer matrix produce the light emission under alternating-current (AC) bias, audible sound-wave is generated via an actuation of dielectric elastomer matrix along with input sound signals simultaneously. The stretchable sound-in-display devices show highly robust and reliable EL sound performance that can be repeatedly stretched and released without severe degradation due to the use of strain-insensitive silver nanowire electrodes. This study demonstrates stretchable electronics including light emission and acoustic system in a single device, which could be further expanded for the realization of sound-in-display electronics.

SB01.03.23
Thermoresponsive Smart Surfaces as Color- and Texture-Changing Sensors and Actuators
Ayoung Choe, Jeonghee Yeom and Hyunhyub Ko; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Stimuli-responsive smart materials are promising for the detection of various stimuli, such as temperature, pH, or light intensity. Under the external stimuli, the smart materials abruptly change their physicochemical properties. Above all, colorimetric smart materials have great advantages in direct detection and real-time visualization of stimuli. Here, we present a thermoresponsive colorimetric sensor based on the hybrid structure of plasmonic gold nanoparticles and thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) microgels. The color of smart hydrogel film shifts from ruby red to grayish violet with a large extinction peak shift of 176 nm in 1 second for the temperature change from 25 to 40°C. Through the analysis of color shift, the colorimetric sensor array shows a high thermal resolution of 0.2°C. Furthermore, the thermoresponsive colorimetric sensor can be stretchable up to 90% when the hybrid plasmonic microgels are embedded in a stretchable polyacrylamide. In addition, both color- and texture-tunable smart surfaces can be fabricated by using shape memory polymers (SMPs) and thermochromic dyes. We design a thermoresponsive color- and texture-changeable smart surface based on polylactic acid/polyurethane SMP and thermochromic dyes. Here, the pyramid-patterned SMPs (py-SMPs) with fluorinated silica nanoparticles exhibit thermoresponsive change of surface texture and wettability (water contact angle change from 98° to 144°), and thermochromic dye displays thermoresponsive color change. The suggested concept of smart surfaces can be extended to the fields of sensors, actuators, and smart coating by using various adaptive polymers.

SB01.03.24
Injectable Triblock Copolymer Hydrogel for Cryogenic Preservation Combined with Polymeric Dipole Interaction and Quadruple Hydrogen Bonding
Jewon Choi¹, Seyoung Kim¹, Soo-Hyung Choi² and Kookheon Chatt¹; ¹Seoul National University, Korea (the Republic of); ²Hongik University, Korea (the Republic of)

Hydrogel has been attracted great attention in biomedical field since this material resembles the feature of extracellular matrices (ECMs). For the successful application of hydrogel for cell culture or tissue engineering, not only providing the stable substrate but also considering the cryogenic preservation of cells or organs is essential to prevent unwanted cellular degeneration. In cryogenic preservation of cells, it is essential to make the water
molecules in hydrogel unfrozen during the freezing process. To this end, synthesized the triblock copolymer hydrogel composed with hydrophobic block, zwitterionic block and quadruple hydrogen bonding moiety was investigated in this research. Due to the synergistic effect of super-hydrophilic nature of zwitterionic polymer and nanoscale domain formation of hydrogen bonding moiety, the large amount of water in this hydrogel did not freeze below the temperature 223K. Furthermore, capitalizing on these dynamic bond, this triblock copolymer hydrogel shows injectable and self-healable property. In addition, it shows plateau modulus in the range of soft tissue. We hope that our basic finding give the design principle on hydrogel for biomedical application such as a tissue engineering.

SB01.03.25
Epoxy Toughening with Core-Shell Bottlebrush Polymer Jin Woong Choi, Joona Bang and Yoon Huh; Korea University, Korea (the Republic of)

Bottlebrush polymers (BBPs) consist of a linear backbone and grafted side-chains. The high branch-to-backbone ratio in these systems causes BBPs to adopt different conformational behavior compared to linear polymers, making them a topic of interest. The most widely used synthetic method for BBPs is the ring opening metathesis polymerization (ROMP) of macromonomers. Here, we synthesized diblock macromonomer via atom transfer radical polymerization and nitroxide radical coupling, and then synthesized core-shell bottlebrush polymer via ROMP. Our diblock macromonomers consist of poly n-butylacrylate (PBA) and poly ethylene oxide (PEO). Here, PBA acts as a rubbery core and PEO acts as an epoxy miscible shell. With only 3 wt% of BBPs addition, epoxy toughening effect of 200% was achieved. The results show that the application of BBPs to the epoxy toughening industry can be expected.

SB01.03.26
Effective Utilization of Moth-Eye Inspired Structures with Different Dimension and Materials Jiseong Choi, Joon Hyung An and Seongmin Kang; Chungnam National University, Korea (the Republic of)

Since the fabrication of flexible anti-reflective (AR) structures has great attention for application, such as solar cells, display, wearable devices and so on, various methods, especially moth-eye inspired technologies, have been developed in decades. However, there is limited study to explain difference of optical properties depending on structure dimensions and materials fabricating ultra-violet (UV) curable polymers or thermal curable polymers. In this works, we fabricated moth eye inspired conical structures with three different-sized dimension using various materials. To compare the dimension and material dependent AR properties, we successfully fabricated 300 nm, 500 nm and 1000 nm moth-eye structures by using UV curable and thermal curable polymers. As a result, we have demonstrated that the anti-reflection effect of the fabricated surfaces is improved depending on the structural dimension and consisting materials of the nanostructures.

SB01.03.27
Programmable Three-Dimensional Curvature of Glassy Polymer Sheet by Photo-Triggered Strain-Engineering Jun-Chan Choi1, Jong Hyeok Lee2, Sukyoung Won2, Jae-Won Lee1, Jeong Jae Wie2 and Hak-Rin Kim1; 1Kyungpook National University, Korea (the Republic of); 2Inha University, Korea (the Republic of)

Shape morphing from two-dimensional (2D) planar sheet to three-dimensional (3D) structure have been attracted great attention for the number of application including packaging, assembly, transport, and mechanical actuation. To obtain programmable 3D structure from a 2D polymer sheet, various types of external stimuli have been used including light, heat, electric/magnetic field, and chemicals. In particular, photo-triggered strain engineering used pre-strained thermoplastic polymer sheet has been widely researched due to its ability to local actuation by harmless near infrared (NIR) light with simple and low cost processes. Generally the ink patterns are printed on the polymer sheet for local heating over glass transition temperature (Tg) of polymer with inducing local shrinkage at the pattern regions.

To control the morphed shape of 3D structures, many kinds of pattern design strategies have been studied. For example, pattern width and spacing of hinge patterns were handled for adjusting the folding angle of 3D folding structures. Moreover, different color of hinge patterns was used with different light sources for sequential folding actuation. Recently, using the large size of hinge patterns, global curvatures were controlled according to pattern location, gradient, and its combinations. However, most of the previous works have limited to morphing the folding shapes or the global curvatures based on simple hinge pattern because they considered the deformation of the pattern.
To morphing the complicated 3D structures using photo-triggered strain engineering, the pattern design should be done in advanced considered the deformation of non-pattern regions as well as pattern regions. Furthermore, the analyzing of intermediate shapes at each time interval should be done because the final morphed 3D structure is defined according to an intermediate one.

In this study, we demonstrated the pattern design strategy for 3D shape morphing considering the deformation of the non-pattern region by localized shrinkage of pattern regions with employing radial hinge patterns and round facet on bi-axially pre-strained polystyrene (PS) sheet with a circular boundary condition. According to pre-designed radial pattern conditions and the existence of the round facet, photo-triggered 3D shape morphing was experimentally discussed. Furthermore, we introduced the finite element modeling (FEM) simulation with consideration on temporal/positional stress distribution and their stress competition effects. Interestingly, the hidden mechanisms of the strain re-distribution effect at the non-pattern regions, associated with the final 3D curvature structuring, could be experimentally visualized with polarizing optical transmittance images of the photo-triggered birefringent PS films and they also could be analytically computed. Based on systematic experimental results and computational analysis for pre-determined radial patterns, complex 3D shape morphing having bio-mimetic shapes of soft-turtle shell and sea shell shapes could be successfully implemented, where the PS sheet actuation behaviors at the non-pattern regions were as important as the photo-actuating pattern regions in the formation of final 3D structures. The results of local curving actuation with quantifiable stress imply to take applicability forward for self-folded architectures embodying curved and linear geometric surface coexist.

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SB01.03.28
In Situ Magnetic Alignment and Cross-Linking of RGD-Modified Alginate-Coated Magnetic Microparticles into Macroscale Bundles for Efficient Cell Alignment Seung Woo Choi1, Youngjin Choi2 and Jaeyun Kim1,2,3; 1Samsung Advanced Institute for Health Sciences & Technology (SAIHST), Sungkyunkwan University (SKKU), Korea (the Republic of); 2Sungkyunkwan University (SKKU), Korea (the Republic of); 3Biomedical Institute for Convergence at SKKU (BICS), Sungkyunkwan University (SKKU), Korea (the Republic of)

Cell alignment is an important factor in the exertion of specific mechanical function originated from its anisotropic structure. Especially, myoblast alignment is critical to form paralleled and organized myotubes in muscle regeneration. Diverse approaches have been proposed in cell alignment based on photolithography, electrospinning, laser-guided cell micropatterning, microfluidic patterning, acoustic cell patterning, and 3D bioprinting. However, there is still a need for an easier method that does not require complicated equipment to increase the efficiency of cell alignment. Here, we propose a facile method for magnetic assembly of arginine-glycine-aspartic acid (RGD)-modified alginate-coated magnetic microparticles for cell alignment, in particular myoblast arrangement. The particles could be aligned along the direction of a weak external magnetic field and alginate chains on the surface of microparticles could be cross-linked via ionic cross-linking. By these effects, stable linear bundle structures of the particles in centimeter-scale could be formed even after removal of the magnetic field. In addition, incorporation of RGD into alginate chains on the surface of microparticles could lead to myoblast adhesion onto cross-linked, anisotropic bundles. The efficient myoblast alignment on the bundles was confirmed by filopodia detection followed by analysis of filopodia orientation. As a proof-of-concept, in vivo demonstration of the alignment of alginate-coated magnetic particles was performed without complicated surgery by subcutaneous injection of the particles followed by an additional injection of a calcium solution for in situ ionic cross-linking under the external magnetic field. In histologic examination, the anisotropic bundle structures of the particles in subcutaneous space were observed even after 1 day of injection. This facile process could be one of the options to fabricate aligned architecture, which could further supply an aligned microenvironment to the cells; for example, myoblasts for muscular system in regenerative medicine and tissue engineering. Moreover, the properties of being able to be simply injected through a needle without extra surgery and being in situ cross-linked can be strong points when this platform is applied to in vivo system.

SB01.03.29
Molecular Structure and Hydration Effect of Human Epithelial Keratin Protein Chia-Ching Chou; National Taiwan University, Taiwan

Epithelial keratin protein, a type of intermediate filament protein, is the key component of epidermis in skin which is
the largest organ in human body. The epithelial alpha-keratin intermediate filaments feature a hierarchical structure, ranging from alpha-helical protein, a dimer composed of alpha-helical coiled coils and two globular C- and N-terminal domains, to full-length intermediate filaments. Epithelial keratins dominate the structural stability and mechanical properties of the skin, also help lock in moisture and bear the external pressure. At the molecular level, the alpha-helical coiled coils are stabilized by clusters of hydrogen bonds. Here we report a study on building a bottom-up molecular based model of one epithelial keratin protein by using the full human keratin type K5 and K14 amino acid sequence. A detailed analysis of geometric and mechanical properties of the full-sequence epithelial protein at different water contents by fully atomistic simulation is presented. We analyze how the protein structure and its properties vary with hydration and investigate the role of water molecules in the epithelial protein. Our results suggest that water molecules play a significant role in achieving the characteristic molecular behaviors, including filament assembled arrangement and mechanical properties of this protein material. We further compare our results with the latest experimental measurements and discuss the opportunity of studying disease states associated with genetic mutations and other structural defects in keratin.

SB01.03.30
Ultra Stretchable and Conductive Electrospun Fibers via Electroplating Reinforcement for Strain Sensor Applications Marco Chu, Hani E. Naguib and Tianhao Chen; University of Toronto, Canada

Electrospinning fibers have allowed for the creation of nanoscale structures with high surface to volume ratio which are ideal for next generation wearable electronic and textile applications. Conductive electrospun films are typically constructed by incorporating conductive nanoparticles such as graphene nanoplatelets (GNP) and carbon nanotubes (CNT). Inherently conductive polymers such as polyaniline or polypyrrole have also been used to fabricate conductive electrospun fibers. However, these methods of creating conductive pathways are insufficient as their conductivity remains several orders of magnitudes lower than any metal. Recent developments have used electroplating to coat the fibers with a thin layer of metal. Herein, an alternative electroplating method has been developed that allows for a coating of copper to be uniformly electroplated throughout the entirety of a highly stretchable electrospun styrene-butadiene-styrene (SBS) film. SBS is a copolymer rubber that possesses high elasticity and durability. When made into an electrospun film, the high aspect ratio amplifies the material's elastic properties and can reach strain ratios greater than 1000% without breaking. In this study, various conductive nanoparticles were explored to identify their effects on electroplating coating properties. The SBS film was ultrasonicated in an aqueous solution of the nanoparticles at varying weight percent to prepare the film for electroplating. The ultrasonication process assisted the conductive fillers to diffuse through the thickness of the film and adhere to the individual fibers. This provided an initial conductive pathway for the copper to deposit onto the fibers. As the conductive fillers were evenly coated on each fiber, the copper was also uniformly coated onto the underlying nanoparticle layer. The resulting conductive electrospun film retains its high elasticity through the mechanical properties of SBS, while the conductive copper and nanoparticle layer provide relatively high conductivity to the film even at high strain ratios. These properties make the film suitable for use as large strain sensors in electronic skins and smart textiles.

SB01.03.31
Nature-Inspired Encapsulation Layers for Soft, Transient Electronics JinMook Chung, Gwan-Jin Ko and Suk-Won Hwang; Korea University, Korea (the Republic of)

Transient electronics is a different form of electronics that can physically disappear and bioresorbable when immersed in water or moisture condition. New options about treatments of transient electronics are essential to create potential applications. Especially, an encapsulation of transient electronics is very important to protect electric devices at prescribed times. However, it is difficult for flexible electronics with encapsulation layers to maintain a soft and protection properties. Therefore, selecting encapsulation layers of transient electronics is an important issue. Usually, soft polymers are used for the encapsulation of electronics. We report some artificial and nature polymers, which have soft, biodegradable and biocompatible properties. On these polymers, we can fabricate electric components and integrated circuits.

In previous studies, thick or multiple encapsulation layers are used for increasing lifetime of device. However, that methods cause film delamination and decrease of flexibility. Therefore, we feel the need for new form of encapsulation layer.

In nature, lotus leaves have a large contact angle through microstructures, which results in a hydrophobic surface. Microstructures of lotus leaves can be applied to encapsulation layers of transient electronics. By tuning surfaces of
encapsulation layers, hydrophobicity of surfaces increases and lifetime of electronics can be enhanced effectively. As a result, softness and lifetime of devices can be controlled by surface-tuned encapsulation layers. And then, it is expected that this research is applied to various applications like wearable, medical devices.

SB01.03.32
Inkjet-Printed High Efficiency Organic Solar Cells as Customizable Energy Harvesting Systems for Autonomous Applications Daniel A. Corzo, Eloise Bihar, Khulud Almasabi, Diego Rosas Villalva, Sahika Inal and Derya Baran; King Abdullah University of Science and Technology, Saudi Arabia

Emerging materials including low-bandgap donors and non-fullerene acceptors are leading organic solar cells (OSC) to reach efficiencies beyond the 16% mark. The increased performance of OSCs along with flexibility, stretchability, and the versatility and low costs associated with solution processing has rendered them attractive as energy harvesting devices for unconventional applications such as conformable and disposable electronics and autonomous sensing. Inkjet printing has proven to be a viable fabrication technique to exploit the advantages of solar cells and transition from laboratory-made devices into consumer-ready products due to its low material usage, customization through digital design, and high-resolution of printed features.

This work demonstrates the fabrication of fully inkjet-printed high efficiency solar cells based on the PCE10:4F and P3HT:O-IDTBR blends for autonomous micro-powered applications. The engineering of functional inks for the different functional layers is centered on tuning the rheological properties for proper jetting, the compatibility of surface energies between the ink and the underlying films, as well as controlling the drying behavior for optimized electronic properties.

The optimization of the printing process results in repeatable devices with efficiencies of up to 12.5%, comparable with that of laboratory coating techniques. Fully printing OSC’s encourages their integration as a power source in combination with other printable electronics as a customizable solution for a wide variety of applications. Fully printed devices allow end-users to design and integrate OSC’s as a power source in combination with other printable electronics throughout a wide range of applications.

SB01.03.33
Reprogrammable Nanomagnets for Shape-Morphing Micromachines Jizhai Cui1,2, Tian-Yun Huang1, Zhaochu Luo1,2, Paolo Testa1,2, Hongri Gu1, Xiang-Zhong Chen1, Bradley Nelson1 and Laura Heyderman1,2; 1ETH Zürich, Switzerland; 2Paul Scherrer Institut, Switzerland

Shape-morphing micromachines have demonstrated significant potential in drug delivery, minimally invasive surgery, cell manipulation, and stenting applications [1]. With current fabrication methods, most micromachines are limited to a single type of transformation determined by their geometric design, which cannot be altered once fabricated [2]. In this work, we have developed a strategy to encode multiple shape-morphing information into transformable micromachines making use of the magnetic configurations of single-domain nanomagnet arrays. Inspired by origami, our micromachines consist of rigid panels carrying the arrays of nanomagnets separated by structured soft creases. The nanomagnets have tailored magnetic switching fields and, by applying a sequence of magnetizing fields, the arrays can be set into a particular magnetic configuration. By customizing the micromachine designs, we can obtain micromachines that perform specific shape transformations in an applied magnetic field.

Based on this strategy, we have built a simple four-pad micromachine with 24 possible magnetic configurations, demonstrating four distinct conformations when actuated by a magnetic field. Further, multicomponent micromachines were constructed by assembling modular units and, by customizing each individual unit, we have engineered a micromachine that can transform between two alphabet letters. We have also created complex folding behaviors, such as bending and twisting, and have implemented these folding modes in a microscale ‘origami bird’ capable of several different flapping modes. This work paves the way for the development of future intelligent microsystems that are reconfigurable and reprogrammable, which is required for biomedical applications and is also of interest for 3D magnetic and optical metamaterials. [3]

Color-Changeable Soft Actuators based on Metal Nanowire Network Transparent Heaters and Anisotropic Polymer for Biomimetic Soft Robotics

Hyeonseok Kim¹, Habeom Lee² and Seunghwan Ko¹; ¹Seoul National University, Korea (the Republic of); ²Pusan National University, Korea (the Republic of)

To overcome lack of functionality and limitation in conventional soft robots, we demonstrate a highly anisotropic color changeable soft actuators for the first time. Due to the huge anisotropic thermal expansion mismatch, the suggested actuators has a highly anisotropic bending with very large curvature (2.5 cm⁻¹) at considerably low temperature (=40 °C) compared to the previous electrothermal soft actuators. Low temperature operating condition enables the remarkable long-term durability during more than 10000 times actuating at the maximum curvature. In addition, the optical transparency of metal nanowire network heaters and polymer bilayer allow the incorporation of the thermo-chromic dyes to fabricate color-changing actuators. We demonstrate various color-changing biomimetic soft robots such as color-changing blooming flower, flapping butterfly, and color-changing twining tendril. Along with high anisotropic behavior, large bending curvature with low temperature operating, long-term durability, color-changing function, the actuators offer tremendous possibility for biomimetic soft robotics.

SESSION SB01.04/SB04.04: Joint Session: 3D/4D Printing of Stimuli-Sensitive Materials

Session Chairs: Marc In het Panhuis and Andreas Lendlein
Tuesday Morning, December 3, 2019
Hynes, Level 3, Ballroom A

8:00 AM *SB01.04.01/SB04.04.01
Gels for Bioprinting—Finding, Functionalising, Formulating, Printing and Characterising Gordon Wallace; University of Wollongong, Australia

The ability to create 3D printed structures containing living cells is providing a route to the creation of "living" systems that might be useful for bench top drug testing or implantables that facilitate tissue regeneration.

However, the realisation of a useful printed structure based on hydrogels is not a simple task. While we can build on the extensive knowledge that has accrued through cell-gel interaction studies to date, there are a number of dimensions that add to the challenge.

Central to these is that the gel containing the cells must undergo a reasonably rapid phase transformation. In addition, with some applications multiple cells and other bioactive entities need to be strategically distributed in 3 dimensions. Sterilisation of the components and/or the final structure is also of critical importance and finally knowing what we have created without destroying it remains a challenge.

Returning to the start of this process we encounter perhaps the most neglected aspect - most of the emerging hydrogels finding use in bioprinting are naturally occurring. So where do we find them - how do we ensure a reliable high quality source?

8:30 AM SB01.04.02/SB04.04.02
Novel Hybrid Approach to 3D-Print Graphene/Polymer Composites Xuechen Shen, Taylor J. Morrison, Hani E. Naguib and Tianhao Chen; University of Toronto, Canada

Current 3D printing uses a wide range of plastic, metal, and ceramic materials, with no significant effort to integrate these techniques for multi-material fabrication. We previously developed a novel method to deposit non-viscous ink through a stable continuous jet formed by gearing-enhanced peristaltic pumping. This ink deposition technique was used to deposit graphene oxide (GO) ink in a binder jetting (BJ) process to fabricate GO/polyvinyl alcohol composites. In this technique, ink particles are accelerated to speeds of 2-10ms⁻¹ to overcome surface tension forces tending towards pendant drop formation. Gearing is applied to achieve mechanical advantage (MA)<1, enabling high pump velocity. Motor acceleration made up for the lost torque. In recognizing that gearing could be used to
increase torque with MA>1, we realized the potential to perform Direct Ink Writing (DIW) using our ink deposition system. To this end, we DIW-printed viscous graphene/nanocellulose inks. We also recognized that DIW and BJ shared similar layer change, material transport, and gantry motions, allowing the 2 techniques to be implemented in the same system. We designed and built the hybrid 3D printer, implementing transmission to switch gearing ratios. The hybrid printer was demonstrated to print Graphene/polymer composites using both DIW and BJ printing modes.

8:45 AM SB01.04.03/SB04.04.03
Three-Dimensional Printing with Silica Cages Jen-Yu Huang¹, Tangi Aubert¹,², Ulrich Wiesner¹ and Tobias Hanrath¹; ¹Cornell University, United States; ²Ghent University, Belgium

Material scientists have now developed an extensive library of nano-sized building blocks, offering a vast panel of properties (optic, magnetic, plasmonic, catalytic, etc.). Nevertheless, combining these building blocks for the realization of multifunctional materials while controlling their structure from the nano- to the micro- and all the way to the macroscale still remains an open challenge in order to fully exploit their potential. In parallel, new material processing techniques such as 3D printing technologies are emerging for the fabrication of macroscopically highly engineered parts and devices. In this work, newly discovered silica nanocages are combined with digital light processing 3D printing technique for the rapid fabrication of mesoporous parts with arbitrary shapes and tunable internal structures. Complementary strategies are then deployed for the implementation and deliberate positioning of various functionalities throughout 3D printed objects with high control on the microstructure and macroscopic architecture of the superstructures. This approach paves the road for innovative device concepts and designs, that will benefit from the unique properties of nanomaterials and from the micro- and macroscale manufacturing capability of 3D printers.

9:00 AM SB01.04.04/SB04.04.04
Magnetically Navigable 3D Printed Multifunctional Microdevices for Water Quality Control Roberto Bernasconi¹, Elena Carrara¹, Marcus Hoop², Fajer Mushtaq², Bradley Nelson², Salvador Pani², Caterina Credi¹, Marinella Levi¹ and Luca Magagnin¹; ¹Politecnico di Milano, Italy; ²ETH Zürich, Switzerland

Water contamination, either chemical or biological, is one of the main problems for public healthcare in many parts of the world. Contaminated water is a source of a great number of diseases caused by pathogens or by chemical agents. Many techniques are available to improve water quality, but in many cases these methods are not entirely environmentally friendly. Current research efforts are directed toward the use of harmless substances and safer methods. From the pathogens control point of view, silver is one of the most used non-antibiotic agents. Regarding chemical pollutants elimination, one of the most promising techniques is photodegradation mediated by titania (TiO₂). This material photocatalytically generates reactive radicals able to oxidize pollutants upon exposure to an electromagnetic radiation. Functional layers of silver and titania can therefore be used to provide efficient water remediation.

An interesting approach consists in manufacturing multifunctional materials that exhibit both antimicrobial and photocatalytic activities. A fabrication technique able to yield this type of materials is electrolytic codeposition of particles with metals or alloys [1]. For example, thanks to this wet deposition technique, a matrix of silver with embedded titania particles can be easily obtained. The final composite layer exhibits both antibacterial and photoactive properties. Water cleaning possibilities can be further expanded if the antibacterial and the photodegradation action is performed by microdevices covered with silver/titania composites. An example of such devices are the so-called microrobots [2], which can be wirelessly guided using magnetic field and placed exactly where the water decontamination action is needed. Examples of microrobots presenting photocatalytic [3] or antimicrobial activity [4] are available in literature, but none of them combines these two actions on the same device.

The aim of this work is the realization of cylindrical shaped microrobots combining biokilling and photodegradation thank to the presence of a bifunctional composite on their surface. Such microrobots are produced using 3D printing, more specifically microstereolithography, and are subsequently metallized using wet techniques. Two functional layers are applied on the surface of the 3D printed device: a CoNiP magnetic alloy and an Ag/TiO₂ composite. The first makes possible the movement of the device under the influence of an external magnetic field, while the latter imparts the biocidal/catalytic activity to the device. We demonstrate that these devices exhibit antimicrobial activity toward methicillin resistant Staphylococcus aureus bacteria. Moreover, from the pollutants removal point of view,
we prove that they can efficiently photodegrade a model molecule like rhodamine B when exposed to ultraviolet radiation.


9:15 AM
SB01.04.05/SB04.04.05
Macroscale Double Networks—A Universal Method for Improving the Strength and Toughness of Soft Materials Daniel R. King, Tsuyoshi Okumura, Riku Takahashi and Jian Ping Gong; Hokkaido University, Japan

The double network concept has been revolutionary in its ability to turn soft, brittle hydrogels into tough, robust materials with mechanical properties that match the best synthetic elastomers. Double network hydrogels consist of two interpenetrating networks, where each network has a specific mechanical response: the “first network” acts as a sacrificial network, consisting of a rigid, extended network, and the “second network” is a globally percolated, stretchable network. When a double network hydrogel is stretched, covalent bonds of the first network break, dissipating energy; this process continues with increasing strain, until the sacrificial network is completely broken and the second network ruptures. The goal of this research is to demonstrate that the “sacrificial bond concept” is applicable at length-scales beyond the molecular scale. We aim to incorporate this design concept universally for application in structural and medical devices.

Like double network hydrogels, our system consists of a rigid “first network,” 3d printed polyurethane/polyacrylate grids, embedded in a soft and stretchable “second network,” silicone rubber. We found that when the strength of the matrix exceeds the strength of the grid, local fracture occurs in the grid, and stretching is isolated to the rubber in the fractured region. As stretching increases, the force increases, and when the local force exceeds the global strength of the grid, fracture will occur elsewhere in the composite. This process continues sequentially throughout the sample until all grid fracture sites are exhausted, and the matrix ruptures. By tuning the stiffness of the grid, we can independently control the yield strength and fracture strain of the composite, until a point where the grid strength exceeds the matrix strength, and the multiple fracture process no longer occurs.

We also systematically studied the interfacial interactions between the matrix and the reinforcing grid. Both interfacial adhesion as well as topological interlocking are important towards developing a robust composite. By adhesive interactions alone, only minimal fracture of the reinforcing phase occurs; topological interlocking is required to maximize fracture. Based on this result, we systematically change the grid size to modify the number of fracture events. In the optimized form, an increase in work of extension of ~50% over the neat matrix was achieved, representing a ~70% toughening efficiency versus the calculated maximum toughness. These results demonstrate that macroscale double networks can dramatically increase the toughness of soft materials.

9:30 AM *SB01.04.06/SB04.04.06
4D Printing Thermoplastic Polyurethane Hydrogel-Elastomer Trilayers for Structural Applications Richard S. Trask; University of Bristol, United Kingdom

Hydrogels represent a class of engineering materials that have great promise for integration within the human body; particularly by optimising and functionally grading their biophysical and biochemical properties. The ability to construct complex architectures through 3D printing is now common place but introducing the ability to transform a planar architecture into a new configuration once manufactured opens up the potential to minimise manufacturing complexity but maximising the design potential. This presentation will detail our latest design thinking utilising a multifunctional materials design methodology and 4D printing research for producing a diverse range of complex architectures utilising thermoplastic and hydrogel trilayer constructs. This unique methodology permits the viable construction of dynamically robust and complex bilayer and trilayer origami architectures for a new generation of active structures. In our study the resulting creations transform from flat 2D parts to 3D structures through submersion in water and return to their original configuration through dehydration. This technique uses commercially available materials and printers to enable a controlled and predictable actuation method that is more accessible and affordable than previous examples of hydration triggered 4D printing. We show the ability to create tessellated origami patterns, such as the Miura-ori origami fold pattern and the waterbomb configuration; the latter
being a design that has not previously been realised with 4D printing. These new designs demonstrate how the integration of multiple trilayers into a single 3D print enables through-thickness control of actuation resulting in the formation of active structures with complexity beyond what has previously been achieved with 4D printing. The research will now be extended by the generation of curved-layer morphing origami architectures (i.e. individual layers with variable z-component actuation) to enable selective structural buckling; the generation of tubular bilayer/trilayer architectures; and, the generation of sequential actuation through the addition of porogens (i.e. dissolvable particles used to create porous hydrogel structures) such that the rate and magnitude of actuation can be further programmed in the design phase.

10:00 AM BREAK

10:30 AM *SB01.04.07/SB04.04.07
Extreme Hydrogel Technology Xuanhe Zhao; Massachusetts Institute of Technology, United States

While human tissues and organs are mostly soft, wet and bioactive; machines are commonly hard, dry and biologically inert. Bridging human-machine interfaces is of imminent importance in addressing grand societal challenges in health, security, sustainability, education, and joy of living. However, interfacing human and machines is extremely challenging due to their fundamentally contradictory properties. At MIT Zhao Lab, we propose to harness “extreme hydrogel technology” to form long-term, high-efficacy, compatible and seamless interfaces between humans and machines. In this talk, I will first discuss the fundamental mechanisms to design extreme properties for hydrogels, including extremely tough, resilient, adhesive and anti-fatigue, for long-term robust human-machine interfaces. Then I will discuss a set of novel hydrogel technologies, including i). hydrogel bioelectronics capable of electro-opto-fluidic interrogating single neurons and continuously monitoring gastric physiological conditions over the long term; ii). tissue double-sided tapes that give instant strong adhesion of wet tissues and devices. I will conclude the talk with a perspective on future human-machine convergence enabled by extreme hydrogel technology.

11:00 AM *SB01.04.08/SB04.04.08
Smart Hydrogels from Mechanistic Design to Practical Applications Jie Zheng; University of Akron, United States

Synthetic polymer hydrogels as soft-wet materials, consisting of three-dimensional cross-linked networks and a large amount of water (50–90%), possess many unique properties such as swelling/deswelling, stimuli-responsiveness, shock absorption, and low sliding friction, making them as potential excellent biomimetics for substitution of soft living materials. However, conventional hydrogels often suffer from weak mechanical properties, which greatly limit their extensive uses for many other applications. In this talk, we will present different design strategies to prepare tough and multifunctional hydrogels with unconventional polymer network architectures and extraordinary properties. Guided by our design principle, we will demonstrate different hydrogels with high mechanical properties, self-healing, actuation, antifouling, and/or wound healing to mimic cartilages, artificial muscles, and mussel-inspired glues. In parallel, molecular simulations will be presented to given atomic-details of structure-properties relationship. Finally, several unique aspects for future development of tough hydrogels will be suggested.

11:30 AM SB01.04.09/SB04.04.09
Design and Understanding Dynamic Hydrogel with Hydrazone Crosslinks for 3D Printing Junzhe Lou, Sean Friedowitz, Christopher Lindsay, Sarah C. Heilshorn, Jian Qin and Yan Xia; Stanford University, United States

Dynamically crosslinked hydrogels received increasing interest for their adaptive mechanical behaviors under stress and deformation and wide applications for cell scaffolding and delivery. We present a new concept of modulating the dynamics of hydrogel systems crosslinked by hydrazone bonds via a biocompatible organic catalyst. The catalyst accelerates the exchange kinetics of hydrazone bonds for over two orders of magnitude, resulting in identical network structure with widely tunable viscoelastic behavior. The catalyst control of network dynamics enabled quantitative and unambiguous correlation between the network parameters and mechanical properties of dynamic polymer networks, which can be generalized to provide design principles to engineer their viscoelastic properties.
We also applied this system for 3D bio-printing to modulate the dynamic properties of hydrogels at different time points of application to have both high injectability and high stability. The incorporated catalyst enhanced the exchange of dynamic crosslinks to achieve high injectability during printing process, but rapidly diffused away from the hydrogel after ejection to retard the exchange and improve the long-term stability for cell culture.

11:45 AM SB01.04.10/SB04.04.10

**Chemical Pumps for Soft Autonomous Robots** Junsoo Kim¹, Kai Luo² and Zhigang Suo¹; ¹Harvard University, United States; ²Beijing Institute of Technology, China

Soft robots can be untethered by carrying a chemical fuel of pneumatic actuators. However, it has a fundamental design restriction; the fuel pressure should be higher than the actuator pressure to transport the fuel. Given that the fuel part occupies most of the volume, the robot becomes pressurized as much as the actuating pressure and requires stiffer materials for the fuel part, making entire robots stiffer. Here, inspired by the pit in plants, we decouple the pressures of the fuel part and the actuator while providing a fuel against the pressure gradient by introducing an isolator between them, thereby liberating from the design constraint. This isolator consists of a hydrophilic nanoporous membrane made of a hydrogel and a micro-porous wall made of a nylon mesh, that correspond to the pit membrane and the cellulose wall at the pit respectively. The mechanical integrity of the structure according to the geometry is studied by finite-element analysis to establish a design rule and the pneumatic power is extensively characterized experimentally with various parameters. Finally, the isolator is implanted to the conceptual soft robots to demonstrate the merits of the isolator.

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**SESSION SB01.05: Applications of Multifunctional Materials: From Design to Advanced Manufacturing**

Session Chairs: Michael Dickey and Pablo Valdivia y Alvarado
Tuesday Afternoon, December 3, 2019
Hynes, Level 3, Ballroom A

1:30 PM *SB01.05.01

**3D Printing of Soft (Hydrogels) and Hard (Surfboard Fins) Materials** Marc In het Panhuis; University of Wollongong, Australia

Surfing is an iconic sport that is extremely popular in coastal regions. Current surfboard fin manufacturers produce high end products using an expensive injection moulding process to create hydro-foil shaped fins. This process, however, does not allow for easy customisation or rapid prototyping.

Hydrogels are smart and multifunctional materials with a real potential for use novel applications including soft robotics, (edible) sensors and bionic implants. Consisting of a highly swollen polymer network, hydrogels are typically soft and brittle meaning they are not compatible with many traditional techniques used to process materials into structures.

I will demonstrate a variety of (extrusion-based) 3D and 4D printing techniques for processing soft materials (hydrogel inks) alongside other inks of structural polymers to create composite architectures including a smart valve, an artificial cartilage meniscus, an artificial tendon, brain-like structures, edible electronic circuits, stretchable devices, soft robotic devices and edible/living hydrogels.

I will discuss the development of surfboard fins (a hard material) using a performance feedback loop. This loop involves the unique combination of computational fluid dynamics, computer aided design, 3D printing of hard materials, stiffness/flex testing, ocean testing (surfing the waves), embedded sensors / wearables, the Internet-of-Things, and surfers’ perceptive experiences.

Time permitting I will finish my talk with our progress on measuring the mechanical flex behaviour of surfboards, including vibration analysis.

2:00 PM SB01.05.02
**Oxygen-Responsive 3D Printing Inspired by Insect Cuticle Sclerotization** Kyueui Lee¹, Patrick A. Ruehs², Phillip Messersmith¹,¹ and Haeshin Lee³; ¹University of California, Berkeley, United States; ²ETH Zürich, Switzerland; ³Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Insects adopt phenolic molecules as molecular cross-linkers that tether internal proteins and/or polysaccharides (such as chitin) to form mechanically strong cuticles functioning as protective armor. The tethering mechanism is triggered by ambient ‘oxygen’ which induces oxidative polymerization between the phenols and the amine-based polymers (proteins or chitin) at the air/water interface. Motivated by this mechanism, we designed a new type of 3D printing system that can be controlled by an unusual external stimulus, ‘oxygen’. The ink for 3D printing is a mixture of pyrogallol (representative phenol), polyethyleneimine (amine-rich polymer), and a scaffolding material. It is initially fluid but immediately hardened after extrusion. By adjusting the air/water interfacial rheology, we were able to control the ink to be cured in 1 second in ambient air conditions. This was a suitable condition for the material to be stacked without falling. The advantage of this 3D printing system is material independence. Activated carbon has been applied to the system to print conductive 3D objects for demonstration, but it can be applied virtually to any colloidal materials on demand.

**2:15 PM SB01.05.03**

**Development of Programmable, Multi-Functional Composite Materials through Additive Manufacturing Techniques to Produce Carbon Capture Devices for Space Travel** Jamie Thompson¹,²,³, Gregory L. Whiting¹ and Camille Petit²; ¹University of Colorado Boulder, United States; ²Imperial College London, United Kingdom; ³Xerox PARC, United States

Multi-material, layer-by-layer additive manufacturing approaches provide a route to the fabrication of complex, structured, and multi-functional composite materials. These composites can be applied in many spaces, including using biomaterials for tissue scaffolding, zeolites for reversible gas capture, and various stimuli-responsive materials for a range of sensing applications.

Here, we present examples of additively manufactured multi-functional materials, including co-printing of conductive and non-conductive adsorbent paste formulations using a direct-ink writing approach to produce devices capable of performing thermal-swing reversible CO₂ capture and release. These printable composites show gas adsorption characteristics in-line with what is expected from the bulk material. Additionally, when an external potential is applied, the printed composites resistively heat to sufficient temperature to desorb captured CO₂. This potentially enables reduced mass and complexity, as well as in-situ manufacture for life-support systems in remote, enclosed, off-planet environments. This approach is further extended beyond the two discrete materials described above through the integration of inline mixing hardware. Multiple pre-functionalized inks were combined within a print head to enable digitally controlled continuous gradient blending of several different functional materials in order to deposit a programmable multi-functional composite. Components of varied resistivity across a spatial region are demonstrated allowing a high degree of thermal control to be achieved post print. This enables the coupling of desired thermal effects to specific chemistries in the design phase to optimize devices for performance, as well as energy efficiency. This is a key step to unlocking the higher potentials of simulation and multiscale modeling approaches used in prototype design.

Finally, implementation of basic closed-loop analysis of the deposition of these multi-functional materials was studied, by including in-line electronic and optical metrology tools on the print platform. By taking account of the specific effects of additive manufacturing processes, such as spatial resolution and geometry, on-the-fly design optimization is achieved, allowing for the degree of ink functionality to be measured and calibrated. This technique should be applicable to a wide range of functional inks thus unlocking the ability to rapidly prototype parts optimizing for multiple complex physical/chemical properties.

**2:30 PM SB01.05.04**

**Low-Temperature Sintering of Inkjet Printed Metal Nano Particles for Additive Manufacturing—Chemical and Morphological Assessment** Gustavo F. Trindade, Yinfeng He, Feiran Wang, Christopher Tuck, Ricky Wildman, Clive Roberts and Richard Hague; University of Nottingham, United Kingdom

Additive Manufacturing (AM) is nowadays employed in a wide range of industries utilising various materials alongside constant developments in terms of geometrical complexity. However, in addition to exploiting geometry, a
multi institutional and multi industry project [1] seeks to augment these products three-dimensional functionality through the co-deposition of both functional and structural materials contemporaneously. Material jetting is key for developing such next generation multi-material/multi-functional AM due to their ability to jet a wide range of materials from polymers, to inks containing metal nano particles (MNPs). In recent years, the use of inks containing silver MNPs has been explored for printing multi-material 3D objects by means of contemporaneous in-situ curing of a polymer and sintering of MNPs using near infrared (NIR) or ultraviolet (UV) light that is absorbed by the NP, triggering their sintering process [2, 3]. As a consequence of their high surface-to-volume ratio, silver MNPs are sintered typically at 120–200 °C, which is as low as 20% of the melting temperature of the metal [3]. Such an advantage enables the printing of metal structures on flexible polymer substrates such as PET or polyimide [4]. A common problem involving low temperature inkjet printing of MNPs is poor conductivity of 3D printed structures and the reason for such problem may lie on the chemistry and morphology evolution during the low-temperature sintering process. Past works have reported conductivity change as a function of annealing temperature and related it to morphological changes [2, 3], however, none has carried out a thorough chemical characterisation of these printed materials. This work describes the development of a protocol for assessing, chemically and morphologically, the sintering process of 3D printed silver nano-particles under different sintering conditions and strategies. Single-layer silver samples were produced by inkjet printing a commercial MNP ink and sintering at different temperatures and high specificity, surface sensitive techniques (time-of-flight-orbitrap secondary ion mass spectrometry – ToF-Orbi-SIMS and X-ray photoelectron spectroscopy – XPS) were employed to track chemical changes. Ambient scanning electron microscopy (SEM) has also been carried out to track in-situ morphological changes in function of sintering temperature.


2:45 PM SB01.05.05
2D-Macromolecular Heterostructures Enabled Colloidal State Machines Albert T. Liu, Pingwei Liu, Daichi Kozawa, Jingfan Yang, Volodymyr Koman and Michael Strano; Massachusetts Institute of Technology, United States

Arming nanoelectronics with mobility and self-awareness opens new opportunities in macromolecular science. Originally referred to as electronics based on chemically synthesized nanostructures, nanoelectronics today can also be fabricated following conventional top-down approaches that scale with Moore’s law. Although the subject has been studied intensively for the past two decades and finds application in a variety of disciplines from computing to energy generation, examples of nanoelectronics with mobility and on-board logics remain elusive. As an emerging paradigm that calls for several scientific and engineering disciplines to work in unison, it is necessary to establish a strong narrative that sets the field apart from similar concepts with explicit, unambiguous functions. In this context, I will discuss how the growing library of 2D-soft material composites, with the suite of exotic properties they command, has facilitated the symbiotic engraftment of electronics onto mobile colloidal particles[1] thus paving the way towards next-generation microrobotics with both low energy consumptions as well as complex functions.[2]

I will focus on our recent efforts in synthesizing such 2D-macromolecular heterostructures, using a novel fabrication technique named autoperforation, owing to the spontaneous perforation of the grafted 2D materials around a pre-designed polymer template.[1] This method lay the foundation of building the proposed colloidal state machines. We have demonstrated, for the first time, that nanoelectronic devices can be grafted onto and/or embedded within colloidal microparticles, creating autonomous machines capable of complex operations in a particulate form.[1] The characteristic mobility of a colloidal system integrates seamlessly with the modularity that comes with modern digital electronics, enabling information collection and recording in enclosed spaces – such as the human gastrointestinal (GI) tract,[3] microfluidic channels, and chemical/biosynthetic reactors – as well as remote locations like oil and gas conduits, waterbodies, soil, or the atmosphere.[1] Ultimately, we envision an intelligent colloidal microrobot that collects, manipulates, and stores information autonomously, extending electronic systems into traditionally inaccessible environments.
Ferromagnetic Soft Robots—Multifunctionality Enabled by 3D Printing and AI

Xuanhe Zhao; Massachusetts Institute of Technology, United States

Soft materials capable of transforming between three-dimensional (3D) shapes in response to stimuli such as light, heat, solvent, electric and magnetic fields have applications in diverse areas such as flexible electronics, soft robotics and biomedicine. In particular, magnetic fields offer a safe and effective manipulation method for biomedical applications, which typically require remote actuation in enclosed and confined spaces. In this talk, we will present ferromagnetic soft robots capable of untethered remote actuation, model-guided design, and AI-based control. We fabricate the soft robots by 3D printing the soft-robot bodies together with programming ferromagnetic domains in the robots. We develop a physics-based model capable of quantitatively predicting the deformation of the robots under applied magnetic fields. Based on the model, we obtain a massive amount of simulation data of various applied magnetic fields and deformed configurations. By training deep neural networks with the simulation data, a machine-learning algorithm is further developed to autonomously navigate the soft robots in complicated environments such as vascular systems. We will demonstrate multiple previously-inaccessible functions of the ferromagnetic soft robots, such as autonomous minimally invasive surgeries, enabled by the synergy of 3D printing, quantitative model and AI.

Sequential Shape-Shifting Capability of 3D Printed Shape Memory Polymers with Broad Glass Transition

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4D printing, i.e. the application of 3D printing technology to stimuli-responsive materials, and in particular to shape memory polymers (SMPs), is gathering large attention among the researches on smart materials. Such an approach would lead to important improvements towards design flexibility, allowing to achieve complex or customized 3D printed structures with externally-triggered shape evolutions. The behavior of SMP-based structures consists in significant dimensional variations occurring when the polymer, after being deformed and fixed in a given temporary shape, recovers its permanent shape thanks to an external stimulus, typically involving heating above specific temperatures [1]. Inspiring aims of 4D printing pioneering works were the realization of active structures based on origami theory and of mechanisms capable of sequential self-folding motions [2].

In order to obtain sequentially moving structures, i.e. structures in which different parts undergo dimensional changes at different times upon the application of the same external stimulus, various approaches may be adopted. Research efforts were mainly based on technological and design tools, as the employ of multi-material 3D printing techniques and the realization of functionally-graded structures [3]. An interesting alternative approach to achieve sequential motions is based only on the material, by employing specific SMP families, as in the case of multiple shape memory polymers (i.e. polymers possessing more than one glass transition or melting temperature) or of polymers featuring the so-called temperature-memory effect. These latter systems, thanks to a broad distribution of the glass transition or melting region, are able to “memorize” not only a shape but also the temperature at which the deformation of the temporary shape was performed, so as to trigger the recovery of the permanent shape at a temperature strictly correlated to the deformation temperature [4,5].

In this work the temperature-memory effect, displayed by a commercial resin, featuring an inherent broad glass transition region, was investigated, with particular interest towards the characterization of the effect and its exploitation for sequential motions of 3D printed geometries. A comprehensive experimental characterization is carried out on simple material specimens and on more complex structures (bars; cubes; self-locking mechanism; reverse-honeycomb auxetic structures) printed by stereolithography. In particular, their shape memory behavior was studied after thermo-mechanical deformation history (or “programming”) properly designed to investigate the material response in case of different deformation temperatures and of multi-step deformation histories. Multiple
deformations performed at different parts of a same specimen/structure and at different deformation temperatures enabled in fact the achievement of a controlled recovery process with the presence of distinct and sequential motions. The shape memory response was studied as a function of temperature and in isothermal conditions, these latter being employed to attempt, through the application of a time-temperature superposition scheme, a master curve full description of the time-dependent shape recovery process. The aim is to depict the dependence of the recovery on the deformation temperature both on the temperature and time scales in order to identify best conditions for multiple deformations allowing sequential recovery motions. As a final proof-of-concept and application example, a self-locking clamp was realized and properly “programmed”, so that locking motions were triggered on distinct time scales by the same thermal stimulus applied.

References

4:15 PM  SB01.05.08  
**Thermal and Laser Sintering of Liquid Metal Nanoparticles for Stretchable Electronics**  Shanliangzi Liu¹² and Rebecca Kramer-Bottiglio²; ¹Purdue University, United States; ²Yale University, United States

Gallium-based liquid metal nanoparticle inks have shown great potential in creating printed soft and stretchable electronics. Despite their metallic composition, as-printed liquid metal nanoparticles form a nonconductive film because the liquid metal cores of each particle are surrounded by a nonconductive metal oxide shell. Hence, these films require a sintering process to recover their conductivity. Our group previously demonstrated mechanical sintering of liquid metal nanoparticles, although this sintering process put a lower bound on both the size of the particles and softness of the substrate that may be utilized. In this work, we present two thermally involved sintering methods - laser and thermal sintering - to attain conductive liquid metal nanoparticle films. By comparing laser and thermally sintered films with respect to electrical conductivity, surface morphology and elemental composition, crystallinity and surface composition, we reveal the oxide rupture-induced mechanisms that enable electrical conductivity of liquid metal nanoparticles using both methods. We show that thermal and laser sintering under different conditions generate highly conductive liquid, solid or solid-liquid composite films with desired properties that can be used for different applications such as soft robotics, wearable electronics, or broader semiconductor and electronics applications. We also demonstrate high-resolution laser sintered patterns that can be implemented to create high-density electronic devices on soft substrates.

4:30 PM  SB01.05.09  
**3D Printed Objects with Functional Coatings**  Bhavana Deore, Chantal Paquet, Nathan Kredentser, Thomas Lacelle and Patrick Malenfant; National Research Council Canada, Canada

3D printing is an emerging additive manufacturing technology poised to transform both design and manufacturing due to its ability to customize design and generate structural complexity not possible using traditional manufacturing processes. Commercial examples of 3D printed objects using monolithic materials, such as GE’s fuel nozzle, illustrate early success of this technology by enabling new designs and significantly reducing the number of parts and supply chain required for manufacturing. However, only marginal progress has been made to demonstrate multi-material printing and as such it remains a low technology readiness level research endeavour at the moment with enormous potential for innovation and commercial impact. Multi-material 3D printing would increase the complexity and functionality of printed objects and pave the way for 3D structural electronics. The challenge is that most 3D printing techniques cannot print multiple disparate materials into one object. For instance, 3D printing techniques of stereolithography (SLA) and digital light processing (DLP) can generate 3D printed objects with high resolution, high quality surface finish and dimensional accuracy, and it does so using photo-active polymerizable resins as precursor material. However printing objects with functional coatings that are distinct from the core of the object has not been developed. Examples of multi-material 3D structures made from SLA and DLP have been made but the approaches typically result in a composite structure throughout the object and if functional surfaces are desired, this typically involves coating the objects post-printing with functional materials. The drawback of coating
post-printing is that it requires multiple steps with different coating apparatus and does not consistently yield coatings with the desired function or robustness, which will depend greatly on adhesion. In this presentation, we demonstrate multi-material printing using SLA 3D printing yielding an object with a functional coating.

4:45 PM SB01.05.10
Additive Manufacturing of 3D Architected Multifunctional Metal Oxides Daryl Yee, Michael Citrin, Max Lifson, Bryce Edwards and Julia R. Greer; California Institute of Technology, United States

Multifunctional metal oxides represent an important class of materials used in modern society. These materials exhibit unique properties such as piezoelectricity, superconductivity, and semiconductivity, rendering them useful in virtually every type of micro/nanosystem device technology. Most current device designs utilize metal oxides as thin film stacks because patterning these materials have mostly been limited to using traditional planar lithography, or various casting methods, which substantially limits the geometries that can be achieved. However, in recent years, 3D printing of these multifunctional metal oxides has become a significant area of interest as new experimental devices that have been able to utilize these 3D materials have demonstrated substantial improvements in performance. While many different techniques have been developed to achieve these architected materials, additive manufacturing (AM) has recently emerged as a frontrunner for the fabrication of three-dimensional metal oxide structures with almost arbitrary geometries.

In particular, additive manufacturing processes involving photolithography have emerged as one of the most promising ones due to the high resolution and small feature sizes achievable. These photolithography systems typically consist of photosensitive slurries, where metal oxide nanoparticles are dispersed in a photosensitive organic binder. The slurry is then patterned using a variety of lithography techniques to create 3D nanocomposite structures, which are then calcined to burn off the organic matrix and to sinter the metal oxide particles together. The advantages of these systems are that it’s simple and versatile – as long as the desired metal oxide nanoparticles can be obtained, the slurry can be made and the part 3D printed. However, the high loading of nanoparticles needed results in a host of other issues, such as increased viscosity, homogenous dispersion of the nanoparticles, and light scattering. To circumvent these, hybrid inorganic-organic photoresins, which contain polymers with metal heteroatoms in their backbone, have been developed. These photoresins can be patterned and then calcined in the same way to produce 3D metal oxide structures, but without the challenges associated with the inclusion of nanoparticles. A key disadvantage of this approach is that these photoresists are often not commercially available and sometimes require a complex multi-step synthesis. To fabricate arbitrarily shaped 3D metal oxide structures, a process that combines the beneficial aspects of existing approaches: (1) the simplicity and versatility of the slurry method and (2) the high resolution afforded by the organic-inorganic photoresists, has to be developed.

In this presentation, a new photopolymer system that circumvents the problems of both existing techniques is demonstrated. The photopolymer system is facile to prepare and can be easily modified to fabricate various multifunctional metal oxides. As an example of this technique, we demonstrate the printing of a few different metal oxides at a variety of scales by fabricating zinc oxide (ZnO) and lithium cobalt oxide (LCO) architected structures with sub-micron and sub-millimetre features respectively. Characterization of these structures using X-ray diffraction, energy-dispersive spectroscopy and transmission electron microscopy indicate that the structures are indeed comprised of the appropriate material. Compression of the ZnO structures results in a voltage response, exhibiting the piezoelectric behaviour of these structures. Electrochemical cycling of the LCO structures showed efficient performance as a lithium ion battery cathode over greater than 100 cycles. This ability to fabricate these multifunctional 3D materials could open up the field of smart devices and change how we design them.
SB01.06.01 Matrix- and Morphology-Dependent Electronic Responses of Nanocarbon-Polymer Composites
Chen Chi¹, Toshiyuki Sato², Yoshitaka Kamata², Daisuke Hashimoto², Pawel Czubarow³ and Howard E. Katz¹; ¹Johns Hopkins University, United States; ²NAMICS Corporation, Japan; ³eM-TECH Inc., United States

Nanocarbon-polymer composites offer the advantages of functional electronic response combined with facile processing, thermal stability, and mechanical flexibility. In this presentation, we consider two nanocarbon morphologies, carbon nanotubes and nano-carbon spherical particles, and four polymer matrices, two of which are entirely aliphatic and two of which are rich in aromatic rings. We find that simple current-voltage curves, thermoelectric responses, and perturbations by the oxidizing vapor NO₂ are consistent with the best interconnection and greatest responsiveness associated with carbon nanotubes in aliphatic matrices. In particular, these latter composite types using poly(methyl methacrylate) (PMMA) matrix showed bulk conductivities >1 S/cm and small, concentration-independent Seebeck coefficients <5 µV/K at or below the percolation threshold <5%. At <1% incorporation in epoxy, conductivity was injection-limited rather than bulk-limited, with currents consistent with a 1 S/cm conductivity. Exposure of 1% carbon nanotube-in-PMMA samples to 10 ppm NO₂ resulted in a steady, cumulative p-doping response of about 2% per hour. No such response was observed from nano-carbon spherical particles mixed into PMMA at the same concentration. Insulating polystyrene and semiconducting poly(bisdecylquaterthiophene) (PQT12) matrices resulted in much lower conductivities with carbon nanotubes, with the polystyrene samples essentially insulating with 1% carbon nanotubes, and PQT12 showing moderate conductivities and increased Seebeck coefficients consistent with significant traps, barriers, and aggregates formed by the carbon nanotubes. The results taken together suggest that moderately polar but nonaromatic matrices yield the highest and best controlled environmental responses from nanocarbon composites.

SB01.06.02 3D Reconfigurable Liquid Crystal Elastomers via Dynamic Bond Exchange
Emily C. Davidson, Arda Kotikian and Jennifer A. Lewis; Harvard University, United States

We report a method to create 3D liquid crystal elastomers (LCEs) that exhibit programmed shape morphing capabilities which can be ‘locked-in’ on demand via dynamic bond exchange. Specifically, we have created printable inks composed of oligomer-based LCEs with main-chain rigid mesogens and allyl dithiol chain extenders. Their programmed director alignment, which is uniquely defined by print path, gives rise to a reversible actuation response when thermally cycled above and below their nematic-to-isotropic transition temperature, TNI. By incorporating light-activated dynamic bonds, we ensure that the external stimulus for bond exchange is orthogonal to that required for their reversible actuation. When actuated above TNI, UV light can be used to “trigger” allyl disulfide bond exchange within these printed LCEs in response to the pre-programmed internal stress to “lock-in” their actuated state. Our results offer a pathway towards reconfigurable, adaptive actuators with controlled shape-morphing capabilities and high specific energy density.

SB01.06.03 Simultaneous 3D Printing and Frontal Polymerization for Rapid Manufacturing of Multifunctional Nanocomposites
Leon Dean, Jia En Aw, Allen Guo, Douglas Ivanoff, Samya Sen, Randy Ewoldt and Nancy R. Sottos; University of Illinois at Urbana-Champaign, United States

Thermoset polymers and composites exhibit excellent specific stiffness and strength, thermal stability, and chemical resistance. However, the manufacturing of high-performance thermosets and composites typically requires lengthy cure times at elevated temperatures, which presents significant challenges for 3D printing. Recently, we demonstrated a technique that combines frontal polymerization (FP) with extrusion-based direct ink writing to simultaneously print and cure neat polymer parts with minimal energy input. This system relies on the ring-opening metathesis polymerization (ROMP) of partially cured endo-dicyclopentadiene (DCPD). Here we expand this approach from the printing of neat polymers to the printing of nanocomposites. We investigate the shear and extensional rheology of nano-inks composed of DCPD monomer and either carbon or silica nanoparticles. From
these data, we define a suitable window for direct ink writing in terms of monomer degree of cure and nanoparticle loading. We also use thermal imaging to characterize the FP of printed nano-inks, including front velocity and front temperature, in a variety of printing conditions. Finally, we report on the multifunctional properties of printed nanocomposites, including enhanced mechanical and electrical properties, as well as potential applications based on their multifunctionality.

SB01.06.04  
**Multi-Dimensional and Multi-Length Scale Assembly of Functional Biomaterial**  
Pu Deng and Xiaocheng Jiang; Tufts University, United States

Electrochemically active bacteria (EAB) such as *Shewanella* and *Geobacter* are capable of performing long-range charge transport through a variety of evolutionally developed electron pathways. While these biodevived electroactive systems represent intriguing building blocks for a range of bioelectronic applications, their applications to date are still limited by the lack of effective structural and functional integration at meaningful scales. Here we present our recent effort toward the multi-dimensional assembly of these living materials. Core-shell, EAB-encapsulated hydrogel fibers were manufactured by the multi-inlet coaxial microfluidic devices for 1D assembly. Inside these core-shell fibers, the cellular interactions and microenvironments can be precisely modulated to engineer the developments of the protein-based conductive materials. Based on the results, closely contacted bacteria promote the development of high-density, sub-micron protein structures at cellular interfaces which can be directly translated to the increase of conductivity (16.2 mS/cm) as compared with low-density, micrometer long protein structures generated by the isolated bacteria (6.4 mS/cm). Furthermore, bioprinting was applied to assemble these bacterial cables into functional bioelectrochemical systems, where the 3D structure, including xx, yy and zz, can be programmed and optimized to overcome the intrinsic charge and mass transport limits in native biofilms. The current work represents an important strategy to achieve spatial organization of electroactive living materials with precisely engineered functions and could open up new possibilities to design and construct a biosynthetic functional system from the bottom-up.

SB01.06.05  
**Microfluidic Manufacture and Use of 3D Multi-Material Microparticles for Uniform Fluid Compartmentalization and Bioassays**  
Ghulam Destgeer, Mengxing Ouyang, Chueh-Yu Wu and Dino Di Carlo; University of California, Los Angeles, United States

Biosensing accuracy suffers from low signal above background at low analyte levels and random variations in sensor performance at higher analyte levels which limit quantitation. Conventional detection schemes, e.g. enzyme-linked immunosorbsent assays (ELISA), overcome low analyte level challenges through enzymatic signal amplification, however these assays typically measure the bulk signal from a single or few reactions, leading to compromised detection sensitivity and accuracy. Microfluidics has provided promising tools for uniform compartmentalization of a sample fluid volume into many smaller reactions, however skilled users or specialized and costly commercial instruments are required for implementation. Here, we present a versatile platform to compartmentalize and perform reactions in uniform nanoliter-scale volumes based on the fabrication of microscale multi-material particles (e.g. hydrophobic outer layer and hydrophilic inner layer ring-shaped particles) that form a single droplet per particle with design flexibility of particle structure and droplet shape. Our “dropicle” system provides uniform compartmentalization, customizable shape-coded particle for multiplexing, flexibility to be scaled up, and ease of implementation with existing amplified assay workflows, enabling hundreds to thousands of parallel reactions.

We manufacture the multi-material particles using a 3D printed device to run a hydrodynamically stable co-flow of four different streams of fluids including polymer precursors. The inlet ports of the device are connected using intricate channels such that the outlet flow streams take a cylindrical co-axial shape. Density-matched flow streams consist of Poly(propylene glycol) diacrylate (PPGDA), PPGDA and photo-initiator (PI), Poly(ethylene glycol) diacrylate (PEGDA) and PI, and PEGDA, from the outermost to the innermost stream, respectively. At the device outlet, a square glass capillary is attached to provide a region where fluid streams are exposed to UV source through a patterned mask when the flow is stopped. The two streams with PI are cured into ring-shaped multi-material particles with the inner and outer layers made of PEGDA and PPGDA, respectively. The size of particles are readily controlled by adjusting the fluid-flow rate ratios at the inlets and mask design; whereas the shapes are altered by customization of 3D printed device and mask design for UV exposure.
We have fabricated particles with four distinct cross-sectional shapes and different thickness. These particles with a hydrophilic inner hollow layer and hydrophobic outer layer provide a versatile and scalable platform to form highly uniform aqueous droplets in the center of the particles suspended in an oil phase holding a volume of 1-6 nL depending on the particle design. Capture antibodies for target analyte or other immobilization anchors such as biotin are added to the PEGDA layer during the fabrication process. We successfully implemented an HRP-based fluorescent immunoassay using the dropicle system and demonstrated a limit-of-detection of 10 pg/ml (i.e., 100 fM) with a dynamic range of at least 3 orders of magnitude. Fluorescent-based imaging of the droplets after reaction enabled both end-point measurements and real-time amplification with simultaneous tracking of large numbers of single particles over time. Furthermore, multiplexing was shown without crosstalk, where two types of particles with different outer polymer shapes and inner droplet shapes maintained their individual fluorescent signals. In addition to be used as a “swarm” of analog assays by correlating fluorescent intensity with target analyte concentrations, our dropicle system is also promising to serve as a digital platform by scaling up the number of particles and reducing their size. Finally, signal readout using a portable imager are being explored to extend assay capability to point-of-care settings without relying on expensive instrumentation.

SB01.06.06
Controlling the Perception of Softness in Haptic Interfaces—The Role of Indentation Depth and Contact Area Charles Dhong1 and Darren J. Lipomi2; 1University of Delaware, United States; 2University of California, San Diego, United States

In contrast to sight and hearing, we are relatively weak at recreating the sense of touch. To address this gap, we have conducted several studies to decompose tactile (touch) sensations into their fundamental components, with the goal of recreating arbitrary tactile sensations. Using micropatterned elastomeric slabs of precise thicknesses and psychophysical testing with human subjects, we systematically investigated the role of indentation depth and contact area on the human perception of softness.1 By decoupling the indentation depth from the contact area, we developed explicit equations to design and tune the perceived softness of haptic interfaces so that, for example, one object feels twice as soft as another. We provide strategies such as designing materials to feel “softer”, while keeping the Young’s modulus constant. These findings provide specifications for designing new materials to interface with the sense of touch and how these materials can be actuated to reproduce tactile sensations.


SB01.06.07
Lattice Fluidics—A New 3D Microfluidic Platform for Tuning of Multiphase Interfaces Nikola Dudukovic, Joshua DeOtte, Hawi Gemeda, Maira H. Ceron, Sarah Baker and E.B. Duoss; Lawrence Livermore National Laboratory, United States

Conventional microfluidic devices are often limited to enclosed channels and planar geometries, which hinders their usefulness in multiphase reaction or transport processes. We present a novel platform based on capillary fluid flow in three-dimensional open-cell lattices. Using deterministic cell and lattice design and additive manufacturing, we fabricate complex 3D structures with tuned porosity. This approach enables selective placement and direction of liquid flow into predetermined continuous paths through the structure, as well as optimizing the occurrence of gas-liquid or gas-liquid-solid interfaces. We demonstrate the application of lattice fluidics for CO2 capture by incorporating a liquid sorbent into a 3D lattice with high gas-liquid interfacial area. ***This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 within the LDRD program 19-SI-005. LLNL-ABS-778327.

SB01.06.08
Exploring Natural Photonic Crystals in Prawn Exoskeletons as a Template Material Fiona Sander1, Dominic Melvin1, Adrian Ting Ho2, Stefano Angioletti-Umberti1 and Ahu Gumrah Dumanli2,1; 1Imperial College London, United Kingdom; 2University of Manchester, United Kingdom

Chitin structures can be found in a variety of organisms in nature and show unique mechanical and optical properties in combination with biodegradability and nontoxicity. One of those species is Penaeus setiferus (King Prawn) with
an exoskeleton made of chitin which is conformed into a bouligand/helical structure that is a photonic crystal. *Penaeus setiferus* uses this structure mainly to form a strong network as a part of exoskeleton and the optical appearance of the shrimp seems to do not reveal the interesting chiral optics of such organisation. However, when the proteins and calcium minerals were removed from the shrimp exoskeleton, the residual chitin film show quite remarkable iridescent appearance with strong circular polarization. This isolated helicoidal framework is much more porous than the starting material and provides an exciting foundation as a template for exploring chiral photonics using different deposition methods. With the goal of transferring this intricate network, the iridescent chitin shell is used in this study to decorate with metal nanoparticles using wet chemical methods and in a separate study conformally coated with TiO$_2$ using atomic layer deposition techniques. It is shown that the helicoidal organization of the iridescent shrimp shells can be conformed and transferred in to higher refractive index materials with distinctive macroscopic combination of optical effects.

**SB01.06.09**  
*Water-Processable and Biodegradable Bioplastic from Engineered Microbes* Anna Duraj-Thatte$^{1,2}$, Avinash Manjula Basavanna$^{1,2}$ and Neel Joshi$^{1,2}$; $^1$Harvard University, United States; $^2$Wyss Institute for Biologically Inspired Engineering, United States

Over 335 million tons of plastic is produced globally every year and nearly 80% of it have accumulated in landfills and water-bodies. Contamination of non-biodegradable plastics and microplastics (<5 mm fragmented particles) are causing potentially irreversible damage to our ecosystems and global health, including that of humans. Herein, we report a new class of microbialy produced biodegradable bioplastic that is water-processable. *E. coli* was genetically engineered to produce biopolymers under ambient conditions to produce bioplastic that can withstand strong acid/base and organic solvents. In addition, our bioplastic can be healed and welded to form three-dimensional architectures by using water. These unique features of our bioplastic are believed to inspire further exploration and the development of much needed alternatives to conventional plastics.

**SB01.06.10**  
*Towards Biomimetic Programmable Material Systems—Creating Responsive and Intelligent Biomaterial Assemblies to Address an Environment under Stress through Botany, Biology and Charismatic Design* Emelia E. Erland and Raymond Oliver; Northumbria University, United Kingdom

We are experiencing a global environment under stress and if not ‘capped’, will lead to both a biodiversity failure in addition to global warming and adverse greenhouse gas content in the atmosphere. Looking at natural material design we can see a vast range of intertwined materials and biocomposites performing an enormous and impressive range of tasks, utilising often easily obtained and renewable resources. Biological systems are argued to be superior to technological ones in terms of biology’s utilisation of information and structure over energy and materials. There are many opportunities for biogeochemical cycles to inspire a Design:STEM approach that can simultaneously address the opportunities and challenges created by the global resource and waste crises, greenhouse gas emissions, expanding urban populations and environments, and consumer engagement in environmental behaviours.

As part of our work in BioDesign:STEM Integration, we are examining the role that both biology and botany can play in replacing synthetic single use polymers for plastic packaging of foods, consumer products and luxury items. The paper will outline the choice of bio and phyto materials development and the development of multi component composites that are both resilient, have controlled release and targeted delivery behavioural characteristics, and through an LCA methodology can be reused, refunctioned and recomposted after primary use. We are investigating the creation of a biomimetic yarn drawn from examination of the cross sections of plant stems, where each element is analysed and then substituted for a biomaterial with tailored and enhanced properties.

Natural materials are presumed to have enhanced biocompatibility with humans and, from a financial and timing perspective, provide a good material base for enhancement and modification to fit the current manufacturing methods. Their use allows for aims to include desirable and complex materials properties with biodegradable and biocompatible characteristics, as well as providing the opportunity to identify resources that are naturally abundant, renewable and cost effective. Currently major issues for bio-based packaging are the requirements for water and oxygen barriers and so the project aims include identification of structures, processes and biodegradable materials that can achieve water and oxygen barriers for flexible materials, preferably from a renewable source. Another way to ensure cost-effectiveness and resource sustainability is to use the least amount of material possible through
enhancement of material properties and through investigation into structures such as foams. From a design perspective, charismatic effects and aesthetics are being explored through investigations into ideas of elegantly simple, traditionally crafted and overtly natural fabrications concealing a novel, non-intuitive responsive element that adds great functional and experiential value. This interactive behaviour, drawn from our work with thermoresponsive gels, ensures easily repurposable packaging fabrications that engage the consumer. The facile efficiency which the resultant packaging fabrications can achieve serves to inspire the consumer with the potential of natural materials and the natural environment at large.

SB01.06.11
Investigation of Dissolution Temperature of Gold Nanorods Depending on the Size of the Modified Polymer
Tatsuya Fujiwara and Tsuyohiko Fujigaya; Kyushu University, Japan

As a promising candidate for photothermal therapy material, gold nanorods (AuNRs) having high photothermal conversion efficiency, strong absorption and scattering in the near infrared region excellent in biotransparency have been studied. However, one of the problems in practical photothermal therapy application is a burning of organs and/or skin by heating upon light irradiation. Previously, we demonstrated the mechanism which can avoid the overheating even if AuNRs is overirradiated (Autonomous overheat suppression mechanism); namely phase transition of the polymer modified on AuNRs upon heating induced an aggregation of AuNRs and resulted in the shift of AuNRs photoabsorption wavelength [1]. However, in the living body, diffusion of AuNRs is slower compared to that in solution, and rapid aggregation might be difficult. Therefore, in this research, in order to achieve the mechanism of suppressing the overheating of AuNRs itself without involving the change of the aggregation state, we focused on the shortening of AuNRs by the oxidative elution of Au ion from the AuNRs surface [2]. Since the longitudinal absorption wavelength of AuNRs depends on the aspect ratio, the absorption peak will shift to a shorter wavelength by the shortening of AuNRs, and it is considered that the absorption of the irradiation light decreases to suppress the overheating. Therefore, in this study, we studied the shortening temperature of AuNRs depending on the size of modified polymer, in which the density of the polymer coating on AuNRs is expected to change the stability of the Au on AuNRs.

Polymers (RAFT-PEG188, RAFT-PEG500, RAFT-PEG1500) were synthesized by Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization using polyethylene glycol methyl ether methacrylate (PEGMA) ($\text{M}_n=188, 500, 1500$) having different ethylene glycol length. After the reduction of the polymers to generate -SH group in the polymer terminate, the polymer solution was added to AuNRs aqueous solution. The obtained AuNRs aqueous solution (PEG188-AuNRs, PEG500-AuNRs, PEG2000-AuNRs) was heated from 35 to 115 °C, and the change of the longitudinal absorption peak upon heating was monitored by UV-vis spectroscopy. A blue shift of the longitudinal absorption peak was observed in the PEG-modified AuNRs, while shift of the longitudinal absorption peak was not observed in the excess CTAB-removed AuNRs (CTAB-AuNRs) measured as a comparison. The peak shift onset time was earlier as the side chain length of the polymer was longer. We found that the onset temperature of the AuNRs with RAFT-PEG2000 was lower than that of AuNRs with RAFT-PEG500.

Conclusion
AuNRs was modified by SH terminated polymers having different side chain length synthesized by RAFT polymerization. Heating experiment of AuNRs solution revealed that the onset temperature of the shortening of AuNRs was lowered when the AuNRs was modified by the polymer with longer side chain. We considered that the lowering of the modification density lowered the stability of Au on the surface of AuNRs, resulting the lowering of the shortening temperature.

References

SB01.06.12
A Cross-Linking Reagent Derived from 2-Mercaptonicotinic Acid and Its Application to Photoadhesive Materials
Masahiro Furutani, Kentaro Nakayama and Koji Arimitsu; Tokyo University of Science, Japan

Adhesives are one of essential materials for manufacturing industry, especially for that of composite products. Different kinds of parts made from metals, ceramics or polymers are adhered by adhesives, which contributes to
designing, processing, and weight saving. For adhesion of two adherends of dissimilar materials, modification of their surface with laser, plasma or chemicals has been used in general. On the other hand, adhesives having catechol or its analogue moieties have been paid attention, because polymers having catechol moieties show high adhesive strength toward various kinds of adherends. Adhesives of this type are inspired by proteins having DOPA residues in adhesive components of mussels.

2-Mercaptopyridine has a similar chemical structure with catechol, while it is not found in chemical structures of natural proteins. Nevertheless, it has a pyridine ring and a sulfur atom, and these chemical moieties would also interact with kinds of adherends including late transition metals. In this work, a disulfide dimer derived from 2-mercaptobenzonic acid (compound 1) is used as a diacylate cross-linking reagent for radical UV curing of 2-hydroxyethyl acrylate (HEA). The curing system is applied to photoadhesion of dissimilar materials, which enables to adhere two different substrates quickly and selectively under mild temperature conditions. Quantitative consumption of acryloyl groups was confirmed after 4 J/cm² of UV irradiation, by FT-IR spectral measurement (decrease of peak area at 1637 cm⁻¹). The UV-cured products were found to be insoluble to THF. Shear stress of in the range from 0.27 to 1.2 MPa was recorded, and the value for glass was higher than for metals. Triplicate value for the glass-copper sample comparing with glass-aluminum sample would indicate better interaction of sulfur (and nitrogen) atoms from compound 1 with substrate of late transition metals.

Samples preparing with compound 1 showed much higher adhesive property than the control samples. Shear stress was apt to be kept during extension in the cases of glass-glass samples. This is probably due to hydrophilic interaction between glass substrate and hydroxyl groups of the adhesive layer. Furthermore, the UV-cured adhesive layer was stretched before breaking of the sample. This would be due to exchange reactions between disulfide bonds. On the other hand, the difference was much clear in the cases of glass-copper samples. Cross-linking moieties of compound 1 would contribute to both cohesion in bulk of the adhesive layer and interaction in the interface. Intertacial fracture was observed on the glass-copper sample of compound 1, which the UV-cured residue was remained on the both sides.

To investigate chemical states of the nitrogen and sulfur atoms in the UV-cured glass-copper sample of compound 1, XPS spectral measurements were performed. A model compound for compound 1 had simple spectral charts where a peak at 398.8 eV for N1s and a peak pair at 163.4 eV for S2p were observed. The former peak is assigned to nitrogen atom of pyridine. The latter peak pair is assigned to sulfur atom of disulfide. In the N1s spectra of UV-cured adhesive sample of compound 1, new peaks are observed at 400.5 and 402.6 eV on the side of copper substrate. This indicates that a part of nitrogen atoms of the dipyridyl disulfide moiety from compound 1 would interact with the copper surface. In comparison, new peaks are observed in the lower binding energy region, around 162 eV in the S2p spectra of the adhesive sample. This implies the presence of electron-rich sulfur atoms on the both sides. Although the mechanism for generation of such sulfur atoms is still unknown, these sulfur atoms may contribute to the adhesion via hydrophilic interaction (on the glass side) and coordination (on the copper side).

**SB01.06.13**

**Smart Materials for the Corrosion Inhibition of Metal Artefacts**

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Chitosan-based coatings turned out to be very promising for the development of sustainable and safe multifunctional systems for the corrosion protection of metal artifacts. A promising strategy to achieve long-term efficacy and specific action against corrosion is represented by the encapsulation of corrosion inhibitors inside stimuli responsive nanostructure. With this aim, herein we investigated the effect of the addition of Layered Double Hydroxides (LDHs) smart nanocarriers on the protective performance of chitosan-based coatings. These systems consist of stacks of positively charged layers between which the inhibitor compound can be intercalated. LDHs act as inhibitor reservoir and allow to control its release only in the presence of corrosion related stimuli, i.e. presence of chloride species and acidic pH. Moreover, these systems are able to slow down the photodegradation of the guest molecules, thus prolonging their protective action. Benzotriazole (BTA) and mercaptobenzothiazole (MBT) were used as inhibitor compounds since they possess a recognized anticorrosion efficiency for different metal substrates. In addition, alkaline nanoparticles, deposited at the coating/metal interface, were used to contrast the acidity coming from the environment and/or produced during corrosion pathways. To assess the efficacy of these nanostructured polymer layers accelerated corrosion tests were performed on the coated and uncoated bronze substrates. The coatings with the inhibitors freely dispersed into the polymer matrix were used as reference. The surface properties of bare alloy and of the alloy with the protective coatings were investigated before and after the accelerated
treatments. The obtained results showed that the encapsulation of inhibitors inside LDHs smart nanostructures allow to achieve a specific action against corrosion and also protect the active molecule from photodegradation, thus improving the stability and the protective performance of the coatings. Alkaline nanoparticles with high surface area and reactivity to acids are also able to provide a local buffer action against pH changes at the metal surface, further enhancing the corrosion resistance of the system. It is worth noting that the developed protective materials possess better performance compared to commercial products based on acrylic resins and are also easy to be applied and removed by using not toxic (water-based) solvents.

The multifunctional active coatings containing LDHs smart nanocarriers, corrosion inhibitors and alkaline nanoparticles guarantee a long-term, safe and sustainable protection of metal works of art exposed to indoor environment conditions. These systems combine different functional capabilities: the physical barrier properties of the polymer matrix and the UV/light shielding action of the inorganic fillers, the stimuli responsiveness of the smart nanocarriers and the chemical protective action of corrosion inhibitors.

This research activity has been carried out within the EU H2020 Nanorestart project “NANOmaterials for the REStoration of works of ART” and has also received the “Young Investigator Award 2018” prize in the area of Chemistry for Cultural Heritage from the Department of Chemical Science and Materials Technology (DSCTM) of the Italian National Research Council.

SB01.06.14
Piezoelectric Materials for Autonomous Charge Generation in Biomedical Implants
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The ability to convert an electrical field into a mechanical perturbation and vice versa makes piezoelectric materials versatile components for industrial applications in a range of fields covering vibration control in airplanes, ultrasound applications in marine and medical devices or pickups for musical instruments [1].

In recent years, the value of piezoelectric materials for biomedical applications has been unfolding [2-4]. They can act as self-sustained suppliers of charge for nerve and bone tissue repair or as autonomous in vivo energy harvesting components powering electronic implants. Depending on the specific application, biocompatibility and stable performance in the presence of body fluids determine a materials potential for the task. In some cases, it is necessary that living cells form a close interface with the implanted material and when hard- and/or soft-tissue integration of the implant material is desired, a piezoelectric implant that provides large, open pores allowing the ingrowth of cells and blood vessels, provides a clinical benefit.

The potential areas of application for piezoelectric materials in the biomedical context are manifold, but for their transfer into clinical routines safe and reliable functionality has to be ensured. A fundamental step on this way is to clarify the influence of the rather unusual biochemical boundary conditions of the body as well as the standardized pre-surgery handling routines on chemical and functional stability of the materials.

We have been investigating two promising piezoelectric ceramic systems – BaTiO3 and (K,Na)NbO3 - regarding their potential as functional implants due to their low degree of cytotoxicity. Microstructural features, such as grain size and porosity, influence the dielectric and piezoelectric performance. While a high degree of open porosity is necessary to allow tissue integration and the development of a stable tissue-implant interface, it can be detrimental for the piezoelectric properties. This can be counteracted by grain size adaption allowing optimization of the materials functionality.

The fluidic environment at an implant site triggers chemical interactions that can influence the implants surface chemistry, functionality and reliability. This is especially important for porous materials providing a large surface to volume ratio. The sensitivity of the functional properties on soaking differs significantly for the two systems investigated. This holds promise that both long-term stable as well as bioresorbable compositions can be developed. Apart from reliable functional performance and low cytotoxicity, compliance with pre-surgery routines has to be guaranteed, to transfer a novel material from the lab bench to the surgery room. We investigated the impact of disinfection routines and plasma sterilization on the piezoelectric performance of both material systems. The distinct differences between them are correlated to their Curie temperatures and their electromechanical response.

References
Protein-Based Piezoelectric Nanogenerators for Wearable and Implantable Electronics

Narendar Gogurla, Biswajit Roy and Sunghwan Kim; Ajou University, Korea (the Republic of)

Harvesting electronic energy from biomechanical motions of a living body is important for health monitoring and biomedical applications. Most tissue surfaces are inherently soft and constantly in motion. Piezoelectric devices enable new electromechanical interfaces with human tissue for monitoring motion signals. However, the electronic devices should be ideally soft and conformal to the tissue surface. Silk protein is one of the finest biopolymer with intriguing properties such as softness, biocompatibility, flexibility in thin film form, and potential to fabricate wearable and implantable electronic devices.

Herein, we present a stretchable, bendable, and biocompatible piezoelectric nanogenerator using silk protein and ZnO nanorods (NR) to monitor and harvest electrical energy from biomechanical motions. Silk protein without ZnO NR produced an open-circuit voltage of ~1.5 V and a short-circuit current of ~5 nA. With the incorporation of ZnO nanorods into silk protein matrix, the output electrical performance is enhanced 8-fold (open-circuit voltage of ~12 V and a short-circuit current of ~0.04 μA). Due to the noncentrosymmetric structure in the wurtzite form and large electromechanical coupling of ZnO, it can produce large piezo-potential in the crystal under strain condition thus lead to higher output performance for ZnO-silk devices. With this high output electrical performance, it can activate small power consumed commercial electronic device (stop-watch). Owing to the softness and stretchability of the devices, they can be contacted conformally to the biological tissue to generate an output voltage of ~7 V from the tissue motions. The study indicates the potential use of biocompatible ZnO-silk devices in harvesting the power from the human body and tissue motion that may be provide an alternative power source for implantable biomedical devices.

Instability-Induced Pattern Formations in Soft Magnetoactive Composites

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We study magnetomechanical instabilities in magnetoactive elastomer (MAE) composites undergoing finite strains in the presence of a magnetic field. In particular, we consider MAE composites with chain-like microstructure. We analyze the influence of the applied magnetic field along the chains on the stability of the MAE composites at both microscopic and macroscopic length scales [2]. To this end, we develop a numerical scheme to detect the onset of instabilities at the long wave and finite length-scales. By applying the developed numerical technique, we analyze the influence of the materials microstructure geometrical parameters and applied magnetic field on the onset of instabilities in soft MAEs. We found that identical MAE composites with periodically distributed particles can switch to a variety of new patterns with different periodicity under particular levels of the applied magnetic field. The post buckling analysis is performed to numerically realize the newly formed patterns dictated by the magnitude of the applied magnetic field.

References
carry the required drug payload and can serve as a flexible implant particularly when the fibers are made from FDA approved biodegradable materials. However, the proper formulation of the drug-polymer composite and the ability to control their release require a better understanding of the polymer-drug interaction which would determine the kinetics of release.

Mechanism of drug release can also be influenced by the intrinsic properties of the encapsulated drug, such as its molecular weight, hydrophobicity and the drug-polymer formulations. In these cases, the choice of the polymeric matrix and method of electrospinning, play a crucial role in the final release pattern. In the same vein, combining electrospinning with other fabrication techniques, can provide a multifunctional property as well as various means of control over the release mechanism of the enclosed drug.

As a first step we focused on electrospinning process parameters namely flow rate, applied voltage and capillary to collector distance. The voltage field and combination of the polymer/drug and solvent concentration that determines the viscosity, surface tension and electric conductivity were evaluated to obtain the proper fiber morphology with the drug blended in it. We have demonstrated that by applying proper means of control, various stages of drug release can be manipulated, such as initial burst release, final plateau stage and on demand release. Control over the initial burst release of the drug, was applied by controlling the diameter and morphology of the obtained fibers, as well as the level of dispersity of the loaded drug. Meanwhile, the sustained release of the drugs were manipulated by choosing the proper polymeric matrix with appropriate disintegration time. Finally, on demand release of the loaded drugs were investigated by utilizing combinatory techniques with electrospinning.

In this study, we have evaluated the influence of polymer choice with different molecular weights ranging from 40,000 to 240,000 (PLGA 50:50, PCL, PLGA 85:15), morphology of the electrospun polymers, and the combination of various technique with electrospinning, for obtaining desired release mechanisms of three hydrophobic drugs, namely biphenol containing small molecule cancer drug, Honokiol, and peptide based, nitroxide radical containing antioxidants JP-4-039 and XJB-5-131, with different molecular weights, from 200 to more than 900. Drug release is characterized through first order burst release followed by controlled release over time using various techniques. Our choice of drug was driven by their applications. XJB and JP are mitochondrial targeting antioxidants being explored for the treatment of cardiac recovery post myocardial infarction. Honokiol is a natural drug being tested for kidney cancer. Sustained and controlled release locally from patches would be beneficial for these drugs. The effectiveness of each polymer used and combinatorial technique, in providing various spatiotemporal control over the release of the aforementioned drugs have been demonstrated.

SB01.06.18
**Efficient Molecular Design as Regioregular-block-Regiorandom Poly(3-hexylthiophene) Copolymer for Highly Electrical and Mechanically Robust Semiconductors** Junghun Han, Hyeonjung Park, Boo Soo Ma, Jin-Seong Kim, Youngkwan Kim, Hyeong Jun Kim, Donguk Kim, Taek-Soo Kim and Bumjoon Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

In this work, we demonstrate poly(3-hexylthiophene) regio-block copolymers (block-P3HTs) that show both great electrical performance and mechanical robustness. block-P3HTs are composed with crystalline regioregular block (rrre block) for providing efficient charge transport and the amorphous regiorandom block (rra block) for flexibility. To clarify the architecture effects of block-P3HTs, a series of block-P3HTs was prepared to have similar number-average molecular weight (\(M_n\)) of rre block with different \(M_n\) of rra block, while the regioregularity (RR) of each block are the same. The hole mobility (\(\mu_h\)) of all the block-P3HTs are comparable high because the rre blocks confined with the rra blocks provide efficient crystalline domains resulted in fast charge transportations. Especially, the highest \(\mu_h\) (1.5 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) is obtained in block-P3HT, rather than rre P3HT. The mechanical robustness of block-P3HTs are highly improved with the higher \(M_n\) of rra block. The elongation at break of block-P3HT finally reach at 100 times higher values than that of brittle rre P3HT. The study of block-P3HTs serves an efficient strategy of organic active materials for the coexistence of electrical performance and mechanical robustness.

SB01.06.19
**Implantable Solar Cells Using Upconversion Nanoparticles for On-Demand Controlled Drug Delivery Devices** Seulgi Han, Woong Sung, Taeyeon Kim, Kilwon Cho and Sei Kwang Hahn; Pohang University of Science and Technology, Korea (the Republic of)

On-demand drug delivery devices (DDDs) have been widely investigated for spatiotemporally controlled therapy with greatly improved patient compliance. However, the power system to operate the DDDs is still a serious
limitation, constraining their clinical applications. Here, we developed implantable solar cells using upconversion nanoparticles (UCNPs) for on-demand controlled DDDs. Although skin-penetrating near infrared (NIR) light cannot be used for flexible organic solar cells, UCNPs can convert NIR light to visible light for their operations after implantation to the body. We designed the UCNPs of NaYF\(_4\):Yb/Er@NaYF\(_4\):Yb, which were doped on flexible organic solar cells [PEN/ITO/ZnO(ETL)/Pbdbt:itic(active layer)/MoO\(_3\)(HTL)/Au]. They could generate current flow upon NIR irradiation and used for on-demand DDDs based on the gold (Au) dissolution to AuCl\(_4^-\) by the applied electrical current. The on-demand DDD was fabricated with a SU-8 photoresist on the flexible polyethylene terephthalate (PET) substrate. After that, the on-demand DDD was interconnected with the UCNP coated flexible organic solar cell and passivated with a flexible PET substrate. The successful fabrication of NIR-triggered implantable DDDs was confirmed by TEM, SEM, photoluminescence and absorbance spectrum, current density-voltage (J-V) characteristics, and drug release tests. This new paradigm on-demand DDD might greatly contribute to the progress of light-triggered medical devices and the relevant phototherapy.

SB01.06.20
Nanomeshed Si Nanomembranes Xun Han, Kyung Jin Seo, Yi Qiang and Hui Fang; Northeastern University, United States

One of the biggest challenges in stretchable electronics is to achieve high-performance stretchable semiconductors. Here, we introduce an innovative concept of nanomeshed semiconductor nanomembrane which can be regarded almost as intrinsically stretchable to conventional microelectronic layouts. The nanomembrane is a dense network of fully connected, high quality, inorganic semiconductor traces of nanoscale line width. By making a silicon film into homogeneous nanomeshes with spring-like nano traces from a lift-off and transfer process using a Si-on-insulator (SOI) wafer, we demonstrated a high electron mobility of 50cm\(^2\)/Vs, and moderate stretchability with a one-time strain of 25% and cyclic strain of 14% after stretching for 1000 cycles, further improvable with optimized nanomesh designs. A simple analytic model covering both fractional material and trace sidewall surfaces well predicted the transport properties of the silicon nanomesh transistors, enabling future design and optimizations. Besides potential applications in stretchable electronics, this semiconductor nanomesh concept provides a new platform for materials engineering and is expected to yield a new family of stretchable inorganic materials having tunable electronic and optoelectronic properties with customized nanostructures.

SB01.06.21
Thin, Flexible P(VDF-TrFE) Nanosheet Based Pressure Sensor Artificial Dragon Fly Wings Haruka Harazaki, Ganesh Kumar Mani and Kazuyishi Tsuchiya; Tokai University, Japan

Unmanned aerial vehicles have received tremendous attention for potential use in various real time intelligent systems. Also, many people use these kinds of systems for their hobbies and business using autopilot technology. Due to the increase in number of unmanned aerial vehicles, several accidents happened in recent years due to loss of control. To solve this problem, researchers mimicking the dragonfly wings. Dragonfly gets attraction due to its rapid acceleration, rapid turning, hovering. Therefore, development of a microminiature flying object that imitates the shape and flight method of the dragonfly is being promoted. However, there is a problem with the miniaturized dragonfly type vehicle currently under development. It is said that, the attitude of the projectile becomes unstable and falls when taking off. Thus, continued flight is difficult. Therefore, to maintain the attitude of the flight, wings pressure needs to be precisely monitored without adding much weight to the wings. Hence, this research work is focused on developing lightweight, thin and ultra-flexible P(VDF-TrFE) nanosheet based pressure sensor. Spin coating and thermal evaporation techniques were used to prepare nanosheet and contact electrodes. Finally, bulge tester was used to apply pressure to the nanosheet and evaluated the electro motive force (emf). Also experiments were performed with various thickness of P(VDF-TrFE) to identify the desired pressure sensor with high capability.

SB01.06.22
Functionalized Boron Nitride Nanomaterials as Reinforcement for Polymer Aerogels Haley B. Harrison\(^1\)\(^2\) and Jeffrey R. Alston\(^1\)\(^3\); \(^1\)The Joint School of Nanoscience and Nanoengineering, United States; \(^2\)University of North Carolina at Greensboro, United States; \(^3\)North Carolina Agricultural and Technical University, United States

Boron nitride nanomaterials (BNNTs) and hexagonal boron nitride platelets (h-BNs) have received considerable...
attention for aerospace insulation applications due to their exceptional chemical and thermal stability. Aerogels have
great potential for use as insulation materials but their practical use is limited. Presently, matrix compatibilization of
BN nanomaterials is tricky and BNNTs are difficult to covalently functionalize. In this work, we present novel
sonochemical techniques to covalently attach fluoroalkoxy substituents to the surface of BN nanomaterials.
Attachment is confirmed via FT-IR, solvent compatibility and the use of x-ray photoelectron spectroscopy (XPS).
Presently, BN nanomaterials have limited uses in composite development. Covalent functionalization can enable
BNNTs to crosslink with polymer and composite matrices, improving their mechanical and thermal properties. We
also utilize sol-gel synthesis to incorporate BN nanomaterials into multifunctional polymers composites. Here, we
develop a light weight and flexible BNNT reinforced and crosslinked aerogel that can be effectively integrated into
insulation materials for structural reinforcement.

SB01.06.23
Novel 3D Cell Culture Method Using Thermally Reversible Liquid Culture Medium Composition Daisuke
Hatanaka; Nissan Chemical Corporation, Japan

Regenerative medicine, which has been extensively studied in recent years, requires a large amount of cells.
Therefore, development of a method for efficiently culturing cells is actively promoted, and a three-dimensional
culture method is attracting attention. In the efficient culture method of cells, it is not only just culture of a large
amount of cells, but also efficiently collecting cells cultured in a large amount without damaging the cells is also an
important issue.
A cell culture substratum for controlling the culture and recovery of cells by changing temperature has been studied
as one of the efficient culture methods, but many conventional cell culture substratum having temperature
responsiveness are limited to use in two-dimensional cell culture (e.g. flat culture), and there are few reports that can
be applied to three-dimensional (3D) cell culture (e.g. suspension culture). Therefore, in this study, we performed
the preparation of a thermally reversible liquid culture medium composition that is possible to culture cells three-
dimensionally in a floated state at 37°C and further to be easily recovered cells without damaging the cells in a room
temperature, and then we developed novel 3D cell culture method using the medium composition. The preparation
of the medium composition was performed by blending xyloglucan from which galactose residues was partially
degraded by β-galactosidase into a basal liquid medium at a specific concentration. By using the medium
composition, (1) cells can be preferably cultured in a 3D state maintaining liquidity at temperature over the sol-gel
transition point, and (2) it has been found that the cells and the medium composition can be efficiently separated at
temperature below the sol-gel transition point.

SB01.06.24
Development of a Compliant Bipolar Electrostatic Chuck Having 3D-Printed Elastically-Deformable Beams
for Handling Large Film Terumichi Hayashi, Yuki Taoka, Pasomphone Hemthavy, Kunio Takahashi and Shigeki
Saito; Tokyo Institute of Technology, Japan

In this study, we propose a new system concept of 3D-printed modular compliant bipolar electrostatic chuck for
handling large film. The prototype of the system consists of 3D-printed modules of bipolar electrostatic chuck with
surface flexibility by collective elastically-deformable beam structure. The proposed system is expected to
effectively grip thin film-like objects because the compliance avoids any excessive stress which results in damage of
target objects. The module performance was experimentally evaluated to investigate influence of beam compliance
on attractive force to a target object.
New handling techniques of large thin film/textile materials such as polymer films and papers have been required to
manufacture devices using Organic Electro-Luminescence and many other applications. However, conventional
electrostatic chucks cannot handle those objects because they typically aim to handle flat and hard wafer in semi-
conductor fabrications. Recently, our research group has been developing compliant bipolar electrostatic chucks.
Previous researches validated a concept of module of bipolar electrostatic chucks with surface flexibility by
collective elastically-deformable beam structure, which has been prototyped by 3D-printer. In addition, other studies
shows that the attractive force is greatly increased by smoothing the beam tips. As a next step toward handling large
film, it is necessary to increase effective area of attractive surface of grippers. Therefore, this research proposes
stacking the modules by layers for that purpose and investigate influence of stacking the modules on attractive force.
For proof of the concept, the authors developed two types of bipolar electrostatic chuck modules which have either
high or low compliant beams. By stacking five each of those modules by layer, we synthesized a compliant bipolar
electrostatic chuck having 3D-printed elastically-deformable beams for handling large film. We determined the
maximum attractive force per unit area of each of the single modules and the stacked modules by obtaining force curves for glass surface. Both modules have 3D-printed beam structure and consist of four-sublayer (conductor-insulator-conductor-insulator) structure. The outer insulation layer prevents the beams from contacting each other and energizing when modules are stacked. Carbon-mixed and PLA (poly lactic acid) resin are used for conductor and insulator, respectively. Each module consists of 11 beam-assembly and a support board connected with beams. The 80mm-long bipolar beams are arranged at 45-degrees to effective surface which corresponds array of beam tips. In low-compliance module, both a cross section of a beam and a tip of the beam are rectangle of 1.2 mm × 2.0 mm. In high-compliance module, a cross section of the beam is a rectangle of 0.6 mm × 2.0 mm and each tip of the beams is a rectangle of 1.8 mm × 2.0 mm. By this difference of beam width, high-compliance module has greater compliance than low-compliance.

The results validated that the concept increases the effective area and absolute values of attractive force. In addition, we confirmed that the slide glass (4.2 g) was lifted by the high-compliance system which has the smoothed beam tips. However, the results show stacking modules decreased the attractive force per unit area of a system from a single module regardless the compliance because the beam tips of each module are not perfectly aligned to a flat surface. Especially, the reduction ratio of low-compliance was 30% while that of high-compliance was 10%. This indicates that increasing the beam compliance is a valid design strategy in enlarging the effective area by stacking the modules.

In conclusion, our concept, layer-by-layer bipolar electrostatic modules, was verified to increase the effective area of attractive force. The results suggest that it is necessary to increase beam compliance for the concept to maximize performance of compliant bipolar electrostatic chuck.

SB01.06.25
Soft Robotic Materials Integrating Strain-Sensing and Photo-Actuation Chiao-Yueh Lo¹, Cheolgyu Kim¹, Yusen Zhao¹ and Ximin He¹,²; ¹University of California, Los Angeles, United States; ²Arizona State University, United States

To realize self-regulation for robot automation, robots are usually equipped with sensors, actuators and data-processing component to operate synchronically. Particularly, the signal (i.e. position, image and temperature) is gathered by sensor and processed, finally sent to actuators for a specific action. In spite of many new soft sensors and soft actuators, self-sensing materials that can monitor their own motions are highly desirable but proven challenging to realize. In this work, we present a photothermally-responsive electrically conductive soft material that can serve as a strain sensing and a photo-actuation, simultaneously owning two key functions essential to artificial muscle materials. The nanostructured hydrogel is synthesized into interpenetrating double network, leading to great enhancement of stretchability and responding speed. Photo absorbers are integrated into the hydrogel, enabling to be controlled by remote illumination and achieve various complex photo-driven anisotropic locomotion. At the meantime, the strain produced from the controlled motion can be sensed by the actuator itself in real time. With this unprecedented capability of sensing the magnitude of the strain that the actuator produces, the robust, stretchable, and ultra-sensitive conductive hydrogels will lead to the next-generation soft robots with self-diagnostic feedback-controlled, higher level of autonomy.

SB01.06.26
Inkjet-Printed Electrochromic and Electrofluorochromic Biodegradable Displays Gerardo Hernandez-Sosa¹,²; ¹Karlsruhe Institute of Technology, Germany; ²InnovationLab, Germany

Electro(fluoro)chromic devices (EFCD) have received increased research attention in investigation in the past years because of their potential applications in multifunctional optical devices. Particularly, their simple device architecture, low power consumption, and processability by industrial relevant printing techniques provide great opportunities for the fabrication of low-cost displays and smart window devices. Furthermore, these exceptional properties can be extended with the use of biocompatible and biodegradable materials for the fabrication of transient devices aimed to the reduction of electronic-waste or potential medical applications.

In this work, we report on the fabrication of inkjet-printed EFCDs consisting of biocompatible and biodegradable components on cellulose/gelatin flexible substrates. The electro(fluoro)chromic layers were comprise of two different polymer materials, either a polyindenofluorene-8-triarylamine (PIF8-TAA) or poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). Additionally, we compared the performance of two
different solid polymer electrolytes, on the basis of gelatin or Poly(D,L-lactide-co-glycolide) (PLGA) in
combination with the non-fluorinated biodegradable salt tetrabutylammonium bis-oxalato borate (TBABOB). The
devices were fabricated in a planar architecture utilizing inkjet printed Au electrodes. The fabricated devices were
characterized in terms of contrast, efficiency and lifetime.

Finally, by subjecting the devices to a standardized composability test, we demonstrate their potential application in
short-lifecycle biodegradable electronics.

SB01.06.27
A Hydrogel-Based Smart Garment for Electrooculography S. Zohreh Homayounfar, Soha Rostaminia, Ali
Kiaghadi, Deepak Ganesan and Trisha L. Andrew; University of Massachusetts Amherst, United States

Eye tracking through novel eye-based assistive wearable devices is considered as a valuable input modality to be
used in different sorts of applications; e.g. medical applications such as visual fatigue, sleep studies and diagnosing a
variety of disease states; as well as human-computer interface applications. However, the most popular method to
detect eye movement is video-based eye trackers in which, generally, a video camera is mounted on a headset to
record the images of the eye, and then, the images are processed to calculate the gaze position. Due to the
considerable computational power cost, this technique cannot be applied for portable on-batteries long term
applications. As an alternative, electrooculography (EOG), through a more convenient wearable device, was
considered as a lightweight, accurate eye-tracking method with low-power consumption. This technique is based on
measuring the corneoretinal biopotential of the eyes, which can be modeled as a constant electrical dipole. The
eyeball rotation leads to the change in the dipole orientation which subsequently gives rise to the change in the EOG
signal amplitude. This signal is generally measured through two pairs of electrodes located in periorbital positions
close to the eyes with respect to a ground electrode.

Different variety of wearable EOG devices have been attempted recently, however, due to ergonomic issues and
limitations exposed by the current bioelectrodes to be mounted close to the eyes, there still exists a tradeoff between
comfortability and the detection of the signal with a high signal to noise ratio. Although the presence of gel is
necessary to improve the signal acquisition, wearing the conventional Ag/AgCl electrodes is not aesthetically
pleasing. In addition, since the signal decades, once the gel is dried out, these electrodes are disposable and cannot
be applied for long-term applications. Considering all the wearable devices recently developed for detecting eye
motion using EOG, none of them allows for an accurately long-term monitoring along with comfortability and low
motion artifact caused by daily activity. Herein, the role of the electrodes, i.e. the interface between the body as the
signal source and the computers as the processing units, is profoundly important. This is the electrode who receives
the charges in the ionic form from the body and injects them as electrons through the wires. Since in EOG, the
electrodes must be attached close to the eyes, designing a pleasing electrode, both aesthetically and comfortably,
which is capable of damping artifacts for efficient data acquisition is still a dire need to be fulfilled.

In the current study, we introduce a novel methodology to fabricate a smart eye mask embedded with a first-in-its-
kind fabric-based hydrogel electrode which can be feasibly adopted to daily life. We synthesized a mechanically
stable, biocompatible, and fully recoverable hydrogel, through initiative chemical vapor deposition of
poly(hydroxyethyl acrylate) on the silver gel. In the retro-design of this electrode, we got inspiration from the
conventional Ag/AgCl electrodes, which, despite all the drawbacks, is still second to none in the market. We have
successfully addressed all those drawbacks in our hydrogel electrode along with reaching to high signal to noise
ratio in long-term data acquisition, wash-stability, breathability, no skin irritation, and is capable for further
miniaturization to be embedded in other wearable platforms rather than the sleep eye mask. The success of the
proposed wearable hydrogel-based EOG device is illustrated through several controlled experiments revealed by a
comparative study between the designed bioelectrode, the standard electrodes, and the dry silver plated fabric ones
based on their biopotential strength and the corresponding signal to noise ratio.

SB01.06.28
Membrane Distillation with Controllable Membrane Pore Size Using Stretchable Superhydrophobic
Membrane Seong Kyung Hong1, Hyonguk Kim2, Seong Jin Cho2 and Geunbae Lim1; 1Pohang University of
Science and Technology, Korea (the Republic of); 2Chungnam National University, Korea (the Republic of)

Membrane distillation (MD) has attracted significant attention as a rapidly emerging water treatment technology
owing to its utilization of low-grade energy. Extensive studies have been carried out in both theoretical and
experimental aspect of this technology. These previous studies, however, focus only on either theoretical or
experimental aspect rather than incorporating both sides for a deeper understanding. It is impossible to perform a comparison study between theoretical and experimental results without being able to reliably control crucial MD membrane parameters, namely the pore size. This remains a critical limitation of most superhydrophobic membranes that the membrane parameters are not versatile once the fabrication process is set. Here, we suggest a stretchable superhydrophobic membrane of which the pore size can be readily controlled through the application of mechanical strain. The membrane was fabricated through simple electrospinning/electrospraying process and was tested of various membrane parameters including pore size, contact angle, and liquid entry pressure. The MD performance of the membrane according to the applied mechanical strain was studied both theoretically and experimentally by comparing the experimental separation flux to that of the predicted value from the computing simulation of MD. As expected, the separation flux was enhanced with increasing the pore size of the membrane. However, the lifespan of usage was shortened with larger pore sizes as it was wetted easily compared to its counterpart with smaller pore sizes. By varying the applied mechanical strain, the optimal pore size in terms of both separation flux and lifespan was found for the MD process.

SB01.06.29
Vertical MEMS Micro-Actuators with Vanadium Dioxide Chengzi Huang, Zhen Zhang, Shriram Ramanathan and Dana Weinstein; Purdue University, United States

Vanadium dioxide (VO$_2$) under goes insulator-metal phase transition (IMT) at 68 °C, accompanied with giant electrical, optical and lattice changes. Combining high Young's modulus (around 140 GPa), large IMT strain shrinkage and moderate IMT temperature, the distinct performance before and after phase transition makes VO$_2$ a competitive candidate for multi-functional MEMS actuators. For VO$_2$ actuators reported to date, lateral structures were used where two electrodes are placed above the phase change material, and current flows via in-plane direction. In this work, a vertical multilayer VO$_2$ MEMS micro-actuator device is reported. Though such configuration is being actively studied for memory devices, there is currently no literature discussing VO$_2$ vertical stack actuators. Here we will report on experimental and simulation studies of the vertical stack on the performance of the VO$_2$ actuator, toward the goal of IC integration for applications benefiting from reduced size, weight, power, and cost.

The VO$_2$ actuator is composed of 3 vertically stacked layers, where a 150 nm thick VO$_2$ layer is sandwiched between top Pt and bottom ITO electrodes. An equivalent thermal circuit is developed with a thermal response time of 0.39 ms. With the IMT of VO$_2$ generating volume change, a 35 μm long VO$_2$ actuator experiences 2 μm deflection across the phase transition driven by heating, and 0.22 μm deflection when electrothermally actuated. COMSOL finite element analysis is performed to determine spatial distribution of current flow and temperature profile, and to verify experimental measurements of strain induced bending in this multilayer vertical structure. The obtained experimental result shows a good fit with simulation analysis, which can in the future be utilized to develop a generic understanding of such vertical MEMS devices incorporating phase changing systems.

SB01.06.30
Self-Directed Self-Assembly of Block Copolymers Hejin Huang and Alfredo Alexander-Katz; Massachusetts Institute of Technology, United States

Self-assembly of block copolymer (BCP) serves as a powerful tool to fabricate complex 2D nanopatterns. Block copolymer are comprised of two or more chemically distinct subchains, which are linked together by covalent bonds. Upon annealing, these different blocks are phase separated into regimes, which forms nanostuctures of different morphologies such as spheres, cylinders and lamellae. By introducing graphoepitaxy such as trenches, post arrays, researchers can ‘direct’ the self-assembly process to form uniform and device-oriented 2D nanostructures. Over the past two decades, researchers have achieved all different thin film patterns through directed self-assembly of BCP. Despite the various 2D structures obtained from BCP, the variety of 3D nanostructures that have been so far achieved is limited. In this work, we present a novel way to fabricate uniform 3D nanostructures using a layer-by-layer approach. We test this new method using dissipative particle dynamics (DPD) to show its promise. Various multilayer structures consisting of spheres, cylinders and lamellae aligned and stacked on each other were achieved. Furthermore, different experimental parameters, which affect the uniformity of the structures, have been studied in the model.

SB01.06.31
Hierarchical Assemblies of Dendrimers Embedded in Networks of Lanthanide-Based Supramolecular
**Polymers**  
*Jianan Huang;* East China University of Science and Technology, China

Supramolecular assemblies of dendrimers, with defined structures and tunable functionalities, are promising functional materials. Here we report a ternary system (lanthanide ion/bis-ligand/PAMAM dendrimer) capable of assembling in a cooperative way by forming a complex between anionic (metal−ligand) coordination polymers and the cationic PAMAM dendrimers. In off-stoichiometric mixtures, charge-stabilized spherical nanoparticles of ~100 nm appear; they have either negative or positive surface charges depending on what the excess component is. Introducing different trivalent lanthanide ions, Ln(III), in the coordination allows tuning both the luminescence emission spectrum and the magnetic relaxivity without affecting the assembly process or the final structure of the particles; this makes them interesting in the context of application. Moreover, the incorporated dendrimer allows us to add functional nanocargo, for example, Au nanoparticles in the cavities of these molecules, again without disturbing the assembly. In this novel way, we obtain versatile, multilevel hierarchical supramolecular dendrimer-containing assemblies with good control over their structures and functionalities. This is very difficult to achieve with conventional covalent compounds but becomes possible because of the supramolecular nature of the coordination polymers and the strong cooperative assembly.

**SB01.06.32**  
**Development of a ReaxFF Force Field for Acrylated Photopolymer Resins in Volumetric Additive Manufacturing**  
*Yihan Huang and Roland Faller;* University of California, Davis, United States

Light-driven and photo-curable polymer based additive manufacturing (AM) has a huge potential due to its high resolution and precision. Unlike point- and layer-wise photopolymer AM technologies, volumetric AM forms the entire part all at once, which produces parts much more rapidly and overcomes such as stair step surface artifacts and inhomogeneous mechanical properties. Acrylated radical chain-growth polymerized resins are widely used in photopolymer AM due to their fast kinetics, and volumetric AM technology readily leverages this set of materials. However, for successful control of the reaction in 3D, the molecular basis of polymer network formation must be understood in detail. We present an optimized ReaxFF force field for acrylates polymer resin to account for the radical polymerization thermodynamics and kinetics, and the polymer network structure and composition. The force field is trained against our extensive training set including density functional theory (DFT) calculations of reaction pathways along the radical polymerization from methyl acrylate to methyl butyrate, C-C and C=C bond dissociation energies of methyl acrylate and methyl butyrate, and structures and partial charges of all molecules and radicals. The parametrization process utilizes a parallelized search algorithm, and the resulting model is able to study polymer resin formation, crosslinking density, chain length and distribution, and residual monomers of the more complex poly(ethylene glycol), diacrylate (PEGDA)/bisphenol a glycerolate (1 glycerol/phenol) diacrylate (BPAGDA) mixture.

**SB01.06.33**  
**Design of Microparticle-Based Soft Electronic Devices for Tactile Sensing**  
*Hyejin Hwang and Unyong Jeong;* Pohang University of Science and Technology, Korea (the Republic of)

While microparticle (MP) assemblies have long attracted academic interest, few practical applications of assembled MPs have been achieved because of technological difficulties related to MP synthesis, MP position registration, and absence of device concepts. The precise positioning of functional MPs in a proper stencil can produce flexible/stretchable electronic devices, even when the MPs themselves are rigid. In recent years, remarkable progress has been made in the programmable position registration of MPs, production of functional MPs, and concepts for MP-based, pixel-type electronic devices. For example, flexible tactile sensors have been intensively studied for healthcare and electronic skin devices.

Non-close-packed MP assemblies on a flexible electrode act as a pressure sensing material like a cartridge film. The cartridge film is made by filling the holes of a stencil film (one MP in each hole) with conductive microparticles (MPs). Using the cartridge film, the sensing material can be cut-and-pasted on electrodes and transferred to other electrodes for reuse. This study analyzes the electrical responses of the sensors made of the cartridge film on the basis of the Hertzian contact theory, and also correlates the sensing performance of the sensors with the conductivity of the MPs and the degree of protrusion of the MPs from the stencil surface.

On the other hand, stretchable strain sensors are manufactured with close-packed MP assemblies. We proposes a dry process of fabricating single crystal-like monolayer which consists of conductive MPs in large area of rubber substrate. Due to their complete two-dimensional assembly, the current map measured by a conductive atomic force...
microscope (C-AFM) provides information to understand the rapid resistance change in small elongation
deformations. Within 15% of elongation strain, the stretchable sensor distinguishes 0.3% fine strain due to high
gauge factor (average value ~ 124.5) and detects sensitively the pulse on a wrist.

SB01.06.34
Optical Design and Electrohydrodynamic Jet Printing of Polymer Photonic Crystals Brian Iezzi1, Zahra
Afkhami2, David Hoelzle1, Kira Barton2 and Max Shtein1; 1University of Michigan--Ann Arbor, United States;
2University of Michigan–Ann Arbor, United States; 3The Ohio State University, United States

A challenge faced in the creation of increasingly complex and miniaturized sensing platforms is the need for
multiple lithographic masking steps to achieve a particular pattern. In this work, we design and manufacture
microscale arrays of one-dimensional photonic crystals without masking via electrohydrodynamic jet printing.
Transfer matrix simulations are first used to design interference-based, polymer optical filters with reflectance
exceeding 60% in imaging-relevant bands of the visible wavelength range. We describe the material selection rules
and process conditions allowing for multilayered micro-filters with individual layer thickness control from 0.1 to 1
μm, filter edge length less than 50 μm, and compositions using commercially-available polymers with varying
refractive index. A microspectrophotometry tool and process are developed to aid the characterization ex and in situ,
allowing for rapid iterative processing to negotiate optical, interfacial, and rheological constraints of the system.

SB01.06.35
Evaluation of Antifouling Property of Surface Microstructures by Dynamic Wettability in Liquid Media
Maria Inukai and Daisuke Ishii; Graduate School of Engineering, Nagoya Institute of Technology, Japan

Fish skin is covered with a lot of scales which have microstructures on surfaces. It is considered that surface
microstructures are functioned as antifouling property, self-cleaning ability and reduction of fluid resistance. In the
conventional study, antifouling property and self-cleaning ability were evaluated by static wettability analysis.
However, it is not sufficient for the practical evaluation because actual liquid movements cannot be determined by
the static method. Therefore, we suggested a novel experimental method, called “dynamic wettability analysis in
liquid media”, to observe behaviors of air bubbles and micro-droplets in liquid media. The values of dynamic
wettability improved evaluations of antifouling property and self-cleaning ability. We fabricated a series of micro-
structured water channels on silicon wafers by photolithography. The surfaces of water channels were modified
hydrophilic by an excimer lamp. It is thought that antifouling property and self-cleaning ability are changed not only
by surface microstructures but also by surface wettability changes. The surface wettability was measured by static
water/hexadecane contact angles. The abilities of antifouling and self-cleaning of the micro-structured surfaces were
evaluated by the behaviors of the air bubble and the hexadecane droplet in water media. In addition, we investigated
how long hexadecane droplet was easy to invade within micro-structured surface in water media. The surface
microstructures enhanced the water/hexadecane wettability and the movements of the air bubble in liquid media.
The air bubble behaviors in liquid media on micro-structured and flat surfaces were differing unexpectedly. It is
generally thought that liquid droplets or bubbles move easily on surfaces having larger static contact angles, but
these results were not agreed so. We tried to control the movements of the air bubble and the droplet in liquid media
by gradually hydrophilic treatment. The movements of the air bubble and the hexadecane droplet in water media
were improved by hydrophilic treatment. These results indicate that the movements of the air bubble and the droplet
in liquid media become able to evaluate the antifouling property and the self-cleaning ability.

SB01.06.36
Fine-Tunable and Injectable 3D Hydrogel for On-Demand Stem Cell Niche Ki Hyun Hong1,2, Young-Min Kim1
and Soo-Chang Song1,2; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Korea University of
Science and Technology, Korea (the Republic of)

Stem cell based tissue engineering requires increased stem cell retention, viability, and control of differentiation.
The use of biocompatible scaffolds encapsulating stem cells typically addresses the first two problems. To achieve
control of stem cell fate, fine-tuned biocompatible scaffolds with bioactive molecules are necessary. However, given
that the fine-tuning of stem cell scaffolds is associated with UV irradiation and in situ scaffold gelation, this process
is in conflict with injectability. Herein, we develop a fine-tunable and injectable 3D hydrogel system with the use of
thermosensitive poly(organophosphazene) bearing β-cyclodextrin (β-CD PPZ) and two types of adamantane-
peptides (Ad-peptides) that are associated with mesenchymal stem cell (MSC) differentiation that serve as
stoichiometrically controlled pendants for fine-tuning. Given that complexation of hosts and guests subject to strict stoichiometric control is achieved with simple mixing, these fabricated hydrogels exhibit well-aligned, fine-tuning responses, even in living animals. Injection of MSCs in fine-tuned hydrogels also results in various chondrogenic differentiation levels at three weeks post-injection. This is attributed to the differential controls of Ad-peptides, if MSC preconditioning is excluded. Eventually, our fine-tunable and injectable 3D hydrogel could be applied as platform technology by simply switching the types of peptides bearing adamantane and their stoichiometry.

SB01.06.37
Negative Mechanical Materials and Metamaterials James N. Grima-Cornish, Joseph N. Grima and Daphne Attard; University of Malta, Malta

‘Negative mechanical materials / metamaterials’ refer to materials and/or engineered systems that exhibit anomalous macroscopic thermo-mechanical properties that emerge due to the structure of their subunits, rather than the specific chemical composition. As a result of their design/construction, they may exhibit anomalous macroscopic properties such as zero or negative Poisson's ratios (auxetic), moduli and/or indices. Such zero/negative properties are not normally manifested by their conventional counterparts and may thus potentially be used in applications where typical materials cannot. This work will look into some of the more recent developments made in this field, focusing on how existing materials (e.g. crystals) are providing the blueprint for the design and manufacture of novel 'negative materials'.

SESSION SB01.07: Soft Actuators
Session Chairs: Ximin He and Mingming Ma
Wednesday Morning, December 4, 2019
Hynes, Level 3, Ballroom A

8:00 AM SB01.07.01
Low Voltage, High Power-Density, Molecularly Ordered Drivers for Untethered Microrobotics Junfeng Gao, Angel Martinez, Arul Clement and M. Ravi Shankar; University of Pittsburgh, United States

Liquid crystal elastomer (LCE) films can be programmed by an array of stimuli, such as light, heat, interaction with alignment layers and mechanical deformation. Well aligned, monodomain films can produce large mechanical strains via order-disorder transitions caused by heating and, thus, high power – density actuations can be realized with low-cross-linked LCEs. Here, we focus on developing the material composition, alignment via mechanical deformation and Joule heating for achieving a low-voltage (<5V), high power-density (~kW/m³) response using LCE actuators. The material design process involved modulating the cross-linker and spacer monomer structure, as well as varying the molar concentrations among mesogenic matrices to simultaneously achieve optimal actuation and stability of the mesophase. To elicit ultrafast actuation by Joule heating, we developed the elements of the microfabrication protocols to integrate electrodes (2nm Ti + 30nm Ag), patterned onto a curved PET shell in mechanical designs. By utilizing non-linear mechanical instabilities (snap-through) in curved shells, an experimental platform was developed for creating millisecond scale actuation. In our experiments, 50um thick LCE films were synthesized and attached to a curved, electrode-patterned 23um PET shell by silicone glue. An Arduino system was used to provide current pulses for periodic heating and a current sensor was integrated to track the actinic current as a function of time. To characterize the actuation, USB digital cameras were used to record the deformation from front and side views and a FLIR infrared camera was positioned to monitor the actuator temperature variation from above. The dynamics of snap-through time (ms) was characterized using high speed imaging. Repetitive actuation over tens of cycles was demonstrated.

8:15 AM SB01.07.02
Untethered Soft Robotic Matter with Passive Control of Shape Morphing and Propulsion Arda Kotikian¹, Connor G. McMahan², Emily Davidson¹, Jallilah Muhammad¹, Robert Weeks¹, Chiara Daraio² and Jennifer A. Lewis¹; ¹Harvard University, United States; ²California Institute of Technology, United States

There is a growing interest in creating untethered soft robotic matter that can repeatedly shape-morph and self-
propel in response to external stimuli for use in exploratory robots and adaptive structures. Towards this goal, we use multimaterial 3D printing to fabricate active hinges composed of liquid crystal elastomer (LCE) bilayers with orthogonal director alignment that interconnect polymeric tiles. When heated above their respective actuation temperatures, printed LCE hinges exhibit a large, energy-dense, and reversible bending response. Their actuation temperature and bending angle are controlled by employing LCE inks with disparate nematic-to-isotropic transition temperatures ($T_{NI}$) and hinge geometry, respectively. Through an integrated design and additive manufacturing approach, we demonstrate passively controlled, untethered soft robotic matter that adopts task-specific configurations on demand, including a self-twisting origami polyhedron that exhibits three stable configurations and a “rollbot” that assembles into a prism and self-rolls in programmed response to thermal stimuli.

8:30 AM *SB01.07.03
Liquid Crystalline Vitrimer Actuators Mohand O. Saed and Eugene M. Terentjev; Cambridge University, United Kingdom

Covalent crosslinking of a polymer network forms a distinct reference state, with respect to which the changes in liquid crystalline order in elastomers (LCE) could produce significant and reversible actuation. However, it was difficult to process the LCE materials into useful actuating shapes. Vitrimer networks offer a way to make processable plastics with shape-memory properties: with the plastic regime above vitrification temperature, re-shaping and re-alignment of LCE is now possible. Also possible is the joining-together and assembling of complex actuator structures via the bond-exchange reaction across the contact interface. In this talk we present a range of new (exchangeable) xLCE materials, including different bond-exchange chemistry, and also the dual vitrimers where a certain fraction of the polymer network remains permanent – and demonstrate their remarkable physical properties in large reversible actuation, and switchable dynamic adhesion. This new generation of the LCE and xLCE materials, showing both nematic and smectic phases of main-chain LC polymers, is very robust: with strain to break exceeding 150-200% and stress to break exceeding 0.8-1 MPa. The Young modulus of 0.7-1 MPa is found both in the non-aligned polydomain state, and in the aligned monodomain. With the reversible (equilibrium) thermal actuation strain amplitude of over 100%, the density of mechanical work delivered on the full thermal cycle reaches MPa levels, with the speed of response is only limited by the rate of heat diffusion into the elastomer body. We present and discuss practical thermo-mechanical devices using the heat-moulded xLCE as reversible actuators.

9:00 AM SB01.07.04
Light-Induced Athermal Shape Memory Effect in Liquid Crystal Elastomers Chongyu Zhu, Xiao Zhang, Jia Wei and Yanlei Yu; Department of Material Science, Fudan University, China

Shape memory polymers (SMPs) are promising candidates in the emerging fields of biomedicine, aerospace, flexible electronics and nanofabrication thanks to their programmable deformation.1 To date, the shape adaptations in most SMPs are triggered by external heat, which is not favored or feasible in bio-applications. Light-induced SMP has shown potentials owing to its temporal, localized, remote and isothermal triggering and actuation.2,3 However, the current light-induced SMP requires long activation time and the shape fixity rate remains low. Herein, we develop a new strategy to activate shape memory effect (SME) by light. Unlike triggering the thermal SMP by changing the external temperature, we switch the transition temperature of the photoresponsive polymer by light under ambient temperature to realize SME. To demonstrate this strategy, an azobenzene-based liquid crystal elastomer (azo-LCE) with dynamic covalent bonds is designed and synthesized via ring-opening metathesis polymerization. Upon sequential UV and visible light illumination, azo-containing mesogens undergo trans-cis-trans photoisomerization,4 varying the glass transition temperature of azo-LCE,5 thus to allow for the athermal processing of temporary shape. By exploring the SME of LCE, we realize various light-induced actuations with high shape fixity and recovery rate in 2 minutes without generating significant heat. In particular, we demonstrate the programmable shape recovery of artificial *mimosa* from the temporary shape to the original shape upon UV irradiation, mimicking the stimulus-response performance of natural mimosa. Moreover, the employment of dynamic covalent bonds is capable of altering the topology of the network, endowing this cross-linked LCE with excellent processability.6 Therefore, we manage to obtain and reshape different 2D and 3D structures from the same azo-LCE, solving the manufacture issue of conventional SMPs. We expect this light-programmable SMP provides potential applications for the future soft robotics and automation equipment.

References
Stimulus-responsive polymers are attractive for microactuators because they can be easily miniaturized and remotely actuated, which enables untethered operation. Inspired by biology, artificial cilia have been investigated for applications in sensing, microfluidics, and controlled wettability. Functional artificial cilia usually respond to applied stimuli but require maintaining the applied stimulus or are programmed to perform one-way processes that cannot be reset. Reconfigurable artificial cilia are desirable, whose shape can be set, locked, unlocked, and reconfigured. In this work, magnetic iron microparticles were dispersed in a thermoplastic polyurethane shape memory polymer matrix and formed into artificial, magnetic cilia by solvent casting within the vertical magnetic field in the gap between two permanent magnets. In this template-free method, interactions of the magnetic moments of the microparticles, aligned by the applied magnetic field, drive self-assembly of magnetic cilia parallel to the field direction. The resulting magnetic cilia respond simultaneously to magnetic fields and light. Temporary shapes obtained through combined magnetic actuation and photothermal heating can be locked by switching off the light and magnetic field. Subsequently turning on the light without the magnetic field drives recovery of the permanent shape of the magnetic cilia. These cilia are therefore reconfigurable rather than merely responsive. The permanent shape of the cilia can also be programmed after fabrication by applying mechanical constraints and annealing at high temperature. Spatially controlled actuation of cilia is demonstrated by applying a mask for pattern transfer into the array of magnetic cilia. Developing a theoretical model to predict the response of shape memory magnetic cilia elucidates physical mechanisms behind observed phenomena, enabling the design and optimization of ciliary systems for specific applications. Remote reconfiguration enabled by combining applied magnetic fields and light enhances the capabilities and broadens the applications of magnetic cilia.

Switchable Friction Coefficient on Shape Memory Photonic Crystals Yifan Zhang and Curtis Taylor; University of Florida, United States

Friction force on soft material usually is not linearly dependent on normal load because of the nonnegligible adhesion force or surface energy. As the adhesion force is proportional to the real contact area, friction force can be switchable by changing the surface roughness of the material. Here, we introduce a shape memory photonic crystal (SMPC) which is polymeric inverse opal structure and made of polyethylene glycol diacrylate (PEGDA) and ethoxylated trimethylolpropane triacrylate (ETPTA) co-polymer. The original ordered structure of SMPC providing a smooth surface can be programmed into a temporary disordered structure providing a rough surface by water swelling. The disordered structure can be recovered by ethanol swelling. Both programming and recovery are under room temperature. The previous studies demonstrate that this unusual athermal shape memory effect is caused by the competing between the elastic modulus (E) of material and the surface tension (µ) of the chemical solution. During the swelling, the porous structure is order because the polymer chains are lubricated by chemical solution and have high mobility. In this case, polymer chains tend to recover to their original conformation which is ordered porous structure. During the evaporation of the chemical solution, the capillary force from the surface tension (µ) of the solution will deform the porous structure into disordered status if µ is large (such as water) enough to compete with E. On the other hand, the structure will stay order if µ is not large (such as ethanol) enough. In this work, we first characterize the optical property of both ordered and disordered SMPCs by reflection spectra. The SMPCs show an obvious photonic band gap with ~530 nm wavelength in ordered (recovered) status and no
photonic band gap in disordered (deformed) status. Then, atomic force microscopy (AFM) and micro-indentation are used to characterize surface roughness and adhesion, respectively. The adhesion force on recovered SMPCs with a smooth surface is about three times larger than that on deformed SMPCs with a rough surface. Finally, a reciprocating sliding test is conducted on SMPCs by a spherical stainless steel tip under different normal load (0.5mN ~ 7mN). The friction coefficient on the recovered SMPCs can be 14 times higher than that on the deformed one. The mechanism behind this friction coefficient change will be discussed in this presentation.

9:45 AM SB01.07.07
Homogeneous Freestanding Luminescent Perovskite Organogel with Superior Water Stability
Yusen Zhao, Yucheng Zhang and Ximin He; University of California, Los Angeles, United States

Metal-halide perovskites have become appealing materials for optoelectronic devices. While the fast advancing stretchable/wearable devices require stability, flexibility and scalability, current perovskite still suffers from ambient-environmental instability and incompatible mechanical properties. To break the hindrance, recently perovskite–polymer composites have shown improved in-air stability with the assistance of polymers as the embedding media. However, their stability remains unsatisfactory in high-humidity environment or when immersed in water. These methods also suffer from limited processability with low yield (2D film or beads) and high fabrication cost (high temperature, air/moisture-free conditions), thereby limiting their device integration with complex structures and broader applications. Herein, a one-step scalable method is developed to produce freestanding highly-stable luminescent organogels, within which perovskite nanoparticles (NPs) are homogeneously distributed. The perovskite-organogels present a record-high stability, maintaining their high quantum yields for >110 days immersing in water at different pH and temperatures. This paradigm is universally applicable to broad choices of polymers, hence casting these emerging luminescent materials to a wide range of mechanical properties tunable from rigid to elastic. With intrinsically ultra-stretchable photoluminescent organogels, flexible phosphorous layers were demonstrated with >950% elongation. Rigid perovskite gels, on the other hand, permitted the deployment of 3D-printing technology to fabricate arbitrary 2D/3D luminescent architectures.

10:00 AM BREAK

10:30 AM *SB01.07.08
Photodeformable Liquid Crystal Polymers and Soft Actuators
Yanlei Yu; Fudan University, China

Photodeformable liquid crystal polymers (LCPs) that adapt their shapes in response to light have aroused a dramatic growth of interest in the past decades, since light as a stimulus enables the remote control and diverse deformations of materials.1-3 LCPs, especially the ordered ones, have demonstrated their potentials to dramatically increase the photodeformation extent and construct light-driven soft actuators because they possess fascinating features combining the entropic elasticity of polymeric elastomers and the ability to undergo a reversible and alignment dependent shape-change behavior of liquid crystals (LCs). Much effort was made to develop new photodeformable LCPs, including their basic actuation mechanisms, the various deformation modes, the newly designed molecular structures, and the improvement of processing techniques.4-6 In this report, special attention is devoted to the novel molecular structures of LCPs, which allow for easy processing and ordering. The soft actuators with various deformation modes in response to light are also covered with the emphasis on their photo-induced bionic functions and potential applications in optofluidics and optoelectronic devices.


11:00 AM SB01.07.09
A Multifunctional Shape Morphing Elastomer with Liquid Metal Inclusions
Michael Ford¹, Cedric Ambulo², Taylor Ware² and Carmel Majidi⁴; ¹Carnegie Mellon University, United States; ²The University of Texas at Dallas, United States
Wearable computers, stretchable electronics, soft robotics, healthcare, and other areas of research that require physical human-machine interactions demand materials that are inherently multifunctional. Human-made materials typically lack diverse multifunctionality that is more widely observed in nature, where a material can be soft and stretchable as well as responsive and adaptable to its environment. One promising class of materials is liquid crystal elastomers (LCEs), which are compliant, deformable, and undergo a thermally-activated liquid crystal phase transition resulting in macroscopic shape change. However, LCEs are electrically insulating with low thermal conductivity. Rigid fillers can improve relevant materials properties of LCEs and introduce additional functionalities, but at high loading (greater than a few weight percent), rigid fillers reduce shape-morphing capabilities of the LCE. In the multifunctional composite described in this work, functionality is retained at 50 vol. % (83 wt. %) loading of liquid metal microparticles (LM). Mechanical properties were characterized by mechanical testing and dynamic mechanical analysis. The LM inclusions do not degrades the compliance nor deformability of the LCE matrix, while rigid inclusions increased stiffness and prevented actuation. Thermal conductivity measurements showed improved heat dissipation capabilities of the LM-LCE composite relative to the unfilled material, critical for thermally-activated shape-morphing. Electrical conductivity of the LM inclusions enabled the possibility of Joule-heated actuation. Joule-heated actuation is uniform, robust, and resilient; the composite could actuate even after significant physical damage and could actuate for $>15,000$ cycles at 50 % strain and $>100,000$ cycles at 2.5 % strain. Shape change can be programmed for zero-stress actuation of irregular form factors. A soft crawling entity and architectures that demonstrates sensing, actuation, and traditional electronics interfacing highlight the potential use for this multifunctional composite in active areas of research.

11:15 AM SB01.07.10
Independent Multi-States of Photo-Responsive Polymer/Quantum Dot Nanocomposite Induced via Different Wavelengths of Light Jiyeon Lee, Wonsik Lee, Dongjun Kim, Myungjun Kim and Jiwon Kim; Yonsei University, Korea (the Republic of)

Stimuli-responsive systems are attractive since their properties can be controlled by external stimuli and/or surrounding environment. Recently, more than one stimulus is utilized in order to enhance the performance of systems, or to bypass undesired effects. However, most of previous research on multi-stimuli has been focused on enhancing or inducing changes in one type of response. Herein, we developed a nanocomposite material with independent multi-states composed of photo-responsive polymer and quantum dots (QDs), in which its properties can independently be controlled by different wavelengths of light. More specifically, azobenzene-incorporated poly(dimethylsiloxane) (AzoPDMS) triggers photobending (PB) by 365 nm light and uniformly dispersed methylammonium lead bromide perovskite (MAPbBr3) QDs show photoluminescence (PL) by light below 500 nm. The PB and PL could be simultaneously and independently controlled by the wavelength of applied light creating multi-states. Our approach is novel in that it creates multiple independent states which can further be used to transfer information such as logic gates ($00(2)$, $01(2)$, $10(2)$, $11(2)$) and possibly widen its application to flexible and transparent opto-electric devices.

11:30 AM SB01.07.11
Design Optimization of Liquid Crystal Elastomers with Programmable Stiffness David Yoo¹, Seung-Yeol Jeon², Andrew S. Gillman³, Sung H. Kang² and Phil Buskohl³; ¹UES, Inc, United States; ²Johns Hopkins University, United States; ³Air Force Research Laboratory, United States

Elastomeric lattices are widely applicable for energy absorption, impact protection, and signal propagation, due to their capability to undergo large, reversible strains and energy-dissipating buckling instabilities. In particular, architected liquid crystal elastomers (LCEs) combine the structural properties of lattice-based design with programmability of the material stiffness, offering tailored energy absorption properties. The stiffness of the LCE is locally programmed by the applied strain field, which orients the director (mesogen) of the LCE. However, the set of physically accessible strain profiles is regulated by the shape and spacing of the LCE beams within the lattice, creating a large design space to navigate. To address this challenge, a Bayesian optimization framework is utilized to design the shape of the LCE beams to achieve specific spatial strain distributions under applied loading. The beams are parametrized with a Fourier-series expansion, which controls the thickness as a function of beam length in terms of the magnitude, periodicity, and phase of the top and bottom layers. The Bayesian optimizer utilizes the posterior
distribution of the response surface that is obtained by a Gaussian process, creating a less expensive surrogate model for optimization and visualization. Representative 2D lattices for both bending and stretching dominated behavior under uni-axial loading were prescribed. The strain field within the designed LCE beams was calculated using a nonlinear finite element simulation to capture the geometric and material nonlinearities of the model. After calculating the strain field, statistics of the spatial distribution were compiled to predict the average stiffness increase of the lattice due to LCE director programming. The mean, variance and number of modes of the strain distribution were evaluated as objective functions for optimization. Preliminary results suggest uniform thickness beams with a range of lower periodicity (< 4) increases the variance of the strain distribution in the LCE. In contrast, beam designs with regions of narrow thickness result in lower variance of the strain distribution, but have larger differences in the maximum to the minimum strain difference, as the strain fields become more localized. Collectively, this design tool provides an initial framework to explore the coupling between geometry, strain and material programmability in the LCE system and has potential to inform the design of other material systems with strain-based patterning mechanisms.

11:45 AM SB01.07.12
Precise Network Polymerized Ionic Liquids for Low-Voltage, Dopant-Free Soft Actuators
Christopher Evans, Chengtian Shen and Qiujie Zhao; University of Illinois, Urbana-Champaign, United States

There has been substantial research interest in ionic liquids and polymerized ionic liquids (PILs) over the past decade due to their potential applications in energy storage, ion exchange membranes, gas/liquid separation membranes, and stimuli-responsive devices. Typically, a trade-off is observed between ionic conductivity and mechanical properties. Polymers provide a route to improve flexibility and mechanical properties of electrolytes but generally at the expense of conductivity. Here we report a new class of electroactive polymer that was designed and synthesized based on covalently crosslinked network PILs (n-PILs) to decouple conductivity and mechanical strength. Through molecular engineering, we are able to precisely control the spacing between ions, crosslinking density and linker polarity (hydrocarbon or oligoether). The resultant n-PILs exhibit low $T_g$ (~ -40°C), tunable ionic conductivity (> $10^{-5}$ S/cm under ambient conditions), and are self-standing (Young’s modulus 0.2-2.2 MPa) at room temperature. These n-PILs were investigated as dopant-free, single ion conducting actuators and showed bending strains as large as 0.9% under DC testing conditions which is comparable to the best performing ionic liquid swollen block copolymers. A large electrochemical window (±3 V) and absence of water or solvent allows our n-PIL actuators to retain >85% of the original bending strain after 1000 cycles under 3V, 0.1 Hz AC current. Modulus controls the response under DC conditions while the AC measurements are dependent on the ionic conductivity as well.

SESSION SB01.08: Multifunctional Hydrogels
Session Chairs: Michael Dickey and Richard Trask
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Ballroom A

1:45 PM SB01.08.01
A Multifunctional Anti-Icing Hydrogel for Controlling Ice Nucleation, Propagation and Adhesion
Zhiyuan He¹, Ximin He², Jianjun Wang¹ and Mutian Hua; ¹Chinese Academy of Sciences, China; ²University of California Los Angeles, United States

The ice formation processes on solid surfaces are complex and diverse, which makes it a daunting challenge to design an iceophobic material functional under different icing conditions in complex varying real-life environment. Developing an effective iceophobic material surface with multiple anti-icing functions through simple design and large-scale production is highly desirable. Biological antifreeze proteins (AFPs) offer a great example of multifunction integrated anti-icing materials that excel in all the three key aspects of anti-icing process, i.e., they can depress the freezing temperature, prevent the ice growth, and inhibit the ice recrystallization simultaneously by tuning the structures and dynamics of interfacial water. Inspired by antifreeze proteins (AFPs), a multifunctional anti-icing platform based on polydimethylsiloxane (PDMS)-grafted polyelectrolyte hydrogel is reported. The properties of interfacial water can be controlled via tuning the synergy of hydrophobicity and ion-specificity, which provides us a
promising route to integrate various icephobic advantages into one material. The controllability of interfacial water
grants the polyelectrolyte hydrogel coating high performance in inhibiting ice nucleation (ice nucleation temperature
lower than -30 °C), preventing ice propagation (ice propagation time higher than 500 s/cm²), and decreasing ice
adhesion (ice adhesion strength lower than 20 kPa). These low-cost hydrogels can be large-scale coated onto
different inorganic and organic materials, such as metals, plastics, oxides and ceramics. The simplicity, mechanical
durability, and versatility of these smooth hydrogel surfaces make it a promising option for a wide range of anti-
iccing applications.

References

2:00 PM SB01.08.02
Stretchable Distributed Waveguide Sensor with Deformation Differentiation Capability Hedan Bai, Shuo Li,
Yaqi Tu, Jose Barreiros, Clifford Pollock and Rob Shepherd; Cornell University, United States

Soft materials deform in a distributed fashion and in various modes. Although stretchable sensors have been
developed to sense the deformations of soft-bodied robots or human organs, each sensor can only sense one
deformation, and offers limited knowledge about the deformation’s mode and location. Advanced mechanical
sensing with richer information is usually achieved through sensor networks, or machine learning techniques, which
are complex on a systematic or computational level. In a step toward reducing complexity associated with advanced
mechanical sensing, we present a compact and low-cost design of a stretchable optical waveguide sensor, which
achieves the goal through sensing the rich information carried by light. The waveguide, composed of multi-core
structure and patterned with absorbing dyes, differentiates the deformations’ modes among stretching, bending and
pressing, and senses deformations’ location and magnitude. Furthermore, the sensor is capable of decoupling
deformations happening at multiple locations at the same time, and decoupling different modes of deformations.
These features are demonstrated in a 3D printed glove, which can use one waveguide sensor to sense in real time the
bending angles of the three joints on a finger, and simultaneously detect location and magnitude of an external press.

2:15 PM SB01.08.03
Light-Degradable Hydrogels as Dynamic Triggers in Implantable Devices Ritu Raman, Tiffany Hua, Declan
Gwynne, Joy Collins, Siddartha Tamang, Vance Soares, Tina Esfandiary, Jianlin Zhou, Simo Pajovic, Alison
Hayward, Robert Langer and Giovanni Traverso; Massachusetts Institute of Technology, United States

Introduction: There is a critical need for a safe, non-contact, and dynamically activated trigger for actuating
implantable devices. Inducing on-demand degradation of these devices enables tuning treatments to the needs of
individual patients, diseases, and recovery schedules. Triggers based on other stimuli, such as heat, pH, or enzymatic
chemicals, have been employed in some in vivo applications, but come with many restrictions that limit their use for
several disease use cases. Light-triggerable materials offer non-contact on-demand degradation with high spatial and
temporal resolution. We have developed a tough light-triggerable hydrogel with tunable mechanical properties and
modular design that can be degraded in a safe and non-contact manner in vivo. We apply these materials to two
applications in the gastrointestinal tract: a bariatric balloon and an esophageal stent. We demonstrate
biocompatibility and on-demand triggering of the material in vitro and in vivo. We characterize performance of the
system in a large animal model with an accompanying ingestible LED. This is, to our knowledge, the first
demonstration of light-degradable hydrogels in vivo.

Methods: We custom-manufactured an acrylated ortho-nitrobenzyl (oNB)-based compound and used it as a linker
to polymerize hydrogels from a range of materials, including polyacrylamide (PAAM) and poly (2-acrylamido-2-
methylpropane sulfonic acid) (PAMPS) single network gels and tough PAMPS/PAAM double network gels.
Cytotoxicity of the materials and degradation byproducts was evaluated on two cell lines. Mechanical properties
were measured using rheological testing and compression testing. Materials were degraded in vitro and in vivo
(porcine model) using custom-made LED arrays and ingestible light-emitting pills.

Results & Discussion: The mechanical properties of our material far exceeded previously reported properties for
light-degradable gels (>100 times stronger) and enabled, for the first time, their in vivo use. The mechanical
properties and degradation timelines of these materials could be tuned using a variety of parameters, such as gel composition and light wavelength, intensity, and distance from the material. The material could be dissolved within minutes of irradiation and its degradation byproducts, as well as degradation light wavelengths (365-405 nm) were proven biocompatible. We showcased the advantageous properties of our material in two use cases: a gastric resident bariatric balloon and an esophageal stent. In the gastric resident device, we triggered light-activated reduction in the size of an ingestible space-filling balloon in vivo using an ingestible LED pill. If employed in a patient, this functionality could enable on-demand passage of the space-filling device when residence is no longer required. This would provide a significant advantage over the current clinical standard, which requires an invasive endoscopic procedure to retrieve the balloon. Similarly, we have developed a triggerable gel-linked esophageal stent in which light irradiation provides a non-contact method for safely dissolving and removing the stent from the esophagus without risking off-target detrimental effects to the tissue lining that arise from mechanical-, heat-, or chemical-based triggers. This could be used to treat benign and malignant stenoses or strictures. Our material enables dynamic, biocompatible, spatially controllable, and non-contact degradation in vivo.

Conclusions: Triggerable materials stand to transform our capacity to precisely control biomedical device activity and performance while reducing the need for invasive interventions. Our light-triggerable hydrogels have the potential to be applied broadly throughout the GI tract and other anatomic areas. By demonstrating the first use of light-degradable hydrogels in vivo, we provide engineers and clinicians with a novel, safe, dynamically deliverable, and precise tool to design dynamically actuated implantable devices.

2:30 PM BREAK

3:30 PM SB01.08.04
Efficient Fabrication of Stimuli-Responsive PNIPAM Hydrogels and Programmable Soft Actuator Jingwei Liu, Xuhao Fan, Yufeng Tao, Chunsan Deng, Wenguang Zhang and Wei Xiong; Huazhong University of Science and Technology, China

Stimuli-responsive hydrogels have been widely used in many fields, including soft robots, bioengineering, and smart sensors, due to their excellent flexibility, stimuli responsiveness, and shape change performance, which have attracted extensive attention. However, the tedious and time-consuming preparation process, low response speed, and requirement of toxic additives/solvents severely limit their practical application. Here, we reported a cost-efficient two-step synthetic method for stimuli-responsive Poly(N-isopropylacrylamide) (PNIPAM) hydrogel with additive-free, fast response, large swelling ratio, and high fatigue resistance. Results show that the overall performance of the as-synthesized PNIPAM hydrogels is among the top level compared with other reported work despite the significantly shortened preparation time. Moreover, we have also achieved large photo-thermal response and remote control capabilities by introducing multi-wall carbon nanotubes (MWNTs) into the PNIPAM hydrogel, demonstrating precise tuning of the bending angle and deformation geometry of the nanocomposite hydrogel under infrared laser irradiation. Lastly, we designed and integrated the stimuli-responsive hydrogels with stretchable circuits to make an electric-driven soft actuator, which is capable of multi-mode programmable electric-driven actuation. It is expected that the electric-driven soft actuator could have great potential for the application of artificial muscles and aquatic soft robots.

3:45 PM SB01.08.05
How Smart and Actuatoric Hydrogel Systems Can be Developed by High-Energy Electron Treatment Stefanie Riedel1,2 and Stefan G. Mayr1,2; 1Leibniz Institute for Surface Modification, Germany; 2Universität Leipzig, Germany

The development of smart biomaterials is a challenging task. Via the promising high-energy electron treatment, biological relevant hydrogels such as gelatin can be engineered to become smart materials. Due to their original biocompatibility and cytocompatibility, they show a high potential for applications in biomedicine and related fields. Therefore, reagent-free methods to develop smart hydrogels are required. A highly favorable technique is high-energy electron treatment, which can be used to develop smart and stimuli-responsive hydrogels. Within this contribution, we will present two different preparation processes utilizing high-energy electron treatment to develop effective thermo- and hydration-responsive gelatin hydrogels. Since high-energy electron treatment is highly advantageous for reagent-free modification of biological hydrogels, the resulting smart hydrogel materials have a great potential for applications in biomedicine and related fields.
4:00 PM SB01.08.06
AFM Assessment of the Mechanical Properties of Stem Cells During Differentiation
Jie Zou¹,², Weiwei Wang¹, Xianlei Sun¹,³, Wingtai Tung¹,³, Nan Ma¹,² and Andreas Lendlein¹,³; ¹Helmholtz-Zentrum Geesthacht, Germany; ²Free University of Berlin, Germany; ³University of Potsdam, Germany

During tissue formation and regeneration, the dynamic mechanical force transmitted through microenvironments continuously impacts on the mechanics of cells. Cellular mechanical properties are closely related to genes and proteins expressions [1, 2]. The mechanical properties would alter during the procedure of stem cells differentiating into different lineages. At different stages of stem cell differentiation, the cells display varying levels of mechanical properties in response to surrounding microenvironments, which depends on the composition and organization of subcellular structures, especially the cytoskeleton and nucleus. The mechanical properties of cell nucleus affects the proteins folding and transport as well as the condensation of chromatin [3], which further regulates cell fate. However, few studies have assessed stems cells mechanical property during differentiation. In this study, the mechanical properties change of human bone marrow mesenchymal stem cells (hBMSs) during the procedure of adipogenic and osteogenic differentiation were determined by atomic force microscopy (AFM) at different time points. Simultaneously, the change of histone modification level and cytoskeleton were characterized by laser confocal microscopy and flow cytometry. Through comparing the mechanical properties of the nuclei at different stages of cell differentiation found that the stiffness of nuclei increased with the induction time prolongation. Immunofluorescence results show that the intensity of H3K27me3 significantly increased over the differentiation. Our results indicate that AFM is a facile and effective method to monitor stem cells differentiation.

Key words : stem cell, cell mechanics, AFM

Reference

4:15 PM SB01.08.07
Wood-Inspired Aligned Hydrogels with Structural Control for All-Solid-State Supercapacitors
Yusen Zhao and Ximin He; University of California, Los Angeles, United States

Wood in nature has well-defined vertical structure with low tortuosity to facilitate the mass transport. Inspired from the wood structure, we designed anisotropic hydrogels with alignment to increase the ionic conductivity of materials. The pore size can be rationalized and reduced even smaller than natural wood to increase the specific area, while maintaining the alignment. Conducting polymer, owing to its mesoporous structure and high electrical conductivity has been widely used for supercapacitors. By incorporating the conducting polymer in hydrogel-based matrix, the all-solid-state supercapacitor with high electrochemical performance can be fabricated. Such conducting polymer-hydrogel composites exhibit unprecedented ionic conductivity, areal supercapacitance, power density, energy density, capacitance retention and cyclic stability. Besides, the hydrogel matrix also provides excellent flexibility under cyclic bending, making it possible for flexible electronics.

4:30 PM *SB01.08.08
Multifunctional Hydrogels as an Emerging Platform for Sustainable Energy and Environmental Technologies
Guihua Yu and Xingyi Zhou; The University of Texas at Austin, United States

Given their intrinsic hierarchical micro-/nano-structures, unique chemical/physical properties and tailorable
functionality, hydrogels and their derivatives have emerged as an important class of materials for many exciting applications beyond their traditional biomedical applications. Bottom-up synthetic strategies to rationally design and modify their molecular architectures enable functional hydrogels to address critical challenges in renewable energy and environmental technologies.

In this talk, I will present our recent advances made in nanostructured functional hydrogels, particularly those based on conjugated polymers, as an emerging material platform for sustainable energy and environmental technologies, including high-energy-power batteries and supercapacitors, and solar water desalination and atmospheric water harvesting. I will further illustrate ‘structure-derived multifunctionality’ of this special class of materials.

SESSION SB01.09: Poster Session III
Session Chairs: Andreas Lendlein, Barbara Mazzolai and Philippe Poulin
Wednesday Afternoon, December 4, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB01.09.01
Evaluation of Anisotropic Dynamic Wettability and Liquid Movement on Cuticle Structure
Nozomi Ito, Daisuke Ishii and Shingo Ito; Nagoya Institute of Technology, Japan

Introduction
Many animals including humans have a lot of hairs on their body surface in order to protect their body surface. The outermost surfaces of the hair have cuticle structures in a scaly overlapping manner from the root to the tip of hair. The cuticle plays an important role as protection of the interior of the hair against external irritation. Furthermore, it is said that it plays a role of transporting the sebum secreted near the root to the tip of hair. Anisotropic surface structure such as cuticle greatly contributes to wettability. However, we have a question about the direction of sebum transport phenomena due to the fine cuticle structure.
In this research, we tried to investigate dynamic wettability of the cuticle structure, to clarify regularity in this fine structure, and to consider correlation with the liquid transport phenomenon. To elucidate the wettability of anisotropic surface structures can be expected to apply to microfluidic devices, hair cosmetic products, and antifouling coatings.

Experimental Method
Dynamic wettability toward water droplet of 3 to 40 pL such as a receding angle and a droplet evaporating behavior was measured by using Microscopic Contact Angle Meter (MCA-3 type I). Distilled water, which is a volatile liquid, evaporates in less than 30 sec. The receding angle can be measured during the evaporation process. The amount of the droplet during the measurement is kept much smaller than the capillary length at which the liquid begins to be affected by gravity, it is possible to measure dynamic wettability of the cuticle structure excluding the influence of gravity.

Results and Discussion
The dynamic wettability of the cuticle structure toward to picolitter-scaled water droplets indicated that, an anisotropic pinning effect was observed at the cuticle structures in the case of the longer diameter of water microdroplet than the interval of cuticle. The receding angle from the tip side to the root side of the hair was measured during evaporation of the water microdroplet. This result also indicated that the anisotropic water spreading from the tip to the root of hair was depended on commonly consideration of sedum transporting on the cuticle from a root to a tip of hair surfaces. The water manipulation learning from this mechanism will help to produce biomimetic fluidic devices.

SB01.09.03
Facile Method to Synthesize Ultra-Stretchable Light Managing Soft Materials for Performance Enhancement of Optoelectronic Devices
Hanmin Jang, Kang Won Lee, Sungwon Jo and Dong Rip Kim; Hanyang University, Korea (the Republic of)
We report the synthesis method of ultra-stretchable soft materials for effective light modulation of optoelectronic devices such as solar cells and light emitting diodes. We controllably generate multi-scale pores within soft materials (e.g., silicone rubber) to effectively control their light reflection properties by using the water-streaming method, which can be extended to ultra-stretchable soft materials. Specifically, formation of the pores on the surfaces of soft materials enables to fabricate the anti-reflective soft materials with light reflection of less than 4% in the visible wavelengths. In addition, multi-scale pore generation within the soft materials leads to achieve light reflection of more than 95% in the visible wavelengths without incorporation of metallic or ceramic components. The fabricated soft materials exhibit ultra-stretchable properties of up to ~300% engineering strain. Those layers are assembled to commercial organic solar cells as anti-reflective and back-reflective layers as such they significantly increase the light absorption and the light energy conversion efficiency of the solar cells due to the enhanced light trapping effects. Our all-polymer platform with effective light managing properties can be readily applied to commercial optoelectronic devices for their enhanced performance with diverse applications.

Acknowledgement
This research was supported by the International Research and Development Program (NRF-2018K1A3A1A32055469) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT of the Republic of Korea.

SB01.09.04
Patterning Magneto-Actuation of Polymer Composites Microarrays Jisoo Jeon1, Jeong Eun Park1, Sei Jin Park2, Sukyoung Won3, Hangbo Zhao3, Sanha Kim1, Bong Sup Shim1, Augustine M. Urban4, Anastasios J. Hart3, Zahyun Ku2 and Jeong Jae Wie1; 1Inha University, Korea (the Republic of); 2Lawrence Livermore National Laboratory, United States; 3Massachusetts Institute of Technology, United States; 4Wright-Patterson Air Force Base, United States

Magneto-responsive materials are emerging sources for packaged shape reconfigurable devices owing to its rapid contactless actuation by the external magnetic field. While programmability of magneto-responsive materials enables multi-modal actuation such as bending, twisting, and their hybridized actuation mode, most reports are limited to demonstrate of single actuation mode in a single sample. Herein, we report patternable actuation modes within a single sample by utilizing the patterned magnetic field to align the magnetic component. Furthermore, we also demonstrate programmability of actuation modes in a single sample by adapting a masking technique for arbitrary patterned actuation of the microarray. Remarkably, reversible magnetic actuation of patterned microarrays is achieved 100 actuation cycles. The programmable magneto-responsive microarrays could be served as a general platform for shape reconfigurable tunable microdevices.

SB01.09.05
Biomimetic and Bioinspired Structures for Energy Harvesting and Sensors in Piezoelectricity Chang Kyu Jeong; Chonbuk National University, Korea (the Republic of)

Elastic composite-based piezoelectric energy harvesting technology is highly desired to enable a wide range of device applications, including self-powered wearable electronics, robotic skins, and biomedical devices. Recently developed piezoelectric composites are based on inorganic piezoelectric fillers and polymeric soft matrix to take the advantages of both components. However, there are still limitations such as the weak stress transfer to piezoelectric elements and the poor dispersion of fillers in matrix. In this talk, a highly-enhanced piezocomposite energy harvesters (PCEH) is representatively developed using a three-dimensional (3D) interconnected electroceramic skeleton by mimicking and reproducing the sea porifera architecture (although the speaker will introduce other research examples and achievements). This new mechanically reinforced PCEH is demonstrated to resolve the problems of previous reported conventional piezocomposites, and in turn induces stronger piezoelectric energy harvesting responses. The generated voltage, current density and instantaneous power density of the biomimetic PCEH device reach up to ~16 times higher power output than that of conventional randomly-dispersed particle-based PCEH. This work broadens the further developments of high-output elastic piezocomposite energy harvesting and sensor application with biomimetic architecture.
An Optimized Spring Roll Dielectric Elastomer Actuator Design for Various Situational Applications

Seung Mo Jeong and Ki-Uk Kyung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Dielectric elastomers are a type of electro-active polymers that have been investigated for its use in artificial muscle-like stretchable actuators. Dielectric elastomers are characterized by their high energy density, large strain rate, fast response, softness, lightweight, and low cost [1]. There have been many attempts at harnessing and utilizing these characteristics. To apply elastomers in various conditions and structures, numerous actuator configurations were designed, such as spherical, cylindrical/tubular, and zipping actuators [2][3]. Also, to produce a larger linear motion or to maintain stability, soft actuators combined with other actuation mechanisms, such as hydraulics and magnetism, have been fabricated [4][5]. A spring roll actuator is composed of a thin dielectric elastomeric sheet wrapped around a spring core. This configuration converts the dielectric membrane’s expansion into linear motion. As a result, upon activation, a muscle-like movement is produced. Designing of spring roll actuators based on models has been attempted, to obtain an optimal design and to increase the performance [1][6-8]. Although the model-based approach was effective, experimental results did not completely match with model predictions, due to nonlinear properties. We propose a model-based spring roll actuator design, which considers both static and dynamic conditions. Using strain energy functions, a viscoelastic material model of the actuator is established. Then, overall governing equations are derived from the Helmholtz free energy equation and the viscoelastic model. With fabricated spring roll actuators, the proposed actuator model is experimentally verified in static and dynamic conditions. In conclusion, we present a general model of spring roll dielectric elastomer actuators and its optimized fabrication parameters for specific operating conditions.


Reconfigurable Microswarm Mimics the Structure and Function of Ant Bridges for Electronic Applications

Dongdong Jin, Jiangfan Yu and Li Zhang; The Chinese University of Hong Kong, Hong Kong

Ant colonies in nature are able to cooperatively accomplish complex tasks that are beyond the capabilities of individuals through self-organizing into sophisticated and functional structures. For example, to traverse difficult terrain, ants grip firmly the bodies of each other, and constitute a living, flexible and robust chain-like ant bridge to march across the gaps beyond the reach of individuals.

Emulating natural collective behaviors promises benefits in various engineering fields, and has been partially realized through elaborate algorithm and physical designs in traditional large-scale robotic swarms. Further downsizing the swarms to micro-/nanoscale is envisioned to expand their applications in the hard-to-reach regions for humans, such as targeted delivery, microelectronics, and so on[1, 2]. However, to date, developing microswarms with group-level functionality still remains a challenge.

Previously, our group has developed various magnetic actuation strategies for microrobotic systems[3-5]. Herein, we present a magnetic microswarm that emulates the collective behaviors of ant bridges for electronic applications[6]. The building blocks of microswarm are fabricated by functionalizing Fe₃O₄ nanoparticles with a continuous gold surface layer, so that they are both paramagnetic and electrically conductive. Under a programmed oscillating magnetic field, the building blocks are reconfigured into a ribbon-like microswarm, which can perform reversible elongation with a high aspect ratio. Through elaborately tuning the magnetic field parameters, we apply the microswarm to self-assemble a chain-like conductive pathway for electrons between two disconnected electrodes with the bodies of building blocks, thus mimicking both the structure and function of ant bridges. We demonstrate that the microswarm is capable of serving as a microswitch, repairing broken microcircuits and constituting flexible circuits with the advantages of customizable controllability, high precision and long-term stability. This work
provides an example of how science and technology can be inspired by nature. Further adjusting the surface functionalization process may endow the microswarm with new collective behaviors and functions, thus paving the way for better understanding the complex collective behaviors of living systems.

ACKNOWLEDGMENT
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REFERENCES

SB01.09.08
Tantalum Oxide Nanoparticles as a Contrast Agent for Articular Cartilage Imaging Anisha Joenathan1, Taylor Lawson1, Janne Mäkelä2, Brian Snyder1,4 and Mark Grinstaff1; 1Boston University, United States; 2University of Eastern Finland, Finland; 3Boston Children's Hospital, United States; 4Beth Israel Deaconess Medical Center, United States

Cartilage consists of a collagen network coupled with a hydrated matrix of negatively charged sugars known as glycosaminoglycans (GAGs). GAGs are responsible for attracting and immobilizing water within the tissue as well as providing high resistance to compression due to charge repulsion. A decline in GAG content is an early indication of osteoarthritis (OA), a disease that deteriorates the mechanical integrity of cartilage. To date, early diagnosis of OA remains nearly impossible. Using contrast enhanced computed tomography (CECT), tissues such as cartilage can be visualized to ascertain properties such as thickness, morphology, and biochemical states of various tissues. Nanoparticles (NPs) are of particular interest as a CECT contrast agent due to their modifiable properties such as composition, diameter, high surface area, and confined electronic structure. NPs containing gold, bismuth, and tantalum have been used as X-ray contrast media for CECT. Tantalum is biocompatible, can be functionalized with a variety of silane ligands, and absorbs a greater fraction of X-rays compared to conventional iodinated contrast agents, making it an attractive contrast agent material for CECT. We have synthesized a new positively charged tantalum-oxide nanoparticle (Ta2O5 NP) as a contrast agent for CECT assessment of cartilage health and integrity. The NPs were synthesized with positively charged tetra-ammonium ligands to bind to anionic GAGs and a short polyethylene glycol layer to improve biocompatibility. We have successfully imaged naturally occurring osteoarthritic defects in ex vivo human metacarpal phalangeal joints using CECT with NPs with different surface charges. Additionally, we measured NP diffusion into tissue and subsequently characterized the biochemical and biomechanical state of the entire cartilage.

SB01.09.09
Self-Assembly of Polysaccharide LC Domains over Millimeter Scale During Evaporation and Their Anisotropically Swelling Hydrogels Gargi Joshi, Kosuke Okeyoshi, Maiko K. Okajima and Tatsuo Kaneko; Japan Advanced Institute of Science and Technology, Japan

Self-assembly of biopolymers like proteins and polysaccharides, through their liquid crystalline (LC) state, provides reconfigurable structures in nature. These are effectively mimicked by researchers to develop highly ordered architectures through various self-assembly processes. We reported the self-assembly of polysaccharides, sacran and xanthan gum upon drying their aqueous LC solution from a limiting interface as an example of instability-driven pattern formation. By controlling the cell width, the polysaccharide deposited to form multiple vertical membranes, bridging the millimeter-scale gap between the substrates, partitioning the available space. The interesting aspect is the size of the LC structural unit (mesogen) of sacran. It has been reported to be 1 µm in diameter and < 20 µm in length, the aspect ratio being more than 20, when compared to other popular biopolymers like CNF, DNA. The size and interactions between these mesogenic units have not been considered. The basic
theory is that as the receding air-water evaporative interface reaches their location, the domains are formed like a crust/ skin-layer. In order to create a new surface, energy is needed which comes from the supplied temperature as thermal energy. They experience capillary forces towards the substrate-wall as well as strong interparticle capillary interactions. In this competition of forces, the interparticle interaction is long-ranged and also stronger, resulting in bridging depositions. In this study, we have explored the effect of the size of the LC domains of the polysaccharide solution in the space partitioning phenomenon.

[REFERENCES]

[ACKNOWLEDGEMENTS]
G. J. is grateful for the JSPS Fellowship and the KAKEHNI Grant #JP18J11881.
Then, we have fabricated LCE lattice structures based on the design guidelines and characterized their mechanical behaviors. We synthesized main-chain LCEs in a replica mold of the desired shape through a two-stage thiol–acrylate reaction. Before the second stage reaction, the LCE structures were detached from the mold and different amount of strain was applied to the structures. In accordance with generated strain distribution, mesogens were differently aligned inside the structures. As a result, different modulus distribution was achieved. After that, the alignment was fixed with UV light and the structures were restored to their original shape by heating. Then, we investigated mechanical behaviors of differently “programmed” structures using universal testing system and found that the structures show different mechanical behaviors depending on the changed modulus distribution as a result of “programming”. For example, a structure with the same shape changed its behavior from positive stiffness to almost zero stiffness, i.e. stresses maintained nearly constant within broad strain range, after programming. In addition, we will present our characterization results of strain distribution in the LCE lattices and resulting modulus change to compare with the prediction from Bayesian optimization as well as our studies of combining different types of programmed structures to achieve various mechanical behaviors.

We envision that our findings can contribute to enabling the next generation meta-materials by providing the capability to manipulate the mechanical behaviors of lattices through a simple programming procedure with applications including load bearing (positive stiffness), energy absorbing (negative stiffness), and large actuation with minimum input energy (near zero stiffness). It can also contribute to improving an engineering system efficiency by enabling multi-functionalities from one component.

SB01.09.12
Facile Fabrication of Micro/Nano-Structured Wrinkles by Controlling Viscoelasticity of Soft Elastic Substrates Eun Seon Kim1,2, Sung Hyun Kim1, Sang-Jin Lee1, Dong Hack Suh2 and Woo Jin Choi1; 1KRICT, Korea (the Republic of); 2Hanyang University, Korea (the Republic of)

Wrinkling rendered by the buckling of a strained stiff layer attached to a soft elastomer substrate has been widely used in various applications such as smart adhesion, optical grating, precision metrology, surface engineering, stretchable electronics, and antifouling coating. This is because it is an efficient and low-cost strategy to control surface morphology. There were many researches on the formation of wrinkle surface in film/substrate bilayers through compressive stresses by various factors such as mechanical compression, thermal expansion mismatch, lattice mismatch, solvent-induced swelling, capillarity force, environmental stimulus, and bubble inflation, etc. Especially, the method of strain mismatch leads to thermal stress from a difference in the coefficient of thermal expansion between thin films and soft substrates for producing a wrinkled structure which has been extensively investigated throughout theoretical and experimental approaches. Bowden et al. first reported that complex surface patterns are formed by depositing a metal thin film onto a polydimethylsiloxane (PDMS) due to thermal contraction of the soft substrate by electron beam evaporation1. Stafford et al. observed that the formation of complex surface patterns can be controlled by elastic modulus depending on the difference in thermal expansion when the ultrathin amorphous polymer on a soft elastic substrate2. Im et al. have theoretically studied that the viscoelastic properties of thin polymer films play an important role in fabricating ordered structures by modeling3. However, rheological properties of viscoelastic substrates for developing wrinkle structures by the sputtering system are still insufficient up to now.

In this research, we report the controlled surface morphologies of fluorocarbon thin films deposited on soft elastic substrates by a mid-frequency sputtering using the sputtering target of carbon nanotube/polytetrafluoroethylene composite polymer. The fluorocarbon thin films deposition and particle bombardment can produce heat the PDMS substrates greatly during the sputtering process. We demonstrate a one-step method to obtain the micro/nanostructured wrinkles by changing the viscoelastic properties of PDMS substrates. The viscoelasticity of substrates was controlled with various amount of curing agent and different curing conditions such as temperature and time. The surface morphology for these samples strongly depended on the viscoelastic properties of PDMS substrates. The rheological properties and surface morphologies were systematically studied and discussed. This study provides a facile and effective method for fabricating different wrinkle structures by controlling the viscoelasticity of PDMS substrates.

References
The nanocomposite coating system was constructed by a composite film composed of inorganic polymer and graphene for metal protection. The anti-corrosive technology for metal protection is essential in contemporary industry. Although the metal species such as copper (Cu), aluminum (Al), stainless steel, etc., have a very important role in wide commercial application fields including building, automobiles, electronics, etc., they are susceptible to corrosion; spontaneous degradation reaction showing similar mechanism to electrochemical reaction at the interface between electrode and electrolyte [1]. This kind of reaction leads to undesirable deterioration of own functional properties by structure deformation of materials and a lot of financial losses. So far, most researches have been focused on the fabrication of insulating coating barrier as one of the candidates to break through this problem [2,3]. However, the necessity which requires multifunctional roles not only defending main materials but also having additional functionality such as electrical conductivity and thermal conductivity came to the fore. Furthermore, selectivity properties against various environmental factors for protective barrier layer are issues in recent semiconductor electronics, many devices including anti-icing, electromagnetic shielding (EMI) and energy storage systems [4-6].

With this consideration, we studied about dual function behaviors of electrically conductive anti-corrosion coating layer which is composed of inorganic polymers such as polysiloxane (PSX) or polysilazane (PSZ) and graphene. Inorganic polymer, PSX or PSZ, was used as a main barrier matrix with excellent chemical stability and defect covering agent for graphene and graphene, a 2-dimensional carbon allotrope, was applied as a conductive filler and a stress relaxation agent of composite matrix. The Inorganic polymer-graphene nanocomposite shield layer was fabricated on metal substrate such as Cu or Al by a simple coating process using a metering rod or a doctor blade. After curing process, the inorganic polymer-graphene nanocomposite barrier film showed enhanced corrosion inhibition properties when they were exposed to seawater (3.5 wt% NaCl) or sulfuric acid (H2SO4) comparing to both of bare Cu or Al substrates. To be specific, the corrosion rate of inorganic polymer-graphene nanocomposite film was prominently decreased (minimum 1/40th compared to bare Cu in 3.5 wt% NaCl solution and 1/2000th compared to bare Al in 0.5M H2SO4 solution) and charge transfer resistance was noticeably improved (minimum 2×10^4 times higher than bare Cu in 3.5 wt% NaCl solution and 2.77×10^6 times higher than bare Al in 0.5M H2SO4 solution). Furthermore, this coating film exhibits the electrical conductivity enhancement as increase of conductive carbon filler to maximum 1.70×10^3 S m^-1 on Cu and to 35 S m^-1 on Al. With the result of this study, the inorganic polymer-graphene nanocomposite coating layer exhibits superior multifunction properties including anti-corrosion and electrical conductivity with the synergetic effect between inorganic polymer and graphene.

We believe that further understanding and modifying inorganic polymer-graphene nanocomposite coating system has the potential to broaden the area of application which needs multifunctionality in the field of thermal interface materials, EMI, anti-icing and etc.

References
cross-linkers to make solid-state chemical ion gels. We fabricated stretchable ion gels that can be applicable to various electronic/optoelectronic devices by controlling the crosslinking density of the network polymer. By modifying the interface of the target substrate, stretchable devices could be stick to various substrates including SiO₂, metal, plastic, and rubber surfaces, which clearly demonstrates versatility of the adhesive ion gels for E-skin devices. We introduced adhesive ion gels to fabricate flexible strain sensors. Electrical properties of the flexible sensors including sensitivity, linearity, transmittance, and durability were systematically investigated. The resulting sensors using adhesive ion gels performed better than normal ion gel sensors without adhesive functionality. Furthermore, we controlled the structure and morphology of the adhesive ion gels to enhance the sensing performance.

SB01.09.15
Compositional and Morphological Study on a Polyaniline (PANI) Hydrogel for a 3D Porous Electrode Ji Hye Kim¹, Ju-Hee So², Sungkon Kim³ and Hyung-Jun Koo¹; ¹Seoul National University of Science and Technology, Korea (the Republic of); ²Korea Institute of Industrial Technology, Korea (the Republic of); ³Chonbuk National University, Korea (the Republic of)

Since any electrochemical reactions occur at surface of electrodes, an electrode with well-defined porous structure, and therefore high surface area, would be preferred. Upon crosslinking with phytic acid, polyaniline (PANI) forms a conducting hydrogel with a hierarchical 3-D porous structure. Such a PANI-based hydrogel could be a promising electrode for various electrochemical applications. Here, we present the effect of compositions in preparation of PANI on its pore morphology and electrical property. It turns out that the composition of monomer, initiator, and crosslinker in preparation has a significant influence on the morphology of the PANI hydrogel. As initiator/crosslinker increase or monomer decreases, the PANI conducting hydrogel has denser morphology with decreased pore size, resulting in higher electrical conductivity. The PANI conducting hydrogel with 3-D porous morphology could serve as an efficient electrode of an electrochemical capacitors. In the 3-electrode configuration, the PANI hydrogel electrode prepared at the optimized compositions exhibited 294 mF/cm² of capacitance with ~50% retention rate after 5000 cycles. Finally, we fabricated a practical capacitor with two symmetric PANI hydrogel electrodes, which shows 195 mF/cm² of capacitance with improved cycle stability of 80% retention rate.

SB01.09.16
Type 2 Nanotheranostics—MRI Guided Hyperthermia Using Magnetic Softness Tuned γ-Iron Oxide (MSTIO) Nanoprobes Jiwook Kim and Seongtae Bae; University of South Carolina, United States

Theranostics is a combination of the terms diagnosis and therapeutic. This concept was further developed to Nano-Theranostics with advancements in nanotechnology over the last decade. In the Nano-Theranostics, nanoscale imaging module, targeting module, or therapeutic module were incorporated into a single system by chemical conjugation or encapsulation methods. However, the multiple compositions and complex structure of these Nano-Theranostics agents (we call this “Type 1 Nano-Theranostics agent”) have several hurdles (i.e., low reaction yield, high synthetic cost, and difficulty in verifying their toxicity) for biomedical applications. Here, we introduce next-generation of Nano-Theranostics agent, called “Type 2 Nano-Theranostics” which is MRI guided hyperthermia using magnetic softness tuned g-iron oxide (γ-Fe₂O₃, MSTIO) Nanoprobes. While the conventional magnetic nanoparticle-based agents are optimized for the individual function of MR effect or heat induction power, MSTIO possesses both exceptionally high intrinsic loss power (ILP, ~ 7.0 nHm²kg⁻¹) at a biologically safe range of AC magnetic field (H_{appl} f_{appl} = 5.0×10⁶ Am⁻¹s⁻¹) and a significantly enhanced r2-relaxivity of MRI (r₂ = 647.94 mM⁻¹s⁻¹). The enhanced hyperthermic antitumoral effects and T₂-MR contrast imaging of MSTIO tested in rat models are primarily due to the dramatically increased saturation magnetization (M_s), resulted from the precisely controlled occupation of Ni²⁺/Zn²⁺ cations in T₂ and O₃ sites. We also found that 20-30 nm of the γ-Fe₂O₃, nanoparticles with ultra-thin surface layer shows best heat induction performance under the bio-safe range of AC magnetic field (f=100 kHz, H=120 Oe) from the numerical simulations and experimental results. Due to their excellent dual functionalities implemented in a simple system, we believe that MSTIO nanoprobe will be one of the best candidates of Type 2 Nano-Theranostics for future nanomedicine.

SB01.09.17
Reconfigurable Photonic Surfaces Assembled by Amphiphilic Photonic Tiles at the Air-Water Interface Jong Bin Kim, Gun Ho Lee and Shin-Hyun Kim; KAIST, Korea (the Republic of)
Many organisms in nature have a photonic epidermis composed of an assembly of iridophores, iridocytes, or iridoplasts rather than a monolithic photonic layer. The cell assembly enables the organisms to reorganize the photonic surfaces during dynamic transformation and growth. Inspired by the organisms, we propose the two-dimensional (2D) assembly of amphiphilic photonic tiles at the air-water interface to provide unprecedented reconfigurability that has never been achieved with a conventional film format of the colloidal lattice. The photonic tiles are prepared using a photocurable dispersion of silica particles in a carefully-selected resin as a photonic ink. In the ink, the silica particles spontaneously form nonclose-packed face-centered cubic (fcc) lattice due to the interparticle repulsion caused by the solvation layer. The nonclose-packed lattice is instantly captured in a polymeric matrix upon photopolymerization of the resin, where the shape of the colloid-polymer composite is featured to a hexagonal disc by photolithography. The silica particles are selectively etched out from the hexagonal disc, which results in a porous internal structure with strong iridescence. To render the photonic discs amphiphilic, the top side surfaces of the tile are subjected to reactive ion etching with sulfur hexafluoride gas, which makes the surfaces highly porous and hydrophobic according to Cassie-Baxter model. As a result, the photonic tiles sit on the air-water interface while exposing the body of the tile to the air. This configuration significantly deforms the interface by the action of gravity, which leads to the strong capillary attraction between the tiles. Therefore, the tiles assemble to form a dense photonic layer without large voids under gentle agitation. The assembly of photonic tiles rapidly adapts to the dynamic undulation of the interface and shape transformation of the container as the individual tiles can rearrange while the capillary force holds the tiles assembled. The assembly can be applied to a shape-shifting reflective display. The assembly can be also transferred onto a solid substrate by either using the Langmuir-Blodgett method or forming an elastomer on the top of the assembly. The two methods construct a highly reflective photonic coating on a wide range of substrates, which can also make a flexible photonic device. In addition, the tiles can be assembled on the surface of the water drop, forming a photonic liquid marble. It potentially serves as a reservoir for cells and algae and helps the organisms to be photo-protected and photosynthetically efficient, which is modeled after nature mentioned in the introduction. We believe that the interfacial assembly of amphiphilic photonic tiles will provide new means to create high-quality photonic coatings on wide solid supports as well as highly reconfigurable photonic surfaces at free interfaces.

SB01.09.18
Colloidal, Nanoelectronic State Machines Based on 2D Materials as Smart Aerosolized Probes and Recorders
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A here-to-fore unexplored property of two-dimensional (2D) electronic materials is their ability to graft modular electronic functionality onto colloidal particles so as to access local hydrodynamics in fluids to impart mobility and enter spaces inaccessible to larger electronic systems. Herein, we demonstrate the design and fabrication of fully autonomous state machines (only 100x100x1 µm³ in size) built onto a SU-8 particles powered by a 2D material-based photodiode. The on-board circuit connects a chemiresistor element and a memristor element, enabling the detection and storage of information after aerosolization, hydrodynamic propulsion to targets over 0.6 m away, and large area surface sensing of triethylamine, ammonia and aerosolized soot in inaccessible locations. An incorporated retro-reflector design allows for a facile position location using laser-scanning optical detection. Such state machines may find widespread application as probes in confined environments, such as the human digestive tract, oil and gas conduits, chemical and biosynthetic reactors, and autonomous environmental sensors.


SB01.09.19
Control of Liquid Transport Velocity of Open-Type Micro-Blade Arrays Inspired by Wharf Roach
Rikima Kuwada, Koji Muto and Daisuke Ishii; Nagoya Institute of Technology, Japan

Recently, microfluidic devices are much paid attention, because these are used in many ways such as bio analysis, chemical synthesis and heat pipe devices. However, current microfluidic devices have some problems, that these need high pressure to transport liquid, since these are composed of some closed tubes. And more, these are susceptible to bubble entrapment, inpurities, and consequently variation in the metered volume. In order to solve these problems, we focused on a coastal animal wharf roach that has open-type flow micro-passages on the legs which can transport water to their gills spontaneously by the surface free energy. It was found out that the flow passages were composed of micro-blades oriented in several parallel lines. We fabricated a series of flow passages
composed of micro-scaled epoxy blades on silicon wafer by photolithography inspired by those on legs of Wharf Roach. Fabricated samples can also transport liquid spontaneously against gravity. The purpose of this research was to clarify the factors controlling the velocity of liquid transport by changing several parameters defined the size, gap and arrangement of the micro-scaled blades. The velocity through these flow passages was experimentally determined by measuring the vertical rise of liquid column across a series of vertical microstructure surfaces with varying characteristic dimensions. The plot of transport distance to elapsed time is accurately approximated by the equation of motion for the capillary rise of liquid in a porous medium using Darcy law.

From these results, it was found out that the velocity of liquid transport through these flow passages was determined by the balance of the capillary pressure, the weight of the liquid column, and the pressure loss defined by the kinematic viscosity, the porosity and the permeability. Furthermore, it is suggested that the capillary pressure, the porosity and the permeability can be controlled by several parameters of the sample, and the liquid transport velocity can also be adjusted.

SB01.09.20
Transparent Wearable 3D Touch—Self-Generated Multiscale Structure Engineered by Laser-Induced Thermal Gradient Kim Kyun Kyu and Seunghwan Ko; Seoul National University, Korea (the Republic of)

Pressure-sensitive touch panels provide an intuitive and natural method to sketch and write with new levels of control and interactivity. However, they require a combination of sensors or a stylus-based interface to identify 3D signals, which prevents their implementation in a wide spectrum of applications. Here, we report a transparent and flexible 3D touch which operates in a single device with the assistance of multiscale structures and a nanowire percolation network. The device could assign functionalities to objects without reference to any varying surfaces. Rigorous theoretical analysis allowed us to achieve the target pressure sensitivity, and successful 3D data acquisition was carried out through the 6-wire measuring technique

SB01.09.21
A Degradation-Induced Shape Memory Elastomer Melodie Lawton1,1, Caitlin D'Ambrosio1, Meaghan Yant1, Devon A. Shipp2 and Patrick T. Mather1; 1Bucknell University, United States; 2Clarkson University, United States

Tasking polymeric materials with functionalities beyond their primary (often load-bearing) role has gained significant interest in the development of smart materials. We have recently developed a reconfigurable shape memory elastomeric composite (Re-SMEC) featuring a water-degradable, elastomeric polyanhydride (PAH) matrix that, unlike most polymeric shape memory systems, features an original geometry that can be thermomechanically altered at will. In our past work, we reported that this reconfigurability was possible since the constituent bonds of the polyanhydride elastomeric network undergo dynamic covalent exchange between neighboring anhydride groups. This exchange enables one to customize the geometry of the “target” shape during shape memory activation. Taking advantage of these new properties, we present a new shape memory elastomeric composite featuring elastic fibers as the permanent, memory retaining phase, and a polyanhydride-based elastomer matrix as the fixing phase. Unlike other fiber-reinforced shape memory systems, where the fibrous phase typically serves to temporarily fix geometry, this design utilizes a reconfigurable matrix as the shape-fixing phase. Moreover, this new design enables recovery of the original shape in response to degradation of the matrix. We report on the degradation profile of this composite, with quantification of mechanical properties and the effect of fiber orientation on this new shape memory phenomenon.

SB01.09.22
Nanofiller Particles Migration to Polymer Composite Melt Boundaries—Experimental and Numerical Studies Oleg V. Lebedev1,2, Leonty A. Mukhortov1,2 and Alexander N. Ozerin2; 1Moscow Institute of Physics and Technology, Russian Federation; 2Enikolopov Institute of Synthetic Polymer Materials, Russian Federation

In this work a study of an effect of nanofiller particles migration to the polymer composite melt surface was conducted. The effect’s nature was investigated and methods of its control and diagnosis were developed. The results of the work allowed to controllably obtain materials with properties of surface layer drastically different from the properties of the bulk. Such composites are considered as functionally graded materials that attract a lot of attention in recent years from research society and industry.

To experimentally investigate the process of nanosized particle migration, series of composite mixtures were prepared, based on polymer matrix of different types (polypropylene, polyethylene, polystyrene, etc.) and carbon
nanofillers of different aspect ratio, such as single- and multi-walled carbon nanotubes, graphite nanoplatelets, and electroconductive carbon black. Mixing of the components was performed using melt mixing method for a wide range of the filler concentrations values below percolation threshold, which was determined beforehand for each matrix/filler pair. The resulting compounds were processed further into samples of cylindrical shape in a heated press-form with minimal heating and cooling times.

To constantly monitor the filler particle migration to the surface the electrical conductivity measurements were conducted for the melted in a closed heated press-form samples. This allowed to observe steady increase of the material electrical conductivity over time, possible due to the inherited high electrical conductivity of the nanoparticles chosen. The effect of conductivity increase was present for each matrix/filler combinations. Analysis of the filler geometry influence on the characteristic times of the electrical conductivity changes respectively to the percolation threshold values was conducted. Dependencies of the process dynamics on the melt temperature, number of cycles of melting and cooling, etc. were additionally investigated.

Removal of a thin surface layer (< 10μm) of the pre-annealed and instantly cooled solid composite samples demonstrated that the high conductivity is provided by the composite boundary layers enriched with nanoparticles in the course of the annealing, which was also confirmed by the analysis of electron microscopy data of the samples’ fracture surfaces.

To help developing an analytical model describing the process of nanofiller migration to the composite material surface, a numerical model was proposed based on the experimental results for the electrical conductance measurements. The simulations were performed for nanotubes using molecular dynamics methods for ranges of modelling parameters, such as inter-nanoparticle interaction force values, force between the particle and surface, and the temperature of a medium. Different conductivity calculation methods for simulation boxes allowed to plot the dependencies of conductivity of the material on time, which was successfully correlated with experimentally obtained results.

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SB01.09.23
Ultraflexible and Transparent Pressure-Imaging Skin Using Cellulose/Nanowire Nanohybrid Networks for High-Information-Density Human-Machine Interfaces

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Electronic skin realizes seamless interfaces between human and computers, enabling mechanical and chemical sensing on human skin with applications for healthcare/monitoring devices and user interfaces for augmented reality. Multifunctional devices that can map high-resolution pressure distribution over arbitrary surfaces would enable novel applications such as skin prosthesis, artificial nerve systems for soft robotics, and advanced human-machine interfaces. For this reason, many studies on conformable force sensors have tried to map spatial pressure by employing matrix design and sensor pixels. However, they show poor spatial fidelity mainly due to their low pixel density, crosstalk among pixels, and bulky electrical wires for data acquisition. Furthermore, pressure distribution could be severely distorted by device structures such as uneven or thick sensing layers, structural inhomogeneity, and limited conformability. Therefore, the new homogeneous and conformable design should be developed to bridge the fidelity gap. However, existing methods for flexible or soft pressure sensors show limited design freedom to satisfy the demand due to their impractical fabrication process. Although pressure sensors exploiting contact resistance between engineered micro-/nano-structures and conductive films are promising due to their high stability and fast response time, reported works cannot offer viability because they need bulky micro-fabricated or pre-established structures such as a sponge and tissue paper.

In this work, we propose a homogeneous and ultrathin device structure to autonomously capture and image pressure distribution over 3D surfaces with high spatial fidelity, and appropriate materials and a manufacturing method for highly sensitive and transparent pressure sensors that can be readily integrated into the proposed device.

Specifically, we develop a solution-processable nanohybrid network of nanocellulose and conductive nanowires for ultrathin and transparent piezoresistive pressure sensors. As compared to previously reported cellulose-based piezoresistive pressure sensors where microfibers are coated with conductive nanowires, our nanohybrid network features a nanostructured surface morphology where dense nanocellulose encircles each conductive nanowire. This unique nanostructured surface results in unprecedentedly high sensor sensitivity (> 1000 kPa⁻¹), a fast response time (< 1 ms), and high transparency (~80%). We combine the transparent piezoresistive network coated on an ultrathin
(~1 μm) colorless polyimide (PI) film with a quantum dot-based electroluminescent film. The two functional films conform to each contact object and effectively form conductivity distribution in a continuous domain with minimal distortion of contact pressure. This patterned conductivity brings out high-resolution (> 1000 dpi) electroluminescent imaging of the pressure distribution without the need for pixel structures. The spatial resolution depends only on the thickness of the films, whose effect on output images is systematically investigated by a finite element analysis and measuring images of spatial pressure applied with micropillar arrays. We further demonstrate the feasibility of our approach by constructing high-information-density human-machine interfaces such as a transparent touch interface that can identify the user in addition to touch information. This study provides a new pathway to high-fidelity stimulus imaging with potential applications for bio-imaging, wearable human-machine interfaces, and force-sensing deformable displays. The detailed methods and results will be discussed later.

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**SB01.09.24**

**Octopus-Inspired Light-Responsive Smart Adhesive Pads for Macroscopic/Microscopic Applications**

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Smart adhesive system which easily adhere to and release from a target surface on demand by external signals can be employed in broad applications in medical industry, robotics, industrial transporting system, and smart printing. By employing light-responsive actuation of hydrogel composites and octopus-sucker-like microstructure of elastomer, here, we demonstrate a high-performance light-responsive smart adhesive pad, in which the adhesive properties can be actively and remotely controlled by external light stimulus. The light-responsive hydrogel composite, which consists of a thermo-responsive hydrogel (poly(N-isopropylacrylamide) (pNIPAM)) and photothermal carbon materials, acts with a switchable motion of shrinking/swelling by turning on/off a near IR light. This hydrogel composite on the octopus-sucker-like microcavity-patterned elastomer (polydimethylsiloxane (PDMS)) can generate/remove a differential pressure between the inside and outside of microcavity, which can induce/withdraw an adhesive force to grab/release a foreign target surface. Finally, the light-responsive smart adhesive pad shows a switchable adhesive performance through the control of irradiation of near-IR (NIR) light, enabling the switchable adhesive strength from 0.15 kPa (NIR light ‘off’) to 26.32 kPa (NIR light ‘on’) with an on/off switching ratio of adhesion of 175 in fast response to the remote NIR light without any preload. Thanks to these superior adhesive properties, the smart adhesive pad can be applied to broad macroscopic/microscopic applications such as an adhesive patch which can endure a weight or a micromanipulation to easily pick and release micro/nano-membranes of semiconductors by the remote control of NIR light.

**SB01.09.25**

**Control of Lateral Buckling in High Aspect Ratio Structures by Bilayer Formation**

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Buckled structures originated from the compressive stress on a film have been exploited to generate randomly or regularly grating patterns, or as a method to fabrication of foldable or stretchable devices. Laterally buckled structures, which is resulted from the compression of high aspect ratio line patterns have been reported for an academic interest or an application about the anti-counterfeit patterns generated by a mechanical response. In the presentation, we show the control of the features of laterally buckled patterns by the manipulation of the compressed area in the bilayer system. In addition, we demonstrate a potential application to absorb the mechanical stress by using the unique spring-like structures of lateral buckling.

**SB01.09.26**

**Fluorinated Epoxy Siloxane Hybrid Materials for Bio-Fluidic Barrier on Flexible Electronics**

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The barrier is a key component of bio-integrated electronics, protecting the device from the bio-fluid environment and enabling high performance without degradation over time. Recently, the bio-fluidic barrier on the ultra-thin device offers reliable measurement of various bio-signals from even on skin or organ due to the defect-free passivation layer[1]. To meet the requirement of low water permeability, inorganic material based bio-fluidic barriers such as thermal grown SiO2 [2] and bilayer of SiO2/SiNx[3] have been exhibited superior barrier performance. However, the inorganic materials for the barrier have process incompatibility, including high processing temperature and harsh etching conditions. Thus, the organic materials based on bio-fluidic barriers, such as polyimide[PI][4] and SU-8[5] have been also investigated due to their process compatibility. But such organic-based barriers are unstable under the water environment, resulting in unreliable ultra-thin devices for the bio-applications. Therefore, hybrid material for the bio-fluidic barrier that has advantages of both organic and inorganic is needed.

Here, we demonstrate the siloxane(inorganic) based fluorinated epoxy(organic) hybrid materials(FEH) for the bio-fluidic barrier and confirm the barrier performance for the flexible system by using the solution-processed oxide thin-film transistor(TFT)s on ultra-thin polyimide film. Our sol-gel derived FEH is inorganic-organic hybrid materials for the bio-fluid barrier, which is capable of simple spin-coating and UV-patterning by cationic polymerization without additional etching process. Furthermore, FEH exhibits superior water repellency and hydrophobicity compared to other conventional organic films due to the fluorine functional group, which can be confirmed by magnesium soaking test and water contact angle. To evaluate the electrical stability of the barrier in the bio-fluidic environment, we confirm no leakage through defects of films using electrical impedance spectroscopy analysis. To verify the barrier performance in real-time, we demonstrate the solution-processed indium oxide TFTs with the FEH barrier and measure the transfer characteristics in the phosphate-buffered saline (PBS). The oxide TFT, which is vulnerable to water, passivated by FEH barrier films exhibits transfer characteristics with no dramatically change during 16 hours in the PBS. Furthermore, to realize the FEH barrier for flexible systems, we demonstrate the solution-processed oxide TFTs on 1μm-thick polyimide film with the FEH barrier and successfully measure the transfer characteristic, which is consistent with the result of TFTs on rigid glass wafer. In conclusion, we envisage the potential of our FEH as a bio-fluidic barrier for future bio-integrated devices and advanced electronics.


SB01.09.27
Promotion of Crystallinity and Actuation of Polyvinylidene Fluoride/Single Walled Carbon Nanotubes Composite for Soft Robotics Applications
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Piezoelectric materials are extensively used as actuators in various sectors such as biomedical, manufacturing and robotics. This is due to its piezoelectric property that allows the material to actuate when an electrical field is applied. Compared to traditional electric motors, piezoelectric polymer actuator, Polyvinylidene Fluoride (PVDF), offer advantages such as conformability, ease of processing, better biomimicking ability, lower cost, higher power-to-weight ratio, increased control, and response time. PVDF is a semi-crystalline polymer where its zigzag all-trans (TTT) b crystal phase is responsible for the actuation ability. To promote this unique crystal phase, there has been research on processing methods, such as the addition of fillers to align and stabilized the TTT conformation on the surfaces of the nanofillers. The current study investigates the use of single-walled carbon nanotubes (SWCNT) in a PVDF matrix to increase: (i) its piezoelectric property for enhanced actuation and (ii) its mechanical property to withstand the environmental conditions of various actuation applications. The weight percentage (wt.%) of SWCNT within the PVDF matrix and its dispersion, enhanced actuation displacement, and response time due to higher conductivity were explored with parametric studies. This study also reports on the effects of popular processing
methods (i.e., mechanical stretching) in promoting the alignment of the fillers, resulting in an alignment of the crystal structures. Initial results found an optimal weight percentage of SWCNT to be 0.5 and 3%, where both mechanical, electrical, and actuation properties excelled. At 1 wt.% CNT, the composite increased its conductivity by 4 magnitudes, and its density and ultimate yield strength increased by a factor of 70%. While its b content at 1 wt.% had no significant change, at 2 wt.% CNT, the b phase increase to 40%, 10% higher than that of the pure PVDF sample. With an increase in conductivity and piezoelectric property, the material’s actuation can be performed with greater displacement and lower power. This study provides insight to future research utilizing piezoelectric materials for actuation application that can advance into soft robotics.

SB01.09.28
Antibacterial Surface with Novel Biocompatible Metal-Ceramic Composite Material via Sputtering Method for Wearable Devices Joon-Min Lee1,2 and Chan-Hwa Hong2; 1University of Science and Technology, Korea (the Republic of); 2Electronics and Telecommunications Research Institute, Korea (the Republic of)

Antibacterial surface coatings have become a primary solution for preventing device-associated infections (DAIs). Even though extensive progress reducing DAIs has currently been made, recent antibacterial surface coating methods are complicated and do not effectively kill infectious bacteria.

In this research, we propose novel biocompatible metal-ceramic composite material that exhibits selective bacteria-killing properties. Because the metal-ceramic composite surface was coated by a sputtering method known as physical vapor deposition (PVD) at room temperature, this method can be applied to flexible and stretchable substrates of wearable devices.

We confirmed the metal-ceramic composite surface exhibits a damaging effect to both Gram-positive bacteria (S. aureus) and Gram-negative bacteria (E. coli). Thus, the biocompatible metal-ceramic composite material surface which induced in this research can be a good candidate for the antibacterial solution of biomedical and wearable devices.

SB01.09.29
Continuous Gradation of Multi-Material Biopolymer Hydrogels Nicolas A. Lee1, Ramon Weber1, Joseph Kennedy1, Jorge Duro-Royo1 and Neri Oxman1,2; 1Massachusetts Institute of Technology, United States; 2Massachusetts Institute of Technology, Media Lab, United States

We present advancements to a water-based digital fabrication and design platform that allow for the continuous gradation of mechanical properties, biocompatibility, and biodegradability in pectin-based biopolymer hydrogels. Continuous gradation of these properties across scales ranging from centimeters to meters are achieved using the same fabrication methods and computational workflow. Fabrication parameters including extrusion pressure and feedrate are assigned and varied without discretization, allowing material proportions to be precisely tuned by graded computational inputs. Localized diffusion of extruded materials further increases the continuity of multi-material transitions beyond the limits of mechanical resolution.

Both functionally graded and homogeneous combinations of silk, pectin, and chitosan hydrogels are presented and characterized with a focus on the ability to tune stiffness, dissociation rate, and the proliferation rate of biological agents as independent variables The implemented digital-fabrication system further enables the real-time modification of extrusion parameters through feedback-driven control logics, thereby allowing the further customization of hydrogel properties in response to environmental parameters. These capabilities constitute a set of methods by which a diverse array of material properties can be precisely tuned and spatially templated from a relatively limited material palette for the creation of functionally-graded multiscale hydrogels.

SB01.09.30
Colorimetric Recording of Thermal Conditions Using Thermal Creep Behavior of Polymeric Inverse Opals Seung Yeol Lee, Joon-Seok Lee and Shin-Hyun Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

It is important to record thermal history in our daily lives. Although conventional digital-based thermometers have a high accuracy of temperature measurement and its recording, they usually consist of electronic circuit board, battery,
and display as well as temperature sensor, which are expensive and not disposable. Moreover, the electronic thermometers have difficulties on applying to an infant skin for monitoring long-time fever or applying to packages of edible products and cosmetics for checking staleness, causing intense demand for disposable, patch-type thermal recorders. The non-electronic, disposable thermal recorders can be prepared by using materials that have colorimetric response for temperature. Metallic nanoparticles, thermochromic dyes, fluorescent dyes, or liquid crystals have been used as constituent materials for the temperature recording. However, it is elusive to decouple temperature and time from color change of the materials.

Here, we design photonic films that record thermal condition through irreversible structural deformation and intuitively display the thermal condition as color patterns. The photonic films are polymeric inverse opals whose frameworks are made of negative photoresist. When the polymeric inverse opals are heated up, they experience creep deformation due to the large surface energy at the pores, causing shrinkage. Polymeric inverse opals attached on a solid substrate show the shrinkage along the direction normal to the substrate while maintaining regularity of their cavity array. This anisotropic shrinkage leads to a blue-shift of the structural color. The rate of the blue-shift or equivalently rate of deformation strongly depends on the temperature. The relation between the rate and temperature can be described by time-temperature superposition principle or Williams-Landel-Ferry (WLF) model. That is, time and temperature are equivalent so that it is difficult to separately estimate time and temperature from the single magnitude of the blue-shift. To decouple and separately estimate temperature and time for isothermal heating, crosslinking density of the negative photoresist is regioselectively adjusted by controlling ultraviolet (UV) dose, which determines thermal and mechanical properties of the photoresist. As the different crosslinking density provides different time-temperature relation, several independent relations can be obtained from a set of distinct UV doses. For isothermal heating, an invisible pattern with regioselective UV doses turns into a multicolor pattern. Using the multiple structural colors of the single inverse opal film, multiple superposition equations are deduced, from which temperature and time are separately estimated. To the best of our knowledge, there has been no thermal recorder that is able to decouple temperature and time. Our patch-type inverse opal is potentially useful as the disposable thermal recorders for various applications.

SB01.09.31
A Facile Fabrication Method for Bio-Inspired Compound Eyes with Printing and Dry-Phase Rubbing Process Seunghwan Lee, Byeongmoon Lee and Yongtaek Hong; Seoul National University, Korea (the Republic of)

Bio-inspired compound (BIC) eyes have been emerging as a main component of optical systems, and many researchers have been interested in their unique optical characteristics such as wide field-of-view, low-aberration, and high sensitivity to light [1,2]. To fabricate BIC eyes structures, several methods are generally used such as precision machining, thermal reflow, and femtosecond laser writing [3-5]. However, these methods are time-consuming and involve high-cost associated with photolithography and etching. Self-assembly of microparticles in liquid can be an alternative method [6] because it does not require vacuum system. But it is not appropriate for large-area fabrication and has a disadvantage in that the process control is difficult.

In this work, we report a facile fabrication method for BIC eyes with printing and dry-rubbing assembly process. Firstly, a hemispherical lens is fabricated by dispenser printing method, which is suitable for rapid-processing of optical components [7]. After that, we adopt dry-rubbing process, which is one of the methods for arranging microparticles in dry-phase [8], to form microparticle monolayer onto the surface of hemispherical lens. This hierarchical microstructure is used as a template of BIE eyes, and replicated in soft materials including polydimethylsiloxane and ultraviolet-curable epoxy resin. Because the BIC eyes structure is fabricated from soft materials, it has stretchability, thus it is expected that the optical properties can be easily tuned by applying mechanical strain. We believe that our method can be applied to the various imaging systems such as cameras, endoscopies, and light-emitting devices. Detail fabrication process and experimental results will be discussed at the conference.

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References:
SB01.09.32
Facile Synthesis of Thermo-Plasticized Cellulose via Graft of ε-decalactone in Ionic Liquid
Woojin Lee, Yongjun Ahn, Dae-Yeon Won and Seung-Yeop Kwak; Seoul National University, Korea (the Republic of)

Natural polymer is one of the most promising material to reduce dependence on petroleum-based polymer. Cellulose is the most abundant natural polymer on the planet. In particular, the use of cellulose is not only a fundamental solution to the focused microplastic problem, but also is high utilization value as industrial material due to high strength, biodegradability and thermal stability. However, it is well known that cellulose does not have $T_g$ and melting temperature because of their strong hydrogen bonding network and chain rigidity. These limitation makes difficult to be thermally formed as certain shape and control mechanical properties to apply industrial fields. Therefore, it is necessary to develop technology capable of controlling strength, flexibility, and stretchability by inducing thermoplastic properties. Many researchers have studied methods of microstructural change to develop thermo-plasticized cellulose by introducing macromolecules on cellulose backbone. However, those methods have critical limitation because of low efficiency of plasticization and complex process that precedes the synthesis of cellulose derivatives.

In this study, we developed method to efficiently plasticize cellulose via change of grafting architecture which composed of ester molecules. To control chain flexibility and free volume, three different types of grafting molecules were employed; ε-caprolactone (ε-CL) / Cell-g-PCL, ε-decalactone (ε-DL) / Cell-g-PDL, and L-lactide / Cell-g-PLLA. The grafting molecules were synthesized at hydroxyl groups on cellulose backbone via ring-opening polymerization in 1-buthyl-3-methyl-imidazolium chloride, which was observed by $^1$H NMR and FTIR. Furthermore, degree of polymerization (DP) of grafted molecules was controlled to confirm effect of side chain size on plasticization performance. The microstructure of cellulose was significantly disrupted by grafting molecules. This deconstruction behavior became more clear when the size of grafting molecules was larger. Despite of similar molecular weight of grafted molecules, the branched architecture easily dissociated the cellulose crystalline. This results led to decrease of glass transition temperature ($T_g$) of cellulose. ε-DL-grafted cellulose exhibited $T_g$ at 30°C, while $T_g$ in ε-CL and L-lactide-grafted cellulose was not observed in similar DP. This results suggested that the grafting molecules with branched structure was more effective to hinder intra- and inter-chain network of cellulose, compared to linear structure.

SB01.09.33
Femtosecond Laser-Assisted Etching for Anti-Biofouling and Anti-Fogging Endoscope Lenses with Physical and Chemical Durability
Yeontaek Lee1, Jaeho Park2, Hojeong Jeon2 and Jungmok Seo1; 1Yonsei University, Korea (the Republic of); 2Korea Institute of Science and Technology, Korea (the Republic of)

Clear endoscopic vision is essential for laparoscopic surgery. However, body fluids such as blood and peritoneal fluid cause sight loss, which make the surgical operation difficult. Conventional methods such as irrigation, rubbing lenses, and particle-based porous coating infused with lubricant have been conducted to prevent sight loss, but functional stability issues are not solved[1]. Here, we present directly engraved nano-microstructure lubricating (DENL) method, which demonstrates anti-biofouling and anti-fogging ability without any additional device and strong physical and chemical durability due to engraved nano-microstructure. DENL method involves the formation of robust nano-microstructure on the endoscopy lenses via etching with a femtosecond laser. After the process, Fluorine-based self-assembly monolayer (SAM) was applied on the substrate to enhance the chemical affinity of the substrate to perfluorocarbon-based lubricant. We further demonstrated that the developed lens maintained a transmittance of 80% in the visible light region and confirmed its anti-biofouling and anti-fogging ability via dipping (>5 cycles) and fogging (>30 mins, >RH 90%) test using various body fluids. Also, the clear vision was
secured even in extreme condition where various attempts were made to damage the developed lenses via exposing it to various chemical solutions and mechanical stresses. We believe that the endoscopic lenses produced by DENL method bring excellent benefits in endoscopic surgery compared to a conventional method by securing clear sight for stable operation and miniaturizing the endoscopic instrument for minimally invasive surgery.

Reference

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SB01.09.34
Optimizing Optical and Thermal Properties of Polyethylene Aerogels for Radiative Cooling Arny Leroy, Bikram Bhatia, Lin Zhao and Evelyn N. Wang; Massachusetts Institute of Technology, United States

Radiative cooling enables passive cooling of terrestrial objects to sub-ambient temperatures by rejecting thermally emitted infrared radiation to the cold outer space through the infrared (IR) transparent window of the earth’s atmosphere (8-13 µm). However, achieving low sub-ambient emitter temperatures and high cooling power during the day under direct sunlight remains a challenge due to significant absorption of solar irradiation and high parasitic heat gains from the ambient environment. In this work, we address these challenges by developing polyethylene aerogels (PEAs) covers that are optimized to achieve high solar reflection, near-perfect infrared transmittance and ultra-low thermal conductivity which can minimize solar absorption and parasitic heat gains at the emitter. The PEA samples were fabricated using thermally induced phase separation of polyethylene in a solvent followed by supercritical CO₂ solvent extraction. The optical and thermal properties were optimized by altering the nanoporous structure of the PEA using different solvents (decalin, paraffin oil or paraffin wax) and varying the density (between 10 and 80 kg/m³) of the aerogel. The optical characterization of the fabricated samples revealed a solar-weighted reflectance as high as 92% and a mid-infrared (8-13 µm) transmittance as high as 80% for a 6 mm thick sample. We also performed a detailed thermal characterization of PEA samples using a custom-made guarded hot plate thermal conductivity setup and measured thermal conductivity as low as 28 mW/mK. By performing measurements under different gas pressures and boundary conditions (optically black or reflective boundaries), we were further able to experimentally decompose the total thermal conductivity \( k \) of PEA into its three subcomponents – solid \( k_s \), gaseous \( k_g \), and radiative \( k_r \). Finally, we performed outdoor experiments to demonstrate the benefits (ultra-low thermal conductivity and high solar reflectivity) of our optimized PEA for daytime radiative cooling. Under direct sunlight at solar noon, we measured a sub-ambient cooling of up to 13 °C for an emitter covered with 12 mm thick PEA – greatly surpassing the performance (1.7 °C sub-ambient cooling) of a similar emitter without PEA.

SB01.09.35
Macroscopic Actuators Based on Super-Aligned VO₂ Nanowire @ CNT Bimorph Yuxing Liang, Pengcheng Chen and Chun Cheng; SUSTech, China

Vanadium dioxide (VO₂) is an ideal inorganic driving material for actuators with outstanding performance due to its giant power density (7 J/cm³) and ultrafast response (~ picosecond). Single-crystalline VO₂ nanowires (NWs) have demonstrated supreme actuation capabilities while the VO₂-based flexible devices up to centimeter-size toward macroscale robotics are rarely explored. Here, we develop a kind of macroscopic, flexible and all-inorganic bimorph actuators composed of super-aligned VO₂ NWs and carbon nanotube (CNT) films for the first time. Super-aligned VO₂ NW films in large scale (several square centimeters) were achieved by assembling and post-annealing ultra-long \( \text{H}_2\text{V}_2\text{O}_5 \) NWs. The as-grown highly-anisotropic VO₂@CNT films showed tailoring direction-dependent bending morphologies and actuation performance, in which giant displacement/length of 0.83; high power density of 3.2 J/cm²; two orders of magnitude higher than mammalian muscle, fast response up to ~15 Hz, and long lifetime more than 1 million actuation cycles were demonstrated. The excellent thermal/electrical conductivity and light absorption of CNT thin films enable the actuators highly responsive to multiple stimuli including heat, light, and electricity. Notably, the whole-inorganic structure as well as remarkable anisotropy allow the remarkable actuation of VO₂ NWs in a macroscopic scale mechanical device with fantastic performance for versatile applications, including biomimetic geometry, mini jack, inspect wing, mini elephant trunk, torsional artificial muscle, etc.
SB01.09.36
Gapless Total Transfer for Skin Electronic Devices Jong Tae Lim, Bock Soon Na, Himchan Oh, Yun-Jeong Kim, Hye-Jin Kim, Sung Haeng Cho, Chi-Sun Hwang, Kang-Ho Park, Seong Hyun Kim, Seong-Deok Ahn and Jeong-Ik Lee; Electronics and Telecommunications Research Institute, Korea (the Republic of)

Our bodies and smartphones will be connected to the bodyNET in the near future [1]. Electronic devices that can stretch, from circuits and batteries to sensors and screens, will realize with the demand of such bodyNET and will extend our senses and abilities. To fabricate devices within our clothes and accessories, attached to our skin and implanted in our bodies, a new platform transfer technology is required. In particular, the technique of forming conformal contacts, which remove air at the interface, is of paramount importance. Air trapping at the interface cause air to bulge due to small thermal changes during the device driving and even during post-processing such as vacuum, ultraviolet curing, heating and plasma processes, etc. The interfacial air-bulging problem could lead to not only delamination but also the breaking of films and metal interconnections in the devices. As a result, the interfacial expansion of air damages the electrical characteristics of the device. Meanwhile, the degree of air-bulging at the interface could be increased as Young’s modulus of a stretchable materials is low.

In this talk, we introduce how to remove air in the interfaces for the fabrication of skin electronic devices (skintronics). It is possible by using a gapless vacuum laminator with a stretchable jig. Skintronics were designed to the wrinkled structure, to impart stretchiness in one axis direction without destroying the function of the device while stretching or compressing the device. The gapless laminating process consists of a first step of removing air from the interface and a second step of applying pressure. Skintronics are fabricated by four essential fabrication steps. First, polyimide (PI) is spin-coated on a carrier glass. Second, the functional layers constituting the device are individually fabricated on a sample of glass/PI. Third, a sacrificial film (SF) is fabricated on a sample of glass/PI/device, followed by a laser lift-off process to detach a glass from a sample of glass/PI/device/SF. Finally, a sample of PI/device/SF is totally transferred on pre-stretched elastic substrate by a gapless vacuum lamination [2]. Spontaneous wrinkles are formed on skintronics, which has the structure of elastic substrate/PI/device, after both removing a SF and relaxing a stress. Here, we prove that the devices fabricated by a new total transfer method are stable and reproducible in the electrical property during a device driving. Also, we demonstrate that this excellent electrical property of the device is due to the reduction of a long-range-order deformation as well as a formation of conformal contact at the interfaces.

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SB01.09.37
Photothermal Effect of Fe3O4 and Fe3O4@Cu2-xS Nanoparticles Coating for Energy-Efficient Applications Jou Lin, Yuan Zhao and Donglu Shi; University of Cincinnati, United States

Energy saving in buildings is a critical problem due to the poor thermal insulations, especially for windows in cold climates. The conventional approach mainly relies on a double-pane design. We have previously reported a concept that by applying photothermal coating on single-pane windows, the thermal insulation property (U-factor) can be dramatically lowered. Both Fe3O4 and Fe3O4@Cu2-xS nanoparticles coatings have shown promising photothermal effect, maintaining good transparency. By comparison of the same average visible transmittances (380-760 nm) of Fe3O4 and Fe3O4@Cu2-xS coatings, Fe3O4@Cu2-xS shows better photothermal effect under simulated solar irradiation (0.1 W/cm²). This is due to the better NIR absorbance of Fe3O4@Cu2-xS nanoparticles compared to Fe3O4 nanoparticles. Similar results were also found through monochromatic irradiations (785 nm laser, 0.1 W/cm²).

Therefore, under the same requirement of visible transmittance, a photothermal coating with better NIR absorbance will perform the better photothermal effect, as well as better thermal insulation improvement for the coated single-pane window.

SB01.09.39
Forming Diverse Pollen-Like Particles from Liquid Crystalline Oligomers via a Biological Pathway Jiaqi Liu, Asja Radja, Yuchong Gao, Rui Yin, Alison Sweeney and Shu Yang; University of Pennsylvania, United States

Synthetic microparticles have been widely used in drug delivery, imaging, light scattering, pigmentation, cell
mimicking, and understanding of cell phagocytosis. Surface patterns could play important roles in their functions, yet it remains challenging to reproduce spherical microparticles of diverse surface patterns with submicron resolutions. In contrast, nature uses a bottom-up mechanism, via phase separation of extracellular material mechanically coupled to an elastic cell membrane, to create infinitely replicable but diverse surface patterns on spherical cells, such as fungal spores, insect cuticles, and pollen grains. Here, taking the biological pathway that nature has perfected over evolutionary history, we design and fabricate liquid crystal elastomer (LCE) microparticles (diameter, 1 ~ 10 um) with various surface patterns including holes, stripes and spikes, recapitulating the key features in pollen pattern formation that involves phase separation and kinetic arrest of polysaccharides of different chemistry and elasticity at the extracellular membrane. Our approach takes advantage of the anisotropy of liquid crystal oligomers (LCOs) and mixture of different chain lengths in a single droplet. While the chain length of LCOs determines the surface energy and elasticity, thus surface anchoring behaviors at the interface; the heterogeneity of LCOs leads to chain segregation within droplets, thus, facilitating kinetic arrest of LCOs at the interface. Diverse surface patterns are formed after UV curing of the LCO droplets, which are not seen from non-LCOs. Our study also confirms that heterogeneity can be a feature but not a bug in self-assembly. The ability to form diverse and complex surface patterns on microparticles could not only improve our understanding of the general rules about self-assembly in micro- and nano-environments, but also open doors to mass production of functional nano-/micromaterials.

**SB01.09.40**

**Optical Engineering of Polymer Composites for Simultaneous Color and Thermal Management** Luis M. Lozano¹,², Yoichiro Tsurimaki³, Yi Huang¹, Gang Chen¹ and Svetlana V. Boriskina¹; ¹Massachusetts Institute of Technology, United States; ²Tecnológico de Monterrey, Mexico

For centuries, optics and photonics have been key enabling technologies in art, design, and architecture in a manner that architects and designers, in their struggle to enrich visible light with color, have experimented with adding pigments, textures, and nanoparticles to construction materials. However, the sunlight not only brings bright visual illumination and color to the building exteriors and interiors, but also radiative heat, which can either be used to warm the buildings or needs to be reflected to avoid overheating. Ideally, the two functions can be combined in one material or a single structural design concept. Recent development of spectrally-selective nano-structured materials and meta-surfaces has opened opportunities to manage both visible light and radiative heat year-round with conventional window and rooftop designs. In this regard, lightweight, flexible, and durable polymer materials, as well as organic-inorganic composites are increasingly replacing conventional natural materials across different sectors of economy, including new construction, historical buildings retrofitting, and design of new multi-functional wearables. Here, we report on the design, fabrication, and characterization of polymer-based organic-inorganic composites with tailored broadband spectral properties, and controllable thermal conductivity. We show that by varying the degree of crystallinity of ultrahigh molecular weight polyethylene (UHMWPE) and the composition of nanoparticle fillers, we can achieve simultaneous control over optical and thermal properties of the resulting composite material. The development of new optical functionalities that go beyond normal light diffusion in disordered polymer-based materials are also explored by introducing pseudo-random order to the material internal meso-structure.

**SB01.09.41**

**Multi-Material 3D Fabrication—CNT-Polymer Hybrids with Controlled CNT Alignment and Multifunctionality** Mostakima M. Lubna, Philip Bradford and Jakub Sciora; North Carolina State University, United States

The development of today’s smart devices not only focused on the miniaturization of complex material systems also the design flexibility, adaptability, and sustainability of a product are major concerning areas for researchers. The great opportunities offered by the nanomaterial-polymer systems from nano-micro to mesoscale have engendered scientists to design innovative structures with multifunctionality. Recently, carbon nanotubes (CNTs) are extensively used to fabricate multifunctional structures for wearable electronics, robotics, as well as in a wide range of other textiles and biomedical applications. CNTs hold substantial promise for fabricating the ideal multifunctional system; owing to their inherent properties of high aspect ratio, conducting network formability, thermal stability, compatibility with different polymers, ultralow-density and design flexibility. Though significant researches have been done previously regarding CNT-polymer hybrid structures, the superior nano-properties offered by CNTs are not fully being harness yet due to the randomness variability and complexity of multi-step processing. Typically, in fabricating CNT-polymer hybrids, solution-based dispersion or/inorganic acid assisted chemical surface
modification of CNTs were done prior to the addition of a specific polymer. These approaches of CNT processing routes are fully selective regarding the hydrophobic/hydrophilicity of a polymer and specifically customized focusing the system thus no design flexibility. Considering the percolation threshold and electrical property prediction uncertainty of the final CNT-polymer structure due to CNTs randomness, and allowance of a broader range of polymer incorporation possibility we have innovated a simple strategy with the inverse design approach. At first, we fabricated a stable ultra-low-density 3D anisotropic CNT foam structure with dry spinnable CNTs followed by pyrolytic carbon coating (PyC), where we can control the interconnected CNT network alignment directions within the structure which eliminate the CNT dispersion randomness limitation. And then, infiltrate polymer within the CNT structure, where the density of the final product can be tuned in a wide range by varying the polymer solution concentration. Very short-duration (few second) corona treatment was done on the dry CNT foams if hydrophilic polymers were to be infiltrated. The polymer infiltration technique is the same regardless of the polymer types (hydrophobic or hydrophilic). We have fabricated low density, stable and multifunctional 3D CNT-polymer hybrid structures using several different polymers, e.g., polydimethylsiloxane, polycarbonate, and polyvinyl alcohol. The results showed better structural stability in several hundred successive dynamic cyclic compression loading, tuneable low-density ranging from ~8.8 mg/cm³ to ~107 mg/cm³, ultra-porosity up to ~99.89%. The multifunctionality of CNT-polymer hybrids was successfully demonstrated in piezoresistive sensing for human motion detection, in electromagnetic interference shielding performance with thickness only 1 mm S21 is 63.4 dB for X-band and oil absorption applications. This 3D design provides the benefit of easier multi-material incorporation with controllable interconnected CNT alignment which can be used as a platform for the development of multi-nanomaterials systems.

SB01.09.42
OPEN SLOT

SB01.09.43
Biomimetic Fibronectin Fibrillogenesis at Air/Water Interface Thanga Bhuvanesh Vijaya Bhaskar1,2, Rainhard Machatschek1, Burkhard Schulz1,2, Nan Ma1,2 and Andreas Lendlein1,2; 1Institute of Biomaterial Science, Teltow, Germany; 2Institute of Chemistry, Germany

Fibronectin (FN) fibrillogenesis plays crucial roles in vivo by orchestrating embryogenesis, tissue organization by promoting the assembly of other extra-cellular proteins such as collagens, fibrillins, and tenasin-C and cell adhesion and growth [1]. This process is initiated by binding of FN to the cell surface through integrins and subsequent association with polyanionic proteoglycans (PGs) such as chondroitin sulphate resulting in FN unfolding from compact form to an extended form [2]. FN-self association through N-terminal domains and additional binding sites after FN unfolding result in fibril growth stabilized through non-covalent FN-FN interactions. To realize FN fibrillization artificially in vitro, the assembly of FN at the air-water (A-W) is an attractive solution [3]. The 2D confinement and high local concentration at the A-W interface enhances the FN-FN association essential for fibril growth and the acidic pH of the subphase can mimic the negatively charged PGs to promote FN unfolding. It is hypothesized that FN assembly at the A-W can simulate the FN assembly on cell membranes and result in fibril formation. FN was spread as droplets from concentrated solution (1 mg/mL) on subphase pH 2 in a circular trough (diameter 9 cm) and the assembly process was followed using in situ characterization tools. Surface pressure increases with time plateauing at 11 mN/m after 350 min and this indicates that surface adsorption is favorable on the subphase with pH 2, which is a pre-requisite for self-assembly. In parallel, the assembly process was investigated by polarization-modulation infrared reflection absorption spectroscopy (PM-IRRAS) to get information about the conformation of the FN layer. Amide I peak shifted from 1627 cm⁻¹ to 1621 cm⁻¹ after 30 min indicating unfolding of the FN from the compact native form. Finally, FN self-crosslinking was proven using interfacial rheology by the increase in interfacial elastic modulus and interfacial loss modulus with time (upto 16 h). The elasticity of FN fibrils was confirmed from the much higher elastic modulus (6 mN/m) than loss modulus (1 mN/m). Therefore, FN fibrillation can be realized in a cell-free environment using the A-W interface as a platform for assembly and such fibrils can be produced artificially in a facile manner on large-areas (12 cm²). We envision that such FN fibril networks can be transferred onto substrates for stem cell differentiation or as biomimetic scaffolds for tissue engineering and regenerative medicine.

References


SB01.09.44
**Mosquito Bite Inspired Miniaturized Sensor Technology for Healthcare Applications** Ganesh Kumar Mani and Kazuyishi Tsuchiya; Tokai University, Japan

Always there is great demand for *in vivo* testing to understand more about body metabolism to provide effective diagnosis and therapy. Currently no industrial technology available for single cell especially for pH, temperature or other cell metabolites. Compared to conventional sensors, research on single cell microneedle sensor is still in its infancy due to their difficulty in fabrication, poor flexibility, toxicity, scarcity of nanomaterials, instrumentation difficulty and poor stability. Meanwhile painless micro/nano needles have been widely used for extraction skin interstitial fluid, vaccine and drug delivery over the past two decades, but their potential as sensor remains largely unexplored. Therefore we aim to develop single microneedle based sensor for detection of pH and other cell metabolites in single cell. A ~4.8 µm pH sensor was fabricated and tested it *in-vivo/in-vitrosensing* capability was demonstrated. High stability and sensitivity make this novel pH sensing microneedle is a cost effective and easy fabrication tool for biological sensing especially at the single cell level. The developed sensor exhibited the Nernstian response of ~46 mV/pH. The fabricated microneedle sensor ability is proven by in vivo testing in mice cerebrospinal fluid (CSF) and bladder. The pH sensor reported here is totally reversible and results were reproducible after several routine testing. This type of sensor development definitely will bring new innovative ideas that have the huge potential for drug development while continuous metamorphosis observation.

SB01.09.45
**Active Microfluidic Substrates Based on Electroactive Electrospun PLLA Membranes** Ricardo Pereira¹, Eduardo Pimentel¹, Estela Carvalho¹, Pedro Martins¹, Senentxu Lancers-Mendez² and Vanessa Cardoso¹; ¹Universidade Do Minho, Portugal; ²Basque Centre for Materials, Applications and Nanostructures, Spain

Microfluidic paper-based analytical devices (µPADs) represent a promising platform for fast, portable, low-cost and easy-to-use analytical tools for point-of-care (POC) devices. Cellulose’s hydrophilicity, combined with patterned hydrophobic microfluidic channels generate sample flow from the inlet to a defined location for subsequent analysis. Nevertheless, the entry of µPADs into a real-life application is still minimal, mainly due to the inherent limitations of the materials used for the manufacture of µPADs, including their passive role as support element with no control on the fluid flow.

The present work develops microfluidic substrates based on piezoelectric electrospun poly(L-lactic acid) – PLLA membranes, optimised and properly characterised in terms of morphology, physicochemical properties and capillary flow rates. Oriented PLLA electrospun membranes were first produced to mimic the structure of commercially available *Whatman®* papers, commonly used in the fabrication of µPADs. Further, oriented PLLA membranes were also produced to study the effect of fibres orientation. As proof of concept, a disposable PLLA microfluidic system was designed and fabricated for the detection and quantification of glucose.

Acknowledgements

SB01.09.46
**Mechanically Induced Hydrophobic Recovery of PDMS for Patterning Surface Wettability** Ali J. Mazaltarim, Jay M. Taylor, Abhiteja Konda, Michael Stoller and Stephen Morin; University of Nebraska-Lincoln, United States

Silicone elastomers are widely used in “stretchable” technologies (e.g., wearable electronics) that require the elastomeric components to accommodate varying magnitudes of mechanical stress. Understanding how mechanical
stress influences the surface chemistry of these elastomeric components is therefore critical to the performance of these materials. We treated silicone films (polydimethylsiloxane; PDMS) with oxygen plasma and systematically exposed these films to various magnitudes of tensile stress while studying the associated surface chemical changes using contact angle measurements, X-ray photoelectron spectroscopy, and gas chromatography-mass spectrometry. We discovered that mechanical stressing oxidized PDMS films resulted in the on-demand restoration of the film’s hydrophobicity due to: i) cracking of the brittle surface oxide layer, ii) migration of uncured monomers from the bulk towards the surface, and iii) surface rearrangement. We utilized these understandings to develop a facile method for the rapid, on-demand switching of surface wettability and the generation of surface wettability patterns and gradients. These findings are broadly applicable to the fields of microfluidics, soft robotics, printing, and to the design of adaptable materials and sensors.

**SB01.09.47**

**Controlled Release from Core-Shell Electrospun Gelatinous Scaffolds** Adnan Memic, Tuerdimaimaiti Abudula, Kalamegam Gauthaman, Ahmed AlShahrie, Numan Salah, Angelo Chianese, Pierfrancesco Morganti and Ali Tamayol; ¹King AbdulAziz University, Saudi Arabia; ²Sapienza University of Roma, Italy; ³University of Naples, Italy; ⁴University of Nebraska–Lincoln, United States

Non-healing, chronic wounds have placed an enormous stress on both patients and the healthcare systems that served them. Severe complications induced by these wounds can lead to limb amputation or even death. Treatment of the hostile wound environment requires effective drug delivery systems able to overcome current limitations. Electrospun biomaterial scaffolds have showed a great potential for in both wound healing (i.e. as wound dressing materials) as well as controlled drug delivery applications. More specifically, electrospun gels due to their high moisture adsorption capacity and ability to interact with wide ranges hold a lot of promise. Previously, we developed bio-waste derived chitin-lignin gels, and demonstrated that they can be integrated as a native tissue-like fibrous membrane. However, their clinical application was limited by solubility and undesired burst release. Here, we developed a coaxial electrospinning approach to first encapsulate the gels with polycaprolactone (PCL). Presence of a PCL shell layer provided longer shelf life for the chitin-lignin gels in moisture environments and provided a sustainable release of drug molecules. Model drug and antibiotics were loaded into core-shell fibrous platform, which effectively inhibited both gram -positive and -negative bacteria without inducting observable cytotoxicity. Therefore, these PCL coated chitin-lignin fibrous gel platforms may be a good candidate for controlled drug release based wound dressing applications.

**SB01.09.48**

**Dynamic Wetting of Dandelion Pappus and Its Bioinspired Applications** Qingan Q. Meng, Huan Liu, Masao Doi and Lei Jiang; Beihang University, China

Learning from nature is the important fountain for the materials development. In recent years, the biomimic functional materials and structure have been paid more attention. Taraxacum officinale, often simply called dandelion, is a common composite perennial Asteraceae species with the capitulum containing a white ball of fluff composed of many pappi in an arrangement of horizontal radial geometry when the dandelion seeds are ripe. The most attractive feature of the dandelion is that the seeds are easily to be detached from the mother plant by wind after maturity and then start the new generation somewhere the seeds were parachuted. Interestingly, we observed another intriguing but less studied feature that the geometry of the pappus changed from open state (paratrute) to closed state, even a big water droplet could be encapsulated by the pappi of the dandelion seed after raining. However, the mechanism of the pappus undergoing hydro-actuated configuration alteration and water encapsulation in high efficiency have been unknown. Starting from the dynamic phenomenon of dandelion pappus in response to wet environment, we reveal the mechanism of dynamic wetting behavior of the pappus. Then drawing inspirons from above, we design and develop the intellgent materials and devices for realizing highly efficient liquid capture, transport and realizing stimuli-responsive spatial movement to the environment humidity, offering novel strateries for the development of highly efficient and controllable liquid transfer and intellgent aircrafts.

**SB01.09.49**

**A Comparative Analysis of Mechanical Properties and Release Characteristics of Drug Eluting Bone Cements** Lydia M. Mensah and Brian Love; University of Michigan-Ann Arbor, United States

We have been producing and testing aqueous amphiphilic copolymer polyether solutions, formulated with varying
amounts of a third constituent added with the notion of forming higher-throughput, drug-loaded gels. These gels have also shown potential in localized drug delivery and displace drug-eluting bone cements and spacers. So long as there are no structural requirements for the spacers, the cement matrix can be loaded with more than a few percent of the mass of the spacer with an antibiotic. To establish baselines of drug release in drug eluting cements, their transport attributes have been assessed either in terms of directly qualitatively observing an infection response clinically, or by measuring drug release into a tissue, or a receiving solution to mimic the tissue. Direct assessments of reduced infection by imaging or indirect protocols using a spacer interacting on a bacterial culture plate and resolving a zone of death emanating from the spacer are both indications of transfer of some antibiotic from the spacer and into the surrounding medium allowing some sort of assessment of a minimum inhibitory concentration (MIC). To assess the elution features of gentamicin and vancomycin incorporated into bone cements, we probed the spacer and into the surrounding medium allowing some sort of assessment of a minimum inhibitory concentration.

Hemocompatible Hybrid Magnetic Block-Copolymer Nanocapsules—UV Light Triggered Morphological Conversion from 3D Nanocapsule to 2D Nanowire-Network

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Chemical versatility of polymers provides a wide range of functionalization inputs onto the shell of the nanocapsules that play an essential role in the interactions with their surroundings. Moreover, the polymeric shell enhances the lifetime of the encapsulated drugs by protection from harsh environment factors such as pH value, enzyme activity, and avoids side effects of the cargo molecules to the living environment by decreasing rapid leakage. For this purpose, the development and engineering of smart polymeric nanocapsules have gained a high interest. Various materials have been adopted for encapsulation, and a variety of chemical and physicochemical methods have been developed in order to prepare hollow spheres with controlled size and shape. Although each method has its own merits and demerits, they all need either a preorganized structure or template to shape a hollow shell structure, and furthermore require time-consuming and laborious multi-step processes including removal of core or templates. Moreover, in polymers, dye/drug release can be achieved by introducing a photo-sensitive segment, whose activation leads to either rupture or modification of the diffusive properties of the capsule shell, allowing the delivery of the encapsulated material. Considerable efforts have been thus devoted to prepare stimuli-responsive hollow capsules which undergo a structural transition in response to small changes in the environmental conditions such as pH, temperature, redox-state, medium, and ionic strength. However, polymer nanocapsules which change the morphology from 3D nanocapsule to 2D nanowire-network on UV light exposure are not reported. Herein, we have developed a new, direct synthetic method for polymer nanocapsules without need of any template, pre-organized structure, or core removal. Wherein, introduction of the ferrocene-based moiety into the copolymer induced the formation of the nanocapsules. We demonstrate the switchable encapsulation and release of a fluorescent dye, when exposed to UV light. This process which is fully reversible and is due to transformation of spherical morphology into nanowire network.

Polymer nanocapsules were obtained by self-assembly of poly(styrene-b-vinylpyridine) (PS-b-P2VP) block copolymer and poly(chlorostyrene-co-vinylferrocene) (CIPS-co-PVF) in a mix solvent of THF/methanol without addition of any surfactant. The nanocapsules are paramagnetic in nature; this helps easy separation of polymer nanocapsules from solution by application of external magnetic field. Encapsulation of the fluorescent dye occurs during self-assembly step. Upon triggered with UV light for 2 h, the capsules gradually shrink and fuse into each other to transform into a nanowire-network and release the fluorescent dye gradually. The polymer nanocapsules were treated with human blood, which showed good hemocompatibility and did not cause any platelet aggregation.
This has good implications for the development of the drug carriers. In conclusion, we have synthesised a new hemocompatible, hybrid magnetic light responsive polymer nanocapsules with a controlled dye releasing capacity by a facile and robust preparative protocol in one pot. It is anticipated that this material will find applications in target specific drug delivery systems responsive to light and other external stimuli.

References

SB01.09.51
Highly Fluorescent Dynamic Hydrogels Via 2:2 Cucurbit[8]uril Host Guest Complexation Stefan Mommer and Oren A. Scherman; University of Cambridge, United Kingdom

Hydrogels are an important class of materials and have until now spread over a variety of fields in modern sciences. Other than covalent networks, non-covalent hydrogels consist of transient physical cross-links and have the inherent advantages that they are flexible and show self-healing as well as shear-thinning behaviour. Specific binding motifs have to be chosen to render a hydrogel non-covalent. Beside hydrogen bonding, electrostatic interactions or metal complexations, the self-assembly between a host and a guest molecule can be a powerful tool to mediate gelation in a given material. Cucurbit[8]uril represents such a host molecule and can complexate a variety of guest molecules. Recent reports have shown, that depending on the aromatic guest structure, complexes of 1:1:1, 2:1, 2:2 and even 2:3 (guest:host) stoichiometry can be formed. In this work we harvest the capacity of Cucurbit[8]uril to form 2:2 complexes, where now 2 modified viologen derivatives are stacked and handcuffed by 2 Cucurbit[8]uril macrocycles. The used guest molecules are fluorophores of aromatic nature and show unique optical and electrical properties. Once brought together, charge transfer complexes are formed that are glued together by the Cucurbit[8]uril macrocycles and therefore the optical and electrical properties dramatically change. By copolymerizing acrylamide with only little amounts of these fluorophores, polymers are obtained that readily form hydrogels upon addition of Cucurbit[8]uril to the system. The resulting highly fluorescent hydrogels show unique mechanical properties that are supported by rheological data. Due to their high elasticity and fluorescent properties, hydrogel materials based on these 2:2 Cucurbit[8]uril host-guest complexes hold promising potential for imaging applications in biomedical systems or as self-reporting materials.

SB01.09.52
Metal Deposition-Made Intrinsically Stretchable Conductors on Strain Absorbable Surface Structures and Their Use in Analog Position Sensors Sungmin Moon, Hyejin Hwang, Wonjeong Suh and Unyong Jeong; Pohang University of Science and Technology, Korea (the Republic of)

Intrinsically stretchable conductors are essential components for soft electronics, a new field of electronics, which includes deformable displays, stretchable transistors, energy storages, and health care devices. Most of the cases, they were usually made in the form of the conductive composite using percolation networks; conductive filler and intrinsically stretchable polymer matrix. Although they show great performance with high conductivity and large deformability, in terms of the fabrication process, their process is far from the conventional electronic fields where sputtering deposition is widely used. If the sputtering process can be applied to the manufacturing process of soft electronics, the potential for industrialization and commercialization will be greatly enhanced.

In this presentation, therefore, a bridge between the industry field and the new electronics will be suggested; stretchable conductors are made by metal deposition method on strain releasable structured substrates [1-3]. The intrinsically stretchable substrates (Styrenic block copolymers (SBC)) dissipates strain during the elongation through their surface network structures (microfibrils network, nanofiber network).

With these substrates, the deposited brittle conductive metal lines can maintain their network and conductivity
during harsh deformation condition (up to biaxial stretched ~ 100 %, ~ 20 Ω/sq). To demonstrate the advantages of the deposition method, tunable conductivity (i.e. strain sensitivity), patternability with various pattern width, areal uniformity and practical application are proposed. In addition, in order to clarify the fundamental mechanisms for maintaining the conductivity during the deformation, various experimental results and finite element method (FEM) focusing on mechanical deformation were investigated. Finally, a novel but simply designed tactile sensor fabricated only through metal deposition method on a single substrate will be presented that reacts to pressure and detects 2-D position information.

Reference

SB01.09.53
**Dynamic Transport of Liquid Droplets Using Mechano-Adaptive Chemical Gradients** Stephen A. Morin and Ali J. Mazaltarim; University of Nebraska-Lincoln, United States

Spatial variations in the wettability of surface-chemical gradients has been used to transport liquid droplets along predefined paths at predictable velocities. In these demonstrations the chemical gradients were synthesized, almost exclusively, on rigid, planar substrates which limit their adaptability. We have pioneered a set of techniques which enable the facile synthesis of large-area surface-chemical gradients on soft elastomers (e.g., PDMS) with mechanically switchable surface microtopography. These advances enabled the fabrication of, for the first time, mechano-adaptive soft surfaces capable of controlling the transport of liquid droplets dynamically. We provide an analytical model which predicts droplet velocity based on critical parameters such as strain state, droplet radius and viscosity, surface microroughness, and steepness of the wettability gradients. Further, we demonstrate the use of these mechano-adaptive gradients in the performance of functions directly relevant to surface-fluidic applications. We believe these findings are generally applicable to the generation of mechano-adaptive surfaces with dynamic, programmable surface-liquid interactions and chemical reactivity and directly useful to, for example, the design and fabrication of surface fluidic systems, adaptive surface coatings, and smart textiles.

SB01.09.54
**Hybrid Additive Manufacturing of Poly(caprolactone)-Modified Bone-Ligament Composite Scaffolds for Interface Tissue Engineering** Lorraine Mottishaw, Christopher Buksa, Marissa Perez, Nafisa Elghazali, Ruben Trujillo, Serafina Lopez, Fermin Prieto, Matthew N. Rush and Christina Salas; The University of New Mexico, United States

In a ligament rupture reconstruction, a tendon autograft is used to restabilize the bones around it. This procedure requires: surgically removing a portion of a tendon adjacent to the site of injury, drilling holes in the bones at the ligament insertion sites, funneling the tendon through the bones, pulling them taut, and restraining them with bone anchors. In addition to being fraught with limitations, this procedure and reconstructed joint cannot recapitulate the functionally-graded biochemical and biomechanical bone-ligament interface. Precise control of material properties and architecture could be the solution to reproducing native tissue properties at the bone-ligament interface.

3D bioprinting (3DBP) has shown promise for creating tissue engineered scaffolds with excellent resolution and controlled architecture. Commonly made from bioinks of biocompatible polymer-based solutions, these 3DBP scaffolds can be optimized to match the structural competency needed for bone tissue regeneration. Additionally, near-field electrospinning (NFE), an additive manufacturing technique, can produce smaller feature sizes than 3DBP. By applying a voltage between the build surface and the needle of the bioink syringe, the solution can be drawn from the syringe using electrostatic potential and thinning of the bioink filament. This system produces highly controlled, high-tensile resistant fibers very similar to ligament tissue fibers. Using a custom platform that merges the two manufacturing systems, we can fabricate complex composite scaffolds with fully integrated bone (3DBP) and ligament (NFE) phases. The current study focuses on optimization of the biochemical and biomechanical properties of each distinct phase of the composite scaffolds and characterization of the mechanical capability of the composite.

Poly(caprolactone) (PCL) in chloroform with decellularized bone particles was used as a bioink for the fabrication of the 3DBP bone phase scaffold. PCL in chloroform was mixed with Hexafluoro-2-propanol (HFIP) as a bioink for
the NFE ligament phase. 3DBP and NFE scaffold deposition parameters (extrusion rate and print speed) were characterized as a function of viscosity and solvent evaporation using an Anton-Paar rheometer. Bone phase 3DBP scaffolds of PCL only, PCL w/10% bone, and PCL w/40% bone were mechanically tested for compressive strength using an MTS servohydraulic actuator. Ligament phase NFE fibers were evaluated for tensile strength in 0° uniaxial, 90° biaxial, and 45° biaxial configurations using dynamic mechanical analysis. Cell viability of 3DBP and NFE scaffolds using NIH/3T3 fibroblasts was conducted along with cytoskeletal structural analysis through immunocytoskeletal staining and confocal imaging. Furthermore, the mechanical response of the 3DBP/NFE composite scaffolds were mechanically characterized and the microscopic structure examined using scanning electron microscopy.

By combining the 3DBP and NFE additive manufacturing techniques, we’ve created a structurally integrated composite scaffold for bone and ligament phase tissues. The hybrid system can create functionally graded architectural features that mimic bone and ligament tissue by altering scaffold geometry. Adapted bioink composition can tune the mechanical properties of the scaffold for fabrication of biologically relevant bone-ligament tissues.

SB01.09.55
Modelling of Carbon Nanotubes Based Multilayered Dielectric Elastomer Actuators
Seshadri Reddy Nagireddy and Aftab M. Hussain; International Institute of Information Technology (IIIT) - Hyderabad, India

Dielectric Elastomer Actuators (DEAs) are emerging as pseudo-muscular actuators for applications in the field of soft robotics. DEAs work on the principle of actuation due to electrostatic pressure. Because DEAs are electromechanical transducers based on capacitive architecture, all the components in the actuator (namely the dielectric elastomer and electrode) must contract and stretch. In order to achieve the requisite stretchability, carbon nanotube (CNT) based electrodes are used, which retain conductivity even at large strains. The CNT thin film consists of a large number of individual CNTs interwoven into a mesh. When these films undergo strain, the CNTs merely slide on each other increasing the lateral dimensions of the film without loss of conductivity. However, this interwoven structure causes the thin film to resemble a perforated film instead of a continuous conductive film, which causes the electrostatics to be complex. Apart from the need for compliant electrodes, another key disadvantage of DEAs is their high driving voltage of 0.3-4 kV. To reduce the actuation voltage without reducing the thickness, or increasing the relative permittivity of the dielectric material, multilayered structures can be used. These structures increase the actuation force without the need to increase driving voltage. This can create complex electric field patterns especially with perforated CNT-based thin films. In this work, we study the electrostatics of such multi-layered structures focusing on screening or lack of screening of electric fields created by ad-joint capacitors made of perforated CNT thin films and the effect it has on the observed capacitance of the system. Under theoretical treatment, it has been found that for an n-layered interdigitated structure with uniaxial perforation the capacitance of the system can be estimated by the equation: $C_n = C_0[n - 2(n-1)\beta + 2(n-2)\beta^2 - ... + 2(-\beta)^{n-1}]$, where $n$ is the number of layers, $\beta$ is the constant dependent on perforation ratio, $C_0$ is the capacitance of single layer with all solid electrodes. Further, the above theoretical model is verified using finite element analysis (FEA) in both 2D and 3D space. The perforated electrode is modelled as a charged metallic electrode with gaps in 2-dimensional case, and a metallic sheet with circular holes in 3-dimensional case. The analysis is carried out on an interdigitated structure to obtain capacitance of multilayered structure (up to 10 stacked layers). The electric field is seen to briefly fringe very close to the perforations as there is discontinuity in charge at these points. At large distances from the perforations, the electric field is approximately constant as predicted by Grosser and Schulz [1]. From these results it has been found that $\beta$ is independent of number of layers and is dependent only on electrode perforation. The obtained data closely matches the theoretical analysis results for normalized capacitance, which is calculated to show the percentage change with that of a capacitor with solid electrodes. The drop in normalized capacitance increases as the perforation ratio increases, while the normalized capacitance decreases with increase in number of layers but saturates afterwards. The change in capacitance due to perforations in the electrode system is limited (<0.5%) for an electrode area coverage of more than 90%. We believe this modelling and analysis is important to develop robust, reliable CNT based DEA structures.

Preparation of α-synuclein-Mediated Multi-Component Nanofilm Comprised of CNTs, AuNPs and MNPs and Its Use as Stimuli-Sensing Element for Shape Deformation

Funjeong Nam1, Yeji Kwon1, Jong Tak Lee1, Jung Hee Lee1,2 and Seung R. Paik1; 1Seoul National University, Korea (the Republic of); 2AweXome Ray Inc., Korea (the Republic of)

Integration of various nanomaterials into one multi-component system is prerequisite to produce multifunctional materials. In this study, a self-assembly protein of α-synuclein (αS), an amyloidogenic protein responsible for Lewy body formation found in Parkinson’s disease, has been employed to fabricate the multi-component nanofilms containing carbon nanotubes (CNTs), gold nanoparticles (AuNPs), and magnetic nanoparticles (MNPs). Ultra-thin 2D film of CNTs was prepared with the αS-CNT conjugates in which the N-terminal region was demonstrated to form α-helix on the hydrophobic CNT surface while the acidic C-terminus was exposed outward as determined by CD and NMR spectroscopy. Following a slow vacuum filtration of αS-CNTs through a polycarbonate membrane filter, chloroform was then used to unleash the CNT film by dissolving the underlying filter membrane, which also facilitated the αS-αS interactions by forming enhanced anti-parallel β-sheet and α-helix as evaluated with FT-IR. The light-responsive CNT film ornamented with or without αS-AuNPs in the presence or absence of αS-MNPs was transferred to the surface of a thermo-responsive double network hydrogel sheet composed of poly-N-isopropylacrylamide (PNIPAAm) and alginate, and sandwiched with a passive polymer layer of Ecoflex. Upon a near infra-red laser irradiation to trigger the photothermal effect of CNT, the entire triply structure exhibited a distinct shape deformation via a heat-induced shrinkage of the CNT immobilized area. In addition, the MNP co-localized films were shown to cause unique locomotions in the triply form under a rotating magnetic field. These multi-component nanomaterial films are therefore suggested to be utilized as a stimuli-responsive element to cause the shape deformation of hydrogels, which could serve as a critical part for the development of various areas including soft robotics, theranostics, and human-machine interfaces.

SB01.09.57
A Fully Integrated 3D Deformable Heterogeneous Sensors Based Biomedical Device for Clinical Emergency

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Wearable wireless sensor technologies are of greater concern for delivering the real-time healthcare information through personalized smart mobiles. Despite significant developments in active components, device geometry, sensors and efforts have been made to introduce new forms of natural inspired mechanical architectures that can accommodate large strains and geometrical deformations that are subjected to complex stress environments. Herein, we introduce, a fully integrated wearable wireless sensory patch system with strain-free mechanically robust structures inspired from both natural kirigami and serpentine patterns that are sticky, conformable, and mechanically robust to achieve high-levels of sensing performances. The present work addresses the challenge of all-day continuous monitoring of human body biological signals by introducing the well-equipped breathable (water permeability ~ 80 gm-H/1h), excellent adhesion to the skin (peel strength < 200 gf/12mm), bio-compatible, and conformable smart patch that can absorb the moisture (sweat) generated from the skin without any harshness and allowing the users’ to continuously monitor the early detection of diagnosis. Moreover, the hologenous stretchable temperature and humidity sensors have been introduced with high electrical properties and sensitivity under various temperature and relative humidity (%RH) scales. Theoretical and experimental results highlight the importance of sensor structural designs under various mechanical loading and deformations. The integrated sensory systems are equipped with breathable, bio-compatible patch, and protective layers, so that the user can conformably wear through the day for continuous analysis of early diagnosis, thereby allowing the patients to improve healthcare problems at different stages through mobile monitoring. Furthermore, the proposed integrated sensor enables the wireless sensing capabilities in response to a rapid variation equipped with customized circuit design, low power Bluetooth (BLE) module and signal processing integrated circuit (IC), thus, establishing a unique platform for multifunctional sensors to interface with hard electronics and emerging opportunities in the biomedical field and internet of thing (IoT) applications as well.

SB01.09.58
Polydopamine-Mediated Surface Modification Promotes the Adhesion and Proliferation of Human Induced Pluripotent Stem Cell

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Therapies, Helmholtz-Zentrum Geesthacht, Germany; ²Helmholtz Virtual Institute – Multifunctional Biomaterials for Medicine, Germany; ³Freie Universität Berlin, Germany; ⁴University of Potsdam, Germany

With their abilities of self-renewal and pluripotency to differentiate into all three germ layers, human induced pluripotent stem cells (hiPSCs) are promising cell sources for cell-based drug and implant testing [1, 2]. However, the large-scale expansion and maintenance of hiPSCs require adhering to strict conditions [3, 4]. Sample systems for the cultivation of high-quality hiPSCs are highly demanded to meet the application requirements. In this study, we probe the possibility of modifying the polymeric substrates for maintaining the self-renewal and pluripotency of hiPSCs. Here, polydopamine (PDA), typically used to join two materials including a wide range of inorganic and organic materials [5, 6], was employed to immobilize the Laminin 521 (LN521) onto the surface of polyethylene terephthalate (PET). An aqueous solution of dopamine with concentrations ranging from 0 to 2.0 mg/mL was applied on PET surfaces. These PDA-modified surfaces were further functionalized with LN521. Surface wettability was evaluated by measuring the water contact angle (WCA) and surface properties of the modified substrate were analyzed using an atomic force microscope (AFM). Initial hiPSC attachment (1h after seeding) and cell proliferation were evaluated by counting the total cell number. The maintenance of pluripotency was evaluated at different time points. WCA of the PDA-LN521 surfaces gradually decreased from 62.1°±6.3° to 8.1°±2.9°. The maximum peak-to-valley height roughness (Rt) of PDA-LN521 modified surfaces determined by AFM increased in a dopamine-concentration-dependent manner, ranging from 43.9±1.6 nm to 126.7±7.6 nm. Young's modulus of PDA modified surfaces was substantially increased from 0.980±0.36 GPa to 4.810±2.41 GPa. There was a significant enhancement (13.0±7.2% and 24.2±8.1%) of hiPSC adhesion on PDA-LN521 (dopamine concentration at 0.125 and 0.25 mg/mL). When increasing the dopamine concentration to 0.5 and 1.0 mg/mL, there was no further increase in hiPSC adhesion on PDA-LN521 surfaces. Moreover, hiPSCs proliferation was remarkably enhanced on PDA-LN521 surface (dopamine solution at concentration from 0.125 to 1.0 mg/mL). Pluripotent gene expression of hiPSC, including Oct-4, Sox2, and SSEA4, was not affected by PDA treatment. PDA modification did not impair the pluripotency of hiPSCs. In conclusion, polydopamine-mediated surface modification is an effective approach for the robust expansion and maintenance of hiPSCs on polymer substrates.

Reference

SB01.09.59
An All-Polymer Biofuel Cell for Bioelectronic Applications Georgios Nikiforidis, David Ohayon, Achilleas Savva, Shofarul Wustoni and Sahika Inal; KAUST, Saudi Arabia

All electronic devices require a power source to operate. The need to have portable power sources becomes more crucial for miniaturized bioelectronic devices that detect biological signals such as the heartbeat, muscle movements, as well as critical biomarkers. We herein present an all-polymer enzymatic biofuel cell to power such bioelectronic devices. The anode is an NDI-T2 copolymer (P-90) consisting of alternating naphthalene dicarboximide (NDI) acceptor and bithiophene (T2) donor subunits with randomly distributed alkyl and ethylene glycol side chains, while the cathode is a p-type thiophene-based copolymer P(EDOT-OH-EDOT). The enzyme (glucose oxidase) has efficient electrical communication with the n-type polymer film, rendering P-90 suitable as an anode for the enzymatic biofuel cell. The p-type cathode material demonstrated stable catalytic activity towards oxygen reduction reaction (ORR). Upon introduction of glucose into PBS, the former is oxidized to gluconolactone by GOx, producing electrons that are transferred to the P-90 anode. These electrons then travel through the external
circuit to the cathode which reduces dioxygen to water generating power from glucose and oxygen in aqueous media. The biofuel cell exhibited a cell open circuit potential of 0.3 V when operated at physiologically relevant glucose concentrations, enough to power organic electrochemical transistors (OECTs), state-of-the-art sensor configuration of organic bioelectronics. The powering device is stable for 35 days in a membrane-free configuration and yields a power density of 20.7 mW.cm⁻² at 100 µM of glucose. Implementing an OECT sensor that can be indefinitely powered by glucose through the biofuel cell can lead to self-reliant devices.

**SB01.09.60**
**Temperature-Responsive 4D Printing with Fast, Controllable and Reversible Self-Deformation** Je Hoon Oh¹, Jongbeom Kim¹, Je Jun Jeong¹, Kyu Hwan Oh¹ and Myoung-Moon Moon²;¹ Seoul National University, Korea (the Republic of);² Korea Institute of Science and Technology, Korea (the Republic of)

4D printing is a technology that makes the 3D printed structures deformed by responding to external stimuli such as temperature, pH, UV, and magnetic field. Recently, 4D printing has been actively explored for the application in several field such as soft robotics or biomedical devices such as a stent or a sensor that detects and reacts under the biofluidic environment. However, there are still many challenges. One is that it is difficult to control the deformation speed and the other is irreversible deformation which changes only in one direction.

In this study, we present a temperature-responsive 4D printed structure deformed by controlling the two distinct memory effect of ‘strain memory’ and ‘stress memory’. Shape memory has two concepts: one is 'strain memory' and the other is 'stress memory'. 'Strain memory' means to remember the shape of the structure and to be restored to that shape by the stimuli condition. 'Stress memory' means that the structure accumulates and memorizes the stress, not just the shape. Even if the same structure deforms to the same strain, the stress that acts on the structure can also be programmed differently by the material of the structure, 3D printing conditions, and additional processes.

When a 3D printed structure is deformed, the external strain applies to each of the printed thermoplastic fibers composing the structure. The strain applied to a 3D printed SMP (shape memory polymer) with a rubbery state at Tg or higher would be stored in a glassy state when cooled. Stress memory inside the printed structure can be residually controlled by stacking output layers with different recovery stresses. By programming the stress acting on each layer in the process of returning to the memorized shape, it is possible to make the stress more than necessary in the shape recovery process differently for each layer. We shows that by alternatingly programmed with the layer with stress memory effect on top of the upper layer with strain memory effect, it is possible to make a reversible structure in deformation. By relieving the stress memory, the structure in the high temperature is transitionally deformed into programmed shape with a faster speed, then by the strain memory effect, the programmed shape returns to the original shape that was initially memorized at the 3D printing process. Through this study, we demonstrate this concept for a structure similar to the stimuli responsive plants behavior like Mimosa, which rapidly self-deforms to instantaneous external stimuli, and gradually restores to its original structure even when the external conditions are intact.

**SB01.09.61**
**Reversible Nanoscale Switch with Short Responsive Time** Seoyeah Oh, Myungsoo Han, Jihyeon Park and Jiwon Kim; Yonsei University, Korea (the Republic of)

Nanomaterials with high specific surface area and nanoscale detection capability via reversible process is promising for real-time monitoring. In nanoscale detection, the system needs to show long-term stability, rapid response, precise detection, and high ON/OFF ratio. Herein, we present a nanoscale switch which is reversible with short response time and stable for many cycles. Switch is composed of gold nanoparticles(NPs) functionalized with carboxylic functional group (11-mercaptoundecanoic acid; MUA) and tert-ammonium functional group ((11-mercaptoundecyl)-N,N,N-trimethylammonium bromide; TMA) with 5:1 ratio. These NPs were stable in both acidic (pH 3) and basic (pH 11) conditions, and surface charges rapidly changed by changes in the environmental pH. We propose two models to monitor changes in surface charges upon changes in environmental pH via zeta potential: ‘dilution model’ and ‘conservation model’. In dilution model, the pH control solution was directly injected into the NP system, which showed rapid response (< 30 s) with ~30 cycles. In conservation model, NPs were isolated in a semipermeable membrane in order to avoid accumulation of counterions. Conservation model showed relatively slower response time (< 5 min) compared to the dilution model, but the stability improved to 45 cycles. NP-based nanoscale system showed high ON/OFF ratio of 1.3 due to the high surface area, and reversibly switched with fast response time (< 30 s) with ~30 cycles. We believe this system will provide significant advances in the field of real-time nanoscale monitoring (e.g. in vivo monitoring where the environment changes in real time due to homeostasis)
and receptors for molecular communications which quickly respond to continuously delivered messenger molecules.

**SB01.09.62**

**Zeolite-Templated Carbon Network—A Beta Zeolite Case Study**  
Eliezer F. Oliveira¹, Leonardo D. Machado² and Douglas S. Galvão¹; ¹State University of Campinas, Brazil; ²Federal University of Rio Grande do Norte, Brazil

3D structures formed from carbon nanotubes could present interesting mechanical and electronic properties [1]. Some studies have shown that these structures are dominated by the topology of the carbon nanotubes networks, which makes their properties tunable [1]. However, up to now the synthesis of such structures has been very limited [2,3]. It has been previously shown that it is possible to grow carbon nanostructures inside the channels of the zeolites [2,3]. Among the large number of possible zeolites [4], good candidate structures to allow the synthesis of 3D carbon nanotubes network are the beta zeolites [3], as they have interconnected channels. In this work we report a preliminary study, based on molecular dynamics simulations about 3D carbon nanotube networks that could be formed inside beta zeolites. We investigated their structural stability and mechanical properties. Our results show that from all possible carbon nanotubes that can be embedded inside the channels of the beta zeolite, the one with chirality (6,0) is the most stable. Using the carbon nanotube (6,0), it is possible to built 3D structures with both all (higher density) and only partially (lower density) filled zeolite channels. The 3D low-density carbon nanotube networks are anisotropic and can be stretched along the direction in which all nanotubes are perpendicular up to 130% of strain without fracture. Also, the porosity and network stiffness can be tuned depending on the amount of carbon nanotubes filling the zeolites channels.

References:

**SB01.09.63**

**Development of “Fullerene Nanowhisker-Composite Paper”**  
Taku Onishi and Takahide Oya; Grad. Sch. of Eng. Sci., Yokohama National University, Japan

We propose a new functional paper containing fullerene nanowhiskers (FNWs), i.e., an “FNW-composite paper.” It is known that FNWs have an n-type semiconducting property and are used in a diverse range of applications, including field-effect transistors, solar cells, chemical sensors, and photocatalysts. Therefore, many studies have been conducted until now by lots of researchers. However, because the FNW is a nano-scaled material, so that it is difficult to handle, generally. In this study, we develop an “FNW-composite paper” by mixing FNWs with pulp fibers (raw materials of papers) and solve the problem. Since a paper is lightweight, easy to process, inexpensive, and familiar material for us, the “FNW-composite paper” can be expected to be applied to various things. It is well known that the FNW is prepared using the method of liquid-liquid interface precipitation (LLIP). In this method, it is necessary to put a poor solvent of fullerenes above a good solvent saturated solution of them and form an interface between them. After a while, thin cylindrical shape substances are grown at the layer and FNWs are reduced.

In this study, we use the LLIP. As a first step of fabricating our “FNW-composite papers,” pulps (150 mg) are stirred in pure water (10 ml) for 60 minutes to prepare a pulp dispersion. Then, C₆₀ (fullerene, 40 mg) is dispersed in m-Xylene (10 ml), which is a good solvent of fullerenes, to prepare a fullerene dispersion. After that, the pulp dispersion and the fullerene dispersion are poured in a square case. Since water has a greater specific gravity than m-Xylene, the layer of the fullerene dispersion is above it of the pulp dispersion. Then, isopropyl alcohol (IPA, 10 ml), which is a poor solvent of fullerenes, is poured from above the dispersions carefully to form an interface between the fullerene dispersion and IPA. After that, the prepared liquid is left for 112 hours at 4 °C. Next, the liquid is heated to evaporate moisture. Finally, the material in the case is pressed to finalize the making process. As results, we could gain a sample in this way and confirm that FNWs existed on the pulps by SEM. FNWs have a lot of great features as we showed above. We expect to prepare the paper which has an n-type semiconducting property and use it as a field-effect transistors, chemical sensors, and so on.

**SB01.09.64**
Bioactive Glass Nanoparticles as Antibacterial Tool against Antibiotic-Resistant Infections Natalia Pajares Chamorro1, Yadav Wagley2, Neal Hammer1, Kurt Hankenson2 and Xanthippi Chatzistavrou1; 1Michigan State University, United States; 2University of Michigan–Ann Arbor, United States

Infections are a major concern in orthopedics. Bacteria colonization is often the reason for prosthetics failure that causes biofilm formation and induces bone degenerative diseases. The emergence of resistant bacteria has hindered the ability of common antibiotics to fight these infections. For example, Staphylococcus aureus (S. aureus) is able to encode methicillin (i.e. MRSA strains) and it is responsible for 60% of sepsis implant failure. The elevated morbidity and mortality associated with resistant infections support the need for innovative approaches that not only improve treatment outcomes but also reduce the risk of developing further antibiotic resistance. Antibacterial agents such as silver ions are of great interest as broad-spectrum biocides to overcome and prevent the development of resistance in many pathogenic strains. We have developed Ag containing bioactive glass-ceramics with advanced antibacterial and bioactive properties. The synthesis of bioactive nanoparticles (BGN) with complicated composition remains a big challenge. In this work, this challenge is addressed, as we deliver nanoparticles in the desired composition. These nanoparticles are expected to show enhanced antibacterial and bioactive behavior compared to their microsize counterparts due to the increase in their surface area. Here, a modified Stöber method is presented for the successful incorporation of ions that play a key role in the bone regenerative properties of the BGNs. Synthesis parameters were systematically modified in terms of solvent, reagent addition order and stirring time to accomplish particles of the nominal composition being below 100 nm in size and with moderate dispersity. A final protocol was optimized for the synthesis of silver-doped BGN (Ag-BGN) containing SiO2-CaO-P2O5-Al2O3-Ag2O. Characterization techniques such as SEM-EDS, TEM, FTIR, XRD, and solid-state MAS-NMR were used to demonstrate the composition, morphology and structure of the BGN and Ag-BGN synthesized. The antibacterial properties were also evaluated against MRSA by colony forming unit quantification after direct exposure. The cell-material interaction was studied using human marrow-derived mesenchymal progenitor cells. In conclusion, this work addresses the challenges in the development of nanoparticles with multiple ions in nominal concentrations and presents the advancements in antibacterial and bioactive characteristics.

SB01.09.65 Preparation and Degradation Analysis of Multifunctional 3D-Architectured Gelatin-Based Hydrogels Jun Hon Pang1, Christian Wischke1 and Andreas Lendlein1,2; 1Helmholz-Zentrum Geesthacht, Germany; 2Potsdam University, Germany

Mimicking the native extracellular matrix (ECM) using multifunctional materials is a promising approach to direct tissue regeneration in vivo. In particular, pure biomaterial-based strategies without further incorporation of growth factors or surface functionalization are desirable, owing to lower production cost and complexity.

Targeted towards clinical translation of an implant capable of modulating regenerative processes in vivo, a one-pot synthesis of 3D-architected gelatin-based hydrogels was designed, in which the biomolecule is chemically functionalized [1]. These structured hydrogels exhibit essential properties and functions including presentation of cell adhesive sequences, interconnected porous architecture, degradability, dimensional stability upon swelling, as well as tailorable elastic properties. The gelatin-based hydrogels were manufactured in a cleanroom facility. While it is known that such scaffolds are degradable in vivo, there is limited understanding on the contribution of different degradation mechanisms, particularly in relation to the role of crosslinks.

In this study, samples of 1.5 x 1.5 cm2 with thickness of ~3.5 mm were incubated at 37 °C with mild agitation in solutions simulating pure hydrolytic degradation (phosphate buffered saline, PBS), oxidative degradation (3 % v/v H2O2) and enzymatic degradation (0.2 U/mL Collagenase I), which are supplemented with 0.01 % w/w sodium azide to exclude microbial contamination. The hydrolytic and oxidative buffer conditions simulate real-time degradation [2]. Collagenase I was selected to elucidate enzymatic degradation due to its presence in damaged tissue and reports of degrading other gelatin-based materials [3]. The influences of the three degradation conditions on mass loss, morphological and chemical properties of the scaffolds were investigated.

The scaffolds degraded rapidly under oxidative and enzymatic conditions, with endpoint of >95 % mass loss achieved in 2.5 weeks. In contrast, the scaffolds were relatively resistant to hydrolytic degradation, with merely mass loss of 20 % after 20 weeks. SEM analysis indicated varied degradation behavior among the different sample groups based on changes in porous structure alongside crack formation.
We discuss degradation mechanisms and products in relation to the chemistry of the scaffold, specifically on the role of the involved crosslinks. Oxidative and enzymatic degradations were shown to be the key mechanisms for in vivo degradation of our gelatin-based hydrogels. Such analysis is vital for biodegradable implants to elucidate degradation behavior and products, both of which are essential for translation of novel biomaterial-based implants.

Reference:

**SB01.09.66**

**Effects of Geometry on Magnetic Actuation of Micropillar Arrays**

Jeong Eun Park1, Jisoo Jeon1, Sukyoung Won1, Jehwan Hwang2, Sang Jun Lee2, Augustine M. Urbas2, Zahyun Ku3 and Jeong Jae Wie1; 1Inha University, Korea (the Republic of); 2KRISS, Korea (the Republic of); 3Wright-Patterson Air Force Base, United States

Reversible shape-reconfiguration of magnetic composites has been demonstrated by pre-programming the alignment of magnetic particles within micropillar arrays. The alignments of magnetic particles determine the magnitude and directionality of magnetic-actuation dependent to the offset angle from the external magnetic field axis. Previous reports on magnetic microstructures have mostly been employed symmetric cylindrical or rectangular geometry, resulting in balanced stress distribution for actuation by the external magnetic field. Herein, we demonstrate the effects of asymmetric geometry on magnetic actuation with the rectangular and triangular form factor. Upon the external magnetic field, the magnetic torque generates concentrated magnetic momentum in anisotropic micropillars, resulting in enhanced magneto-mechanical actuation. To elucidate the relationships between geometry factors of pillars and magnetic-actuation, we will discuss structure-property relationships of triangular and rectangular micropillars for both bending and twisting actuation.

**SB01.09.67**

**Time-Controlled Nanoscale Delivery System**

Jihyeon Park, Seoyeah Oh, Dongjun Kim and Jiwon Kim; Yonsei University, Korea (the Republic of)

Delivering cargoes at desired time points and positions in nanoscale is necessary in order to precisely control the time-dependent reactions. For example, each drug needs to be delivered at desired time point in order to increase the efficacy of multi-drugs. The delivery time and position also need to be finely controlled if cargoes should be combined before they degrade for activation. However, it is difficult to develop a spatio-temporally controlled delivery system (especially for multi-cargos, delivery time difference with a short period time (< a few minutes)) due to random walk motion of cargoes, difficulty of applying two different driving forces on the same type of nanoscale delivery system, and an interference between cargoes. Herein, we designed two (or more) types of nanomotor which can travel at different speeds upon a single magnetic stimulus. Nanomotors were composed of nickel head – silver flexible filament – gold tail encapsulated with N-isopropylacrylamide (NIPAm) based hydrogel. The difference in speed was quantitatively controlled by adjusting the length of each compartment whereas the cargo releasing time was regulated by optimizing the thickness of encapsulating hydrogel. Our nanomotor based nanoscale delivery system demonstrated sequential cargo delivery with time-difference of a few minutes. This delivery system can possibly increase the gene editing efficiency (e.g. CRISPR/Cas9 system) and efficacy of multi-drugs by allowing drugs or genetic materials to be activated at different time points. Furthermore, our time-controlled delivery system in nanoscale can also be applied in molecular communication via applying sequential (bio)material transmission as a signal.

**SB01.09.68**

**Controlling Microstructure of Bombyx mori Silk for Water-Responsive Actuation**

Yaewon Park1, Yeojin Jung1,2, Raymond Tu1,2 and Xi Chen1,2; 1Advanced Science Research Center at City University of New York, United States; 2The City College of New York, United States

Water-responsive (WR) materials that swell and shrink in response to changes in relative humidity could serve as high-energy actuators, providing new engineering opportunities for soft robotics, sensors, and energy harvesting devices. Spider silk has been shown to be a WR material and has a higher energy density than conventional
actuators. However, natural silk’s relatively low production efficiency and variations in water-responsiveness limit their practical applications. Bombyx (B.) mori silk is also reported to have a WR property, but B. mori silk has a lower energy density than that of spider silk. Here, we demonstrate that the processing of the B. mori silk can dramatically increase regenerated B. mori silk’s WR energy density. To control the grain size and volume ratio of Silk II structures, we treated regenerated B. mori silk films with water vapor and methanol under various conditions which yield higher volume ratios. FTIR and AFM experiments subsequently confirmed the variation of Silk II structures resulted from these post-treatment methods. We found that Silk II structures’ crystallinities, sizes, and distributions define the silk’s WR behaviors. For example, as the volume of Silk II increases, regenerated silk’s WR energy density increases and reach ~500 kJ m⁻³, which is comparable to that of spider silk. This work is a proof-of-concept that a powerful WR actuator can be fabricated with cost effective and naturally abundant B. mori feedstocks.

SB01.09.69
Humidity Sensing Microfibers Containing Conducting Nanofillers in an Agarose Matrix and Impedance Analysis on Their Opposite Humidity Response Ye-Jin Park¹, Yangwoo Lee¹, Ju-Hee So², Sungkon Kim³, Bongjun Yeom⁴ and Hyung-Jun Koo⁵; ¹Seoul National University of Science and Technology, Korea (the Republic of); ²Korea Institute of Industrial Technology, Korea (the Republic of); ³Chonbuk National University, Korea (the Republic of); ⁴Chonbuk University, Korea (the Republic of); ⁵Hanyang University, Korea (the Republic of)

Inspired by a human or animal hair as a natural humidity sensor, two types of humidity sensing microfibers based on an agarose polymer as a hydrophilic matrix and conducting fillers are reported. The microfibers are fabricated with simple extrusion of the agarose composites containing two different conductive nanofillers: (1) graphene oxide (GO, chemically reduced after extrusion)/silver nanowires (AgNWs) and (2) carbon nanotubes (CNTs). Both microfibers at optimum filler content exhibit the enhanced electrical conductivity and mechanical properties, due to intrinsic property of CNT or synergistic contribution of AgNWs and reduced GO (rGO) as 1D and 2D nanofillers, respectively. As a result, the microfibers have 3~4 times higher values of Young’s modulus than commercial nylon-6 and polyamide and are flexible enough to be knotted. The composite microfibers have an ability to be humidity sensors owing to their humidity-dependent conductivity. The microfiber containing rGO/AgNWs shows positive dependence of its conductivity on environmental humidity, upon ionization of water molecules by rGO. On the other hand, the microfiber with CNT shows negative dependence of its conductivity on humidity, due to decreased junction density of CNT resulting from swelling of the hydrophilic agarose matrix at high humidity. In order to delve into the opposite humidity response of two composite fibers, we performed impedance analysis of the fibers at various humidity conditions, which will be discussed. The composite microfibers show reliability, reversibility and feasibility of humidity sensing demonstrated by repetitive changes in humidity and practical usages such as human breathing. The humidity sensing microfibers could have applications to smart textile and wearable devices.

SB01.09.70
Artificial Synapses and Resistive Switching Memory Based on Biomaterials Youngjun Park, Min-Kyu Kim, Dongshin Kim and Jang-Sik Lee; Pohang University of Science and Technology, Korea (the Republic of)

Biocompatible and implantable electronics have gained increasing attention due to growing interest in health care. The advances in the electronics require the development of biocompatible and implantable memory that performs the data processing and storage. However, conventional memory devices are not suitable for this purpose because they are not biocompatible and sometimes even toxic. We present the memory devices and artificial synapses based on natural, biocompatible, and biodegradable materials on flexible polyethylene terephthalate substrates [1]. Multi-bit data storage capability is achieved by controlling maximum reset voltages and compliance current. The switching behavior is thought to be related to the carbon atoms in the active layer, which could form the carbon filament. Synaptic functions including analog switching behavior and potentiation/depression are realized by controlling the formation and rupture of filament [2]. By properly modulating the stimulation pulses, both short-term plasticity and long-term plasticity of biological synapses can be achieved. Moreover, the devices can be stably operated under mechanical bending stress. These researches will offer a new possibility for biomaterials to be used in next-generation memory devices and neuromorphic systems. In this presentation, characteristics of biomaterials for application to memory devices and artificial synapses will be presented in detail.

SB01.09.72  
**Multifunctional and Biodegradable Self-Propelled Protein Motors**  
Abdon Pena-Francesch, Joshua Giltinan, Metin Sitti and Ugur Bozuyuk; Max Planck Institute for Intelligent Systems, Germany

A diversity of self-propelled chemical motors, based on Marangoni propulsive forces, has been developed in recent years. However, most motors are non-functional due to poor performance, a lack of control, and the use of toxic materials. To overcome these limitations, we have developed multifunctional and biodegradable self-propelled motors from squid-derived proteins and an anesthetic metabolite. The protein motors surpass previous reports in performance output and efficiency by several orders of magnitude, and they offer control of their propulsion modes, speed, mobility lifetime, and directionality by regulating the protein nanostructure via local and external stimuli, resulting in programmable and complex locomotion. We demonstrate diverse functionalities of these motors in environmental remediation, microrobot powering, and cargo delivery applications. These versatile and degradable protein motors enable new design, control, and actuation strategies in microrobotics as modular propulsion sources for autonomous minimally invasive medical operations in biological environments with air-liquid interfaces.

SB01.09.73  
**Programming Tri-Peptides Water-Responsive Materials**  
Roxana Piotrowska1,2, Travis Hesketh3, Alan Martin4, Deborah Bowering4, Chunhua Hu5, Haozhen Wang1, Xi Chen7 and Rein Ulijn1; 1Advanced Science Research Center, United States; 2The City University of New York, United States; 3University of Strathclyde, United Kingdom; 4University of Strathclyd, United Kingdom; 5New York University, United States

Water-responsive (WR) materials that exert significant forces in response to changing hydration levels are receiving growing interest due to their potential applications, including use as actuators for energy harvesting devices, artificial muscles, and soft robotics. Reported examples include biological and synthetic materials with abilities to efficiently convert chemical potential of water into mechanical actuations. However, these systems are typically complex, and consequently, their WR mechanisms are not well-understood thus preventing rational design and optimization. Here, we demonstrate that tri-peptides, which are modular organic building blocks with precisely tunable non-covalent interactions, spontaneously associate to form hierarchical ordered crystalline structures, which exhibit WR behavior that is strongly dictated by their building blocks’ chemical nature and consequent organization. Our tripeptide crystals, with intrinsic water channels in nanoscale, has the ability to swell and shrink in response to changes in relative humidity (RH). The crystals also exhibit outstanding mechanical properties including a stiffness of 0.5 - 2GPa depending on RH, leading to a high WR energy density of more than 80kJ/m³. Due to its biodegradability and relative simplicity, this system could not only serve as an excellent platform to enhance understanding of such material’s WR mechanisms, but also holds much promise for programing better WR materials for future applications.

SB01.09.74  
**Effect of Mechanical Mismatch on Failure Mechanism of Substrate-Electrode Systems in Stretchable Electronics**  
Reihaneh Jamshidi; University of Hartford, United States

All-organic electronics have gained increasing attention due to their biocompatibility, intrinsic flexibility, as well as lower cost compared to inorganic materials. It is hypothesized that the similarity of mechanical properties between the electrode and substrate in all-organic electronics, facilitates improved mechanical performance in these structures. Here, we report the comparison between failure mechanism of an all-organic bilayer and a metal-polymer bilayer to demonstrate the effect of inherent properties of layered structures on the overall mechanical performance of the system.
High-Performance Actuators for Untethered Applications Seyed M. Mirvakili, Robert Langer and Ian W. Hunter; Massachusetts Institute of Technology, United States

In this work, we are presenting a simple approach for the fabrication of high-performance muscle-like actuators (artificial muscles) for untethered applications. Artificial muscles are exploited in various applications, including soft robotics, bio-medical devices, and even energy harvesting systems, to name a few. One of the limitations of such actuators is the need for wiring, pressurized gas tanks, electrolytes, etc. Here we are demonstrating how we can make wireless actuators that can perform as good as the tethered counterparts.

Emerging Materials Robotics S.K. Smoukov1,2; 1Queen Mary University of London, United Kingdom; 2University of Cambridge, United Kingdom

Molecular robots are all around and inside us – from viruses injecting their RNA and highjacking cellular machinery for replication, to myosin contracting our muscles, to the ribosome translating our DNA. Such invisible machinery is key to us being alive. Can we start growing functional nanomachines artificially? In this talk I will outline progress we have made towards this goal. From creating programmable materials that can move, sense and respond to their environment in complex ways, to artificial morphogenesis – we have the ability to shape particles and our future. & much of this story is based on liquid droplets.

Our work on topological inter-penetration of functional materials[1] replaced unpredictability in multifunctional synthesis with combinatorics - choosing 3 phases of 20 already optimized functions would lead to over 8000 trifunctional materials. We demonstrated new supercapacitor architectures,[2] as well as emerging self-sensing artificial muscles.[3] We also discovered artificial morphogenesis – transformation of liquid droplets into a large variety of complex regular micro- and nanostructures. Our methods of growing from single molecules many shapes, including octahedra, hexagons, rhomboids, triangles and fibers[4] have yielded a polymerization process[5] that could potentially replace the expensive infrastructure and waste of lithography. We have classified dozens of pure[6] and mixed component systems (including triglyceride oils) capable of shape-change[7] which could let us synthesize novel shaped lipids or polymer drug carriers. We use thermodynamic understanding and mathematical modelling to predict and control the observed shapes[8]. Transforming almost 100% of a liquid droplet into a final shape is ideal for sustainability and for space manufacturing.

Current projects aim to move beyond manufacturing static shapes. By combining bottom-up growth with multifunctional polymer synthesis, we aim to produce functional micro- and nanoparticles with autonomous behaviour, e.g. movement, sense and response to environmental stimuli, as well as on-board energy storage. Surprisingly, some of our artificial systems already mimic life by repeatedly harnessing thermal fluctuations in the environment, and storing energy by breaking up into smaller and smaller emulsion droplets.[9] I will outline implications for further fundamental discoveries and for potential applied explorations.


9:00 AM SB01.10.03
Printed Wearable Multi Sensors on Soft Robotic Gripper for Detection of Tactile Signals Tomohito Sekine1, Yi-Fei Wang1, Yasunori Takeda1, Daisuke Kumaki1, Santos Fabrice Domingues Dos2, Atsushi Miyabo3 and Shizuo Tokito1; 1Yamagata University, Japan; 2Piezotech, France; 3Arkema K. K., Japan

Tactile sensing is required for a dexterous feedback system of an object in robotic-skin applications. Moreover, an ability to monitor various physical forces such pressure and shear in real time is a key technology for a slip detection with fragile objects. As a way of solving the above, a flexible printed sensor will be invaluable. Because these possess great potential advantages for the robotics-skin applications due to high sensitivity. Previously, fabrication of soft sensors and their application for robotic skins was reported by many groups; however, realization of a multi-sensing devices by printing methods remain a challenging task. Recently, we reported flexible and soft sensors that were fabricated using a ferroelectric polymer, P(VDF-TrFE) and Carbon nanotube (CNT) by printing methods for shear and pressure detection. Furthermore, we developed a printed temperature sensor using PEDOT:PSS. Integration of these sensors on a one-tip-substrate will enable realization a physical multi-sensor for tactile signals. Here, we report a wearable and printed soft robotic multi sensor composed of shear, pressure and temperature sensors for detection of tactile signals.

The various shear, pressure and temperature sensors were fabricated on a flexible film by printing methods. First, we fabricated the shear sensor using P(VDF-TrFE) by Screen printing method. A cross-linked poly(4-vinylphenol) (PVP) solution mixed with the PVP and 1-methoxy-2-propyl acetate as the solvent was formed by spin-coating onto the substrate as the planarization layer. Lower and upper electrodes of the sensor were formed using conductive polymeric materials and annealing at 140 °C for 30 min. The P(VDF-TrFE) layer was formed as the detecting layer of shear force by screen printing and annealed at 135 °C for 1 h. The polarization and the coercive electric point of the sensor were 7.0 µC cm⁻² and 50 MV m⁻¹. These performances are reasonable as printed ferroelectric devices. Next, we fabricated the pressure sensor using the CNT solution mixed with a 4-dodecylbenzenesulfonic acid by Dispense equipment. The electrodes of this sensor were formed by the Ag nanoparticle ink and annealing at 150 °C for 30 min. The CNT layer was formed as the detector of pressure force by Dispensing and annealed at 100 °C for 12 h. The initial resistance value of this sensor was 10 kΩ. Finally, the temperature sensor using PEDOT:PSS was fabricated by Screen printing. After formation the PEDOT:PSS layer, the substrate was annealed as 100 °C for 12 h. The output voltage of the shear sensor linearly displayed a clear correlation with the applied shear force and the output voltage. It showed approximately 50 mV in the shear speed of 200 mm s⁻¹. Similarly, the relationship between applied pressure and output voltage in the pressure sensor was measured. The pressure was applied by using a pressure tester to the sensor. This resistivity was changed from the initial value to 1 kΩ when pressure of 2.0 N applied. These results indicate that the fabricated various devices will be candidate for tactile sensors of a robotic-skin due to high sensitivity.

Robotic controlling experiments were performed demonstration the use of our sensors to monitor tactile signals in real time. The gripper can grip various objects by a pneumatic driving system. Moreover, our multi sensor were attached on a soft robotic gripper. An oscilloscope recorded the signals of output voltage from the sensors. We can estimate tactile signals of shear, pressure and temperature at the same time when the gripper handled objects. From these outcomes, the information obtained from the fabrication of the multi sensor used in this study further illustrates the potential in an elaborate robotics controlling system with a closed loop feedback.

9:15 AM SB01.10.04
Stimuli Responsive Microscale Architectures—Two Photon Lithography with Shape Memory Polymers Luizetta V. Navrazhnykh, Erika Salzman and Julia R. Greer; California Institute of Technology, United States

Shape memory polymers (SMPs) can respond to heat by generating programmable movement, which can enable multiple technological advances in deployable structures, biomedical device placement, and sensing applications. Many of these technologies could benefit from miniaturization: deployable micro-sized drug delivery vehicles, neural probes and stents could enable minimally invasive access to targets that are currently surgically inaccessible. The shape change requirements of drug delivery have motivated the development of isolated three-dimensional (3D)
SMP structures through molding and emulsion techniques, resulting in relatively simple geometries: spheres, cubes and boomerangs with whose critical dimensions are 1-35 µm\(^1\text{-}^3\). Many other applications require shape transformations to occur in structures with substantially more complex geometries, i.e. a stent or neural probe, which drives the need to synthesize complex architected shape memory structures with sub-micron resolution.

We developed a benzyl methacrylate-based photosensitive resin that polymerizes into programmable 3D shapes with minimal dimensions of 650nm using two photon lithography direct laser wiring (TPL-DLW). We synthesized this resin for shape memory actuation via a glass transition, i.e. the produced structures transform from glassy to rubbery state in response to increased temperature to enable shape programming and recovery. Dynamic nanomechanical analysis (DnMA) was performed through the 22°C to 87°C temperature range on individual TPL-sculpted SMP cylindrical pillars with diameters of 10µm and revealed the initiation of a glass transition at 60°C. We performed shape memory programming by first applying a 400µN load to individual pillars at 77°C and then cooling them to the glassy state at 42°C while maintaining the mechanical load. After load removal, the structures retained their shapes over 7 days at room temperature and recovered to their original dimensions when heated to 87°C within 5 minutes. This shape memory occurred in all 3D micro-architectures that we programmed, including pillars, cubic lattices, and flowers, with a characteristic shape recovery ratio of 86% +/- 4%.

This technique provides a promising pathway to miniaturize shape memory devices and to develop stimuli responsive microscale mechanical metamaterials. Utilizing shape memory polymers as constituent materials could enable miniaturization of existing macroscale shape memory devices, as well as the development of stimuli responsive materials that display amplified and unusual mechanical properties that stem from emergent nano-size effect in materials.


9:30 AM SB01.10.05
**Biodegradable Soft Robotics and Electronics** Florian Hartmann, Melanie Baumgartner, Michael Drack, David Preninger, Daniela Wirzl, Lukas Lehner, Stepan Demchysyn, Robert Gerstmayr and Martin Kaltenbrunner; Johannes Kepler University, Austria

Cephalopods, caterpillars and other soft creatures inspired a broad spectrum of bio-nimetic actuators capable of sensing and adapting to their complex erratic environments. Yet, they are missing a feature of nature’s designs: biodegradability. Soft robots that degrade at the end of their life cycle reduce electronic waste and are paramount for a sustainable future. At the same time, medical (robotic) technologies benefit from biodegradable materials since they are often single-use devices and have to address hygiene requirements. We therefore develop biodegradable hydrogels (biogels) for single-use wearable electronics and transient soft robots that are reversibly stretchable, are able to heal, and are resistant to dehydration. Soft machines and robots – built from biogels with tuned mechanical properties – are designed to be operated in ambient conditions and degrade after use. An equally compostable electronic skin provides our soft actuators tactile feedback and temperature sensing, directly processed with a recyclable on-board computation unit. Besides progressing stand-alone soft machines, our advances in the synthesis of biodegradable hydrogels bring bionic soft robots a step closer to nature.

9:45 AM SB01.10.06
**Origami-Designed Artificial Muscles (O-DAM) Electroactive Soft Robotic Actuators** Madison B. Emmett, Shardul Panwar, Jillian Jakubiec and Michael Rowe; Toyota, United States

Electroactive artificial muscles actuators are unique and lightweight devices that will revolutionize automotive applications by their large strain (120%) and high specific power (160 W/kg), but still require improvement in energy density to be commercially viable. Through design aided by finite element analysis (FEA) and material research, these in-house fabricated artificial muscles were improved by recursive optimization. This led to a new origami-inspired design for a compact, foldable electrode stack that consists of an inner zig-zag structure suspended in dielectric fluid, surrounded by an outer double helix of electrode leads. We refined the electrical insulative material to increase the breakdown voltage per micron of film thickness by more than 30%. This improvement enables actuators to operate at higher voltages, thus increasing the maximum actuator force. Our origami-designed artificial muscles (O-DAM) increase the active electrode surface area which enhances the performance of the device. These soft robotics actuators promise to revolutionize the future of human-machine interactions.
**10:00 AM BREAK**

**10:30 AM *SB01.10.07***  
**Cell-Sized Robots** Marc Miskin¹², Alejandro Cortese², Kyle Dorsey², Paul McEuen² and Itai Cohen²; ¹University of Pennsylvania, United States; ²Cornell University, United States

This talk presents an approach for fabricating cell-sized robots massively in parallel. By building upon existing microelectronics technology, we show how to overcome the key challenges for miniaturizing robotic systems. We use this approach to build and deploy microrobots that walk, are fully untethered, are individually addressable, and wirelessly receive power and instructions through light. They use a new class of voltage controllable, electrochemical actuators made from nanometer thick membranes of platinum. Our fabrication process is completely compatible with silicon microelectronics processing and results in millions of microrobots per four-inch wafer. Combined, these results present a broad platform that can unite mechanical systems, information processing and control to make autonomous robots the size of cells.

**11:00 AM SB01.10.08***  
**Graphene – Carbon Nanofibers Hybrids for Stretchable and Healable Electronics with Application in Soft Robotics** Pietro Cataldi, Dimitrios Papageorgiou, Robert Young, Mark A. Bissett and Ian Kinloch; University of Manchester, United Kingdom

The advancement of stretchable electronics is instrumental for new-generation compliant and wearable devices. High-performing strain sensing technologies have already been realised by exploiting the high gauge factor of graphene-related materials coupled with elastomers [1,2]. Nevertheless, the manufacture of graphene-based electrodes that display outstanding electrical features which remain constant during mechanical deformation, is still challenging [3,4]. On this basis, we fabricated a deformable electrode by simply spray-coating nitrile rubber with graphene-based elastomeric conductive inks. Painting stretchable polymer dispersions carrying graphene nanoplatelets (GnPs) or hybrids of GnPs and carbon nanofibers led to the production of novel electrodes with low sheet resistances (~10 Ω sq⁻¹). The hybrid electrodes that were prepared in this work, exhibited enhanced electrical conductivity at low nanofiller loadings and upgraded performance after repeated bending and folding cycles, compared to the GnP-based electrodes. Both conductors sustained repeated washing cycles and preserved 50% of their initial electrical conductivity at 12% elongation. The strain stability of their electrical properties was enhanced by pre-stretching the rubber substrate before spraying the conductive ink. With this approach, both GnP- and hybrid-based electrodes preserve more than 70% of their initial electrical conductivity at 12% stretch. In this case, at 80% elongation the hybrid material displays electrical conductivity 4 times higher than the GnPs conductor. This is because the GnP-based coating forms cracks already at 30% elongation while the hybrid shows a crack-free morphology even at 100% strain. Repeated stretch-release cycles produced an electro-mechanical deterioration that can be restored simply through a heating treatment. The healing procedure also restored the electromagnetic interference shielding efficiency that was normally reduced after repeated stretch-release cycles. The developed technology finds application as stretchable parallel-plate capacitive touch sensor [4]. Tactile forces as low as 0.03 N and as high as 5 N can be detected by the device bended over curvilinear surfaces or under elongation.

References:

**11:15 AM SB01.10.09***  
**Magnetically-Triggered Ultrafast Soft Robots with Embedded Magnetic Cognition and Feedback Control** Xu Wang, Gilbert Santiago Canon Bermudez, Jürgen Fassbender and Denys Makarov; Helmholtz-Zentrum Dresden-Rossendorf, Germany

In the last years, soft robots have been designed and developed to fulfil demands of better malleability and adaptability to changing environment [1-2]. They can be made of various stimuli responsive materials, which respond to magnetic field [3], light [4], temperature [5], electric fields [6], chemicals [7], pressure [8], etc. In
contrast to other actuation mechanisms, magnetic fields are appealing for numerous application scenarios (e.g. environmental, biological, medical), where their long-range penetration, easy accessibility, and controllability [2, 9, 10] offer exciting advantages. Despite the significant advances in soft magnetic actuators, real-time monitoring and precise feedback control [11-13] remain a challenge for magnetic soft robots.

Here, we present a soft robotic system capable of precisely controlling its deformation degree by means of embedded highly compliant, high-performance magnetic sensors. Our ultrathin (7-100 μm) and ultrafast soft robots that can be actuated by in external magnetic fields pulsating at rates of up to 200 Hz. The high-performance magnetic field sensor is based on the giant magnetoresistive effect and is prepared on ultrathin polymeric foils [14-17] to assure its high mechanical stability combined with mechanical imperceptibility. The latter is crucial to avoid any disturbance of the soft actuator due to the presence of magnetic sensing device. The self-sensing function is realized by monitoring the change of the sensor signal upon approaching it to a magnetic patch applied to the soft robot. This concept of an entirely soft and integrated sensor-actuator system enables contactless self-tracking of motion for magnetic soft robots and can be readily extended to other stimuli-driven soft actuators. These developments will pave the way towards intelligent soft robots, autonomous and reactive soft devices, and new types of human-robot interaction.


**SB01.10.10 Soft Dielectric Materials for Sensing and Energy Harvesting Applications** Philippe Poulin; CNRS University of Bordeaux, France

High permittivity and efficient electromechanical coupling are critical to perform energy storage or conversion between mechanical and electrical energy for various applications of electrostrictive polymers. We report a giant electrostriction effect in liquid crystalline graphene doped elastomers. The materials are formulated by an original phase transfer method which allows the solubilization of graphene oxide monolayers in non-polar solvents. It is shown in particular that liquid crystal transition leads to an increased percolation threshold. Because of their unique liquid crystal structure, the resultant composites show a giant electrostriction coefficient ($M\sim \times 10^{-14}$ m$^2$/V$^2$ at 0.1 Hz) coupled with good reproducibility during cycles at high deformation rates. This work offers a promising pathway to design novel high performance soft dielectric materials for sensing or energy harvesting applications. We will also discuss recent developments concerning dielectric foams and multilayers systems that allow ultra-low pressure sensing via piezo-capacitive effects.
1:30 PM *SB01.11.01
Programmable Composites for Stiffness-Changing and Shape-Shifting Soft Robots
Rebecca Kramer-Bottiglio; Yale University, United States

Soft robots have the potential to adapt their morphology, properties, and behavior to different tasks or changing environments. This adaptive capability is often inspired by biological systems. For instance, humans can transition between forceful and gentle tasks by controlling the stiffness of skeletal joints through co-contraction of antagonistic sets of muscles. In another example, the remarkably dexterous motion achieved by skeleton-free animal parts such as elephant trunks, octopus arms, and human tongues is attributed to selective contraction of layers of uni-directional muscle fibers. During this talk, I will present recent work towards programmable composites that address variable stiffness properties and variable trajectory motions inspired by these capabilities in animals. First, I will present a particulate additive designed to undergo a repeatable solid-liquid phase change within a polymeric matrix and demonstrate its use to achieve unprecedented changes in bulk material stiffness and elasticity. The solid-liquid phase change of Field’s metal inclusions allows a composite to dramatically adjust its mechanical response, as demonstrated in two matrix materials: a thermoset epoxy and a silicone elastomer. Second, I will describe a soft composite lamina comprised of an elastic matrix with uni-directionally embedded inextensible fibers and an adhesive backing, which was inspired by soft body control strategies using fiber-architectures. In contrast to existing soft actuators with fixed deformation trajectories, this composite is simply placed on the surface of an inflatable body to govern its deformation trajectory, can be re-arranged in-situ to change this trajectory, and is created using a high throughput, automated manufacturing process. Finally, I will speculate on how these two composites could be combined to achieve new capabilities in next-generation soft robots.

2:00 PM SB01.11.02
Freeform Fabrication of Dielectric Elastomer Actuators for Soft Robotics Applications
Theo Calais, Elgar Kanhere, Siddharth Kumar, Thileepan Stalin and Pablo Valdivia y Alvarado; Singapore University of Technology and Design, Singapore

The emergence of soft robotics has given rise to new challenges in both the development of functional materials and the design of innovative versatile manufacturing techniques. Additive manufacturing is generally cited when discussing promising versatile fabrication processes. Indeed, a wide range of materials, such as thermoplastic polymers, metals, elastomers, biomaterials, and yarns, can be used for freeform fabrication and integration into complex structures using different additive manufacturing techniques. Among these techniques, the extrusion of materials is the most commonly adopted due to its relative simplicity. However, the choice of materials has been limited to materials exhibiting a phase transition at appropriate temperatures (e.g. thermoplastics) or to thixotropic materials that flow under stress. Hinton et al. reported the use of a support bath, made of a microparticulate hydrogel (Carbopol), allowing the freeform embedding of PDMS in the liquid state before reticulation of the elastomer. After curing, the hydrogel is dissolved by changing the pH, and the 3D-printed object is released. However, Carbopol is highly sensitive to the ionic composition and pH, thus excluding various materials with incompatible chemical compositions. In this contribution, we present the use of a new aqueous-based support bath made of nanoclay suspension for the printing of functional devices. This new support enables the printing of a wider range of materials, including thermosensitive and UV-curable materials, that can be combined into functional devices. We illustrate the advantages of this economical and reusable support by fabricating dielectric elastomer actuators (DEAs) inspired by the Peano-HASEL actuator published by Keplinger’s group. In a facile and fully integrated process, we used the aqueous-based support bath to print advanced muscle-like actuators. First, the dielectric liquid is encapsulated by printing an elastomeric envelope. Electrodes, made of a UV-curable polyacrylamide hydrogel, are successively integrated into the elastomer before curing. Finally, materials are left for curing at room temperature for about 24 h and the support bath is washed away. This facile method allows the assembly of multiple actuators with various complex forms. We present the rheological properties of the support bath, its compatibility with a wide range of materials, and the fabrication and characterization of a DEA device.

Polymeric actuator materials are able to shift their shape reversibly and repetitively in response to an environmental stimulus. Shape-memory polymer actuators function by utilizing the crystallization-induced elongation and melting-induced contraction of an actuation domain, the orientation of which is maintained by a rigid skeleton domain. The interconnection between the domain-forming segment chains is provided by a network of cross-links, which are usually of a covalent nature and therefore preventing the reprocessing of the material after fabrication. The implementation of physical cross-links, based on e.g. hydrogen bonding, thermally stable crystals or ionomers, aims to provide a solution to this problem. In this work, we introduce shape-memory polymer blend actuators, where the cross-links are formed by the physical interaction between a multiblock copolyester and an oligoester. By utilizing this supramolecular interaction, we create a rigid structure, stable up to 200 °C, formed in a one-step process without any post-treatment. The blending approach allows us to tune the actuation performance of the materials simply by adjusting the composition.


Plant-Like Robots are Growing Up

Barbara Mazzolai; Istituto Italiano di Tecnologia, Italy

A rich literature exists in bioinspired robotics and recently the use of soft materials and variable stiffness technologies represents an emerging way to build new classes of robotic systems that are expected to interact more safely with natural unstructured environments and with humans, and that better deal with un-certain and dynamic tasks. Despite the big achievements in this field, robotic technologies are still inadequate to mimic the biological system capabilities in changing their morphology and adapting their body and functionality during their lifetime. Growth is a very interesting feature of living beings that can inspire a generation of robots with new and unpredictable abilities of movement. Noteworthy, plants represent an alternative model of movement in robotics based on growing.

We propose a new generation of self-creating plant-like robots that are able to move adding new material to their bodies while adapting to external conditions. We also focus our research on designing and developing innovative actuation solutions taking inspiration from unexplored biological phenomena, such as osmosis. In this field, we propose the first soft robot mimicking plant tendrils. The robot is able to curl and climb, using the same physical principle determining water transport in plants (osmosis).

The potential impact on society of plant-like self-creating robots could be huge and wide, e.g., in rescue, medical applications, space, or environmental monitoring. Since the design of these robotic solutions is deeply based on a few selected plant features, a new view of robots for biology can be envisaged, with the goal to give insights on the organisms themselves and open new exciting opportunities both in science and engineering.

Bio-Inspired Multifunctional Materials Systems—Plants as Concept Generators for Soft Robotics and Architecture

Thomas Speck; University of Freiburg, Germany

Plant organs and tissues represent from a materials science point of view hierarchically structured multifunctional adaptive materials systems which in addition typically are equipped with various self-x-functions including for example self-repair. This makes them to interesting role models for many potential applications in high-end
technologies including soft robotics, aviation and space flight, automotive, and future-bound green architecture, but also for sports equipment and for prostheses or orthoses. An often overlooked potential of bio-inspiration from plants are complex motions found in the not at all static and immobile plants. These motions can either be actively actuated (by turgor or growth processes) or can be passively actuated (by changes in humidity). In the latter case, motion patterns are imprinted in the structure of fiber-reinforced plant materials systems allowing for one, two and three-phase motions.

Novel methods for quantitative analysis and simulation of the form-structure-function relationship at different hierarchical levels provide fascinating insights into multiscale mechanics and other functions of plant material systems. New production methods such as 3D & 4D-printing, laser sintering and melting, and 3D braiding pultrusion make it possible - similar to biology - to produce from small to large and to functionalize different hierarchical levels. This allows cost-effectively to convert many outstanding properties of biological models into innovative biomimetic products. The examples presented include the development of material systems for a novel type of soft robots that climb like plants and adapt to their environment. The “GrowBot” research groups aim to transfer the skills of climbing plants who can find suitable support structures with their stems in complex, unknown 3D environments. Their different anchoring strategies allow the plants to attach themselves to different surfaces. In a first phase the transfer of stems structure and of the various attachment system (e.g. roots or tendrils) into bio-inspired (self-)adaptive materials systems for soft-robots is intended. A second example are anti-adhesive materials systems and surfaces inspired by plant surfaces on which insects cannot find grip and slip off. These bio-inspired micro-structured surfaces can be embossed on adhesive tapes that can help protect food or medicines from pest insects. Further examples are based on plant movements and aimed for the development of novel bio-inspired motile materials systems, e.g. for architecture. They include one and two phase motion patterns found in pinecone scales (Pinus spp.) and three phase motions occurring in the involucral bracts of the silver thistle (Carlina acaulis). These organs combine sensor, actuator, reactive movable element, and support structure in one materials system, do not consume energy (i.e. move entirely passive), show high level of functional integration and display extraordinary high functional resilience and robustness. Active motion processes served as role model for the biomimetic façade shading system flectofold which was inspired by the trap movement of the waterwheel plant (Aldrovanda vesiculosa), and by the wing folding patterns of the Italian striped bug (Graphosoma italicum). The waterwheel plant together with the Venus flytrap (Dionaea muscipula) served additionally as concept generator for adaptive biomimetic actuator systems reacting to various stimuli and combining two biological snap-trap mechanics. The bio-inspired demonstrators not only incorporate the actuation principles and movement behaviours of the two carnivorous plant species but also show adaptive responses to different environmental triggers. In the presented actuator systems we succeeded to implement several plant movement, actuation and deformation systems into one versatile adaptive technical compliant mechanism.

4:00 PM SB01.11.06

**Light Responsive Magnetic Cilia for Local Actuation**  Meng Li, Taehoon Kim, Giulia Guidetti, Yu Wang and Fiorenzo Omenetto; Tufts University, United States

Cilia are thin hair-like structures that cover living surfaces for motion and swimming. Numerous studies have been focused on replicating the properties of these morphologies by exploring artificial biomimetic cilia for applications in microfluidic propulsion/mixing[1], surface property modification [2], catalytic reactions [3], microrobots/swimmer [4] among many others.

Among multiple possibilities for actuation, magnetic fields present an opportunity given their advantageous properties for quick response and wireless operation. However, localizing the actuation of only a small area of the cilia structure or even individual pillars, presents a challenge since the magnetic field is not localized and does not present defined confining boundaries. In this work, we use light as a wireless and localized stimulus to modulate the magnetic force and control the movement of a small fraction of cilia within a large magnetic cilia array. Chromium dioxide (CrO₂) is a black ferromagnetic material with lower Curie temperature than other commonly used magnetic fillers. By taking advantage of the high absorbance and temperature-sensitive magnetic susceptibility of CrO₂, we have demonstrated a novel mechanism by combining light and magnetic field to actuate soft actuators [5]. In this work, the technique is applied in the microscale to high aspect-ratio arrays of pillars that form magnetically responsive cilia. The cilia are fabricated with CrO₂ and PDMS mixture using silicon molding techniques and present a 9:1 aspect ratio (i.e. 5 μm in diameter and 45 μm in height) over a 1 cm 1 cm patch.

The cilia move in accordance with the external magnetic field and exhibit a deformation-dependent transparency. Because of the periodic pattern of the cilia, the structure also exhibits far-field diffraction patterns from whose
diffraction efficiency can be wirelessly tuned with the magnetic field. With the measurement of the change of
diffraction efficiency, a theoretical estimation of the cilia movement can be made. Furthermore, by taking advantage
of the high light absorption and good photo-thermal properties of CrO$_2$, the cilia array can be locally heated through
light irradiation. Along with its thermal-demagnetization effect, embedding CrO$_2$ in the structure grants the uniform
magnetic cilia array unique properties: cilia can be actuated locally and at the same time globally with untethered
stimuli – light and magnetic fields yielding three distinct modes of controls that can be used to actuate the cilia
array- (a) only with light, (b) only with magnetic field, and (c) with both in combination. By using light only,
accurate actuations can be made even with individual cilia while the rest remains unperturbed; with the sole use of
the magnetic field, all the cilia are synchronized and move together. When using light in concert with the magnetic
field, one can modify the cilia movement locally on top of a global cilia movement. This is hard to achieve with
either only light or magnetic field on a uniform sample without imposing material constraints to generate a material
gradient during synthesis and material fabrication. Among potential applications, this concept cilia composite can
add utility in soft-robotic approaches, or biomimetic microrobots with higher control degree-of-freedom when
combined with other non-reciprocal cilia designs.


4:15 PM SB01.11.07
*Magnetically Addressable Shape-Memory and Stiffening in a Composite Elastomer* Paolo Testa$^{1,2,1}$, Robert
Style$^1$, Jizhai Cui$^{1,2}$, Claire Donnelly$^{1,2}$, Elena Borisova$^2$, Peter Derlet$^2$, Eric Dufresne$^1$ and Laura Heyderman$^{1,2}$;
$^1$ETH Zürich, Switzerland; $^2$Paul Scherrer Institute, Switzerland

With a specific stimulus, shape-memory materials can assume a temporary shape and subsequently recover their
original shape, a capability that renders them relevant for applications in fields such as biomedicine, aerospace and
wearable electronics. Shape-memory in polymers and composites is usually achieved by exploiting a thermal
transition to program a temporary shape and successively recover the original shape. This may be problematic for
heat sensitive environments and when rapid and uniform heating is required. In this work, a soft magnetic shape-
memory composite is produced by encasing liquid droplets of magneto-rheological fluid into a polydimethylsiloxane
matrix. [1] Under the influence of a magnetic field, this material undergoes an exceptional stiffening transition, with
an almost 30-fold increase in shear modulus. Exploiting this transition, fast and fully reversible magnetic shape
memory is demonstrated in three ways, by embossing, by simple shear and by unconstrained three-dimensional
deformation. Using advanced synchrotron X-ray tomography techniques, the internal structure of the material is
revealed, which can be correlated with the composite stiffening and shape-memory mechanism. Based on this
simple emulsion process, this material concept can be extended to different fluids and elastomers, and can be
manufactured with a wide range of methods.


4:30 PM *SB01.11.08
*Programmable Multi-Responsive Soft Actuators Based on Conductive Polymer Composites* Mingming Ma;
University of Science and Technology of China, China

Conductive polymers such as polythiophenes, polyanilines and polypyrroles, have been widely studied for many
potential applications, such as organic photovoltaic cells, organic electronics, supercapacitors and actuators. One
major barrier that restricts their application is their poor mechanical properties. The poor mechanical properties of
conductive polymers are mainly due to their conjugated molecular structure, which makes the main chain very rigid.
Inspired by the structure of bones, where rigid hydroxyapatite crystals and soft collagen fibers cooperate to form
strong and tough materials, we proposed to incorporate ‘soft’ polymers into rigid conductive polymers to improve the
mechanical properties. The soft polymer ingredients are designed to interact with rigid conductive polymers through
supramolecular interactions, such as hydrogen bonds, charge-charge interactions, dynamic covalent bonds and so on.
Upon a large stress, the weak supramolecular interactions between soft polymers and rigid conjugated polymers
would break to help dissipate destructive energy, which would greatly improve the toughness of the materials. Beyond that, the dynamic nature of supramolecular interactions could also enable the conductive polymers stimuli-responsive properties. Herein, we report two examples of utilizing conductive polymers composite to make programmable soft actuators that are responsive to multiple stimuli.

In the first case, PEDOT, PAA-AMPS and PVA are crosslinked by hydrogen bond, electrostatic interaction and coordination to form a supramolecular network. In response to environmental moisture, the resulted composite PPA can not only generate powerful actuation with a contractile stress up to 13 MPa, but also perform programmable helical motions. PPA films with internal stress along the radial directions were prepared by a simple solution casting method. Driven by moisture, rectangular stripes cut from the same PPA film but with different cutting angles can perform direct bending, left-handed or right-handed helical motions, demonstrating the generation of chirality from asymmetric internal stress. By modulating the distribution of internal stress in PPA stripes, their moving direction and speed are readily prescribed. The powerful and programmable PPA stripes can be used to make soft devices, such as moisture-responsive switches and transporters.

In the second example, we report a multi-responsive polymer composite (PHP) based on poly(N-isopropylacrylamide) (PNIPAm), polyaniline (PANI) and polydimethylsiloxane (PDMS). PNIPAm shows reversible volume change in response to the change of temperature, humidity and ionic strength. PANi can efficiently absorb visible light and convert the light energy to heat. PDMS is a transparent and robust elastomer, with a high positive coefficient of thermal expansion. PNIPAm and PANi are incorporated together to give the PNIPAm-PANI hydrogel, which is coated with a PDMS layer to give the PHP bilayer film. Owing to the synergistic effect of these three functional polymers, the PHP bilayer film can perform rapid and reversible transformation between multiple complex shapes (upon global stimuli) and patterns (upon localized stimuli), driven by four types of stimuli: light, heat, humidity and ionic strength. The transformation of PHP is well programmable by using different orders of sequential stimuli. With its powerful actuation and excellent repeatability, the programmable PHP bilayer actuator can be utilized as environment-sensitive devices, such as switches and smart curtains.

By these examples, we wish to demonstrate that the supramolecular approach could be a general method not only improve the mechanical properties of rigid conductive polymers, but also enable good stimuli-responsive properties to conductive polymer composites. These programmable multi-responsive actuators are promising for fabricating smart soft robotics.

SB01.12.01
Efficient Shockwave Energy Dissipation in Self-Healing Dynamic PDMS Rubber Jaejun Lee, Brian Jing, Laura Porath, Nancy R. Sottos and Christopher Evans; University of Illinois, Urbana-Champaign, United States

Polymer networks containing dynamic bonds have received increasing attention over the past decade. Depending on the specific bond, a certain amount of energy is required for the bonds to undergo an exchange process. We hypothesize and demonstrate that dynamic bonds in polydimethylsiloxane (PDMS) networks can be used as an effective mechanism for dissipating energy, in particular from a shockwave. The density of dynamic bonds can be controlled which controls the modulus while the network Tg is unchanged. Using a classical laser induced shockwave technique, superior energy dissipation is observed in a PDMS dynamic rubber compared to the benchmark polyurea. The dynamic PDMS also outperforms covalently crosslinked PDMS and shows a monotonic improvement in dissipation performance with increasing density of dynamic boronic ester bonds. In all cases, the Tg is invariant in the different networks (-125 °C) implying a minimal role of segmental dynamics on dissipation in these specific networks. The dynamic networks can be shocked multiple times with invariant performance due to their self-healing ability, suggesting the mechanism is non-destructive and related to bond exchange rather than
Porous Carbon Fibers from Blends of Polyacrylonitrile and Sacrificial Polymers by Gel Spinning

Jyotsna Ramachandran, Mingxuan Lu, Pedro J. Arias-Monje, Mohammad Hamza Kirmani and Satish Kumar; Georgia Institute of Technology, United States

High strength and high modulus carbon fibers are produced by carbonization of polyacrylonitrile (PAN) precursor fibers processed through continuous gel spinning [1]. The density of solid carbon fibers made from PAN precursors is in the range of 1.73-1.93 g/cm³. Further reduction in the density of the carbon fibers and increase in specific surface area are possible by introducing porosity. Controlling the pore size and distribution in the porous carbon fiber are ways to tailor the mechanical and structural properties. This study explores the conditions to introduce porosity in carbon fibers produced by continuous gel spinning of blends of PAN and sacrificial polymer, with good mechanical properties. Sacrificial polymers including poly(acrylic acid) (PAA), poly(methyl methacrylate) (PMMA), poly(styrene-co-acrylonitrile)(SAN), are chosen based on their incompatibility for blending with the carbon source, PAN. Pore size, distribution and morphology in the carbon fibers are found to be dependent on factors including the choice of sacrificial polymer, blend ratio, solvent and coagulation conditions used for spinning. The influence of the above mentioned processing factors on the mechanical and structural properties of the precursor and resulting carbon fibers are evaluated in this study. This comparative study paves the way for identifying the optimal PAN-sacrificial blend system for production of gel spun porous carbon fibers that are strong, light and possess uniform network of porosity. Porous carbon fibers from gel spun precursor, possessing high mechanical strength could create a spectrum of applications of lightweight, self-sustaining structural reinforcements with energy storage or filtering capabilities. One could envision the body of an aircraft or car made with porous carbon fiber that could store energy and lead to energy efficient smart vehicles.


Scalable and Low-Cost Preparation of Smart Textiles with CuO and ZnO In Situ Synthesis Using Cyclodextrin Functionalized Cotton Fabrics

Wellington M. Rangel, Rozineide A. Boca Santa and Humberto G. Riella; UFSC, Brazil

Smart textiles are a topic of growing interest combining traditional uses of clothes with functional properties. The increasing number of antibiotic-resistant microorganisms and consequently its infection diseases frequency, and the rising of skin cancer incidence are two examples of smart textiles applications. Antimicrobial properties and UV blocking could be developed in fabrics by using metallic oxides. The broad range of metallic oxides properties and their stability are of great interest, and the methods for its grafting in textile substrates are divided into two groups: ex-situ and in-situ.

In this work, cotton weave fabric samples were prior treated with enzymatic desizing, and a scouring/bleaching simultaneous process to develop a high absorbing material. A factorial experiment suggested a treatment procedure with 0.2% NaOH and 2% otw of H₂O₂ for best results of weight loss, whiteness index and water absorption rate (warp and weft directions).

Then, a new two-step method is proposed to prepare in-situ copper oxide (CuO) and zinc oxide (ZnO) inside the cotton fibers in the pre-treated textile fabric, and after grafting with a reactive monochlorotriazine (MCT) beta-cyclodextrin. The grafting of MCT-beta-cyclodextrin in cotton fibers was made by the pad-dry method. Copper and zinc sulfates were used as precursors, to achieve concentrations of copper and zinc ions from 1% to 5% inside the fibers (until copper sulfate solubility limit). These methods are low-cost and scalable into the textile industry finishing process.

The main purpose of this work is to prepare a smart textile with a never reported method. Using water-soluble precursors applied by a pad-dry process. Followed by a reduction wet process to prepare nanostructured metallic oxides inside cotton fibers. The change of solubility from the precursors to the prepared oxides is proposed as a mechanism to improve the washing fastness and durability of the treatment.

The new materials were characterized using FTIR, SEM, EDX, TEM, DRX and thermogravimetric analysis to understand the structural properties and nanostructured particle morphology.
A Water Activated Switch Using a Kirigami-Inspired Robotic Finger

Jihyun Ryu, Mehdi Tahernia, Maedeh Mohammadifar and Seokheun Choi; State University of New York at Binghamton, United States

We created a kirigami-inspired self-folding robotic finger with a microfluidic capillary force in paper. When water was sprayed on hydrophilic regions patterned on paper, the 2-D sheet of the kirigami-based finger was controllably self-folded and popped up to touch/connect two electrodes and switch on LEDs. When the water in the paper evaporated, the popped-up structure was unfolded into its original planar sheet. The fold-to-pop-up structure can be readily fabricated via a double-sided wax printing method, forming a bilayer structure of the hydrophilic regions and the hydrophobic wax, in which these two layers have different swelling and shrinking properties. This novel activation technique enabled a flat paper finger to self-fold with desired angles by controlling hydrophilic/hydrophobic patterns and their lengths. The patterned paper performed folding actuation with water and unfolding behavior with evaporation without being mechanically manipulated by external forces or moments. This proposed technique will be advantageous for many applications (e.g. humidity sensors) inexpensively and autonomously in remote and resource-limited environments. Soft robotics is recently considered as one of the most exciting research topics because of their deformability, flexibility, and adaptability to environmental changes. Soft actuators have been one of the most significant core technologies to enable autonomous capabilities for various soft robotic applications like rehabilitation and training robots, surgical robots, and diagnostic robots. Several promising soft actuators have been proposed including shape memory alloys, electro active polymers, fluidic elastomer actuators, and electro-magnetic actuators, achieving multiple degrees of freedom and delicate object manipulation. However, these techniques are very complicated, expensive, and inefficient in terms of energy use [6]. This work demonstrated an innovative self-actuating method with a microfluidic capillary force in paper through rapid and low-cost prototyping. Through the prescribed planar design of patterned folds and cuts, we demonstrated a kirigami-inspired programmable self-folding of the robotic finger with defined curvatures. The operating principle of the fluidic actuation in paper, which consists of a swelling process with sprayed water and a drying process with evaporation. This actuation used a two-layer configuration with one passive wax layer and one active water layer. The passive layer developed a negligible mechanical move compared to the active layer with the water-based swelling process. This difference in expansion or contraction between the two layers generates localized bending of the paper finger and touches/connects two pre-patterned electrical wires (conductive PEDOT:PSS polymers) for LEDs lighting. The bilayer of the hydrophobic and the hydrophilic regions had drastically different swelling behavior in response to water spraying, spontaneously folding-up and actuating from the 2-D pattern on the paper, turning on the LEDs. The folded structure can also unfold itself with evaporation, turning off the LEDs. Electronics components (i.e. resistors, LEDs and SN75468 IC) were mounted on the paper printed circuit boards. Under repeated swelling and drying processes, the designed paper successfully folded and unfolded without any mechanical degradation. The length of the hydrophobic wax was controllably increased, reducing the ratio of the wax to the hydrophilic part of the paper and controlling the switching duration with water sprayed. The stability and conductivity of the electrical wires were significantly enhanced by the addition of graphene even under repeated folding and unfolding deformations.

Sub-Nanoscale Self-Assembly of Block Copolymers by Local Heating Using Magnetite Nanoparticles

Smriti Sahu, Natalia da Silva Moura, Tochukwu Ofoegbuna and James A. Dorman; Louisiana State University, United States

The growth rate of next generation advanced electronic devices revolves around the formation of high-resolution patterns on semiconductor substrates. Lithography is the most widely used patterning technique that has enabled progressive miniaturization of semiconductor industry and development of the incredibly small technology node of ~7nm till date. However, this top-down scaling comes at a compromise with the cost and tedious processing steps. Hence, the propensity of block copolymers (BCPs) to self-assemble at nanoscales have attracted significant interest of researchers from diverse fields. BCPs assemble into various morphologies viz. spherical, lamellar, cylindrical etc. when treated with heat. Self-assembled periods as small as ~50nm have been reported, that can be used for templating nano-features over macroscopic areas. In addition, BCPs are extremely flexible in terms of their morphology, block size and phase formations, that can be controlled by tuning molecular weights, Flory-Huggins interaction parameter and the degree of polymerization. Although having an interesting property portfolio, the integration of BCP self-assemblies in practical nanoelectronic device designing is still a challenge. The controlled
placement of the nanodomains require conjunction with nano-imprint lithography, that itself is a complex process. Hence, our work focuses on further reducing the period sizes and providing an independent nanoscale control on BCP domains by generating localized heat using RF-actuated magnetic nanoparticles. We have used magnetite (Fe₃O₄) nanoparticles of diameter ranging from ~20-100 nm, that are known to generate heat when placed in an RF magnetic field. The experiment is performed with combinations of various BCPs and different shapes and sizes of nanoparticles to thoroughly study the localized heating effect and its efficiency in transferring this heat to self-assemble the BCP films coated on top. This local heating strategy of the BCPs would prove to be a step towards further scaling down of the device features and meet the needs of current technology node, with using traditional cumbersome lithographic techniques.

SB01.12.08
Silicone-Based Membrane-Interface-Elastomer (MINE) Structures for Ultrasoft Wearable Electronics Kory Schlingman and Tricia B. Carmichael; University of Windsor, Canada

Soft and stretchable electronics present opportunities to change how humans interact with technology, promising improvements to healthcare monitoring, communications, and accessibility. Stretchable devices, particularly those designed to be worn on the human body, require soft, deformable elastomeric substrates that can withstand torsional, shearing, and multiaxial strains in addition to normal wear and tear. The elastomer polydimethylsiloxane (PDMS) has been widely used: It is soft, stretchable, biocompatible, transparent, and easy to mold. Most importantly, PDMS possesses surface properties that make it easy to integrate with functional electronic materials for stretchable device fabrication. Plasma oxidation increases the wettability of the PDMS surface by generating a hydrophilic surface silicate layer, enabling the deposition of functional materials from solution and chemical surface modifications via the chemisorption of organosilanes. Still, bulk PDMS suffers from mediocre tear strength, a relatively high Young’s modulus of 1.5-2.0 MPa and an elongation at break of ~140%. Replacing PDMS with other elastomers that offer useful properties such as high dielectric strength, edge-tear resistance, extreme stretchability, and ultra-low modulus is a challenge due since they often lack the ideal surface chemistry of PDMS necessary for device integration.

Our approach to solving this fundamental problem fuses two different elastomers together to form a layered structure, transforming the elastomeric substrate into a multifunctional element that combines different properties, providing functionality that a single elastomer cannot deliver. We previously demonstrated the idea using an organosilane-based “molecular glue” to adhere a thin membrane of PDMS onto the surface of a transparent butyl rubber substrate. The resulting membrane-interface-elastomer (MINE) structures uniquely combine the surface chemistry of PDMS with the intrinsically low gas permeability of butyl rubber for the fabrication of robust stretchable device. This structure enables functionalization of the PDMS surface with conductive metal films while retaining the gas impermeability of the butyl rubber below. Interestingly, metal films deposited on this structure remain conductive to 85% elongation by generation of microcracks in the surface in a way that is not observed in native PDMS. In this presentation, we describe new MINE structures fabricated by adhering a PDMS membrane to the elastomer Ecoflex. The low Young’s modulus (68 KPa) of Ecoflex is similar to human skin, making this elastomer ideal for skin-mounted electronics. However, we show that the silicone oils and low molecular weight petroleum plasticizers that make Ecoflex so stretchable also cause poor surface chemical properties: Plasma oxidation of Ecoflex results in migration of these low molecular weight additives to the surface, disrupting the formation of a hydrophilic silicate layer. The fabrication of PDMS-Ecoflex MINE structures uses the platinum-catalyzed crosslinking chemistry common to both elastomers, producing a covalently-crosslinked interface between the two elastomers.

We show that together, the layered MINE structure exhibits the best properties of PDMS and Ecoflex: The PDMS membrane surface can be plasma oxidized to increase the wettability and support subsequent chemical modification, whereas the mechanical properties of the Ecoflex elastomer dominate mechanical behaviour of the composite. PDMS-Ecoflex MINE structures demonstrate stretchability to 400% elongation before delamination of the PDMS layer, as well as a Young’s modulus at the surface of 100 KPa, comparable to Ecoflex alone. We also demonstrate the use of pre-strained PDMS-Ecoflex MINE structures to fabricate gold films that retain conductivity to 300% elongation.

SB01.12.09
Active Membranes for Ionotronic Systems Thomas B. Schroeder and Joanna Aizenberg; Harvard University, United States

Final Program 1/13/2020 2404
Ionotronic systems consist of hybrid electrical circuits that use both ions and electrons as charge carriers. The constituent materials of synthetic ionotronic systems, such as hydrogels and dielectric elastomers, often exhibit properties such as softness, transparency, stretchability, and biocompatibility that are desirable in a range of contemporary applications such as soft robotics and biological interfaces. Recent years have seen the development of ionotronic sensors, actuators, and power sources that leverage these characteristics. Such engineered systems often share their function, morphology, or mechanism with excitable biological tissues, which also use ions as charge carriers in aqueous media.

Membranes are a key component of both biological and synthetic ionotronic systems, owing to their utility as selective barriers and capacitors with variable properties. Electrolyte gradients across selectively permeable membranes provide the driving force for the generation of electrical potentials such as the resting potential of a cell membrane, and capacitive membranes between electrolyte-bearing reservoirs can laterally transport electrical signals quickly in the manner of a transmission cable or an axonal segment between nodes of Ranvier in a neuron. In this work, we trigger selective permeabilization events within an insulating membrane in response to various stimuli in order to generate and transmit electrical signals within soft materials in the manner of a dendrite. We compare the voltage decrement along such membranes with that of an electrotonus in excitable tissues. This bioinspired transduction scheme leverages the toolkit of stimuli-responsive chemistry to enable the development of systems that produce fast electrical responses to a range of environmental changes. The ionotronic systems described here may be useful as sensors when interfaced with existing electronics or, when coupled with actuators, may serve as functional elements of autonomous systems exhibiting homeostatic or oscillatory behavior.

References:

SB01.12.10
The DAGS-Chemistry—Droplet Assisted Growth and Shaping of Polymeric Nano- and Microstructures for Design of Multifunctional Materials

Stefan Seeger, Naeem-ul-Hasan Saddiqi, Sandro Olveira, Xiaotian Zhang and Georg Artus; University of Zurich, Switzerland

The synthesis of nano and microstructures are an emerging field in chemistry and materials science. They can be made from a large variety of materials, for example metals, semi-metals, or polymeric substances. Usually, these particles exhibit a comparable simple shape, for some are high temperature is required and for many (except polymers) of them no covalent bonds are formed during formation /1/.

Some years ago, we have presented the synthesis of silicone nano filaments in particular for coatings delivering superhydrophobic, superoleophobic, or superamphiphobic surface properties (fig. 1) /2, 3/. Also, nano- and microstructures different from filaments have been synthesized in a reproducible manner /4/.

Recently, we have shown a reaction mechanism, the Droplet-Assisted Growth and Shaping, explaining how this one-dimensional growth is initiated by a delicate interplay between surface properties, phase equilibrium, and reactivity /5/. Based on this new scheme we are able to synthesize nano- and microparticles of different shapes depending on the reaction conditions.

The DAGS approach is not only applicable to silicon containing polymers. Recently, we could show that DAGS also leads to ermaniumoxide structures and Alumina containing nanostructures.

In this presentation, we will give an overview about this novel synthesis scheme. Applying appropriate reaction conditions allows for the directed growth of nano- and microstructures of complex shape. We believe that this reaction scheme is very promising in chemical synthesis and material science, since it enables us to form complex nano and microstructures from polymeric materials at room temperature in aqueous medium. Beyond this, we also draw the attention on multifunctional materials obtained by strategies implementing DAGS chemistry, e.g. wetting
and electric conductivity features.

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SB01.12.11
One-Touch Embeddable Microneedles for Hair Loss Treatment
Keum-Yong Seong1, Min Jae Kim1, Hye Seon Lee1, Seung Soo Lee2, Hoon-Soo Kim1, Beum-Soo An1 and Seung Yun Yang1; 1Pusan National University, Korea (the Republic of); 2SNvia, Korea (the Republic of)

With increasing clinical needs for painless and easy administration of therapeutic drugs through a transdermal route, microneedles (MNs) have been extensively exploited as a new technique for facilitating percutaneous drug delivery in a minimally invasive manner. However, a precise control of dose and the risk of secondary infection through punctured holes by MNs have remained unsolved. Here we present a bullet-shaped, swellable MNs prepared by crosslinked biopolymers, enabling shear-induced implantation inside skin following distal swelling of MN tips by absorbing body fluids. The embeddable MN patch was prepared by a solvent-casting with a mold and the swellable tip height of MNs to be embedded was controlled by the concentration of polymer solutions. After insertion into skin, swollen MN tips of more than 90% were separated from the patch following simple shear actuation and the embedded swollen MNs in skin offered a superior barrier function by tight sealing of punctured holes. For potential applications, the biodegradable embeddable MN platform were investigated for promoting hair growth by effective intracutaneous delivery of minoxidil (MXD), commonly used for the treatment of androgenetic alopecia. The MXD-loaded MN tips embedded in animal skin tissue achieved a prolonged release of MXD more than 48 h. In pilot animal studies, the MXD-loaded MN group (1 MN patch application/3day) showed better hair growth efficacy compared to topical MXD treatment group (2 topical application/1day).

SB01.12.12
Efficacy of Thin-Film MgO and SiO2 Layers in the Prevention of Mo Diffusion at Elevated Temperature
Kevin Shah and Harry Efthathiadis; SUNY Polytechnic Institute CNSE, United States

Thin-film layers deposited on flexible metal foils can offer functionality for many applications, including semiconductors, detectors, refractory shielding, insulators, catalysts, and optical layers. With favorable manufacturability and low cost of thin-film deposition, various stacks of thin-films can be layered to produce multifunctional properties. For processes that require high temperatures, in this case up to 1450°C, it is imperative to limit the diffusion from the underlying metal foil substrate into the functional top layer thin-film, to reduce impurity contamination that may otherwise degrade the performance of the functional layer(s). Here, thin-films of MgO and SiO2 were deposited onto molybdenum metal foil and heated to 1410°C in a controlled vacuum environment with argon gas. Mo impurity concentration was characterized by dynamic secondary ion mass spectrometry (SIMS) depth profiles, both before and after high temperature annealing, and compared for MgO and SiO2 diffusion barriers. The films were also examined in secondary electron spectroscopy (SEM) to assess the impacts of high temperature annealing on film adhesion and cracking, XRD to measure effects of annealing on film crystal structure, and AFM to determine topography.

SB01.12.13
Identical Material-Based Self-Powered Triboelectric Sensors via Ferroelectric Polarization
Young-Eun Shin, So-Dam Sohn, Huijun Han, Hyung-Joon Shin and Hyunhyub Ko; Ulsan National Institute of Science and Technology, Korea (the Republic of)
In a triboelectric system, two different materials with large difference of polarity in triboelectric series are generally required for the enhanced triboelectric output performance. This requirement of contact pairs restricts the selection of triboelectric materials and the use of identical materials for contact electrification. In addition, it impedes the facile fabrication of triboelectric devices with enhanced performances. Here, we demonstrate a facile approach for the development of triboelectric devices based on an identical material for the contact pair by switching the triboelectric polarity of ferroelectric copolymer, poly (vinylidenefluoride-co-trifluoroethylene) (P(VDF-TrFE)). The aligned dipoles in P(VDF-TrFE) have a great effect on the triboelectric polarity, which relies on the applied bias direction during electrical polarization. This approach does not need any additional chemical functionalization or mechanical modification to fabricate identical material-based triboelectric devices with remarkably enhanced output performances. The inversely-polarized P(VDF-TrFE) device exhibits ~106 times higher output currents and ~126 times higher output voltages than those of non-polarized P(VDF-TrFE) devices. Moreover, the high sensitivity of our triboelectric device in the subtle pressure range enables the simultaneous monitoring of weak pulse pressure of the carotid artery. This work demonstrates a facile fabrication to realize identical material-based triboelectric device with outstanding output performances via dipole-alignment of ferroelectric polymers. Our proposed strategy provides the capability to tune the triboelectric polarity of identical material without additional complicated process, paving the way for the development of high-performance triboelectric devices.

**SB01.12.14**
Dynamic Wavelength Tunable Functions of Near Infrared Photoluminescent Single-Walled Carbon Nanotubes by Local Molecular Functionalization

**Tomohiro Shiraki, Yasuto Nakagawa, Naotoshi Nakashima and Tsuyohiko Fujigaya; Kyushu University, Japan**

Single-walled carbon nanotubes (SWNTs) with semiconducting features show near infrared (NIR) photoluminescence (PL). Recently, locally functionalized SWNTs (lf-SWNTs) that are synthesized by local chemical functionalization of the tube structures have been developed as new types of NIR PL nanomaterials.[1-8] Therein, by the chemical reactions, new emissive sites that have different electronic structures from non-modified SWNTs are created on the tubes. As a result, the lf-SWNTs emit red-shifted PL with high efficiency (E$_{11}$*) compared to original PL (E$_{11}$) of the non-modified SWNTs. Furthermore, the E$_{11}$* PL of lf-SWNTs is found to show different PL wavelengths depending on the modified molecule structures.[1-5] Thus, this feature would be promising to create multifunctional NIR PL nanomaterials based on molecular functionalities of the modified molecules.

Here we report dynamic E$_{11}$* PL wavelength tuning techniques by covalent modification of functional molecules on the local functionalized moieties of lf-SWNTs. In this technique, driving forces for the wavelength shifts are designed based on molecular functions including molecular recognition[6,7] and dynamic covalent bond formation[8]. It allows us to control lf-SWNTs that response to various external stimuli with NIR PL shifting features.

Firstly, phenylboronic acid (PB), which binds sugar molecules selectively, so-called “sugar recognition”, was functionalized to SWNTs through diazonium chemistry to synthesize phenylboronic acid-modified lf-SWNTs (lf-SWNTs-PB).[6] The E$_{11}$* PL of lf-SWNTs-PB appeared at 1138 nm. When D-fructose was added to the aqueous solution of lf-SWNTs-PB, the E$_{11}$* peak was blue-shifted to 1124 nm according to the increase in the D-fructose concentration. This shifting was induced by electronic property changes of the functionalized PB moiety through boronate ester formation with D-fructose. As another molecular recognition motif, azacrown ether groups were functionalized to lf-SWNTs (lf-SWNTs-CR).[7] The lf-SWNTs-CR showed spectral red-shifts of E$_{11}$* PL by silver ion inclusion and protonation of amine part (pH variation), and, interestingly, the shifted wavelengths were different between these two systems. In the dynamic covalent bonding system, arylaldehyde groups were introduced in lf-SWNTs (lf-SWNTs-CHO).[8] When aniline derivatives having different substituents were mixed with the lf-SWNTs-CHO, wavelength shifts of the E$_{11}$* PL occurred, which provided different wavelengths depending on the chemical structures of the bound aniline derivatives. This wavelength shifts were induced by the imine bond formation (condensation reactions between amine and aldehyde groups). Moreover, additional chemical reactions including dissociation and exchange reactions of the bound aniline derivatives, and the Kabachnik-Fields reaction realized further wavelength changes in the E$_{11}$* PL. Thus, the present approach using imine chemistry at the functionalized sites achieves multistep PL modulation.

Therefore, molecular design of the local functionalized sites produces multifunctionalities in lf-SWNTs that response to various stimuli and environmental changes, which would be applicable to biological sensing and environmental monitoring by using their NIR PL features.

SB01.12.16
Fully Printed Metal-Free and Complex-Shaped Sensors via Direct Functional Microparticle Writing Leonard Siebert1, Maik-Ivo Terasa1, Mattia Mirabelli2, Maik Tienken1, Philip Schäfer1, Sören Kaps1, Oleg Lupan1,2 and Rainer Adelung1; 1Institute for Materials Science – Functional Nanomaterials, Germany; 2Department of Microelectronics and Biomedical Engineering, Moldova (the Republic of)

3D-printing has become one of the most fascinating subjects of research during the last decades because of the sheer amount of different design strategies and the implied manufacturing philosophies it has enabled.[1] Crucial to the impact of additive manufacturing is the possibility to freely design devices and structures without the necessity for highly complex technologies by combining standard materials science with standard mechanical engineering on varying levels of technological profoundness. Especially the fields of biomedical engineering and printed electronics profit from the simplicity of 3D-printing, allowing for sophisticated material design and advanced circuitry.[2] Additionally, microparticles with complex shapes and integrated functionalities have been used in a broad range of applications since their geometry cannot be easily reproduced with clean room technology to implement structural benefits in a microscopic range.[3] Here, combining both of these aspect, we demonstrate multiple, microparticle based architectures for both biomedical and electronic applications. The benefit of using microparticles is the multitude of well grounded, standard techniques for their usage and the possibility to elevate their functionalities by integrating them into 3D structures. Custom geometries of metal-free sensors for different signals have been fabricated, just using metal oxide microparticles from materials science in a common Direct Ink Writing (DIW) approach. As an example, a heterojunction net of CuO/Cu2O/Cu has been grown by simple step integration of copper microparticles on glass substrates and additional rapid thermal annealing, exhibiting high sensitivity for acetone, enabling its use as a sensor for breath analysis. Another example is the usage of complex-shaped single crystalline ZnO tetrapodal microparticles, which are highly sensitive towards UV light and are used as UV-sensors without the necessity for clean room technology. For the field of biomedical engineering, ZnO-biopolymer composite printed constructs show antibacterial properties for potential applications as functional wound dressing. These findings only hint at the much larger potential of the DIW of microparticles into functional devices which will enable more simple fabrication techniques for future challenges.


SB01.12.17
Self-Limiting Electrospray Deposition for Postprocessing of 4D Printing Lin Lei, Dylan Kovacevich, Christianna Kuznetsova, Daehoon Han, Howon Lee and Jonathan P. Singer; Rutgers University, United States

Electrospray deposition is a spray coating process that utilizes a high voltage to atomize a flowing solution into charged microdroplets. These self-repulsive droplets evaporate as they travel to a target grounded substrate, depositing the solution solids. We have classified a regime of self-limiting electrospray deposition (SLED) that enables the coating of surfaces hidden from the spray needle’s line-of-sight. In this regime, the deposited solids are insulative and have minimum mobility at the substrate, causing charge to gradually accumulate. Future generations of droplets are redirected to uncoated areas, yielding more uniform coverage of the entire substrate. In this study, we used stimuli-responsive hydrogel 3D structures fabricated through projection micro-stereolithography as our substrates to demonstrate the effectiveness of SLED for the coating of 4D-printed structures. We first examined model metallic geometries to classify the limits of the SLED phenomenon, including gaps and rapid bends. These revealed that SLED could readily enter gaps of less than 100 µm and undergo bends at a rate of an estimated 500 rad/s. We then coated 3D printed octet-truss lattices. The lattices had edge lengths of ~1 cm and struts of ~250 µm.
diameters and were coated with hierarchically-structured styrene-butadiene-styrene block copolymer-toughened polystyrene. By monitoring coated and uncoated lattices were enclosed in a camera-monitored humidity chamber, the swelling-driven dimensional changes in lattice over time were recorded. The polymeric coating acted as both a moisture barrier and mechanical coating, both reducing the extent and regulating the rate of hydrogel swelling. This represents a means of decoupling the surface and bulk properties of 4D-printed materials to provide for surface-gated control of the final structures.

SB01.12.18
Morphological and Mechanical Properties of Polymer Composites Created by Self-Limiting Electrospray Deposition Lin Lei, Luc Bontoux, Christiana Kuznetsova, Dylan Kovacevich, Max Tenorio, Assimina Pelegri and Jonathan P. Singer; Rutgers University, United States

The electrospray process utilizes the balance of electrostatic forces and surface tension within a charged spray to produce charged microdroplets with a narrow dispersion in size. By adding dilute solids to the spray, electrospray deposition can be employed for the manufacturing of nano- to micro-scale coatings. We have identified a regime of the spray of insulating materials onto conductive substrates where a limiting thickness emerges where the accumulation of charge that repels further spray. Self-limiting electrospray deposition (SLED) can uniformly cover complex multiscale structures with a variety of morphologies, including nanoshells and nanowires. Here, we investigate the application of polymer blends to modify the morphology and, through nanoindentation, the mechanical properties of the spray films for different applications. On the morphological side, blending immiscible non-self-limiting materials can alter the fill and porosity of the shell structures or the length and alignment of wire structures by tuning the droplet phase evolution. In mechanical properties, we demonstrated that the addition of a miscible curing agent to an epoxy resin can maintain the hierarchical spray structure to result in a tougher and stiffer coating for protective barriers. Further, the porosity of these films can be tuned spatially or programmed into the spray composition. In contrast, to make films that are more flexible for compliant surfaces, blends of plastic homopolymers and elastomeric block copolymers were sprayed. The net result of elastomeric blending was a coating that could enhance adhesion and sustain ~17% strain in the underlying structure.

SB01.12.19
Manufacturing Biohybrid Textiles through a Robust Fiber Based Cell-Free Expression System Rachel S. Smith, Miana Smith, Susan Williams and Neri Oxman; MIT, United States

The emergent field of biohybrid fiber systems has derived several techniques to entrap, encapsulate, or adsorb living or bioactive agents within woven and non-woven constructs, to simultaneously benefit the survivability of the biological agent and augment the functionality of the fiber. However, these techniques remain largely incompatible with existing textile manufacturing technology and lack the robustness of commercial woven fabrics. The incorporation of bacteria-derived [SS1] biosynthesis systems into fibers that can survive industrial spinning, weaving, or knitting processes is a method of producing biocomposite textiles across scales, and further, for using textile patterning methodologies for fiber templating and distribution.

To achieve the necessary preservation of biological activity within industrially-workable threads, we experiment with techniques such as lyophilization and the use of cell-free expression systems. The efficacy of a PURExpress cell-free system soaked into commonly used natural and artificial fibers is first demonstrated using the expression of Green and Red Fluorescent Protein (GFP, RFP). The cell-free system is then preserved on the fibers via lyophilization and the output is compared to that of the fresh system using the difference in the expression of GFP/RFP as determined by the intensity of fluorescence. The expression of more functional genes, such as the one which produces serratiopeptidase, a proteolytic enzyme that dissolves silk and other proteins, is then tested using the cell-free fiber system.

To assess their industrial usability biohybrid threads are used in established textile manufacturing techniques, and monitored for robustness and for the controlled spatial distribution or patterning of biofunctional properties into woven or knit textile structures. We hypothesize that when preserved onto silk fibers, the expression of serratiopeptidase would create a subtractive process by which the biosynthesized outputs of a silk textile would actively alter the geometry of the textile. We envision future textiles with a controlled patterning of biosynthetic compounds via biohybrid threads could have applications ranging from autonomous modifications in fabric structure, to wound care and the promotion of the migration of other pharmaceutical agents to areas of interest.
SB01.12.20
Interfacial and Mechanical Properties of Different Organosilane-Treated Ceramic/Photopolymer Resins for SLA 3D Printing Se Yeon Song1,2, Jung Woo Lee2 and Ji Sun Yun1; 1Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of); 2Pusan National University, Korea (the Republic of)

Silane coupling agents (SCAs) with different organic functional groups were used to investigate the interface and mechanical properties of highly dispersed ceramic resins for stereolithography (SLA) 3D printing. The different organic functional groups of the SCAs used in this study were vinyl group, acryloxy, methacryloxy, and acrylamide groups. The Al2O3 ceramic particles were uniformly coated by various SCAs through a hydrolysis and condensation reaction, and then highly dispersed in commercial photopolymers based on interpenetrating networks. The uniformly coated surface and coating thickness were observed by FE-TEM, and similar coating properties were observed in all SCAs. The dispersion stability and interface properties of Al2O3/photopolymer composite resins with different SCAs were investigated by Turbiscan, relaxation NMR, and Rheolaser Master, and the resins with Al2O3 coated by the acrylamide group showed the best dispersion stability and viscoelastic behavior. The best dispersion stability and strong viscoelastic behavior of the resins contributed to improve the mechanical properties of the 3D-printed objects.

SB01.12.21
Versatile Soft Robotic Web Inspired by Spiderweb Won Jun Song, Younghoon Lee and Jeong-Yun Sun; Seoul National University, Korea (the Republic of)

Nature is the best pioneer of science based on their optimized functions for thousands of years. Spiders and spider webs, among them, have been tremendously attracted for prey capturability optimized by sensing of prey approaching, vibration cleaning the surface from droplets. Although spider web have provided various inspiration, simultaneous mimicry of the functions in a simple structure meets challenges due to needs of complex mechanism and proper materials. Here, we explored a multi-functional ionic spider web, which is electrostatically capturable, cleanable and self-powered sensible dielectric elastomer actuators optimized by behavioral inspiration of spider web. To combine the multi-functions resulting in increase of capturability, ionic spider web was driven by a stretchable and translucent electroactive structure made of dielectric elastomer and ionically conductive organogel. The electric field generated by the potential difference between a pair of ionic spider tube induces polarization in an adjacent target to realize electrostatic adhesion. Self-powered sensing by electrostatic induction from a naturally electrificated target to ion in the tube realized switchability to ionic spider web to avoid from undesirable contamination on the surface, resulting in increase of capturability. Furthermore, electrostatic vibration of ionic spider web driven by alternating electrical attraction and repulsion forces readily cleaned droplet on ionic web, leads increasing capturability. Plasma and (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane treatment on dielectric elastomer readily increased (sensibility) and cleanability and it prevented the evaporation of organogel, which leads increase of durability of ionic spider web. We demonstrated the integrated approaches with autonomous ionic spider web sensing approaching targets and robustly capturing various materials after cleaning the surface. Ionic spider web lays the foundation for multi-functional robots inspired by nature.

SB01.12.22
Adaptive Self-Strengthening and Actuation via Multiphasic Composite Materials Nicholas Vishnosky and Rachel Steinhardt; Syracuse University, United States

Materials that respond to stimuli by moving and/or changing modulus are needed for emerging applications in fields ranging from soft robotics to medicine. To fill this need, we create composite materials consisting of regions of heterogeneous physical phases: liquid or gas vesicles encapsulated in a solid or complex fluid matrix. Through incorporation of energy transferring nanoparticles and coatings at the interphase of these phases, we are able to actuate microscale phase transitions that result in a macroscale change in morphology/modulus of the material. This property may lead to tetherlessly actuated robotics, and new medical devices.

SB01.12.23
Mechanics of a Three-Dimensional Spider Web Isabelle Su1, Zhao Qin1, Tomás Saraceno2, Roland Mühlethaler2, Ally Bishop2, Evan Ziporyn1 and Markus J. Buehler1; 1Massachusetts Institute of Technology, United States; 2Studio Tomás Saraceno, Germany
Spiders are abundant in most ecosystems in nature, making up more than 47,000 species. This ecological success is due to the web architectures and the exceptional mechanical properties of spider silk. Silk’s combination of strength, elasticity, toughness, and robustness originates from its hierarchical structure and has been a template for high-performance material design. In particular, spiders have optimized and adapted their web architecture to survive in their environment.

The most studied and familiar spider web is the 2D orb web which is composed of radial and spiral threads. However, 3D webs, such as sheet, funnel, or cob webs, are more common in nature. In contrast to 2D webs, where the spider is vulnerable to attacks, 3D webs surround the spider and offer a defensive advantage by warning the spider of intruders, blocking its predators and entangling prey.

Here, we investigate the mechanical properties of a Cyrtophora citricola 3D web, the architecture of which has been digitally modeled with micron-scale details from images of full-scale laboratory experiments (Su, Qin, Saraceno, Krell, Mühlethaler, Bisshop, Buehler, Royal Society Interface, 2018). Extending this work, we use a coarse-grained bead-spring model based on the 3D spider web network model and silk fiber properties to study the response of a realistic web structure to mechanical loads and the interplay between material and performance.

Understanding the roles of structure, material, and web spinning process, in the functionality and evolutionary fitness of spider webs could lead to innovative 3D spider web-inspired structures such as high performance lightweight long-span structures or fiber reinforced composite materials.

SB01.12.24
Miniaturized Flexible Capacitive Shear Force Sensor Using Ion Gel Wonjeong Suh and Unyong Jeong; Pohang University of Science and Technology, Korea (the Republic of)

A soft shear force tactile sensor is essential for sensitive stretchable e-skin as well as pressure sensor. Especially, small size shear sensor has large potential of development in surgical robots which need delicate movement and grasping. However, capacitive type shear sensor has limit to miniaturization because the signal is weak in pF when it gets smaller. Here, we enable miniaturization of capacitive shear sensor using ion gel. Ion gel constructs electrical double layer (EDL) so that the sensor can make big signal at a small size. It provides nF scale capacitance which is about 10^4 ~ 10^5 times bigger than general polymer dielectrics. Also, our sensor has simple structure composed of well-shaped wall and pillar in the center. The ion gel located between wall and pillar make it possible to detect 4 different directions with high accuracy according to movement of pillar. Moreover, the sensor itself is made of conductive Ag ink and polydimethylsiloxane (PDMS) so it has high mechanical flexibility and stability. The single sensor has 5 x 5 mm^2 area and 2 mm height pillar and produces up to 100 nF. Finally, we demonstrate practical application of shear force sensing with 3 x 3 array in 27 x 27 mm^2. This flexible tactile sensor shows great promise for delicate robot finger which needs careful touch and sensitivity.

SB01.12.25
Sinking-Floating Control on a Hydrophilic-Hydrophobic Pattern Inspired by a Surface of Dixidae Larvae Naoya Tagata and Daisuke Ishii; Nagoya Institute of Technology, Japan

Dixa Longistyla is a family of flies and the larvae can float for a long time on water. A hydrophobic-hydrophilic pattern presents on the surface of larvae’s abdomen. The hydrophobic region is ring-shaped and the inside is hydrophilic. When the larvae float on water, a water droplet is held inside of the hydrophobic ring. Due to the drop, it is considered that the larvae sink down to water easily and need lower energy than the completely hydrophobic surface. Moreover, a bubble ring is formed on the hydrophobic region in water and the maggots can float up more easily than completely hydrophilic objects. Therefore, they have a both hydrophobic and hydrophilic region in terms of floating and sinking to water. Applying the pattern, we can control sinking and floating properties. The purpose of this study was to mimic the hydrophilic-hydrophobic pattern and to examine the effect of the pattern on water sinkability.

Sample were fabricated by oxygen plasma treatment of hydrophobic sheets through ring-shaped masks. The sheet surface under the mask was not oxidized, so that a hydrophobic region was remained after the plasma treatment. The sinking position, which was related with interaction on the hydrophilic-hydrophobic pattern, was measured using by surface tension balance. If the sinking position is shallow, it seems that the sample easily sinks into water. Two
different shapes of mask, annular and disk, were prepared and the samples were fabricated by using of each mask. Moreover, in the case of measurements of the annular sample, volume of water held inside the hydrophobic ring was changed systematically. There was almost no difference in sinkability between ring pattern without any water droplet inside the ring and disc pattern. On the other hand, the sinkability of the sample improved as volume of water inside the ring increased. The experimental results indicated that volume of water inside the ring affects the sinkability. The reason why the ring-shaped pattern and the disk-shaped pattern did not have a difference in the sinkability is considered that water was not sufficiently held inside the ring-shaped pattern.

**SB01.12.26**

**Formulation of Filled Direct Ink Write Resins for Shockwave Applications** Samantha J. Talley¹, Brittany Branch², Cynthia F. Welch¹ and Kwan-Soo Lee¹; ¹Los Alamos National Laboratory, United States; ²Sandia National Laboratories, United States

Polymer foams are widely utilized in the aerospace and defense industries for applications including structural support, vibrational dampening, and shockwave mitigation. Through a materials-by-design approach, the Direct Ink Write (DIW) additive manufacturing (AM) method is an attractive approach for the design and fabrication of porous structures capable of achieving controlled mechanical response of the underlying deformation mechanisms. Two geometries of porous, periodic AM pads were printed using new DIW resin formulations containing up to 25 wt.% of functional filler (TiO₂, Al₂O₃, or graphite). All AM pads were characterized using chemical (FTIR, MS, NMR), thermal (TGA, DSC), and mechanical techniques (DMA, compression). Dynamic compression experiments coupled with time-resolved X-ray imaging were performed to obtain insights into the role of filler interactions in the *in situ* evolution of shockwave coupling in these functional, periodic porous polymers.

**SB01.12.27**

**Noise Control and Vibration Energy Harvesting with Soft Acoustic Blackhole Based on Hyperuniform Disorder Scatters** Hanchuan Tang, Zhuoqun Hao and Jianfeng Zang; Huazhong University of Science and Technology, China

Living creatures and artificial objects like engines that possess dynamically varying and highly unconventional geometries are full of elastic waves. Such elastic energy with different frequencies could be power source of devices while few work demonstrates the elastic energy utilization on curved surfaces. The difficulties include that elastic waves in human beings and artificial objects are dispersed and relatively weak at local parts. Meanwhile, unconventional geometries and multiple frequencies of elastic waves require soft materials and more complicated structures of devices.

The acoustic blackhole (ABH), generally made of wedge structures, could damp the induced elastic wave velocity into zero, due to its power-law profile change in the thickness. ABHs have great potential for mitigating vibrations and noise. However, the fabrication limitation of the wedge may greatly affect the ABH performance. Besides, the rigid irregular structure of traditional ABHs reduces the strength of the whole device and limit their application in complex scenarios.

Here, we demonstrated an ABH mode with soft hyperuniform disordered structure that dramatically concentrate elastic wave energy and eliminate reflections on uneven surface. Hyperuniform disordered structures exhibit acoustic bandgap, and its randomness showing potentials to design novel devices. While this topic draw increasing attentions, application based on which is few. We arranged hyperuniform pattern with a smooth power-law profile edge in the soft matrix to realize the hyperuniform disorder acoustic blackhole (HABH). The numerical simulation shows good suppression of reflection and concentration of energy at the tip. The design method of HABH and double layer HABH is discussed. The HABH doesn’t require delicate process build while shows convincing ABH effect. The soft matrix of HABH makes it possible to attach on uneven surface. Our work provides a prominent solution to realize energy harvesting on human beings and noise reduction in automotive or architecture with lightweight, strong compatibility and low cost. Besides, the combination of hyperuniform structure and traditional configurations like ABH bring the unprecedented characteristic of devices, which can be translated to photonic crystals or other wave controlling systems.

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SB01.12.28
Real-time Characterization of the Degradation and Chemi-Crystallization Phenomenon in Natural-Based
Polymers at the Air-Water Interface—The Story of Bacterial Polyesters

Natalia Tarazona1, Rainhard
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of Potsdam, Germany

Interest in natural-based degradable polymers has placed bacterial polyhydroxyalkanoates (PHAs) under the
spotlight. PHAs are linear and isotactic polyesters composed of (R)-hydroxyalkanoic acid monomers. The
knowledge of degradation and crystallization mechanisms of PHAs, which leads to shifts in their mechanical
properties, is of critical importance for application development.

Naturally, biodegradation of a material starts at its surface. Using the Langmuir monolayer degradation technique,
combined with in situ Brewster Angle Microscopy (BAM), several aspects of the degradation of polymer materials
were directly observable. Since degradable polymer films at the air-water interface form water-soluble degradation
products, the concentration of chain segments at the surface decreases during degradation leading to a decline of the
surface pressure1.

Thin polymer films of poly(3-(R)-hydroxybutyrate) (PHB) and poly[(3-(R)-hydroxyoctanoate)-co-(3-(R-
hydroxyhexanoate)] (PHOHHx) were exposed to a degrading medium consisting of i) phosphate-buffered saline
(PBS, pH 7.4), ii) KOH (pH 10-13) and iii) KOH plus a PHA depolymerase enzyme (pH 10). In Langmuir layers,
both polymers were highly stable in PBS and up to pH 12, demonstrating that the hydrolysis of PHAs ester bonds is
only catalyzed at very highly alkaline conditions. At low packing densities of the films, the molecular degradation
curves at pH >12 suggested a chain-end scission mechanism with an almost linear decrease of the surface pressure.
This process did not induce a drastic shift in the crystallization state and therefore in the mechanical properties of the
polymers, as observed by BAM and interfacial rheology measurements.

PHB with high initial degree of crystallinity (Xc = 55–65%), showed slightly faster degradation curves when
compared to PHOHHx. Most likely, the amorphous polymer chains entrapped by the PHB spherulites (interlamellae
amorphous regions) degraded faster than free amorphous polymer chains, as established in semi-crystalline poly(L-
lactide)2.

The degradation of PHAs by a specific PHA depolymerase showed a typical and fast random scission mechanism
for both polymers. However, the PHA-degrading enzyme was more efficient on PHOHHx with longer side chain
and lower degree of crystallinity. Interestingly, the degradation of PHB followed a two-steps mechanism that could
be observable at the air-water interface. In the first stage, a decrease in the mechanical strength was observed, which
was followed by a second step that agrees with a secondary crystallization process or chemi-crystallization.

We present the Langmuir degradation technique as a potential standard to characterize and compare several
functionalities of polymers of different origin, structure and composition.

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SB01.12.29
Understanding the Effect of Solution Spinning Processing Parameters on the Structure and Properties of
Carbon Nanotube Fiber

Lauren W. Taylor, Oliver S. Dewey and Matteo Pasquali; Rice University, United States

Since their discovery in 1991, carbon nanotubes (CNTs) have been of great interest for multifunctional materials due
to their outstanding electrical, thermal, and mechanical properties. Unfortunately, it has been challenging to translate
the excellent properties of single CNT molecules into macroscale materials. A promising technique for obtaining
high performance fiber materials is wet-spinning solutions of CNTs in chlorosulfonic acid (CSA). CSA and other superacids overcome the strong van der Waals forces between the CNTs by protonating the sidewalls of the CNTs to individualize the molecules to form a true solution. The CNTs in solution follow classical soft matter physics behavior; the solutions are isotropic at low concentration and liquid crystalline at sufficiently high concentration. The transition between these phases depends on the aspect ratio (the ratio of the length of the CNT to the diameter). Here, we study how the rheology and phase behavior of the solutions affect the spinning process and the electrical and mechanical properties of the resulting fibers. We have examined this experimentally by varying key processing parameters such as solution extrusion rate, CNT solution concentration, fiber draw ratio, and choice of coagulant. We find that spinning at lower concentrations yields significant improvement in tensile strength but no change in conductivity. Preliminary tensile testing data demonstrates that fibers spun from lower concentration solutions have a higher elongation at break. This suggests that the improvement in tensile strength can be attributed to the formation of larger bundles of CNTs within the fiber. Continued research of the fluid behavior will enable us to create the next generation materials for sensors, electrodes and wiring.

SB01.12.30
A Soft Ultra-Flexible Tactile Sensor for Robotic and Prosthetic Applications Andrei Nakagawa Silva1,2, Deepesh Kumar2, Tomoyuki Yokota3, Takao Someya3, Nitish Thakor2,4 and Alcimar Soares1; 1Universidade Federal de Uberlândia, Brazil; 2National University of Singapore, Singapore; 3The University of Tokyo, Japan; 4Johns Hopkins University, United States

SOP: In this paper, we present the development of a novel ultra-flexible tactile sensor that makes use of such organic photo diodes (OPDs) embedded into a soft skin construct, measuring force based on its deformation. Our goal is to integrate this sensor with robotic and prosthetic fingers for improved sensing and control. Developing an electronic skin (e-skin) that is highly flexible, durable and scalable is a highly desired goal. We model the e-skin sensor design and application after human hand and skin. Our skin provides a sophisticated sense of touch, contact-based information, as well as perception of texture, shape, etc. Beneath the skin, mechanoreceptors act as transducers, generating precisely timed spikes that are informative of contact forces and surface properties such as textures, edges and curvatures. A wide variety of sensors based on piezoresistive, capacitive and optical principles have been proposed with varying degrees of resolution, sensitivity and sizes. However, the development of flexible sensors that can be attached to robotic fingers and e-skins is still an unresolved issue. OPDs, especially designed on flexible substrates, constitute a new technology for applications to robotic and prosthetic hands.

Methods: The sensor is composed of 3 layers: The top one is formed by a matrix of 3x2 light-emitting diodes (LEDs), the middle layer is made of a soft elastomeric material (Ecoflex) that serves as the transduction layer and the bottom layer is formed by an ultra-flexible, ultrathin OPD 3x2 array. The transduction layer was painted with black pigment and has six cavities through which each LED target one OPD directly. Deformation of the soft layer induces changes in the light received by the OPDs and is informative of the applied forces over the skin. We performed a compression test to characterize the output voltage of the OPDs. From this relationship, we built a neuron model that mimics the activity of Merkel Cells (SA-I) akin to physiological data.

Results: The compression test demonstrated that it was possible to detect deformations of at least 0.5 mm. The relationship between compression and voltage was mostly linear and the sensitivity can be improved by making use of a programmable amplifier. The firing rate of SA-I afferents is associated with indentation depth according to a sigmoidal function. We applied such function to map indentation to a proper input to the SA-I neuron model. Our results demonstrated that it was possible to obtain firing rates that were similar to the physiological behavior of SA-I, where larger indentation amplitudes led to higher firing rate.

Conclusion: The proposed ultra-flexible tactile sensor paves way for improved e-skin design in robotics and prosthetics, especially for soft robotics where flexibility is a must. This sensor can also be used for improving the tactile perception of textures and shapes, besides dexterity in manipulation. The conversion of the signals into spiking activity of SA-I afferents that are more faithful their biological counterpart is also promising for delivering more naturalistic touch feedback from prosthetic hands to amputees via nerve stimulation.

SB01.12.31
Soft Robotic Steerable Microcatheter for the Treatment of Cerebral Aneurysms Gopesh C. Tilvawala1, Jessica Wen1, David Santiago-Dieppa1, Bernard Yan2, Alexander Norbash1, Alexander Khalesi3 and James Friend1; 1University of California San Diego, United States; 2Royal Melbourne Hospital, Australia

Nearly one-fourth of neuro interventions fail to treat cerebral aneurysms, imposing a significant sociological and
economic burden. Treatment is beneficial but was limited to surgical clipping until the advent and broad clinical adoption of endovascular coiling [1, 2], now a preferred, relatively inexpensive, and statistically more successful option [3]. It involves deploying platinum detachable coils into the aneurysm through a microcatheter; the coils aid formation of blood clots within the aneurysm, excluding it from circulation. However, the current microcatheters lack the much-needed steerability for precise tip positioning. Magnetic [4], piezoelectric ultrasonic [5], and wire-pulley [6] devices have been proposed in the past, but have not found broad acceptance. The existing panoply of passive guidewires and catheters, cannot be steered in vivo resulting in treatment failure, principally due to the difficulty in navigating tortuous vasculature, accessing, and optimally placing the microcatheter tip in the aneurysm dome for coil deployment.

Balloon catheters, which represent a crude form of soft-robotics, are broadly accepted in clinical use. However, fabrication of soft-robotic devices at length scales between 50 micrometers and 1 mm – the critical length scale which endovascular neurosurgical catheters demand – remains a challenge because both photolithography and 3D printing are inadequate. We combine innovative micro-fabrication techniques with intuitively engineering hyperelastic polymers, and direct hydraulic microactuation to provide steerable catheters for endovascular neurosurgery to overcome the high failure rate of current devices. Our novel fabrication methods enable delivery soft-robotic devices at the small length scales (<100 μm) with aspect ratios over 400. This delivers complete 3D hemispherical and direct handheld control of the microcatheter tip orientation to the neurointerventionist. We further test and validate the performance of the soft robotic steerable catheter in CT-Angiograms based silicone models to provide a representative test bed. The representative ex vivo silicone phantoms of vasculature start from the femoral artery, through the aortic arch to the internal carotid artery and the aneurysm, and include non-Newtonian blood flow analog with pulsatile pumping to mimic the heart. The testing in silicone models is used to iteratively improve performance paving the way for in vivo tests in porcine. The resulting data shows that the technology demonstrates promise through quicker treatment with fewer mistakes in comparison to the existing gold standard devices.


SB01.12.32
Multifunctional Magneto-Fluorescent Core-Shell SPIONs for Single Particle Fluorescence Imaging, Magnetic Resonance Imaging and Targeted Drug Delivery Ashish Tiwari and Jaspreet Randhawa; Indian Institute of Technology, India

Developing multimodal imaging probe without compromising their properties for different imaging modalities is essential but very challenging. Superparamagnetic iron oxide nanoparticles (SPIONs) have shown great potential as magnetic resonance (MR) contrast agent. However, lack of fluorescence in SPIONs restricts their applications as multimodal imaging probe. Here, we demonstrate a single step synthesis of carbon coated core–shell multifunctional fluorescent SPIONs with excellent magnetic susceptibility, inherent fluorescence, multicolor emission and high photostability. MR imaging shows significant potential of SPIONs as a contrast agent in cancer diagnosis. Single particle fluorescence imaging revealed that SPIONs show high photon counts and a single step photobleaching than the commonly used Cyanine dye. After evaluating the multimodality, these SPIONs were formulated as drug carrier for targeted cancer therapy. In vitro cytotoxicity and MR imaging studies on cancer cells showed the active targeting ability of SPIONs nanocarriers. Biocompatibility of SPIONs nanocarriers was ascertained ex-vivo by hemolysis and serum stability studies. Thus, the synthesized SPIONs nanocarriers, a multimodal imaging probe, illustrate great potential in targeted drug delivery to improve the existing cancer theranostics.
SB01.12.33
Drug Delivery Microneedles Coated with Electrosprayed Micro/Nanoparticles for Cosmetic and Medical Skin Treatments Serdar Tort, Daewoo Han and Andrew J. Steckl; University of Cincinnati, United States

Microneedles (µNeddles) are an attractive option for painless drug delivery vs. hypodermic needles. µNeddles have gained popularity for cosmetic and medical applications because they create micro-punctures without damaging the skin epidermis and deliver drugs or nutrients deeper into the skin layer. Coating the microneedles is an interesting approach for delivering specific drugs and/or nutrients. Electrospraying is a versatile method to produce micro/nanoparticles and can control the particle size by changing process parameters or solution properties. Electrospraying process was used for producing micro/nano particles of insulin, folic acid, titanium dioxide, antimicrobial agent before. However, limited studies are available on coating of microneedles. In this study, we have demonstrated microneedles can be controllably coated with an electrospraying method. The effect of electrospraying process parameters (electric field, electrospraying time) and solution parameters (molecular weight, solvent properties) were evaluated using two dermarollers with µneedle arrays 0.25 and 2.00 mm in height. To determine the solution parameters of the electrospraying process, two different molecular weight of poly(ethylene oxide) (Mn 100 kDa and 1000 kDa) and two different solvents (water and ethanol) were used. Water soluble Keyacid Red (KAR) dye was used as a model molecule. For successful electrospraying, a solvent with high surface tension and low vapor pressure, high electric field between nozzle and collector, low polymer molecular weight are required. Because a limited amount of particles can be coated on microneedles, optimizing polymer to drug ratio is critical to incorporate the required amount of drug into microneedles. The loaded dye was released completely within 5 min. As expected, dye loading was increased with electrospraying time up to 60 min, after which loading on the µneedles no longer increases as the particles begin to accumulate and branch on top of each other.

Further research is being carried out to determine the performance of the nanoparticle coated microneedle delivery system in ex vivo and in vivo studies.

SB01.12.34
Mo⁶⁺ Doped Ag/Ag₃PO₄ System—Influence of Femtosecond Laser Irradiation on Its Structural, Photocatalytic and Antimicrobial Properties Aline B. Trench, Thales Machado, Mayara M. Teixeira and Elson O. Longo; Federal University of Sao Carlos, Brazil

The development of functional materials has been widely investigated due to its large range of applications. In the heterogeneous photocatalysis field, one of the most interesting material is the silver phosphate (Ag₃PO₄), which presents a remarkable photocatalytic activity using visible light irradiation. Herewith, several methods of modification aiming to improve the Ag₃PO₄ properties have been performed. The doping modification has been proved as an effective method for improvement and modulation of properties of semiconductor materials. In addition, another powerful method for improvement of properties is the irradiation with a femtosecond pulsed laser, which tends to generate structural changes and semiconductor/metal interface. Therefore, the main proposal of this work was to investigate the influence of concomitant Mo doping and femtosecond pulsed laser irradiation in Ag₃PO₄ in its structural, photocatalytic, bacterial and photoluminescent properties. The material was characterized by X-ray diffractometry (XRD), ultraviolet-visible absorption spectroscopy (UV-Vis), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray spectroscopy (EDX). The photocatalytic activity was evaluated for the degradation of rhodamine B under visible light irradiation. The results showed that the photocatalytic activity of the samples modified by doping and nanoparticle growth showed a promising result, degrading 100% of the pollutant in 2 minutes while the pure sample degrades about 53% in the same time interval. The bactericidal activity was tested for Escherichia coli bacteria, and the results showed that the modified samples have a superior antimicrobial activity than the pure ones. Thus, both the improvement in the photocatalytic and antimicrobial activity can be explained by the synergic effect between the silver nanoparticles obtained by irradiation in femtoseconds with the different cluster of the material.

SB01.12.35
Cellulose-Based Materials for Magnetic Paper Ana C. Trindade¹, João Canejo², Sergio H. Toma², Susete Fernandes², Maria Helena Godinho², Koiti Araki³ and Jon O. Fossum¹; ¹Norwegian University of Science and Technology, Norway; ²Universidade NOVA de Lisboa, Portugal; ³University of São Paulo, Brazil

It is known that iridescent solid films can be produced from cellulose nano crystals (CNCs) solutions in the presence
of the earth Magnetic field, [1] after solvent evaporation. The CNCs have a negative magnetic susceptibility, which allows the production of aligned solid films, with the cellulose nano rods main axis aligned parallel to the air interface, after the evaporation of the solvent.

Cellulose derivatives, for example cellulose acetate (AC), can form homogenous solutions with CNCs, from which films and fibers can also be prepared [2], the CNCs align their main axis along the main axis of the fibers, which translates into the enhancement of the mechanical properties of the electrospun micro/nano fibers [3]. To investigate the broken symmetry of the system CNCs rods were mixed with symmetric particles, spheres of iron oxide metallic nanoparticles (IONs).

The IONs were chosen due to their shape and because they are magnetic [MG2] nanoparticles, with diameters of the order of 10 nm, and can be conjugated with different other agent nanoparticles [4]. We prepared micro/nano fibers from AC with different quantities of IONs conjugated with CNCs and determined the critical concentration of IONs needed to induce magnetic properties to the fibers.

The precursor suspensions and the micro/nano electrospln fibers were investigated by using different techniques as scanning electron microscopy (SEM), atomic force microscopy (AFM), polarizing optical microscopy (POM), X-ray, small angle X-ray scattering (SAXS), and nuclear magnetic resonance spectroscopy (NMR). The mechanical properties as well as water contact angle measurements, of the electrospun membranes, were also investigated, with and without the nanoparticles.

This work demonstrates that it is possible to produce magnetic paper by adding a low amount of magnetic cellulose-based nanoparticles, which opens new horizons to the design and control of mechanical and magnetic properties of cellulotic materials.

References:

SB01.12.36
Continuous Chaotic (Bio)Printing—Using Simple Chaotic Flows to Continuously Fabricate High-Resolution Complex Lamellar Micro- and Nanostructures Carolina Chávez-Madero1,1,2, María Díaz de León-Derby1,1, Carlos F. Ceballos-González1,1, Edna J. Bolivar-Monsalve1, Mohamadmahdi Samandari2,3, Christian C. Mendoza-Buenrostro1, Sunshine Holmberg1,4, Norma Garza-Flores1,1, Mohammad Almajhadi4, Ivonne González-Gamboa1, Juan Yee-de León5, Sergio Martinez-Chapa1, Ciro Rodriguez-González1,6, Kumar Wickramasinghe1,4, Marc Madou1,4, Yu S. Zhang1,2,7, Mario M. Alvarez1,1,8 and Grissel Trujillo-deSantiago1,1,8; 1Tecnologico de Monterrey, Mexico; 2Harvard Medical School, United States; 3Isfahan University of Medical Sciences, Iran (the Islamic Republic of); 4University of California, Irvine, United States; 5Delee Corp., Mexico; 6Laboratorio Nacional de Manufactura Aditiva y Digital, Mexico; 7Harvard-MIT Division of Health Sciences and Technology, United States; 8MIT, United States

The fabrication of complex microstructure at high resolution and speed continues to be a technological challenge. We introduce continuouschaotic printing—the use of chaotic flows to continuously print hydrogel fibers with a high amount of internal (lamellar) microstructure at high resolution (a few microns) and speed (~1.0 meters of fiber/minute). We coextrude two inks (i.e., a suspension of microparticles, dispersed in a hydrogel) through a printing head that contains a miniaturized Kenics mixer (a simple on-line mixer) that contains multiple helicoidal mixing elements.

The diameter of the printing head and the number of mixing elements determines the number of internal lamellae produced according to a process of successive bifurcations that yields an exponential generation of inter-material area. By using 7 internal elements, 256 lamellae of average widths of 4 µm can be generated in a 1 mm cross-section fiber, and an inter-material area of ~ 0.067 m² cm⁻³ can be achieved. These values for microstructure resolution, internal surface area density, and fabrication speed all exceed the capabilities of any of the currently available commercial microfabrication techniques (i.e., commercial 3D printers) for the creation of microstructure.

In the present work, we include several application examples. We demonstrate the feasibility of reinforcing alginate fibers by precise engineering of lamellar arrays of graphite microparticles. We calculate the distribution of the
relevant length scales (i.e., the distance between lamellae) and demonstrate that the process of creation of microstructure is robust, reproducible, and self-similar. In addition, we demonstrate the possibility of designing living societies of bacteria, finely ordered in well-defined lamellae within the same construct, so that different cell types share a substantial contact interface. This enables, for example, the facile fabrication of complex bacterial community models for biomicrogeography studies. In proof-of-principle experiments, we demonstrate the bioprinting of mammalian cell-laden fibers in gelatin-methacryloyl (GelMA), a commonly used hydrogel for cell culture applications.

In an exciting further development, we demonstrated that the output of a continuous 3D chaotic printing head can be fed into an electrospinning head. We have shown that the microstructure created by 3D chaotic printing can be further scaled down by three orders of magnitude. A comparison of our experimental and computational results demonstrates that the output of the chaotic printing process is robust, predictable, and amenable to mathematical modeling.

The simplicity and high resolution offered by chaotic printing could enable novel biomedical and electronic applications, including the fabrication of tissue-like structures and reinforced or super-catalytic materials.

**SB01.12.37**

**Analysis of Nanofiber Formation for High-Throughput and High-Quality Electrospinning Process**

Kenya Uchida¹, Ikuo Uematsu¹, Yasutada Nakagawa¹, Tomomichi Naka¹ and Hidetoshi Matsumoto²; ¹Toshiba Corporation, Japan; ²Tokyo Institute of Technology, Japan

A nanofabrication including nanofiber formation gives novel functions to materials. Due to the large surface area, interconnected framework, and pore structures, nanofibers and nanofiber membranes show superior properties in the applications such as sensors, catalysts, filters, protective clothes, and biomaterial scaffolds(1). An electrospinning is a straightforward and versatile fabrication method for the nanofiber membrane from polymer solutions and melts. One major advantage of this method is applicable for a wide range of materials, such as inorganic materials, synthetic polymers and biological materials. Recently, the development of high-throughput and high-quality electrospinning system is strongly required. The process of nanofiber fabrication during electrospinning is too complicate to clarify the mechanism.

Some researchers reported the direct observation of fiber formation during electrospinning by using a high-speed camera. Few reports, however, deal with the analysis of the electrified-jet behavior in bending instability region(2). We performed quantitative analysis of nanofiber fabrication process during electrospinning. The electrified-jet phenomenon from the nozzle to the substrate was observed by a high-speed camera(3). To analyze electromagnetic and kinetic parameters, the flying velocities of the electrified-jet were measured and the electric potentials were obtained from a finite element method analysis of an electric field. The charge density and a size of the electrified-jet in the bending instability were determined by solving the equation of motion for the electrified–jet. By using this analytical approach, the effects of the applied voltage and the addition of an electrolyte to the spinning solution on nanofiber formation were demonstrated. The insights obtained here enable precise design of the high-throughput and high-quality electrospinning process.

In addition, we carried out theoretical analysis of liquid impregnation behavior into well-defined nanofiber membranes. The determining factors for controlling liquid impregnation is investigated using numerical analyses based on the Kozeny-Carman equation.

Finally, an application of nanofiber membrane derived from material properties and nanofiber morphology is demonstrated to show the advantages of electrospinning technology.


**SB01.12.38**

**Pattern Formation in the Heterostructured Gel by the Ferrocyanide-Iodate-Sulfite Reaction**

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Coupling of reaction and diffusion forms a spontaneous pattern. Turing theoretically predicted that stationary pattern forms in reaction-diffusion systems and stated the formation conditions of stationary patterns. In reaction-diffusion
systems, the medium is an important. The diffusion coefficients of the activator and the inhibitor are important for pattern formation. We have tried to control pattern formation in the Ferrocyanide-Iodate-Sulfite (FIS) reaction, which is pH-oscillating reaction, by controlling solute diffusion via the network density of polymer gel. In this study, we reported the pattern formation in heterostructured gels with different network densities by the FIS reaction. The chemical states of the gel depend on the diffusivity, which in turn depends on the network density of the gel. Consequently, a pH pattern reflecting the heterostructured gel emerged. Furthermore, adjusting the condition produces novel patterns in the heterostructured gel.

A heterostructured gel was prepared by a two-step synthesis method with photo polymerization. Acrylamide (AAm), the cross-linker N,N'-methylenebisacrylamide (MBAAm), and the photopolymerization initiator Irgacure 2959, were used. Two gel precursor solutions with different monomer contents were prepared. The monomer contents of gel precursor (20) and gel precursor (10) were 20 and 10 wt%, respectively. A continuous stirred tank reactor (CSTR) covered with a gel was constructed. The gel was set in the space between reactor. The temperature of the reactor was set at 50 °C with a thermostatic bath. Solution A ([NaIO₃]₀: 75 mM, [H₂SO₄]₀: 3.6 mM, [NaOH]₀: 0.25 mM) and solution B ([Na₂SO₃]₀: 89 mM, [K₄Fe(CN)₆]₀: 25 mM) were fed separately into reactor with HPLC pumps. By controlling the flow rate, the difference in the diffusivities in the heterostructure gel was converted to a difference in the pH states via the FIS reaction. Furthermore, the boundary conditions given by the striped heterostructured gel gave rise to stationary linear patterns, which are formed in the reaction-diffusion system. In this way, pattern formation in the FIS reaction was controlled by the artificially designed heterostructured gel.

SB01.12.39
Isolation of Chloroplasts from Grass to Design Photobioreactors by Using High Internal Phase Emulsions
Andrea E. Vaca, Alicia E. Sommer and Renata A. Montero; Universidad de Investigación y Tecnología Experimental Yachay Tech, Ecuador

The deficient disposition of the pruning waste from grass (Poaceae), has been converted into a considerable environmental problem in Ecuador since it is discarded in common garbage dumps. As a result, gases and lixiviates are generated producing a negative impact on the environment. This project takes advantage of these residues to isolate their chloroplasts, with the aim of subsequently developing bioreactors to make the absorption of CO₂. Several investigations have been carried out in order to encapsulate chloroplasts obtained from other species, in inorganic matrices[2,3], since these molecular machines transform light energy into chemical energy, through the process of photosynthesis[1]. However, it is still a challenge to find an adequate method to encapsulate them and to maintain their vital function. In this work we present, for the first time, the encapsulation of grass chloroplasts into silica monolith with a hierarchical texture, using high internal phase emulsion (HIPE). Based on the results obtained, it was demonstrated that it is possible to extract chloroplasts from the grass with high yield. The chloroplasts extracted were encapsulated into silica monolith. The synthesized samples were analyzed by optical and scanning electron microscopy, as well as by DRS-UV-Vis and Fluorescence spectroscopy to monitor the photosynthetic activity of chloroplasts and it was shown that it was possible to keep it up to more than 90 days.


SB01.12.40
Micro-Structuring of Multilayered Thin Films Enables Stretchable Interconnect Technology
Nicolas Vachicouras, Christina Tringides, Yohann Thenaïs, Florian Fallegger and Stephanie P. Lacour; École Polytechnique Fédérale de Lausanne, Switzerland

We propose a new strategy to engineer elasticity in otherwise rigid materials by structuring them with specific patterns. This happens spontaneously at the microscale on stretchable thin gold films on silicone that display dense distributions of Y-shaped cracks to favor out-of-plane deformation. We drew inspiration from these cracks to pattern Y-shaped cuts and engineer reversible elasticity in a multi-layer of metallic and plastic thin films. First, the geometry and density of the Y-shaped patterns were first optimized using finite element analysis and macroscopic models. Next, we developed the fabrication process enabling the micro-patterning of thin polyimide/platinum/polyimide interconnects with microscopic Y-shaped cuts (branches of dimensions ~15 μm, thickness < 10 μm). Encapsulation in silicone rubber completed the fabrication of stretchable interconnects that can be easily manipulated.
The micro-structured metallic films exhibit a sheet resistance of $\sim 15\text{--}20 \ \Omega/\text{sq}.$ and display surprising deformability and stability compared to non-micro-patterned interconnects of identical thickness. 200 µm wide, 17 mm long, Y-shaped metallic tracks mechanically fail at 80 % tensile strain albeit do not fail electrically while plain tracks of identical geometry fail both mechanically and electrically at only 3 % applied strain. The micro-patterned interconnects sustain repeated cycling at 10% tensile strain for 1 million cycles with remarkable electrical stability. Moreover, this technology allows for the patterning of tracks down to 20 µm in width and complex layouts on a wafer-level scale. Through pattern optimization, mechanical gradient may be engineered across the structure, defining non-deformable to elastic areas, thereby providing an interesting platform for the hybrid integration of stiff and rigid components with stretchable interconnects. Finally, we verified the micro-structured tracks impact only minimally the mechanical properties of the silicone carrier in terms of apparent elastic modulus (apparent elastic modulus increased from 2.3 MPa to 3.2 MPa).

We have implemented this soft technology to prepare stretchable micro-electrode arrays for neural recordings but we anticipate this strategy will be implemented in a range of wearable and implantable bioelectronic interfaces.

SB01.12.41
Characterization and Evaluation of Antibacterial Activity of Hydrothermaly Synthesized Iron Oxide Coatings
Svetlana Vihodceva1, Jurate Siugzdaite2 and Andris Sutka1; 1Riga Technical University, Latvia; 2Lithuanian University of Health Sciences, Latvia

As surface contamination can contribute to transmission of bacteria, the development of surface enhanced coatings that causes sanitization of the surface is an important development in reducing hospital acquired infections. To develop antimicrobial coatings with “sharp” Z-scheme photocatalytic nanoarchitectures. Hematite (Fe2O3) as non-toxic narrow band gap semiconductor with broad absorption in the visible light, will be used as the main element in coating, “sharp” structures offering a long optical path for efficient light harvesting, that will increase photocatalytic efficiency of structures. Similar “sharp” structures proved it effectiveness in bacteria killing by piercing into the bacterial cell wall and as repelling surfaces that resist bacteria attachment. Thereby, in this work an antimicrobial activity of Fe2O3 coatings was studied by Agar diffusion and JIS tests. Hematite coatings were obtained by one step hydrothermal method. Ferric chloride and urea were dissolved in a distilled water, this solution was transferred into autoclave containing an rubber substrate fully immersed into the solution. Then the autoclave was placed in a hot air oven at constant temperature 150 C for 3 hours in air. Finally, substrate with coating was taken out from the autoclave and washed in DI water and dried in air at room temperature. Obtained coating were characterized by SEM, FTIR and XRD.

Escherichia coli ATCC 25922, Staphylococcus aureus ATCC 2593, Staphylococcus epidermidis ATCC 12228, Staphylococcus saprophyticus ATCC 15305, Pseudomonas aeruginosa ATCC 10145, Bacillus cereus ATCC 11778, Enterococcus faecalis ATCC 29212, Listeria monocytogenes ATCC 13932, Salmonella typhimurium ATCC 14028 were used as a test cultures. The microbiological testing results show the efficiency of the hematite coatings against all test microorganisms.

SB01.12.42
GER Driven Artificial Muscles—Nano-Catalyst Laden Filament for 3D Printed Pneumatic Actuators
Marcos Villeda Hernandez, Charl F. Faul and Michael P. Dicker; University of Bristol, United Kingdom

Soft Robotics offers solutions to problems where human or animal-like architectures and materials are needed. Tasks requiring strength yet finesse, currently only achieved through human operators, may in the future be automated by developments in soft robotics. Further than just mimicking biological systems in performance, the aim of soft robotics is to develop robots which are both safe and compliant for human interaction. Pneumatic actuators are widely studied in soft robotics as the compliant actuation of these systems is comparable to that found in Nature. However, conventional pneumatic actuators are powered by externally tethered hard air compressors or accumulators.

Gas Evolution Reactions (GER) are widely found in biochemical processes [1,2]. Hydrogen peroxide is a sub-product of cellular metabolism that protects the cell against anaerobic pathogens. Given its reactivity, it must be quickly transformed into less harmful or reactive compounds. In vivo, the decomposition of hydrogen peroxide to water and oxygen is catalysed enzymatically by catalase [3]. Soft, porous catalytic nanocomposites can perform a similar function to enzymes while also mimicking the desirable compliance of biological systems.

Platinum is a catalyst used in the decomposition of hydrogen peroxide [4]. This work reports the development and
characterisation of a Platinum nano-catalyst laden 3D printing filament, created by loading a commercially available porous filament (POROLAY LAYFOMM 40) with platinum nanoparticles. The nanocomposite filament is used to create a one-step multi-material 3D-printed GER pneumatic soft artificial muscle. The resulting pneumatic actuator with embedded catalysts converts energy-dense liquid chemical fuel (hydrogen peroxide) into actuating gases (oxygen). Actuator geometries for optimising the amount of oxygen harnessed from the hydrogen peroxide decomposition are explored through finite element analysis. The potential for the configuration to create a fully soft untethered device capable of gentle movements for locomotion or handling of delicate objects is discussed. Developing such advanced methods for manufacturing and powering soft robots is critical in order to realise their potential to generate real societal impact.


SB01.12.43
Bacterial Cell Walls Exhibit High Water Responsive (WR) Pressures and Energy Densities Haozhen Wang1,2, Zhi-Lun Liu3 and Xi Chen1,3; 1Advanced Science Research Center (ASRC), The City University of New York, United States; 2PhD Programs in Physics, The Graduate Center of the City University of New York, United States; 3The City College of New York, United States

Nature has developed remarkable WR systems that dramatically deform in response to changes in relative humidity (RH), such as the actuation of pine cones opening and releasing their seeds and wheat awns propelling their seeds into the ground. Such WR actuations can be extremely powerful, and have a great potential to power modern engineering systems. Here, we present our discovery of bacterial cell walls that exhibit extremely high energy density of 72.6 MJ/m3 and power density of 9.1 MW/m3, surpassing that of existing actuator materials and artificial muscles. By using our customized AFM, we characterized WR properties of bacterial cell walls from three species, including Bacillus subtilis, Staphylococcus aureus, and Saccharomyces cerevisiae. We found that cell walls from these three species have significant water-responsiveness, and their WR strains reach 27.2%, 19.1%, and 11.2%, respectively. To measure their WR energy densities, we have created a thermodynamic cycle where applied forces and RHs can be varied to maximize cell walls’ WR work. Using this method, we have measured their energy densities to be 72.6 MJ m-3, 47.9 MJ m-3, and 29.9 MJ m-3. Considering their cycle period (8s), cell walls’ power densities are estimated to be 9.1 MW m-3, 5.9 MW m-3, and 3.7 MW m-3, respectively. We also note that, while these cell wall structures share similar molecular structures, they possess diverse water-responsiveness, motivating further studies of cell walls’ WR fundamental mechanisms.

SB01.12.44
Highly Sorptive and Breathable PIM-1-Based Fabrics with Enhanced Mechanical Strength for Chemical and Biological Protection Siyao Wang1, Natalie Pomerantz2, Erin Anderson3, Todd Miller2, Saad Khan1 and Gregory Parsons1; 1North Carolina State University, United States; 2U.S. Army Combat Capabilities Development Command – Soldier Center, United States; 3Battelle Memorial Institute, United States

Recently, Polymers of Intrinsic Microporosity (PIMs) have attracted attention as a novel class of high free-volume polymers with highly rigid and contorted molecular structure. Most research on PIMs has focused on fundamental material and membrane properties, with only a few studies on materials in fiber form. In this study, PIM-1 polymer fiber mats were fabricated by electrospinning using different solvent systems consisting THF, DMF and toluene. The resulting fiber mats showed excellent breathability and high porosity, indicating potential for applications in protective clothing. The surface area of the PIM-1 fiber mats was typically 650 m2/g, which is close to 750 m2/g measured for the starting neat powder. A problem, however, is that the produced fiber mats have very poor mechanical integrity due to low interchain interactions of PIM-1, hindering their practical use. In our work, we have
developed a unique PIM/PAN hetero-structure synthesis approach by incorporating PAN fibers as a structural reinforcing material into the PIM fiber matrix. The as-prepared PIM/PAN composite fibers exhibit 40 times improvement in tensile strength compared to the PIM fibers, with a net surface area of 360 m²/g, indicating only a moderate loss in porosity. In addition, metal-organic framework (MOF) particles with the capability of degrading toxic chemicals, such as chemical-warfare agent (CWA) simulants, were integrated into the composite fibers. The resultant PIM/PAN/MOF composite fibers show 2-3 times higher removal capacity of dimethyl methylphosphonate (DMMP) than the baseline material and demonstrate the detoxification of 4-nitrophenyl phosphate (DMNP) as monitored by UV–vis spectroscopy, among which DMMP and DMNP are both chemical nerve agent simulants. These findings indicate that functionalized PIM-1-based fabrics are a promising material for applications in chemical protection and detoxification.

SB01.12.45
Application of Janus Graphene Nanofluids for Enhanced Oil Recovery Wei Wang and Sehoon Chang; Aramco Research Center-Boston, United States

Anisotropic nanomaterials composed of two halves with different structure, chemistry, or polarity, known as Janus nanomaterials, have distinct properties when compared to symmetrically functionalized analogues. These materials have recently gained significant attention in many applications such as electronic thin films, drug delivery, sensors, optics, oil/water separation membranes, photoactivated micromotors, photocatalysts, and interfacial modification. Among the many Janus structures, two-dimensional (2D) Janus nanomaterials with high aspect ratio in rod-like or planar (i.e., nanosheets) morphologies, are especially intriguing considering their interfacial properties as well as their ability to assemble into higher order and hybrid structures. In this research, we describe an approach to mass synthesis of Janus graphene nanosheets in highly controllable ways via a novel “Interfacial Nanoreactor” system. We have characterized and proven the asymmetric structures of the synthesized Janus graphene nanosheets by Langmuir-Blodgett (LB) surface pressure-area (π-A) curves, fluorescence spectroscopy, contact angle measurement and scanning electron microscope (SEM) characterizations. The Janus graphene nanosheets with two chemically different compartments show very unique behaviors at liquid interfaces. We observed surfactant-like interfacial phenomena of the Janus graphene layer when its surface density increases, which is similar to the way that micelles or lipids form in a bulk phase above the critical micelle concentration (CMC). The one of applications for the nanofluids of Janus graphenes is to be a chemical agent for enhanced oil recovery (EOR). To demonstrate this applications, we used a microfluidic-based reservoir-on-a-chip model to understand oil-water-rock phase interactions and visualize the fluid transport processes in micropores, and more than 10% improvement in oil recovery was observed using the Janus graphene nanofluids in comparison to just using seawater flooding. The 2D Janus graphenes also present great opportunities to further create tailored and functional hierarchical structures of interest to molecular biology and medicinal chemistry.

SB01.12.46
Transparent and Flexible Pressure Sensor for the Human/Machine Interface Elena E. Watts1, Ning Xu2 and D. Jason Riley1; 1Imperial College London, United Kingdom; 2ROLI, United Kingdom

With the movement towards flexible and transparent electronics[1] for use in displays[2], electronic skins[3] and wearable healthcare monitoring[4], electrical components such as pressure sensors must evolve alongside circuitry and electrodes to ensure a fully flexible and transparent system. In the past, piezoresistive pressure sensors made with flexible electrodes have been fabricated, however, many of these systems are opaque.[5]

For the first time, we present a technology that exploits the natural self-assembly of polystyrene nanospheres to reproducibly create optically transparent pressure sensors with sensing performance comparable to industry standards. We have demonstrated flexible sensors with transparencies as high as 79.3 % transmission, fast relaxation times of <50 ms, and sensing response up to 200 kPa.

The performance of the piezoresistive pressure sensor relies on uniform elastic nano-dome arrays. A thin and homogenous lining of PEDOT:PSS renders the domes conductive and retains the transparent and flexible qualities of the underlying polymer. The highly tunable multi-step fabrication procedure establishes the potential for the mechanical properties of the sensor to be tailored and tuned.

This presentation will include the design, fabrication details and scale-up potential of the sensor. Alongside this, the
performance metrics will be demonstrated, and the pressure sensing mechanism analysed with reference to some preliminary in-situ SEM compression testing.


SB01.12.47
Thin Hydrogel Coatings by Enzyme-Catalyzed Mechanism Christian Wischke1, Marlin Kersting1,2, Alexander Welle2, Ludmila Lysyakova1, Steffen Braune3, Karl Kratz1, Matthias Franzreb2 and Andreas Lendlein1,3; 1Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz-Zentrum Geesthacht, Germany; 2Institute of Functional Interfaces, Karlsruhe Institute of Technology, Germany; 1Institute of Chemistry, University of Potsdam, Germany

Technologies for modification of material surfaces to create specifically envisioned interfacial properties are of high technological interest, particularly when it comes to in situ thin layer coatings with very hydrophilic materials, i.e. hydrogels, on hard materials. While spin coating of precursors and crosslinking of reactive moieties via UV irradiation may be applicable to flat materials [1], alternative approaches are of interest that conceptually would be applicable to any surface shape by initiating hydrogel formation from the surface itself [2]. In this context, the capability of enzymes to crosslink polymeric precursors to form hydrogels [3] may be applied to realize a “coating-from” rather than a “coating-to” approach for functional interfaces.

Based on previous experience of relatively slow conversion of substrates by mushroom tyrosinase after surface immobilization [4], here horseradish peroxidase was selected and successfully coupled to amino-functionalized glass or gold surfaces by use of glutaraldehyde. When exposed to solutions of hydrophilic 4-arm star shaped telechelics from poly(ethylene glycol) bearing end groups derived from aromatic amino acids, the envisioned in situ formation of thin layer hydrogel coatings was achieved.

Contact angle and zeta potential analyses were applied to determine physicochemical properties of the surfaces. A qualitative proof of hydrogel deposition was provided by time-of-flight secondary ion mass spectrometry (ToF-SIMS), showing ethylene glycol repeat units as well as the crosslinkable aromatic moieties at higher concentrations for enzyme triggered crosslinking conditions as compared to pure adsorption of the precursor. A quantitative assessment of the coating thickness was performed by atomic force microscopy (AFM) and quartz-crystal microgravimetry, suggesting very thin homogeneous hydrogel layers of 100 - 250 nm being formed. As a key function needed for hemocompatible devices, low thrombogenicity of the hydrogel coating similar to clinical accepted implant materials was demonstrated with human blood from several donors according to the protocol approved by the ethics committee (# EA2-018-16; Charité University Medicine Berlin, Germany).

This “coating-from” approach may in the future be applied to various shapes of surfaces, e.g. for cell culture, protein/biofilm repellency in technical applications, or in flexible electronics.


SB01.12.48
Multimodal Magnetomotility of Multiple Soft Robots Sukyoung Won1, Sanha Kim2, Jeong Eun Park1, Jisoo Jeon1 and Jeong Jae Wie1; 1Inha University, Korea (the Republic of); 2Korea Institute of Science and Technology, Korea (the Republic of)

Magnetic soft robots facilitate battery-free contactless control of sub-mm soft robots. However, simultaneous programming of magnetic field is required in both 3-axial direction and magnitude to navigate through obstacles. Hence, parallel control of multiple soft robots becomes prohibitive. Herein, we demonstrate maneuverability of multiple polymeric microbots capable of on-demand orbital navigation inspired by hierarchical rotation and revolution of our Solar System planets. Here, the hierarchical magnetomotility for soft robots is achieved by planar rotations of permanent magnet. Simple change of rotational speed of magnets allows reversible control of trimodal
rotation including rotating, pivoting, and tumbling. Remarkably, different orbital radius and/or velocity for each soft robot can be achieved in multi-body system due to aspect ratio dependent magnetic motility of soft robots. The hierarchical magnetomotility promotes adaptable self-correcting locomotion since blocked rotations shift revolution pathway, providing multi-terrain navigation functionality including stairs and uphill climbing as well as underwater and above water swimming. We will also discuss collective behaviors of the magnetic soft robots to accomplish a certain mutual goal.

SB01.12.49
Dual-Porous Cellulose Nanofibril Aerogels for Organic Pollutant Removal and Silver Ion Recovery from Wastewater Tingting Wu1,2, Qinghua Zhang1 and Gustav Nyström2,3; 1Donghua University, China; 2Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; 3ETH Zürich, Switzerland

The growing world population and the related increase of chemicals used in daily life leads to higher concentrations of chemical substances in our water reservoirs. It is therefore crucial to develop green, stable and efficient absorbents for purification of contaminated water. In this work, an anionic cellulose nanofibril (CNF)-based hierarchical aerogel with high specific surface area (up to 430 m²/g) was prepared via a combined directional freeze-thawing (macro-pores) and supercritical drying (meso-pores) method. By adjusting physical and chemical cross-linking, we can obtain a high Young's modulus (711 kPa) and hydrophobic performance (contact angle ~120°), which help to maintain the stability of aerogels in aqueous conditions. The cationic dye methylene blue (MB) was chosen as a model organic molecule to investigate the absorption properties of the aerogels by changing the pH, absorbent dosage, initial dye concentration, and contacting time during the adsorption process. The aerogels showed a maximum adsorption of MB up to 234 mg/g, and remain intact in the dye solution even after 24 h of shaking during the adsorption test. Inspired by the excellent adsorption performance of cationic MB, we selected Ag⁺, a metal ion that has been rarely studied in the literature for ionic adsorption. The maximum adsorption of Ag⁺ was found to be 116 mg/g. A high specific surface area and a strong electrostatic interaction are the prominent mechanisms behind the good adsorption capacities to both MB and Ag⁺. These results indicate that the prepared macro- and meso- dual porous CNF aerogels are promising candidates for wastewater purification. Considering the economic factor, a reduction reaction was performed on the aerogels after the Ag⁺ adsorption enabling a conversion of ionic to metallic Ag. This allows for a recovery of the extracted silver and a potential reuse of the materials within antibacterial or catalytic applications.

SB01.12.50
Rapid and Facile Fabrication of Self-Similar Hierarchical Broccoli-Like Structures Zhigang Wu, Shuo Zhang and Qin Jiang; Huazhong University of Science and Technology, China

Cross-scale micro-nano hierarchical structure in the living systems often provides unique features on surface and serves as an inspiration source for artificial materials or devices. Among them, artificial made broccoli-like structure demonstrates excellent surface performance such as ultra-high hydrophobicity or hydrophilicity in various situations.

In this work, by introducing a solvent-assisted UV laser treatment, we establish a rapid yet facile approach to fabricate self-similar hierarchical broccoli-like micro-nano structures on silicon with super hydrophilicity and high light absorbance. Specifically, through adjusting the operating parameters of the UV-laser (scanning speed, v and space between adjacent scanning lines, ΔL) and immersing solvents, we can tune the surface morphology of the surface, such as surface roughness and height difference, to obtain uniform, robust surface topography. According to micro-views, we observe regular microgrooves consist of abundant “peaks” and “valleys” that stack vast broccoli-like structures. We also investigate the forming mechanism of such broccoli-like structures. It is found that phase change, micro-/nano-particles sputtering and depositing, disintegration and re-depositing, and solvent evaporating etc are important issues during the forming process of self-similar structure.

Through optical test of UV-treated Si samples, the results reveal that such broccoli-like structures have a consistent high light absorbance (>90%) in an ultra-broad spectrum from ultraviolet to infrared spectrum (in 200-2 500 nm spectral range). It may provide a low-cost way to fabricate black Si for solar energy harvesting in common laboratory environment.

Further, the patterned silicon can be used as a master for capillary assembly of soft electronics on elastomeric substrates with water/liquid alloy-amphiphilic zones, or as a self-cleaning surface and a heat transfer surface. The demonstrated facile way for a broccoli-like structure fabrication may encourage more researchers to investigate unique features of self-similar micro-/nano surfaces, and further exploit their great potential in applications towards
diverse directions.

**SB01.12.51**

**Tactile Sensor for Magnitude and Direction Detection Based on a Liquid Alloy Droplet**

Zhigang Wu¹, Wenci Xin¹ and Bei Wang¹,²; ¹Huazhong University of Science and Technology, China; ²Uppsala University, Sweden

To perceive the tactile signals, such as magnitude, strain and especially direction, researchers have developed various types of sensors. However, these devices are either only could obtain single signal or super complex in structure. This work presents a novel soft tactile sensor with capacitance between liquid alloy based hemisphere and planar electrodes. Due to the nature high surface tension and flowability of liquid alloy droplet, the dynamic re-distribution of charges on electrodes can achieve high sensitivity, wide range and abundant functions, e.g. magnitude or direction of external force.

In demonstration, a flexible tactile sensor based on morphological deformation of liquid alloy was fabricated. The bottom electrode was a hemi-sphere liquid alloy droplet pinned on a circle copper pad, which was surrounded with liquid alloy phobic substrate to avoid the adhesion of liquid alloy during deforming. While the upper electrode was made of planar liquid alloy, which was divided into several isolated equal sections. Hence, the entire device can be viewed as several capacitance sensors with a shared fluidic electrode. In intact situation, most of the charges would concentrate on the top of hemisphere at first. With the approaching of the electrodes, the charges would disperse to a wider contacting area, which was reflected on the change of capacitance in each sector. Thus the information of the tactile signal could be calculated according to the results from all of the capacitances, and the magnitude and direction were acquired at the same time. Without the constraint of wrapped materials, the droplet is only limited by its high surface tension, which leads to a high sensitivity. At the same time, the charges dispersion following the deformation also contributes to the sensitivity. The impact parameters including the amount of liquid alloy, the size of bottom and upper electrodes, and the fabricating technique also were studied. The response time, repeatability, hysteresis etc. demonstrated the performance of this novel tactile sensor.

**SB01.12.52**

**Facile Fabrication of Flexible Discrete Magnetization Soft Robot via Laser-Tuned Selectively Adhesive Transfer Printing of Anisotropic Magnetized Silicone Cells**

Zhigang Wu, Xingxing Ke and Shuo Zhang; Huazhong University of Science and Technology, China

This work presents a facile method to assemble discrete magnetization soft robots via laser-tuned selectively transfer printing different patterned anisotropic magnetized silicone cells. This technique could be simply implemented via anisotropic magnetization, magnetized cells cutting and transfer printing of magnetized cells in three major steps. It is very promising to parallelly flexibly input magnetization information into a three-dimensional structure for diverse applications.

Spatial preset of specific properties in a configurable way is a key to develop active devices running in dynamic scenarios such as that in soft robotics, biomedicine, functional materials and four-dimensional (4D) printing. Despite success in recent development, current fabrication technique still too complicated to implement in a facile and rapid way enabling flexible spatial preset of magnetization in soft materials.

In this work, by introducing a laser-tuned selectively adhesive transfer printing of anisotropic magnetized silicone cells, we present a facile fabrication technique to flexibly preset discrete magnetization in soft materials for making fast-transforming untethered magnetic robots. Such a preset of magnetization pattern can be easily tuned during the transfer process by alignment adjustment or laser parameters tuning. Different magnetized cells can be selectively picking up by tuning the surface morphology and hence adhesiveness of magnetized film with a different laser-treatment parameter setting. Spatial preset of magnetism can be achieved by geometrical alignment and configuration adjustment of different magnetized cells. Moreover, magnetization in each layer can be easily tuned in arbitrary direction on demanded and thus empower the independent addressability to different magnetized cells in a global actuating magnetic field. Further, we can use planar structure to achieve complex 3D structures and the flexibility of the re-assembling based this method enable it ease of geometrical re-configuration, which can totally change its response behavior accordingly.

Finally, two demonstrations are presented: 1) the re-assembling process of sub-robots together with its responding behavior in different geometrical configurations, and 2) a targeted drug delivery of a hollow 3D structure with excellent passibility and flexible steering inspired by tumbleweed.

**SB01.12.53**
Fabrication of Seamless Integrated Perception Layer for Fully Soft Robots via a Conformal Masked Printing
Zhigang Wu and Shuo Zhang; Huazhong University of Science and Technology, China

Nowadays, intelligent home robots are meeting a giant demand in people’s daily life, including healthcare detecting, environment monitoring and so on. Among them, fully Soft robots are attracting huge attentions due to its great adaptability in various environments and enhanced safety, particularly when interacting with people. Therefore, it’s important to improve the comfort level of human-robot interaction rather than a rigid or statistic contacting, where diverse soft functional circuits are needed to be integrated on the 3D complex surfaces for environmental perception and to endow soft robotics with more features. However, present approaches for perception layer are almost based on planar techniques in a very limited area, or costly equipment to print 3D circuits but time-consuming, cannot satisfy the demanding from soft robots without seamless integration without hindering the great adaptability and dynamic 3D morphology. Hence, direct conformal print of perceptive circuits on arbitrary robots’ external surfaces is one of the most effective and convenient solution to achieve excellent environmental perception for soft robots. In this work, we present a method of fabricating intuitive perceiving layer integrated on soft robots with a conformal masked printing combined with UV-laser patterning and liquid alloy (Galinstan) circuits spraying. Specifically, an ultra-flexible and sticky elastomer is employed as a mask to be conformably attached on the target surfaces under a gentle pressure after laser patterning. Following with liquid alloy sprayed and mask peeled, the liquid alloy circuits are completely conformal printed on arbitrary surfaces of soft robots, including developable/non-developable surfaces, curvilinear surfaces with sharp edges and other 3D complex surfaces. Finally, through connecting with functional component units and sealing via dip-coating, we can obtain the fully soft robot with soft/conformal functional layer.

Upon this technique, we employ a soft robot hand integrated with functional layer, which consists of liquid alloy connections and component units, such as thermistors, to detect pressure, strain or near-field heat source. Further, combining with a feedback circuit and soft actuator, the soft robot hand could help monitor human healthcare signal when we touch/shake with it. In addition, it can be actively away from heat source because of temperature sensor module. That would be a great potential for endowing soft robotics with more functionalities.

SB01.12.54
Electrically Modulated Highly Switchable Adhesion of N-Doped Graphene Interfaces for Robust Micromanipulation
Yiyang Wan¹, Yong Gao² and Zhenhai Xia¹; ¹Univ of North Texas, United States; ²Northern Polytechnical University, China

Smart surfaces or interfaces, which can turn their adhesive force on and off spontaneously under natural or provoked stimuli, renders them appealing for many applications. We demonstrated a smart interface, N-doped graphene, with highly switchable adhesion and robust micromanipulation capability triggered by external electric signals. Upon applying a small DC or AC electrical bias, this nano-textured surface can collect environmental moisture to form a large number of water bridges between the graphene and target surface, which lead to a drastic change in adhesive force. Turning on and off the electrical bias can control this graphene interface as a robust micro/nanomanipulator to pick up and drop off various micro/nano-objects for precise assembling. Molecular dynamics simulation reveals that electrically induced electric double layer (EDL) and ordered ice-like structures at graphene-water interface strengthen the water bridges and consequently enhance force switchability. In addition to the micro-/nanomanipulation, this switchable adhesion may have many technical implications such as climbing robots, sensors, microfluidic devices, and advanced drug-delivery.

SB01.12.55
Biocompatible Nanocomposite Fibrous Membranes Fabricated by 2D-Controlled Close-Range Electrospinning
Siyu Xiong and Kwang-leong Choy; University College London, United Kingdom

Electrospun fibrous membranes have been investigated by many biomedical researchers due to their extraordinary biomimetic morphology and superior biocompatible performance, which promote the compatibility between the biomaterials and the host environments. Active materials have been adapted for the electrospun fibrous membranes for various applications, including catalysts, absorbents, cell supports, and drug carriers. In this presentation, silicon oxide (SiO2), titanium oxide (TiO2), chitosan (CS), and graphite were incorporated with polycaprolactone (PCL) to produce highly interactive fibrous membranes by a 2D-controlled close-range electrospinning method. The electrospun membranes were characterized using a combination of scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) for the surface morphology and chemical composition analysis. The
2D-controlled close-range electrospinning warrants the production of fine fibers with well-controlled microstructure and diameter, and the active materials were well dispersed along the fibrous matrix to facilitate their applications. The relationships among process, structure, and property of the electrospun biocompatible nanocomposite fibrous membranes will be presented.

SB01.12.56
Fine-tuning of Rat Mesenchymal Stem Cell Senescence via Microtopography of Polymeric Substrates Xun Xu1, Weiwei Wang1, Yan Nie1,2, Karl Kratz1, Nan Ma1,3 and Andreas Lendlein1,2,3; 1Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz-Zentrum Geesthacht, Germany; 2Institute of Chemistry, University of Potsdam, Germany; 3Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany

The therapeutic potential of mesenchymal stem cells (MSCs) has been demonstrated in regenerative therapies. However, their therapeutic efficacy could be attenuated when undergo cellular senescence caused by various environmental stressors. The senescent MSCs could remain viable but presented an irreversible growth arrest and deficient proliferation. Tissue regeneration would be impaired due to their influence on the function of neighboring cells via altered secretome profile [1, 2]. MSCs can be modulated by not only the biochemical signals but also the physical cues such as the substrate topography [3, 4]. However, little is known about the influence of the topographic cues on cellular senescence of MSCs. In this study, the influence of microscale roughness on MSC senescence was investigated on the poly(ether imide) (PEI) substrates as a model system. Three distinct levels of roughness were created in the bottom of PEI inserts via injection molding: smooth surface R0 (root mean squared roughness (Rq): 0.2 ± 0.1 µm); R1 (Rq: 3.9 ± 0.2 µm) and R2 (Rq: 22.7 ± 0.8 µm). The senescence and proliferation of rat MSCs on the substrates were examined using senescence-associated β-gal assay and a cell counting kit. The paracrine effect of MSCs on different substrates was studied using a transwell system. MSCs were cultured in PEI inserts, then the MSC-laden transwells were put into the insert. The proliferation of cells inside the transwells was assessed via CFSE staining followed by flow cytometry analysis. After 5 days of culture, MSCs in different inserts showed high cell viability and similar spindle-shaped morphology. The lowest senescence ratio was observed in MSCs cultured on R1 (35 ± 4% decreased compared to R0). Cells on R1 presented the highest proliferation rate (5.1 ± 0.2 fold increase of cell number), as compared to cells on R0 (4.3 ± 0.5) and R2 (3.9 ± 0.4). The MSCs cultured on different substrates could effectively influence the proliferation of cells inside the transwell via their paracrine effect. The R0 secretome inhibited cell proliferation compared to R1 secretome (1.8 ± 0.2 fold decrease after 20 days of culture). In summary, the PEI substrate with roughness R1 provided a more superior surface environment for MSC culture, which inhibited cellular senescence and promoted cell proliferation. Such a microscale surface roughness can be considered as a key parameter for surface design of stem cell culture device and implants to improve the quality and therapeutic potential of stem cells.

References:

SB01.12.57
Syringe-Injectable and Self-Expandable Shape Memory Polymer Ultrathin Films Kento Yamagishi1, Akihiro Nojiri2, Eiji Iwase2 and Michinao Hashimoto1; 1Singapore University of Technology and Design, Singapore; 2Waseda University, Japan

We developed ultrathin films of polyurethane-based shape memory polymer (SMP) as a syringe-injectable and self-expandable platform for implantable medical devices. Free-standing polyurethane ultrathin films with the thickness less than 1 µm and the flexural rigidity less than 10^-2 nN m have been demonstrated as a promising material for a minimally-invasive platform for the delivery of molecular and cellular drugs. Despite their potential merits, however, conventional nanosheet technologies based on polymers such as poly(lactic acid) (PLA) and poly(lactic-co-glycolic acid) (PLGA) are yet limited by (1) the size of needle that injects nanosheet from syringe (maximum lateral size of 15 mm could be ejected from a 19G needle (inner diameter (I.D.) = 0.7 mm)), (2) the ability to expand after injection and (3) the ability to control the motion after injection. To address these limitations, we developed free-standing SMP nanosheets embedded with magnetic nanoparticles (MNP), termed MNP-SMP nanosheets. The
temperature-mediated shape memory effect (SME) of the SMP with the glass transition temperature ($T_g$) of 25°C provided following four capabilities to the 710-nm-thick MNP-SMP nanosheet; (1) syringe-injectability through the medical needles (a nanosheet with the lateral size of 15 mm could be ejected from a 20G needle (I.D. = 0.6 mm)), (2) self-expandability after injection to aqueous media, (3) conformability and removability on the biological surfaces, and (4) guidability in an external magnetic field. In addition, the MNP-SMP nanosheets were readily interfaced with an additional layer of PLGA to extend the functionality as a carrier of molecular and cellular drugs without compromising the demonstrated capabilities. The MNP-SMP nanosheets will contribute to the development of advanced syringe-injectable medical devices as a platform to deliver drugs, electronics, biological cells and engineered tissues to the specific site or lesion in the body for minimally invasive diagnosis, therapy and regenerative medicine.

**SB01.12.58**

**Cellulose/BaTiO$_3$ Nanocomposite Dielectric Films with High Energy Density**

Quanling Yang, Chenggang Zhang, Yanan Yin and Chuanxi Xiong; Wuhan University of Technology, China

Cellulose/BaTiO$_3$ nanocomposite films were fabricated by incorporation of BaTiO$_3$ nanoparticle (BTNP) or BaTiO$_3$ nanofiber (BTNF) in regenerated cellulose (RC) via simple blending in aqueous NaOH/urea solution. The results showed that a proper addition of BTNP or BTNF could improve the dielectric constant, breakdown strength, energy density of RC and reduce the dielectric loss simultaneously. Meanwhile, RC-BTNF composites exhibited better dielectric and mechanical properties than RC-BTNP. Especially, the RC-2BTNF composite film with 2 vol% BTNF exhibited an ultrahigh discharged energy density of 13.14 J/cm$^3$ at breakdown strength of 370 MV/m. Moreover, the discharged energy density of 9.45 J/cm$^3$ at 300 MV/m of RC-2BTNF is the highest discharged energy density of reported polymer-based dielectric films at 300 MV/m (close to actual electric field strength when film capacitors work). Therefore, these flexible cellulose-based dielectric materials are promising in the field of novel high-performance film dielectric capacitor.

**SB01.12.59**

**Temperature-Sensitive Hydrogels for the Local Delivery of Antibiotics**

Rong Yang$^1$, Michelle Calabrese$^2$, Bradley Olsen$^3$ and Daniel Kohane$^4$; $^1$Cornell University, United States; $^2$University of Minnesota, United States; $^3$Massachusetts Institute of Technology, United States; $^4$Harvard Medical School/Boston Children's Hospital, United States

Hydrogel with reverse thermal gelation has been an important tool in drug delivery. Some of them, such as poloxamer 407 (P407), have been approved by the FDA for various biomedical applications. Despite the clinical importance of P407, its assembly in the presence of therapeutics and other bioactive molecules was not well understood, deterring rational design and improvement of hydrogels and limiting their implementation in the clinical practice. We have bridged this gap by elucidating the effects of some molecules, which are commonly delivered using P407 (chemical permeation enhancers, antibiotics, and anesthetics), on the hydrogel gelation mechanism. We also charted a path forward to manipulating these interactions and thus rendering the gelation more robust in biomedical applications, achieved by chemical modifications to the polymer.

As a proof-of-principle, chemically modified P407 was used to treat otitis media (OM), the most common reason for antimicrobial prescription to US children. The current standard of care is a requisite 7-10 day course of oral antibiotics. The treatment is challenging to deliver in children, entails potential systemic toxicity, and encourages selection of antibiotic-resistant bacteria. Building upon the modified P407, we developed a drug delivery system which, when applied once to the tympanic membrane (TM) through the external auditory canal, delivers an entire course of antimicrobial therapy to the middle ear. The pentablock copolymer was designed to flow easily during application then form a hydrogel on the TM. Chemical permeation enhancers within the drug delivery system then assisted flux of the antibiotic ciprofloxacin across the TM. This drug delivery system successfully treated OM from non-typeable *Haemophilus influenzae* (NTHi) and *Streptococcus pneumoniae* in chinchillas. Biocompatibility was excellent, and ciprofloxacin was undetectable in blood, implying no systemic drug exposure in treated patients.

**SB01.12.60**

**Harnessing Kirigami Shells for Ultra-Thin Flipper-Like Soft Gripper**

Yi Yang, Katherine Vella, Peter Zink and Douglas Holmes; Boston University, United States
Harnessing soft materials and compliant structures to build robotic grippers has pushed the boundary in advancing robotic systems and materials science. Mimicking the morphology and grasping mechanisms found in biological systems has attracted tremendous attention in the design of soft grippers. Although hand morphology of primates inspired a variety of soft gripper designs, due to the complexity, bio-mimicking the thumb–index hand morphology is limited and challenging. In contrast to the hand morphology of primates, marine tetrapods, such as sea turtles, utilized their flipper-like articulating limbs to capture and manipulate prey. This simple posture for holding and pinching could be effectively achieved by utilizing the underactuated deformation of compliant structures, such as kirigami. In this talk, we present a novel design of an ultra-thin soft gripper that mimics the grasping posture of marine tetrapods using kirigami shells. Through a combination of mechanical modeling and experiments, we demonstrate the morphology and principle of grasping, and characterize the performance of the kirigami shell gripper by picking up a various objects with different shapes and examining the loading capacity. We find that the kirigami shell gripper can perform a variety of grasping tasks which cannot be easily accomplished by current soft gripper designs. The gripper is low-cost, scalable, ultra-thin, and ultra-lightweight with a payload to weight ratio of 270, and provides a novel approach to the design of soft robotic grippers.

SB01.12.61
3D Printing of Soft Responsive Structures Incorporating Stimuli-Responsive Microcapsules Seon Ju Yeo1, Sangchul Roh2 and Orlin D. Velev1; 1North Carolina State University, United States; 2Cornell University, United States

The design of inks for three-dimensional (3D) printing of actuatble structures is of importance since the principles of ink design have a great influence on the response and the general materials characteristics. Thus, creating new types of ink materials with a programmable response is an ongoing challenge. This study demonstrates a new class of stimuli-responsive inks for 3D printing containing microcapsules, which contain small droplets of an aqueous solution of water and glycerol in the core. Polydimethylsiloxane (PDMS) capsules are generated by using water-in-oil-in-water double emulsions as templates. PDMS microcapsules can swell in deionized (DI) water by the difference in osmotic pressure between the inner and the outer phases of the complex emulsions. The swelling ratio in DI water can be controlled by the ratio of water to glycerol in the inner phases, and it is closely related to the resulting mechanical properties of the composite materials. In addition, they exhibit shape memory behavior due to inhomogeneous swelling behavior of the composites. Subsequently, the generated PDMS microcapsules are connected to each other by capillary bridging with liquid PDMS precursor for use as 3D printing inks. The composition of the outer phases (i.e., with glycerol or without glycerol, the molecular weight and the concentration of the surfactants) is varied to understand the relationship between rheological properties and printing performance. Overall, by taking advantage of controlled swelling and shape memory behavior of composite inks containing osmotically sensitive capsules, complex architectures capable of actuating can be fabricated, which opens up new opportunities in soft robotics and stimuli-responsive materials.

SB01.12.62
Soft Artificial Tongue Detecting Astringency Jeonghee Yeom, Ayoung Choe and Hyunhyub Ko; Ulsan National Institute of Science and Technology, Korea (the Republic of)

A tongue is a soft muscular organ which is one of the most sensitive and flexible human body parts transducing vital chemical information for the survival and health. One of the unique functions of the tongue is perceiving astringency, which is resulted from the strong association of the ingested astringent molecules and saliva proteins covering the tongue. Previously, artificial tongues are presented based on the lipid/polymer membranes, human taste receptors, and stripped epithelium cells. However, these works are hardly emulating human tongue due to the low selectivity for the target tastes, bulky and rigid structures. Here, we present a soft artificial tongue mimicking the mechanism of the human astringency perception based on the polyacrylamide hydrogel containing mucin (MUC) as secreted protein and lithium chloride as electrolyte. The thickness of soft hydrogel layer is comparable with that of actual saliva layer (70-100 μm) on the tongue, enabling efficient absorption and diffusion of astringent compounds (tannic acid, TA). Moreover, a flexible artificial tongue is fabricated by the polymerization of soft astringent hydrogel on the polyethylene-naphthalate (PEN) film, exhibiting stable sensing performances even after bending. Our resistive-type astringent sensor exhibits wider sensing range (10 g/L–0.001 g/L) and lower threshold sensing concentration (0.001 g/L) compared with the panel tests and other evaluating methods such as potentiometry, turbidity, and tribology. In addition, the astringent hydrogel shows better selectivity (ΔI/Io) for the TA compared with the same concentrations (5 mM) of other tastants and derivatives of TA. Finally, as a proof-of-concept
demonstration, we fabricate the artificial tongue sensor array which can be utilized as a portable taste sensing pad for the taste mapping and wipe-and-detection performance.

**SB01.12.63**  
**Realization of Bio-Inspired 3D Structures by Deformation of Soft Structures** Jaekyoung Kim, Hyemin Lee and Hyunsik Yoon; Seoul National University of S&T, Korea (the Republic of)

In decades, there have been many efforts to study the superb functions of unique structures in Nature. Researchers have tried to fabricate the artificial structures inspired from moth eyes, lotus leaves, gecko’s feet, wings of Morpho-butterfly and developed nano-, micro- and hierarchical structures. However, most of the features in Nature have 3D structures and they show more sophisticated functionality such as high adhesion in a wet condition of octopus and robust oleophobic surfaces inspired from springtails. In this talk, I explained a simple method to realize 3D structures by using the structures deformed by the mismatch of volume expansion of two different materials. Furthermore, I demonstrate the functions of oleophobicity, adhesion in dry and wet conditions, etc.

**SB01.12.64**  
**Inkjet Printing of Latex Based High-Energy Microcapacitors** Fernando Torres-Canas, Jinkai Yuan, Isabelle Ly, Wilfrid Neri, Annie Colin and Philippe Poulin; Ctrde Recherch Paul Pascal, France

Micro-energy storage devices are appealing, and highly demanded for diverse miniaturized electronic devices, ranging from microelectromechanical system, robotics, to sensing microsystems and wearable electronics.[1,2] However, making high-energy microcapacitors with currently available printing technologies remains challenging. Herein, we show the possibility to use latex polyvinylidene fluoride (PVDF) as aqueous ink for making dielectric capacitors on the microscale. The dielectric properties of printed microcapacitors can be optimized based on a novel approach, i.e., mixing PVDF latex with polyvinyl alcohol (PVA) to realize dielectric organic nanocomposites. The PVA prevents the coalescence of PVDF nanoparticles and serves as a continuous matrix phase with high dielectric breakdown strength. While the well-dispersed PVDF nanoparticles serve as highly polarizable and isolated domains, providing large electric displacement under high fields. Consequently, a high discharged energy density of 12 Jcm⁻³ is achieved at 550 MVm⁻¹. [3] These printed microcapacitors demonstrate mechanical robustness and dielectric stability over time.


**SB01.12.65**  
**Formulation of Lightweight Cement-Based Materials for 3D-Printing in Warmer Climates** Lyn Zemberekci¹, Wael Ali Saeed Aldulaimi², Can Akaoglu¹, Hay Rotana³, Kemal Celik² and Ozge Akbulut¹; ¹Sabanci University, Turkey; ²NYU Abu Dhabi, United Arab Emirates

Recent developments have allowed for the layer-by-layer deposition or 3D-printing of cement-based materials, which promise i) a decrease in the total duration of a construction process and labor costs, ii) a customizable design, and iii) elimination of the use of formwork. Here we report a lightweight cement composite that contains cenosphere, white cement, and white silica fume to be used in 3D printing. We designed a poly(carboxylate ether)-based additive to enable the rheological control such that the mixture is i) 3D-printable—extrudable through a nozzle and can be layered successfully, ii) lightweight—resulting in a decrease in the total dead weight of the structure, iii) high-strength, and iv) thermally insulating, which is useful for warmer climates. This mixture, which contains a significant amount of recycled materials, was optimized with respect to its rheological and mechanical properties and we have reached high compressive strength up to 80 MPa and an 11.5 % reduction in dry hardened density. According to ACI, this formulation is classified as high performance (>55 MPa) and lightweight (320 – 1920 kg/m³).

**SB01.12.66**  
**Multifunctional Semi-Liquid Surfaces with Durable Liquid Repellency** Lei Zhang, Xianming Dai, Zongqi Guo and Jyotirmoy Sarma; The University of Texas at Dallas, United States

Liquid repellent surfaces have attracted broad interests in both fundamental studies and engineering applications.
The current state-of-the-art liquid repellent surfaces are centered on either superhydrophobic/superoleophobic surfaces (rely on air lubricant) or liquid infused surfaces (rely on liquid lubricant). However, these surfaces suffer from severe durability issues: air/liquid lubricant loss or topography damage. Here, we present a semi-liquid surface(s) (SLS) that shows ultralow contact angle hysteresis ($\leq 1.0^\circ$) to liquids with surface tensions in the range of 10-72.8 mN m$^{-1}$ including perfluorinated liquids like FC72 and Krytox101, as well as complex fluids like urine and crude oil. Such a surface is made by tethering a flexible polymer on a solid substrate with a one-step self-catalyzed grafting method. The mobile molecular chains of the flexible polymer behave as liquid-like lubrication on a solid substrate. The liquid repellency can be maintained after heating at 105 $^\circ$C for more than three months, as well as 1000 cycles of abrasion and adhesion tests. The SLS can be fabricated on various substrates, such as silicon, glass, and metals. We have demonstrated that the SLS, owing to its tethered mobile molecular chains, outperforms superhydrophobic surfaces and liquid infused surfaces in fog harvesting and self-cleaning under durable operations. Such a semi-liquid surface may open up new opportunities for scientific studies and engineering applications related to polymer, surface chemistry, wetting, adhesion, fluid dynamics, anti-biofouling, anti-icing and heat transfer owing to the exceptional liquid repellency and durability. It is anticipated that such a surface can be developed to meet emerging needs in energy efficiency, water harvesting, bio-adhesion, advanced heat exchangers, drag reduction, and other areas that are beyond the reach of existing liquid repellent surfaces. Therefore, it will be of great interest to interdisciplinary areas.

Reconfigurable Architectured Materials through Hybrid Design and Manufacturing

Pu Zhang, Fanghang Deng and Quang Nguyen; SUNY Binghamton, United States

Reconfigurable architectured materials exhibit tunable shapes and functionalities that are of great interest to modern engineering like aerospace, robotics, wave control, sensing, etc. Most of the reconfigurable architectured materials are composed of only single phases of materials with their shapes manipulated by external mechanical, thermal, pneumatic, electrical, and magnetic stimuli. In this presentation, we report a new type of reconfigurable architectured materials composed of two materials organized in a co-axial way. This hybrid design enables the architectured materials with thermal-tunable shapes and properties. The developed architectured materials are fabricated by combining 3D printing, molding, and coating. The mechanical properties and reconfigurability of these architectured materials are studied via experimental testing. We expect that this new type of dual-phase architectured materials will greatly expand the current realm of architectured materials and bring about novel functional applications.

Artificial Synaptic Behavior of Aloe Polysaccharides-Based Device with Au as Top Electrode

Zhe Xi Lim1, I. A. Tayeb1, Zuratul Ain Abdul Hamid1, M. F. Ain1, A. M. Hashim1, J. M. Abdullah1, Feng Zhao4 and K. Y. Cheong1; 1Universiti Sains Malaysia, Malaysia; 2Universiti Teknologi Malaysia, Malaysia; 3Universiti Sains Malaysia Health Campus, Malaysia; 4Washington State University, United States

Formulated, processed, and dried Aloe polysaccharides thin film sandwiched between ITO as bottom electrode and Au as top electrode has been adopted as an artificial synapse to emulate behavior of neuromorphic computing. The synaptic plasticity or weight has been modulated with this simple metal-insulator-metal structure by applying voltage sweep and voltage pulse, with excitatory postsynaptic current being monitored. Synaptic potentiation and depression has been demonstrated by applying 6 consecutive sweeps of voltage in positive and negative polarity, respectively. By varying number (10 – 50) of voltage pulses, variable synaptic weight has been measured with paired pulse facilitation and post-tetanic potentiation indexes of 4.38x10$^{-9}$ and 1.30x10$^{-6}$, respectively. The short-term plasticity and long-term potentiation can be clearly revealed when applying 40 pulses and beyond, with extracted time constants of approximately 28 s at 40 pulses and 90 s at 50 pulses.

Effective Reduction of Building Heat Loss without Insulation Materials via the Photothermal Effect of a Chlorophyll Thin-Film Coated “Green Window”

Yuan Zhao1,2, Andrew W. Dunn1,3, Jou Lin1, Enhe Zhang2, Julian Wang2 and Donglu Shi1; 1University of Cincinnati, United States; 2The Pennsylvania State University, United States; 3Cincinnati Children's Hospital Medical Center, United States

One of the critical components of energy savings in buildings is thermal insulation, especially for windows in cold
climates. The conventional approach mainly relies on a double-pane design. In this study, a new concept of “Green Window” has been designed for single-pane applications that lower the U-factor. The “Green Window” is structurally and simply composed of a thin film window coating of chlorophyll that exhibits pronounced photothermal effect, while remaining highly transparent. We demonstrate a new concept in “thermal insulation” via optical means instead of solely through thermal insulators or spectral selectivity. This concept lifts the dependence on insulating materials making single-pane window highly possible.

SB01.12.70
Photo-Regulated Motion for Solar Harvesting and Autonomous Locomotion Xiaoshi Qian, Yusen Zhao, Yousif Alsaid and Ximin He; 1University of California, Los Angeles, United States; 2California Nanosystems Institute, United States

Stimuli-responsive materials are a class of materials that can be implemented for robotics using power supplies. Particularly, photo energy has widely been used for generating motion due to the versatility, ubiquity and properties (wavelength, intensity, polarization) for optimization of precise spatial and temporal control. While many smart materials exhibit nastic behaviors in response to light, no synthetic material can intrinsically detect and accurately track the direction of stimuli, i.e., exhibit phototropic behaviors. Other than the phototropic in dynamic equilibrium state, self-sustained oscillation under constant stimuli have recently been reported in liquid crystalline networks system. However, no work can realize the self-sustained oscillation to generate locomotion due to its low operation force under damping environment. We, however, report an artificial phototropic actuator and a self-sustained oscillator by using the same light-sensitive hydrogel system. On one hand, the phototropic behavior of hydrogels can instantaneously aim to incident light in three-dimensional space over broad ambient temperatures. The array of phototropic pillars can successfully harvest solar energy for omnidirectional solar vapor generation, achieving high energy harvesting enhancement over non-tropistic materials by maintaining normal to oblique illuminations. On the other hand, the photo-triggered oscillation showcases large force and long-lasting properties. The photo-regulated soft-swimmer is further made by using the oscillation to self-propel away from light source, showing high-speed and controllable locomotion.

SB01.12.71
Oxidative Chemical Polymerization of Functionalized PEDOT:PSS Erjin Zheng, Priyesh Jain, Hao Dong, Zhiyin Niu, Emerson Chen and Qiuming Yu; University of Washington, United States

Poly(3, 4-ethylenedioxythiophene) (PEDOT) is one of the most successful conductive polymers. The commercial available PEDOT is synthesized by chemically polymerizing 3,4-ethylenedioxythiophene (EDOT) monomer in the presence of polyelectrolyte poly(styrene sulfonate) (PSS), giving the water-soluble PEDOT:PSS. Many applications of PEDOT:PSS have been developed such as solar cells, photodetectors, light emitting diodes, smart windows, biosensors, fuel cells, and wearable electronics. The conventional PEDOT:PSS, however, is lack of functionality. The functionality of PEDOT:PSS can be introduced by replacing the counterion PSS or adding a functional group onto the ethylenedioxy ring in the PEDOT backbone. In order to develop functionalized PEDOT:PSS using oxidative chemical polymerization method, it is crucial to understand the interaction between functionalized EDOT monomer, counterion, oxidant, and catalyst during the reaction.

In this work, we selected three monomers, EDOT, EDOT-methylhydroxyl (-MeOH) and EDOT–methylchloride (-MeCl), and polymerized them using oxidative chemical polymerization. We investigated the interaction between EDOT monomer, -MeOH and -MeCl functionalized EDOT monomer with PSS counterion and Fe^{3+} catalyst during the reaction. For EDOT, monomers and PSS formed micelles with monomers inside PSS shells when dispersed in water. The deprotonated, negatively charged PSS, due to adding an equal molar amount of KOH, attracted Fe^{3+} ions to the micelles, which preferentially polymerized EDOT monomers inside micelles. PEDOT polymers were mostly doped by PSS counterions, resulting in an aqueous soluble product. Adding less or no KOH led to partially negatively charged PSS and thus less attraction to Fe^{3+} ions to micelles. As a result, Fe^{3+} ions polymerized EDOT monomer both inside the micelles and in the water phase, where PEDOT polymers were doped by PSS and SO_{4}^{2-}, respectively. Final products were partially soluble in water. We characterized the thin film morphology, chemical structure, and conductivity of the PEDOT:PSS synthesized with different amount of KOH using AFM, Raman spectroscopy, and four-point probe measurement, respectively. The thin films of PEDOT:PSS synthesized with equal molar KOH to PSSH exhibited smooth morphology, quinoid structure dominated PEDOT backbones with linear-like conformation, and low conductivity of 9.06 × 10^{-4} S/cm. The thin films of PEDOT:PSS synthesized with less or no KOH exhibited rough morphology with large aggregates, benzoid structure dominated PEDOT backbones
with coil-like conformation, and gradually increased conductivity to the highest value of $1.76 \times 10^{-1}$ S/cm with no KOH added.

For functionalized EDOT monomers, the -MeOH group formed hydrogen bonding with PSS, which makes EDOT-MeOH monomers stay inside micelles or closer to PSS. However, EDOT-MeCl monomers tended to be away from PSS due to the electrostatic repulsion. Because of the high electronegativity of both types of the functional groups, the oxidative polymerization occurred with a triple amount of oxidant and catalyst, and no KOH added. PEDOT-MeOH polymers were mainly doped by PSS, yielding a water-soluble PEDOT-MeOH:PSS. However, PEDOT–MeCl were doped by PSS and $\text{SO}_4^{2-}$, resulting in a mixture of water-soluble PEDOT-MeCl:PSS and insoluble PEDOT-MeCl:SO$_4$ precipitates. PEDOT-MeOH:PSS thin films exhibited smooth morphology, quinoid structure dominated PEDOT-MeOH backbones with a linear-like conformation, and a conductivity of $1.17 \times 10^{-3}$ S/cm. PEDOT-MeCl:PSS thin films showed large aggregates on surfaces, benzoid structure dominated PEDOT-MeCl backbones with a coil-like conformation, and a conductivity of $4.71 \times 10^{-4}$ S/cm.

This study provides insights into the polymerization of EDOT with functional groups using the oxidative polymerization method and can be widely applied in designing the oxidative chemical polymerization reaction for synthesizing PEDOT:PSS based conducting polymers.

SB01.12.72
**Designing Hydrogel-Based Solar Evaporators for Seawater Desalination and Water Purification** Xingyi Zhou and Guihua Yu; The University of Texas at Austin, United States

Hydrogel materials with unusual physical/chemical properties are becoming critically important in a wide range of applications from electronics, biomedical devices, renewable energy to environmental technologies. To enable significantly improved or even unprecedented properties, the chemical composition, micro/nanostructures and physical interactions of hydrogel materials need to be delicately controlled. Here we will present our representative works on rational design and molecular engineering of hydrogels and their applications in solar powered water purification. We designed hybrid hydrogels composed of a hydrophilic polymer framework and solar absorption materials to harvest solar energy and remove contaminants. By tuning the micro/nanostructures and chemical/physical interactions between components, the hybrid gels exhibit attractive synergistic characteristics including high solar absorption, reduced energy demand for water evaporation, fast water transport, effective thermal management and antifouling property. I will also discuss our latest work on architecting the highly hydratable polymer networks to tune the water state, activating water molecules and facilitating water evaporation. These works provide fundamental design principles regarding material selection, molecular engineering and structural modification of these emerging hydrogels for the development of next-generation solar evaporators for seawater desalination and water purification.

SB01.12.73
**Development of a Facial Thermal-Releasing Drug Delivery Gold Nanoparticles under Ambient Conditions** Jun Zhu and R. B. Lennox; McGill University, Canada

The emergency of nanotechnology has a profound impact on clinical therapeutics recently. One promising candidate is using gold nanoparticles, which has unique optical property, low toxicity, and in vivo stability. Previous researches are focused on using gold nanoparticles as a drug carrier. In this talk, a thermal labile drug delivery linker is developed, using an endo/exo adducts from furanic and maleimide derivatives, and incorporated onto a model gold nanoparticle surface for drug delivery/releasing. Model drug loads can be effectively released at physiological temperature when endo- linker is applied via a retro-Diels-Alder reaction (rDA). In addition, second-stage controllable temperature dependent drug release can be achieved at elevated temperatures through the rDA of exo-linker. This drug delivery strategy has promising applications for the development of novel drug-delivery and thermal triggered drug releasing. This methodology can be easily extended to other nanomaterials.

SB01.12.74
**Biomimetic Nanoemulsions as a Blood Substitute for Oxygen Delivery In Vivo** Jia Zhuang, Ronnie Fang and Liangfang Zhang; University of California, San Diego, United States

Blood transfusion is oftentimes required for patients suffering from acute trauma or undergoing surgical procedures in order to help maintain the body's oxygen levels. The continued demand worldwide for blood products is expected to put significant strain on available resources and infrastructure. Unfortunately, efforts to develop viable
alternatives to human red blood cells for transfusion have generally been unsuccessful. Herein, a hybrid natural–synthetic nanoemulsion platform is developed which combines the biocompatibility of natural red blood cell membrane with the oxygen carrying ability of synthetic perfluorocarbon. By coating perfluorocarbon emulsion with red blood cell membrane through a facile process, the resulting biomimetic nanoemulsion could serve as a more stable and easy way to store and mimic red blood cells for transfusions. Specifically, the nanoemulsion can be stored for over three months at room temperature and exhibits a high capacity for oxygen delivery, helping to mitigate the effects of hypoxia. In an animal model of hemorrhagic shock, mice are resuscitated at an efficacy comparable to whole blood infusion. Furthermore, uncompromised biosafety profiles with pronounced biocompatibility and minimal immunogenicity are demonstrated owing to the incorporation of red blood cell membrane. By leveraging the advantageous properties of its constituent parts, this biomimetic oxygen delivery system may have the potential to address critical needs in the clinic, especially in places that lack ideal storage conditions, such as remote villages and the battlefield. In general, this biomimetic oxygen delivery system could be a robust candidate for next-generation blood substitute, as well as a versatile platform for a variety of biomedical applications such as ultrasound imaging and photodynamic therapy upon further functionalizations.

SB01.12.76

Molecularly Engineering One-Dimensional Assemblies of Optoelectronic Peptide Nanostructures Herdeline Ardona1, Tejaswini Kale2, Zhe Qi3, Christopher Stanley4, Christopher Jaroniec3 and John D. Tovar2; 1Harvard University, United States; 2Johns Hopkins University, United States; 3The Ohio State University, United States; 4Oak Ridge National Laboratory, United States

The applications of functional supramolecular assemblies continue to expand into a broad range of fields, such as from electronics to tissue engineering. The proper molecular design of monomers for such assemblies can enable the rational engineering of their macroscale material properties. Here, studies on systematically controlling the coassembly behavior and corresponding functional heterostructures formed by pi-conjugated peptidic monomers under completely aqueous conditions will be presented. The influence of (i) local fields due to the flanking peptide moieties, (ii) torsional constraints within the central pi-system core, and (iii) lengths of peptide monomers on assembly behavior were studied using photophysical investigations, solid state NMR (ssNMR) and small-angle neutron scattering (SANS). Our results show that within the coassembly volume of peptide-pi-peptide and peptide-alkyl-peptide triblock monomers, a hydrophilic tripeptide sequence (Asp-Asp-Asp, DDD-) sequence promoted isolation/dilution of minority pi-electron components in the matrix of aliphatic peptides, while a beta-sheet promoting sequence (Asp-Val-Val, DVV-) led to blocks of the two components distributed within larger 1D-nanostructures. To demonstrate that torsional constraints within stacked pi-units may affect the overall nanostructure formation, we used quaterthiophene units with inherently different geometries: relatively planar 2,2':5',2''-quaterthiophene (OT4) and twisted 3',4'-dimethyl-2,2':5',2''',5''',2'''-quaterthiophene (OT4dM). The peptides bearing dimethylated quaterthiophene units showed spectral signatures which suggest minimal interchromophore exciton coupling due to perturbed pi-stacking. Finally, ssNMR and SANS characterization of the polymorphic coassemblies suggest that peptide length matching between the monomer components of peptide heterostructures can affect the degree of co-mixing or self-segregation within the nanostructures formed. These insights on structure-property relationships and assembly principles for optoelectronically-active peptide nanomaterials contribute towards developing more innovative strategies for molecularly designing functional regenerative scaffolds for electrically-active cells, such as neurons and cardiomyocytes.

SB01.12.77

Multiple Tridimensional Janus Peptide Dendrimers with Manipulable and Dramatic Multivalency Uimin Hwang, Sung-ju Choi, Soo Hyun Kwon and Yong-beom Lim; Yonsei University, Korea (the Republic of)

The self-assembly of peptides facilitates the construction of self-assembled peptide nanostructures (SPNs) with chemical composition analogous to those of natural proteins; nonetheless, the structural complexity and functional characteristics of SPNs are far different than those of natural proteins. One of the most fundamental challenges in fabricating more exquisite SPNs lies in developing building blocks that are simultaneously more complex and comparatively easy to synthesize. In this poster, the development of self-assembling Janus peptide dendrimers is reported, which have fully tridimensional structures akin to those of globular proteins. For the trustworthy and convenient synthesis of JPDs building blocks, a solid-phase bifurcation synthesis system is devised. The self-assembly behavior of Janus peptide dendrimers is unique because only the generation of dendrimer and not the weight fraction determines the morphology of SPNs. The co-assembly of two JPD building blocks presents an
opportunity not only to enlarge the morphological repertory in a foreseeable manner but also to discover SPNs with uncommon and interesting morphologies. Because JPD assemblies have dual multivalent property, i.e., supramolecular and unimolecular multivalency, the JPD system facilitates the statistical selection of materials with great avidity for the possibly any target receptors and desired cell types.

SB01.12.78
Preparation of Bioactive Glass-Calcium Phosphate Composites and Evaluation of Their Biodegradation in SBF Zivile Stankevičiute, Gabija Zarembaite, Laurynas Alinauskas, Lauryna Sinusaite, Aleksej Zarkov, Edita Garskaite and Aivaras Kareiva; Vilnius University, Lithuania

Biomaterials for bone repair receive considerable attention worldwide and the global bone grafts and substitutes market is projected to grow over forthcoming years. Bioactive glasses (BGs) are group of biomaterials which show relatively fast dissolution after the implantation. BGs are generally based on various oxides containing calcium, sodium, phosphorous, and silicon. Calcium hydroxyapatite (Ca10(PO4)6(OH)2, HAP) – a biomaterial of calcium phosphates (CaPs) group – is similar to the main inorganic constituent of bone and teeth tissue. Synthetic HAP is applied in constructing artificial bone grafts for long-term usage and drug delivery systems. Contrary to the BGs, the crystalline HAP has the slowest degradation rate compare to the other CaPs.

The fundamental properties of bone grafts are osteogenesis, osteoinduction, osteoconduction, and structural support. Therefore, in this work the synergy between BGs and CaPs as a potential materials for bone scaffold engineering was studied. Herein, BG composed of Na4Ca4(Si6O18) and NaCaPO4 phases was synthesized by a sol-gel method at 700 °C. This semi-crystalline BG was then homogeneously mixed with HAP and pressed mechanically to cylindrical-shaped specimens. Bioactivity of prepared BG-HAP composites (wt% relations of BG:HAP were 100:0, 75:25, 50:50, 25:75 and 0:100) was studied in vitro for 1, 3 and 7 days at 37 °C in a simulated body fluid (SBF). The amount of elements after the dissolution was determined using ICP-EOS technique. Morphological features and elemental distribution of a newly-formed ceramic layer on the BG-HAP composites were evaluated using SEM-EDS. XRD and FTIR spectroscopy analyses revealed the rapid phase transformation of bioactive glass to the amorphous carbonated calcium phosphate upon exposure to a SBF solution. It was also shown that substance dissolution rate and topography of newly-formed ceramic layer depends on the wt% of the bioactive glass. Results indicated that BG-CaP composites produced via biomimetic processing route have potential for the exploration of broader range material properties in the field of regenerative medicine. In order to resemble bone implants as closely as possible the biomimetic bone apatite the coatings of these BG-CaP composites would be very promising for application to bone implants.

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SB01.12.79
Preparation of Antibacterial Hybrid Hydrogels of Polysaccharides (Sacran/CNF) Gargi Joshi, Qiang Han, Maiko K. Okajima and Tatsuo Kaneko; Japan Advanced Institute of Science and Technology, Japan

Hydrogel-type wound-dressing materials require strength and water absorbability appropriate for applying to the injury. However, control of the water absorbability, water retention degree, and mechanical strength of the materials are very important for this application. In this respect, our group is studying cyanobacterial exopolysaccharide, sacran. It has an ultrahigh molecular weight over 10 MDa, high water-retention capability, and anti-inflammatory properties. We have adjusted properties by hybridizing sacran with cellulose nanofibers (CNF) with varying the ratio of sacran:CNF solution. The solvent-casted hybrid films were macroscopically homogeneous and easy to handle. The Young’s modulus of the hybrid film increased with increasing the content of CNF. By thermally annealing by films, physically-crosslinked gel matrices were prepared which showed high swelling ratios. To impart these films with antibacterial properties, aminated silver nanoparticles were synthesized and incorporated in the hybrid solution before solvent casting. The prepared nanocomposite dressing showed high antibacterial activity against both gram-negative and -positive bacteria.

SB01.12.80
Voxelated Molecular Patterning in Three-Dimensional Freeforms Mohsen Tabrizi1, Taylor Ware2 and M. Ravi Shankar3; 1University of Pittsburgh, United States; 2The University of Texas at Dallas, United States
In recent years, there has been an increasing interest in smart structures that can be manipulated by utilizing ambient stimuli. Liquid crystalline polymer (LCP) is, in particular, an interesting candidate for making these structures due to the ability to reversibly generate large work densities through changing the molecular order. The ability to pattern the molecular director enables us to program the shape morphing behavior of LCP structures. In this study, we exploited the combination of anisotropic magnetic susceptibility of the LC monomers and spatially-selective photopolymerization approach by utilizing a digital micromirror device (DMD) in an inverted (bottom-up) 3D printing configuration to fabricate LCP structures at scales ranging from the micro to the macro-scale. This gives us a level of flexibility to vary the orientation of the nematic director in all three dimensions (within and between layers), which is not possible with other methods. We developed and optimized different compositions that can be used for printing light and/or heat responsive structures. This platform enables us to modulate the composition and integrate responses to multiple stimuli. We demonstrated this by building a multi-responsive robotic arm that can deform in two different directions independently, in response to light and heat. The proposed fabrication method breaks out the confines of prior approaches and extends the applications of liquid crystalline polymers in the field of soft robotics, biomedical devices, and optomechanical systems.

**SB01.12.81**

**High-Resolution Electrical Probes with Single Nanoparticle Pick-Up Resolution** Eugene Soh, Benjamin Porter, Judy Kim and Harish Bhaskaran; University of Oxford, United Kingdom

Single particle manipulation opens up the possibility to create new device structures and experimentally test new physics that are currently only possible through computer simulations [1]–[3]. Currently, atoms have been precisely manipulated in a scanning tunnelling microscope at low temperatures and high vacuum [4]. Microparticles are usually manipulated with optical tweezers [5] and microgrippers [6]. However, it becomes increasingly difficult and complicated to manipulate particles in the nanoscale regime, especially in ambient conditions. Most methods use a combination of pushing and pulling of particles on a surface with an atomic force microscope (AFM) [7]. For three dimensional pick up, electric fields have been used [8]. However, clusters of particles are picked up irrespective of probe size or voltage used due to stray fields which extend beyond the probe’s tip.

In this work, we manufacture high resolution AFM probes in-situ through nanoscale phase switching of configurable thin films coated probes. These configurable coatings are germanium-antimony-tellurium (GST) and amorphous-carbon; materials known to undergo electric field-induced non-volatile switching. By forming localized conductive filament(s) through phase transition, we are able to confine the electric field to a nanoscale region at the probe apex. And by using dielectrophoresis, we demonstrate the picking up of nanoparticles with single particle resolution. This results are a promising start to developing a truly three dimensional pick and place technique at the nanoscale in ambient conditions.


**SB01.12.82**
Ultraviolet-C Persistent Luminescence in Pr\textsuperscript{3+}-Activated Silicates

Xianli Wang\textsuperscript{1}, Yafei Chen\textsuperscript{1}, Feng Liu\textsuperscript{2} and Zhengwei Pan\textsuperscript{1}; \textsuperscript{1}University of Georgia, United States; \textsuperscript{2}Northeast Normal University, China

Visible-light and infrared-light persistent phosphors have been extensively investigated and are being widely used as self-sustained glow-in-the-dark tags in darkness. However, persistent tags working in bright environments (daylight and artificial light) are not available. Here we report a persistent phosphor, Pr\textsuperscript{3+}-activated strontium yttrium cyclosilicate, that emits broadband persistent luminescence at solar-blind ultraviolet-C (UVC: 200–280 nm) spectral region. The UVC persistent phosphor can be effectively charged by a standard 254 nm lamp and emits intense, long-lasting afterglow (>12 h) at ~270 nm. The UVC persistent luminescence is easily distinguishable from the ambient light (daylight and artificial light) via a corona camera and can be used as self-sustained glowing tags in bright environments. This is the first use of persistent phosphors in bright environments.

Surface Morphing of Geometrically Patterned Active Skins

Yujin Park and Kenneth J. Loh; University of California, San Diego, United States

The design of high-performance surfaces and structures has been inspired by many nature’s creations, such as shark skins with minimal drag coefficients, self-cleaning hydrophobic lotus leaves, and dry adhesives on a gecko’s feet. In addition, recent advancements in additive manufacturing have opened new opportunities for fabricating unprecedented, multi-scale, architected materials with unique properties. However, most of these architected materials only focus on enhancing a specific material property or functionality. This limitation highlights the difficulty of controlling the individual architected units, as well as the surface topology of architected materials. This study introduces a new class of instability-induced morphable structures, which is within the scope of mechanical metamaterials that exhibit unique functionalities by harvesting their extrinsic instabilities. Herein it is referred to as Active Skins, which enables on-demand, reversible, surface morphing through buckling-induced out-of-plane feature deployment activated by in-plane loading. By taking advantage of a preconceived auxetic unit cell geometrical design, mechanical instabilities were introduced to induce out-of-plane deformations when in-plane strains are applied. Here, geometrical imperfection, or notches, were introduced at judiciously chosen locations in an array of 3D-printed and connected unit cells for eliciting unique patterns of out-of-plane deformations and for controlling bulk Active Skin behavior. These purposefully designed imperfections were employed for facilitating full out-of-plane shape morphing with lower applied tension as compared to unnotched Active Skins, as well as selectively actuating them for applications ranging from camouflage to surface morphing to soft robotic grippers.

Oxytocin-Derived Metal Ion Biosensors

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Peptides are commonly used as recognition elements for biosensing. These peptides are usually attached to surfaces as label-free recognition ligands by multistep processes. The outcome of these tedious processes is a modified peptide that, in many cases, doesn’t preserve many of its features. Using functional groups in native peptides for their assembly on surfaces without affecting their biological activity can facilitate the preparation of biosensors. Herein we present several strategies to modify gold surfaces with peptide layers. Exposure of modified surfaces to metal ions induces conformational changes in the peptide layer and thus can affect the electronic and electrochemical properties of the device. We used this phenomenon for biosensor design. Our approach utilizes the neuropeptide Oxytocin which is a known native metal ion chelator. While one functional group is used to anchor the peptide to Au surface, the peptide still preserves the ion-binding properties. The chelation event was monitored using various electrochemical methods and surface chemistry analysis and supported by theoretical simulations.

Liquid Layer Generator with Excellent Dynamic Icophobicity at Extremely Low Temperature

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Ice formation and accretion on road, aircrafts, electrical transmission cables, wind turbines et al can cause huge
problems. A large amount of human source and energy are required to clear ice away. Therefore, designing and deploying material surfaces that can remove ice easily is in great demand. State-of-the-art icephobic surfaces fail at low temperature reaching a threshold of around -50 °C, which can lead to multiple orders of magnitude increase in ice adhesion strength. Strategy for such low temperature is missing, which is critical for the ever increasingly important Arctic area. In this work, with the combination of theoretical and experimental studies, a new strategy, termed liquid layer generator (LLG), were designed and fabricated targeting low ice adhesion strength at unprecedentedly low temperature. The molecular dynamic simulation firstly predicted the great potential of using ethanol as lubricating layer in lowering ice adhesion under extremely low temperature. The carefully designed LLGs were able to constantly release interfacial ethanol that convert ice contact from firm solid-solid to weak solid-liquid-solid mode for more than 250 days, and demonstrated super low ice adhesion strength of ~1 kPa. The liquid layer generator can also overcome the challenges of rough surfaces and surface hydrophilicity, and survive at temperature of down to -60°C, showing great potentials for practical applications.1,2

References:

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Non-Equilibrium Morphologies in Stimuli-Responsive Gels Subjected to Topographical Confinement Cathy T. Zhang1, Ya Liu2, Cindy Wang3, Xiaoguang Wang4, Stefan Kolle1, Anna C. Balazs2 and Joanna Aizenberg1; 1Harvard, United States; 2University of Pittsburgh, United States; 3Opalux, Canada; 4Ohio State University, United States

Stimuli-responsive "smart" polymers have generated significant interest for introducing temporal control into the properties of antifouling coatings, smart membranes, drug capsules, switchable adhesives and cell manipulation substrates. Switchable surface morphologies formed by confining stimuli-responsive gels to topographically structured substrates have shown potential for a variety of interfacial applications. However, to date, most studies have focused on exploring the equilibrium morphologies that can be obtained from such materials. We conduct a detailed investigation into the non-equilibrium morphologies that emerge from a composite surface consisting of a temperature-responsive gel cured to a bumpy substrate as it is heated along different heating paths. Through harnessing non-equilibrium behavior in this hybrid, temperature-responsive surface, we can control the assembly kinetics of colloidal particles and microalgae. Confining stimuli-responsive gels to topographically-structured surfaces not only enables temperature-programmable control over the local curvature of the surface, but could also introduce temperature path-dependent dynamics into actutable antifouling, cell manipulation, and liquid manipulation surfaces.

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Liquid Crystal-Based Composite Materials for Neuromorphic Applications Ik-Jyae Kim, Min-Kyu Kim, Youngjun Park and Jang-Sik Lee; Pohang University of Science and Technology, Korea (the Republic of)

Recently, neuromorphic electronics has attracted much attention as a candidate to overcome the von Neumann bottleneck, due to its energy-efficient and smart data processing ability achieved by the massive parallelism and fault-tolerant properties. While much attention has been paid on neuromorphic electronics, artificial synapses that can exploit diverse synaptic functions are still desirable for bio-realistic neuromorphic electronics, as complex biological functions often require cooperative effects of synaptic functions. Here, we demonstrate liquid crystal-carbon nanotube composites as a resistive switching material that can serve as an active material for artificial synapse. The artificial synapse based on liquid crystal-carbon nanotube composite showed resistive switching characteristics with long retention time by its unique resistive switching mechanism, which is electric-field driven carbon nanotube alignment and aggregation. By properly modulating the stimulation pulse and device structure, diverse synaptic functions such as analog switching, homosynaptic potentiation, heterosynaptic potentiation, and heterosynaptic facilitation were emulated. Moreover, synaptic weight normalization, which is an essential synaptic function in the biological brain, was also emulated by tuning the synaptic plasticity using a modulatory electrode. Artificial synapses that exploit multi-functionality of liquid crystal-carbon nanotube composites will offer a new possibility for uses in next-generation neuromorphic devices.
In Vitro Antimicrobial Activity for Bone Repair Scaffolds Formed by 3D Printing in β-TCP and Borate Bioglass—A Comparison between Autocombustion and Sol-Gel Routes
Carlos Paucar, Natalia Jaramillo, Isabel Moreno, Niza Otero, A. Peláez-Vargas and Claudia P. Garcia; Universidad Nacional de Colombia, Colombia

Pathologies such as dental demineralization, dental resorption, and root canal treatments have a high impact on dentistry. The use of ceramic materials such as calcium phosphates and bioglasses with adequate characteristics of size, porosity, degradability, and compatibility are a suitable option for their solution. Nevertheless; Due to oral lesions, it is necessary to contemplate the behavior of these materials against pathogens oral. These effects can be diminished by doping the ceramic material with elements that have an essential role in bone repair and / or regeneration and that also have an antimicrobial effect, such as magnesium (Mg). Doping also has an effect on the process of reabsorption of the material due to the release of ions.

Here, the antimicrobial activity of two types of ceramic materials was studied, borate bioglass (BGb) obtained via sol-gel and Auto-combustion within the X B2O3 [100-X] system (61SiO2 9 P2O5 30CaO) and of calcium phosphate (β-TCP) with 5% by weight of magnesium (Mg) obtained via Auto-combustion. The characterization of ceramic powders was obtained by X-ray diffraction (DRX) and Infrared Spectroscopy (FTIR). Biological characterization includes an antimicrobial activity of borate bioglass (BGb), β-TCP and β-TCP with Mg+2 (5% by weight), this was evaluated against Streptococcus mutans (ATCC25175) and Candida albicans (ATCC90028) strains and its coculture through the technique of disk diffusion and growth curves in the presence of biomaterials. X-ray diffraction for the bioglass indicates crystalline phases associated with doping with Boron, corroborating the obtaining of a semicrystalline (ceramic) material. The FTIR shown a form associated with the crystallization of β-TCP according to the vibrating bands of calcium phosphates (PO4)³⁻, in addition, the intensity related to Al-OH, Mg-OH, is reduced. The in vitro growth inhibition shown better antimicrobial efficacy of (BGb) obtained by self-combustion than BGb by sol-gel. Against a concentration of 1x10⁸ UFC/ml of C. Albicans, β-TCP without doping had a better effect than β-TCP with Mg. The results that the use of ceramic materials is promising as devices in bone regeneration.

Computational Modelling of Electrical Discharge Machining (EDM) for Tuning Surface Roughness and Curvature
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Electrical Discharge Machining (EDM) is a processing method to create rough surfaces on metallic substrates. The surface is modified by recurring current discharges between an electrode and a substrate separated by a dielectric. The extent of roughness is dependent on the applied current and the distance between electrode and substrate. The process of EDM provides a stochastic method for creating a randomly generated surface. In order to phenomenologically understand how such certain topographies are generated and what surface parameters may change, a predictive model was created for further understanding.

The model assumes that impacts on an arbitrarily sized surface are stochastic and independent of previous impacts. The underlying shape change during the process was deemed most crucial, thus heat transfer and surface charge were not taken into account. A number of input parameters such as number of impacts, size of impact, depth of impact, volume fraction were chosen. Subsequently, Abbott-Firestone curves were used to evaluate both surface roughness and surface curvature. In addition, equilibria for a given set of parameters were determined – i.e. a surface reaches its final form and undergoes no further significant topographical change.

For each iteration a point was randomly chosen as the point of impact. Subsequently the surface was deformed according to an ellipsoid-torus model for crater formation, which was based on a previously reported model of Micro Wire Electrical Discharge Machining (Micro-WEDM). A fraction of the removed volume was used to form the torus ridge surrounding the crater. This process is then repeated for the given number of impacts. The script for the modelling was written in Python 3.7 with packages NumPy for algebraic calculations and CUDA libraries for parallelization were used for faster computation:

The application of such a computational model may be useful in predicting how a surface is deformed, and what input parameters to use to create a surface with certain desired surface function. Future improvements of the model may include volumetric changes, surface charge and heat transfer.
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Multicomponent Soft Material Far from Equilibrium Self-Assembly for Functional Systems
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The self-assembly of cationic gelator molecules can be controlled by the composition of the solvent used for their formation. In these water-ethanol media, the dominance of enthalpy or entropy of formation leads to fibres of very different morphology but identical fibre structure. The route used to make these fibres and the resulting gels can be exploited to incorporate functional molecules - such as drugs for controlled release, dyes for singlet oxygen generation, or molecular switches for responsive materials - in a simple ion-exchange and solvophobic driven assembly route. Emergent properties are seen as a result of this new assembly method. The enhancement of singlet oxygen generation by a chromophore localised precisely in the fibres is observed, and the positioning of the fluorescent molecule determined using a unique method for this kind of material. Also, new results will show a three-component system containing dye and photoswitch, wherein the fibres that are formed by the gelator undergo dramatic changes in their morphology upon irradiation. All components of the system are necessary for the response to light to be observed.

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First Results of the Mucosa Reconstruction in an Animal Model with a Polymeric Implant Material
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The availability of polymeric biomaterials, whose properties and function can be adjusted to fulfill the anatomical, physiological and surgical requirements, facilitate the development of novel therapeutic options in different medical fields. Recently, multifunctional polymeric biomaterials were designed, which shall modulate regeneration in soft tissue. The increasing number of HPV- (Human Papilloma Virus) induced carcinoma of the upper aerodigestive tract in younger patients requires therapeutic strategies with reduced functional loss concerning verbal communication and deglutition. Both are distinctly reduced in case of a pharyngeal reconstruction by myocutaneous flaps. The reconstruction of the pharynx with a polymeric biomaterial would be a novel therapeutic option in oncological Head and Neck Surgery especially when a fast and complete integration of the material in surrounding tissue would minimize the risk for pharyngeal fistula.

Results
The surgical procedure and the postoperative course were without complications in all animals of the implantation and control group (n=63). Gastrointestinal complications like fistula, perforation or peritonitis did not occur in any animal of the implantation group (n=42) and the control group (n=21). A liquid- and gas-tight anastomosis between the copolymer network and the adjacent stomach wall existed in all animals of the implantation group. The intragastric pressure was measured after explantation of the stomach with maximal dilatation of the stomach by air insufflations in order to test the impermeability between the implant material and adjacent gastric wall. The measurement of the intragastric pressure did not show statistically significant differences between the implantation, the control and the baseline group after 1 week, 4 weeks and 6 months. To investigate systemic responses to inflammation leucocytes and acute-phase proteins α1 -acid glycoprotein (AAG) and Haptoglobin were determined at the different times. No statistically significant differences were found in the number of leucocytes and the concentration of AAG and Haptoglobin between the implantation and control group after 1 week, 4 weeks and 6 months.

Discussion
Pharyngocutaneous fistulas are a serious complication after surgical oncological procedures in Head and Neck Surgery, leading to a severe adverse impact for the patient and social activity. Oncological goals cannot be reached when a radiation therapy cannot be started because of pharyngocutaneous fistula. In this model the mortality of the gastric breakdown of the degradable copolymer network and/or sutures and fistula implying local or generalized peritonitis are comparable to the mortality of insufficiencies and salivary fistula of the pharynx. The adequate chemical, enzymatical, bacterial and mechanical stability of the polymeric material was shown under the extreme conditions of the stomach. The impermeability between the implant material and adjacent gastric wall, the missing
gastrointestinal complications and the concentration of the leucocytes and acute-phase proteins suggest that the polymer network did not induce impairment of the wound healing rather support the tissue regeneration. In further investigations, the mechanisms of the integration of the biomaterial in surrounding tissue as well as the degradation of the polymer and the process of the tissue remodeling should be analyzed. Especially, the correlation of the concentration of AAG and Haptoglobin with intraperitoneal cytokines levels should be investigated.

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Para-Aramid Nanofiber Sheets—Overcoming the Trade-Off between Mechanical and Thermal Protection
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Extreme environments require simultaneous protection from multiple threats. For example, astronauts need space suits that can provide both thermal and fragmentation protection to survive in these harsh environments while in outer space. These suits are traditionally made up of several layers of materials working in concert with one another to provide multiple modes of environmental protection. Chief among these are aramid-based compounds, such as Kevlar and Nomex, which were used in the Apollo missions to provide fragmentation and thermal resistance respectively. However, one result of using multiple protection layers is that spacesuits are often complex, and bulky. One way to potentially avoid this is by incorporating multiple functionalities into a single material layer. However, this incorporation is traditionally difficult to achieve in high-performance para-aramid fibers due to a trade-off in protective properties. For example, mechanical protective para-aramid Kevlar fibers are an order of magnitude higher than the thermal insulating meta-aramid Nomex but have orders of magnitude lower thermal insulation. To overcome this trade-off, we hypothesized we could combine the mechanical properties of continuous fibers with the thermal properties of porous aerogels by manufacturing a porous network of aligned fibers with a fiber diameter an order of magnitude smaller than commercial high-performance fibers. Choosing a para-aramid polymer as the base building block due to its high mechanical properties, we spun para-aramid solutions using the recently developed immersion Rotary Jet Spinning platform to fabricate our goal structural material. To ensure continuous fiber formation, we engineered the precursor solution to be fluid like during fiber spinning and solid like during fiber formation. This precursor solution allowed for the fabrication of porous, continuous fiber sheets with diameters and single fiber mechanical properties an order of magnitude lower than commercial para-aramid but had a higher sheet insulation value. With these synergistic properties, the nanofibers sheets act as a multifunctional material that can provide personal protection not only to astronauts but also for those exposed in other extreme environments such as firefighters and warfighters.

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Multifunctional Silk Biomaterials for Bioinspired Electronics
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Bioinspired materials provide exciting opportunities to develop physiologically compliant bioelectronic systems and scaffolds for tissue regeneration. They can serve not only as the structural, but also as the functional components of such devices. Functional bio-composites with properties of mechanical robustness and flexibility, transparency and importantly, biocompatibility and biodegradability provide a unique palette of properties for biointerfaceing sensors and electronics. Previously, our group demonstrated photopatternable silk inks that can be combined with the conducting polymer PEDOT:PSS to form high resolution microstructures, and flexible micropatterned surfaces.[1-3] We further demonstrated electroactive coating materials for conventional electrodes, flexible electrodes, biosensors, and energy storage devices.[4-7] In recent work, we have been able to successfully fabricate multifunctional designs of this biomaterial leading to engineered elastic behaviors and out-of-plane deformations [8]. This has been facilitated by the use of kirigami inspired cuts in silk films. This biodegradable and biofunctional silk kirigami is mechanically flexible, free-standing, and optically transparent, with precisely defined microscale cuts that can be easily formed using a single-step photolithographic process. We will discuss how, as composites with conducting polymers, intrinsically electroactive, stretchable, and flexible biomaterial sheets can be formed. The silk-kirigami sheets are biocompatible, can serve as substrates for cell culture, and be proteolytically resorbed. The unique properties of the kirigami suggest
a host of applications as transient, “green”, functional biointerfaces and flexible bioinspired electronics.

References:

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Morphology, Growth and Defect Dynamics in Cylindrical Colloidal Crystals Nabila Tanjeem, William Wilkin, Christopher Rycroft and Vinothan N. Manoharan; Harvard University, United States

Curvature and topology of a substrate have significant impact on crystal morphology and growth dynamics. For example, it is well known that a crystal that grows on the surface of a sphere incorporates topological defects and closure catastrophe. Topological defects arise due to the Gaussian curvature of the sphere. Closure catastrophe, in which accumulation of defects prevents the crystal from growing, arises due to the finite size of the sphere. To distinguish between the effects of Gaussian curvature and closure catastrophe, we study crystallization on the surface of a cylinder.

A cylinder has a zero Gaussian curvature, but a finite circumference, which requires a crystal to loop back on itself and be content with closure. Cylinders with certain diameters can accommodate a perfect crystal around their circumference. These crystals emerge with different chirality depending on the diameter of the cylinder. Common examples of this type of chiral structures are Carbon nanotubes. Cylinders with other diameters, which fail to accommodate a perfect crystal, satisfy the closure constraint by either incorporating asymmetry in the crystal structure, or by incorporating a line-slip defect. In previous work, it was predicted that line-slip defects satisfy the maximum packing condition in case a perfect crystal fails to form (A. Mughal, PRL, 2011).

We design an experiment in which colloidal spheres with an average diameter of 700 nm self-assemble to form a crystal on the surface of a tapered optical fiber (diameter range 1.5 μm– 5.5 μm). The crystallization is driven by a short-ranged depletion interaction. We observe crystals with different chirality; this observation is consistent with previous theory and experiment on cylindrical crystals. We observe line-slip defects with different chirality as well, which were only predicted in theory previously. A line-slip defect consists of a line of particle pairs where each particle has one less number of contacts, compared to other particles in the crystal.

Surprisingly, we find a new form of a line-slip defect with kinks. The kinks incorporate vacancies that are “fractional” - one full particle cannot be fit in the free volume provided by these vacancies. By observing crystal growth dynamics, we find that the kinked line-slip structures are a result of crystal growth – when a line-slip defect fails to follow the crystal growth, it can appear in a separate, parallel line, incorporating kinks and fractional vacancies. We do not observe relaxation of the kinked defects in experimental timescale. We calculate the equilibrium number of fractional vacancies assuming Boltzmann distribution, which shows that we find a greater number of fractional vacancies in experiment that are expected in equilibrium. This further proves that the kinks and fractional vacancies are kinetic traps and are not equilibrium structures.

Moreover, we find that the line-slip defects that form a larger angle with respect to the cylinder radial axis have fewer number of fractional vacancies compared to the ones forming smaller angles. We explain this observation by modeling and tracking crystal growth in time using Brownian dynamics simulation. Since growth of a crystal is limited in the radial direction due to the finite diameter and unrestricted in the axial direction, line-slip defects that are aligned with the axial direction find it easy to grow without incorporating kinks.
In conclusion, we observe unprecedented crystal morphology and growth dynamics in cylindrical colloidal crystals. We conclude that certain aspects of crystal morphology can only be explained from careful consideration of growth dynamics. This study can further help us understand the growth mechanism of various cylindrical structures that exist in nature and in artificial materials, such as – virus, microtubules, nanotubes, etc.

SB01.12.95

**3D Printed Composites of Polymer and Multiferroic Materials** Emery Utterback, Naga Korivi and Vijay Rangari; Tuskegee University, United States

There is great interest in 3D printing-based fabrication techniques for multi-functional materials. We report on the development of composites of polydimethylsiloxane (PDMS), and nano-particles of barium titanate, and cobalt ferrite by 3D printing for applications in advanced multiferroic devices. The fabrication involved the mechanical blending of liquid PDMS pre-polymer and its curing agent with the barium titanate and cobalt ferrite nano-particles. The blend was subsequently loaded onto an extrusion printing head of a commercial 3D printer and printed on a base plate maintained between 75 – 90 °C to yield solid composite layers. Characterization of the solid composite layers by electrical and magnetic studies, and observations from scanning electron microscopy, transmission electron microscopy, x-ray diffraction, differential scanning calorimetry, thermogravimetry will be presented. To the best of our knowledge, this is one of the earliest reports of a 3D printing approach to fabricate polymer multiferroic composites, and represents a significant technological advance.

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**Rheological Study on Using Graphene Oxide as Printing Aid to Enable 3D Printing of 2D Materials for Energy Storage Applications** Jiacheng Wang\(^1\), Subrata Ghosh\(^1\), Pei Yang\(^1\), Ian Kinloch\(^1,2\) and Suelen Barg\(^1\); \(^1\)University of Manchester, United Kingdom; \(^2\)National Graphene Institute, United Kingdom

Graphene, a type of 2D materials, with large specific surface areas and high electrical conductivity can be used as electrode materials for high-performance supercapacitors [1–2]. However, the re-stacking of 2D graphene sheets during conventional electrodes fabrication can lead to insufficient use of the surface area and blockage of electrolyte ion transport which degrade the capacitance and rate performance of supercapacitors. 3D printing allows fabrication of 3D graphene electrode architectures with well-tuned porosity and interconnected channels that favour the retention of large electrolyte ion accessible surface area and fast ion transport within the electrodes [3–5]. Graphene oxide (GO) aqueous suspensions in specific concentrations were shown to have not only adequate rheological properties for 3D printing [6] but also the capability to process polymers, ceramics, metals [7] and graphite [8]. A study also showed that the addition of graphene nano-platelets into GO inks enhanced the rate performance of printed electrodes [4]. However, there is a lack of study on using GO to process 2D materials for 3D printing. This work conducts a thorough study of the rheological properties of GO-graphene nanoplatelets (GnP) composite inks. GnP was chosen to represent 2D materials with inert chemistry and a strong tendency to re-stack. The theory can be expanded to other 2D materials. 3D graphene supercapacitors have been printed and their performances have been compared with the conventional graphene supercapacitor cells.

Hydrogel Paints for Repairing Articular Cartilage Defects in Osteoarthritis

Wei Wei, Xudong Yao, Wenyan Zhou, Yuanzhu Ma and Hongwei Ouyang; Zhejiang University, China

Osteoarthritis (OA) is causing pain in millions of people's joints. In clinical, the joints with see partial-thickness cartilage defects on their surface. Partial-thickness cartilage defects can not self-repair due to the avascular, aneural, and alymphatic nature of cartilage. Herein, inspired by painting technique, we designed a new kind of hydrogel system consists of the components of cartilage ECM to treat partial-thickness cartilage defect in osteoarthritis. The resultant hydrogel paint is tissue adhesion, compression resistance, cell affinity, and easy operation. Controlled chemical modification allows each component to achieve the above functions while maintaining biological activity. We found the hydrogel paint support adhesion of stem cell and can maintain phenotype of chondrocytes. In vivo results show that the cartilage was regenerated on the defect site while the control group was developed to osteoarthritis. Therefore, we consider such hydrogel paint is a biomaterial that is promising for repairing partial-thickness cartilage defects.

Smart Membranes

Liang-Yin Chu; Sichuan University, China

Membranes are playing paramount roles for sustainable development in myriad aspects such as energy, environments, resources and human health. However, the unalterable pore size and surface property of traditional porous membranes restrict their efficient applications. The performances of traditional membranes will be weakened upon the unavoidable membrane fouling, and they cannot be applied to the cases where self-regulated permeability and selectivity are required. Inspired by the natural cell membranes with stimuli-responsive channels, artificial stimuli-responsive smart gating membranes are developed by chemically/physically incorporating stimuli-responsive materials as functional gates into traditional porous membranes to provide advanced functions and enhanced performances for breaking the bottlenecks of traditional membrane technology. The smart gating membranes, integrating the advantages of traditional porous membrane substrates and smart functional gates, can self-regulate their permeability and selectivity via flexible adjustment of pore sizes and surface properties based on the "open/close" switch of the smart gates in response to environmental stimuli. This presentation introduces the recent development of stimuli-responsive smart gating membranes, including the design strategies and the fabrication strategies that based on introduction of the stimuli-responsive gates after or during membrane formation, the positively and negatively responsive gating models of versatile stimuli-responsive smart gating membranes, as well as the advanced applications of smart gating membranes for regulating substance concentration in reactors, controlling release rate of drugs, separating active based on size or affinity, and self-cleaning of membrane surfaces. With self-regulated membrane performances, the smart gating membranes show great power for global sustainable development.

References
Multifunctional Materials with Self-Adaptive Mechanical Properties and Regeneration

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Nature provides numerous examples of advanced materials with remarkable properties, synthesized in sustainable ways. Inspired by natural systems, there have been active efforts to understand design principles of natural materials and to synthesize bioinspired multifunctional materials with outstanding properties. We have been inspired by natural structural materials with outstanding mechanical properties such as bone, coral reef, and wood that can adapt to their surrounding environment. For instance, bone can control mineral quantity proportional to the amount of stress. It becomes stronger in locations subjected to the higher mechanical loads, and vice versa. This leads to the formation of mechanically efficient structures for optimal biomechanical and energy-efficient performance.

However, it has been a challenge for making synthetic materials that can change their structures and properties to adapt to the changes of loading conditions. Moreover, materials degrade over time due to fatigue damage occurred during use and damages accelerate the degradation rate, resulting in reduction in the lifetime of the materials and increase of the maintenance costs. If materials can repair damages, we can have more efficient use of materials with reduced associated costs. Synthesizing materials with self-adaptable mechanical properties and regeneration capability can help us to use materials for a broad range of loading conditions with extended lifetime and reduced costs.

To address the challenge, we are inspired by previous findings that bones are formed by mineralization of organic scaffolds using ions from blood. We report a multifunctional material system that triggers mineral synthesis from simulated body fluids onto organic scaffolds upon mechanical loadings and/or damages so that the material can modulate its mechanical properties to adapt to loadings and regenerate upon damages. For example, we observed \(~40\%\) increase in the modulus of the material upon periodic loadings for 3 days. We also observed that the material could repair damages generated by removing \(~5\) \(\mu\)m thick minerals from the matrix, in 7 days. In addition, we demonstrate a simple way of making functionally graded material based on stress distribution within a material that results in graded deposition of minerals. We envision that our findings can open new strategies for making multifunctional materials with self-adaptable mechanical properties and regeneration capability as well as tuning material properties on-demand.

Self-Healable Electronics Based on a Paper-Like Thin PVA/CNC Nanocomposite Film

Jung Wook Kim and Jeong Sook Ha; Korea University, Korea (the Republic of)

Wearable electronics including skin-attachable devices in the form of thin and soft film made for conformal attachment to clothes or skin, are prone to be damaged by external forces during usage. In order to increase the lifetime, there have been extensive efforts to develop self-healing materials that can restore the original properties after being damaged and be implemented to wearable electronic devices.

We report a fabrication of a paper-like thin, foldable and self-healable electronics based on poly vinyl alcohol/cellulose nanocrystal (PVA/CNC) composite film through a facile vacuum filtration method. For self-healing conductive electrodes, polyaniline/multi-walled carbon nanotube and gold nanosheet (AuNS) percolated network are deposited onto the PVA/CNC film. Via contacting the bisected surfaces and spraying water, the damaged area can be self-healed due to formation of hydrogen bonding. By controlling the composition of PVA/CNC film, pH, and temperature, the maximum self-healing efficiency can be optimized. On the PVA/CNC self-healing film, integrated circuit of a supercapacitor and a temperature sensor is fabricated using AuNS interconnections. Both the supercapacitor and temperature sensor show mechanical stability; 100\% recovery of capacitance and sensitivity after 100 repetitive folding deformation and \(>80\%\) recovery of capacitance and sensitivity after 5 repetitive self-healing cycles. These results demonstrate the potential application of our paper-like thin PVA/CNC film based self-healable devices to future highly durable and deformable electronics with longevity.
Living tissues are an integrated, multi-scale architecture consisting of dense cell ensembles and extracellular matrices (ECM) that cooperatively enable the outstanding mechanical properties and rapidly dynamic responsiveness. One key challenge in designing tissue-like materials is to identify cell-like building blocks that can synergistically respond to external stress with existing ECM-like polymer platforms. Therefore, we designed a granular material-enabled hybrid gel, including cell-like starch granules embedded in ECM-like synthetic hydrogel matrices that readily exhibited dynamic reconfigurable effects upon mechanical training. Multi-scale and in-situ characterizations reveal that the synergistic cooperation between nanoscopic (chemical bonding) and mesoscopic (physical friction) interactions from three-dimensional hierarchical architecture give rise to the tissue-like properties, such as rapidly dynamic responsiveness, strain-stiffening, and self-healability. Our results suggest that granular materials, a largely ignored component for biomimetics, could be critical in enabling dynamic behaviors in artificial tissue-like materials, meanwhile it also provides a brand new opportunities for exploring adaptive and active materials.

9:45 AM SB01.13.05
A Theory of Photoactive Nematic Liquid Crystal Elastomers Ruobing Bai and Kaushik Bhattacharya; California Institute of Technology, United States

Liquid crystal elastomers containing photochromophores such as azobenzene can undergo large deformation when illuminated by light of certain wavelength. Since its first discovery in 2001, this phenomenon has attracted extensive research and inspired new applications of large-deformation actuation by light. In such a system, the deformation couples optics, chemistry, and mechanics, leading to a multi-scale, multi-physical process. The process includes the photoisomerization of chromophores, the interaction between mesogens and polymers, and the anisotropic, entropic elasticity of the polymer network. Continuum models have been developed in recent years to study this photochemistry-induced actuation. However, the theoretical studies up to date have been incomplete to fully capture the coupling in the system, which further hinders the discovery of new actuation modes, or exploring the general anisotropic and inhomogeneous material response under complex loading conditions. This talk presents a theoretical modeling on the large deformation of photoactive nematic liquid crystal elastomers actuated by light illumination and mechanical force. The model starts from the statistical mechanics of the photoisomerization, nematic mesogens, and the polymer network. The total free energy landscape is plotted under different light intensities and mechanical loads. We show two generalized actuation modes due to light illumination and mechanical force. The coupling between the two modes induces various deformation. The transition between the two modes gives rise to microscopic stripe domains formed in the material. The opto-chemo-mechanical process readily leads to photomechanical instability.

10:00 AM BREAK

10:30 AM *SB01.13.06
Integrated Soft Materials Zhigang Suo; Harvard University, United States

An integrated circuit achieves its function by integrating dissimilar components, and so does a living organ. Soft materials—tissues, elastomers, hydrogels, and ionogels—are under intense development for immediate and far-reaching applications. Examples include tissue regeneration, synthetic biology, drug delivery, soft robots, ionotronics, bioelectronics, skin-attached and implanted devices, active textiles, as well as wearable and washable devices. Nearly all applications require the integration of dissimilar soft materials. This talk describes several recent examples of integrated soft materials that achieve unusual functions. Also highlighted are fundamental challenges to the mechanics and chemistry of materials, such as adhesion, fatigue, and seal. Integrated soft materials open opportunities to reinvent our disciplines and ourselves.

11:00 AM SB01.13.07
An Origami-Patterned, Flexible Pressure Sensor Fabricated with Vacuum Forming Kris Dorsey, Mariel Jones, Huiying Huang and Alysha de Silva; Smith College, United States

A common flexible sensor modality employs a change in sensor layout and device capacitance to detect mechanical
deformation. A challenge for this sensor type is in determining what type of deformation (e.g., bending, strain, pressure, torsion) caused the signal. While multiple sensors may be placed in a bridge or rosette configuration to improve selectivity or directionality, the sensor substrate also offers a route to identifying deformation type. Here, we present origami-patterned, polyethylene-based pressure sensors. In comparison to flat polyethylene-based sensors, which can only undergo small strains before plastic deformation occurs, the origami patterns allow the sensors to remain compliant at high strain (>45%) while exhibiting pressure sensitivity. Such sensors may have applications to gesture detection and activity classification, which require flexible and conformal sensors that can distinguish modes of mechanical deformation.

The mechanical properties of origami may be tuned through the material choice, the pattern, and the initial geometry. Paper is most commonly associated with origami, but novel processes such as self-assembly, 3D printing, and casting now enable a wide variety of origami patterns in fabrics and polymers [1]. We directly pattern the material by vacuum forming, which eliminates the multiple steps required to buckle or cure the material in self-assembly fabrication processes. To fabricate the sensors, we designed and generated a 3D printed form with the pattern using a custom Python script interfaced with AutoDesk Fusion 360. We heated commercially available carbon black filled polyethylene (Linqstat, Caplinq) at 60°C for 10 s before placing it onto the 3D printed form and custom vacuum former. The 3D printed form is slightly porous and permits suction of the polyethylene onto the form. After cooling, the conductive polyolefin retains the shape. To fabricate the capacitor, two conductive polyethylene sheets were formed and placed on either side of a formed layer of high-impact polystyrene sheet with a thickness of 0.25 mm.

We characterized the pressure sensitivity of the Miura fold, which is a pattern of repeated chevrons [2], and the double arrow pattern, which is similar to the Miura fold with a taper at the edge of each chevron. The unit cell has a width and length of 20 mm with a height of 7.5 mm. When pressure is applied, the Miura pattern deforms at the pattern folds and flattens out, while the double arrow pattern is stiffer and only deforms at the arrow points. The Miura capacitance increased by 17.8% under a mass of 6.5 g placed on the sensor (5.5 Pa), while the double arrow capacitance increased by 0.25%. As the pattern faces do not appreciably expand when the Miura pattern unfolds, the increase in capacitance may represent both an increase in the fringing field capacitance and a decrease in the electrode separation.

Vacuum forming conductive polymers into origami patterns has the potential for the rapid fabrication of sensors with novel mechanical properties, limited only by the capabilities of 3D printers and the draft angle requirements of the vacuum forming process. Forming conductive polyethylene into other origami patterns, such as those with low bending compliance and high planar compliance, may yield selectivity to other modes of mechanical deformation. This work has implications for designing flexible and multimodal sensing systems for wearable sensing and soft robotics applications.


11:15 AM SB01.13.08
Dry-X Paste for Body-Fluid-Resistant Instant and Strong Wet Adhesion Xinyu Mao, Hyunwoo Yuk and Xuanhe Zhao; Massachusetts Institute of Technology, United States

Tissue adhesives are able to bond wet and dynamics tissue surfaces, yet adhesion on body-fluid-covered wet tissues remains to be a challenge. While there are a wide range of tissue adhesives targeting sealing of damaged tissues, most of commercially available glues and patches only take effect on clean tissue surfaces, and generally completely fail to form adhesion on surfaces covered with large amount of body fluids such as blood and mucus. Conventional hemostatic agents enable adhesion with bleeding tissues, such as hemostatic gauze and topical hemostats. However, their adhesion is based on accelerated coagulation of blood and subsequent formation of blood clots. These conventional approaches are relatively slow and lack robust sealing capability for compromised tissue walls due to weak and unstable adhesion formed by blood clots, both of which may pose several practical challenges and limitations. In this talk, we will present our new a dry-crosslinking (Dry-X) paste for instant, strong, and body-fluid-
resistant adhesion on diverse wet tissues to address all abovementioned challenges. Our Dry-X paste incorporates a unique bio-inspired mechanism and materials design that are distinguishable from all known tissue adhesives as well as hemostatic measures, which yields superior capability of instant and strong adhesion on blood- or mucous-covered tissues. These new capabilities enabled by the Dry-X paste will provide a simple, facile, and effective solution to critical clinical and biomedical applications such as traumatic tissue sealing and hemostasis as well as new opportunities such as a tissue-adhesive drug delivery platform for challenging locations such as GI tract.

11:30 AM SB01.13.09
Bioinspired 3D Microscale Suction Cups for Dry and Wet Adhesion to Human Surfaces
Sangyul Baik, Heon Joon Lee and Changhyun Pang; Sungkyunkwan Univ, Korea (the Republic of)

Research in the adhesive phenomena of natural organisms has inspired developments in biocompatible and skin/organ-attachable adhesives for various medical applications such as wound protection, diagnosis, and therapeutics. Examples of such include gecko feet pads, beetle forelegs, and needle structures of endoparasites, which rely on physical interactions of the multiscale architectures on their topologies. However, such adhesive strategies rely on mechanical interlocking or molecular attractions between surfaces, which suffer upon contact with liquids. The development of adhesives which are easily fabricated and perform robustly and repeatedly under both wet and dry conditions without leaving chemical contaminations on the engaged surfaces has been a major challenge. In addition, achieving high conformity against the three-dimensionally (3-D) rough and curved surfaces of the human body remains difficult for further medical applications of wound protection, diagnosis, or therapeutics. To overcome such challenges, much research in recent years has been focused on octopus suction cups due to their unique anatomical features which enable stable fixation onto rough, dry, and wet surfaces. Although previous reports have presented hypothetical studies for the anatomy of octopus suckers, the detailed mechanisms underlying their enhancement of wet adhesion remain largely unexplored due to the difficulty of precise mimicry. Further detailed investigation of the complex architecture of octopus suckers, including the dome-like protuberance, cup-shaped protruding rim, and soft wrinkles, have revealed their roles in establishing dry and wet adhesion. To mimic the 3D architectures of suction cups, we utilized a facile, solution-based, air-trapping technique within microscale molding without any sophisticated chemical syntheses or surface modifications. Applying these bioinspired architectures as interfacial adhesive layers may benefit the development of skin-attachable or implantable bioelectronics for health diagnosis, controlled drug therapeutics, and multifunctional devices for ubiquitous-healthcare systems.

SESSION SB01.14: Smart Electronic Materials and Sensors
Session Chairs: Ximin He and Zhigang Suo
Friday Afternoon, December 6, 2019
Hynes, Level 3, Ballroom A

1:30 PM *SB01.14.01
Design Skin-Inspired Electronic Materials and Their Applications
Zhenan Bao; Stanford University, United States

In this talk, I will discuss several design concepts on realizing conductive and semiconductive electronics materials with skin-like properties, such as stretchability, self-healing and both properties. These materials have enabled stretchable circuits, displays and sensors. Several examples of applications will be discussed.

2:00 PM SB01.14.02
Multi-Responsive Flexible and Stretchable Robotic Skin for Soft Robot Hands
Jooyeun Ham, Amy K. Han, Jayoung Kim, Zhiao Yu, Naoji Matsuhisa, Mark R. Cutkosky and Zhenan Bao; Stanford Univ, United States

Recent advances in soft robot hands have demonstrated its unique capabilities, such as handling randomly-shaped or fragile-soft objects, which have been addressed as limitations of conventional rigid robotics. Despite recent progress, the majority of soft robot hands are still limited in dexterous activities, which need tactile and thermal detection for feedback control. Here, we present a highly flexible and stretchable multi-responsive sensory network for soft robot
hand applications. Unlike previously developed embedded tactile systems for soft robot hands, in present work, laser-assisted fabrication techniques allow low-cost and rapid-one-step fabrication of multiple sensors and wires, and modulating the width of a pattern of each sensor and wire enables it to easily tune its sensitivity, sensing range, and expandability. The sensor network further integrated with highly expandable and irregularly-shaped soft robot hands and demonstrated successful tactile sensing performances during grasping actuation of robotic hands undergoing expansion and compression due to high conformity on curved surface and stretchability. The sensor network integrated soft robot hand measured tactile and thermal stimuli distribution, and analyzes multiple stimuli in real time simultaneously in various grasping scenarios. The reproducibility of the sensor network was further evaluated by continuous measurement during repeated grasping action.

2:15 PM SB01.14.03
A Body Area Wireless Sensor Network by Stretchable Passive Tags Simiao Niu¹, Matsuhisa Naoji¹², Xiaodong Chen*² and Zhenan Bao¹; ¹Stanford University, United States; ²Nanyang Technological University, Singapore

Body area sensor network (BodyNET) is a promising platform for next-generation healthcare and realizing its full potential requires seamless hybridization between on-body sensors and both rigid circuits for signal readout, conditioning and wireless transmission components. Rigid sensors based BodyNET has already been demonstrated due to its fabrication compatibility with existing integrated circuit technologies while the integration of soft on-skin sensors into the BodyNET still remains a grand challenge. So far, the integration of rigid silicon circuits and stretchable sensors on a single substrate has only been realized through the introduction of rigid islands and stretchable interconnects. However, the weak interfaces between soft and rigid parts severely compromise the robustness of such systems. Therefore, physical separation of stretchable sensors from rigid readout circuits that completely eliminate all fragile interfaces may be an effective strategy towards an intimate and robust BodyNET system.

Here, we demonstrate a bodyNET system comprised of battery-free and chip-free stretchable sensors attached on multiple skin locations to gather human physiological and movement signals, which are wirelessly operated by silicon readout circuits attached to textiles. The physically-separated stretchable sensors and silicon readout circuit are communicated via passive radio frequency identification (RFID) technologies. The stretchable sensor tags are fabricated via printing intrinsically stretchable materials on elastic substrates, and are completely free from rigid silicon chips and batteries to avoid potential stress concentrated regions and improve system robustness. The main technical challenge encountered here is the strain-induced changes of both sensor antenna inductance and resistance that can affect readout effectiveness. We address this issue by adapting an unconventional detuned RFID tag design and verify its appropriateness by both simulation and experiments. Our design enables the bodyNET system to maintain full functionality even when the on-skin sensors are stretched to 50% strain. To further enable multiple sensors in one RFID tag, we have fabricated and integrated a high frequency intrinsically stretchable rectifying diode and low voltage driven intrinsically stretchable ring oscillators for RF energy harvesting and frequency modulation. Finally, the bodyNET is demonstrated by connecting multiple sensor nodes and smartphone through Bluetooth. Our hands-free bodyNET could continuously, simultaneously and accurately monitor human’s respiration, pulse and body movements. Thus, this platform constitutes a powerful tool in analyzing relevant human activities and physiological signals, hence enabling critically-needed possibility for real-time physiological studies.

Reference:

2:30 PM SB01.14.04
Visually Imperceptible Liquid-Metal Circuits for Transparent, Stretchable Electronics with Direct Laser Writing Chengfeng Pan¹, Kitty Kumar¹, Jianzhao Li², Eric J. Markvicka¹, Peter Herman² and Carmel Majidi¹; ¹Carnegie Mellon University, United States; ²University of Toronto, Canada

Electrically conductive films that are optically transparent have a central role in a wide range of electronics applications, from touch screens and video displays to photovoltaics. These conductors function as invisible electrodes for circuit wiring, touch sensing, or electrical charge collection and are typically composed of transparent conductive oxides (e.g. indium-titanium-oxide, ITO), polymers (PEDOT:PSS), metal grids, or nanocomposite
polymer thin-films (graphene, carbon nanotubes). However, most transparent conductors have either poor electrically conductivity or are mechanically stiff and/or inelastic – i.e. stretching the material will cause it to break apart and lose electrical functionality. Such inability to support strain or electrical conductivity greatly limits the role of these existing materials for emerging applications in wearable computing, soft bioelectronics, and biologically-inspired robotics.

Here, we introduce a materials architecture and laser-based microfabrication technique to produce electrically conductive films (sheet resistance = 2.95 Ω/sq; conductivity = 5.65×10⁵ S/m) that are soft, elastic (strain limit > 100%), and optically transparent. The films are composed of a grid-like array of visually imperceptible liquid metal (LM) lines on a clear elastomer. Unlike previous efforts in transparent LM circuitry, the current approach allows for fully imperceptible electronics that have not only high optical transmittance (>85% at 550 nm) but are also invisible under typical lighting conditions and reading distances. This unique combination of properties is enabled with a direct laser patterning technique that results in LM grid patterns with a line width and pitch as small as 4.5 μm and 100 μm, respectively. This yields grid-like wiring on a transparent polydimethylsiloxane (PDMS) elastomer substrate that has adequate conductivity for digital functionality but is also well below the threshold for visual perception. To help adhere the LM and PDMS, a “bi-phasic” architecture is adopted in which a thin metal film – in this case sputter deposited Cr/Cu – was coated on the PDMS prior to LM deposition and patterning. The fabricated LM wiring can be readily interfaced with conventional circuit components (e.g. lead wiring, packaged microelectronics, or LED chips) to enable optically clear digital electronics.

2:45 PM SB01.14.05
Chemo-Mechanical Self-Oscillation Based on Dynamic Buckling Mutian Hua, Cheolgyu Kim and Ximin He; University of California, Los Angeles, United States

Self-oscillating materials have drawn great attention from both fundamental science and application endeavors. Its unique capability of generating sustained motion from static energy source or inputs without intervention has inspired numbers of interesting and impactful applications in the field of energy conversion and robotics. Several attempts for creating self-oscillating materials has been made using chemical oscillators coupled with stimuli responsive hydrogels and liquid crystalline networks. However, these systems suffer from limitations such as of careful molecule alignment within the material, limited choice of materials and high requirements for stimuli (e.g. chemical oscillators, polarization, wavelength). On the contrary, oscillatory patterns occurring in nature are much less restrict with the choice of reaction and materials. Chemical and mechanical dynamics in cell division, cilia motion, cardiac rhythms and peristalsis can perpetually occur from wide selections of rudimentary processes such as acid-base neutralization, metal-protein chelation and ion concentration change.

Inspired by nature, we look into the universal strategy for constructing self-oscillating materials systems out of rudimentary reactions and homogenous/isotropic materials. We demonstrate a self-oscillating materials system based on dynamic buckling. The asynchronized swelling and deswelling of hydrogel in the flow direction of the stimuli leads to a cascade of buckling in the hydrogel strip such that different regions will consecutively go through cyclic deformation in succession. This synergistically leads to the self-oscillation of the material. This provide a new general principle of generating oscillation through self-regulated chemical-mechanical energy transductions. The customizable modular design offers opportunities for creating various other forms of self-oscillatory systems.

3:00 PM BREAK

3:30 PM *SB01.14.06
Photonic Capsule Sensors—New Platform for Monitoring Microenvironment and Its Spatial Distribution Shin-Hyun Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Sensor technology based on electronic circuits has led the current IoT era. However, the conventional sensor platform is inadequate for monitoring the microenvironmental condition and its spatial distribution. In the film “Twister (1996)”, a thousand of 10 cm-sized sensor balls are suspended in a tornado, from each of which local information is gathered to provide the spatial distribution. Inspired by the film, we design photonic-crystal-laden microcapsules to make a new sensor platform for monitoring microenvironment and its spatial distribution. As the microcapsule sensors can be injected, suspended, and implanted in any target sites, their array provides the spatial distribution, in a similar manner to the sensor balls yet at the three-orders of magnitude smaller length scale. In this
early stage of development, we aim to monitor microenvironmental temperature and its spatial distribution, which is achieved using thermochromic colloidal photonic crystals.

The microcapsules are produced to have a hollow core and solid shell using microfluidically-prepared water-in-oil-in-water (w/o/w) double-emulsion drops as a template. In the inner water drop, thermoresponsive-responsive colloids composed of a polystyrene core and a poly(N-isopropyl acrylamide-co-acrylic acid) shell are encapsulated in the presence of sodium chloride and depletant of poly(acrylamide-co-acrylic acid) at low concentrations. As the oil shell phase, a thermo-curable silicone precursor is used. To assemble the core-shell colloids, the double-emulsion drops are subjected to a hypertonic condition. The water is selectively pumped out from the core, thereby concentrating the encapsulants. This strengthens the depletion attraction and lessens electrostatic repulsion, resulting in the formation of crystallites with a close-packed array along the interface. Interestingly, the crystallites exclusively have hexagonal close-packed (hcp) lattice rather than face-centered cubic (fcc) lattice. The double-emulsion drops are finally converted into microcapsules with an elastomeric shell through curing of silicone precursor. The microcapsules display a brilliant diffraction color developed by the colloidal crystallites.

The volume change of core-shell particles causes the shift of diffraction color. In particular, the volume change of individual colloids fully influences the change of lattice constant in the close-packed array, resulting in a wide shift. Although the colloidal crystallites are fragile against mechanical stress and chemical impurity, the silicone shell completely isolates the core from the surrounding, making shear- and impurity-free environment in the core. Therefore, the microcapsules show a thermochromic property without degradation of performance. More importantly, each microcapsule reports the microenvironmental temperature through the diffraction color and the array shows the temperature distribution through the color map. We demonstrate this using a convection cell at which temperature gradient causes the flow. The microcapsule sensors can be further developed to measure other conditions or detect small molecules and used for various applications.

4:00 PM SB01.14.07
Cortisol Immunosensor Integrated in Soft, Smart Contact Lenses for Point-of-Care Testing Minjae Ku, Joohee Kim, Young-Geun Park and Jang-Ung Park; Yonsei University, Korea (the Republic of)

Since psychological stress has been demonstrated to have a direct impact on health, extensive research has been conducted to analyze stress levels quantitatively by measuring stress hormones. Various methods have been reported to detect cortisol, the stress hormone, by means of immunoassay and chromatography. However, this method cannot be used in the point-of-care testing (POCT) because it requires bulky equipment and graph analysis. Thus, we propose a cortisol immune sensor integrated into a soft contact lens that can monitor the cortisol level in tears using the POCT platform. This approach makes it possible for smart contact lenses to measure cortisol levels in real time and transmit the data wirelessly to smart mobile devices. The cortisol sensor uses a channel bonded with cortisol monoclonal antibody (C-Mab) as a transducer and the field effect transistor structure to measure electrical signals according to the cortisol concentration. The limit of detection of the sensor was 1 pg/ml, which is sufficient to detect cortisol level in tears ranging from 1 ng/ml to 40 ng/ml. In this study, we used live rabbits for in-vivo testing, and the results confirmed the reliable, wireless operation of the sensor for in-vivo testing as well as its biocompatibility and its safety with respect to the absorption of electromagnetic energy. A cortisol sensor on a wearable platform that is compatible with smart mobile devices provides a new protocol for self-care.

4:15 PM SB01.14.08
Multi-Functional and Flexible Energy Storage Devices with High Safety Yang Zhao, Ye Zhang, Yifan Xu, Hao Sun and Huisheng Peng; Fudan University, China

Flexible energy storage devices are critical for the next-generation electronics and have attracted extensive attention. With the fast-growing requirements of portable and wearable electronic equipment, great efforts have been made to develop flexible batteries and supercapacitors. However, the energy densities of these devices are still urgent to be further increased. Furthermore, most of the reported flexible batteries and supercapacitors employ either strong acid/base or toxic flammable organic solutions as electrolytes, which poses potential safety issue for being worn by humans or implanted into the bodies. Therefore, the energy density, safety concerns and compatibility of the flexible energy storage devices are still urgent to be improved to meet the practical application requirements.

Herein, we have developed a new family of multi-Functional and flexible energy storage devices including fiber-shaped aluminum-air battery with superior energy density, self-healing and multi-functional aqueous batteries with high safety, and a novel multi-functional compression-sensing supercapacitor. 1. The all-solid-state fiber-shaped
aluminum-air batteries showed a specific capacity of 935 mAh/g and an energy density of 1168 Wh/kg. They are also flexible and stretchable and can be further woven into a variety of textiles. 2. After breaking, the flexible self-healing batteries can be healed to recover the normal functionality by simply contacting the two breaking parts for seconds. The electrochemical performance of these batteries can be well maintained after repeated cutting and self-healing. 3. The flexible aqueous sodium-ion batteries exhibit high volumetric energy/power density and high flexibility. When the normal saline or cell culture medium is used as electrolyte, these batteries can still work well, indicating an application prospect in implantable electronic devices. 4. The novel compression-sensing supercapacitors can store energy and tolerate and sense the external strain change with high performance. These flexible and multi-functional energy storage devices can be woven into lightweight and flexible electronic textiles to effectively meet the requirement of the modern electronics including electronic skins and advanced bioelectronic devices.

Reference
Zhao, Y.; et al. J. Mater. Chem. A 2018, 6, 3355-3360. (Co-first author)

4:30 PM SB01.14.09
Reversible Humidity-Driven Optical Tuning of PS:PEG-Based Porous Polymer Films in Oxygen Sensors
Soyeon Lee and Jin-Woo Park; Yonsei University, Korea (the Republic of)

Recently, polymers have been used as actuators or energy generators because they have good responsivity to external stimuli such as heat, light or environmental factors due to their flexible chains. In particular, inspired by the various movements and activities of the living organisms, widely existing environmental humidity variation has been vigorously used as an external stimulus for controlling the artificial polymers. However, in a polymer-based wearable sensor, the humidity responsive behavior of polymer may jeopardize an accurate detection of a chemical element other than moisture because there are variations in optical and mechanical properties and gas permeability of the polymers upon exposure to the humid atmosphere. For example, in the wearable luminescent oxygen (O2) sensor, where the sensing film is composed of O2-sensitive dyes embedded in polymer matrices, a sensing signal is obtained based on the changes in light intensity. Under humid condition, the variation in gas permeability of the polymer matrix changes the flux of the O2 molecules inside the sensing films, which varies the photoluminescence (PL) of the films. Simultaneously, the water adsorbed in the polymer matrix changes the reflectance of the films, and both the PL and reflectance variations are detected as a photocurrent signal, which leads to signal drift in O2 concentration. Therefore, there is a need to systematically study the origin of humidity-driven optical changes of the sensing films in addition to the change in O2 permeability. In this study, the humidity-driven optical changes in a porous structured luminescent O2 sensing film were examined in two aspects: changes in O2 permeability and light scattering in the polymer matrix. The luminescent O2 sensing films are composed of an O2-sensitive dye (PtOEP) within porous polymer matrices, where the porous structure is formed via phase separation between immiscible polystyrene (PS) and polyethylene glycol (PEG). Different types of polymer films were made by the drop-casting method and samples are prepared by considering the three main factors: 1) the presence of an PtOEP within the films, 2) the PS:PEG phase-separated porous films and PS-only solid films, and 3) the different rinsing time of porous films in deionized (DI) water. These three factors were established to identify the humidity-driven optical changes in a porous structured luminescent O2 sensing film as a function of the variation of O2 permeability, porosity in films and hygroscopicity of PEG inside the pore. Here, the porous structured polymeric films were identified by the FE-SEM image, and the amount of PEG inside the polymeric films was identified by absorption peak intensity in FT-IR spectra based on the Lambert-Beer law. Finally, with comparisons of the polymeric films by in-situ measurement of both the photocurrent signal and diffused reflectance under different relative humidity (RH) levels ranging from 20 to 80 % RH, a decrease in light scattering intensity is a major contributor to the humidity responsive photocurrent decrease of 22.5% in our porous structured sensing films. In the phase-separated porous
structured polymer film, the hygroscopic PEG distributed inside the polymer matrix swells and fills up the pores as the RH level increases. Therefore, the light refraction at the polymer matrix-air interface was replaced by the polymer matrix-swollen PEG interface, which reduced the Mie scattering coefficient and increased the light transport mean free path, and finally reduced the light scattering of the porous films. The fully reversible humidity-driven tuning of the light scattering properties in porous polymeric films will make various applications possible, such as dual monitoring of O2 and RH in wearable sensors, responsive coating or smart windows that require optical tuning without extra energy.

4:45 PM SB01.14.10
New Oxygen Sensors and Pressure Sensitive Paints Based on PDMS-Containing Block Polymers Jiayan Shi,
Ke Zhong and Yanqing Tian; Southern University of Science and Technology, China

In wind tunnel and aircraft experiments, it is important to know the aircraft’s surface pressure, which provides the aerodynamic performance of aircrafts[1]. In traditional pressure test, punching holes on the model surface and installing pressure transducers into these holes are required. Though this method is simple and accurate[2], the pressure information obtained in this way is non-continuous, and the measurement is also limited by the model structures and the interference/interval between adjacent holes[3]. To alleviate these drawbacks of traditional pressure test method, a non-contact and non-destructive measurement technique is needed. Pressure sensitive paint (PSP) provides a non-destructive method for air pressure measurement by using oxygen sensitive probes in suitable matrices, which is based on the oxygen quenching principle[4]. The distribution of air stress on the sample surface can be deducted from the emission changes of PSP. Compared with the traditional pressure measuring method, this type of optical measuring technology has the following advantages: high spatial resolution, no damage to the model surface, short test cycle, high economic benefits, and being able to get continuous measuring results[5]. Almost all of the polymers used for PSP studies belong to random polymers in previous reports. In this study, we reported new PSP materials derived from block polymers. And we investigated the influence of polymer structure on oxygen sensing activity.

The new PSPs with block polymeric structures were prepared by using a kind of controlled living polymerizations - atom transfer radical polymerization (ATRP). Polymers composing of polydimethylsiloxane-b-poly(isobutylmethacrylate) (PDMS-b-PolyIBMA)s act as the matrices for the platinum porphyrin-based phosphorescence probes, which were copolymerized in the matrices. The polymers were characterized by using ^1H-NMR and GPC. The sensitivity and response time to oxygen and/or pressure were investigated. Results showed that copolymers with suitable compositions can have higher sensitivity. The influence of polymer structures on oxygen sensing activity was also investigated. Results showed that polymer structures have no significant effect on their oxygen sensing performance. This is the first time to apply PSPs with block polymer structures, which will broaden the PSP functional materials’ design.

References

SYMPOSIUM SB02
Multiscale Materials Engineering Within Biological Systems
December 2 - December 5, 2019

Symposium Organizers
Benjamin Almquist, Imperial College London
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Ritchie Chen, Stanford University
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SESSION SB02.01: Biomolecular and Biomimetic Materials
Session Chairs: Benjamin Almquist and Ritchie Chen
Monday Morning, December 2, 2019
Hynes, Level 2, Room 200

8:00 AM SB02.01.01
Unraveling the Effect of Morphological Features and Hierarchy on the Performance of Diatoms-Inspired Structures
Flavia Libonati1,2, Filippo Gallina1, Daniele Origo1, Kai Guo2, Laura Vergani1 and Markus J. Buehler2;
1Politecnico di Milano, Italy; 2Massachusetts Institute of Technology, United States

Diatoms are single-cell algae that form a hard silica/organic composite with a honeycomb-like structure. The fascinating and sophisticated structure of these algae, which is responsible for the multifunctionality of these organisms, has attracted several scientists and engineers for various reasons. Multiple functions and properties (e.g., mechanical, chemical, and optical) are achieved through a combination of different factors, such as compositions, geometrical features, and hierarchy. A characteristic feature of the diatoms is the protective shell, which has an optimal strength-to-weight ratio, especially if compared to other biological materials, offering enough resistance to predators’ attacks and preventing sinking. These characteristics make the shell an interesting biomimetic model for the design of lightweight structural materials. Here we focus on one of the most relevant and interesting diatom species, the Coscinodiscus, that is a centric diatom with radial symmetry. Keeping the effective density constant, we use numerical modeling, experimental testing, and additive manufacturing study the effect of systematically varying the size of the relevant geometrical features on the overall bending stiffness. The overarching hypothesis of this work is that the morphological features, like pores and hierarchical layers, drive the mechanical response of diatoms exoskeleton and are designed by Nature to simultaneously fulfill different functions. We build a simplified FE-model of a diatom-inspired architecture and we study the mechanical behavior under three-point bending and compressive loading. We evaluate the effect of the hierarchical level and the effect of material distribution amongst the hierarchical level on the overall bending stiffness and resistance to buckling. The numerical simulations are validated through experimental tests, carried out on polymeric geometries fabricated using multi-material 3D-printing. The results of this study reveal how the natural geometry is optimized to simultaneously provide lightweight, bending stiffness, and structural integrity, limiting local buckling and providing different dissipation mechanisms to absorb energy, thus preventing catastrophic failure. Ongoing studies are carryout on the effect of the pore distribution on both the mechanical behavior, with particular attention to fracture, and on the fluid-dynamics properties. Ultimately, this research offers an innovative perspective in terms of design and fabrication of multifunctional diatom-inspired materials for diverse applications, from drug delivery to membrane filtering and solar cells. Moreover, given the large diatom diversity and the plethora of architectures, there is great potential of applying machine learning algorithm for the design of novel diatom-like topologies with a novel set of properties.

8:15 AM SB02.01.02
Engineering Microbes to Produce Water-Processable, Biodegradable and Coatable AquaPlastic
Anna Duraj-
Thatte; Harvard University, United States

Over 335 million tons of plastic is produced globally every year and nearly 80% of it have accumulated in landfills and water-bodies. Contamination of non-biodegradable plastics and microplastics (<5 mm fragmented particles) are causing potentially irreversible damage to our ecosystems and global health, including that of humans. Herein, we report AquaPlastic, a new class of microbiologically produced biodegradable bioplastic that is water-processable. We genetically engineered *E. coli* to fabricate AquaPlastic with minimal processing steps. AquaPlastic is entirely water-processable and aqua-healed by the addition of water. Additionally, it can be aqua-welded to create robust three-dimensional architectures by using water as a glue. It also readily forms well-adhered coatings on a wide variety of surfaces and is resistant to strong acid/base and organic solvents. AquaPlastic films can be imprinted with surface patterns with topographical features as small as a few tens of nanometers. These unique features of AquaPlastic are believed to inspire further exploration and the development of much-needed alternatives to conventional plastics.

8:30 AM *SB02.01.03
Biomimetic Nanocomposites for Biomedical Technologies Nicholas A. Kotov; University of Michigan, United States

Design of stimuli responsive and structurally versatile materials with finely controlled combination of properties represent the key bottlenecks of nearly all biomedical technologies. The central challenge for the design and realization of biologically inspired materials with such demanding set of properties is harnessing the processes of self-organization involving molecular, nanoscale, and microscale components. This challenge can be addressed using integration of several methods of self-assembly producing hierarchically structured composites.

Replication of load-bearing and functional nanocomposites will be described for three examples of bioinspired nanomaterials: nacre; enamel and cartilage. Nacre-like composites allow for multidimensional design of materials properties: toughness, stiffness, strength, transparency, ion transport, and biological response. These type of hierarchical nanocomposites resulted in biomimetic neuroprosthetic implants. Replicating tooth enamel, we recently learn that the mechanics and other properties of this material can be replicated combining out-of-plane nanoparticle assembly into columns and molecular-scale self assembly of polymers between them. These composites reveal remarkably high vibrational damping unusual for stiff materials that imparts them resilience to aging. Replication of cartilage gives example how to nature reconciles load-bearing and transport properties. Versatile cartilage-like nanocomposites based on aramid nanofibers (ANFs) will be discussed in details.

9:00 AM SB02.01.04
An Introduction to the Cephalopod Protein Reflectin for Biomedical Applications Atrouli Chatterjee and Alon Gorodetsky; University of California, Irvine, United States

Cephalopods possess unrivaled camouflage and signaling abilities that are enabled by their sophisticated skin, which alters the texture and coloration of their skin to blend into their surroundings. The color-changing capabilities of cephalopods, in particular, are enabled by multiple dermal layers, which contain chromatophore pigment cells (as part of larger chromatophore organs) and different types of reflective cells called iridocytes and leucophores, which function synergistically to alter the appearance of the cephalopods for both communication and signaling. The optical functionality of these cells (and thus cephalopod skin) critically relies upon subcellular structures partially composed of a class of unusual structural proteins known as reflectins. Reflectins have been found to have a unique amino acid sequence, but very little secondary structure. We will highlight studies that have investigated reflectins’ structure-function relationships, within the context of cell-reflectin interactions. We will also discuss these proteins’ multi-faceted material properties, associated challenges, and future potential. Our findings hold relevance for the development of biomedical technologies based on and inspired by reflectins.

9:15 AM SB02.01.05
Biomimetic Thermally Responsive Self-Assembled Hierarchical System Ju Hun Lee1,2, Seungwook Ji3,2, Byoung Duk Lee1,3 and Seungwuk Lee1,2; 1University of California at Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3Samsung Display, Korea (the Republic of)
Out-of-equilibrium self-assembly of biomolecules is one of key processes to forming organisms in nature. Spatial and temporal activation energy switches the biochemical properties of biomolecules, and altering the interactions between biomolecules results in self-assembled structures and, eventually, the construction of a functional organism. To explain the self-assembly mechanism in nature, biophysicists have constructed a variety of theoretical and experimental models. These models assume no interactions between biomolecules in general because it is not trivial to design an interaction-controllable system; this basic assumption, however, is highly simplified and does not represent the reality of nature. We demonstrate our recent efforts to design a biomimetic interaction-controllable self-assembly system. M13 bacteriophage possesses a long fibrous shape with a helically-arranged protein surface, analogous to naturally existing basic building blocks such as collagen, cellulose, and chitin. As a result of amplification through bacterial infection, M13 bacteriophage is identical, homogenous, and can be easily genetically engineered to make M13 bacteriophage a promising biomaterial in designing a biomimetic system. In this study, we genetically engineer M13 bacteriophage to install a thermally responsive peptide (TRP) at the end of the major capsid protein p8 to tune interactions between biomolecules during self-assembly. TRP phage self-assembles into a highly ordered structure with increasing temperature that is counter-intuitively inverse thermal response than usual liquid crystals. The temperature dependent phage transition of TRP-phage in solution is investigated by a macroscopic turbidity measurement. The phage transition temperature is decreased with increasing TRP phage concentration and ionic strength of solution. The microscopic nucleation and growth of TRP phage’s helical, fibrous, and smectic structure is observed by polarized optical microscope. To evaluate the temperature dependent orderedness of the TRP phage structure, small angle x-ray scattering measurement of (100) peak is utilized. TRP phage in solution shows 7.8 nm interspacing at 42°C, and this peak is decreased to 6.9 nm at 68°C, while there is no peak from room temperature to 42°C. From atomic force microscopy and He-ion microscopy, the final nanostructure is the helically assembled TRP. The role of individual amino acids, especially valines in different positions, is also investigated through the turbidity measurement by inducing point mutations.

9:30 AM SB02.01.06
Environmental Remediation and Biofuel Production through Nanoparticle Stimulation of Yeast Shalmalee Pandit, George Sun and Angela Belcher; Massachusetts Institute of Technology, United States

Artificially photosynthetic systems aim to store solar energy and chemically reduce carbon dioxide. These systems have been developed in order to use light to drive processes for carbon fixation into biomass and/or liquid fuels. We have developed a hybrid-biological system that manages both genetically controlled generation of products along with the photoactivability of a semiconductor system. We show an increase in the production of ethanol, a common biofuel, through the electron transfer stimulated by biologically produced cadmium sulfide nanoparticles and light. This work provides a basis on which to improve the production of many metabolites and products through endogenously produced nanoparticles.

9:45 AM SB02.01.07
Mechanical Energy Transmission in Collagen Segments Mario Milazzo1,2, GangSeob Jung1, Serena Danti1,2,3 and Markus J. Buehler4; 1Massachusetts Institute of Technology, United States; 2Scuola Superiore Sant'Anna, Italy; 3University of Pisa, Italy

Collagen is the most abundant protein in humans and animals with more than twenty-five different variations. Among them, Collagen Type I (COL1) is the main component of bone and skin. Owing to its structural nature, previous studies have investigated different mechanical perspectives, including strength, elasticity, toughness and viscoelasticity. An interesting avenue of research, still poorly understood, is the capability of collagen to transfer mechanical energy when exposed to impulsive displacement loads. This topic is particularly relevant due to the tremendous implications for developing new biomimetic and bioinspired materials to be employed in bioengineering. Specifically, the energy transfer applications in the auditory apparatus are most interesting since this organ possesses abundant collagen and its physiological role is specific to mechanical energy transmission from sound waves. In this work, we study a collagen peptide (with GXY triplets) at the molecular level to understand the role of hydration in the material behavior under impulsive loads. We employ molecular dynamics simulations to investigate wave speeds and energy dissipation. We prepare a (GPO)_{20} collagen peptide with Triple-Helical collagen Building Script with a length of about 180 Å. Both dry (DS) and the wet (WS) structures are equilibrated via LAMMPS aiming at relaxing the topology and
reaching a convergence of the potential energy and RMSD (Root-mean-square deviation).

To study the behavior of COL1 along and perpendicularly to the helix axis, wave transfer analyses are performed on both the DS and WS by fixing the peptide at one end and by applying two different impulses: longitudinal case (LC) and transversal case (TC).

As for the LC, we load the free end with an axial impulsive displacement of 10 Å. In contrast, for the TC, we perform a preliminary slow stretching of the triple helix at the free end (up to 10% of the tensile strain) before applying a transversal impulsive displacement of 10 Å.

Our results for the LC show higher wave speeds for the DS than the WS’s (3082 m/s vs. 2190 m/s) with correspondent Young’s Moduli of 8.05 GPa and 4.07 GPa.

We discover that the kinetic energy is markedly dissipated, similarly for the DS and WS, and it results annihilated before the travelling wave reaches the fixed edge. We estimate for both the DS and WS a relaxation time in the order of 100 ps.

Concerning the TC, instead, the material behavior is strongly affected by the pre-strain applied before the impulsive load. We compare the results with the vibrating string analytical model to study the relationship between the wave speeds at different tensile strains and the Young’s Moduli. Our results show a monotonically increase of the travelling wave speed with the tensile strain (up to 1400 m/s and 829 m/s for DS and WS, respectively). A direct comparison of the Young’s Modulus vs. strain curves with previous works confirms the validity of our approach.

Concerning the dissipating phenomena, our results show a quasi-elastic propagation of the wave along the DS with a dissipation about five times smaller than the WS’s in the same loading conditions (i.e., relaxation time: 429 ps vs. 80 ps). We believe that, during transversal perturbations, water plays a key role in enhancing the kinetic energy dissipation, otherwise driven by only hydrogen bonds.

This study represents a first step in understanding collagenous material properties under transient loading conditions in view of applications related to bone physiology and replacement, and to the auditory apparatus where COL1 is abundant.

This work has received funding from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement COLLHEAR No 794614.

10:00 AM BREAK

SESSION SB02.02: Molecular and Nanoscale Materials for Medical Applications I
Session Chairs: Benjamin Almquist and Polina Anikeeva
Monday Morning, December 2, 2019
Hynes, Level 2, Room 200

10:30 AM SB02.02.01
Core-Shell Carriers for the Controlled Release of Multiple Active Pharmaceutical Ingredients Dina M. Silva¹, Anabela F. Gonçalves², Andre da Costa³, Andréia Gomes³, Raul Machado³, Jitraporn Vongsivivut³, Mark J. Tobin¹ and Vitor Sencadas¹,²,¹,⁴; ¹University of Wollongong, Australia; ²University of Minho, Portugal; ³Australian Synchrotron (ANSTO), Australia; ⁴Illawarra Health and Medical Research Institute, Australia

Drug delivery systems have been extensively investigated for the last decade, with research in the field of microparticles, nanoparticles, micellar, lipid and hydrogel vesicles [1-4]. Unlike traditional drug formulations which typically consist of a raw drug dispersed within a matrix, encapsulating reservoirs present the advantage of sustained drug release with high efficacy, in an attempt to alleviate the risks of toxic side effects and overcome the challenges of providing an optimised therapy both in space and time [1, 5]. Such challenges are the driving force behind the design of novel drug delivery systems aiming to revolutionise the way drugs exert their actions. One example is the modification of the release behaviour of core-shell carriers for the combined administration of drugs, within a safe therapeutic window [1, 6].

This work presents a novel route to process polymer-based core-shell microparticles, composed by an outer shell of poly(vinyl alcohol) (PVA) encapsulating ciprofloxacin (CPx), and a core comprising a curcumin (CM) loaded poly(e-caprolactone) (PCL) particle. The obtained core-shell particles size was in the range of 1 – 6 μm, making them ideal candidates for inhalable drug delivery systems.

The release patterns for both CM and CPx from the simple PCL or PVA particles took less than 72 h to being fully
released. The core-shell microparticles, on the other hand, presented a biphasic release pattern, showing that the CPx was released over the first 24 h followed by the release of the curcumin from the core PCL particle, being the last one fully released after 15 days. Thus, the polymer layers worked as a physical barrier, preventing drug-drug interaction and modulating the release behavior.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy coupled with synchrotron infrared (IR) beam was used to obtain the chemical mapping of the drug distribution within the individual core-shell particles. This technique demonstrated that the PCL particles were inside of the PVA layer, and that there was a distinct and traceable distribution of the both drugs inside the particles. Finally, the bioactivity and compatibility of the formulated particles were confirmed by antimicrobial and viability assays. These novel polymer-polymer core-shell systems proved to be biocompatible and able to deliver, in a controlled fashion, two different drugs without compromising their bioactivity, hence offering unique properties for multidrug therapies.

Acknowledgements
This research was undertaken on the Infrared Microspectroscopy (IRM) Beamline at the Australian Synchrotron, part of ANSTO, under the project number M14463. This work was supported by the strategic program UID/BIA/04050/2019 funded by Portuguese national funds through FCT I.P.

References

Statement of Purpose: Cancer related deaths are the second leading cause of death with more than 10 million new cases each year. Conventional treatment often affect both healthy and cancerous cells, causing severe adverse side effects. Moreover, systemic delivery of chemotherapeutic drugs requires higher doses of drugs which lead to higher toxicity to healthy cells. Therefore, biomaterials have been used to enable localized and effective delivery of therapies to avoid side effects and reduce the effective dose. Biomaterials engineering was used to develop a variety of drug delivery vehicles for different chemotherapeutic drugs. We hypothesize that by incorporating single walled carbon nanotube (SWCNT)-liposome complexes in hydrogels, a drug delivery system capable of controlling timing and sequence of multiple drug deliveries can be developed. Utilizing near infrared (NIR) lasers, SWCNTs can be preferentially heated to disrupt liposomal bilayers, resulting in drug release. Since NIR absorbance spectra of SWCNTs is dictated by their \((n,m)\)-chirality, e.g. distinct Gaussian profiles with \(~15\) nm full-width at half maximum (FWHM), multiple formulations of single-chirality SWCNT-liposomes can be developed for the multiplexed release of drugs triggered by different NIR lasers. Finally, these SWCNT-liposome complexes will be retained in 3D hydrogel structures, enabling the localized delivery of chemotherapeutic drugs.

Methods: Single-stranded DNA was used to wrap the SWCNTs and disperse them in aqueous solutions. For each dispersion, 1 mg of raw HiPco nanotubes was added to 2 mg of desalted ss(GT)\(_{15}\) oligonucleotide with 1 mL of 100 mM NaCl. The mixtures were then ultrasonicated using a 1/8" tapered microtip for 2 hours at 40% amplitude, with an average power output of 8 W, in a 0 °C temperature-controlled vial. After sonication, the dispersion was ultracentrifuged for 30 min at 250,000 xg and the top 80% of the supernatant was extracted. 1,2-dioleoyl-sn-glycerol-3-phosphocholine (DOPC) and 1,2-dioleoyl-3-trimethylammonium-propane (DOTAP) were mixed at a 1:1 molar
ratio in chloroform at 10 mM and rotary evaporated to form a thin lipid film. 10 kDa FITC-Dextran was dissolved in DI water at 1 mg/ml and used to hydrate the lipid film for 5 minutes. The solution was then vortexed and extruded through polycarbonate membranes with 200 nm pore size to form unilamellar positively charged liposomes. DNA-wrapped SWCNTs were mixed with the liposomes using two-barrel syringe and syringe pump to form SWCNT-liposome complexes. Different ratios of SWCNT to liposome were used to minimize aggregation (measurable by polydispersity index (PDI)). These SWCNT-liposome complexes were further encapsulated into alginate hydrogels. Dynamic light scattering (DLS) was used to characterize the SWCNT-liposome structures. Confocal fluorescence microscopy was used to verify the homogenous distribution of SWCNT-liposome structures in the alginate hydrogel.

**Results & Conclusions:** We verified the fabrication of SWCNT-liposome complexes using dynamic light scattering (DLS) to measure the size and zeta potential of these structures before and after fabrication. Different ratios of SWCNT to lipid were used and the optimal ratio for minimizing aggregation was identified. Furthermore, cryo-transmission electron microscopy (Cryo-TEM) was used to visualize the structure of SWCNT-liposome complexes. Confocal fluorescence microscopy demonstrated the retention of model drug in the complexes over a two-week period. In summary, SWCNT-liposome complexes were fabricated, characterized and their retention in a 3D hydrogel scaffold was demonstrated. Furthermore, drug retention in these complexes over a 14-day period was verified and drug release vs. time was quantified. We believe that these complexes can be useful for controlling the drug release by using NIR lasers. More studies need to be conducted to analyze the effect of different NIR wavelengths on release profiles.

**11:00 AM SB02.02.03**

**Towards Nanoparticle Oral Administration—Stable Silica Nanoparticles Crossing Intestinal Barrier** Iris R. Ribeiro¹,², Nathalia d. Indolfo¹, Talita M. Marin¹ and Mateus B. Cardoso¹,²; ¹Brazilian Center for Research in Energy and Materials (CNPEM), Brazil; ²Universidade Estadual de Campinas (UNICAMP), Brazil

Over the last 20 years nanomedicine has drastically evolved with consequent approval of 51 FDA nanomedicines which are currently in the market. Most of these nanomedicines are applied intravenously, although oral administration propitiates comfort to patients, reduced infection risks and invasiveness, easy application, and low cost. Therefore, one critical challenge that remains in the pharmaceutical industry is the development of nanomedicines that can be orally administered.

Intestine is likely the key barrier facing oral administration-based medicines. Thus, the interaction and transport of nanoparticles (NPs) across this barrier is of paramount relevance. Currently, intestinal barriers production resembling human tissues involves the co-cultivation of human colon carcinoma epithelial (Caco-2, non-mucus secretion) and human colorectal adenocarcinoma (HT-29, high mucus secretion) cells at 9:1 ratio, respectively. While this co-culture leads to production of intestinal epithelia that mimics the human intestine with higher reliability, few reports have assessed the passage of nanomedicines across non-ideal models of intestine either dealing exclusively with Caco-2 cells or with non-optimized Caco-2:HT-29 ratios. Further drawbacks in these works include the use of NPs undergoing aggregation in biological environment and/or protein-free culture media, which lead to intestinal transport results of low biological relevance. Herein, we quantify the transport of stable fluorescent silica nanoparticles (SiO₂NPs) in complex culture medium across an optimized model of intestinal epithelium (Caco-2:HT-29).

SiO₂NPs were synthesized from the mixture of rhodamine B isothiocyanate dye precursor, tetraethyl orthosilicate (TEOS) and ammonia catalyst in ethanolic solution. A silica shell was produced around the pre-formed fluorescent cores and the resulting particles have approximately 90 nm-size according to electron microscopy. These particles remained stable for more than 24 h of incubation in DMEM supplemented with 10.0% fetal bovine serum enabling reliable analyses of the SiO₂NP transport across the intestinal epithelium since aggregates can prevent this passage and hide accurate quantitative results.

The artificial intestine was formed by co-cultivation of Caco-2 and HT-29 at 9:1 v/v ratio and confocal images confirmed the structure of the intestine. SiO₂NPs at 0.5 mg mL⁻¹ were added on the top of the transwell allowing NPs to interact with intestine. After 24 h, samples from top and bottom (after passing through intestine) compartments were monitored by fluorescence spectroscopy. Quantitatively, 19 ± 2% (n=3) of the SiO₂NPs crossed the intestine through paracellular and transcellular pathways, 44 ± 8% remained at the top of the transwell, whereas roughly 37% were retained either in the transwell polycarbonate membrane or inside intestine cells. Cell viability assays further revealed these SiO₂NPs are non-toxic to intestine cells.

In addition to high stability and low toxicity, the SiO₂NP transport assays were performed using optimized intestine model. The obtained results are important towards a more reliable comprehension on the behavior of SiO₂NPs when
in contact with intestinal barriers, then contributing for new advances related to the development of oral nanomedicines.


11:15 AM SB02.02.04
Micromotors Set in Motion by Disassembling Polymer Multilayers Marina Fernandez Medina1, Xiaomin Qian1, Ondrej Hovorka2 and Brigitte Stadler1; 1Aarhus University, Denmark; 2University of Southampton, United Kingdom

Micro and nanomotors are entities extensively present in nature where they perform complicated tasks in a simple way, making their artificial development interesting as it holds promise in a wide range of applications in the biomedical context, food science or environmental monitoring. Artificial micro and nanomotors are micro or nanoscale sized devices able to exhibit motion in response to different stimuli or power sources. These motors can either employ fuels to move1 or they can require external energy.2 However, they still need to overcome some difficulties, in the former case often toxic compounds in high concentrations were used to propel motors with high thrust. Biocompatible systems with high enough operational lifetimes and speeds to perform their envisioned tasks remain scarce.

We have designed a polymer-based system to address the latter challenge.3 It consists of micromotors formed by polymer-multilayers assembled through hydrogen bonds via the layer-by-layer technique. They exhibit pH-dependent disintegration that results in micro-motors motion, outperforming the Brownian randomization expected for swimmers of these sizes.

The mobility properties of these micromotors have been assessed experimentally and theoretically based on their trajectories and velocities with the aim to yield micromotors with high thrust. We demonstrated their self-propulsion and directed motion for steep pH gradients, while more shallow gradients resulted in random enhanced motion. Interestingly, velocities were predominantly increased for lower micromotors masses, and higher amounts of adsorbed polymer multilayers in their surfaces. All these characteristics as well as their shape and time related dependence have been summarized.

Micromotors capabilities were further evaluated biologically based on their toxicity and mucus penetration ability within cells. We demonstrated an improvement in cell uptake for micromotors compared with their uncoated counterparts.

These micromotors can exploit the existence of different pH regions in the human body. Their high thrust at short times and their biocompatibility make them suitable to cross biological barriers.


11:30 AM SB02.02.05
Ultra-Deformable Platelet-Like Particle Promote Hemostasis and Improve Wound Healing Ashley Brown1,2; 1North Carolina State University and the University of North Carolina at Chapel Hill, United States; 2North Carolina State University, United States

Platelets perform a variety of functions during the wound healing process, including targeting to wound sites,
binding fibrin and promoting clotting following injury. Following cessation of bleeding, platelets also release cytokines and antimicrobial peptides and reorganize the fibrin clot through a process known as clot retraction. Clot retraction significantly decreases clot size, alters clot organization and increases clot stiffness, thereby promoting ongoing wound repair. The fibrin clot acts as a provisional matrix for cellular infiltration and tissue remodeling during the inflammation, proliferation, and migration stages of wound healing, and platelet-mediated reorganization of the fibrin network after hemostasis may be an important factor in promoting cellular infiltration. In cases of traumatic injury or disease, platelets can become depleted or dysfunctional, impairing their ability to promote hemostasis and contribute to subsequent healing. To that end, we have developed a biomimetic platelet-like-particle (PLP) that mimics native platelets by homing to injury sites in vivo, augmenting clot formation at sites of injury, and recapitulating platelet clot retraction in a tunable process. We hypothesized that PLPs would stiffen clot matrices as a result of this ability to induce clot retraction. Increased matrix stiffness has been shown to promote cell migration. Therefore, we also hypothesized that PLPs would subsequently improve in vitro cell migration and in vivo wound healing responses when incorporated into fibrin matrices. In these studies, we evaluated the ability of PLPs to reorganize fibrin clots, increase clot stiffness, and enhance cell migration and healing outcomes in healthy healing models, as well as in combinatorial therapies, infection models, and a deficient healing (hemophilia) model. We evaluated our base PLP design and an antimicrobial PLP design. Finally, PLPs were also applied in combination with ultrasound in order to determine whether this combinatorial therapy could be used to minimize the time required to bring about clot structural changes, as well as minimize the therapeutic dosage of PLPs required for treatment. To create PLPs, ultralow crosslinked poly(N-isopropylacrylamide) microgels co-polymerized with acrylic acid were synthesized using precipitation polymerization and following purification, were conjugated to a fibrin-specific IgG antibody through EDC/NHS coupling. Antimicrobial PLPs were also created by incorporation of nanogold or nanosilver into the base PLP design. The effect of PLPs on clot structure and stiffness were evaluated using confocal microscopy, cryogenic scanning electron microscopy, and atomic force microscopy. The influence of PLP-mediated clot retraction on cell migration was evaluated within 3D in vitro models of wound healing in both normal and hemophilia-B like conditions of deficient healing. The ability of antimicrobial PLPs to decrease bacterial burden was evaluated in a colony forming unit assay using both Escherichia coli and Methicillin-resistant Staphylococcus aureus. Finally, the ability of PLPs to augment hemostasis following trauma and promote healing were evaluated in a mouse liver laceration model and a full-thickness dermal injury model, respectively. Incorporation of PLPs into fibrin matrices increased clot density, stiffness, fibroblast migration in vitro, and markers of wound healing in vivo. Both normal and antimicrobial PLPs significantly decreased blood loss in vivo. Antimicrobial PLPs decreased bacterial burden in vitro and in vivo. Finally, co-application of ultrasound and PLPs increased clot density, stiffness, cell migration, and wound healing markers, but at lower dosages and time scales relative to those required with PLPs alone. Overall, these results demonstrate that PLPs are beneficial for augmenting hemostasis and promoting healing.
The vortex configuration of spins emerges in anisotropic magnetic nanomaterials with certain dimensions in the absence of an external magnetic field (MF). This configuration enables rapid control over a particle’s magnetization direction and magnitude. Nanoparticles supporting vortex spin configuration possess near zero net magnetization in the absence of MF, which affords greater colloidal stability in suspensions. This property makes magnetic vortex particles uniquely suited for applications in biological systems. Guided by micromagnetic simulations, we predict and experimentally demonstrate magnetic vortex states in an array of colloidally synthesized magnetite nanodiscs (MNDs) 100–250 nm in diameter. The vortex state in MNDs was measured directly via electron holography. Following phase transfer into physiological solutions, we applied these MNDs for remote control of activity of sensory neurons with weak (7–26 mT), slow-varying (1–5 Hz) MFs. The latency of this magnetomechanical neuronal excitation was correlated to the MND volume and the applied MF amplitude and frequency. Consistent with MNDs geometry and magnetite chemistry, MNDs exhibit direction-dependent hysteresis loops, which results in their hysteretic heating in high-frequency (100s kHz) alternating MFs. We determined MNDs capability of heat dissipation with efficiency (specific loss power) up to 1000 W/g in MFs with frequencies of 75-150 kHz. This is on par with record reported efficiencies for the isotropic magnetite nanoparticles, but observed at 10-50 times lower particle counts owing it to the MND volumes. This characteristic allows for targeted activation of heat-gated ion channels in neurons upon application of high-frequency alternating MFs. With their large induced magnetic moments in slow-varying MFs and high heating efficiencies in alternating MFs, MNDs allow for multiplexed stimulation of neurons by selectively activating mechanoreceptors or thermoreceptors.

2:15 PM SB02.03.03
Flame Nanoparticle and Device Engineering for Biomedicine Georgios A. Sotiriou; Karolinska Institutet, Sweden

Nanoscale materials show great potential in the biomedical field as they can serve as superior bioimaging contrast agents, diagnostic and therapeutic tools while a key element for the successful implementation of nanoscale materials in clinical applications is multi-functionality. However, the two main bottlenecks for the successful commercialization of such nanotechnologies, that are often neglected in studies, are scalability and reproducibility. Here, a few recent examples will be shown of how flame nanoparticle synthesis, a nanomanufacture process famous for its scalability and reproducibility, may be employed for the production of sophisticated nanoscale materials to tackle important medical challenges.

We focus on nanoparticle formation by flame spray pyrolysis, a highly versatile nanomanufacture process and advance the knowledge for synthesis of complex nanoparticles and their direct integration in multi-scale biomedical devices. We place specific emphasis in multifunctional and responsive nanoparticles that may be used either as transducer elements or as diagnostic probes to monitor biological processes.

We synthesize nanoparticles with high purity and controlled sizes as a basis for functional nanoparticles. We have demonstrated functionalization of luminescent nanoparticles with targeting proteins, whose receptors are overexpressed in cancer cells, and detected them by fluorescence cell imaging. We have also recently explored the potential of flame-made nanoparticles in H2O2 biosensing, using enzyme-mimetic luminescent CeO2:Eu3+ nanoparticles that exhibit catalase-mimetic activity and decompose H2O2. We have also shown the potential of stimuli-responsive nanoparticles as both photothermal agents by near-IR irradiation as well as superparamagnetic nanoparticles for the enhanced triggered-drug-release from alginate beads by hyperthermia. Flame aerosol reactors for nanoparticle synthesis are a powerful toolbox for the scalable and reproducible production of sophisticated nanoparticles with properties not easily attained by other nanomanufacture processes. Their systematic employment in biomedicine has the potential to open up several avenues for nano-enabled solutions to medical challenges.

Acknowledgements
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and the Åke Wiberg Foundation (M16-0098) is kindly acknowledged.

References

2:30 PM SB02.03.04
An Electrochromic Paper-Based Device as a Diagnostic Test for Cystic Fibrosis Elvira Fortunato and Rodrigo Martins; FCT-UNL, Portugal

Cystic Fibrosis (CF) is an inherited disorder affecting more than 70000 people worldwide, especially Caucasian populations with a carrier prevalence of 1/3000. Currently, it has no cure but an early diagnosis remains a critical issue for an optimistic prognosis. Sweat chloride test has been the gold standard to diagnose CF since the affected present higher sweat chloride concentrations than healthy individuals (≥ 60 mM). In this work, a planar electrochromic point-of-care device, based on WO 3 nanoparticles produced by microwave assisted hydrothermal synthesis, was developed for CF low-cost diagnostic testing especially in resource-limited environments. For electrodes patterning, a CO 2 laser technology was used in a PET/ITO sheet. The device presents a design that allows the NaCl-based electrolyte deposition, used as artificial sweat, only on time of usage directly on the nanoparticles or in a paper pad. By applying an operating voltage of 3 V for 1 min, the nanoparticles change their optical properties according to NaCl concentration, presenting a blue colouration with different intensities for different NaCl concentrations. The device is able to differentiate between a positive and negative diagnosis within few minutes, obtaining an RGB channel ratio of 1.37±0.03 for 60 mM of NaCl, when imaged.

2:45 PM SB02.03.05
Size- and Functionalization-Dependent Transport of Silica-Based Drug Delivery Vehicles across Cellular Barriers Using an Optimized Class of Cell-Penetrating Peptides Isabel Gessner, Annika Klimpel, Merlin Klußmann, Ines Neundorf and Sanjay Mathur; University of Cologne, Germany

While the translocation of cargos across biological barriers is the key issue for therapeutic applications, cell-penetrating peptides (CPPs) have demonstrated to be highly useful for the transport of molecules and even nanomaterials into cells. Herein, we studied how the intracellular delivery of silica nanoparticles can be modulated after decoration with differently active CPPs. The latter were obtained after an Ala scan of the recently developed CPP sC18. Out of the 16 peptides obtained, two were selected for further studies: the first displayed a higher positive net charge and enhanced amphipathicity resulting in significantly higher internalization rates than sC18. The second one demonstrated reduced cellular uptake efficiencies, and served as a control. Attachment of these CPPs to silica nanoparticles of different sizes (50, 150 and 300 nm) was performed electrostatically to preserve the secondary alpha-helical structure of the peptides, which was confirmed by CD-spectrometry. Flow cytometry studies showed that all conjugates were efficiently internalized into HeLa cells revealing a particle size-dependent uptake. Moreover, similar to the free peptides, a peptide-dependent internalization could be observed according to the position of the alanine residue in the biomolecular sequence. These results demonstrate the huge potential of sequential fine-tuning of CPPs and provide more insights into their interaction with inorganic nanocarrier surfaces.
3:00 PM BREAK

3:30 PM *SB02.03.06
Engineered Nanomaterials as Medicines for Traumatic Brain Injuries Ester J. Kwon; University of California at San Diego, United States

Traumatic brain injury (TBI) affects ~1.7 million Americans every year and is the largest cause of disability-adjusted life-years lost worldwide. Treatments available in the clinic remain palliative, with no strategies that address the long-term brain health of patients. There is therefore an urgent need for new therapeutics. One hallmark of TBI is vascular damage, which is observed through clinical imaging modalities such as magnetic resonance imaging and X-ray computed tomography. We are engineering nanometer scaled materials to exploit this vascular damage in order to gain access to the injured tissue for the delivery of both diagnostic and therapeutic payloads. In addition, we are interested in studying and developing strategies to target nanomaterials to specific cell-types and structures within the injured brain.

We first explore the time window in which vascular damage allows the infiltration of nanomaterials into the brain tissue, and determine that we can deliver material into the brain when delivered hours after injury. Furthermore, we can exploit this transient window of vascular disruption to deliver targeted nanomaterials that carry therapeutic nucleic acids with neuronal specificity. We next explore the size range of materials that can infiltrate the brain after injury and find that similar to the enhanced permeation and retention (EPR) effect observed for nanomaterials in cancer, there is an optimal size for materials to accumulate in the injured brain. We leverage this accumulation in the injured brain for the delivery of a diagnostic payload that generates signal in response to an enzyme that has elevated and deleterious activity in brain injuries. We observe increased activation of this nanosensor in the context of TBI compared to uninjured brains. Collectively, we are engineering nanomaterials that provide diagnostic and therapeutic capabilities to provide new medicines for TBI.

4:00 PM SB02.03.07
Design of High-Aspect-Ratio Nanoneedle Arrays with Tunable Sharpness for Interfacing and Influencing Biological System Hyejeong Seong, Stuart G. Higgins, Jelle Penders, James P. Armstrong, Axel C. Moore and Molly Stevens; Imperial College London, United Kingdom

Bioengineered systems often employ physical cues arising from intrinsic properties of the substrate in order to mimic specific physiological conditions. In particular, materials with micro- and nanoscale topographies are known to be regulators of cell adhesion, morphology, migration, proliferation, and differentiation. Of these topographies, high-aspect-ratio nanostructures have emerged as versatile platforms for facilitating drug/biomolecule delivery, and intracellular sensing.1,2,3

Here, we present a new approach for the microfabrication of high-aspect-ratio, nondegradable silicon nanoneedle arrays that can support the long-term culture of human mesenchymal stem cells (hMSCs).4 Through a combination of different etching processes, we were able to finely control the sharpness of the nanoneedles from 20 to 700 nm. This enabled us to investigate the influence of the nanoneedle tip diameter upon the phenotype of interfaced hMSCs. High-content, image-based profiling of 100,000 individual cells cultured on different nanoneedle arrays revealed that the nanoneedle tip diameter could be used to influence cell shape, nuclear size, and actin alignment in a controllable manner. In particular, the polarization of actin on sharp nanoneedles was found to be mediated by the Rho-GTPase pathway. Mechanoresponsive cell behavior, including altered expression of lamins, Yes-Associated Protein (YAP) target genes and focal adhesion genes, could also be tuned by altering the tip diameter. These results were correlated to increased nuclear membrane impingement by the sharp nanoneedles, as shown by volumetric, superresolution imaging using focused-ion beam scanning electron microscopy (FIB-SEM).

Taken together, these observations demonstrate the importance of nanostructures for controlling the cell interface and phenotype. Our method of fabricating high-aspect-ratio nanostructures will be broadly applicable to the design of nanotopographical interfaces for biomedical devices, such as bioelectrodes and diagnostic platforms.

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3 C. S. Hansel, S. W. Crowder, …, M. M. Stevens., ACS Nano 2019, 13, 2913
4 H. Seong, …, M. M. Stevens, Submitted
Renal Clearable Catalytic Gold Nanoclusters for In Vivo Disease Monitoring Colleen Lovnachan¹, Ava Soleimany², Sangeeta Bhatia² and Molly Stevens¹; ¹Imperial College London, United Kingdom; ²Massachusetts Institute of Technology, United States

Ultra-small gold nanoclusters (AuNCs) have emerged as agile probes for in vivo imaging, as they exhibit exceptional tumour accumulation and efficient renal clearance properties. However, their intrinsic catalytic activity,¹ which can enable increased detection sensitivity, has yet to be explored for in vivo sensing. By exploiting the peroxidase-mimicking activity of AuNCs and the precise nanometer size filtration of the kidney, we designed multifunctional protease nanosensors that respond to disease microenvironments to produce a direct colorimetric urinary readout of disease state in less than 1 h.²

Our nanosensor is comprised of renal clearable catalytic AuNCs (< 2 nm) tethered to a larger protein carrier via peptide linkages, that is disassembled in response to dysregulated protease activity at the site of disease. We demonstrated that the peptide-templated AuNCs can be filtered through the kidneys and excreted into the urine with high efficiency and retain catalytic activity in complex physiological environments. To demonstrate the modularity of the system, we synthesized functionalized peptide substrates shown to be specifically cleaved by either the serine protease thrombin or the zinc-dependent matrix metalloproteinase 9 (MMP9), which play a critical role in cardiovascular disease or cancer, respectively. We demonstrated the response of our protease nanosensors both in vitro and in vivo, achieving sensitive disease detection with a rapid, colorimetric urinary readout using our MMP-responsive nanosensors. We monitored the catalytic activity of AuNCs in collected urine of a mouse model of colorectal cancer where tumour-bearing mice showed a 13-fold increase in colorimetric signal compared to healthy mice. Nanosensors were eliminated completely through hepatic and renal excretion within 4 weeks after injection with no evidence of toxicity.

Our system exhibited a dual amplification platform: leveraging both in vivo protease activity and inorganic catalytic activity of AuNCs to provide a visual readout of disease state directly in urine. With this method, we demonstrate that these AuNCs are small enough to be filtered efficiently through the kidneys and retain catalytic activity in cleared urine, thus providing a versatile disease detection platform that is compatible for deployment at the point-of-care (PoC). Our adaptable nanocatalyst amplification platform should be applicable in low-resource settings for rapid detection of a diverse range of diseases by exploiting their specific enzymatic signatures and will democratize access to advanced and sensitive diagnostics.


Therapeutic Applications of Graphene Quantum Dots for Central Nervous System Disease Byung Hee Hong¹, Je Min Yoo², Donghoon Kim², Hanseok Ko³ and Kyungsun Kang¹; ¹Seoul National Univ, Korea (the Republic of); ²Biographene Inc., Korea (the Republic of); ³Johns Hopkins University, United States

Graphene quantum dots (GQDs) are 2–3 nm sized nanoparticles that have a hydrophobic 2D graphitic domains with hydrophilic oxygen-containing functional groups along the edges. The carboxyl groups on GQDs can be modified to amine groups through simple organic chemistry to be decorated with many different small molecules. In our recent study, the application of GQDs as a therapeutic agent has been demonstrated to alleviate Parkinson's disease by degrading pre-existing α-synuclein fibers as well as by preventing its fibrillization. It is also proven that GQDs have negligible long-term toxicity in animal models as they are excreted through urine in a few weeks (D. Kim et al., 2018, Nat. Nanotechnol., 13, 812-818). Thus, GQDs are gaining growing interests in the field of nanomedicine by virtue of such novel capability to prevent or remove undesirable aggregation of biomolecules that causes various diseases. In this talk, we will introduce our recent finding that GQDs treatment considerably decreases the accumulation of intracellular cholesterol through physical interactions both in vitro and in vivo, resulting in a therapeutic effect against impaired functions in Niemann-Pick type C disease (NPC). The GQDs are found to induce...
autophagy to restore compromised autophagic flux, which eventually reduces the atypical accumulation of autophagic vacuoles. Moreover, GQDs injection prevents the loss of Purkinje cells in the cerebellum with decreased microglial activation. The finding that GQDs alleviate impaired functions in NPC provides a promising potential for the treatment of NPC and related lysosomal storage disorders (LSDs). In addition, it will be shown that the aggregation of amyloid beta and tau protein fibrils related to Alzheimer's Disease has been successfully prevented by GQDs in vitro. We suppose that the thermodynamic equilibrium can be repositioned by adding GQDs as they interfere with aggregating molecules in terms of enthalpy and entropy, leading to the change the Gibbs free energy to block or reverse the fibrosis. We expect that this new thermodynamic approach to treat the central nervous system disease would be expanded to other fibrosis diseases in liver, lung, and kidney in the future.

4:45 PM SB02.03.10
Engineering the Cas9 Protein via a Chemical Route for Nonviral Delivery Hyun Jung Chung and Yoo Kyung Kang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The CRISPR/Cas9 system has been one of the most innovative tools for genome editing. For therapy, viruses expressing Cas9 and sgRNA have been used, but show limitations in safety due to off-target effects and difficulty in viral packaging. Recently, strategies for nonviral, in vivo delivery have been developed, however problems reside due to the need of using excess carrier amount which causes toxicity. To solve this problem, we have developed conjugate systems of the Cas9 ribonucleoprotein, to safely deliver the cargo in vivo. Cas9 from Streptococcus pyogenes (SpCas9) was covalently conjugated with cationic polymers or lipids, to enhance delivery by increasing the net charge or hydrophobicity of the ribonucleoprotein. Mixing the Cas9 conjugates with sgRNA resulted in the formation of nano-sized complexes, which showed enhanced cellular uptake and genome editing efficiencies compared to the native complexes, demonstrated in various human cell lines and bacteria. To improve the versatility of Cas9 as a platform for chemical modification, we have also generated a bioorthogonal Cas9 protein by incorporation of unnatural amino acids. Incorporation of azidohomoalanine could increase the number of functionalities for further modification, while azidophenylalanine allowed site-specific conjugation. Our platform technologies present a versatile platform for engineering the Cas9 ribonucleoprotein using a chemical route, which can be used as a therapeutic for various human diseases, such as cancer, infections, and genetic disorders.

SESSION SB02.04/SB05.04/SB07.03: Joint Session: Bioelectronics
Session Chairs: Mohammad Reza Abidian, Ritchie Chen, Sahika Inal and Bozhi Tian
Tuesday Morning, December 3, 2019
Hynes, Level 3, Ballroom B

8:00 AM SB02.04.01/SB05.04.01/SB07.03.01
Graphene Based Health Monitoring Dmitry Kireev and Deji Akinwande; The University of Texas at Austin, United States

The modern healthcare and biomedical systems show a clear trend towards personalized, predictive, and preventive medicine. Development of the concept, commonly known as mobile health (mHealth), means that a huge shift in the paradigms of medical device architectures is to be expected in the near future thanks to the increased portability of medical devices as well as increase in number of specific mobile-based apps. An ideal wearable device should possess a set of important requirements, such as (i) low cost of fabrication, (ii) being conformable and compatible with human skin, and (iii) multifunctionality. The latter is of special importance if the goal is to build not just a single specific device, but to rather develop a technology and basis for scalable fabrication of devices that are capable to detect a plurality of vital signals (HR, EEG, ECG, hydration, galvanic response, etc.). In order to develop the universal technology that meets all three requirements mentioned above, we propose to utilize graphene in combination with epidermal technology. The conventional epidermal biosensors are based on metal and silicon based thin films that are patterned into special structures for softness and stretchability and embedded into soft biocompatible polymers. The choice of two-dimensional materials is the most natural due to their ultra-thinness, allowing extreme flexibility, transparency, and conformability to almost any rough surface, including skin [1]. Graphene based passive electrodes have been successfully used to epidermal sensing of electrocardiograms (ECG), electromyogram (EOG), electroencephalogram (EEG), skin temperature, and skin
hydration [1], [2]. It is important to emphasize that the research work is based on large-area CVD-grown graphene, allowing us to develop low-cost, wearable, and fully conformable to skin devices. Furthermore, large area fabrication gives an ultimate promise for future devices fully based on 2D materials to be available on market. In terms of possible applications, the proposed technology can be easily expanded towards other fields of healthcare biosensing, such as in vivo electrophysiology, UV exposure sensing, pressure sensing, or even towards building electronic skin, and prosthetics.


8:15 AM SB02.04.02/SB05.04.02/SB07.03.02
Multifunctional Fiber Based Neural Probes with Integrated Neurotransmitter Detection Atharva Sahasrabudhe1, Tural Khudiyev1, Tomo Tanaka1,2, Kyoungsuk Jin1, Marc-Joseph Antonini1,3, Andres Canales1, Yoel Fink1,1, Karthish Manthiram1 and Polina Anikeeva1,1; 1Massachusetts Institute of Technology, United States; 2NEC Corporation, Japan; 3Harvard-MIT Division of Health Science and Technology, United States

One of the major challenges in deciphering the fundamental principles of cognition is the lack of appropriate tools for seamless interfacing with neurons across all their signaling modalities. Gaining holistic understanding of neural circuits and their control of behavior requires invention of neural probes that can simultaneously record and modulate electro-chemical activity of neurons while evoking minimal inflammatory response for periods ranging from minutes to years. Multifunctional fibers have recently emerged as a promising platform for integrating multiple functional elements to probe and control neural activity that also minimizes the foreign body response.

In my presentation, I will describe our efforts in further expanding the multifunctionality of polymer-based fiber probes by incorporating an electrochemical sensor that enables real-time tracking of neurotransmitter dynamics in behaving animals. This is achieved by introducing a carbon nanotube (CNT) based electrocatalytic electrode within the multifunctional fiber-based probes during their fabrication via thermal drawing process. The resulting devices can be implanted chronically and perform electrical recording and stimulation of neurons, light delivery through waveguides for optogenetics, drug and gene delivery via microfluidic channels, and voltammetry via the CNT electrodes for dynamic detection of dopamine. We envision that these multimodal, miniature, and mechanically compliant probes will facilitate understanding of the neurophysiological underpinnings of dopamine-dependent behaviors including reward, addiction, and motor control.

8:30 AM *SB02.04.03/SB05.04.03/SB07.03.03
OPEN SLOT

9:00 AM *SB02.04.04/SB05.04.04/SB07.03.04
Chronic Recordings from Behaving Animals Using Microwire-CMOS Technology Nicholas Melosh; Stanford University, United States

Mammalian brains consist of billions of neurons operating at millisecond time scales, which current recording techniques only capture a tiny fraction. Recent advances in CMOS device design have led to high-recording quality planar probes, with diminishing sizes to ameliorate the extent of tissue damage. Matching these powerful silicon electronics to the inherently three dimensional architecture of the brain has remained challenging however, as devices are constrained to the planar two dimensional surfaces required for silicon processing. Here we describe a chronic interface using arrays of microwires read out by CMOS-based devices with a low-tissue damage, and controllable, three dimensional distribution of recording sites. The core concept is using a bundle of insulated microwires mated to a large-scale CMOS microelectrode array, such as found in modern camera chips or displays. We show recent results on the mechanics and tissue damage from microwire insertion scales strongly with wire diameter. Microwires with <25µm diameters are shown to have minimal to no vascular disruption or bleeding, as opposed to more conventional 75 to 100 µm devices. These microwires are then arranged into bundles to control the spatial arrangement and three dimensional structure of the distal (neuronal) end, while providing a robust parallel contact plane on the proximal side which is interfaced to a planar pixel array. The modular nature of the design enables a wide array of microwire types and size to be mated to a variety of different CMOS chips, making the same
fundamental platform scalable from a few hundred electrodes to tens of thousands. We thus link the rapid progress and power of commercial multiplexing, digitisation and data acquisition hardware together with a bio-compatible, flexible and sensitive neural interface array. We present recent massively parallel recording using mouse and rat models, showing both spiking activity from single neurons and local field potentials within both chronic and acute settings.

9:30 AM *SB02.04.05/SB05.04.05/SB07.03.05
Membrane Curvature at the Interface between the Cell Membrane and Nanoscale Electrodes Bianxiao Cui; Stanford University, United States

The interaction between the cell membrane and the measuring electrode is crucial for crucial for sensitive measurement of cell electric activities. We are interested in exploring nanotechnology and novel materials to improve the membrane-electrode coupling efficiency. Recently, we and other groups show that vertical nanopillars protruding from a flat surface support cell survival and can be used as subcellular sensors to probe biological processes in live cells. The nanopillar electrodes deform plasma membrane inwards and induce membrane curvature when the cell engulfs them, leading to a reduction of the membrane-electrode gap distance and a higher sealing resistance. As an electrode sensor, nanoelectrodes offer several advantages such as high sensitivity, subcellular spatial resolution, and precise control of the sensor geometry. Furthermore, we found that the high membrane curvature induced by nanoscale electrodes significantly affects the distribution of curvature-sensitive proteins and stimulates several cellular processes in live cells. Our studies show a strong interplay between biological cells and nanoscale topography, which is an essential consideration for future development of interfacing devices.

10:00 AM BREAK

10:30 AM *SB02.04.06/SB05.04.06/SB07.03.06
Engineering Skin-Like Soft Electrical Interface with Biological Systems Zhenan Bao; Stanford University, United States

In this talk, I will discuss several projects related to engineering conductive materials and developing fabrication methods to allow electronics with effective electrical interfaces with biological systems, through tuning their electrical as well as mechanical properties. The end result is a soft electrical interface that has both low interfacial impedance as well as match mechanical properties with biological tissue. Several applications of such electronics will be presented.

11:00 AM *SB02.04.07/SB05.04.07/SB07.03.07
Soft Materials in Wireless Closed-Loop Neuromodulation Systems for Treating Organ Dysfunction John A. Rogers; Northwestern University, United States

Bioelectronic medicines targeted at the peripheral nervous system have the potential to address a wide variety of diseases, from diabetes to bladder dysfunction. The foundational concepts have existed for decades but implementation has been limited and fraught with persistent challenges, including lack in target specificity, nerve interface biofouling, and inability to acquire real time physiologic signals for conditional delivery of corrective stimuli, leading to excess and unnecessary stimulation. Here we present a set of materials, a treatment strategy and supporting technology platform that address many of these challenges, using bladder control as model system. Specifically, we report capabilities for continuous monitoring of bladder function using an ultralow modulus, stretchable strain gauge to measure dimensional changes, real-time data analytics to identify pathological behavior based on the resulting data, and automated, closed-loop optogenetic neuromodulation of bladder sensory afferents to normalize bladder function in the context of acute cystitis, with generic applicability to many other organ systems and conditions.

11:30 AM *SB02.04.08/SB05.04.08/SB07.03.08
Miniature, Wireless Bioelectronics by Harvesting Energy from Magnetic Fields Jacob T. Robinson; Rice University, United States

Miniature, wireless bioelectronic devices enable less invasive surgical implantation and the ability to target tiny nerves or brain areas. However, as these neural stimulators become smaller, we must engineer new ways to deliver
power. Conventional power deliver relies on long wires to deliver power from an implanted battery or subcutaneous antenna. These leads can limit device placement and cause device failure due to lead breakage or infection. Conventional wireless power delivery through biological tissue is difficult when devices are miniaturized and placed deep in the body. Here we show that magnetic materials can effectively harvest energy from magnetic fields and power millimeter-sized bioelectronics. These materials show excellent power densities even as the devices are made small allowing them to be fully implanted and wirelessly powered. We demonstrate that these mm-sized wireless devices can be used to power different types of conventional stimulation electrodes when implanted in rabbits, pigs, and freely moving rats. Furthermore, these miniature electrical stimulators can be adapted to power many individually addressable stimulation channels while still maintaining a small overall device footprint.

SESSION SB02.05: Bioelectronic and Biomedical Devices
Session Chairs: Ritchie Chen and Yoonkey Nam
Tuesday Afternoon, December 3, 2019
Hynes, Level 2, Room 200

1:30 PM *SB02.05.01
Soft Electronics for Health Monitoring—From the Skin to Below the Skin Sheng Xu; University of California, San Diego, United States

Soft electronic devices that can acquire vital signs from the human body represent an important trend for healthcare. Combined strategies of materials design and advanced microfabrication allow the integration of a variety of components and devices on a stretchable platform, resulting in functional systems with minimal constraints on the human body. In this presentation, I will demonstrate a wearable multichannel patch that can sense a collection of signals from the human skin in a wireless mode. Additionally, integrating high-performance ultrasonic transducers on the stretchable platform adds a new third dimension to the detection range of conventional soft electronics. Ultrasound waves can penetrate the skin and noninvasively capture dynamic events in deep tissues, such as blood pressure and blood flow waveforms in central arteries and veins. This stretchable platform holds profound implications for a wide range of applications in consumer electronics, sports medicine, defense, and clinical practices.

2:00 PM SB02.05.02
Stretchable, Patch-Type Calorie-Expenditure Measurement Device Based on Pop-Up- Shaped Nanoscale-Crack Based Sensor Kiyoon Kwon and Tae-il Kim; Sungkyunkwan University, Korea (the Republic of)

Demands for precise health information tracking techniques are increasing, especially for daily dietary requirements to prevent obesity, diabetes, etc. Many commercially available sensors that detect dynamic motions of the body lack accuracy, while novel strain sensors at the research level mostly lack the capability to analyze measurements in real life conditions. Here, we demonstrate a stretchable, patch-type calorie expenditure measurement system that integrates ultra-sensitive crack-based strain sensor and Bluetooth-enabled wireless communication circuit to offer both accurate measurements and practical diagnosis of motion. The crack-based strain gauge transformed into pop-up-shaped structure provides reliable measurements and broad range of strain (~100%). Combined with the stretchable analysis circuit, the skin attachable tool translates variation of knee flexion angle into calorie expenditure amount, using relative resistance change (R/R0) data from the flexible sensor. As signals from knee joint angular movement translates velocity and walking/running behavior, the total amount of calorie expenditure is accurately analyzed. Finally, theoretical, experimental and simulation analysis of signal stability, dynamic noises and calorie expenditure calculation obtained from the device during exercise are demonstrated. For further applications, we expect our devices to be used in broader range of dynamic motion of the body for diagnosis of abnormality and for rehabilitation.

2:15 PM SB02.05.03
Fabric-Reinforced Elastomer Composites for Neo-Aorta Application in Normothermic Heart Perfusion Devices Dinara Zhalmuratova, Thanh-Giang La, Katherine T. Yu, David Nobes, Darren Freed, Chun-il Kim and Hyun-Joong Chung; University of Alberta, Canada
An ex-vivo heart perfusion device preserves the donor heart in a warm beating state during transfer between extraction and implantation surgeries. One of the current challenges includes the use of rigid and noncompliant plastic tubes, which causes injuries to the heart at the junction between the tissue and the tube. The compliant and rapidly strain-stiffening mechanical property that generates a J-shaped stress-strain behavior, is necessary for producing the Windkessel effect, which ensures continuous flow of blood through the aorta. In this study, we mimic the J-shaped and anisotropic stress-strain behavior of human aorta in synthetic elastomers to replace the problematic noncompliant plastic tube.

Firstly, we measured the mechanical properties of human \( n = 1 \) and porcine aorta \( n = 14 \) to quantify the nonlinear and anisotropic behavior under uniaxial tensile stress from five different regions of the aorta. Here, the human and porcine aortas demonstrated the J-shaped strain-stiffening in uniaxial tensile testing and were stiffer in the longitudinal direction when compared to the circumferential direction. In terms of location dependence, we observed that the porcine aorta appears to be stiffer at the distal sections from the heart when compared proximal regions.

Secondly, fabric-reinforced elastomer composites were prepared by reinforcing silicone elastomers with embedded fabrics in trilayer geometry. The knitted structures of fabric provide strain-stiffening as well as anisotropic mechanical properties of the resulting composite in a deterministic manner. By optimizing the combination between different elastomers and fabrics, the resulting composites matched the J-shaped and anisotropic stress-strain behavior of natural human and porcine aorta. In order to find the optimal combination between the elastomeric matrix and the fabric reinforcement, the uniaxial tensile properties of various commercial elastomers and commercial fabrics/textiles were tested and the data were archived. Here, neat elastomer materials could not mimic the J-shape, nor the anisotropy. Among composite elastomers, knitted rayon/spandex fabric sandwiched by the two layers of Ecoflex 0050 was the best in mimicking both the strain-stiffening and anisotropy features of the aorta. Here, the knitted fabrics played a role of anisotropically crumpled elastin and collagen, which enable low moduli at low strains and a rapid stiffening at high strains.

Thirdly, improved analytical constitutive models based on Gent’s and Mooney-Rivlin’s constitutive model (the elastomer matrix) combined with Holzapfel–Gasser–Ogden’s model (the stiffer fabrics) were developed to describe J-shaped behavior of the natural aortas and the fabric-reinforced composites. Overall, the elasticity of natural aorta at low strains is attributed to the elastin (Mooney-Rivlin and Gent) and stiffening of the curve at higher strains originates from collagen contribution and \( k_1 \) and \( k_2 \) parameters (Holzapfel). In the fabric-reinforced elastomers, the low elastic modulus at low strains comes from the elastomer matrix and the stiffening at higher strains comes from embedded fabric. Moreover, the values of the main parameters, namely \( \mu, k_1 \) and \( k_2 \) for Gent’s model, and stress-like parameters \( C_{10}, C_{01}, k_1 \), and \( k_2 \) and for Mooney-Rivlin’s were very similar between the natural aorta and our fabric-reinforced composites. These support the aorta-like behavior of the developed fabric-reinforced composites.

In a broad context, J-shape and anisotropy are general properties of many soft biological tissues. We anticipate that the suggested design criteria and our proposed analytical models can be helpful in designing biomaterials that mimic properties of complex soft biological tissues with synthetic materials. The material design concept can also be used in emerging engineering fields such as soft robotics and microfluidics, where the Windkessel effect can be useful in regulating the flow of fluids.

**2:30 PM *SB02.05.04***

**Tunable, Implantable Materials that Enable Structural Repair and Functional Augmentation in the Heart**

Ellen T. Roche; Massachusetts Institute of Technology, United States

The enhanced design and fabrication of cardiovascular devices relies on technological advances in implantable materials. In this talk I will discuss the importance of tunable and optimized materials for realizing implantable cardiovascular implants for structural repair, active assistance and biological therapy. I will discuss representative devices, and their component materials, in each of these three areas, each addressing an identified shortcoming of existing technologies. In terms of structural repair devices, I will discuss a minimally invasive delivery system that uses a biodegradable, photo-activated adhesive for atraumatic repair of intracardiac defects. Moving to active assist devices I will discuss the modelling and design of a bioinspired soft active material technology that enabled the fabrication of a robotic direct cardiac compression device whose design mimics the orientation of the heart muscle. In vivo testing of this device has demonstrated that it is possible to improve cardiac output without the need for a
blood-contacting approach in an acute heart failure animal model. Building on the platform of soft robotic approaches to enhance organ function, I will discuss pediatric cardiac assist devices and mechanical devices to enhance respiratory function. Lastly, to illustrate examples of enhanced biological therapy, I will discuss the use of biomaterials as vehicles for cell delivery and a targeted, refillable bio-implant for increasing retention of therapy in the heart, which enables repeated local administration of biological or pharmacological delivery, and some preliminary steps to combine these mechanical and biological therapies in order to improve delivery of drugs and modulate the host response.

3:00 PM BREAK

3:30 PM *SB02.05.05
Engineering Materials for Bioelectronics Molly Stevens; Imperial College London, United Kingdom

An important aim of regenerative medicine is to restore tissue function with implantable, laboratory-grown constructs that contain tissue-specific cells that replicate the function of their counterparts in the healthy native tissue. In this talk I will describe our recent work in the development of materials for bioelectronics including polymers and functionalised nanoneedles. I will also describe our new imaging technologies for monitoring and elucidating the cell-material interface.

4:00 PM SB02.05.06
Bioelectronics for Tissue-Wide Electrophysiology and Cell-Type-Specific Electrophysiological Remodeling Jia Liu; Harvard University, United States

Tissue-wide electrophysiology with single-cell and single-spike spatiotemporal resolution, and cell-type specificity is critical for heart and brain studies. In this talk, I will first discuss the creation of cyborg organoids: the three-dimensional (3D) assembly of soft, stretchable mesh nanoelectronics across the entire organoid by the cell-cell attraction forces from 2D-to-3D tissue reconfiguration during organogenesis. We demonstrate that stretchable mesh nanoelectronics can migrate with and grow into the initial 2D cell layers to form the 3D organoid structure with minimal impact on tissue growth and differentiation. The intimate contact between the dispersed nanoelectronics and cells enables us to chronically and systematically observe the evolution, propagation and synchronization of the bursting dynamics in human cardiac organoids through their entire organogenesis and maturation. Second, I will discuss a general concept of genetically-targeted functional assembly in tissue--in this case through a convergence of protein engineering and polymer chemistry that genetically instructs specific living neurons to guide chemical synthesis of conductive polymers onto the plasma membrane. Conductive polymers were assembled in vivo at genetically- and subcellularly-targeted locations per design specifications, and were demonstrated to achieve intended functionality in the form of newly-created electrical conduction pathways. Imaging, electrophysiology, and behavioral analyses confirmed that in vivo conductive polymer assembly preserved neuronal viability, remodeled cellular membrane properties, and elicited cell-type-specific behaviors in freely-moving animals. In the end, I will discuss the prospects for future advances in bioelectronics to overcome challenges in neuroscience and cardiology.

4:15 PM SB02.05.07
Understanding Ion Dynamics in Organic Semiconductor by In Situ NMR Spectroscopy Yanting Jin, Evan Wenbo Zhao, Christopher Proctor, George G. Malliaras and Clare Grey; University of Cambridge, United Kingdom

Organic semiconductors are widely applied in bioelectronic devices, such as organic electrochemical transistors (OECT) and ion pump for drug delivery. This is largely due to their mixed electronic/ionic conductivity, which enables strong coupling between these two charge carriers in the bulk of the material. While electronic charge carrier transport in these materials is rather well understood, the transport of ions has not been studied to equal depth. NMR spectroscopy is a powerful nuclei-specific technique that can provide atomic structural information as well as quantitative and dynamic information of the disordered polymer system. Here, we report on the interaction between the sodium ion and the poly(3,4-ethylenedioxythiophene) polymer doped with poly(styrene sulfonate) (PEDOT:PSS) using $^{23}$Na NMR spectroscopy. The structure of PEDOT:PSS is heterogeneous, and it mainly consists of PSS-rich region and PEDOT:PSS nano-domains (known as “pancakes” due to the non-sphere shape revealed by X-ray scattering measurement). We found that Na absorbs in the pancakes gives rise to unique NMR patterns due to the strong quadrupolar interaction between the Na and the polymer. Thus, we are able to distinguish Na in aqueous NaCl solution and Na absorbed in the polymer. Then we selectively monitor the absorption and desorption
of the Na⁺ and Cl⁻ ions in the polymer when it is biased to different voltages, in order to elucidate and quantify the species within the polymer. Lastly, the Na⁺ dynamics (self-diffusion coefficient and ion drift mobility) is probed by pulsed-field gradient NMR. The result suggests a fast Na⁺ mobility in the hydrated polymer with notable anisotropy possibly due to the preferred orientation of the PEDOT:PSS nanodomains. This work demonstrates the application of in-situ NMR to probe ion-polymer interactions and to correlate the microstructure of the polymer to ion mobility, which improves our fundamental understanding of mixed conductors and our ability to optimise the performance of their devices.

Reference:

4:30 PM SB02.05.08
Hybrid Scaffolds Based on PEDOT:PSS/Collagen or Carbon Nanotubes for the Next Generation of 3D Cell Culture Janire Saez, Chrysanthi-Maria Moysidou, Donata Iandolo, Charalampos Pitsalidis and Roisin Owens; University of Cambridge, United Kingdom

3D cell cultures in biomimetic environments are finding numerous applications in drug discovery, regenerative medicine, among many other fields. 3D cultures often rely on scaffolds, typically made of polymeric materials, which support cell attachment and favour tissue development. These scaffolds possess certain structural and mechanical properties, such as porosity and stiffness, that mimic the extracellular matrix providing a similar microenvironment to that found in vivo. However, these scaffolds are typically passive, merely providing a templated support. We have been focusing on a synthetic biology approach where we are integrating additional functionality into cell culture scaffolds, by using electroactive scaffolds capable of monitoring cell growth and differentiation. Porous conducting polymer scaffolds made of PEDOT (poly(3,4-ethylenedioxythiophene): PSS were obtained by the freeze-drying method. This method allows the addition of different components to tune mechanical and biochemical properties (e.g., collagen), to enhance conducting properties (e.g., carbon nanotubes), thereby fine-tuning the chemophysical properties of the scaffold to render the system suitable for a variety of biological applications. We demonstrate that these scaffolds support cell growth of a variety of cell and tissue types and that the electroactive properties of the scaffolds can be used to monitor cell growth. Current work is focusing on understanding the role of electrical stimuli on cells growing in the scaffolds, in addition to the typical mechanical and biochemical cues present.

4:45 PM SB02.05.09
Electroconductive Gelatin-Graphene Composite Nanofibrous Scaffolds for Cardiac Tissue Engineering Ebrahim Mostafavi and Thomas J. Webster; Northeastern University, United States

Cardiovascular disease (CVD) is the most leading cause of mortality and morbidity in the USA and costs $300 billion per year. Myocardial infarction (MI or a heart attack) is currently one of the most frequent types of CVD in the world. Among diverse technologies for rebuilding the infarcted myocardium, cardiac patches can adequately and simultaneously meet the biochemical, electrical and mechanical demands of the native heart tissue to promote regeneration following MI. Here, we first engineered a gelatin-based porous scaffold by electrospinning technique. We then incorporated graphene nanofibers (GNFs) to the acellular porous matrices to fabricate a conductive electrospun composite scaffold. The gelatin-graphene fibrous composite scaffolds were engineered by dissolving 10% (w/v) of gelatin from porcine skin into various concentrations of GNFs in the range of 0 to 0.5% (w/v) in hexafluoro-2-propanol (HFIP) and electrospinning of resulting solutions. The effects of GNFs on physical properties (such as mechanical properties, degradation, swelling, surface energy, etc.), electrical conductivity and in vitro cytocompatibility of the scaffolds were evaluated. The results revealed that by increasing the amount of GNFs from 0 to 0.5% there was no significant difference in elongation of the scaffolds, while the tensile modules was increased from 3.2 to 7.02 MPa. Moreover, incorporation of GNFs can bridge the electrically resistant pore walls of the matrices, to support and facilitate the internal electrical interactions between adjacent CMs. Co-cultures of primary
cardiomyocytes isolated form neonatal rats and cardiac fibroblasts grown on gelatin-graphene patches exhibited remarkably better contractile profiles compared to pristine gelatin control, as demonstrated by over expression of the gap junction protein connexin 43. In the next step, some epicardial-secreted factors such as paracrine factors and proteins was incorporated into the conductive patches obtained from the previous stage, with the aim of promoting the myocardial regeneration. It is expected that the integration of conductive GNFs and epicardial factors within 3D scaffolds may improve the therapeutic value of current cardiac patches and will open new avenues for engineering cardiac tissues.

SESSION SB02.06: Poster Session I: Biomedical Sensors, Actuators and Devices
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB02.06.02
Biomaterials of Nylon 6.6 and Trimetaphosphate with Antimicrobial Properties for Dental Applications
Francisco N. Souza Neto¹, Danilo M. dos Santos², Leonardo A. de Morais¹, Thayse Y. Hosida¹, Emerson R. Camargo³, Elisabete Frollini³ and Alberto C. Delbem¹; ¹State university of São Paulo, Brazil; ²University of Sao Paulo, Brazil; ³Federal University of São Carlos, Brazil

Advances in material science during the last decades resulted in a new class of nanocomposite materials through the combination of polymeric matrices and a large number of different nanoparticles. In this context, nylon 6,6 (N6) is one of the most important engineering plastics in biomedical applications and has been investigated as a bone tissue scaffold. Trisodium trimetaphosphate (STMP) can be used as potential candidates for dental applications due to the anticaries action of STMP when present in a biocompatible scaffold as N6. Therefore, the insertion effect of different STMP concentrations in a N6 polymeric matrix was evaluated and correlated to the physicochemical and microbiological properties of nanocomposites. STMP nanoparticles were prepared by mechanical milling for 48h. N6 and its nanocomposites were prepared by electrospinning technique, while, the N6/STMP nanocomposites were processed by adding 2.5, 5 and 10% w/w (TMP:N6). The milling processing reduced the particle size of the STMP powders without affecting its crystalline structure. Particle size was reduced of micrometric to nanometric scale after mechanical milling producing particles with ~70 nm and spherical morphology. The phase structure was analyzed by XPS technique and nuclear magnetic ressonance spectroscopies in solid state. ¹³C NMR all chemical shifts were well resolved and were assigned according to N6. XPS results demonstrated that phosphate groups were bound to C=O groups on N6 by covalent bonds, showing that, STMP was incorporated in N6. The morphology it was analyzed by Scanning Electron Microscopy (SEM) technique. SEM images showed the formation of nanofibers in N6 and its nanocomposites with ~150 nm of thickness for N6 and thickness higher for N6-STMP nanocomposite, showing the presence of STMP homogeneously distributed over the nanofibers. The thermal behavior was analyzed by TGA technique. Thermogravimetry analyses demonstrated improved thermal stability of N6-STMP nanocomposites with higher TMP concentration according to its barrier effect. The mechanical properties were evaluated, and N6-STMP -2.5% nanocomposite presented higher elastic modulus, elongation at rupture and tensile strength, presenting as a potential candidate in dentistry. Additionally, the concentration of the cariostatic agent solution and its microbial effect were positively observed, where the inhibition halos corresponding to Saforide® against S. mutans showed the largest inhibition zone, with 4.18 mm and the nanocomposites were not cytotoxic in the concentrations evaluated. These findings showed a new approach to add STMP nanoparticles by electrospinning in a polymeric matrix, forming stable nanofibers with potential application in dental biomaterials. With this methodology, it was possible with this methodology to insert the STMP nanoparticles in a polymeric matrix and increase the physicochemical properties of the nanocomposites formed.

SB02.06.03
Coaxially Nanostructured Chitosan-Based Nonwovens as a Potential Drug Release Platform for Periodontitis Treatment
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Periodontitis is a chronic dental infection caused by a complex bacterial microbiota that can lead to the progressive destruction of periodontal tissue and loss of teeth. Antimicrobial agents are frequently administrated to prevent/treat bacterial infections in periodontal defects and the development of controlled release drug systems based on nanostructures appears as a promising alternative to enhance the efficiency of such treatment. Here we report the preparation of core-shell nanofibers via coaxial electrospinning by using chitosan as shell layer and poly (vinyl alcohol) (PVA) containing tetracycline hydrochloride (TH) as core layer as a potential system to treat periodontitis. Chitosan samples possessing different average degrees of deacetylation (DD = 82% and 93%) were prepared via ultrasound-assisted deacetylation reaction of β-chitin extracted from squid pens. PVA was chosen because it is a biocompatible, biodegradable and easily electrospinnable polymer, while TH, a broad-spectrum antibiotic presenting activity against both Gram-positive and Gram-negative bacteria, was chosen as model drug. The effects of degree of deacetylation of chitosan and the post-electrospinning genipin crosslinking on physicochemical and biological properties of resulting nonwovens were evaluated. Defect-free and geometrically uniform nanofibers with diameters in the range of 100–300 nm were obtained, and transmission electron microscopy (TEM) revealed the core-shell structures of the produced nanofibers. The mechanical properties and stability of nonwovens in aqueous medium were greatly improved by genipin-crosslinking. As a consequence, a sustained release of TH from these structures was possible for 14 days. The degradation rate and the release profile of TH in the presence of lysozyme can be controlled by properly selecting the chitosan to be used in the shell layer of nanofibers, as the degradation and TH release rate was higher the lower the average degree of acetylation of chitosan. Further in vitro antimicrobial activity demonstrated that the cross-linked nonwovens containing TH showed strong activity against bacterial strains associated with periodontal disease. Additionally, the nonwovens did not demonstrate cytotoxicity toward fibroblast (HDFn) cells, indicating the potential of this novel drug delivery platform for periodontitis treatment.

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SB02.06.04
Controlled Drug Release System from PLGA Nanoparticles Responding to NIR Irradiation
Ryo Yamashita, Ha Sita, Minwoo Kim, Ruda Lee and Takuro Niidome; Kumamoto University, Japan

Controlled drug release responding to external stimulus is an important technique to focus area of drug eluting, and to reduce side effect of the drug at normal tissue. Previously, we modified double stranded DNA on gold nanorods that can be heated by near-infrared (NIR) light irradiation. After heating the gold nanorods by NIR irradiation, single stranded DNA was released [1]. Thus, we succeeded in constructing controlled release system responding to NIR irradiation. However, capacity of loading drugs (DNA) was limited on surface of the nanoparticles. Chu et al. prepared gold nanorods-coated PLGA nanoparticles and achieved controlled release of drugs from the nanoparticles responding to NIR [2]. Large amount drugs could be encapsulated in the PLGA as a payload, but disruption of PLGA by the photothermal effect of the gold nanorods was limited on their surface. Here, we prepared PLGA nanoparticles encapsulating drugs in the nanoparticles and the release efficiency was evaluated. Gold nanorods were coated with disulfiram and dispersed in dichloromethane. The gold nanorods and PLGA were mixed in chloroform, and then added to 1% PVA aqueous solution with sonication. After washing resultant nanoparticles by water, gold nanorods-encapsulated in PLGA nanoparticles (GNR-PLGA NPs) were obtained. TEM observation revealed that some gold nanorods were encapsulated in one PLGA nanoparticles. Mean diameter of GNR-PLGA NPs was about 300 nm. When GNR-PLGA NPs dispersion in water were irradiated by continuous wave (CW) near-infrared laser, dispersion temperature increased and destruction of PLGA nanoparticles was observed. In case of pulsed near-infrared laser, the gold nanorods were converted to spherical form in PLGA nanoparticles by strong heating effect by the pulsed near-infrared laser; however, no temperature increase was observed. After changing the shape, the gold nanospheres have little absorption band at NIR region, therefore, they could not be heated anymore. Next, drug release from the gold nanorods-encapsulated PLGA nanoparticles responding to the CW laser was examined. Curcumin as a model drug was encapsulated in the GNR-PLGA NPs. When the nanoparticles were irradiated by CW NIR laser, release of the curcumin was observed, while little release was observed when the laser had been turned off. We constructed the controlled drug release system responding to NIR laser from GNR-PLGA NPs. Heating from inside of PLGA nanoparticles and destruction of the whole nanoparticles will be advantageous in high contrast on/off control of drugs release.

References
SB02.06.05
Disposable Ink-jet Printed Interdigitated Electrodes Modified with Biomass-Based Composite for Detecting C Reactive Protein
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Capacitive biosensors, combined with inexpensive fabrication technologies and low cost materials, may provide simple, sensitive devices for detecting clinically relevant cardiovascular disease biomarkers. Herein, we report a novel platform for detecting the C reactive protein using low-cost ink-jetted interdigitated electrodes modified with biomass-based composite. First, a comb-like interdigitated silver electrode was inked on a Kapton sheet substrate by using an ink jetting Dimatix. Different parameters were tested: tension (20 to 30V), substrate heating temperature (273.15 to 333.15K), distance between nozzle and substrate (100 to 500mm) and number of printed layers (01-15) for obtaining good electrical characteristics. The electrodes were characterized by SEM and resistivity measurements. The best parameters were set 30V, 313.15K, 300mm and 01 layer. A simple synthesis was used to prepare the biomass carbon derived from bamboo and its composite with ZnO nanorods. The biomass carbon derived from bamboo was prepared by direct pyrolysis of the ground sample at 750°C for 4 hours. For preparing its composite, a quantity of biomass carbon derived from bamboo was added a hexamethylenetetramine and zinc nitrate in the proportion 1:1 in a Polytetrafluoroethylene (PTFE) vessel. The PTFE vessel was placed in silicone bath. The solution was stirred and heated at 90°C for 2 h, aiming to promote the growth of ZnO NRs on the surface of the biomass carbon. The samples were characterized by FTIR, RAMAN, EDX and SEM microscopy. The biomass-based composite consisting of bamboo derived biomass carbon with a high degree of graphitization and ZnO nanorods were deposited on silver electrodes to aid in the immobilization of C reactive protein antibody. Immobilization of the anti-C reactive protein was proven by immunofluorescence confocal microscopy and FTIR. The capacitance was measured in a frequency range of 1 Hz to 1 MHz and diverse analyte concentrations. The modification of the electrode with biomass-based composite significantly improved the analytical performance of the immunosensor. The biosensor exhibited high reproducibility and relatively low limit of detection.

SB02.06.07
Efficient and Targeted Delivery of the CRISPR Plasmid Using Carbon Dot Nanoparticles for Nonviral Genome Editing
Juhee Lee and Hyun Jung Chung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Gene therapy is a promising technology for treatment of human diseases due to the versatility and specificity in designing the drug according to the target. The CRISPR/Cas9 system has been greatly attractive as a gene therapeutic since the target gene can be reprogrammed with high efficiency and selectivity. Non-viral gene delivery methods that can effectively transport the carrier to a target site are important for addressing the safety concerns of viral delivery methods, due to their low toxicity. Herein, we used polyethyleneimine carbon dot nanoparticles (PEI-Cdots) to deliver the CRISPR plasmid efficiently to cancer cells. An all-in-one CRISPR plasmid expressing Cas9 and GAL4UAS-luciferase sgRNA was prepared and allowed to form a complex with the PEI-Cdot by electrostatic interaction. The complexes were then functionalized with hyaluronic acid (HA) to stabilize the complexes and specifically target CD44 overexpressed on tumor cells. HA-functionalized PEI-Cdot/plasmid complexes were characterized by dynamic light scattering and zeta potential measurements. Delivery of the HA-functionalized PEI-Cdot/plasmid complexes into tumor cells were investigated by using an all-in-one plasmid to CD44-overexpressing cancer cell lines. The cellular uptake of the complexes and subsequent knockout of the target reporter gene were determined by confocal microscopy.

SB02.06.08
Ni-Free, Built-In Nanotubular Drug Eluting Stents—Experimental and Theoretical Insights
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Stents used for cardiovascular applications are composed of three main elements; a metal, polymer coating and the specific drug component. Nickel-based metals and polymer coatings currently used in the stent market have
increased the recurrence of in-stent restenosis and stent failure due to inflammation. In this study, a Ti-8Mn alloy was used to fabricate a nanostructured surface that can be used for drug eluting stents to overcome the hypersensitivity of metals that are currently used in stent making as well as introducing a new built-in nano-drug reservoir instead of polymer coatings. Two different systems were studied: titanium dioxide nanotubes (NTs) and Ti-8Mn oxides NTs. The materials were characterized using field emission electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), roughness, wettability and surface energy measurements. Nanoindentation was used to evaluate the mechanical properties of the nanotubes as well as their stability. In-vitro cytotoxicity and cell proliferation assays were used to study the effect of the nanotubes on cell viability. Computational insights were also used to test the blood compatibility using band gap model analysis, comparing the band gap of the materials under investigation with that of the fibrinogen, in order to study the possibility of charge transfer that affects the blood clotting mechanism. In addition, the drug loading capacity of the materials was studied using acetyl salicylic acid as a drug model.

**SB02.06.09**

**Novel Nanoprobe-Combined Fluorescence In Situ Hybridization for Detection of Ampicillin-Resistant *E. coli***

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Antibiotic-resistant bacteria present a global threat because they are increasingly difficult to treat. Therefore, it is highly important to develop advanced methods for the identification of antibiotic resistance gene in the virulent bacteria. Here, we report the development of novel nanoprobes for fluorescence *in situ* hybridization (FISH) and the application of the nanoprobe for detection of ampicillin-resistant *Escherichia coli* (*E. coli*). The nanoprobe was prepared by the modified sol–gel chemistry and consisted of fluorescent dye-loaded poly(d,l-lactide-co-glycolide) (PLGA) and silica nanoparticles. The synthesized nanoprobe showed strong fluorescent signals and pH stability even under natural light condition. For the double-identification of bacteria species and ampicillin-resistance with a single probe *in situ*, the nanoprobes were conjugated to the two kinds of biotinylated probe DNAs; one for *E. coli*-species specific gene and the other for a drug-resistant gene. By using the nanoprobe-DNA conjugants, we successfully detected the ampicillin-resistant *E. coli* through the FISH technique. We anticipate that the nanoprobe-based FISH method will be employed for the detection of various kinds of pathogenic bacteria, and diagnosis of the emergence of the infectious drug-resistance bacteria.

**SB02.06.10**

**On the Structure of Lipid-Based Nanoparticles for Drug Delivery**

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Solid lipid nanoparticles (SLNs) have a crystalline lipid core which is stabilised in solution by interfacial surfactants. They are considered favourable candidates for future drug delivery vehicles as they are capable of storing and release bioactive molecules. However, when stored over time it is thought that the lipids undergo polymorphic transitions which result in the premature expulsion of the drug molecules. To date, significant experimental studies have been conducted with the aim of investigating the physicochemical properties of SLNs, including their long-term stability, but as-of-yet, no molecular scale investigations have been reported on the behaviours that drive SLN formation and their subsequent polymorphic transitions. Using a combination of small angle neutron scattering (SANS) and all-atom molecular dynamics simulations (MD) we have generated a detailed, atomistic description of the internal structure of an SLN formed from the triglyceride, tripalmitin, and the Brij O10 surfactant. In addition to studying the SLN, we have performed further experiments and molecular-dynamic simulations on the formation of a triolein-based liquid lipid nanoparticle (LLN) which is stabilised by the same Brij O10 surfactant. LLNs are, like SLNs, of interest for their potential applications in drug delivery. This has allowed us to characterise the structure of the LLN in a similar manner to the SLN and to compare the two contrasting nanostructures in order to better understand the relationship between a nanoparticle’s internal structure and its role in drug delivery. As well as studying the structure and formation of the nanoparticles, we have conducted molecular dynamics simulations and experiments to characterise and compare the processes involved in the encapsulation and localisation of a steroidal drug, testosterone propionate, by both the SLN and the LLN.

**SB02.06.11**

**Optimisation of 5-Fluorouracil Releasing Graphene Oxide/Chitosan/PVP Electrospun Composites**

Jamie J. Grant1, Suresh C. Pillai1, Tatiana Perova2, Sarah Hehir1, Steven J. Hinder3, Marion McAfee1 and Ailish Breen1;
Electrospun chitosan offers an attractive platform for biomedical applications such as wound healing, drug delivery etc. However, chitosan is an extremely difficult material to electrospin and there are few systematic reports of process optimisation for electrospinning chitosan. Graphene-based materials have potential applications in biomedical engineering, due to its large surface to volume ratio and superior mechanical properties but can show poor biocompatibility. Studies have shown that the biocompatibility of graphene-based materials is improved with the addition of chitosan, which also serves to increase the drug loading capacity of the material.

It is hypothesised that blending graphene oxide (GO) with chitosan (CS) and polyvinylpyrrolidone (PVP) would improve the biocompatibility of the graphene and increase its drug loading capacity, whilst also improving the processability of the CS. The research aimed to investigate if a CS / PVP / GO composite could be electrospun and to test the efficacy of this construct for drug release of an anti-cancer drug.

Solution and process parameters were optimised to perform electrospinning of CS/ PVP and these scaffolds were then characterized. PVP was fixed at 6 wt% concentration while CS concentration varied from 0 wt% to 4 wt%. A solvent system of trifluoroacetic acid and glacial acetic acid in a 9:1 ratio was used. SEM analysis showed that the sample containing 4% CS 6% PVP had a homogenous structure with a mean fibre diameter of 0.653μm. XPS analysis of the surface showed that there were no significant chemical shifts present as CS increased, possibly due to masking of the CS by PVP. Raman and FTIR analysis proved the existence of intermolecular interactions (via H-bonding) between PVP and CS molecules, which increases with the increase of CS content in PVP. This is shown through a meaningful downshift of the carbonyl band in Raman analysis (by nearly 13cm⁻¹) along with the linear increase of the ratio of integrated intensities of CH stretching bands (A₂₉₃₀/A₂₉₈₁) versus CS content in x%CS/6%PVP composites (with x = 0, 1, 2, 3, and 4). In FTIR spectra, the contribution of CS to CS/PVP scaffolds was also confirmed by the less dramatic downshift of a C=O band and by the linear increase of intensity of C-O stretching bands of chitosan at 1034 and 1076 cm⁻¹ with increase of the CS content.

GO was integrated into the system to construct GO/4%CS/6%PVP composites in a concentration range of 0, 0.1, 0.2 and 0.7 wt%. Cell viability testing was performed on A549 cells using a neutral red assay. There was no statistical difference in cell viability between constructs loaded with 0 wt%, 0.1 wt% and 0.2wt% GO. With this, a composition of 0.2%GO/4%CS/6%PVP was chosen for drug studies. The anti-cancer drug 5-Fluorouracil (5-Fu) was loaded in concentrations of 10, 5, 1 and 0.1mg/mL to construct electrospun 5-Fu/0.2%GO/4%CS/6%PVP composites. In this case, a significant decrease in cell viability between 10 mg/mL and 5 mg/ml drug loaded samples compared to control of cells only after 48 hours of exposure was detected. At the same time, no statistical difference was observed between control cells and 1mg/mL and 0.1mg/mL samples, showing the drug released was only significant at higher concentrations and had toxic effects on the cells.

The study concludes that electrospun constructs of 0.2%GO/4%CS/6%PVP were successfully fabricated and showed good biocompatibility; capable of releasing a bioactive drug to cells. Current research is aimed at optimising the drug release system and further assessing cell toxicity.


SB02.06.12
Label-Free Nanosensing Platform for Breast Cancer Exosome Profiling Elvira Fortunato and Rodrigo Martins; CENIMAT|I3N, FCT-UNL, Portugal

Breast cancer accounts for 11.6% of all cancer cases in both genders. Even though several diagnostic techniques have been developed, the mostly used are invasive, complex, time-consuming and can’t guarantee an early diagnosis, something that is key when it comes to the tumour treatment success rate. Exosomes are extracellular vesicles that carry biomolecules from tissues to the peripheral circulation, representing an emerging non-invasive source of markers for early cancer diagnosis. Current techniques for exosomes analysis are frequently complex, time
Raman spectroscopy interest has risen lately due to its non-destructive analysis and little to no sample preparation, while having very low analyte concentration/volume, due to surface enhancement signal possibility (SERS). However, active SERS substrates are needed, and commercially available substrates come with a high cost and low shelf life. In this work, composites of commercial nata de coco to produce bacterial nanocellulose and in situ synthesised silver nanoparticles are tested as SERS substrates, with a low cost and green approach. Enhancement factors (EF) from $10^4$ to $10^5$ were obtained, detecting rhodamine 6G (R6G) concentrations as low as $10^{-11}$ M. Exosome samples coming from MCF-10A (non-tumorigenic breast epithelium) and MDA-MB-231 (breast cancer) cell cultures lineages were tested on the synthesized substrates and the obtained Raman spectra were subjected to statistical Principal Component Analysis (PCA). Combining PCA with Raman intra and inter variability in exosomal samples, data grouping with 95% confidence was possible, serving as a low cost, green and label free diagnosis method, with promising applicability in clinical settings.

SB02.06.13
Paper as a Colorimetric Biosensing Platform for the Detection of Tetracyclines in Milk
Elvira Fortunato and Rodrigo Martins; FCT-UNL, Portugal

Tetracyclines (TCs) are a type of antibiotic that exhibits activity against most gram-positive and gram-negative bacteria. These antibiotics are often added at subtherapeutic levels to the feedstock to act as growth promoters. Since they can cause allergic and toxic reactions and also can lead to an increased antimicrobial resistance, several countries implemented a maximum level of residues for TCs of 0.1 µg/mL in milk, 0.2 µg/mL in cattle muscle, 0.6 µg/mL in cattle liver and 1.2 µg/mL in cattle kidney. The current available methods of TCs detection are based on inhibition tests but most of them are time consuming, expensive and inadequate for field analysis.

In the present work a colorimetric biosensor was developed using paper as platform with gold nanoparticles, for the detection of four types of TCs, presenting an alternative in the performance of point-of-care tests. The construction of the sensors was performed using Lab-on-Paper technology and is based on the synthesis of gold nanoparticles by reducing a gold salt precursor for which tetracyclines constitute the reducing agent itself. Different concentrations of tetracyclines were tested and analyzed using image software, allowing to obtain linear calibration, that correlates the concentration of antibiotics in a range between 0.1 and 10 µg/mL with the color intensity of the gold nanoparticles.

Validation tests of the sensors developed with tetracycline (TC) in milk were also performed., confirming that it is possible to detect this type of antibiotic in pre-treated milk.

SB02.06.14
Polymer-Derivatized Cas9 Conjugates as a Nonviral Genome Editing System for Therapeutic Applications of CRISPR
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The CRISPR-Cas9 system is a very robust platform for genome engineering and has a great impact on applications of gene modulation in various organisms. For their delivery, viral vectors are commonly used which have been shown high efficiency and persistent expression of the edited gene. However, the risk of insertional mutagenesis, immunogenicity and off-target effects, disclosed in clinical trials, poses serious safety concerns. Alternatively, CRISPR-Cas9 can be delivered in the form of ribonucleoprotein (= RNP) to reduce these side effects. Most of the recently reported non-viral delivery methods of Cas9 RNP involve the non-covalent encapsulation in carrier materials, which show limitations due to the cytotoxicity by the need of treating at high doses because of the low packaging efficiency. In this study, we introduce a polymer-derivatized Cas9 by direct covalent modification of the protein with cationic polymer, for subsequent complexation with sgRNA and ssODN. Nano-sized CRISPR complexes (= Cr-Nanocomplex) were successfully formed, in which the functionality of Cas9 endonuclease was well maintained. After characterization of the complex, the Cr-nanocomplex was treated to various types of mammalian cells, which showed enhanced cellular uptake and nuclear localization of both Cas9 and sgRNA compared to the native complex or lipofectamine control. Furthermore, we generated a fluorescent reporter cell line to determine HDR efficiency, through which the Cr-nanocomplex was shown to induce effective and precise genome editing, exhibited by phenotypic changes in the reporter cells. Treatment of the Cr-nanocomplex even at high doses did not cause any cytotoxicity problem, which has been a major hurdle for application of conventional lipid-based formulations. In conclusion, the covalent modification of Cas9 with a cationic polymer shows great potential for the application CRISPR complexes as therapeutics for treating a variety of diseases such as cancer and genetic disorders.
Sub-Nanogram Level Biomarker Detection by Using Nanoporous Microneedle Patches

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Minimally invasive microneedle (MN) patches have shown its potential for the rapid detection of biomarkers toward diagnostic point-of-care testing. However, achieving sufficient detection sensitivity for target molecules is a significant challenge. Here we present a highly sensitive detection platform using nanoporous MNs, enabling a rapid capturing of biomarkers present at sub-nanogram level. The uniform nanopore arrays on the MN surface was prepared by a controlled anodization process and then the nanoporous MNs were functionalized by the immobilization of biomarker-specific antibody to detect a target biomarker based on an immunoassay method. The bio-functionalized MN patch showed a rapid capture of estradiol (E2) known as a biomarker of preeclampsia following 1 min incubation time and exhibited a concentration-dependent change in fluorescence intensity over the E2 range of 0.5 to 1000 ng mL\textsuperscript{-1} after treating fluorescent detection antibodies. Additionally, multiple biomarker detection using a single MN patch was investigated to improve the accuracy of preeclampsia diagnosis. The nanoporous MN platform can be employed to detect diverse biomarkers including metabolites and proteins and could be integrated into a handheld system for point-of-care clinical diagnostics.

Synthesis of Highly Sensitive and Biodegradable Soft Foam Sensors for Human Motion and Soft Robotics Applications

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Skin-mountable and wearable electronic devices have potential scientific and technological applications due to their facile integration, interaction with the human body and long-term monitoring capabilities\textsuperscript{1}. Up to now, efforts in the development of polymer-based strain sensors was performed with a synthetic elastomeric matrix like polydimethylsiloxane (PDMS)\textsuperscript{1}, Ecoflex\textsuperscript{2}, Dragon Skin\textsuperscript{1}, or butadiene-styrene copolymers\textsuperscript{3}. These materials are not biodegradable, and their disposal after usage raises critical issues related to the increasing amount of electronic waste generated and its negative impact on the environment. Polyglycerol sebacate (PGS) which is an elastomer obtained from the polycondensation of glycerol and sebacic acid, has tremendous potential for biomedical applications since it is both biodegradable and biocompatible.

In this work, we showed a novel route to manufacture sustainable porous piezoresistive sensors with an outstanding performance by adding multiwall carbon nanotubes (MWCNTs) to the PGS prepolymer, followed by the curing the elastomeric matrix at 120 °C, during 96 h under low pressure (100 mTorr). The sensors before biodegradation reveal high sensibility, with a Gauge Factor (GF) up to –9, very fast response (≤ 3 ms), negligible mechanical and electromechanical hysteresis, reliability and very long lifetime under cycling loading (> 1,200,000 cycles), and a differential pressure sensibility of 34 Pa. Due to their porous structure, they can detect low and high frequency vibrations (up to 300 Hz), small forces (200 mN) covering from the low detection limit of metallic strain gauges up to the large strains characteristic of elastomeric-based nanocomposites. Overall, these characteristics closely match the properties of the human fingertip and hence pave the way towards tactile and compliant sense elements embedded in prosthetic devices.

After biodegradation in a simulated body fluid (SBF) at physiologic conditions (37 C), a loss in the sample weight of 15% was observed after 8 weeks of incubation. While their GF or hysteresis behavior was not dramatically affected, a decrease in the nanocomposite density and an increase in the sample cross-linking was observed. Furthermore, their vibration detection limit decrease from 300 Hz for the as processed sample down to 50 Hz, after one week of incubation in the SBF solution. These sensors presented no detectable cytotoxic effects against normal human skin fibroblasts, revealing the great potential of these sensors for the fabrication of wearable electronics.

Overall, this work demonstrates prospective applications of novel sustainable soft resistive foam sensors that meet the future challenges of soft robotic systems\textsuperscript{4,5}.

Acknowledgments
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References
Graphene quantum dots (GQDs) are 2–3 nm sized nanoparticles that have a hydrophobic 2D graphitic domains with hydrophilic oxygen-containing functional groups along the edges. The carboxyl groups on GQDs can be modified to amine groups through simple EDC/NHS chemistry to be conjugated with many different small molecules. Recently, the application of GQDs as a therapeutic agent has been demonstrated to alleviate Parkinson's disease by degrading pre-existing α-synuclein fibers as well as by preventing its fibrillization. It is also proven that GQDs have negligible long-term toxicity in animal models as they are excreted through urine in a few weeks (D. Kim et al., 2018, *Nat. Nanotechnol.*, 13, 812-818).

On the other hand, kidney disease occurs due to the weakening of the filter function of a glomerulus, and while it can be cured by early diagnosis, a full recovery is almost impossible when CKD (Chronic Kidney Disease) proceeds. When the symptom gets severe, dialysis or even transplantation is required. About 15% of adults in the US are suffering from CKD, and the population has been steadily increasing (National Chronic Kidney Disease Fact Sheet, 2017). When a kidney is injured, it loses tubular cells and to fill in space, an excess amount of ECM (Extracellular Matrix) is synthesized, which results in fibrosis. EMT (Epithelial-Mesenchymal Transition) occurs during fibrosis, and myofibroblasts make more ECM proteins, causing the kidney to become stiff and lose its function. Renal fibrosis is a typical and inevitable histological symptom of CKD.

Herein, we develop a method to employ GQDs as a therapeutic agent to prevent or reduce renal fibrosis. GQDs was treated to human kidney cells at the concentration of 5~200 μg/ml and did not show significant cytotoxicity according to the MTT assay. rTGFβ was added to TECs (Tubular Epithelial Cells) to provoke fibrosis and measured whether GQDs can alleviate this process. After rTGFβ treatment, the level of fibronectin and collagen (I), which are major components of the ECM were increased. When GQDs was treated at 2~10 μg/ml, a decrease in the ECM proteins was observed from the immunofluorescence. The increase in E-cadherin confirmed GQDs' role in preventing cell death. Collagen (I) monomers were incubated for 24 hours with and without GQDs, and thicker collagen (I) fibers were formed when GQDs was treated. GQDs quenched the emission of photoluminescence of collagen (I), showing a physical interaction between the protein and particles.

A UUO (Unilateral Ureteral Obstruction) mouse model was used for generating AKD (Acute Kidney Disease), and GQDs were intravenously injected at the concentration of 20 mg/kg. The level of fibronectin and collagen (IV) were significantly reduced after GQDs treatment, while an increase in E-cadherin was observed. TGFβ, as a key profibrotic factor, is linked with diverse signaling pathways, and we focused on the TGFβ-Smad pathway. Smad2/3 promotes fibrosis by directly binding to the promoter region of collagen and triggers its production. Smad7 is an inhibitory regulator that suppresses TGFβ via negative feedback. GQDs were shown to decrease the level of Smad2/3, and increase Smad7, which correlates with the less formation of the fibrotic region as confirmed by histological staining. Overall, we demonstrate that GQDs can be used as a therapeutic agent for renal fibrosis, which is expected to provide an alternative route to treat CKD patients without pain.
oleylamine. And ligand exchange process via citric acid were performed to yield water soluble nanoparticles under basic environment (pH >7). These synthesized nanoparticles are characterized by UV-Vis-NIR spectroscopy, fluorescence spectroscopy, XRD, TEM, etc. are also heavily relevant in producing stable and uniform hybrid nanoparticles that lack physical impurities. By further optimizing synthesis conditions, such as altering growth temperatures and precursor reagent ratios, functional hybrid magnetic nanoparticles can be obtained for MRI and other multimodal biomedical applications. Correlations between fluorescent lifetime and sizes, compositions, shapes of hybrid nanoparticles have been studied further as well.

**SB02.06.20**  
*In Situ Nanomechanics of Biomimetic and Biomedical Materials*  
Praveena Manimunda, Douglas D. Stauffer and Asif Syed; Bruker Nano Surfaces, United States

Drug-eluting stents (DES) are favored over bare metal stents due to the low risk of angiographic restenosis. To improve the adhesion strength of drug emitting polymer coatings, surface chemical treatments are often adopted. However, to optimize surface modification, it is important to understand the interface phenomenon and mechanical properties of polymer coatings in a greater detail. Here, a new methodology was adopted where, in situ confocal imaging in combination with nanoDMA and nano-scratch tests were used to determine the mechanical and adhesion strength of polymer coatings on stents that contains pharmacologic agents. Force modulations and real-time contact images are correlated to understand adhesion characteristics. Further, the methodology was extended to characterize the mechanical properties of biomimetic materials.

**SESSION SB02.07: Hydrogel and Tissue Engineering**  
Session Chairs: Benjamin Almquist and Ritchie Chen  
Wednesday Morning, December 4, 2019  
Hynes, Level 2, Room 200

**8:00 AM SB02.07.01**  
*Towards the Construction of Strong Physical Hydrogels—Translating Single-Molecule Behaviors to Macroscale Hydrogel Mechanical Properties*  
David S. Knoff and Minkyu Kim; University of Arizona, United States

Artificial protein hydrogels have immense potential as functional biomaterials, incorporating the intrinsic mechanical and bioactive properties of proteins in the polymer network. However, current artificial protein designs are limited in their ability to translate protein nanomechanics to macroscale materials due to inefficient crosslinking density or weak crosslinkers. Chemical crosslinkers are strong but, in general, the lack of specificity or uncontrollable binding kinetics can lead to a spatially inhomogeneous crosslinking density within the polymer network. Physical crosslinkers have specific self-associations with temporary bonds, capable of rearranging in a timescale dependent on their dissociation constants to form a relatively homogeneous network. However, their low rupture strength limits possible applications due its effect on mechanical properties of the material. With many self-oligomerizing proteins that form quaternary structures available in nature, there is great potential for finding physical protein crosslinkers with high affinity and specificity. Streptavidin, well known for having one of the strongest protein-ligand interactions with biotin, is utilized in diverse biotechnology applications ranging from molecular identification to drug delivery. Four streptavidin monomers naturally self-associate with high affinity physical bonds to form a tetramer quaternary structure. Here, we used streptavidin as a strong and specific physical crosslinker to model its effect on the spatial homogeneity and mechanical strength of artificial protein hydrogels. In addition, biochemical methods and single-molecule studies revealed that biotin binding to streptavidin enhances the thermal and mechanical stability of the tetramer structure. We analyzed how the stabilizing effect of biotin on streptavidin tetramers translates from the single-molecule scale to macroscale hydrogel mechanical properties.

**8:15 AM SB02.07.02**  
*The Application of 3D Printing of Biodegradable Polymers*  
Jane Wang, June-Yo Chen, Yu-Ming Chen and Kaiser A. Villalobos Gorday; National Tsing Hua University, Taiwan
The rising prevalence of organ loss and failure due to acute and long term illnesses, and the lack of available therapies and organs for transplantation has been one of the most critical unmet needs in medicine worldwide. In order to meet this critical need in tissue, the field of tissue engineering has emerged over the last several decade with major efforts focused on the liver, lung, kidney, and heart. However, for any organ regeneration, consistent supply of blood to the targeted regeneration sites is considered the most essential criteria for the initiation as well as continuous regeneration. Most engineered tissues, particularly highly metabolic tissues or those with poor oxygen diffusivity, require an intrinsic microcirculation that reaches to within 100 – 200 m of every cell in the construct. This requirement has spurred the development of angiogenesis induction to create capillary beds. Such approaches are promising but face challenges including the long-term robustness and viability of the vessels and integration with larger vessels in the construct and in the host. As an alternative, this work presents biodegradable scaffolds containing bifurcated microchannels designed to replicate the fluid mechanics and transport properties of organ vasculature through 3D printing of glycerol-based polymers. Vasculatures of varying sizes ranging from aortic to micro-vasculatures are successfully printed and are proven robust for repeated flow. Intrinsic micropatterns from 3D printing are shown to facilitate cell adhesion for vasculature regeneration. This work shows potential in advancing the developments in microfluidics and microfabrication technology enabling the supply of nutrients and waste removal for regenerated tissue.

8:30 AM SB02.07.03
Rapid Manufacturing of Elastic Biohybrid Tissue-Engineered Heart Valves for Transcatheter Pulmonary Valve Replacement Christophe O. Chantre1,2, Sarah Motta1,2, Huibin Chang1, Luca Cera1, Qihan Liu1, Emanuela Fioretta7, Maximilian Emmert2, Simon Hoerstrup7 and Kevin Kit Parker1; 1Harvard University, United States; 2University of Zurich, Switzerland

Valvular heart disease is one of the leading causes of death worldwide and is projected to increase because of our aging population and the lack of effective treatments. Current heart valve bioprostheses are engineered from chemically-fixed animal tissues and are therefore prone to calcification and structural degeneration over time. To overcome these limitations, tissue-engineered heart valves (TEHVs) based on cell-free polymeric scaffold materials have emerged as a promising replacement alternative, as they are designed to leverage the regenerative and self-remodeling capabilities of the host to regrow a living, native-like tissue. Such cell-free approaches can furthermore rely on predictable and low-complexity manufacturing methods, thus further addressing the cost and variability of cell-based TEHVs. However, despite recent advances in synthetic scaffold manufacturing, there remains a lack of automated and scalable platforms for the rapid production of biomimetic TEHVs. We previously designed a nanofiber rotary jet spinning process capable of rapidly fabricating (<15min) fibrous biohybrid heart valve scaffolds. In a proof-of-concept preclinical acute study, we confirmed TEHVs functionality up to 15 h in the pulmonary valve position of a sheep model. Here, we propose to utilize this spinning process to manufacture in a single-step biohybrid TEHVs comprising physiologically-shaped leaflets using a newly synthesized elastomeric polymer. We demonstrate that controlled material composition, mechanical properties, and biocompatibility of TEHVs are essential to promote in-vitro cellular infiltration, as well as sustain in-vitro valve functionality at physiological pulmonary conditions. Future in-vivo acute and chronic studies will demonstrate the feasibility to implant such newly designed TEHVs via transcatheter approaches in a preclinical animal model and confirm long-term functionality and remodeling.

Acknowledgments: The authors thank the Wyss Institute of Biologically Inspired Engineering at Harvard University and the Institute for Regenerative Medicine (IREM) at University of Zurich for their ongoing support throughout this project. The authors also thank Harvard MRSEC (NSF award number DMR-1420570), SEAS Scientific Instrument Shop and Harvard Center for Nanoscale Systems (NNIN member, NSF award number 1541959).

8:45 AM SB02.07.04
Aminolysis-Based Biofunctionalization of Polyesters Nanofibers for Tissue Engineering Applications Oliwia Jeznach, Dorota Kolbuk and Pawel Sajkiewicz; Institute of Fundamental Technological Research, Polish Academy of Sciences, Poland

Aliphatic polyesters nanofibrous scaffolds are very attractive from the perspective of tissue regeneration, because they can mimic structure of native extracellular matrix. Moreover, they have good mechanical properties and can degrade inside the body. However, the main problem is unsuitable scaffold-cells interaction, due to lack of
biological cues and scaffold hydrophobicity. Immobilization of cell-adhesive proteins, such as gelatin or fibronectin on the scaffold surface can improve biological response. Aminolysis-based biofunctionalization is one of the effective approaches.

Three different aliphatic polyesters - poly(caprolactone) (PCL), poly(L-lactic acid) (PLLA), and copolymer PLA-PCL (70:30) (PLCL) in a form of electrospun nanofibers were investigated. First step of functionalization – aminolysis was conducted at 30°C using various ethylenediamine/isopropanol solution concentrations at various time to find optimum process parameters. Then, chosen samples were subjected to activation process with glutaraldehyde solution and immobilization of two types of proteins – gelatin and fibronectin. Effectiveness of aminolysis process was characterized via colorimetric ninhydrin test. Amount of proteins on the surface was evaluated using bicinchoninic acid assay (BCA assay). Modified samples were characterized via SEM observations, mechanical testing, WAXS and water contact angle measurements as well as examination of cells-material interaction.

SEM microscopy observations showed diverse impact of aminolysis conditions on nanofibers morphology, for instance reaction with 10% w/v concentration of diamine at 30 min led to unbeneficial PLCL and PLLA nanofibers fragmentation, while the same conditions did not cause any change of morphology of PCL nanofibers. Ninhydrin test results indicated that aminolysis reaction was the most effective in the case of PLLA nanofibers, and the least in the case of PCL nanofibers – difference of one order of magnitude in the amount of free amino groups on the surface for 10% w/v concentration of diamine at 30 min. Our hypothesis is that PCL needs much stronger conditions of reaction, due to its higher crystallinity on the surface of nanofibers, which hinders aminolysis process. Finally it was shown that optimized conditions of aminolysis and protein immobilization led to obtaining nanofibrous scaffolds with suitable mechanical properties and improved material-cells interaction.

This study shows results of optimization of aminolysis-based biofunctionalization process for three types of electrospun nanofibers and confirms that this kind of modification is an effective way to enhance cellular response to nanofibrous scaffold.

Acknowledgements: This work was funded by the Polish National Science Center (NCN) under the Grant No.: 2016/23/B/ST8/03409. We also thank Kosciuszko Foundation for the support of this work.

9:00 AM SB02.07.05
AFM Method for Studying the Basal Extracellular Matrix in Apical Polarity Cells Applied to the Osteoblast Collagen Matrix Marcos Penedo1, Kiyo-aki Ishii2 and Takeshi Fukuma1; 1Nano Life Science Institute, Kanazawa University, Japan; 2Kanazawa University Graduate School of Medicine, Japan

The extracellular matrix (ECM) is a macromolecular network existing within all tissues. It provides physical scaffolding for the cell while initiating crucial biochemical and biomechanical processes required for tissue morphogenesis, differentiation and homeostasis. Therefore, the study of the ECM is essential to understand the former processes.

Some cells present apical-basal polarity, where the ECM is mainly created on the basal side of the cell. More specifically, in the case of culturing cells with apical polarity, the ECM lies underneath the cells in direct contact to the substrate, which makes it difficult to access it for direct measurements.

In the last years, atomic force microscopy (AFM) was successfully used to study both cells and their ECM. However, when the ECM is synthetized on the basal part of the cell culture, lying between the substrate and the single or multi-layered cell culture, it becomes challenging to introduce the cantilever tip through the cell layer(s) to measure the ECM underneath the cells.

In order to overcome the above, we have developed a novel technique: culturing cells in a standing thin membrane with holes. First, cells are cultured on one side of the membrane and then, the structure is flipped upside-down to measure the ECM produced on the basal side of the cells and spread through the membrane holes. This technique demonstrates that AFM measurements can be performed on unaltered ECM, without any fixation, chemical or temperature treatment. Using this method, we have successfully studied the collagen matrix produced by osteoblasts.
Exploring the Relationship between Material Geometry and Chemistry on Immune Cell Responses Using Three-Dimension ChemoArchiChips and Two Photon Lithography

Le Ma; University of Nottingham, United Kingdom

Two-photon lithography (2PP) is a method of creating three-dimensional micro-structures on photosensitive materials. One of the key capabilities associated with 2PP is the ability to create sub-micrometer resolution materials with intricate shapes and features that are impossible to create using other fabrication techniques. Here we demonstrate a 2PP based approach to create a wide range of 3D structures and geometries to efficiently screen phagocyte cell responses on a range material chemistries (polymers).

Phagocytic cells (including monocytes, macrophages and neutrophils) play a key role in the response to invading pathogens and particulate matter as well as large foreign body implants such as medical devices. Upon encountering such materials in the body these cells will activate and attempt to engulf the foreign material. The physical dimensions and shape of these structures has been identified to play a key role in the response of these immune cells to engulf and encapsulate foreign materials. Therefore the aim of this study is to develop a high throughput screening approach to efficiently study the effect of surface structure size, geometry and complexity on phagocyte interactions and responses.

Initial data shows that complex biocompatible structures down to the micron level can be created which differentially drive the attachment of human monocytes. Up to 90 different chemistries with different micron-size complex structures can be tested in one batch to investigate the combinatorial effect of 3D geometry, shape, chemistry and architecture on cell fate. Furthermore, cells appear to completely remodel their morphology and cytoskeleton as part of this complex interaction with the 3D structures. Further studies are ongoing to understand the effect of these different geometries and chemistries on other cell processes including; differentiation, cellular polarisation and cytoskeletal changes. This fabrication method is fast and economical making it an ideal tool for developing large screening platforms of polymer surfaces and complex surface structures.

Biomaterial Templated Genetically Tractable 3D Models of the Human Brain

Halil Tekin, Sean Simmons, Beryl Cummings, Linyi Gao, Xian Adiconis, Cynthia C. Hession, Sourav Choudhury, Joshua Z. Levin and Feng Zhang; Broad Institute of Massachusetts Institute of Technology and Harvard, United States

Elucidating genetic mechanisms of brain diseases requires tractable in vitro models of the human brain. Three-dimensional (3D) neural tissues are compelling systems to investigate brain diseases, but it has not been shown before how encapsulating materials of these tissues impact the transcriptome of neurons and how these changes relate to the human brain. Understanding how biomaterials and 3D culturing parameters affect the RNA-signature of in vitro neural tissues can help to develop model systems better approximating the gene expression profiles of the human brain.

Herein, we developed 3D human neural tissues using cells directly derived from human embryonic stem cells and characterized how scaffolding materials and wide variety of 3D culturing conditions impact their transcriptome in comparison to that of the human brain. We demonstrate that altering crosslinking density of composite hydrogels of alginate and basement membrane matrix tunes the transcriptomic correlations to particular regions and stages of the developing human brain. Single-cell sequencing revealed that our 3D tissue system transcriptionally recapitulates cell types in the human brain. Finally, we show that our biomaterial-templated 3D tissue system is compatible with CRISPR gene editing and delivery tools to interrogate disease-associated genes. This study interfacing biomaterials engineering with genomics will support the development of more effective models of neurological diseases.

In Vitro Model of the Human Blood Vessel Wall

Jaroslaw Jacak¹, Sandra Mayr¹, Boris Buchroithner¹, Philipp Mayrhofer¹ and Bianca Buchegger²; ¹University of Applied Sciences, Austria; ²Johannes Kepler Universität Linz, Austria

Tissue engineering is a rapidly growing field during the last decade. Cells within an artificial tissue need structural support and guidance for growth. For this purpose, we fabricate polymeric bio-compatible scaffolds by multi-photon lithography (MPL).
In MPL, a femtosecond-pulsed laser focused into a photosensitive resin solution initializes polymerization solely within the focal volume of the laser beam. Hence, sub-micrometer resolution can be achieved in three dimensions. Recently lateral and axial resolution of MPL of below 200nm and around 500 nm have been demonstrated respectively. Hence, its flexible additive manufacturing performance makes MPL a well suited technique for 3D-structuring of biocompatible materials for tissue scaffolds.

The challenge herein is the development of a photosensitive resin that is biocompatible, mechanically stable and can be structured high writing speed. Herein we demonstrate a 2D and 3D biocompatible scaffolds structured onto cell culture membranes, which can be combined with microfluidics. For biocompatibility testing the scaffolds are seeded with cells. In order to promote cell adhesion, we developed strategies to functionalize the scaffolds with biomolecules like antibodies, DNA-linkers or RGD-peptides. This 3D structured cell scaffold within a microfluidic device are seeded with human endothelial cells models of a blood vessel wall. In the future molecular processes like transportation of bio-microparticles or macromolecules will be addressed with our platform.

10:30 AM SB02.07.09
Cell-Biomaterial Interface Visualized at the Nanoscale Laura Matino, Paola Scognamiglio, Valentina Mollo and Francesca Santoro; Istituto Italiano di Tecnologia, Italy

Cell instructive biomaterials interact directly with biological systems, modifying their behavior by fine-tuning the crosstalk at cellular level. Cell spreading, polarization and cellular mechanical tension are only few examples of interface dynamics consequences. Great consideration has been given to the role of the cell membrane and the surface tension induced by the topology of the material in contact with it. In this context, many efforts have been focused in the last decade to characterize the cell-membrane interface, at the relevant scale. Beside the standard optical acquisition that allows imaging with major limitations in resolution (~ 100 nm), electron microscopy based-acquisition exceeds that limit. However, high resolution electron microscopy procedures require long specimen preparation processes as well as the imaging and processing of hundreds of specimen sections. Here, we present an advanced microscopy method (scanning electron microscopy/focused ion beam) based on ultra-thin resin plastification which uniquely allows the visualization of the interface between cells and materials with 5-10 nm resolution (1,2,3). This technique allows for the visualization of a region of interest where the cell is in contact with the biomaterial underneath. The use of focused ion beam allows foretching through a variety of materials. In fact, here we will present relevant adhesion process of cells in contact with organic and inorganic materials, pseudo 3D materials (vertical nanostructures) and 3D scaffolds. Our results could give new insights in designing new efficient 3D structures for tissue engineering purpose and their interaction and effect on cellular ultrastructures at the cell-biomaterial interface.

References

10:45 AM SB02.07.10
Next Generation Scaffolds—Induced Pluripotent Stem Cell-Derived Matrix for Diabetic Foot Ulcer Treatment Francesco Santarella1,2, Rukmani Sridharan1,2, Milica Marinkovic1,2, Ronaldo do Amaral1,2, Brenton Cavanagh1, Avi Smith3, Fergal J. O'Brien1,2,4, Jonathan Garlick1 and Cathal J. Kearney1,2, 1Royal College of Surgeons, Ireland; 2Trinity College Dublin, Ireland; 3Tufts University, United States; 4Advanced Materials and Bioengineering Research Centre, Ireland

Diabetic foot ulcers (DFU) are chronic non-healing wounds that often lead to lower leg amputations1. The gold standard therapy includes surgical debridement and topical antibiotic treatment. Omnigraft (a tissue engineered...
Human pre- and post-iPSF cells were seeded at 16,000 (low) and 64,000 (high) cells/cm², with the addition of 3D porous scaffolds utilizing the 2D matrix; and finally (4) tested the biological function of the scaffold.

Ascorbic Acid (AA) and Macromolecular Crowders (MMC)) that improve and scale-up production; (3) fabricated we have (1) analysed matrix components in 2D matrices from Pre- and Post-iPSF cells; (2) explored factors (e.g., progressive mineralization of the PDL fibers while preventing the downgrowth of gingival epithelial cells are interface. Enabling remineralization of dentin lesion and promoting the regeneration of acellular cementum by analysis of different collagens (Col1, 3 and 4) revealed that Ficoll did not significantly affect their expression. Together, these results suggest that high density, high AA concentrations and the addition of Ficoll increased matrix production in pre- and post-iPSF cells without affecting its composition. In order to fabricate a functional scaffold, we blended equal amounts of the pre- or post-iPSF derived matrix with additional Collagen 1 and freeze-dried the resulting slurry following previously established protocols. The scaffolds had a porous micro-architecture, held their shape when rehydrated and successfully promoted fibroblast migration and proliferation. Ongoing work is focused on assessing the functional capabilities of post-iPSF scaffolds in vascularization and wound healing assays, with the hypothesis that the foetal-like matrix will promote tissue repair. Together, this study has shown that matrix production from post-iPSF cells can be scaled up with optimized cell density, AA concentration and with the use of MMC to successfully produce sufficient amounts of matrix for fabricating porous free-dried scaffolds towards the treatment of DFUs.

Our results demonstrated that post-iPSF cells produced an increased ratio of COL3/COL1 and increased production of fibronectin and LAMA5 compared to pre-iPSF cells, confirming the formation of a matrix with foetal characteristics, known to promote wound healing.

High AA concentration and high cell density enhanced matrix production from both pre and post-iPSF cells, with a 3 fold increase compared to controls. These culture conditions also increased COL1, COL3, COL4, FN1, and LAMA5 production in post-iPSF cells compared to pre-iPSF cells (p<0.05). Moreover, the amount of GAGs was increased in the post-iPSF cells while the overall amount of collagenous proteins was unchanged.

Macromolecular crowders are known to enhance matrix production by aiding in increased collagen deposition. Accordingly, addition of Ficoll in combination with high concentration of AA significantly increased matrix production and collagen deposition in both pre- and post-iPSF groups after three weeks. Moreover, RT-PCR analysis of different collagens (Col1, 3 and 4) revealed that Ficoll did not significantly affect their expression.

Periodontal disease, periodontitis, is a progressive destruction of periodontium including the gingival tissues, cementum, periodontal ligaments and alveolar bone. It is caused by infections, trauma, orthodontic tooth movement as well as certain systemic and genetic diseases. If left untreated, periodontitis leads to wide range of health problems from early tooth loss to severe systemic infections. Current clinical settings focus on stabilizing diseased tissues by removal of local debridement and conditioning with demineralizing agents. While these treatments generally have a positive effect on healing, they often lead to colonization of epithelial cells resulting in the formation of long junctional epithelium that prevents the regeneration of periodontium. A concerted effort in the past 20+ years has developed guided tissue regeneration strategies using bone grafts, cell sheets, tissue scaffolds, and growth factors. Although partially effective, these approaches have not yet led to predictable outcomes, mainly due to their inability to restore the structure and function of cementum and cementum-periodontal ligament (PDL) interface. Enabling remineralization of dentin lesion and promoting the regeneration of acellular cementum by progressive mineralization of the PDL fibers while preventing the downgrowth of gingival epithelial cells are...
requisites of connective tissue regeneration. In this study, the goal has been to adapt machine learning (ML) tools and high-throughput (HTP) screening methods into functional peptide design platform, first, to derive a set of peptides from periodontium related-proteins to form acellular cementum-like hybrid peptide-mineral complex, and then use these peptides with cell attachment/signaling functions to interface with PDL cells to guide cell attachment, proliferation and differentiation leading to generation of acellular cementum (aC) and aC-PDL junction. Using Amelogenin, the key protein in enamel mineralization, we have reported the development of set of Amelogenin-Derived Peptides (ADPs) with mineralization and hydroxyapatite (HAp) binding properties. In particular, using ADP5, we had previously demonstrated the formation of structurally and functionally integrated mineral layer on dentin and enamel tissues with mechanical properties similar to that of cementum. In addition, attachment and proliferation of PDL cells on cemento-mimetic layer has been demonstrated. Towards regenerating the acellular cementum (aC) and aC-PDL junction, the next steps included identification of protein-derived peptides from cell with signaling functions and incorporate them into the newly formed layer in hetero-functional form chimerized with ADP’s as heterofunctional biomolecular constructs that enable to form hybrid peptide-mineral tissue interface facilitating periodontal tissue regeneration. The preferential attachment and differentiation of PDL cells induced by the hybrid peptide-mineral tissue interface within a mixed culture including gingival epithelial cells, are demonstrated. The outcomes of this study provides a practical and effective approach towards the regeneration of periodontal connective tissues. This work is supported by UW-School of Dentistry Spencer Funds.

11:15 AM SB02.07.12
Exploiting Peptide Self-Assembly for the Design of Functional Materials for Tissue Engineering Applications
Aline Miller¹ and Alberto Saiani²; ¹Manchester BIOGEL, United Kingdom; ²University of Manchester, United Kingdom

The use of non-covalent self-assembly to construct materials has become a prominent strategy in material science offering practical routes for the construction of increasingly functional materials for a variety of applications ranging from electronic to biotechnology. A variety of molecular building blocks can be used for this purpose, one such block that has attracted considerable attention in the last 20 years is de-novo designed peptides. Peptides offer a number of advantages to the material scientists. The library of 20 natural amino acids offers the ability to play with the intrinsic properties of the peptide such as structure, hydrophobicity, charge and functionality allowing the design of materials with a wide range of properties. Synthetic peptides are chemically fully defined and easy to purify through standard processes. Being build form natural amino acids they result usually in low toxicity and low immune response when used in-vivo and can be degraded and metabolised by the body. Self-assembling peptide-based hydrogels in particular have encountered increasing interest in the recent years as scaffolds for 3D cell culture or for controlled drug delivery. One of the main challenges is the fine control of the mechanical properties of these materials. The bulk properties of hydrogels not only depend on the intrinsic properties of the fibers but also on the network topology formed. In this work we show how fiber–fiber interactions can be manipulated by design to control the final hydrogel network topology and therefore control the final properties of the material. This was achieved by exploiting the design features of β-sheet forming peptides based on hydrophobic and hydrophilic residue alternation and exploiting the ability of the arginine’s guanidine side group to interact with itself and with other amino acid side groups. By designing peptides based on phenylalanine, glutamic acid, lysine, and arginine, we have investigated how fiber association and bundling affect the dynamic shear modulus of hydrogels and how it can be controlled by design [Biomacromolecules, 18, 826–834 (2017)]. Subsequently the fine tuning of the mechanical properties allowed us to design a family of functional hydrogels able to direct cellular behaviour from neurite sprouting of neuronal cells for nerve repair [Advanced Healthcare Materials under review 2019] and co-culture of oesophageal cells for Barrett’s oesophagus treatment [Advanced Functional Materials, 27, 1702424 (2017)] to direct differentiation of mesenchyme stem cells into osteoblasts for bone repair [Journal of Tissue Engineering, 7, 2041731416649789 (2016)].
Nanophotonic materials promise non-invasive, high-fidelity sensing and imaging of biological processes, provided they can exhibit biocompatibility, longevity in dynamic, aqueous environments, and improved targeting capability. Here we present our research developing nanophotonic imaging tools for bacterial identification, cellular mapping, and inter-cellular force visualization. First, we combine Raman spectroscopy and deep learning to accurately classify bacteria by both species and antibiotic resistance in a single step. We design a convolutional neural network (CNN) for spectral data and train it to identify 30 of the most common bacterial strains from single-cell Raman spectra, achieving antibiotic treatment identification accuracies exceeding 99% and species identification accuracies similar to leading mass spectrometry identification techniques. Our combined Raman-CNN system represents a proof-of-concept for rapid, culture-free identification of bacterial isolates and antibiotic resistance. Second, we describe a new technique for high-resolution vibrational spectroscopy in the TEM: electron-and-light-induced stimulated Raman scattering (ELISR). Unlike conventional stimulated Raman measurements, our technique uses a laser source as the pump and the electron beam as the broadband Stokes excitation. A small plasmonic nanoparticle amplifies the local Raman signature, with the spatial resolution determined by the electron beam spot size and the nanoparticle size. We show how this technique can enable molecular mapping at the nanoscale, en-route to an “atlas” of cellular receptors. Finally, we introduce a new class of \textit{in vivo} optical probes to monitor biological forces with high spatial and temporal resolution. Our design is based on upconverting nanoparticles that, when excited in the near-infrared, emit light of a different color and intensity in response to nano-to-microNewton forces. The nanoparticles are sub-30nm in size, do not bleach or photobleach, and can enable deep tissue imaging with minimal tissue autofluorescence. We present the design, synthesis, and characterization of these nanoparticles both in vitro and in vivo, focusing on the forces generated by the roundworm \textit{C. elegans} as it feeds and digests its bacterial food. Chronic cytotoxicity assays are used to confirm biocompatibility. Our force measurements are coupled with electrical measurements of muscle contractions in both wild-type and mutant animals, providing insight into the interplay between mechanical, electrical, and chemical signaling \textit{in vivo}.

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**SESSION SB02.09: Biophotonic Sensors and Actuators II**

**Session Chairs:** Polina Anikeeva and Yoonkey Nam

**Wednesday Afternoon, December 4, 2019**

Hynes, Level 2, Room 200

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**2:00 PM SB02.09.01**

**Designing Quantum Dots for \textit{In Vivo} Use—Copper Indium Sulfide as a Test Case**  
Joshua Kays\(^1\), Alexander Saeboe\(^1\), Reyhané Toufanian\(^1\), Danielle Kurant\(^2\) and Allison M. Dennis\(^{1,1}\);  
\(^1\)Boston University, United States; \(^2\)Brigham and Women’s Hospital, United States

Near infrared (NIR) emitting quantum dots (QDs) have long held promise as probes of biological systems due to their brightness, deeper penetration depth, and narrow emission profiles, allowing the tagging and multiplexing of many targets simultaneously. However, after several decades of research, there has been limited translation of QD technology to meet biomedical problems. Two key barriers have hindered their use \textit{in vivo}: the accumulation and persistence of QDs in essential organs over months to years, and the use of toxic materials (e.g. lead, arsenic, cadmium) in traditional QD compositions.

To address the latter barrier, copper indium sulfide (CIS) QDs have emerged in the last decade as a non-toxic alternative to traditional QDs.\(^1\) However, all \textit{in vivo} studies thus far have been confounded by the presence of a zinc sulfide (ZnS) shell,\(^2,3\) which traps the core CIS material by preventing degradation and causing accumulation in vital organs. Additionally, the ZnS shell can act as a mask that hides the toxicity of the core material: in hepatocytes, CdSe cores under irradiation cause clear dose-dependent toxicity, while the same QDs with a ZnS shell cause no such toxicity.\(^4\) This bioaccumulation and masking greatly limits potential for clinical translation: of the \~50 FDA approved nanomedicines in the clinic today, all are biodegradable and clear from vital organs quickly.
For the first time, we assess the biodistribution and toxicity of unshelled CIS in a murine model at 1-day, 7-day, and 1-month time points. We show that bare CIS QDs breakdown quickly, with >75% of the initial dose being cleared by 1 month. Surprisingly, we also demonstrate a significant toxic response to these QDs as measured by organ weight, blood chemistry, and histology, in contrast to previous literature on this system. Specifically, we find that CIS particles induce severe hepatotoxicity and splenotoxicity. We also find that CIS particles alloyed with zinc ions before injections demonstrated significant, but lower, toxicity compared to bare CIS, while also degrading slower in several organs, suggesting that the release rate of ions correlates with increasing toxicity. Finally, we explore a new copper based semiconductor material that fully degrades in under a month without significant toxicity.

Overall, our data suggests a shift in perspective in interfacing QD platforms with biological systems. Firstly, QD cores and shell materials must be tested in vivo separately to truly assess the biocompatibility of the materials. Secondly, intentionally designing QDs to break down into biocompatible ions may be the key to future translation of QD platforms for biomedical challenges.


2:15 PM SB02.09.02
Artificial-Nose Inspired High Dimensionality Fingerprinting of Biological Samples Using Surface-Enhanced Raman Spectroscopy Nayoung Kim1, Michael R. Thomas1, Mads S. Bergholt1, Isaac J. Pence1, Hyejeong Seong1, Patrick Charchar2, Nevena Todorova2, Anika Nagelkerke1, Alexis Belessiotis-Richards1, David J Payne1, Amy Gelmi1, Irene Yarovsky2 and Molly Stevens1; 1Imperial College London, United Kingdom; 2RMIT University, Australia

Label-free platform diagnostic technologies hold great promise, capitalising upon their independence of target-specific binding structures and the associated burden of their discovery, complex conjugation and production procedures. Among a number of targeting-free sensing technologies, label-free surface-enhanced Raman spectroscopy (SERS) has attracted considerable attention, enabling direct profiling of physicochemical properties of endogenous biomolecules. Despite the promise of sensitive fingerprinting, reliable label-free SERS sensors are infrequently realized for biological samples due in part to the challenges of highly overlapped signatures in complex environments. Here, we present an artificial-nose inspired approach using an array of differently functionalised plasmonic surfaces to achieve increased output-data dimensionality in a label- and wash-free regime. Supported by molecular dynamics simulation, we propose that each self-assembled monolayer can provide a different physicochemical interface that promotes a diverse range of molecular interactions, resulting in modulated SERS signatures. As an artificial-nose-like sensing approach, the value of the increased information was illustrated using cell lysates where we achieved reliable improvements in mean discriminatory accuracy towards 100% with each additional surface functionality. The versatile, label-free artificial-nose based approach lays the groundwork for a broad range of biomedical applications where complex signatures of differing pathologies could be established through unguided compositional fingerprinting.

2:30 PM BREAK

3:30 PM *SB02.09.04
Photonic Materials for Delivering and Generating Light for Biomedical Applications Seok-Hyun Yun1,2; 1Massachusetts General Hospital, United States; 2Harvard Medical School, United States

Light offers attractive ways to visualize and modulate biological systems. However, due to limited light penetration in tissues, many applications require solutions to deliver and generate light deep in the tissue. Here we present some
of those solutions using biomaterial waveguides, bioluminescence energy transfer, and intracellular lasers.

**4:00 PM SB02.09.05**

**Stretchable Optical Fiber Photometry for Recording Neural Circuit Dynamics** Siyuan Rao, Xinyue Liu, Shaoting Lin, Cindy Shi, Atharva Sahasrabudhe, Xuanhe Zhao and Polina Anikeeva; Massachusetts Institute of Technology, United States

Holistic study of neural dynamics in behaving subjects often demands simultaneous recording of neural activity across multiple organs in the nervous system. However, currently available techniques for the chronic recording of activity of specific neuronal ensembles are unsuitable for mobile regions of the nervous system such as the brain stem or spinal cord due to the rigidity of the probes.

Here we present a stretchable optical photometry platform that allows chronic recording of calcium signals as a proxy for neural activity across multiple regions of the nervous system in freely moving rodents during behavioral assays. We achieved simultaneous photometric readout from genetically identifiable neuronal populations in mice correlated to social interactions over a period of more than 6 months. Furthermore, we integrated microfluidic channels within these stretchable probes to realize chemical perturbation concomitant with optical recording. In targeted regions of the nervous system with high mobility, the stretchable fiber photometry platform provides an extended time window to record neural dynamics underlying complex behavioral phenotypes. We anticipate that the stretchable photometry probes will facilitate investigation of neural circuits across central and peripheral nervous systems in freely moving subjects.

**4:15 PM *SB02.09.06**

**Chemical and Mechanical Interrogation of Biological Systems—And Beyond** Periklis Pantazis; Imperial College London, United Kingdom

In recent years, advances in imaging probes, microscopy techniques and bioinformatics image analysis have markedly expanded the imaging toolbox available to probe biological systems. Apart from conventional phenotypic studies, complex biological systems are increasingly investigated in vivo with improved accuracy in time and space and more detailed quantitative analyses down to the single-cell level (reviewed in1). To get more insight into the elaborate chemical and mechanical dynamics that underlie development and disease progression, my laboratory addresses the growing imaging needs of the biological community by developing assays2, imaging technologies3-5, and reagents6,7 for carrying out imaging with i) high spatiotemporal resolution at the single-cell level and with ii) sensitivities down to individual proteins. Such newly introduced and future imaging tools can then be used as a means of performing qualitative and quantitative imaging in order to mechanistically dissect development, disease progression, and tissue regeneration in vivo.


**4:45 PM SB02.09.07**

**Mapping 2D- and 3D-Distributions of Metal/Metal Oxide Nanoparticles within Cleared Human Ex Vivo Skin Tissues** George J. Touloumes¹, Herdeline Ardon¹, Evan K. Casalino¹, John Zimmerman¹, Christophe O. Chantre¹,
An increasing number of commercial skincare products are being manufactured with engineered nanomaterials (ENMs), prompting a need to fully understand how ENMs in these products interact with their major biodistribution entry route: dermal barriers. Although animal studies show that certain nanomaterials can cross the skin barrier, physiological differences between human and animal skin, such as the lack of sweat glands, limit the translational validity of these results. Current optical microscopy methods have limited capabilities to visualize ENMs within human skin tissues due to the high amount of background light scattering caused by the dense, ubiquitous extracellular matrix (ECM) of the skin. We hypothesized that organic solvent-based tissue clearing (“immunolabeling-enabled three-dimensional imaging of solvent-cleared organs”, or “iDISCO”) would reduce background light scattering from the skin’s ECM to sufficiently improve imaging contrast both for 2D mapping of unlabeled metal oxide ENMs and also 3D mapping of fluorescent nanoparticles. Here, we demonstrate successful mapping of the 2D distribution of label-free TiO$_2$ and ZnO nanoparticles in cleared skin sections using correlated signals from darkfield, brightfield, and confocal microscopy, and micro-spectroscopy. Specifically, hyperspectral microscopy and Raman spectroscopy confirm the identity of label-free ENMs which we mapped within human skin sections. We also present measurements of the 3D distribution of fluorescently labeled Ag nanoparticles in cleared skin biopsies with wounded epidermal layers using light sheet fluorescence microscopy. Overall, our results represent a novel strategy for quantitatively mapping ENM distributions in cleared ex vivo human skin tissue models using multiple image modalities. By improving imaging contrast, we affirm label-free 2D ENM tracking and 3D ENM mapping as promising capabilities for nanotoxicology investigations.

**SESSION SB02.10: Poster Session II: Biomolecular and Polymeric Materials and Computation**

**Wednesday Afternoon, December 4, 2019**

**SB02.10.01**

**Computational Design of Dendron-Grafted Soft Materials-Based Nanoparticles**

Akash Banerjee and Meenakshi Dutt; Rutgers, The State University of New Jersey, United States

Many drug delivery strategies demand the need for the adsorption and transport of charged, therapeutic biomolecules. These requirements can be met by nanoparticles (NPs) encompassing multiple molecular species that endow electrostatically-induced interfacial binding of specific biomolecules. We are interested in understanding the role of the architecture and composition of the molecular species on the morphological characteristics of the NPs. We study multicomponent NPs encompassing phospholipids and amphiphiles bearing hyper-branched polyelectrolytes (namely, polyamidoamine (PAMAM) dendrons) via the Molecular Dynamics simulation technique used in conjunction with a coarse-grained force field. We examine the impact of dendron generation and relative concentration on the mechanisms and processes dictating the morphology of NPs. Furthermore, we examine the theory underlying the organization and conformation of the hyper-branched polyelectrolytes.

**SB02.10.02**

**Controlling the Shape and Mechanical Stiffness of DNA Origami Nanostructures by Module-Based Design Approaches**

Chanseok Lee, YoungJoo Kim, Jae Young Lee and Do-Nyun Kim; Seoul National University, Korea (the Republic of)

The development of scaffolded DNA nanotechnology has enabled the self-assembly of various 2D and 3D DNA nanostructures with nanometer scale precision. The basic principle of DNA origami is the sequence programmability of multiple DNA strands and uniqueness between them. It uses a long scaffold DNA as a template, and hundreds of staple strands programmed to hybridize with the specific binding locations of the scaffold. By utilizing its excellence in shape design with high precision, a number of design methods based on the lattice-packing or lattice-free rules have been established. By contrast, a method for controlling the mechanical stiffness of the DNA origami structures
has been rarely investigated, although the importance and the demand of it has been increased for their various biological application.

Here we provide two design approaches to effectively control the mechanical stiffness of DNA origami nanostructures. The first method uses stiffness-tunable modules consist of up to 11 staple strands. By revising the staple connectivity within the selected module, the location, stiffness, and included angle of hinges can be controlled precisely. Therefore, it enables the construction of dozens of single- or multiple-hinge structures with the minimized replacement of staple strands. The second method uses multiple engineered defects, consist of one to five-nucleotide (nt)-long single-stranded segments as stiffness design components. Systematic spatial distribution of these local mechanical defects with controlled lengths and positions can weaken the stiffness of the entire structure up to 70% while preserving overall structural integrity. Since our methods shown here are based on the basic principle of scaffolded DNA origami, it is anticipated that they are compatible with existing lattice-based or algorithmic routing shape design rules, as well as commonly used design program (caDNAno) and computational shape prediction platform. Therefore, our module-based stiffness design approaches can be widely adopted to biological application such as intracellular delivery carriers and templates of functional nanomaterials for therapeutics.

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References

SB02.10.03
Dissipative Particle Dynamics Simulations Reveal Micelle Shrinkage of a Pluronic Polymer upon Encapsulation of Ibuprofen Gokhan Kacar; Trakya University, Turkey

The encapsulation of hydrophobic drugs at the hydrophobic core of a micelle gives superior properties in drug delivery, such as drug biocompatibility, better solubility and longer circulation times. Pluronic micelles are one of the widely used polymeric materials in drug encapsulation processes. In this work, we employ coarse-grained Dissipative Particle Dynamics simulations with the hydrogen bonds added explicitly to study the drug encapsulation property, structure and interactions of Pluronic L64/Ibuprofen combinations at different mixing proportions. The coarse-grained simulations reveal that the computed total drug encapsulation efficiency is around 80%, where the hydrophobic drug Ibuprofen is mainly kept in the hydrophobic core of the micelle. As for the micelle structure, the simulations show a decrease in the micelle size upon encapsulation of the drug in line with the experimental literature. The computed Radial Distribution Functions point out that the micelle shrinkage can be caused by an increased local packing of the hydrophobic-hydrophilic units around each other, and the absence of water molecules inside the micelles when there are drug molecules present in the system. Overall, the coarse-grained DPD simulations predict the structural and drug encapsulation properties of a polymeric system consistent with the experiments, whereby bringing new insights to its molecular understanding in terms of micelle shrinkage upon inclusion of Ibuprofen. The results confirm the promising role of the simulation procedure reported in this work to study the drug encapsulation, molecular structure and interactions of polymeric micelles used as drug delivery materials.

SB02.10.04
Effect of pH on the Initialization of Ca-Deficient Hydroxyapatite to β-Tricalcium Phosphate Nanoparticles—A Route to Low-Temperature Synthesis Feray Bakan1 and Ibrahim B. Misirlioglu2,1; 1Sabanci University SUNUM, Turkey; 2Sabanci University, Turkey

Calcium phosphate (CaP) nanoparticles are preferred in many applications owing to their excellent biocompatibility, bioactivity and chemical affinity towards biological molecules. Stoichiometric or non-stoichiometric hydroxyapatite (HA or CDHA), β-Tricalcium phosphate (β-TCP) and biphasic calcium phosphates (BCP, mixtures of HA and β-TCP in a variety of ratios) are the most widely used CaP compounds. Non-stoichiometric Ca-deficient hydroxyapatite (CDHA) is the main inorganic component of hard tissues and its synthetic forms are extensively utilized in a large spectrum of bio-applications ranging from hard tissue repairment and scaffolds to targeted drug delivery and gene therapy. Among all CaP compounds, β-tricalcium phosphate (β-TCP) exhibits better
biodegradability hence it can be absorbed better and aid in the generation of new hard tissue or effective release of the nanotherapeutic molecules and/or drugs in the targeted tissue. β-TCP is also a forthcoming structure enabling highly effective osteointegration. In synthetic wet-chemical processes, β-TCP cannot be directly precipitated but only be transformed from CDHA at relatively high temperatures (≥900°C) where it apparently gets stabilized irreversibly upon cooling. Low-temperature sintering of β-TCP, on the other hand, is desired for use as a biocompatible coating on alloy-based load bearing implant structures inside the body, acting as the osteointegration agent between the host tissue and the implant. In this work, we report on a procedure to obtain β-TCP phase from CDHA at temperatures as low as 720°C where the transformation already starts. Low calcination temperatures are favored in order to obtain pure β-TCP phase with finer morphology in adapt to natural skeletal tissue. However, whether or not adjusting pH can be an effective means to allow so has partly remained elusive. We, therefore, decided to systematically explore the range of pH that we thought would allow the low-temperature transformation of CDHA to β-TCP. A full transformation of CDHA to β-TCP at 750°C in under 3 hours from Ca++ and PO₄³⁻ precursor solutions prepared under a pH of 5.5 was observed. The lower temperatures and the shorter sintering time reported herein allow for a fine nanostructured morphology along with high crystallinity, a sought outcome for effective osteointegration. The effect of synthesized β-TCP particles on the cell viability of human osteoblast-like cell line MG-63 was also assessed by using MTT colorimetric assay for verifying the biocompability of the obtained nanomaterials. We finally note that such a substantial lowering of the sintering temperature, when used as a coating on metallic implants, also aids in minimizing the high-temperature corrosion of the substrate alloy as most metals are prone to oxidation at elevated temperatures in addition to changing the intended fatigue-resistant microstructure.

SB02.10.05 Enhanced Silver Nanoparticle Synthesis by Recombinant E. coli Cells Transformed with Metallothionein Gene Qunying Yuan, Brittany Batiste, Oluwafolakemi Meroko, Quenland Pogue and Zhigang Xiao; Alabama A&M University, United States

In this study, the metallothionein gene of Candida Albicans was assembled by PCR, inserted into pUC19 vector, and further transformed into E. coli DH5α cells. The capacity of these recombinant E. coli DH5α cells to synthesize silver nanoparticles was tested. Our preliminary data obtained by UV-Vis spectrophotometer and SEM analysis suggested that the metallothionein gene transformed E. coli DH5α cells were able to synthesize silver nanoparticles earlier and faster than DH5α cells transformed with pUC19 vector. The composition and morphology of the nanoparticles will be further characterized using Fourier-transform infrared spectroscopy (FTIR), energy-dispersive X-ray spectroscopy (EDS), and high-resolution transmission electron microscope (HRTEM). The capacity of metallothionein gene transformed bacteria to produce other metallic nanoparticles will be tested. The details of biosynthesis of nanoparticles and the analyzed results on the bio-synthesized metallic nanoparticles will be demonstrated and reported.

SB02.10.06 Multiscale Analysis and Modeling of DNA Origami Nanostructures Jae Young Lee, Chansook Lee, YoungJoo Kim and Do-Nyun Kim; Seoul National University, Korea (the Republic of)

Structural DNA nanotechnology has proposed a bottom-up approach to assemble various complex structures with the nanoscale resolution based on complementary self-assembly principles. DNA origami method is used to design higher order structures by programming complementary base sequences of DNA strands and the inter-helical connectivity between DNA strands. Accordingly, in order to precisely design and analyze DNA nanostructures, it is important to characterize and model the material properties of DNA structural motifs such as base-pair steps, which is the smallest unit of DNA helix, and Holliday-junctions connecting helices. Here, we first quantitatively investigated the sequence-dependent characteristics of DNA structural motifs at the base-sequence level using the molecular dynamics simulation. The atomic fluctuation of structural motifs consisting of base-pairs was reduced to intrinsic configuration and covariance matrices, providing the elastic properties as mechanical rigidities and coupling coefficients. A significant difference in material properties was observed with respect to the base sequences, suggesting that consideration and modeling of the sequence-dependent properties may play a crucial role in designing and analysis of the DNA origami structures. Furthermore, we developed a finite element model that can consider the base level properties of structural motifs driven by molecular dynamics simulation. It was confirmed that the proposed model was in good agreement with the previous experimental or simulation results, suggesting detailed and accurate insights into complex and highly deformable structures. Our study demonstrates the
importance of characterizing material properties of DNA by atomic simulations, and their proper modeling can contribute greatly to the mechanical analysis of DNA nanostructures. This multiscale strategy developed for DNA origami nanostructures could potentially be applied to various biomolecule system, indicating its generalizability.

Acknowledgment
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SB02.10.07
Single-Chain Atomic Crystals as Extracellular Matrix-Mimicking Material with Exceptional Biocompatibility and Bioactivity Jin Woong Lee1, Sudong Chae1, Jung Heon Lee1,2,3 and Jae-Young Choi1,2; 1Sungkyunkwan University, Korea (the Republic of); 2Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); 3Biomedical Institute for Convergence at SKKU (BICS), Korea (the Republic of)

In this study, Mo3Se3− single-chain atomic crystals (SCACs) with atomically small chain diameters of ∼0.6 nm, large surface areas, and mechanical flexibility were synthesized and investigated as an extracellular matrix (ECM)-mimicking scaffold material for tissue engineering applications. The proliferation of L-929 and MC3T3-E1 cell lines increased up to 268.4 ± 24.4% and 396.2 ± 8.1%, respectively, after 48 h of culturing with Mo3Se3− SCACs. More importantly, this extremely high proliferation was observed when the cells were treated with 200 μg mL−1 of Mo3Se3− SCACs, which is above the cytotoxic concentration of most nanomaterials reported earlier. An ECM-mimicking scaffold film prepared by coating Mo3Se3− SCACs on a glass substrate enabled the cells to adhere to the surface in a highly stretched manner at the initial stage of cell adhesion. Most cells cultured on the ECM-mimicking scaffold film remained alive; in contrast, a substantial number of cells cultured on glass substrates without the Mo3Se3− SCAC coating did not survive. This work not only proves the exceptional biocompatible and bioactive characteristics of the Mo3Se3− SCACs but also suggests that, as an ECM-mimicking scaffold material, Mo3Se3− SCACs can overcome several critical limitations of most other nanomaterials.

SB02.10.08
Synthesis of Biocompatible Silver Nanoparticles and Nanotoxicity in Aquatic Ecosystems Jousen A. Merced, David Medina-Suarez, Gabriela M. Mercado-Guzman and Sonia J. Bailon Ruiz; University of Puerto Rico in Ponce, United States

Silver nanoparticles (Ag NPs) have unique optical, electrical, and thermal properties and are being incorporated into products that range from photovoltaics to biological and chemical sensors. The new generation of silver nanoparticles brings potential applications for antimicrobial coatings, biomedical devices, molecular diagnostics, photonic devices between others. The production of silver nanoparticles has been increasing worldwide in the nanotechnology industry due to the variety of applications mentioned and are very likely to reach aquatic ecosystems damaging them. Due to their small size and high surface area to volume ratio of NPs, they can strongly interact with life cells and cause damage to tested animals. Based on the mentioned previously, it is necessary to evaluate the silver nanoparticle nanotoxicity in aquatic ecosystems to prevent possible ingestion or transfer to humans. Also, the research will benefit aquatic systems due to less pollution around aquatic organisms. The objectives of this research included: i) production and characterization of stable silver nanoparticles in water, ii) characterizing the optical properties by UV-Vis spectroscopy, morphology by HR-TEM, crystalline structure by X-Ray Diffraction (XRD) and the nature of the surface by Infrared spectroscopy. Additionally, Electron Diffraction and Energy Dispersive X-Ray analyses were also evaluated for Ag NPs. iii) Optimize the synthesis of silver nanoparticles by changing the molar ratio of silver/citrate and, iv) evaluate the toxicity of silver nanoparticles in aquatic organisms, i.e Artemia salina. Results obtained evidenced that AgNPs showed absorption peaks in a range of 410 nm and 440 nm. These peaks are due to the phenomenon called surface plasmon resonance (SPR) that are responsible for a variety of phenomena, including nanoscale optical focusing, negative refraction, and surface-enhanced Raman scattering. Also, the concentration of nanoparticles was dependent of the reaction time. HR-TEM measurements evidenced the spherical form of the nanoparticles and its small size at around 12-14 nm and it was confirmed by XRD. In addition, Electron Diffraction analyses suggested the composition of the nanoparticle, which contained only Ag. The toxicity assays were evaluated using different concentration of Ag NPs and a control test. The effect and cytotoxicity of these nanoparticles were studied in the nauplii state of Artemia salina. During the toxicity assay, it was demonstrated that the Artemia salina was able to uptake silver nanoparticles and store it into
SB02.10.09
Patterned Amyloid Materials Integrating Robustness and Genetically Programmable Functionality
Yingfeng Li, Ke Li and Chao Zhong; Shanghai Tech, China

The precise manipulation, localization, and assembly of biological and bioinspired molecules into organized structures have greatly promoted material science and biomanufactoring. Further technological innovation calls for new patternable soft materials with the long-sought qualities of environmental tolerance and functional flexibility. Here, we report a Patterned Amyloid Material (PAM) platform for producing hierarchically ordered structures that integrate these material attributes. This platform, combining soft lithography with generic amyloid monomer inks (consisting of genetically engineered biofilm proteins dissolved in hexafluoroisopropanol), along with methanol-assisted curing, enables the spatially controlled deposition and in situ reassembly of amyloid monomers. The resulting patterned structures exhibit spectacular chemical and thermal stability and mechanical robustness under harsh conditions. The PAMs can be programmed for a vast array of multi-level functionalities, including anchoring nanoparticles, enabling diverse fluorescent protein arrays, and serving as self-supporting porous sheets for cellular growth. This PAM platform will not only drive innovation in biomanufacturing but also broaden the applications of patterned soft architectures in optics, electronics, biocatalysis, analytical regents, cell engineering, medicine, and other areas.

SB02.10.11
Hyaluronic acid-Amphotericin B Nanocomplexes—A Promising Anti-Leishmanial Targeted Drug Delivery System
Ricardo Carvalho1, Catarina Gonçalves2, Ana Isabel Bourbon2, Lorenzo Pastrana2, Pier Parpot3, Ana Tomás4 and Miguel Gama1; 1CEB – Centre of Biological Engineering, University of Minho, Portugal; 2Food Processing group, International Iberian Nanotechnology Laboratory, Portugal; 3Centre of Chemistry, University of Minho, Portugal; 4I3S - Instituto de Investigação e Inovação em Saúde, Universidade do Porto and IBMC - Instituto de Biologia Molecular e Celular, Universidade do Porto, Portugal

Leishmaniasis has been classified as one of the most neglected tropical diseases, causing 50 thousand deaths and 1.5 to 2 million new cases every year, according to the World Health Organization. This disease, promoted by protozoan parasites of the genus Leishmania, has a high incidence affecting 89 countries worldwide. Nowadays, current treatment strategies still rely on the antifungal agent amphotericin B (AmB) but are rather inadequate due to the high prevalence of the disease within low-income population of sub-developed regions, the intracellular location of the parasite and the emergence of parasite resistance. Thus, other strategies have been pursued to improve the therapeutic efficacy and to reduce the toxicity of AmB such as the use of biocompatible polysaccharides as carriers. In this work, a simple and inexpensive production process using hyaluronic acid (HA, 50 kDa) was used in order to develop water-soluble hyaluronic acid-amphotericin B nanocomplex (HA-AmB). HA is the main ligand of CD44 receptor, thus being favorably internalized by macrophages that overexpress this receptor upon infection. Therefore, HA arises as a suitable polysaccharide to target the AmB delivery to the leishmania-infected macrophages. The nanocomplex, obtained by simply processing the mixture of the polysaccharide with the drug in a nanospray dryer (HA-AmB SD), was characterized in terms of size/zeta potential (DLS) and morphology (SEM and Cryo-SEM). Furthermore, an HPLC-MS detection method was optimized and used to determine the AmB content in the nanocomplex. Also, to ascertain the interaction between AmB and the HA, FTIR, DSC and PXRD analysis were performed. Cytotoxic and hemolytic effects were assessed on different cell lines through the resazurin test and in dog’s blood, respectively. Anti-leishmanial activity was assessed in vitro in axenic cultures of Leishmania by resazurin and in infected bone marrow-derived macrophages (BMMΦ) stained with different fluorescent probes using high-content microscopy.

Our results shown that the produced material has a spherical morphology in aqueous solution with a mean hydrodynamic diameter of 318.4 ± 34.7 nm and low polydispersity (0.239 ± 0.02). Moreover, this material that presents an AmB content of 13.56 ± 3.49 %, has a good colloidal stability due to the highly negative surface charge (-39.45 ± 1.12 mV). DSC and PXRD analysis strongly suggested the formation of an amorphous inclusion complex between AmB and the complex polysaccharide chain networks, explaining the high solubility of the drug in water. The in vitro assays showed that compared to free-AmB, the nanocomplex had significantly less cytotoxicity against BMMΦ and HEK293T cell lines, significant less hemolytic effect and inhibited the infection in the Leishmania-infected BMMΦ. Exploratory in vivo assays are being conducted in mice. In conclusion, this work has shown that the hyaluronic acid-AmB nanocomplex is a promising system for the treatment of Leishmaniasis, possessing similar
effects to the free-AmB against Leishmania-infected macrophages and Leishmania axenic cultures, with reduced cytotoxicity. Given the affordability, simplicity, low-toxicity and facile scale up of the developed formulation, the hyaluronic acid-AmB nanocomplex may represent an alternative to the expensive nanoformulations available.

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**SB02.10.12**

RNA Delivery via DNA-Inspired Janus Base Nanotubes for Extracellular Matrix Penetration  
Ian Sands, Jinhyung Lee, Wuxia Zhang and Yupeng Chen; University of Connecticut, United States

RNA delivery into deep tissues with dense extracellular matrix (ECM) has been challenging. For example, cartilage is a major barrier for RNA and drug delivery due to its avascular structure, low cell density and strong negative surface charge. Cartilage ECM is comprised of collagens, proteoglycans, and various other noncollagenous proteins with a spacing of 20nm. Conventional nanoparticles are usually spherical with a diameter larger than 50-60nm (after cargo loading). Therefore, they presented limited success for RNA delivery into cartilage. Here, we developed Janus base nanotubes (JBNTs, self-assembled nanotubes inspired from DNA base pairs) to assemble with small RNAs to form nano-rod delivery vehicles (termed as “Nanopieces”). Nanopieces have a diameter of ~20nm (smallest delivery vehicles after cargo loading) and a length of ~100nm. They present a novel breakthrough in ECM penetration due to the reduced size and adjustable characteristics to encourage ECM and intracellular penetration.

JBNTs are comprised of self-assembled supramolecular structures which are further broken down into guanine and cytosine DNA base pairs. The hollow channels formed by these nanotubes are ideal for drug loading and the six-member rosette comprised of hydrogen bonding is essential for its low cytotoxicity profile. By controlled assembly between our nucleic acid cargos (in this case siRNA) with JBNT solution, long segmented Nanopieces are synthesized. They can be further separated via a regulated sonication process. Nanopiece with formulations were assembled and their material properties were studied using DLS and Zeta potential measurements. Their morphological characteristics and distributions were analyzed by TEM (transmission electron microscopy) imaging. The RNA delivery abilities of Nanopieces with different formulations were determined in vitro using human chondrocytes. Nanopiece binding and ECM penetration was also studied in vitro using fluorescence and confocal microscopy. Results of this study provide in-depth characterizations of these Nanopieces along with evaluating their abilities of RNA delivery. Our data also determines how Nanopieces bind with and penetrate into cell ECM to understand their delivery mechanism.
of non-serum media to replace the fetal bovine serum (FBS) containing media, the non-serum media has their limitations including the lower cell activity and adhesion rates.

In order to overcome those limitations, nano-materials coated tissue culture polystyrene (TCPS) plates, which are commercially available, are suggested as a novel lab-ware to improve cell adhesion on culture plate. However, we suggest a compatible alternative, the single-walled carbon nanotube (SWCNT), which is a seamless cylinder comprised of a graphene sheet with diameter of the order of a nanometer and has no toxicity when it is properly functionalized and treated to mammalian cells [3].

The aim of this study is 1) the fabrication and characterization of SWCNT film based scaffolds having an optimal property for ADSC culture in non-serum media and 2) the analysis and evaluation of ADSC adhesion mechanism on the SWCNT film based scaffolds in this culture condition.

References

SB02.11.02
Controlled Growth of Bacterial Cellulose Films in Laser Printed Micro-Scaffolds Adriano J. Otuka, Rafael R. Domeneguetti, Debora T. Balogh, Sidney Ribeiro and Cleber Mendonca; 1University of Sao Paulo, Brazil; 2Sao Paulo State University, Brazil

Several materials have been developed to meet the growing demand of the technological applications. For instance, biological systems require functional materials with specific features, such as biocompatibility and non-toxicity. Hybrid materials are good candidates for this purpose because it combines the advantages of organic compounds with those of inorganic components, creating a variety of new materials. In this work, aiming potential applications in biological platforms, we prepare liquid hybrid materials which can be sculpted using laser micromachining systems. The host sample is prepared using equal proportions of a silane compound (3-(trimethoxysilyl) propyl methacrylate) and an acrylate monomer (dipentaerythritol pentaacrylate), mixed with an acylphosphine oxide photoinitiator (ethyl-2,4,6-trimethylbenzoyl phenylphosphinate). To produce these biological platforms we used a Ti:Sapphire laser oscillator, centered at 780 nm, operating at a repetition rate of 86 MHz and delivering 100 fs pulses. The laser beam is focused through a microscope objective (10X, NA=0.25) into the sample and scanned in the x-y direction using a pair of galvanometric mirrors, while in the z direction we can move the sample aided by a motorized stage. The biological viability of the three-dimensional micro-scaffolds fabricated was tested from the growth analyses of prokaryotes organisms. We inoculate the bacteria *Gluconacetobacter xylinus* (ATCC 23760) into the microenvironments, receiving all the necessary conditions for their development. These bacteria are responsible for the production of bacterial cellulose, which has emerged as an interesting candidate to fabricate advanced biomaterials, aiming applications in tissue engineering and drug delivery systems. We evaluate the bacterial cellulose growth daily, for one week. As result, we obtained films with different thickness, depending how long the bacteria were inoculate on the platforms. All formed biofilms were characterized morphologically and structurally by scanning electron microscopy, infrared spectroscopy and Raman spectroscopy. The structure and composition of grown bacterial cellulose in the microenvironments are similar than those grown in macro systems. In addition, the grown biofilm also exhibits a nanofibrous porous network highly moldable, with high strength and low density. The results obtained in this work demonstrate that, in respect to the bacteria *Gluconacetobacter xylinus* (ATCC 23760), the hybrid platforms developed in this work are biocompatibles and non-toxicity. Moreover, the use of these matrices do not restricted to gram-negative bacteria, open new opportunities to studies with others prokaryotes and eukaryotes organisms.

SB02.11.03
Design Strategies to Control the Mechanical Properties of Tyrosine Photocrosslinked Hydrogels Christopher Camp, Ingrid Peterson, David S. Knoff, Zhaoyinqian Li, Anne Wertheimer and Minkyu Kim; University of Arizona, United States

Chemically crosslinked polymeric hydrogels are promising biomaterial solutions in many tissue engineering applications due to their more permanent structure compared to physically crosslinked gels, but often lack the spatially homogeneous crosslink density of physical hydrogels due to the uneven mixing of gelators. However, photocrosslinked chemical hydrogels can offer improved homogeneity because the solution can be completely
mixed before the gelation is initiated. Much attention has been given to tyrosine photocrosslinking in polymeric hydrogels because tyrosine photocrosslinking is rapid and more specific compared to other protein chemical crosslinking methods, which is especially important for designs that incorporate proteins that are critical for cell or tissue functionalities: specific tyrosine crosslinking reduces unintentional, random crosslinking on the incorporated proteins that can result in the loss of protein functionality. However, thorough studies of tyrosine crosslinking and the design of tyrosine incorporated polymers taking into account parameters such as potentially toxic photoinitiator and catalyst concentrations for biocompatibility, tyrosine spacing, polymer length, and their effects on hydrogel rheology are not available.

We present a systematic study of tris(bipyridine)ruthenium(II) chloride and ammonium persulfate mediated dityrosine crosslinking using a biologically synthesized polypeptide construct with various parameters. Typically, photoinitiators are used in excess in gelation procedures for rapid crosslinking and better mechanical properties, but we optimized the hydrogel formulations and used rheology to show the effects on mechanical properties. In addition, we used biomolecular engineering to show the effects of spacing between tyrosine residues and polymer length on the hydrogel mechanical properties while maintaining the same molarity of tyrosine residues and tyrosine percentage in each construct. We also showed the photocrosslinked chemical hydrogels can be prepared to have no cytotoxicity for up to 7 days when in culture with human primary fibroblasts and low endotoxin levels. This study guides a biomaterial design that maximizes the benefits of dityrosine crosslinking while controlling mechanical properties and limiting the use of photoinitiators for increased biocompatibility.

SB02.11.04  
Effect of Self-Assembled Molecules on Cardiac Differentiation of Induced Pluripotent Stem Cells  
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Surface chemistry plays an important role in regulating cellular behavior, in vitro. Recent studies showed that functional groups on biomaterial surfaces regulate cellular adhesion, migration, proliferation and differentiation. Self-assembled molecules (SAMs) form organized structures and with these molecules, desired surface properties can be easily generated. In the present study, we aimed to prepare polydimethylsiloxane (PDMS) substrates in natural myocardium-like stiffness range and investigate the effect of their surface modifications with SAMs, having two functional end groups (-CH3 and –NH2) and different wettability properties, on cardiac differentiation of murine induced pluripotent stem cells (mIPS). PDMS (Sylgard 184) substrates were prepared with different ratios of silicone elastomer base and curing agent (10:1 – 70:1) and spin coated on glass slides. Young’s moduli of substrates were characterized with nanoindentation. In low resolution XPS survey spectra of all unmodified and modified PDMS, four characteristic peaks were found as O1s, C1s, Si2s and Si2p at 533, 286, 155 and 104 eV, respectively. -CH3 functionalization of PDMS substrates lead to a remarkable increase in the carbon peak, due to high carbon content of the molecule, whereas N1s peak appeared after modifications with APTES at 401 eV. WCA analysis showed hydrophobic nature of native and –CH3 modified PDMS (104.1±5 and 112.7±5, respectively) and hydrophilic properties of –NH2 modified PDMS (61.9±4). MTT analysis of mIPS cells on these substrates showed no statistical difference between SAMs modified PDMS. Both modified substrates showed higher viability when compared to native PDMS (p<0.05). Western blot analysis results were given in Fig.1 on day 12 of differentiation. Similar to viability analysis, both functional end groups enhanced cardiac differentiation significantly, when compared to native PDMS. Cardiac marker Troponin-T expressions were higher in hydrophilic -NH2 groups. Conventional SAMs modified PDMS substrates in myocardium-like stiffness range were confirmed to be nontoxic to mIPS cells and also these modifications enhanced cardiac differentiation of mIPS cells on PDMS substrates.
We fabricated an artificial oral mucosa using a fish scale-collagen scaffold for clinical applications of oral mucosa defects. Fish derived collagen is appropriate for human use due to zoonotic-free biomaterial. The intrinsic wavy papillary structure of in vivo oral connective tissues was patterned to the collagen scaffold by soft lithography. The soft lithography mold was fabricated from an initial mold fabricated via Si anisotropic/isotropic etching process with the error less than 5%. The histology of artificial oral mucosa with the fish scale-collagen patterned by soft lithography (150 µm in height and 300 µm in pitch) showed a differentiated stratified epithelial layer, similar to the native oral mucosa. Soft lithography can be applied to fabricate a negative molds to create the micropattern mimicking the intrinsic wavy papillary structure of oral mucosa, suggesting a useful technique for developing the proposed biomimetic artificial oral mucosa.

As a remedy of oral mucosa defects, transplantation of the oral mucosa substitutes has been clinically applied. Although collagen scaffolds derived from animals have been proposed, the use of animal derived-collagen may cause infectious diseases by foreign contaminants. Instead, attention has been paid on fish scale-collagen because there is no risk of disease transmission from fish to human [1]. In addition, previous studies on a skin epithelial regeneration revealed that undulating microstructure of the scaffold enables to create the specific microenvironment for epithelial cells. [2] However, microstructuring of the fish scale-collagen has not been reported. In this study, we applied soft lithography to fabricate an artificial oral mucosa using a fish scale-collagen mimicking the topographical structure between oral mucosa epithelium and the underlying the connective tissue. Our proposed artificial oral mucosa with the micropatterned fish scale-collagen facilitates the regeneration of oral mucosa epithelium in vitro.

The microstructure was designed to obtain the wavy papilla structure of oral connective tissues. [3] A polydimethylsiloxane (PDMS) was used as a material for soft lithography mold. First, a Si initial mold was prepared via anisotropic deep-reactive ion etching with a photore sist mask. Subsequently, Si isotropic wet etching was performed to fabricate the wavy structure. The PDMS was molded after applying a release agent on the initial mold by dip coating. Second, a solution of fish scale-collagen was poured and structured by soft lithography with the PDMS mold. Finally, the artificial oral mucosa was constructed by culturing oral keratinocytes on the micropatterned fish scale-collagen tissue.

Results of scanning electron microscope observation showed that the initial mold was successfully patterned with the error less than 5% from the designed value. This result indicates the anisotropic/isotropic etching process enables to fabricate the undulating microstructure similar to oral connective tissue. Furthermore, it was confirmed the PDMS mold was replicated from the initial mold with the error less than 5%. Moreover, our histological examination of the artificial oral tissue revealed the formation of the stratified epithelial cell layer on top of the micropatterned collagen scaffold. The papillary structure with 150 µm in height and 300 µm in pitch was successfully fabricated. The histology of artificial oral mucosa was similar to an in vivo oral mucosa tissue. Consequently, soft lithography can be a useful technique for developing the proposed biomimetic artificial oral mucosa to create micropatterns mimicking the intrinsic wavy papillary structure of oral mucosa.

surface and topological features of the extracellular matrix and as well as support the formation of new viable tissue. However, there are an excessive variety of scaffolds and some of them improve biochemical properties but lack from mechanical strength. Nowadays, fibrous scaffolds have demonstrated excellent potential due they mimic the in vivo physiology, where cells grow and interact according to the spatial and mechanical conditions provided. Here, we prepared a scaffold that incorporated bioglass nanoparticles into the polymeric matrix of electrospun nanofibers. Bioglass nanoparticles were loaded and studied at different concentrations, to induce osteogenic differentiation of human fetal osteoblastic cells (hFOB). Further, we produced a bio-adhesive scaffold, based on mussel-inspired polydopamine (PDA) coating of bioglass-loaded nanofibers. This scaffold not only enhances cell adhesion but also improve its mechanical strength. The chemical composition and morphology of these hybrid composite scaffolds were characterized using Fourier-Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM), respectively. SEM micrographs showed highly interconnected pores, a suitable characteristic for cell penetration and showed the PDA coating transition as a function of time. After the fabrication, mechanical tests were performed, and the properties of the scaffolds were evaluated. Immunostaining assays were conducted to study cell adhesion and differentiation of hFOB cells. Our results indicate that our bio-adhesive and bioactive composite could support tissue growth and is proposed as a scaffold for bone tissue regeneration.

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OPEN SLOT

SB02.11.08
Novel Polymeric Fibrous Material Based on Gum Karaya for Biomedical Applications Martina Rihova1, Ahmet Erdem Ince1, Ludek Hromadko1,2, Lucy Vojtova1 and Jan M. Macak1,2; 1Central European Institute of Technology, University of Technology, Czechia; 2University of Pardubice, Czechia

The human skin prevents our bodies against an entry of various microbes. Once the skin is damaged, its infection can occur via anaerobic and aerobic bacteria. The necessary skin wound dressing must fulfil some properties, such as to create a sufficiently moist environment, to prevent further infection, absorb the wound fluids and exudates, to decrease the wound skin necrosis and to prevent the skin against external harsh conditions. Bandages should be elastic, non-antigenic and biocompatible materials. To further increase their healing functions, they are loaded with antimicrobial, antibacterial and anti-inflammatory agents (1, 2). However, these compounds are also present in some biopolymers, such as chitosan and oxyccellulose, which are used in the form of nanofibers for wound covers (2, 3). Biopolymeric nanofibers possess in general a high porosity, large specific surface area, variable pore size, excellent breathability and also biocompatibility (1). The most common technique to produce nanofibers so far has been electrospinning (4). This technique enables synthesis of various nanofibers with diameters in the range of dozens to hundreds of nm. However, it possesses several drawbacks, such low production rate, sensitivity on temperature and humidity, incomplete utilization of spun solutions. In addition, electro spun fibers often have residual electrostatic charge, which renders their handling difficult. More recent spinning method, known as centrifugal spinning (5), uses only centrifugal force, which eliminates drawbacks of electrospinning. The centrifugal spinning also broadens the pool of fibers to allow spinning of even non-conductive materials (polymers). In this work, deacetylated natural polysaccharide Gum Karaya (GK) was used as the main material for the centrifugal spinning. This biocompatible and biodegradable polysaccharide can be prepared into 3D foams of fibrous materials with great prospects in regenerative medicine (6). Fiber blends of Gum Karaya with other biodegradable polymers, such as poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA), were also investigated. Obtained fibers from aqueous blended from GK/PVA and GK/PEO were characterized by various means (Fourier-transformed infrared spectroscopy, scanning electron microscopy and swelling behaviour). Most importantly, they were characterized for biomedical effect using antibacterial testing and commercial skin analyzer. We show that the newly prepared fibers represent very promising material for the skin wound dressing.

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REFERENCE


**SB02.11.09**

**From Microtissues to Organs-on-Chips—Multi-Scale In Vitro Models for Screening Engineered Nanomaterial Toxicity**

Herdeline Ardona1, John F. Zimmerman1, Feyisayo Eweje1, Seungkuk Ahn1, Blakely O'Connor1, Thomas Grevesse1, Johan Lind1, Karla Rivera1, Dimitrios Bitounis1, Philip Demokritou1 and Kevin Kit Parker1; 1Harvard University, United States; 2Concordia University, Canada; 3Technical University of Denmark, Denmark

While engineered nanomaterials (ENMs) have emerged as important components of various consumer products, human exposure to ENMs has been associated with negative health outcomes, such as cardiovascular diseases. To better understand and quantify the pathophysiological effects of exposure to different ENMs, there is a pressing need to develop in vitro models that faithfully recapitulate the native form and function of cells and tissues. In particular, two platforms developed for screening ENM effects in the cardiovascular space will be presented: 1) micropatterned cell pairs as a minimalistic model of the endothelial barrier; and 2) fiber-based cardiac microphysiological devices for contractile stress measurements. These models allow for a multi-scale assessment of the effects of nano-bio interactions at different stages of ENM biodistribution—from the translocation of ENMs across barrier tissues such as the endothelium, to their delivery towards target tissues such as the myocardium. Geometrically-controlled endothelial cell pair microtissues were produced via protein micropatterning, which allows for a systematic assessment of ENM-induced changes in multiple cellular-level parameters related to vascular barrier integrity. These measurements included changes in cellular morphology, junction protein expression, intercellular gap formation and cytoskeletal network organization upon ENM exposure. On the other hand, our “chip-based” platform can be used for measuring changes in tissue-level cardiac function, such as contractile stress and beat rate, during ENM exposure. Aligned polydopamine (PDA)/polycaprolactone (PCL) nanofibers were used as a tissue scaffold for this device in order to mimic the 3D architecture of cardiac microenvironments under physiological conditions. An instrumented version of this platform with embedded strain sensors will also be presented, which provides a way to continuously and non-invasively monitor the effects of ENM on cardiac tissue contractility at different time points. Together, these next generation in vitro and analytical testing platforms provide physiologically relevant 2D- and 3D-models of ENM exposure routes towards a more comprehensive evaluation of microvascular and cardiac response profiles to different nanomaterials.

**SB02.11.10**

**Endothelial Cell Pairs as a Reductionist Model for Studying the Effects of Engineered Nanomaterials on Vascular Barrier Integrity**

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Engineered nanomaterials (ENMs) are being increasingly used in a variety of products due to their unique physicochemical characteristics. However, the potential hazards that ENMs pose to human health are still not fully understood. These materials are delivered to target tissues by following several biodistribution routes across multiple biological tissue barriers, with different microenvironments that vary from one another. Of particular interest is their impact on the vascular endothelium, which is an important selective barrier that regulates the exchange of materials between the blood and tissues throughout the body. Current studies of ENM toxicity towards the endothelium are conducted using endothelial cell monolayers, which are low throughput and not particularly amenable to quantitative image analysis of changes in local structural features upon ENM exposure. To address this issue, we have used a micropatterning technique to isolate endothelial cell pairs as a reductionist model of the vascular barrier. Cell pairs, or two cells with a shared junction, serve as the basic functional repeating unit of a continuous biological tissue such as the vascular endothelium. The micropatterned cell pair in vitro model enables both higher throughput ENM
toxicity studies, as well as the measurement of a series of quantitative parameters, such as changes in cellular structure, junction protein expression, and cytoskeletal network reorganization (e.g., transition from predominantly cortical actin to 24 stress fiber formation), which are all relevant to barrier function. We used the cell pair assay to evaluate the dose-dependent changes in induced by a library of ENMs (Au, Ag, TiO₂, ZnO, CuO, Fe₂O₃, SiO₂, Al₂O₃, and 2 nanocellulose polymorphs) from 10 to 100 μg/mL exposure dosage. The summative ENM-induced changes in these endothelial structural features were then assessed for their correspondence to effects on cellular viability and tissue-level barrier function. We found that endothelial exposure to some of these materials, such as Ag and TiO₂, induce changes with negative implications on barrier function, including increased formation of actin stress fibers, reduced junction protein expression, and increased intercellular gap formation. Here, a similarity index scoring method is also implemented to quantitatively compare the extent by which a cell pair deviates from the unexposed “healthy” phenotype after an acute 24-hour ENM exposure. Collectively, these results demonstrate that our cell pair assay represents a viable new method for standardizing ENM endothelial toxicity screening.

**SB02.11.11**

**Bacterial Cellulose-Based Microfluidic Device for 3D Skin Modelling (Skin-on-Chip)**

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Paper fluidics is based on patterning hydrophilic paper with channels bounded by hydrophobic barriers. Fluids move along channels by capillarity. Several methods are available for patterning paper, with different costs/resolutions. Paper patterning for microfluidics also used the embossing technique to design open-channel microfluidic devices, fabricated by compressing the sheet of paper with the help of 3D plastic printing moulds. These approaches are adopted in this work to develop a multiwell-microplate paper-based microfluidic, aiming the creation of organs-on-chip, combining complexity and miniaturization. Bacterial Cellulose (BC) represents a source of highly pure and biocompatible cellulose, with huge technological potential in many fields - biomedical, composites, textiles, food and cosmetics textiles - but currently still rather underexploited [Gama et al, 2016; Klemm et al, 2018]. This work describes a novel approach towards the development of a nanostructured and multifunctional cellulose-based device for the continuous culture of animal cells and tissues. A multilayered system of modified BC (hydrophobized and electroconductive) was used to assemble the skin-on-chip, a microfluidic platform, using the lab-on-paper technology intended to mimic vascularization, with controlled flow, to introduce external stimuli, such as electrical or mechanical, and to support multicellular growth.

This chip serves a multifactorial purpose, aiming the control of each part that make up the overall complex 3D system, including dynamic control of physical, chemical and gaseous gradients, ensure mimetic vascularization, introduce favourable stimuli and co-culture of skin cells. This model sustains cell growth and allow real time and in a high throughput manner to assess cellular phenomena, such as cell-cell crosstalk, paracrine factor exchange, ECM production, as well as tissue homeostasis in the presence of chemical, mechanical, electrical and biological stimuli, and also kinetics of substance delivery on/through the skin.

BC hydrophobization was achieved using a new strategy for the surface modification of BC through the combination of oxygen plasma deposition and silanization with trichloromethyl silane. The combined use of the two techniques modifies both the surface roughness and energy and therefore maximizes the hydrophobic effect obtained. These modified membranes were characterized by SEM, water contact angle measurements, FTIR-ATR and XPS, and its cytotoxic potential was investigated using both indirect and direct contact studies with cells. Importantly, this surface modification revealed no short-term cytotoxic effects on L929 and hDNFs cells. This material was used for the construction of a BC-based well plate for cell culture, which can be supplied continuously with culture medium in long term studies (ranging from days to weeks), using a two-layered 3D full-thickness skin equivalent consisting of an epidermal and a dermal tissue layer, cultivated in alginate scaffolds, that can be maintained and studied as a skin surrogate on the SkinChip [Maia et al, 2014].

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**REFERENCES**


**SB02.11.12**
**Investigation of Dental Pulp Stem Cells Differentiation Behaviors on Polybutadiene-Polystyrene Nanopattern Substrate**

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Understanding the triggers of stem cell differentiation furthers the field of tissue engineering and contributes to the applications for implantation and bioprinting. Substrate mechanics and topography effects have been widely studied as factors to trigger stem cell differentiation. In our previous studies, we have shown that monodispersed polybutadiene (PB) is able to form biocompatible thin film with adjustable substrate mechanics depending on film thickness, to which the cells can adhere without additional coatings. A threshold was determined at 2.3 MPa when large amounts of biomineralized deposits were observed after 28 days on substrates with mechanics higher than this value. [1] In this study, we explored the understanding and analyzing how dental pulp stem cells (DPSC) respond to both surface moduli and topography effects in nanoscale. In order to achieve this nanopattern, a mixture of Polybutadiene (PB) and Polystyrene (PS) was used in a 3 to 1 ratio for spin cast. Due to the repulsion between two polymers, phase separated nanopattern was created with mechanics and topography differences on different domains, where PB formed flat and soft film with rounded domain of hard PS forming spikes of ~ 100 nm height. DPSC were cultured onto this substrate and were monitored over 28 days. Through the analysis of the images from the confocal microscopy and SEM at first week, DPSC grew slower on pattern substrate compared to the cells cultured on the pure PB substrate. Furthermore, DPSC appeared to be skinny and elongated, seeming to avoid attaching the spikes of PS on pattern substrates. It suggests that DPSC preferred to attach on PB rather than on PS. The cell moduli were also tested at first week through Atomic Force Microscopy with SMFM mode, where we found three different groups of cell moduli instead of two different moduli for the substrates, indicating that DPSC behaved more complicated in response to external triggers. On day 28, biomineralization were observed by SEM and Raman microscopy, where we found fibers templated mineralized deposits on the substrates. RT-PCR was also performed to determine differentiation pathway with selected markers: Alkaline Phosphatase(ALP), Runt-related transcription factor(Runx), and late markers, Dentin Sialophosphoprotein(DSPP) and Osteocalcin(OCN).

This research explored the combination of substrate mechanics and topography effects for DPSC differentiation, which is important for applying printed scaffolds as dentin/tooth regenerative biomaterials, which surface is rough and the mechanics is not homogeneous.


**SB02.11.13**
**3D Patterning of Micro-Nano-Hydrogel Fibres towards Replicating Extracellular Matrix Cues for Tissue Assembly**

Elisabeth Gill, Yan Yan Shery Huang and Iek Man Lei; University of Cambridge, United Kingdom

The extracellular matrix (ECM) environment of tissues permits 3D cell growth in a complex fibrous protein architecture with delicate mechanical properties. Existing biomaterial fabrication techniques struggle to simultaneously attain: micro/nano-scale fibril feature resolution, low fibre stiffness and the 3D organisation crucially provided by the ECM without comprising cell motility. This work utilises 3D printing and low voltage electrospinning patterning synergistically to address these conflicting engineering challenges and act as a minimalist guide for self-directed 3D cell growth. Low voltage electrospinning patterning was adapted as a sequential process on a modified 3D printer. Applied voltage and 3D printed geometry can modulate the suspended behaviour of hydrogel fibres that span between 3D printed support pillars, a parametric study characterised threshold conditions and established a predictive model for patterning suspended fibres. Applications in 2D fibre patterning and 3D cell culture on suspended fibres were explored, including the creation of in vitro glomerulus membrane, and fibre guidance of glioblastoma cell aggregate outgrowth.
SB02.11.14
Internal Design and Fabrication of Tissue Scaffolds
Ozlem Yasar and Deldrys Gomez Reynoso; City University of New York, United States

In the field of tissue engineering, design and fabrication of precisely patterned, highly porous scaffolds/matrixes are required to guide overall shape of tissue growth and replacement. Although Rapid Prototyping fabrication techniques have been used to fabricate the scaffolds with desired design characteristics, controlling the interior architecture of the scaffolds has been a challenge due to CAD constrains. Moreover, large thick tissue scaffolds have reported limited success primarily due to the inability of cells to survive deep within the scaffold. Without access to adequate nutrients, cells placed deep within the tissue construct die out, leading to non-uniform tissue regeneration. This study aims to overcome these design and fabrication limitations. In this work, research has been expanded to design of scaffolds which have inbuilt micro scale fluidic networks. In this procedure, inbuilt channels serve as material delivery paths to provide oxygen and nutrients for the cells. First of all, negative of a cylindrical shape with a single channel was designed with AutoDesk Inventor and printed with a 3D printer to be used as a mold. Then, 3D printed mold was filled out with Poly(ethylene glycol) diacrylate (PEGDA) which is a photo-curable solution to fabricate the cylindrical hydrogel. Once PEGDA was exposed to UV light with the wavelength of 365nm, polymerization completed in about 3 minutes. After that, the same procedure was repeated for cylinders with two and three channels respectively. Then, their mechanical characterization tests were done to compare the compressive strengths of the scaffolds that has different internal architectures. Our preliminary results indicate that, 3D printing and polymerization techniques can be used together to control the interior architectures as well as the compressive strengths of scaffolds.

SB02.11.15
Production-Scale Fibronectin Nanofibers Promote Wound Closure and Tissue Repair in a Dermal Mouse Model
Christophe O. Chantre1,2, Patrick Campbell1, Holly Golecki1, Adrian Buganza3,4, Andrew Capulli1, Leila Deravi1,3,4, Stephanie Dauth1, Sean Sheehy1, Jeffrey Paten1, Karl Gledhill5, Yanne Doucet5, Hasan Abaci5, Jeffrey Ruberti4, Simon Hoerstrup2, Angela Christiano1 and Kevin Kit Parker1; 1Harvard University, United States; 2University of Zurich, Switzerland; 3Purdue University, United States; 4Northeastern University, United States; 5Columbia University, United States

Severe wounds result in the formation of stiff and fibrotic scars. During embryogenesis, fetal wounds have however the capacity to restore skin tissues to their native scarless configuration. Although the underlying mechanisms of this process are still incompletely understood, several spatiotemporal differences have been observed in fetal and postnatal wounds that provide unique insight for regenerative scaffolds design. Biomaterials that attempt to recapitulate the biophysical and biochemical properties of fetal skin have accordingly emerged as promising pro-regenerative strategies. The extracellular matrix (ECM) protein fibronectin (Fn) in particular is believed to play a crucial role in directing this regenerative phenotype. Accordingly, Fn has been implicated in numerous wound healing studies, yet remains untested in its fibrillar conformation as found in fetal skin. Here, we show that high extensional and shear strain rates in a nanofiber manufacturing system, termed rotary jet spinning (RJS), can drive high throughput Fn fibrillogenesis, thus producing fibrous scaffolds that are used to promote wound healing. Förster resonance energy transfer first confirmed the fibrillar conformation of Fn attained using RJS. Next, when tested on a full-thickness wound mouse model, Fn nanofiber dressings not only accelerated wound closure, but also improved tissue restoration, recovering dermal and epidermal structures and promoting regeneration of skin appendages and adipose tissue. Together, these results suggest that bioprotein nanofiber fabrication via RJS could set a new paradigm for enhancing wound healing and may thus find use in a variety of regenerative medicine applications.

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SB02.11.16
Muscle Tissue Engineering in Fibrous Gelatin—Implications for Meat Analogs Luke A. MacQueen, Charles Alver, Christophe O. Chantre, Seungkuk Ahn, Luca Cera, Grant Gonzalez, Blakely O'Connor, Daniel Drennan, Michael Peters, Sarah Motta, John F. Zimmerman and Kevin Kit Parker; Harvard University, United States

Bioprocessing applications that derive meat products from animal cell cultures require food-safe culture substrates that support volumetric expansion and maturation of adherent muscle cells. This is important, because meat consists of muscle, fat, and connective tissues proportioned according to tissue source, each containing a diverse array of nutrients produced by constituent cells. Cell types composing meat can be cultured in vitro but production scale-up is limited by the anchorage dependence of these cells, which require attachment to culture substrates for survival, proliferation, and maturation. This requirement is especially stringent for muscle maturation, where alignment of densely packed muscle fibers is observed. For this reason, controlling cell phenotypes in volumetric cultures is a key challenge for adherent cell bioprocessing, including emerging strategies for meat production. Here we demonstrate scalable production of microfibrous gelatin that supports cultured adherent muscle cells derived from cow and rabbit. As gelatin is a natural component of meat, resulting from collagen denaturation during processing and cooking, our extruded gelatin microfibers recapitulated structural and biochemical features of natural muscle tissues. Using immersion rotary jet spinning, a dry-jet wet-spinning process, we produced gelatin fibers at high rates and, depending on process conditions, we tuned fiber diameters to values comparable to natural collagen fibers. To inhibit fiber degradation during cell culture, we crosslinked them either chemically or by co-spinning gelatin with a microbial crosslinking enzyme. To produce meat analogs, we cultured bovine aortic smooth muscle cells and rabbit skeletal muscle myoblasts in gelatin fiber scaffolds, then used immunohistochemical staining to verify that both cell types attached to gelatin fibers and proliferated in scaffold volumes. Short-length gelatin fibers promoted cell aggregation, whereas long fibers promoted aligned muscle tissue formation. Histology, scanning electron microscopy, and mechanical testing demonstrated that cultured muscle lacked the mature contractile architecture observed in natural muscle but recapitulated some of the structural and mechanical features measured in meat products. Our results demonstrated that gelatin fibers provide a suitable scaffold to study muscle cell aggregation or formation of 3D aligned tissues. The general nature of cell adhesion to gelatin, and its recognition as a safe edible material, suggest these scaffolds can support a variety of adherent cell types with utility for food bioprocessing. With further research and development, we believe that muscle bioprocessing and tissue engineering will play increasingly important roles in food science.

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SB02.11.17

A Tissue-Engineered Scale Model of the Heart Ventricle Luke A. MacQueen1,1, Sean Sheehy1,1, Christophe O. Chantre1,1, John F. Zimmerman1,1, Francesco Pasqualini1,1, Xujie Liu2, Josue Goss1,1, Patrick Campbell1,1, Grant Gonzalez1,1, Sung-Jin Park1,1, Andrew Capulli1,1, John Ferrier1,1, Turgut Fettah Kosar1, Lakshminarayanan Mahadevan1,1,1, William Pu3,1 and Kevin Kit Parker1,1,1; 1Harvard University, United States; 2Boston Children’s Hospital, United States

Laboratory studies of the heart use cell and tissue cultures to dissect heart function yet rely on animal models to measure pressure and volume dynamics. Here, we report tissue-engineered scale models of the human left ventricle, made of nanofibrous scaffolds that promote native-like anisotropic myocardial tissue genesis and chamber-level contractile function. Inspired by the fibrous extra-cellular matrix of myocardial heart muscle, we produced ellipsoidal 3D ventricle chambers based on blended polycaprolactone (PCL):gelatin fibers with average fiber diameter ~500 nm and circumferential fiber alignment achieved by collecting fibers on a rotating mandrel. Ventricle scaffold porosity enabled cardiomyocyte infiltration and fiber alignment controlled cardiomyocyte shape and tissue alignment. Incorporating neonatal rat ventricular myocytes or cardiomyocytes derived from human induced pluripotent stem cells, the tissue-engineered ventricles had a diastolic chamber volume of 0.5 mL (comparable to that of the native rat ventricle and approximately 1/250 the size of the human ventricle). We measured tissue coverage and alignment, calcium-transient propagation, and pressure-volume loops in the presence or absence of test compounds. Proof-of-concept structural arrhythmia disease modelling demonstrated that stable, pinned spiral waves could be generated by inflicting geometrically controlled injuries. Moreover, we describe a bioreactor for modular assembly of tissue engineered ventricles with optional valves and ventricular assist, providing a path towards inline automated experiments. The model ventricles can be evaluated with the same assays used in animal models and in
clinical settings, suggesting future use in pre-clinical cardiology where patient-derived models are preferred to animal models.

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SESSION SB02.12: Biomolecular Computation and Design
Session Chairs: Polina Anikeeva, Ritchie Chen and Siyuan Rao
Thursday Morning, December 5, 2019
Hynes, Level 2, Room 200

8:30 AM SB02.12.01
Rational Design of Twisted DNA Nanostructures through Mechanical Perturbation Programming YoungJoo Kim, Chanseok Lee, Jae Young Lee and Do-Nyun Kim; Seoul National University, Korea (the Republic of)

Through self-assembly of multiple DNA strands with rationally programmed sequences, DNA nanotechnology enabled us to construct various two- or three-dimensional structures at nanoscale with intricate structural shapes such as bending and twist [1, 2]. These structural features have proved their utility in broad fields including optical metamaterials [3], liposome synthesis [4], drug delivery [5], and synthesis of chiral colloidal liquid crystal [6]. The structural features could be achieved by applying engineered mechanical perturbations induced by geometrical mismatches neighboring helices at inter-helix junctions [2]. Contrary to well-developed techniques for curvature control, however, the resolution of twist rate still remains unsatisfactory lagging the development of optimized twisted structures for target functionality.

Here, we present a mechanical perturbation programming approach for fine control of twisted DNA origami nanostructures [7]. To this end, first, we program mechanical perturbation distributions through just determining the location of inserted or deleted base-pairs. This method can make different twist rates without change in the number of insertion or deletion used. For demonstration, a fine adjustment of twist angle in six-helix bundle was achieved with mean increment of 1.77 degree per a 21-base-pair-long unit block. Also, we found that different twist mechanism occurred depending on engineered mechanical perturbation through molecular dynamic simulations. Second, we locally relaxed the strain energy due to mechanical perturbations by introducing short unpaired nucleotides, which can broaden the range of achievable twist rate varying their length or density.

Our approach is expected to contribute to expanding design space of DNA nanostructures with high structural accuracy and accelerating utilization of various benefits derived from structural twist into the DNA nanostructures. Employing our method, for example, one can design plasmonic nanostructures with tailored optical response or macroscopic soft materials with controlled structural and physical properties and resolve unintended distortions of hierarchically assembled DNA nanostructures.

Acknowledgement
This work was supported by the National Research Foundation of Korea (NRF) grand funded by the Korea
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References

**8:45 AM SB02.12.02**

**VSEPRnet—Structure-Based Encoding of Biomolecules for Functionality Prediction**

Siddharth S. Rath¹,¹,¹, Jonathan Francis-Landau¹,¹, Ximing Lu¹,¹, Roman Gutin¹,¹, Jacob Rodriguez¹,¹, Oliver Nakano-Baker¹,¹, Burak B. Ustundag¹,² and Mehmet Sarikaya¹,¹,¹; ¹University of Washington, United States; ²Istanbul Teknik Universitesi, Turkey

Predictively designing peptides for executing materials science and technology relevant functionalities offers great potential to custom design materials systems with desired physicochemical properties at ambient conditions. While the functionality displayed by the biomolecules, such as peptides and proteins, are dependent on their conformation, traditional bioinformatics tools have largely used sequences of letters and implicit assumption of their physicochemical and structural features. Although heuristically interpretable, upon utilizing letter-based encodings in machine learning algorithms for predictively designing functional sequences for engineering applications, implicit physicochemical and structural features are unseen by the data-driven machine agents. Furthermore, transferring learned models from sequence-based molecules to non-sequence based conjugated biomolecules such as peptidolipids, peptidoglycans, peptide-nucleic acids, and even simple sugars and small molecules becomes impossible. Here we explore and demonstrate structure-based encodings inspired from valence shell electron pair repulsion structures (*VSEPR*), functional groups, and signal-processing to train machine learning algorithms that learn latent features which are transferable to other biomolecules of interest. Our results demonstrate clear progress over state-of-the-art similarity matrix approaches, as well as convolutional neural network approaches which are based on strings of letters. Fingerprints developed herein are peptide length invariant and are generalizable to heterogeneous molecules. We demonstrate the capabilities of VSEPRnet in predicting peptide-epitopes as well as peptidolipids binding to major histocompatibility proteins as well as solid binding peptides with binding and surface assembly characteristics. Such models will be applicable in predictively designing drugs, antimicrobial coatings, chimeric constructs and for sensing applications in disease diagnostics. The research is supported by NSF-DMREF program through the grant DMR-1629071 as part of the Materials Genome Initiative.

**9:00 AM *SB02.12.03***

**Structural DNA Nanotechnology—A Foundation for Programmable Biological Materials**

Eike-Christian Wamhoff, Remi Veneziano, Hyungmin Jun, Tyson Moyer, Sakul Ratanalert, Xiao Wang, Matthew Stone, Darrell J. Irvine and Mark Bathe; Massachusetts Institute of Technology, United States

Structural DNA nanotechnology is the only synthetic materials paradigm that offers the ability to position molecules in nearly arbitrary 3D spatial patterns on the 1 to 100 nanometer scale. While the basic rules for this synthetic materials paradigm have largely been in place for over a decade, only now are computational and synthetic procedures reaching a tipping point at which broad adoption of this materials paradigm by the biological and materials science communities is enabled. For this reason, the next decade should witness an increasing number of researchers engaged in the application of this technology to explore its unique potential in diverse scientific domains. Here, I will begin by presenting advanced computational procedures that now offer the fully automated, top-down geometric design of nearly arbitrary 2D and 3D nanoscale assemblies using DNA. I will also review single-stranded DNA synthesis strategies needed to produce the raw material needed for the fabrication of programmed DNA assemblies, including bacterial, enzymatic, and solid-state approaches. I will then present the application of structural DNA nanotechnology to control the spatial organization of HIV antigens that reveals fundamental aspects of immune cell activation, with potential implications for novel vaccine development.

**9:30 AM SB02.12.04**
DNA nanotechnology allows to create programmable and precisely controlled molecular and nanoscale architectures due to the specific Watson-Crick base-pairing and molecular plasticity. In particular, the superior control over DNA origami structures has opened new venues for biomedical applications such as biosensing and drug delivery. However, protecting the integrity of DNA origami structures in complex biological fluids has remained a major challenge. Here, we demonstrate that hybrid peptoids can decorate 3D DNA origamis and provide an effective protection under different ionic and bio-active conditions. We have investigated two types of hybrid peptoid architectures, “brush” and “block” that were built from positively-charged moieties and oligo-ethylene glycol. We find that the brush-like peptoid design exhibits the best protection of DNA origamis against the damaging factors. Our detailed simulation study reveals the crucial role of electrostatic interaction between peptoids and the DNA backbone for the observed protection effect. Moreover, our systematic study shows that the interactions depend on the peptoid sequence, and that the oligo-ethylene glycol motifs contribute to the rigidity of the duplex DNA. Thus, the architecture of these hybrid peptoids can be optimized for desirable “coating” of DNA origamis. We have applied the developed strategy for creating peptoid-coated origamis that reduce a release of anti-cancer drug, doxorubicin and slow down trypsin digestion of proteins encapsulated in the nanostructure. As a proof of concept, we further show that alkyne-modified peptoids can be conjugated with fluorophores and antibodies. This new approach offers a functional and physiologically stable DNA origami-based for targeted biomedical applications.

Keywords: DNA nanostructure, DNA origami, peptoid, electrostatic interaction, molecular protection, molecular coating, drug release

9:45 AM SB02.12.05
Self-Assembled Hybrid Peptide-DNA and Protein-DNA Nanostructures Nicholas Stephanopoulos; Arizona State University, United States

The ultimate goal of nanotechnology is to build structures on the 10-100 nm length scale, with control of matter down to the atomic level. In recent years, DNA has emerged as a powerful molecular building block for the construction of nanostructure materials due to the specificity of Watson-Crick pairing. However, DNA nanostructures are limited by the physical and chemical properties of oligonucleotides, which can be a hindrance for biological applications, or for attaining higher resolution placement of synthetic functionality. Proteins and peptides, by contrast, are the natural “language” of biology, possess a greater diversity of chemical groups, and can position materials sub-nanometer precision. In this work, we present the novel integration of two self-assembling polypeptide motifs with DNA nanostructures: 1) the coiled-coil, and 2) hetero-trimeric proteins. We have synthesized peptide-and protein-DNA conjugates with high site-specificity, allowing us to integrate these components with self-assembled DNA structures with high precision. DNA tiles, wireframe cages, and DNA origami were modified in specific locations with one of two heterodimeric coiled coil peptides that bind with sub-nanomolar affinity. The coiled coil interaction drove the hierarchical assembly of these components into dimers and one-dimensional nanofibers, providing an orthogonal assembly “code” to DNA hybridization. In addition, we will demonstrate the assembly of hierarchically-ordered 3D cages comprised of trimeric protein vertices with tunable DNA arms linking them. These materials are the first to our knowledge to integrate synthetic, self-assembling peptide/protein-DNA hybrids with well-established DNA motifs, and demonstrate the potential of protein-DNA nanotechnology.
candidates are solid-binding peptides selected for specific inorganic solids by directed evolution techniques. Specifically, these dodecapeptides have been shown to spontaneously form long-range ordered assemblies on two-dimensional solid surfaces, such as graphene. The conformation of the solid-binding peptide is dynamic in solution and depends on the solution conditions, such as pH, temperature, and salt concentration. As self-assembly of biomolecules relies heavily on the molecular conformation of the monomer, we show that it is possible to direct the formation of the equilibrium assembly structure by controlling the labile nature of the peptides in solution via environmental preconditioning. This environmental selection process entails the molecular tailoring of the aqueous peptides’ conformational states towards specific assembly structures at the solid interface. Based on structural kinetic analyses, molecular dynamics simulations and a scanning probe energetic analysis (dubbed Intrinsic Friction Analysis), our results demonstrate that (i) peptide-graphite binding can be tailored via thermal selection of specific conformational states and that the same binding state can be reached for even altered amino-acid sequences, and, (ii) the resulting assembly structure is specific to the most prominent peptide solution conformations. That the thermally selected solution conformation persists upon adsorption will be illustrated with a rational redesigned peptide sequence. Based on these findings, environmental processing of biomolecules may allow for the bottom-up fabrication of active bio-nano interfaces for multifarious applications from bioelectronic devices, biosensors, biomolecular fuel cells, to logic switches. The research was supported by NSF-DMREF program through the grant DMR-1629071 as part of the Materials Genome Initiative.

10:45 AM SB02.12.07 Sugar-Derived poly(D-glucose carbonate)s Block Copolymer Solution Assembly for Functional Nanostructures Jee Young Lee1, Daniel Beltran-Vellegas1, Yue Song2, Karen L. Wooley2, Arthi Jayaraman1 and Darrin J. Pochan1; 1University of Delaware, United States; 2Texas A&M University, United States

Designing the new sugar-derived poly(D-glucose carbonate)s (PGC) is motivated by a need to develop sustainable materials in response to a long-term environmental impact of traditional petroleum-based polymers. A recent work on the self-assembly of glucose-based molecules demonstrates they can assemble into various nanostructures including micelles, nanofibers and vesicles with tunable size and surface charge. Motivated by their potential for building blocks for functional nanostructures, in this work, PGC amphiphilic block copolymers (BCP) with targeted block compositions, chain lengths and side chain chemistries (cationic and anionic) are synthesized by organocatalyzed ROP and assembled into various nanostructures for an in-depth characterization. Their assembly behavior in water is investigated by developing CREASE, an algorithm that reverse-engineers assembled micelle structures based on calculated micelle features (e.g., aggregation number, core size, corona chain structure) from the experimental small-angle neutron scattering (SANS) intensity profile. We further explore the assembly behavior of PGCs using a range of solvent environment (e.g., solvent compositions and pH variation). We find that the PGC BCPs display a unique chain packing that is dependent on the degree of side chain ionization and can transition from micellar to fibrous nanostructures. These findings allow us to discover a variety of robust nanostructures that can be achieved by non-traditional polymers and their potential to be used in various scientific disciplines.

11:00 AM SB02.12.08 Peptide Materials Design via a Hybrid Computational Approach Srinivas Mushnoori, Kassandra Schmidt, Ethan Zang and Meenakshi Dutt; Rutgers, The State University of New Jersey, United States

The area of peptide-based materials has seen a recent surge in interest due to its wide range of potential applications including targeted drug delivery, cancer treatment, tissue engineering, nanoelectronics and batteries. The 20 amino acids, the building blocks of peptides, yields an enormous molecular parameter space which can be used to design peptides with a wide variety of sequences. A fundamental understanding of the impact of peptide sequence on the structure-activity relation of these biological materials will accelerate their development and use, thereby advancing diverse disciplines. We use a hybrid computational approach, which integrates molecular simulations with analytical techniques, advanced sampling and computing tools, to study and develop new biological materials with desired sequence-structure-activity properties in a more time- and cost-efficient way. The biological materials are formed via the self-assembly of amphiphilic ultrashort peptides encompassing aromatic amino acids (namely, diphenylalanine and phenylalanine-asparagine-phenylalanine). The extended spatiotemporal scales connecting molecules to materials is addressed via the use of coarse-grained representations of the molecular species (S. Mushnoori, et al Organic & Biomolecular Chemistry 2018, 16, 2499). The dynamics underlying the self-assembly of these peptides is resolved via the classical Molecular Dynamics simulation method.
11:15 AM SB02.12.09  
**Self-Assembly of Single Random Heteropolymers** Shayna Hilburg and Alfredo Alexander-Katz; Massachusetts Institute of Technology, United States

With inspiration from proteins, we investigate synthetic random heteropolymers through molecular dynamics simulations. We explore the behavior of single macromolecular chains and can relate the impact that monomeric chemistry and sequence have on their morphologies to protein folding. Examination of globule formation and the resulting conformations illuminate how the chains may interact and enable random heteropolymer multifunctionality which has been experimentally shown. By emulating the heterogeneity seen on the surfaces of some biological proteins, hydrophobic and hydrophilic polymer segments create a rich energy landscape, allowing for a variety of dynamic conformations and enabling its unique behavior.

11:30 AM SB02.12.10  
**Coarse-Grained Model of DNA Translocation in Nano-Fluidic Channels** Giovanna Bucci¹,², Karim Gadelrab¹, Christopher Johnson¹ and Alfredo Alexander-Katz²; ¹Bosch Research Center, United States; ²Massachusetts Institute of Technology, United States

There is great potential for genome sequencing to enhance patient care through improved diagnostic sensitivity and more precise therapeutic targeting [1]. To maximize this potential, DNA-sequencing technologies need to be optimized and adapted to clinical requirements. Nano-channel analysis is one of the emerging strategies for non-optical DNA sequencing [2-5]. Each constituent nucleobase is identified via measuring the transverse tunneling current as a single DNA molecule approaches measuring electrodes. Accuracy and throughput are still limited by insufficient control over DNA elongation and transport dynamics. We employ a coarse-grained molecular model, as a robust framework for the simulation of biopolymer dynamics. Our computational model serves as an essential tool for the optimal design of nano-channel platforms offering high-resolution DNA analysis.

The model implementation is targeted towards predicting the degree of linearization of confined DNA molecules, and simulating the DNA uncoiling and entering the nano-channel. Nano-confinement opens the possibility of linearizing much longer DNA molecules that is currently possible. To uniformly stretch DNA chains, the dimensions of nano-fluidic structures should be smaller than the persistence length. (e.g, about 50nm for double stranded DNA in dilute solutions) [6, 7]. Channel size reduction introduces added challenges of DNA loading and fabrication cost. Mediated by channel characteristics and buffer concentration we investigate strategies of micro- and nano-confinement to improve DNA stretching.

In addition to the geometric aspects of sequencing DNA under confinement, controlling DNA electrophoresis is essential to acquiring a clear signal from the sensing device. The frequency of DNA treading can be increased by applying larger voltages. However, this approach can result in DNA transport velocity exceeding the sensor’s sampling rate. Our multiscale approach, combining continuum and coarse-grained models, is informative of the driving forces interplay at various scales. This allows for new design concepts to be numerically studied for feasibility. One strategy to facilitate the transition from a high to a low entropy state consists of introducing structures that provide multiple pathways of increasing confinement for the DNA to unravel [8]. Our systematic study reveals how to design the geometry and applied bias to realize shallow free energy paths for the loading of DNA molecules.

**References:**


11:45 AM SB02.12.11
Self-Assembly of Synthetic Collagen and Silk Bio-Composite System for Biomaterial Applications—A Molecular Modeling Investigation

Atul Rawal¹², Kristen L. Rhinehardt¹² and Ram V. Mohan¹²; ¹North Carolina Agricultural & Technical State University, United States; ²Joint School of Nanoscience & Nanoengineering, United States

Bio-composite materials with optimal mechanical and structural properties and capability of cell differentiation are crucial for tissue engineering. Synthetic collagen proteins with lengths of approximately 10 nanometers, along with natural spider silk proteins provide an opportunity for development of an optimal biomaterial for scaffolding applications in tissue engineering. This combines unique mechanical, structural and biological properties of two of the nature’s best polymer proteins. In the present work, we study the binding capability of these proteins at a molecular level via molecular dynamics modeling. Spider silk and synthetic collagen protein molecular models in biophysical saline conditions under standard pressure and temperature are investigated to understand if natural binding occurs between the two without any other external factors. An initial minimum separation of 10 angstroms between the proteins was used. Binding was observed between the two proteins throughout the dynamic simulation. Molecular dynamics simulations are performed for a minimum of 100 nanoseconds for all systems. The radius of gyration and minimum distance between the proteins shows a decreasing separation between the two proteins until a stable distance of 2.5 nanometers and 0.2 nanometers respectively, is achieved. Binding is further identified by binding observed between the proteins via formation of strong and stable hydrogen bonds. A hydrogen bond between collagen Proline-31 and silk Serine-96 was observed to be the most stable and frequent bond between the single collagen and silk system. Results clearly indicate a self assembly behaviour of these two systems illustrating their potential as a biomaterial for tissue engineering.

SESSION SB02.13: Antimicrobial Peptides and Materials
Session Chairs: Polina Anikeeva, Yoonkey Nam and Siyuan Rao
Thursday Afternoon, December 5, 2019
Hynes, Level 2, Room 200

1:45 PM SB02.13.01
A Series of New Bio-Based Antimicrobial Materials—Poly (3-hydroxybutyric acid) Oligomer and Its Homologues

Ziheng Zhang¹, Jun Li¹, Linlin Ma¹, Xingxing Yang², Bin Fei¹, Polly Leung¹ and Xiaoming Tao¹; ¹Hong Kong Polytechnic University, Hong Kong; ²Hong Kong University, Hong Kong

Bio-based and biocompatible antimicrobial materials have many advantages in term of environmental protection and sustainable development, comparing to common inorganic and organic antimicrobial materials. It has been found previously that fabrics made from bio-based PLA/PHBV blend filament fibers exhibit broad-spectrum bactericidal effects, with no addition of any antimicrobial agents. After extracting and analyzing the antibacterial components, here we first discover that Poly (3-hydroxybutyric acid) (PHB) oligomers with several degrees of polymerization have potent antibacterial and antifungal properties.

Subsequently, two preparation methods for PHB oligomers are described as extraction from biologically fermented PHB polymers and one-step ring-opening polymerization of β-butyrolactone. The topological application of the synthesized PHB oligomer imparts perdurable antibacterial properties to the non-antibacterial fabric.

Furthermore, to test its potential in medical applications, skin sensitization and infected wounds cure of the mice treated with PHB oligomer were observed. The antimicrobial mechanism of the synthesized PHB was revealed as the leakage of intracellular content, inhibition of protein activity and the change of transmembrane potential.

Finally, the antibacterial properties of homologues of PHB oligomer, including polylactic acid (PLA) oligomer and polyglycolic acid (PGA) oligomer, were also discovered incidentally, which has brought a wider map for the exploration of antibacterial materials.
Antibacterial Zinc Oxide—Morphology and Enzyme-Mimicking Activities
Tao Yang1, Alexander N. Zelikin2 and Rona Chandrawati1; 1The University of New South Wales, Australia; 2Aarhus University, Denmark

Zinc oxide (ZnO) particles possess unique semiconductive, photocatalytic, and antimicrobial properties and they have found widespread applications in drug delivery, tissue engineering, and bioimaging. Morphology plays a major role in modulating the properties and activities of ZnO particles; however, gap in knowledge exists in evaluating the effect of capping agents on ZnO growth kinetics. In this contribution, we reported a facile water-based chemical precipitation method to prepare ZnO particles with distinct architectures (i.e. ZnO bowties, flowers, and nests) using zinc nitrate, urea, and polyvinylpyrrolidone (PVP) as building blocks [1]. Our detailed studies uncovered that the preferential adsorption of PVP onto different ZnO facets at different polymer concentration controlled the growth directions of ZnO and hence resulted in varied ZnO morphologies. Serendipitously, we discovered that ZnO particles have enzyme-like activities and demonstrated their ability to decompose exogenous and endogenous prodrugs to produce NO at physiological condition (pH 7.4, 37 °C). We also showed that physiologically relevant NO levels can be realized by varying the concentration of ZnO or NO prodrugs. In addition, we observed that ZnO particles preserved their catalytic capacity even after 6 months when suspended in PBS, which is beneficial for long-term biological applications. NO is a versatile player that participates in nearly every physiological system, such as cardiovascular, immune, central nervous system, and outflow physiology. However, the short half-life of NO in human tissues (approx. 5 s) and its limited diffusion radius (40-200 µm) have hampered the full potential of this molecule [2]. Our findings overcome the aforementioned challenges of NO delivery via utilizing an endogenous NO donor (GSNO) and an enzyme mimic (ZnO). Based on the infinite nature of endogenous NO precursors, NO delivery is therefore “limitless”, and NO can be generated throughout the lifetime of the enzyme mimic.

References

Bioinspired Design of Redox-Active Peptide-Based Antibacterial Gels to Prevent Implant-Related Infections
Galit Fichman and Joel Schneider; NCI/NIH, United States

Infection of medical implants is a serious ongoing problem worldwide, caused by bacterial adhesion and subsequent biofilm formation on the implant interface. To prevent such infection, we designed a set of catechol-functionalized cationic peptide antibacterial hydrogels that were inspired by the lysine- and DOPA-rich mussel foot protein-5. These advanced supramolecular gels are designed to coat implants providing a barrier to surface colonization and can also be injected during surgery directly to the tissue implantation site to inhibit surgical site infection. Furthermore, utilizing the gels lysine rich amino acid composition and the redox-activity of catecholic residues, these gels kill bacteria by two distinctive mechanisms: via a direct contact mechanism between the polycationic gel and the bacterial cell surface and by DOPA-mediated production of hydrogen peroxide (H₂O₂), a known antibacterial agent. We demonstrated that these gels exhibit high bactericidal activity against clinically isolated gram-positive bacteria, including the notorious multidrug resistant bacteria, MRSA. We further showed how amino acid composition and peptide sequence can modify the amount of generated H₂O₂, and consequently alter the antibacterial activity of the gel. Moreover, we characterized the ability of the gels to act as adhesives at the implant-tissue interface by utilizing lap-shear tensile strain tests. Collectively, these results indicate that DOPA-containing hydrogels hold promise as antibacterial adhesives, suitable for implantation at the tissue-implant interface.
Effect of Surface Polarity and Charge on the Adsorption of Amphiphilic Antimicrobial Peptide Self-Assembled Nanofibrils

Zhou Ye, Alexandra Kobe, Ting Sang and Conrado Aparicio; University of Minnesota, United States

Antimicrobial peptides are promising substitutes for conventional antibiotics with increasing bacterial resistance. Our previous work studied the relationship between self-assembly and antimicrobial activity using a designer peptide derived from a human salivary protein. This 13-amino acid amphiphilic and cationic peptide, named GL13K, can self-assemble to supramolecular nanofibrils in alkaline solutions. In our previous work, the coating of GL13K nanofibrils onto biomedical devices (e.g., Ti implant) and natural tissues (e.g., dentin) modified the surface hydrophobicity and showed a long-lasting antimicrobial activity. The amount of adsorbed GL13K was highly dependent on the surface chemistry and solution conditions, which eventually affected the activity of the coating. For example, the etched Ti adsorbed a much higher amount of GL13K than untreated Ti; the adsorption of GL13K predominated in the mineral-rich region on dentin. Separating and quantifying the effects on peptide adsorption of substrate hydrophobicity, charge, polarity, and roughness is a difficult, but critical task to design and control coating manufacturing and (bio)functionality. We hypothesized that surface negative charge is the main property favoring adsorption of self-assembled GL13K peptides.

In this work, we used quartz crystal microbalance with dissipation monitoring (QCM-D) to study in situ adsorption of GL13K self-assembled nanofibrils. The surface chemistry was controlled by coating Au QCM-D sensors with self-assembled monolayers (SAMs) with different terminal groups, including –COOH, –NH2, and –CH3. The SAM-coated sensors with polar terminal groups (i.e., –COOH and –NH2) were more hydrophilic than the one with a nonpolar terminal group (i.e., –CH3). It was observed that a significantly higher amount of GL13K adsorbed on the sensor with –COOH terminal group compared to the one with –CH3. In the alkaline solution where GL13K self-assembled to nanofibrils, GL13K had negligible adsorption on the sensor with –NH2 terminal group because –NH2 was deprotonated. Notably, adsorption of GL13K was largely favored on the same sensor once it was protonated to –NH3+ in lower pH. Self-assembled nanofibrils were found on sensors with deprotonated –COO– and protonated –NH3+ by atomic force microscopy (AFM). This indicated that polarity, not charge, was the critical factor determining the adsorption of these amphiphilic peptide self-assembled nanofibrils. Thus, we rejected our initial hypothesis.

With a better understanding of the adsorption behavior of GL13K, it is easier to control the coating of antimicrobial peptides on natural tissues. As a proof of concept, hydroxyapatite, the main inorganic component in tooth and bone, was also coated on sensors. Since hydroxyapatite is a very polar and hydrophilic material, GL13K adsorbed extensively on the sensor surface observed by QCM-D and AFM. The findings in this study could lead to better designs of coating amphiphilic peptides with different functionalities on biomedical devices and natural tissues.

2:45 PM SB02.13.06
Sustained Delivery of Antimicrobial Metal Ions via Biodegradable Hollow Drug Delivery Vehicles

Eva Krakor, Isabel Gessner, Sven Santernik and Sanjay Mathur; University of Cologne, Germany

The discovery of penicillin in 1940 is one of the most important medical inventions in reducing human morbidity and mortality but the intensive use of all kinds of antibiotics since then has led to an increase in multi-drug resistant bacteria and shows the necessity for alternative treatment options against bacterial infections. Alternatively to antibiotics, the antimicrobial properties of metals have been used for thousands of years, e.g. vessels made of copper or silver for water disinfection and food preservation. In this work hollow mesoporous silica capsules (HMSC) were synthesized using a hard iron oxide template which was coated with a silica shell through cross-condensation reactions. Afterwards the iron oxide core was removed by acidic leaching. Metallic nanoparticles such as Cu and Ag were incorporated into HMSC through the reduction of their metal salts (Ag@HMSC and Cu@HMSC). The formation of as-prepared rattle-type metal-silica particles was proven by TEM as well as XPS and EDX measurements. To determine the controlled leaching of metal ions under physiological conditions at 37°C, free Ag and Cu ions were complexed with dithizon to allow for their visualization and quantification via UV-Vis analyses at 454 nm and 543 nm. Moreover, INT assays revealed that both particle types exhibit a strong antimicrobial effect against gram-positive (B. subtilis) as well as gram-negative bacteria (E. coli), demonstrating their promising potential as antibiotic alternative in the future.
SESSION SB03.01: Monitoring/Regulating Plant Physiology
Session Chairs: Eleni Stavrinidou and Michael Strano
Monday Morning, December 2, 2019
Hynes, Level 3, Room 305

8:30 AM *SB03.01.01
Nanomaterials Enable Delivery of Genetic Material without Transgenic DNA Integration in Mature Plants
Markita Landry; University of California, Berkeley, United States

Genetic engineering of plants is at the core of sustainability efforts, natural product synthesis, and agricultural crop engineering. The plant cell wall is a barrier that limits the ease and throughput with which exogenous biomolecules can be delivered to plants. Current delivery methods either suffer from host range limitations, low transformation efficiencies, tissue regenerability, tissue damage, or unavoidable DNA integration into the host genome. Here, we demonstrate efficient diffusion-based biomolecule delivery into tissues and organs of intact plants of several species with a suite of pristine and chemically-functionalized high aspect ratio nanomaterials. Efficient DNA delivery and strong protein expression without transgene integration is accomplished in mature *Nicotiana benthamiana*, *Eruca sativa* (arugula), *Triticum aestivum* (wheat) and *Gossypium hirsutum* (cotton) leaves and arugula protoplasts [1]. We also demonstrate a second nanoparticle-based strategy in which small interfering RNA (siRNA) is delivered to mature *Nicotiana benthamiana* leaves and effectively silence a gene with 95% efficiency. We find that nanomaterials both facilitate biomolecule transport into plant cells, while also protecting polynucleotides such as RNA from nuclease degradation. DNA origami nanostructures further enable siRNA delivery to plants at programmable nanostructure loci [2]. Our work provides a tool for species-independent, targeted, and passive delivery of genetic material, without transgene integration, into plant cells for diverse plant biotechnology applications.


9:00 AM SB03.01.02
Real-Time Detection of Wound-Induced \( \text{H}_2\text{O}_2 \) Signaling in Plants with Optical Nanosensors

Tedrick T. Salim Lew\(^1\), Volodymyr Koman\(^1\), Seonyeong Kwak\(^2\) and Michael Strano\(^1\); \(^1\)Massachusetts Institute of Technology, United States; \(^2\)Seoul National University, Korea (the Republic of)

As a consequence of their sessile nature, plants have developed complex signaling mechanisms to cope with the highly dynamic environment that they live in. In response to external stimuli, plants can utilize various signaling pathways for intercellular communication to engage different metabolic and genetic machineries involved in the plant defense system. Among the many signaling molecules recently uncovered, hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) represents one of the most versatile signaling molecule in plants in response to environmental stresses such as mechanical wounding. Here, we develop an optical nanosensor platform using DNA-wrapped single-walled carbon nanotubes (SWNT) to monitor the wound-induced \( \text{H}_2\text{O}_2 \) signaling pathway in plants. This approach enables non-destructive, real-time detection of changes in endogenous \( \text{H}_2\text{O}_2 \) level in plants at a remote distance with portable and inexpensive electronics. We demonstrate the versatility of this method to investigate the dynamics between \( \text{H}_2\text{O}_2 \) and electric signalling pathways in different vegetable crops and plant species. A mathematical model describing the self-propagating \( \text{H}_2\text{O}_2 \) wave mechanism will be presented. Our work provides a promising tool to elucidate the complex plant signaling pathways across species to aid botany research and agronomic applications.

9:15 AM SB03.01.03
A Smart Interface between a Light Sensitive Conjugated Polymer and Plant Cells

Gabriele Tullii\(^1\), Alex Costa\(^2\) and Maria Rosa Antognazza\(^1\); \(^1\)Istituto Italiano di Tecnologia, Italy; \(^2\)Università Statale di Milano, Italy

In latest years the use of smart materials and devices started to attract attention for modulating the growth and functions of plant systems. Very recently, devices based on organic conductors have been object of increasing interest, both as actuators and as sensors. Here, we explore the opportunity to establish a functional interplay between light sensitive, organic semiconductors and plant systems. We chose \emph{Arabidopsis thaliana} as a widely accepted plant model, and we study the effect of a work-horse photovoltaic conjugated polymer, polyhexyllithiophene, on guard cells physiology. Cell viability in presence of the conjugated polymer is evaluated. Effects of polymer optical excitation and cell metabolism are also preliminarily investigated and critically discussed.

9:30 AM SB03.01.04
Plant Membrane-on-a-Chip

Susan Daniel, Han-Yuan Liu and Martin Stuebler; Cornell Univ, United States

The plant cell is protected by a complex polysaccharide cell wall composed primarily of cellulose, hemicellulose and pectin. The cell wall is followed by a semi-permeable barrier, the plasma membrane (PM) that serves two main roles: (1) transport of essential molecules in and out of the cell, and (2) sensory transduction of environmental stimuli as well as adaption to external influences. Considerable progress has been made over the past two decades to understand plant membrane proteins from a genetic perspective, but complementary tools for physiological, electrophysiological, biochemical characterization, and for studying protein function are facing unmet demand. This work highlights a new cell-free platform capturing the properties of the plant PM. This platform consists of a supported proteo-lipid bilayer (SPLB) derived from the plant PM. The main advantage of this platform is the compatibility with state-of-the-art surface, bioelectronic, and biophysical characterization tools. We demonstrates three straightforward ways to obtain proteoliposomes, from plant protoplasts. Three different plants (\emph{Arabidopsis thaliana}, \emph{Nicotiana benthamiana} and \emph{Zea mays}) were successfully used for the formation of SPLBs. This plant based approach enables direct incorporation of transgenic membrane proteins into supported lipid bilayers without using detergents and reconstitution processes and provides a novel tool to isolate and study membrane properties, transport phenomena, membrane-proteins, and protein-lipid interactions. We illustrate here the single molecule tracking of plant membrane proteins using this platform. In the future, we anticipate that this platform will allow studies of the plant membrane characteristics that will enable design of the biotic/abiotic interfaces for new sensing applications that merge plant membranes with electro-active materials.

9:45 AM BREAK
**10:15 AM SB03.01.05**  
**Long-Term Plant Electrophysiology Using Vapor Printed Polymer Electrodes** Trisha L. Andrew, Jae Joon Kim and Linden Allison; University of Massachusetts Amherst, United States

We vapor print conformal conjugated polymer electrodes directly onto living plants and use these electrodes to probe the health of actively-growing specimens. The conducting polymer PEDOT can be deposited on the surface of living organisms without damaging their health and self-sustenance. A bioimpedance signal can be portably recorded using these vapor printed electrodes, which can reveal detailed information about the health of the organism. Notably, polymer electrodes can be created directly on living plants, meaning that bioimpedance measurements can be performed on-demand, throughout the growth cycle of a plant without being damaged by environmental conditions such as wind, water, temperature changes and UV exposure. Vapor-printed polymer electrodes, unlike their adhesive thin-film counterparts, do not delaminate from microtextured living surfaces as the organism matures and do not observably attenuate the natural growth pattern and self-sustenance of the plants investigated herein. In particular, deep tissue damage caused by UVA irradiation and Ozone exposure can be reliably detected noninvasively. Long-term plant health monitoring can find strategic use in food farming, crop management and biohazard signaling.

**10:30 AM SB03.01.06**  
**Hydroprinting of Liquid Alloy Circuits for Fragile Plants Organism Monitoring** Zhigang Wu¹, Jiajun Jiang¹, Shuo Zhang¹ and Bei Wang¹,²; ¹Huazhong University of Science and Technology, China; ²Uppsala University, Sweden

To precisely monitor the physiology state of plants, this work presents a gentle non-invasive method to transfer functional liquid alloy circuits on living fragile plants using a water-soluble sacrificial layer. This process can print functional electrical circuits in high fidelity on complex irregularity morphology without introducing any external interventions such as heat flow, pressure, acid or base. The data from the circuits on flowers demonstrates this technique is well suitable for monitoring such kind of scenarios.

Internet of things is emerging in sorts of situations, but the access of live plants is rarely studied. With the internet connecting, people could obtain the real-time health state and various behaviors of plants in the practical or stimulus environments. This can further lead to new customized strategies for crop management and even new approaches for botany research. Nevertheless, many of plant organisms, such as flowers and leaves, are fragile with irregular surface morphology, and their growth are easily affected by external constraints. These features make the integration of functional circuits challenging. Existing methods, such as smart patches, press-on buttons, 3D printing, roll-to-roll gravure, flexographic printing and vapor-printing, either impose external loads to the growing plants and hinder the normal growing process, or may easily harm the plants with external intervention during the complicated process.

In this work, a highly biocompatible polyvinyl alcohol (PVA) film was used as a substrate as well as an intermediate sacrificial layer to transfer the original 2-D liquid alloy (Galinstan) circuits to a vulnerable complex 3-D surface under water pressure. Firstly, the circuit was printed on a PVA film by masked deposition with a method developed by our group. Then the circuit with PVA was placed on water surface. When the PVA film was almost completely dissolved, it would become a PVA/water mixture with super flexibility, stretchability and stickiness. More importantly, this mixture could maintain the shape of circuit, which make the transferring process predictable and controllable. Concurrently, the plant organism was gradually immersed through the circuit with a given angle and immersing speed. Consequently, the liquid alloy circuit pattern was transferred and attached to the plant surface by water pressure and Van der Waals force. The whole process can be conducted in minutes, and there is no obviously interference on plants even after three months. To demonstrate the technique, the Galinstan circuits with resolution ~70 um was transferred on complex surfaces with prominent conformalbility, excellent electricity and repeatability. Further, water content sensors and LED circuits were fabricated on rose petals and bean sprouts by this technique. It was found that the measured results could precisely reflect the change of state in different water content, and the sensor could still work well even with an elongation of more than 200% during growth.

**10:45 AM *SB03.01.07**  
**Organic Bioelectronics to Record and Regulate Signaling and Physiology in Plants** Magnus Berggren, Daniel T. Simon and Eleni Stavrinidou; Linkoping University, Sweden

Organic bioelectronics is a unique platform of devices and materials that can serve as the actuator and recorder of signals at the technology-biology interface. In the e-Plant effort, we are exploring organic bioelectronics by
developing devices that can selectively trigger or sense targeted physiological functions and signaling cascades, at high spatiotemporal resolution. With tailor-made organic electronic ion pumps (OEIP), we have managed to deliver phytohormones to regulate the growth rate of the root hairs of Arabidopsis and to provoke the closure of stomata of Tobacco leaves. With PEDOT-based electrodes we have derived efficient bio-photovoltaic electrochemical cells. And, with organic electrochemical transistors (OECT), including immobilized enzymes, we can monitor sugar concentrations from plants in real time. In the future, this sensor-actuator technology promise for a self-powered plant-area network possible to use in plant biology experiments and also in agriculture.

SESSION SB03.02: Energy Harvesting
Session Chairs: Caroline Ajo-Franklin and Massimo Trotta
Monday Afternoon, December 2, 2019
Hynes, Level 3, Room 305

1:30 PM *SB03.02.01
A NanoBioengineering Approach to Developing Living Photovoltaics Ardemis Boghossian; Ecole polytechnique federale de Lausanne (EPFL), Switzerland

Despite their inspiration in improving synthetic photovoltaics, photosynthetic systems suffer from stabilities and efficiencies that limit their direct use in photovoltaics. While they benefit from autonomous repair and reproduction, photosynthetic systems contain light-harvesting machinery that is optimized for evolutionary purposes rather than photocurrent production. Herein we present bioengineered cyanobacteria capable of enhanced photocurrent production. We introduce genetically encoded exoelectronic pathways that serve as electron conduits for interfacing photosynthetic cells with nanomaterial scaffolds. These conduits further enable researchers to electronically rewire the cell metabolism and reprogram biological cells to perform as artificial electronic devices. The ability to improve photovoltaic performance through both nanomaterials engineering and synthetic biology unlocks new possibilities in achieving a viable technology.

2:00 PM SB03.02.02
Enhanced Extraction of Photosynthetic Electrons from Thylakoid-Electrosprayed SU-8 Micro-Pillar Electrodes SeonIl Kim, Yong Jae Kim, Hyeonaug Hong and WonHyoung Ryu; Yonsei University, Korea (the Republic of)

Photosynthetic bio-solar energy conversion using algae or plant cells has been extensively investigated for the last decades. Photosynthesis occurs in the thylakoid membranes (TMs) that contain photosynthetic apparatus such as photosystem I (PS I) and photosystem II (PS II). In photosynthesis, water molecules are split by PS II and high energy photosynthetic electrons (PEs) are generated. Direct extraction of these PEs without a mediator has been investigated over the last decade to maximize the PE currents. Since PEs are transported along TMs, enlarging contact area between TMs and an electrode is a way to enhance PE extraction. Previously, several approaches have been investigated to maximize contact area using various three-dimensional (3D) electrode designs such as multi-wall carbon nanotubes (MWCNTs) modified electrode, sintered AuNPs on screen printed electrode, indium tin oxide (ITO) modified electrode, or micro-pillar electrodes. Then, TMs were usually drop cast on such 3D structured electrodes. However, it is difficult to have uniform and conformal deposition of TMs over the 3D electrodes by the drop casting method. This often results in unreliable performance of the TM-coated electrodes in particular for electrodes larger than a few mm². In this work, we aimed to enhance extraction of PEs from TM-coated 3D micro-pillar electrodes by electrospraying. We fabricated Si micro-pillar (MP) arrays of aspect ratio (AR) of 1, 1.8 with 1um diameter from metal-assisted chemical etching (MAC-Etching). Then, SU-8 MP arrays of 1 cm² size were replicated from the Si MP array as a master mold. To improve adhesion with a metal layer, the SU-8 MP arrays were immersed in 10 mM of 4-aminothiophenol (ATP) ethanol solution overnight. Au layer was sputter-coated on the 4-ATP modified Si micro-pillar electrodes. Then, TMs were electrosprayed uniformly on the SU-8 MP array electrodes. The electrospraying solution contained 1 mg chl/ml of TMs, 3 mM of ammonium acetate, 10% (v/v) of ethanol as a surface tension reducing agent, and 3% (w/v) of sodium alginate as a viscosity modifier. The morphology of TMs, which were electrosprayed over SU-8 photo-anodes, was observed using confocal fluorescence microscopy and SEM to confirm their coating uniformity. TMs were electrosprayed for various spraying times of 0.5, 1, 2, 4 and 10
minutes in order to maximize extraction of PE currents. PE currents were measured using a three-electrode system, under 10 mW/cm² of halogen illumination and bias potential of 400mV vs. Ag/AgCl. The highest PE currents were measured at 4 minutes of TM-electrospraying time. The measured PE currents were 52, 79, and 109 nA/cm² for flat electrodes, MP electrodes with AR of 1, and AR of 1.8, respectively. It was demonstrated that electrosprayed TMs uniformly and conformally covered the entire electrode surface even for MP electrodes with high ARs. It was also shown that higher PE currents were measured from MP electrodes with higher AR values. This indicates larger contact between TMs and individual MPs were formed, resulting in enhanced direct electrochemical contacts.

2:15 PM *SB03.02.03
Biological Solar Cells Using Photosynthetic Machineries of Higher Plants and Cyanobacteria Ramaraja P. Ramasamy¹ and Randy Duran²; ¹University of Georgia, United States; ²NSF, United States

The light reactions of natural photosynthesis can be manipulated towards electricity generation in electrochemical devices called biological solar cells or photo-bioelectrochemical cells (PBEC) that resemble conventional fuel cells in principle without the requirement of a chemical fuel. The device uses a photo-bio anode and a enzymatic cathode that could convert light energy into electricity by photosynthesis assisted oxidation of water. The photosynthetic reactions occur in the thylakoid membrane and involve a complex set of redox reactions that result in the transfer of electrons between protein complexes. The electrons from the photosynthetic reactions can be channeled towards an external electrode for electricity generation by inhibiting the photosynthetic protein complexes in order to divert the flow of electrons towards to desired electron transport path within the photosynthetic membrane. Investigation using site-specific photosynthesis inhibitors revealed that the electrons generated through water oxidation reaction from photosystem II complex can be diverted to the external electrode for photocurrent generation primarily through the plastoquinone pool. Besides site specific inhibition, other approaches to increase photocurrent generation were investigated. One of those approaches is to engineer photosynthetic organisms such as *Synechococcus elongatus* PCC7942 with an outer membrane cytochrome (OmcS) derived from dissimilatory metal reducing bacteria which increase the photocurrent generation at an external electrode by two fold. This presentation will summarize some of our recent work on multiple different approaches to enhance photocurrent generation through an understanding of electron transport reactions in photosynthetic membranes.

2:45 PM SB03.02.04
Bioelectronic Composites from Self-Doped Conjugated Polyelectrolytes Samantha McCuskey, Yude Su and Guillermo Bazan; University of California, Santa Barbara, United States

Anaerobic bacteria routinely interface with abiotic electrodes to catalyze the interconversion of electrical and chemical energy. Integration of materials at the biotic/abiotic interface has improved electron transfer efficiency and cell adhesion, but charge injection/extraction is still largely restricted to the immediate proximity between bacteria and the external electrode. A three-dimensional organization whereby electronic contact extends beyond the confines of the electrode surface would be desirable. Here, we introduce bioelectronic composites comprised of the self-p-doped conjugated polyelectrolyte CPE-K and *Shewanella oneidensis* MR-1. These composites are simple to assemble and biocompatible. Furthermore, testing in three-electrode electrochemical cells show that the composites can generate ~200-fold greater biocurrent density than control *S. oneidensis* MR-1 biofilms. The impact of CPE-K concentration on bioelectronic composite performance will be discussed, along with an evaluation of electroactive surface area and charge transfer resistance.

3:00 PM BREAK

3:30 PM *SB03.02.05
Simple Circuitry for Microbial Extracellular Electron Transfer—Functional Characterization of Geobacter OmcZs Produced in E. coli Miyuki A. Thirumurthy and Anne K. Jones; Arizona State University, United States

Extracellular electron transfer, in which electrons are transferred from the metabolism of a microbe to an extracellular substrate is an intriguing process that may have applications in living electronics, bioremediation, chemical synthesis, sensing, and microbial fuel cells. Although a number of anode-respiring bacteria can exchange electrons with extracellular electrodes, many genetically tractable model microorganisms, especially those used in synthetic biological applications, cannot. Furthermore, the mechanisms by which microbes interact with
extracellular electrodes and the biological components required remain unclear. Among the hundreds of c-type cytochromes found in *Geobacter sulfurreducens*, OmcZs has been shown to have the largest impact on extracellular electron transfer to electrode surfaces. Herein, we overexpressed OmcZs in *E. coli* and defined its function in vitro. UV-vis absorption and florescence assays show that it can reduce riboflavin. Furthermore, electrochemical measurements show that *E. coli* cells expressing OmcZs are capable of extracellular electron transfer, a function not native to *E. coli*. The activity can be enhanced by inclusion of riboflavin in the experiment. Currents produced are comparable to other, more complex *E. coli* circuits reported by others. We conclude that OmcZs and riboflavin alone are sufficient to create a minimal, functional, synthetic pathway in *E. coli* for extracellular electron transfer.

4:00 PM SB03.02.06
**A Kinetic Model for Redox-Active Film Based Biophotoelectrodes**
Darren Buesen¹, Thomas Hoefer¹, Huijie Zhang¹,² and Nicolas Plumere¹; ¹Ruhr-Universität Bochum, Germany; ²University of Leeds, United Kingdom

Photoactive electrodes based on redox-active films are a promising approach to increasing the active area in which enzymes can be deposited and electrochemically accessed via mediated electron transfer. Beside this, these films are able to entrap the deposited enzyme. A great challenge to increase the efficiency arises from different charge recombination pathways, intrinsically connected to the process of the light-induced electron transfer chain from the electrode to the final solar fuel formation or to the charge carrier for electricity production [1]. Experimental investigation based on electrochemical methods and/or product quantification often have the disadvantage, that they cannot distinguish between the catalytic process and the detrimental effect of different short-circuiting processes. We present a general model constructed from diffusion and reaction processes describing redox-active film based biophotoelectrodes [2]. The model predicts the resulting photocurrent-time curve and distinguishes between the main catalytic process and the contribution of the two proposed short-circuiting pathways. It describes the corresponding time dependent concentration profiles of all involved species which can be analyzed to identify bottlenecks present in the solar fuel or photocurrent generation of a given system. The equations consist of dimensionless groups for a straightforward identification of possible limiting processes. The importance of the model for quantitative understanding of biophotovoltaic processes is highlighted with an example of simulation results predicting the effect of the diffusion coefficient of the charge carrier on photocurrent generation for different charge recombination kinetics.

References:

4:15 PM SB03.02.07
**Direct Functionalization of Plants by Smart Materials for Energy Harvesting in e-Plants**
Samia Zrig¹, Nathalie Bridonneau¹, Vincent Noël¹, Giorgio Mattana¹, Benoît Piro¹ and Eleni Stavrinidou²; ¹Université de Paris, France; ²Linköping University, Sweden

Biofuel cells are one of the most attractive power sources for implantable and microscale devices because of their biocompatibility and ability to operate at near neutral pH and ambient temperature. A typical enzymatic glucose biofuel cell comprises two enzyme-modified electrodes, with Glucose Oxidase (GOx) catalyzing glucose oxidation into gluconolactone at the anode, and Bilirubin Oxidase (BOD) catalyzing oxygen reduction at the cathode. For these enzymes to be recycled, specific redox mediators are necessary, to insure an efficient electron transfer between their active sites and the electrodes. During the process of photosynthesis, vegetal cells use energy from sunlight to convert carbon dioxide and water into glucose and oxygen, which could be both used in a glucose biofuel cell as fuel and oxidant, respectively. Our idea was therefore to integrate the energy harvesting system directly within the structure of a living plant. To achieve this, the direct functionalization of the vascular system containing the plants’ endogenous sugars and oxygen is necessary in order to operate the biofuel cell. The electrodes of such bio-hybrid systems should encompass conductive materials, enzymes and redox mediators.

Our approach is based on the growth of a conductive material (functionalized with enzymes and redox mediators) inside the vascular system of the plant, either through the roots or the leaves. The design, synthesis and characterization of such smart materials will be described and discussed.
We believe that the integration of energy harvesting and storage systems within the living plants could be a major breakthrough for energy applications.

Reference:
Stavrinidou E. et al. PNAS, 114, 2807-2812 (2017)

4:30 PM SB03.02.08
CNT Percolation Network in Thick Photosynthetic Composite Films for Enhanced Harvesting of Photosynthetic Electrons JaeHyounge Yun1, TaeYoep Kim2, Hyeonaug Hong1, Yong Jae Kim1, Yunjeong Park2, Kyunghoon Kim2 and WonHyounge Ryu1; 1Yonsei University, Korea (the Republic of); 2Sungkyunkwan University, Korea (the Republic of)

Photosynthesis produces high energy photosynthetic electrons (PEs) with internal quantum efficiency (IQE) of nearly 100%. Due to this high IQE, bioenergy harvesting using algal cells or photosynthetic organelles such as photosystems (PS I, II) and thylakoid membranes (TMs) has been studied extensively. In the absence of a mediator, the magnitude of harvested PE currents directly depends on an electrical contact between the photosynthetic organelles and an electrode. Thus, thicker deposition of the photosynthetic organelles on an electrode does not increase PE currents despite larger quantity of PEs generated from the thicker photosynthetic film. Even in the presence of a mediator, although a mediator can diffuse between a spot of PE generation and an electrode, PE transportation through the thicker film becomes more difficult.

In this study, we propose formation of electrical percolation networks for PE transport from the surface of the film to an electrode. Electrical percolation network was formed by mixing highly-conductive single-wall carbon nanotubes (CNTs) and thylakoid membranes (TMs). Since CNTs have no charge on the surface, we coated mussel-adhesive protein (MAP) on CNTs to have a positive surface potential due to the exposed amine groups of the MAP. The positive zeta potential resulted in well-dispersed CNTs in an aqueous solution. The exposed amine groups of MAP-CNTs also formed peptide bonds with the carboxyl groups of TMs such that CNTs and TMs were firmly connected. The percolation network in MAP-CNT/TM film was analyzed by cyclic voltammetry (CV), chronoamperometry (CA), electrical impedance spectroscopy (EIS), and linear sweep voltammetry (LSV). CNT percolation networks were achieved when the CNT weight was near 30% of the weight of chlorophyll a (Chl a) in the MAP-CNT/TM composites. Moreover, when the CNT weight was 50% of the weight of Chl a, the composites achieved the highest electrical conductivity without a mediator. Finally, when we increased the amount of TM deposition on an electrode, larger difference of PE current magnitudes was observed between the MAP-CNT/TM and TM-only films. The PE currents from the MAP-CNT/TM composite film became about 100 times larger at the Chl a concentration of 300 μg/cm².
built up smart supramolecular architectures combining multiple enzymes assembled with tailored linkers, which are able to perform manifold functions. Finally, we have explored approaches for integration of RC as the light-responsive material in bio-optoelectronic and electrochemical devices. In particular, we have developed protocols for addressing the RC on thin films of molecular or polymeric semiconductors deposited onto metal electrodes by covalent [6] or weak interactions. Biomimetic polymers, such as polydopamine, have been also investigated as efficient electronic interfaces of RC with electrodes in photoelectrochemical cells.

The lecture will discuss the logic behind designing and synthesizing materials for sunlight photoconversion and for light-triggered bioelectronics, by combination of tailored functional molecules with highly efficient bacterial photoenzymes optimized in billions of years of evolution.

References

9:00 AM SB03.03.02
Unravelling the Mechanism of In Vivo Polymerization of a Conjugated Oligomer in Plants Gwennaël R. Dufil, Daniela Parker, Eleni Stavrinidou and Magnus Berggren; Laboratory of Organic Electronics, Sweden

Plants convert radiant energy from the sun into carbohydrates being the primary resource in our ecosystem. Recently, the use of organic electronic materials allowed interaction with plants in a new way: using the vascular system of plant to form electrical circuits and devices targeting bio-hybrid devices. Firstly, a water-soluble conducting polymer, PEDOT-S has been uptaken by the xylem of a rose, forming self-organized conducting wires in the stem. As a next step a conjugated oligomer, ETE-S was developed with bigger versatility in distribution within the plant due to its small size. The ETE-S in-vivo polymerized within the living tissue forming a network of conducting wires from the stem to the flower. It is well known that plant has developed mechanisms for stability and defense that rely on the polymerization of compounds within the cell wall. The major actor in these processes is called the type III peroxidase. This enzyme can proceed with two different catalytic cycles to reduce or increase the cell wall density. The increase of the cell wall density is achieved through the peroxidative cycle that uses peroxide to crosslink phenolic compounds on the cell wall creating a complex network of various polysaccharides such as lignin or extensin. In this work, we demonstrate the involvement of this peroxidative cycle in the polymerization of the ETE-S oligomer by reproducing the reaction in-vitro. We then follow the kinetics of the polymerization reaction while changing the enzyme or substrate concentrations to understand deeper the underlying mechanism. By understanding the mechanism of in-vivo polymerization we can rationally design materials for plant functionalization as well as optimize targeted functionalization.

9:15 AM SB03.03.03
In Vivo Polymerization of Conducting Polymers in Zebrafish Brain Tissue Xenofon Strakosas¹, Peter Ekstrom², Jennifer Gerasimov¹, David Bliman³, Fredrick Ek², Eleni Stavrinidou¹, Roger Olsson², Daniel T. Simon¹ and Magnus Berggren¹; ¹Linkoping university, Sweden; ²Lund University, Sweden; ³University of Gothenburg, Sweden

Organic bioelectronic devices use conducting polymers as active materials because of their soft nature and mixed ionic and electronic conductivity. Electrode arrays, transistors, and drug delivery devices have taken advantage of the conducting polymers in order to improve their performance for the purpose of diagnosis and treatment. However, the aforementioned devices are commonly being developed by using expensive microfabrication techniques. Moreover, conducting polymers occupy only a part of the whole device geometry, while the rest acts as support. Biology, however, builds biological devices by using its own machinery. Recently, the machinery in plants has shown to polymerize trimers resulting in conducting polymer wires, electrodes, and supercapacitors. Here, we
show *in vivo* polymerization of thiophene based molecules by the machinery in the brain in Zebrafish. Localized areas with conducting polymers exist in different parts of the brain. This process paves the way for the development of self-organized organic electronic devices.

**9:30 AM *SB03.03.04***

**Development of Printed Solar Biobattery for Use in Bioelectronics** Marin Sawa; Imperial College London, United Kingdom

There is an urgent need to develop a sustainable battery technology that is cheap, environmentally friendly, easy to fabricate and to dispose of, especially to tackle the world-wide increase in illegally dumped electronic wastes. Microbial biophotovoltaic (BPV) technology is a renewable bioenergy system currently being developed at the laboratory scale. It generates electricity from the photosynthetic metabolism of cyanobacteria and microalgae and exploits their ability to convert light energy into electrical current using water as the source of electrons. Innovative approaches are needed to solve scale-up issues such as cost, ease of fabrication (particularly the fabrication of the inorganic and biological (microbes) parts).

In this talk, I will report the feasibility of the thermal-inkjet method to fabricate a thin-film paper-based BPV cell consisting of a layer of cyanobacterial cells on top of a carbon nanotube conducting surface on plain copy paper. The digitally printed thin-film BPV system produced electricity both in the light and dark, with a maximum electrical power output of 0.38 mW m⁻² in one system and the sustained electrical current production over 100 hours in another more fully printed system. I will discuss latest efforts in development of the proof of concept and address limitations and challenges as well possible applications in the area of printed bioelectronics.

**10:00 AM BREAK**

**10:30 AM SB03.03.05***

**Application of Nanophosphor Particles in Plant Nanobionics** Pavlo Gordiichuk and Michael Strano; Massachusetts Institute of Technology, United States

The concept of a light-emitting plant, or plant exhibiting chemiluminescence powered from its own stored chemical energy, offers promise to advance off grid illumination and other autonomous photonic applications. In this work, introduce and investigate an additional nanoparticle designed to augment plant light emission in the form of silica coated strontium aluminate nanoparticles as nanophosphore elements. These nanoparticles can adsorb and re-emit generated light at longer times, increasing the duration of light emission, where the particles sizes and concentration are the key parameters of plants brightness tunability. Moreover, such nanophosphores can also scavenge additional energy from solar fluence, increasing and augmenting total light emission from the plant. Infiltreted strontium aluminate particles showed homogeneous distribution inside plants leaves in spongy mesophyll region without penetration inside plants cell, preserving their intact structure, as well as efficient particles infiltration deep into the plant’s stem.

**10:45 AM *SB03.03.06***

**Solar Panels on Yeast—Inorganic Biohybrids for Enhanced Photochemical Production** Neel Joshi¹,², Junling Guo¹,² and Miguel Suástegui¹,²; ¹Harvard Univ, United States; ²Wyss Institute, United States

The intersection between synthetic biology and materials science is an underexplored area with great potential to positively affect our daily lives, with applications ranging from manufacturing to medicine. Inorganic-biological hybrid systems have potential to be sustainable, efficient, and versatile chemical synthesis platforms by integrating the light-harvesting properties of semiconductors with the synthetic potential of biological cells. We have developed a modularbioinorganic hybrid platform that consists of highly efficient light-harvesting indium phosphide nanoparticles and genetically engineered *Saccharomyces cerevisiae*: a workhorse microorganism in biomanufacturing. The InP particles are adhered to the yeast surface using a versatile polyphenol-based chemistry. The yeast harvests photo-generated electrons from the illuminated nanoparticles and uses them for the cytosolic regeneration of redox cofactors. This enables the decoupling of biosynthesis and cofactor regeneration, facilitating a carbon- and energy-efficient production of the metabolite shikimic acid – a common precursor for several drugs and fine chemicals. We observed higher per-cell production of shikimic acid for biohybrids compared to their unmodified counterparts, in a light-dependent manner, and a global metabolic shift toward shikimic acid from other fermentative byproducts, like glycerol and ethanol. Our work provides a platform for the rational design of
biohybrids for efficient biomanufacturing processes with higher complexity and functionality. The biohybrid polyphenol-based fabrication scheme can easily be adapted to virtually any combination of particle and cell type, greatly expanding the range of accessible systems and facilitating the exploration of structure-function relationships. Additionally, the vast toolbox of available genetically modified yeast strains will enable further probing of electron transport mechanisms and applicability to a wide variety of biochemical targets.

11:15 AM SB03.03.07
Semi-Artificial Photosynthesis with Biocatalysts Integrated into Hierarchical Materials for Photoelectrochemical Fuel Synthesis Erwin Reisner; University of Cambridge, United Kingdom

Semi-artificial photosynthesis interfaces biological catalysts with synthetic materials and aims to overcome the limitations of natural and artificial photosynthesis. It also provides an underexplored strategy to study the functionality of biological catalysts on synthetic scaffolds through a range of techniques. This presentation will summarise our progress in integrating biocatalysts in bespoke hierarchical 3D electrode scaffolds and photoelectrochemical circuits. The fundamental insights gained into the function of the water oxidation Photosystem II will be discussed, where (i) unnatural charge transfer pathways have been revealed at the enzyme-electrode interface, and (ii) O₂ reduction that short-circuit the water-oxidation process has been discovered. In contrast to natural photosynthesis, these photoelectrochemical cells allow panchromatic light absorption by using complementary biotic and abiotic light absorbers. As opposed to low-yielding metabolic pathways, the electrochemical circuit provides effective electronic communication without losses to competing side-reactions. Progress in the integration of robust live cyanobacteria in 3D structured electrodes will also be discussed.

Selected References
(1) Kornienko et al., Nature Nanotech., 2018, 13, 890–899
(3) Zhang et al., Nature Chem. Biol., 2016, 12, 1046–1052
(9) Zhang et al., J. Am. Chem. Soc., 2018, 140, 6–9

11:30 AM SB03.03.08
PEDOT:PSS-Based Multilayer Bacterial-Composite Films Daniel T. Simon1, Caroline Ajo-Franklin2, Moshe Baruch2,3, Tom Zajdel4, Gábor Méhes1, Eleni Stavrinidou1 and Magnus Berggren1; 1Linköping University, Sweden; 2Lawrence Berkeley National Laboratory, United States; 3Rice University, United States; 4Princeton University, United States

Microbial electrochemical systems provide an environmentally-friendly means of energy conversion between chemical and electrical forms, with applications in wastewater treatment, biofuel production, and environmental biosensing. However, a major challenge to further development, miniaturization, and deployment is the limited thickness of biofilms, necessitating large anodes to achieve sufficient signal-to-noise ratios. In this talk, we present our recent demonstrations of embedding living electroactive bacteria in electrodes based on organic conducting polymers, enabling truly hybrid bioelectronics with a well-defined biological-to-electronic signal pathway. Our method embeds a large, dense biomass of current-producing bacteria inside a three-dimensional PEDOT:PSS matrix, which we call a multilayer conductive bacterial film. The resulting bio-hybrid electrode provides a conformable electrode interface to each bacterium, provides nutrient-permeability, and permits electron transfer via multiple bacterial mechanisms. As a result, it produces 20× more current than a native biofilm grown on the same substrate. We will discuss how this work can both expand our mechanistic understanding of interfacial electron transfer and enable miniaturization and direct incorporation of living biological materials into electronic devices, such as organic electrochemical transistors and microbial biosensors.
1:30 PM SB03.04.01

Anion Interactions with Vapour Deposited PEDOT

Drew Evans; University of South Australia, Australia

Conducting polymers offer several key advantages over their inorganic counterparts, such as mechanical flexibility, transparency, and material abundance, which can enable low-cost fabrication and novel applications such as printed and flexible electronics. The conducting polymer poly(3,4-ethylenedioxythiophene), PEDOT, is one material which displays (among others) high electrical conductivity [1], enhanced thermal conductivity [2], good electrocatalytic performance [3], as well as thermoelectric behaviour [4]. Enhancing the properties of PEDOT has been achieved through Vapour Phase Polymerisation (VPP), an oxidative polymerization process under vacuum conditions. We report that VPP PEDOT shows interesting interactions with anions, in some examples almost specific ion effects [5]. For example, the uptake of anions from an aqueous solution into electrochemically reduce PEDOT is highly dependent on the anion itself. More interestingly is nitrate is specifically absorbed by PEDOT when present in a mixed electrolyte solution [6]. This selective absorption is hypothesised to originate from anion-π interactions, in part validated by MD simulations [5]. Such interactions, relating to both chemistry and structure, lead to interesting opportunities in energy storage as well as (agricultural) sensing.

References:

2:00 PM SB03.04.02

All-Inkjet-Printed Humidity Sensors for the Detection of Relative Humidity in Air and Soil—Towards the Direct Fabrication on Plant Leaves

Giorgio Mattana1, Walid Ait Mammar1, Samia Zrig1, Nathalie Bridonneau1, Vincent Noël1, Eleni Stavrinidou1 and Benoît Piro1; 1Université de Paris, UFR de Chimie, Laboratoire ITODYS, France; 2Linköping University, Sweden

Relative humidity (RH) detection and quantification play a major role in both agriculture and floriculture, as the water content in air and soil has a strong impact on the plant’s growth, flowering and fruiting. Nowadays, the crop and floral industry are facing unprecedented challenges, especially because of the combination of the rapid increase of the world’s population with the unpredictable effects of global warming: atmospheric and soil humidity monitoring has thus become crucial to avoid production insecurity problems. Research on air and soil RH sensors for agricultural and floriculture applications is now focusing on the development of devices that are low-cost, low power-consumption and easily portable. These needs may be met by utilising printing techniques to fabricate...
simple capacitive sensors on flexible, plastic foils.
The devices presented in our work are fabricated on polyimide foils (Kapton®) by inkjet-printing a capacitive structure consisting in coplanar, interdigitated silver electrodes; cellulose acetate butyrate is subsequently printed onto the interdigitated comb and used as humidity sensing layer.
Impedance spectroscopy (at fixed RH) was used to identify the frequency range where our sensors exhibit the most stable capacity values; the sensors’ response to different RH levels was fully characterised by performing both static and dynamic measurements.
A particularly innovative aspect of our work is the sensors characterisation in soil: the printed devices were dipped inside potting soil at different humidity levels (measured by means of a commercial electronic sensor) and again both statically and dynamically characterised. Their lifetime inside the soil was also investigated.
Finally, we present the preliminary results of a protocol to fabricate the aforementioned printed RH humidity sensors using directly plant leaves as substrate.
Our results could pave the way for the fabrication of the next generation of low-cost, flexible and environmentally-friendly humidity sensors.

References

Porous Silicon Fabry–Pérot Interferometer for Highly Sensitive Detection of Mycotoxins in Field Crops Ilana Freidman1 and Giorgi Shtenberg2; 1Bar Ilan University, Israel; 2ARO Volcani Center, Israel

Food and agricultural commodities contamination by various toxigenic molds (fungi) is a serious neglected problem, affecting ~25% of the world’s crops with staggering economical loses [1]. Regardless of decades of extensive research, mycotoxins continue to penetrate the food chain through food and feed crops and pose health risks both to humans and livestock [2]. Mycotoxins may lead to adverse health effects, including cancer, gene mutation, as well as estrogenic, gastrointestinal and kidney disorders [3]. Some mycotoxins are also immunosuppressant which reduce resistance to infectious diseases [4, 5]. Mycotoxins are secondary metabolites produced by specific filamentous fungi species usually belong to Aspergillus, Penicillium or Fusarium that infect crops at the field level and endure on foods during storage. Due to the increased toxicological effects, many countries have set stringent limits for mycotoxins residues in food and feedstuffs particularly with respect to international trade, including developed and developing countries [1]. Thus, it is rather essential to have an accurate, rapid and sensitive method for multiplex detection of mycotoxins in unprocessed food and feed. An oxidized porous silicon (PSi) nanostructures, a Fabry–Pérot thin film, is synthesized and used as an optical transducer element for the detection and quantification of Fumonisin B1 (FB1, target molecule). The nanostructure is modified with specific robust bioprobes for the validation of fungal contamination and its secreted toxins by indirect immunoassay amplified by FB1-horseradish peroxidase (HRP) conjugates. The catalytic activity is monitored in real-time by reflective interferometric Fourier transform spectroscopy (RIFTS). This technique is sensitive to small changes in the average refractive index of the thin-film induced by enzymatic activity products infiltrating the pores. Optical studies reveal high specificity and selectivity towards FB1, presenting LOD of 0.38 ppm. The main advantage of the presented biosensing concept is the ability to detect fumonisin contamination, at environmentally relevant concentrations, using a simple and portable experimental setup.

The Design of Biodegradable Soil Sensors for Precision Agriculture

Madhur Atreya, Karan V. Dikshit, Gabrielle Marinick, Jenna Nielson, Carson Bruns and Gregory L. Whiting; University of Colorado Boulder, United States

Low cost biodegradable sensors for environmental monitoring can enable the collection of large data sets useful for resource optimization in precision agriculture. Therefore, we have developed wireless soil moisture and nitrogen sensors that are printed from solutions of functional biodegradable materials using scalable manufacturing techniques. These sensors will be placed in the field and remotely interrogated, controllably degrading into the soil over time when no longer needed.

The development of biodegradable sensors presents a complex design problem wherein sensor performance must be constant for several months until a prescribed end of life is reached. We leveraged the complex ecosystem of soil in order to more carefully tune degradation rates of electronic devices. We combined enzymatically degradable polymers, such as poly(lactic acid), polycaprolactone, and polyhydroxybutyrate, with benign conductive materials such as magnesium and carbon, to print conductive lines. Similar polymers were also employed as substrates and encapsulant materials. Techniques such as solvent aging and the addition of various composite fillers were explored and optimized for electronic characteristics and degradation rates. We then fabricated wirelessly readable and fully degradable capacitive soil moisture sensors and report on performance shifts due to degradation.

By integrating and modifying existing enzymatic biodegradation techniques, and developing new accelerated testing approaches, we compared degradation rates in continuous flow with traditional batch techniques. We then compared this data with soil-compost mixtures in incubator conditions. Component materials, such as polymers and metals, were tested independently for mass loss and topological changes; and then printed composites and entire devices were tested to investigate performance loss during degradation. In order to ensure the degraded byproducts have a benign impact on the crops being monitored at the local level and on streams and water tables at the systems level, we analyzed the effluent from these accelerated degradation techniques for ecotoxicity.

Control of Stomata in Tobacco Plant Using Organic Bioelectronics

Iwona A. Bernacka-Wojcik1, Miriam Huerta1, Klas Tybrandt1, Michal Karady2, Yusuf Mulla1, David J. Poxson1, Erik O. Gabrielson1, Karin Ljung2, Daniel T. Simon1, Magnus Berggren1 and Eleni Stavrinidou1; 1Linkoping University, Sweden; 2Umeå Plant Science Centre, Sweden

Technologies that allow manipulation of cellular processes with high spatiotemporal resolution can lead to engineering plants that are tolerant of harsh conditions, which is one of the primary goals of modern plant biology. The organic electronic ion pump (OEIP) provides unique means for the electronically-mediated delivery of phytohormones without fluid flow at the cellular scale. Here the OEIP is used to deliver phytohormones at very high accuracy with respect to rate and spatial resolution directly into leaf tissue. Owing to the capillary form factor and the sub-100 µm diameter of the device, there is no significant wound response from the plant benchmarking the OEIP as minimal invasive tool for regulating plant physiology. The delivery of ABA, the phytohormone that mediates plant’s tolerance to stress, induces closure of stomata, the microscopic pores in leaf epidermis that play a vital role in both photosynthesis and transpiration. High performing OEIP mediated delivery revealed surprising kinetics of the ABA-induced signal. This technology offers a new versatile tool for basic plant research but also potential application in agriculture.

Photocontrolled Release Fertilizer System Using Iron(III) Carboxylate Photochemistry for Sustainable Agriculture

Madugamuwe Hewawasam J. Karunarathna, Kerri M. Bailey, Zachery R. Hatten and Alexis D. Ostrowski; Bowling Green State University, United States

Hydrogels with Fe(III) ions and carboxylate-containing polysaccharides such as alginate and pectin were photoresponsive and showed photoreduction to Fe(II) and oxidative decarboxylation of the polysaccharide1. Interestingly, these Fe(III)-polysaccharide hydrogels showed phosphate uptake capability from aqueous solutions for
pH range 4.8 – 11.5. Different hydrogel beads prepared by changing the polysaccharide combination showed a phosphate uptake more than 1 mg g$^{-1}$ at neutral pH of 7. Reclaiming the phosphate from chemical fertilizers and animal manure applied in agriculture is a challenge, and thus we explored the use of these hydrogels to capture phosphate from waste. The phosphate uptake from 100 ppm solutions at pH = 7 was 99% and and~80% from 800 ppm solutions. For raw manure solutions around same pH and with a phosphate content of 340 ppm, the phosphate uptake was 99%. This showed that the uptake behavior was unaffected by the presence of other ions and dissolved solid particles in manure.

These phosphate-loaded hydrogels were also photoresponsive, and the Fe(III)-carboxylate photochemistry slowly degraded the hydrogel network while releasing the phosphate ions. In addition, the amount of phosphate release could be controlled with light intensity. Nutrient uptake by plants (kale and tomato) from the fertilizer-loaded hydrogels was significant. Compared to the controls, plants treated with our fertilizer hydrogel beads showed enhanced plant growth and fruit formation showing the photo controlled nutrient release mechanism. These results show a promising system for reclamation of phosphate from waste solutions and reusing them as a controlled release fertilizer for sustainable agriculture.

3:45 PM

**SB03.04.07**

**Substrate-Functionalized Carbon Nanotubes as Enzyme Probes for Benchtop and In Situ Study of Soil Health**

Nathaniel Kallmyer, Marshall D. McDaniel and Nigel F. Reuel; Iowa State University, United States

The enzymatic degradation of biomacromolecules is critical to the sustenance of life, whether at the cellular or the ecological size scale. Thus, measurement of hydrolytic enzyme activities is often used to characterize an ecosystem’s capacity to support life, particularly in agriculture, where this rate portends to the long-term return of nutrients and overall health of the soil. While soil hydrolytic activity assays exist, they are often confined to dedicated lab spaces and suffer inconsistencies related to in-house preparation of unstable reagents and variable dynamic ranges. In this work, we present a modular sensor that can be used to evaluate modification of different large, agriculturally-relevant substrates. By suspending semiconducting single-walled carbon nanotubes (SWNT) in an amphiphilic enzyme substrate, we observe enzymatic modification of the substrate through modulation of SWNT fluorescent signal. These substrates may be inherently amphiphilic or may be chemically modified to exhibit hydrophilic and hydrophobic domains. Herein, we demonstrate the throughput and modularity of this nanosensor by measuring proteolytic, cellulytic, and lignin-modifying activity in soil to evaluate health of the soil microbiome. We explore variables including type of crop rotation, microbial carbon content, and soil categorization for each type of enzyme. We also demonstrate this assay’s utility for on-site testing using a custom, portable, battery-powered fluorimeter.

4:00 PM

**SB03.04.08**

**In Vivo Sugar Monitoring in Trees via Implantable Organic Electrochemical Transistors**

Chiara Diacci$^{1,2}$;  
$^1$Linköping University, Sweden; $^2$Università degli studi di Modena e Reggio Emilia, Italy

During photosynthesis, plants convert light into chemical energy, building sugar molecules, using water and carbon dioxide. Glucose is one of the main products of photosynthesis and it holds an essential role in plants function being the fuel for respiration, growth and development. In order to meet the plants energetic demand sugars are transported from source to sink tissues through the phloem vascular tissue, mainly in the form of sucrose. Although it is well known that sucrose is transported via the phloem, there is evidence of sucrose transport in the xylem vascular tissue, that is adjacent to phloem and it is mainly responsible for water transport. Monitoring sugar transport in xylem, has gain interest in the scientific community since sugars can play a vital role in the wood development; however the current understanding is limited. Apart from being energy source sugars are also important signalling molecules, involved in regulation of physiology including stress responses. Currently there are no methods that allow real time monitoring of sugar transport in plants. Sugar detection is based on enzymatic assays, chromatography and/or mass spectrometry; all of these methods require sample collection and preparation. Organic electrochemical transistors (OECTs) are ideal tools for interfacing with organisms, since they can translate complex biological input to an electronic readout signal. OECT sensors can operate in complex media and they can directly detect products from the biological unit. Recently we demonstrated that OECTs are able to measure the export of glucose in real time, from isolated chloroplasts, with a temporal resolution of 1 min. In this work we develop implantable OECT-based sugar sensors for in-vivo, real time monitoring of sugar transport in poplar trees. OECTs are developed with standard microfabrication techniques, with multienzyme functionalized gate for specificity to glucose and sucrose. The OECTs sensors show high device to device reproducibility, stability.
during the operation in the in-vivo environment and most importantly they do not cause a significant wound response in the plant. We demonstrate that OECT-based sugar sensors are attractive tools for studying transport kinetics in plants, in vivo and real time.

4:15 PM SB03.04.09
**Single-Bacteria and Virus Identification Using a Bio-Recognition Nanopore**

Makusu Tsutsui¹, Akihide Arima¹, Kazumichi Yokota¹, Masayoshi Tanaka², Masateru Taniguchi¹, Mina Okochi², Takashi Washio³ and Tomoji Kawai¹; ¹Osaka University, Japan; ²Tokyo Institute of Technology, Japan

Solid-state nanopore is a physical sensor capable of detecting single-particles and molecules. The sensing mechanism involves measurements of the temporal ionic current blockade called resistive pulses by an individual object passing through a nanopore. Combing with machine learning to examine difference in multiple features in each ionic current profile, it enables discriminations of analytes by the size, shape, and surface charge states (M. Tsutsui et al., Sci. Rep. 7, 17371 (2017)). In my presentation, I will present our recent research on peptide nanopore approach for adding bioselectivity to the multimodal single-particle analysis. We synthesized recognition probes of various amino acid sequences designed to possess specific affinity to surface proteins of bacteria and/or viruses. We adhered the peptides on Au nanopore wall so as to render antigen-specific perturbation to single-particle translocation dynamics. We found positive correlation between the single-amino-acid-sensitive peptide-analyte affinity and the single-bacteria and -virus translocation time, which was ascribed to longer residence duration of the bioparticle inside the nanochannel with stronger peptide-protein interaction at the wall surface. Multiphysics simulations revealed the intermolecular-interaction-mediated single-antigen translocation mechanism to involve tensile deformations of the soft envelope via electrophoretic forces. Most importantly, we demonstrated multimodal discriminations of flagellated bacteria (Tsutsui et al., Anal. Chem. 90, 1511 (2018)) and influenza types (Arima et al., J. Am. Chem. Soc. 140, 16834 (2018)) in a high-dimensional feature space that revealed the resistive pulse apex as an effective characteristic for distinguishing the intermolecular-interaction-derived difference in the in-pore translocation motions of the two viruses. As the amino-acid sequence degrees of freedom can potentially offer variety of recognition ability to the molecular probes, the peptide nanopore approach can be a versatile single-particle immonosensor that promises wide applications in bioanalysis including environmental monitoring to infectious disease diagnosis.

4:30 PM SB03.04.10
**Nanowire Force Sensors to Probe the Effect of N-acetylcysteine on X. fastidiosa Single Cell Adhesion and Biofilms**

Aldeliane M. da Silva¹, Alessandro Cavalli², Erick Bakkers², Alessandra A. de Souza³, Carlos L. Cesar¹ and Monica A. Cotta¹; ¹UNICAMP, Brazil; ²Technical University of Eindhoven, Netherlands; ³Agronomic Institute of Campinas, Brazil

Probing cell adhesion forces is one of the approaches used to evaluate bacterial motility and surface interactions, which are crucial to the understanding of microorganism behavior. This work presents the application of Indium Phosphide (InP) nanowire arrays as force sensors to investigate the inhibitory effect of N-acetylcysteine (NAC) on adhered cells of the phytopathogenic bacteria *Xylella fastidiosa*.¹,² These bacteria produce extracellular polymeric substances (EPS), which allow them to adhere on a surface and to form biofilms.² NAC is a cysteine analog assumed to disrupt disulfide bonds and therefore remove EPS, among other antibacterial effects. However, the NAC action mechanisms on adhered bacteria are not yet validated experimentally³. In this work we analyzed in real time the effect of NAC on cells attached to the top of InP nanowires. Adhesion forces are measured by optical detection of nanowire deflections due to the forces exerted by bacterial cells, using Confocal Laser Scanning Microscopy. Nanowire positions are determined using a 2D Gaussian fitting of the laser reflection profile. Adhesion forces can be calculated from the measured displacements within the limits of linear theory of elasticity.² Changing bacterial growth time and NAC concentrations in the liquid cell housing the nanowire sensor, we investigated the NAC action on single cells and biofilms. We observed that the measured forces decreased with increasing NAC concentration. Release of cells and biofilms upon NAC addition to the culture are observed in real time; force values on the nanowires decrease once the cells are free. Furthermore, our results suggest a different behavior for the elongated cells bridging neighboring clusters¹; higher adhesion forces keep them attached to the surface after NAC addition, even after biofilm release.

**References**

¹P. Sahoo et al., Nano Letters (2016), 16, 7, 4656-4664.
Programmable release fertilizers have been intensively investigated in the last decades to regularly deliver nutrients to plants. The most used approach is to coat the nutrients using a polymeric matrix to slow or/and control their release on the environment [1,2]. However, the matrix may affect the soil properties, as conductivity and pH, depending on its composition, as a result bio-based and biodegradable polymer had been applied to avoid the harm [3]. In response to this, nanofibrillated cellulose (NFC) has been considered due to the presence of hydroxyl groups on its chemical structure. Those groups allow chemical functionalization of the NFC’s surface, giving it an anionic or cationic charge, and enable the interaction with ionic compounds, e.g. the potassium nitrate nutrient (KNO3). As an effect, it should hold the nutrient and delay its release depending on the nutrient charge. Also, the spray drying technique was used because of its advantages as versatility, reproducibility, and flexibility of the process. In this work we use two types of nozzles to understand the relation of the produced particle (capsule or sphere [4]) with the release mechanism in water. First, the NFC has been chemically modified using TEMPO-mediated oxidation [5] and quaternary ammonium salts [6]. Then, the encapsulation was done on a Mini Spray Dryer B-290-BUCH (inlet temperature: 180°C, aspirator: 100%) using two-fluid (flowrate: 9ml/min) and three-fluid nozzle (inner flowrate: 1 ml/min, outer flowrate: 10ml/min, approx.) to attain microsphere and microcapsule (core-shell) structure, respectively. The materials were characterized and compared by their structure (Z-potential, conductivity titration, FTIR and XRD), morphology (SEM), thermal properties (TGA) and the nutrient release profile. The nutrient encapsulated by nanocellulose has shown a lower released percentage (in water) as compared to non-encapsulated nutrient (KNO3). Also, the two- and three-fluid nozzles have formed different structure, as well as the three-fluid nozzle provided a delayed release of nutrients compared to two-fluid nozzle microparticles. Furthermore, the releasing rate dropped from 100% to 45% for the nutrient encapsulate by positively charged nanofibrillated cellulose. The reasons for the slower released are attributed to the charge of the NFC and to the core-shell structure. The content of the positive charges of NFC was determined by conductometric titration of chloride ions with AgNO3 and found to be 0.119 mmol g⁻¹ corresponding to a degree of substitution of 0.02 (AGU). For the negative charges, the value of 1.46 mmol g⁻¹ was obtained by conductometric titration of acid groups with NaOH. The Z-potential of anionic NFC was found to be -60.1 ± 2.2 mV and for the cationic NFC, 36.5 ± 0.8 mV (proofs of positive charges were grafted on NFC). After the encapsulation, the charges of cationic NFC decrease to -8.4 ± 0.8 mV and 6.6 ± 0.6 mV for microspheres and microcapsules, respectively; confirming the interaction between NFC cationic and the KNO3. As a result, the nutrient is bond with the cationic NFC in the core and also surrounded by the additional layer of NFC (shell) postponing its release. Our approach has showed the great potential of functionalized NFCs and core-shell structure in the preparation of environmentally-friend systems for programmable release fertilizers.

References:
Transparent wood is an emerging material with the combination of optical functions and mechanical performances, showing promising prospect in energy-saving buildings, smart windows, and photonics applications. [1] Transparent wood is usually prepared by removing the light-absorbing components followed by successful impregnation with a refractive-index-matching polymer such as polymethyl methacrylate (PMMA).[2]–[4] During the process, the hierarchical wood structure is preserved. The synergy between wood and PMMA is observed for mechanical properties. Optical properties of TW are tunable via control of the fabrication process and doping the host wood matrix with various additives. Wood nanotechnology is an efficient approach to fabricate multi-functional transparent wood. Through wood-PMMA interface modulation, transparent wood with superior high transmittance and low haze is obtained, paving the way for centimeter thick transparent wood preparation.[5] Wood cell wall modification with organic dye Rhodamine 6G (Rh6G) before PMMA infiltration results in luminescent transparent wood.[6] Lasing effect was observed with the dye modified transparent wood, extending the application of transparent wood in the photonic area. By incorporating functional particles or polymers into the wood structure, hybrid transparent wood materials could be obtained, such as luminescent transparent wood, thermal energy storage transparent wood etc.[7], [8]


Additive engineering is a well-known effective strategy to obtain high quality perovskite films, which is critical for successful perovskite-based device technology[1]. Some challenges of unclear mechanism, limited material selection still exist for these bulk-incorporated materials. In addition, the toxicity and cost of the reported additives are often ignored, in fact being one barrier for the future large-scale fabrication. Here, we introduce an extremely low cost and green biomaterial, Ethyl Cellulose (EC) into the perovskite films. Versatile beneficial effects including trap passivation, crystallization kinetic modulation, balanced charge mobility, hydrogen bonding interaction, scaffold behavior, etc., are surprisingly observed in the EC modified perovskite layers[5]. Due to these benefits, the resulting solar cells with EC additive exhibit a remarkably enhanced average power conversion efficiency from 17.11% to 19.27% with the increased of all device parameters including Jsc, Voc and FF. The hysteresis index is found to decrease by 3 times. A pronounced retardation on degradation is also realized where the bare devices with EC retain 80% of their initial efficiencies after 30 days in ambient air under 45% relative humidity, whereas the pristine devices without EC are completely degraded under the same condition.
The work provides a promising way using simple, earth-abundant, but versatile cellulose-based biomaterials as additives to improve both efficiency and stability of the perovskite solar cells.


9:15 AM *SB03.05.03
Developing Fractionation Technologies for Making Quality Renewable Carbon Fibers from Plant Qiang Li, Cheng Hu, Mengjie Li and Joshua Yuan; Texas A&M University, United States

Lignin polymer represents a promising alternative of petroleum-derived polyacrylonitile (PAN) polymer as precursor to synthesize carbon fiber, because of the biorenewability, abundance, low cost, and high carbon content of lignin polymer. Lignin is one of the three main plant cell wall components and a major waste from both paper industry and lignocellulosic biorefinery. Converting lignin waste into carbon fiber has been sought after for several decades with attempt to make cheap carbon fiber and return economics and build sustainability for both biorefining and paper industry. Nevertheless, the poor mechanical performance remains to be a major barrier for commercial applications of lignin-based carbon fiber. We have established that the low mechanical performance was attributed to the chemical heterogeneity of lignin polymer, including diverse interunitary linkages, various functional groups, different molecular weight, and polydispersity. Recent advancements of our group in fractionation technologies showed the great potential to reduce lignin heterogeneity and thus enhance lignin carbon fiber performance. We have developed a series of fractionation technologies to process technical lignin, including 1) partly degradation of lignin using laccase-mediator system and autohydrolysis treatment; 2) solvent fractionation using different organic solvents with different solubility of lignin; 3) physical fractionation by dialysis tube according to lignin molecular weight; 4) lignin precipitation against water with gradient pH values. All these fractionation have trimmed lignin chemistry and reduced lignin heterogeneity by deriving lignin fraction with more β-O-4 linkage, less hydroxyl groups, higher molecular weight, and less polydispersity index (PDI). The resultant carbon fiber was found to have both enhanced mechanical performance and electrical conductivity. Mechanistic study have revealed that the improvement in lignin heterogeneity has improved the molecular interactions of lignin with guest molecules, and thus enhanced the growth of the crystallite structures in carbon fiber, resulting in carbon fibers with improved performances. Overall, fractionation of lignin represents a simple and efficient way to regulate lignin chemistry and boost the quality of lignin carbon fibers, which paved an avenue to transform the sustainability of carbon fiber industry and the bioeconomy of biomass refining.

9:30 AM *SB03.05.04
Structural Biopolymers—From Nanotechnology to Precision Agriculture and Food Security Benedetto Marelli; Massachusetts Institute of Technology, United States

The reinvention of structural biopolymers into technical materials has enabled the design of biomedical and optoelectronics devices with unique and compelling properties that can serve at the interface between the biotic and the abiotic worlds. For example, we have previously shown the use of silk fibroin bioinks for the detection of E.coli contamination in food. Silk fibroin, in fact, is an edible and biodegradable protein extracted from B. mori cocoons that can be engineered in several formats ranging from films to particles, foams, and gels. By exploiting silk fibroin essential properties (i.e. polymorphism, conformability, and hydrophobicity) it is possible to design a water-based protein suspension that assembles in nano- to centimeter thick materials that can be nanofabricated using advanced manufacturing techniques, including e-beam, soft lithography, replica molding, and printing. The so formed materials modulate mass transport (e.g. O2 and CO2 diffusion and water vapor permeability) and preserve the function of biological molecules and micro-organisms outside the cold chain. This is possible by controlling protein polymorphism (i.e. formation of random or beta-sheet structures) during and post material assembly. Here, we show how silk materials can be used to address technological challenges in precision agriculture and food preservation to enhance food security. We will present the design of edible coatings that prolong the shelf-life of perishable food by decreasing water evaporation and regulating O2 and CO2 diffusion, effectively reducing oxidative stresses and cell metabolism. The use of silk fibroin coating can also be expanded to seeds to engineer the inoculation of biofertilizers that can mitigate abiotic stress as saline and arid soils. Finally, we will discuss the possibility to use silk-based materials as a vehicle to deliver phytoactive payloads in plants vasculature to modify plant metabolism.
10:00 AM BREAK

SESSION SB03.06 Spotlight Talk: Smart Materials, Devices and Systems for Interface with Plants and Microorganisms
Session Chairs: Drew Evans and Marin Sawa
Wednesday Morning, December 4, 2019
Hynes, Level 3, Room 305

10:30 AM SB03.06.01
Spotlight Talk—Multifunctional SiQD-Embedded Transparent Wood Alden Clemments and Ilya Sychugov; Kungliga Tekniska Hogskolan, Sweden

Recent developments in the fabrication of transparent wood (TW) have shown promise in the field on renewable energy. Impregnation of TW with silicon quantum dots (SiQDs) exhibits promise as light-harvesting composite. However, these advancements are hindered by the ability to selectivity control QD distribution and loading within the porous scaffold. Here, we demonstrate that by employing a variety of chemical methods, improvements in QD loading, distribution, and ultimately optical output are drastically improved.

10:35 AM SB03.06.02
Spotlight Talk—Electronic Functionalization of Roots of Intact Plants via In Vivo Polymerized Conducting Polymer Daniela Parker1,2, Gwennael R. Dufl1,2, Magnus Berggren1,2 and Eleni Stavrinidou1,2; 1Laboratory of Organic Electronics, Sweden; 2Linköping University, Sweden

As our understanding of the surroundings and technology advances so does the way we interact with our environment. Serving as food, improving our health, allowing us material extraction or just decorating our constructions, plants have played a vital role in helping humans thrive to adapt and survive. As new challenges arise, there is still room for creative ways to interact with plants. Recent research has focused on interfacing organic electronics with living plants. Although the plant by itself represents a complex system, the idea is to add an extra functionality.

Initially we demonstrated formation of conducting wires along the xylem vascular tissue of rose cuttings from stem to flower. The wires were formed spontaneously, when the cutting was immersed in aqueous solution of a thiophene based conjugated oligomer, ETE-S. ETE-S comprises key features such as water solubility and small molecular weight for plants to transport through its vascular system. The plant guided the polymerization reaction in the xylem acting as a template and catalyst for the polymerization reaction.

In this work we aim to advance the technology by functionalizing intact plants. We choose the bean as our model system and demonstrate electronic functionalization of roots. The ETE-S polymerizes effectively in the root epidermis forming polymer coating of thickness 1-3um. The functionalized roots exhibit conductivity in the order of 10S/cm and volumetric capacity of 50F/cm3. The plants ability to grow its not impaired from the electronic functionalization, making it an attractive system for biohybrid applications from sensing to energy.

10:40 AM SB03.06.03
Spotlight Talk—Synthesis of a Paracyclophane-Based Conjugated Oligoelectrolyte and Its Interactions with Biological Membranes Jakkarin Limwongyut1,1, Yang Liu2, Gayatri Shankar Chilambi2, Thomas Seviour2, Jamie Hinks2, Yuguang Mu2 and Guillermo Bazan1,1; 1University of California, Santa Barbara, United States; 2Nanyang Technological University, Singapore

Conjugated oligoelectrolytes (COEs) are molecules that can spontaneously interact and modify microbial membrane properties. In this work, a three-dimensional COE containing a [2.2]paracyclophane unit (COE2-3-pCp) in a conjugated framework was synthesized to introduce more dimensionality to the core. Its biological activity was determined within the context of membrane perturbation and biocompatibility in lipid vesicles and microbial cells. Additionally, the effects of COE2-3-pCp in a bacterial membrane model were determined in silico using molecular dynamic simulations. The simulations indicate that, compared to its linear analog (COE2-3C), COE2-3-pCp introduces more lipid disorder with higher extent of membrane thinning. In microorganisms, COE2-3-pCp exhibits...
lower toxicity against *E. coli* K12 and yeast, while maintaining similar levels of membrane permeabilization. These findings suggest a new design of COEs as biocompatible cell permeabilizers.

**SESSION SB03.07: Electron Transfer Processes**
Session Chairs: Ardemis Boghossian and Gianluca Farinola

**Wednesday Afternoon, December 4, 2019**
Hynes, Level 3, Room 305

**1:30 PM *SB03.07.01*  
The Photoelectrochemistry of Photosynthetic Machineries—From Isolated Proteins to Living Cells Jenny Zhang; Univ of Cambridge, United Kingdom

Photoelectrochemistry is a relatively new tool for studying photosynthesis, and the knowledge and tools developed from this platform will form the foundation of emerging technologies utilizing photosynthetic materials for energy conversion. The photoelectrochemistry of purified photosystems have recently benefited enormously from an improved understanding of the interfacial wiring and improved electrode design. Here, I give an overview of this progress with a focus on lessons derived from photosystem II, and show how these lessons can be applied to the photoelectrochemistry thylakoids and whole cells. The systematic comparison of the different components, each being one step removed in metabolic complexity, allows the electron transfer processes at each level to be more effectively teased out.

References

**2:00 PM SB03.07.02  
Bacterial Photosynthetic Reaction Center—Extending the Functionality by Bioconjugation Strategies  
Gabriella Buscemi1, Simona La Gatta1, Francesco Milano2, Roberta Ragni1, Gianluca M. Farinola1 and Massimo Trotta2; 1University of Bari, Italy; 2National Research Council, Italy

Bioconjugation is a process useful for giving natural systems addititional artificial properties belonging to ad hoc newly synthetized organic small molecules or other biomolecules. Protein functionalization is usually achieved via click chemistry reactions or amide synthesis, and the partner molecule can be a lipid, or another protein, a nucleic acid, a polysaccharide or an organic molecule. During the bioconjugation processes, cysteine, tyrosine and lysine residues are typically exploited for anchoring synthetic ligands1. Moreover, if the protein is an enzyme, the creation of a protein-protein or protein-prosthetic assembly can finely modulate the enzymatic activity.

The photosynthetic reaction center (RC) is an ubiquitous protein. Among all the photosynthetic organisms, the RC obtained from the anoxygenic purple bacterium Rhodobacter sphaeroides is often used as a model system, due to its easy isolation and fully charactherized spectroscopic/electrochemical behaviour2. RC is a trans-membrane photoenzyme which efficiently harvests sun-light and converts it in other viable forms of energy by generating charge separated states for fueling cell metabolism.

Biohybrid materials, based on the combination of RC and artificial organic antennas have been already produced to increase the spectral region of the harvested sun light, in order to ameliorate the charge separation aptitude and generation3. Now our research group is focusing on the possibility to covalently link RC with another non photosynthetic protein, the cytochrome c (Cyt C), which is the natural electron donor of these photosynthetic proteins. This is in principle done for ameliorating the electrical communication between RC and Cyt C4.5. This RC-Cyt C bioconjugation is possible by developing a one-step “grafting-to” protocol exploiting specific lysine and organic aliphatic linkers. In a speculative perspective, we will use these biohybrids to better orient RC on devices for
bioelectronic applications.

2:15 PM SB03.07.03
Flavin-Hybridized Carbon Nanotube Electrode for Selective Biocatalytic Oxyfunctionalizations Da Som Choi¹, Yan Ni², Elena Fernández-Fueyo², Minah Lee¹, Hollmann Frank² and Chan Beum Park¹; ¹Korea Advanced Institute of Science and Technology, Korea (the Republic of); ²Delft University of Technology, Netherlands

Biocatalytic oxyfunctionalization of inert C-H or C-C bonds is of special interest in organic synthesis. In particular, unspecific peroxygenases have gained much interests since they catalyze a wide range of selective oxyfunctionalization reactions; however, their broad application is hampered by oxidative degradation of the heme moiety in the presence of even low concentrations of H₂O₂. Typically, this challenge has been met by in situ provision of peroxygenases with suitable amounts of H₂O₂ by catalytic reduction of molecular oxygen using electrochemical¹, photochemical², or enzymatic³ methods. Photoelectrochemical (PEC) reduction of oxygen is an attractive approach to produce H₂O₂ with the use of abundant solar energy and water, avoiding the accumulation of byproducts in the reaction mixture. In this study, we demonstrated a novel, photoelectrochemically boosted peroxygenase catalysis through in situ generation of H₂O₂ via flavin-hybridized carbon single-walled nanotubes (SWNT) photoelectrodes. Flavins can be easily immobilized on the surface of SWNT electrodes via a simple hybridization process while maintaining their redox-active properties of flavins. The hybridization of flavins with SWNTs occurs through π-π interactions between aromatic isoalloxazine moities and graphitic carbons in addition to hydrogen bondings between adjacent flavin molecules. Compared to a pristine SWNT, the flavin-SWNT hybrid photoelectrode exhibited much higher photocurrent density and a marked anodic shift for oxygen reduction reaction, which is attributed to the facilitative effect on charge transfer to oxygen by flavin photosensitizers. As a result, H₂O₂ production rate is enhanced up to 0.15 mM h⁻¹ at -0.3 V (vs. Ag/AgCl) under illumination, which is 2.28- and 2.48-fold higher than control experiments without light or using a pristine SWNT cathode under light, respectively. We successfully coupled the flavin-SWNT-based PEC platform to peroxygenase-catalyzed reactions, such as ethylbenzene hydroxylation, 2-phenoxypypropanoic acid hydroxylation, and indole oxidation.

References

2:30 PM BREAK

3:30 PM *SB03.07.04
Charge Recombination in Semi-Artificial Photosynthesis Nicolas Plumere; Ruhr-Universität Bochum, Germany

The integration of photosynthetic proteins in biophotoelectrodes is envisioned for the production of electricity⁴ or chemical fuels. Redox hydrogels proved particularly suitable as matrices for the immobilization and electrical contacting of photosynthetic proteins to electrodes. We tuned the redox potentials of the electron relays and the properties of the polymeric supporting matrix to enable benchmark photocurrent densities (300 μA cm⁻² for PS1⁵ and up to 400 μA cm⁻² for PS2⁶) at low overpotential⁴. In analogy to the working principle of dye sensitized solar cells, an important feature of biohybrid solar cells for conversion of light to electricity is the charge carriers needed for collection of the high-energy electron from the photosystem⁵. The main limitation in energy conversion efficiency is the recombination of this charge carrier at the photoelectrode, a process that decreases both the photocurrent and the open circuit voltage⁶. Moreover, this charge recombination process is suspected to induce degradation of the photosynthetic protein⁶. We demonstrate that the hydrogel film properties as well as the electrode surface chemistry can be tuned to minimize the various charge recombination pathways.
References:


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SESSION SB03.08: Poster Session: Materials and Devices for Plants and Microorganisms
Wednesday Afternoon, December 4, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB03.08.01
**Spotlight Talk—Electronic Functionalization of Roots of Intact Plants via In Vivo Polymerized Conducting Polymer** Daniela Parker,1,2, Gwennaël R. Dufil,1,2, Magnus Berggren,1,2 and Eleni Stavrinidou,1,2; 1Laboratory of Organic Electronics, Sweden; 2Linköping University, Sweden

As our understanding of the surroundings and technology advances so does the way we interact with our environment. Serving as food, improving our health, allowing us material extraction or just decorating our constructions, plants have played a vital role in helping humans thrive to adapt and survive. As new challenges arise, there is still room for creative ways to interact with plants. Recent research has focused on interfacing organic electronics with living plants. Although the plant by itself represents a complex system, the idea is to add an extra functionality.

Initially we demonstrated formation of conducting wires along the xylem vascular tissue of rose cuttings from stem to flower. The wires were formed spontaneously, when the cutting was immersed in aqueous solution of a thiophene based conjugated oligomer, ETE-S. ETE-S comprises key features such as water solubility and small molecular weight for plants to transport through its vascular system. The plant guided the polymerization reaction in the xylem acting as a template and catalyst for the polymerization reaction.

In this work we aim to advance the technology by functionalizing intact plants. We choose the bean as our model system and demonstrate electronic functionalization of roots. The ETE-S polymerizes effectively in the root epidermis forming polymer coating of thickness 1-3μm. The functionalized roots exhibit conductivity in the order of 10S/cm and volumetric capacity of 50F/cm³. The plants ability to grow its not impaired from the electronic functionalization, making it an attractive system for biohybrid applications from sensing to energy

SB03.08.02
**Antimicrobial Polymer-Peptide Conjugates Based on Maximin H5 and PEG to Prevent Biofouling of E. coli and P. aeruginosa** Eduardo Nicolau, Valérie Ortiz and Jaime Santillan; University of Puerto Rico, United States

Many pathogens, such as *Pseudomonas aeruginosa* and *Escherichia coli* bacteria can easily form biofilms. The formation of such biofilms in surfaces is known represents a problem for membrane-based water purification techniques, the area of biomedical devices among many others. Aiming to provide a plausible solution to this issue, herein we explore on an antimicrobial peptide (AMP’s) polyethylene glycol (PEG) conjugate that prevents biofouling formation. In this research, the anionic and hydrophobic peptide Maximin H5 (MH5, 2.4kDa), which is
an integral part of the defense system of the frog *Bombina maxima*, is coupled to PEG of different sizes (i.e. 2 kDa and 5 kDa) followed by extensive characterization. Scanning Electron Microscopy (SEM) was employed to evaluate the formation of biofilms and its interaction with these conjugates, showing no biofilm formation. After physical and microbial characterization, MH5 was bio-conjugated to PEG followed by size exclusion purification. The reaction confirmation was achieved by SDS-PAGE and MALDI ToF. Moreover, the antimicrobial activity of the MH5-PEG conjugates was performed via the growth inhibition method and SEM. These conjugates have demonstrated potent antimicrobial activity with high inhibition of bacterial growth after 24 hours. Thus, the prepared polymer-peptide conjugates have the potential to be utilized on applications where an antimicrobial coating is necessary.

**SB03.08.03**

**Modification of Cotton Surfaces with Superhydrophobic Nanotextures for Enhanced Healthcare and Hygiene**

Jun Kyun Oh; Dankook University, Korea (the Republic of)

As a result of frequent outbreaks occurring due to poor hygiene and improper sanitation of processing environments, there has been an increasing demand for the development of material surfaces that intrinsically inhibit and reduce likelihood of potential microbial adherence and biofilm formation. Herein, we report the synergistic utilization of surface nanotexturing and chemical modifications with nonpolar functional groups on cotton surfaces to produce coatings having bacterial super-repellent characteristics. Using these coatings, the attachment of *Staphylococcus aureus* as pathogen surrogates was reduced more than 99.0%, compared to the bare cotton surfaces. Moreover, this method is both versatile and scalable, involving inert and biocompatible building blocks. Overall, this study contributes to the field of biomedical applications through the design and development of novel coatings for achieving improved healthcare and hygiene.

**SB03.08.04**

**A Novel Photothermal Nanocomposite for Reducing Bifofilms Associated with Silicone-Based Devices**

Pedro Sanchez, Stanley Green, Madison Greer, Shaina Yates and Nicole Levi-Polyachenko; Wake Forest University Health Sciences, United States

*Staphylococcus aureus* is a common pathogenic bacterium prevalent in a wide variety of diseases, including progressive blood and tissue infections such as chronic ulcers, sepsis and osteomyelitis. Additionally, there exist many *S. aureus* subtypes which have developed resistance to broad-spectrum antibiotics. Part of the acquired antibiotic resistance may be attributed to the capacity for *S. aureus* to thrive in colonies within a protective matrix of polymers, polysaccharides, extracellular DNA and water (biofilm). Biofilm residing bacteria are known to be many times more resistant to select antibiotics than their planktonic counterparts.

One mechanism proposed for mediating biofilm-associated infections is to disrupt the polymer structure of the biofilm, leading to the release of planktonic bacteria which are more susceptible to antibiotic therapy. Chemical agents have been evaluated for accomplishing this; however, physical means, such as heat or ultrasound can serve two purposes by first disrupting the biofilm structure while also altering individual bacterial cell walls. Physical disruption may be especially advantageous for eradicating biofilms associated with implanted medical devices, alleviating the need for their removal and maintaining device function.

Silicone is a biocompatible elastomer that can either compose an entire medical device (catheters) or be used as a pliable surface coating on metal or ceramic implants. For the generation of heat, we have included photothermal donor–acceptor conjugated polymer nanoparticles based on poly[4,4-bis(2-ethylhexyl)-cyclopenta[2,1-b;3,4-b’]dithiophene-2,6-diyl-alt-2,1,3-benzoselenadiazole-4,7-diyl] (PCPDTBSe). The composite materials were evaluated for the killing of planktonic and biofilm-residing *S. aureus*, in either the presence or absence of the antibiotic gentamicin. In the absence of near-infrared laser stimulation of the composite, addition of the nanoparticles exhibited an unexpected bactericidal effect. Stimulation of silicone alone with 612 J/cm2 of 800nm light had no effect on planktonic or biofilm *S. aureus*, whereas ablative temperatures in the nanoparticle doped composites resulted in a 95-100% reduction in viable bacteria. Sub-ablative temperatures resulted in a 75% reduction in planktonic bacteria treated with gentamicin and a 90% reduction in biofilm-residing *S. aureus*, compared to controls treated with gentamicin alone and no infrared stimulation. The PCPDTBSe nanocomposites were then evaluated in a murine model to simulate biofilm infections associated with subcutaneously placed silicone implants. A luminescent variant of *S. aureus* was used to monitor the bacterial burden in the mice before and after laser stimulation with and without antibiotics, and the burden was quantified by measuring colony forming units.
(CFU) following explantation of the nanocomposite. Depending upon the laser parameters used (1.2-3W/cm² for 10-45s) there was a reduction of 33-94% CFUs following treatment with the heat-generating nanocomposite plus antibiotics. Our results demonstrate the potential for heat-generating biocompatible nano-composites to augment antibiotics used to treat S. aureus biofilms. These results offer a new avenue for the use of photothermal nanocomposites to eliminate challenging medical infections associated with in-dwelling medical devices.

SB03.08.05
Metabolically Active Cells of the Photosynthetic Bacterium Rhodobacter sphaeroides Encapsulated in Melanin-Like Structure
Massimo Trotta¹, Danilo Vona², Stefania Cicco¹, Roberta Ragni², Marco Lo Presti², Gabriella Buscemi² and Gianluca M. Farinola²; ¹Consiglio Nazionale delle Ricerche, Italy; ²Università di Bari, Italy

Photosynthetic organisms are the primary producers of energy on planet Earth thanks to their ability to harvest and convert light into other forms of energy viable for virtually all the metabolic needs of any living organism. Exploiting this formidable attitude is a very intriguing possibility for developing innovative and efficient sustainable energy sources based on the conversion of solar energy. Garnishing the photosynthetic enzymes [1,3] to produce hybrid systems formed by biological and organic moieties for energy transduction has been shown to be a promising route. On the other side, being able to use the whole, metabolically active, photosynthetic organisms is even more promising [4]. To this purpose, “wiring” the living organism with conductive systems, either organic or inorganic, is of paramount relevance [5] and, yet, has not been fully addressed. Recently, the encapsulation of living yeasts in polydopamine (PDA)-based structures has been demonstrated [6], with the metabolic activity of the cells preserved in this confinement state because of the lack of any detrimental effect of the polymer. We present here the preliminary results of the entrapping and confinement of active cells of the photosynthetic bacterium Rhodobacter sphaeroides into ad hoc engineered melanin-like polymers using a mild approach in water based buffers. Bacterial growth accompanied by cellular division are retained under photosynthetic anoxygenic condition, although some detrimental effects are registered in the case of some of the polymers investigated.

This work was funded by European Commission through the EU project 800926 - HyPhOE (Hybrid Electronics based on Photosynthetic Organisms)


SB03.08.06
Spotlight Talk—Multifunctional SiQD-Embedded Transparent Wood
Alden Clemments and Ilya Sychugov; Kungliga Tekniska Hogskolan, Sweden

Recent developments in the fabrication of transparent wood (TW) have shown promise in the field on renewable energy. Impregnation of TW with silicon quantum dots (SiQDs) exhibits promise as light-harvesting composite.
However, these advancements are hindered by the ability to selectivity control QD distribution and loading within the porous scaffold. Here, we demonstrate that by employing a variety of chemical methods, improvements in QD loading, distribution, and ultimately optical output are drastically improved.

**SB03.08.07**

**Spotlight Talk—Synthesis of a Paracyclophane-Based Conjugated Oligoelectrolyte and Its Interactions with Biological Membranes**

Jakkarin Limwongyut\(^1,1\), Yang Liu\(^2\), Gayatri Shankar Chilambi\(^2\), Thomas Seviour\(^2\), Jamie Hinks\(^2\), Yuguang Mu\(^2\) and Guillermo Bazan\(^1,1,1\); \(^1\)University of California, Santa Barbara, United States; \(^2\)Nanyang Technological University, Singapore

Conjugated oligoelectrolytes (COEs) are molecules that can spontaneously interact and modify microbial membrane properties. In this work, a three-dimensional COE containing a \([2.2]\) paracyclophane unit (COE2-3-pCp) in a conjugated framework was synthesized to introduce more dimensionality to the core. Its biological activity was determined within the context of membrane perturbation and biocompatibility in lipid vesicles and microbial cells. Additionally, the effects of COE2-3-pCp in a bacterial membrane model were determined *in silico* using molecular dynamic simulations. The simulations indicate that, compared to its linear analog (COE2-3C), COE2-3-pCp introduces more lipid disorder with higher extent of membrane thinning. In microorganisms, COE2-3-pCp exhibits lower toxicity against *E. coli* K12 and yeast, while maintaining similar levels of membrane permeabilization. These findings suggest a new design of COEs as biocompatible cell permeabilizers.

**SB03.08.08**

**M13 Bacteriophage Based Triboelectric Energy Generation for Powering Organic Light Emitting Diode**

Han Kim\(^1\), Byoung Duk Lee\(^2\), Jihwan Yoon\(^2\), Jonghyuk Lee\(^2\), Ju Hyuck Lee\(^3\) and Seungwuk Lee\(^3,1,1\); \(^1\)University of California, Berkeley, United States; \(^2\)Samsung Display, Korea (the Republic of); \(^3\)Biological Systems and Engineering Division, Lawrence Berkeley National Laboratory, United States

Development of a clean and green renewable energy source without sacrificing a carbon footprint is one of most challenging issues that mankind faces in the modern society. Triboelectricity is a charge separation induced by friction through the physical contact of materials with different electron affinities. Recently, triboelectricity materials and devices have shown a promising pathway to harvest ubiquitous mechanical energy to charge mobile and portable electronic devices. M13 bacteriophage (phage) is a promising material to develop a clean and green triboelectric material. M13 phage is benign and non-harmful virus to infect only bacterial host cells. It has a filamentous shape with 880 nm in length and 6.6 nm in diameter. The M13 phage is covered by 2700 copies of major coat protein that encapsulates phage DNAs. Through the genetic modification, we can precisely control the chemical and physical structures of the phage coat proteins. The resulting engineered phage can be easily amplified to produce identical copies of the phage in a large scale. Due to the anisotropic rod-shape, we can self-assemble the phage into various of liquid crystalline structures. Here we developed a novel triboelectric energy harvesting materials and devices using M13 phage. We first created a monolayer thin film of M13 phage and characterized triboelectric properties of the M13 phage. Through direct friction between Ti/Pt coated-AFM tip and M13 phages, we generated the triboelectric charge, and characterized them using Kelvin probe force microscopy (KPFM) measurement. Upon friction generation, we could successfully observe the triboelectric charge generation using the KPFM. We then modified the surface charge through addition of different number of glutamic acids on the M13 phage coat proteins. The phage with higher number of glutamic acids showed a higher triboelectric potential than that of fewer glutamic acids. We also characterized triboelectric charge generation depending on the friction conditions and their discharging behavior. We finally fabricated the large area thin film of M13 phage and developed a triboelectric thin film energy harvesting device. Upon the mechanical force application, the phage-based triboelectric devices can generate 3 V and 5x10^-4 mA. The resulting device also could power the organic light emitting diode devices with thin film encapsulation. Our approach to develop a phage-based triboelectric material is useful to understand how friction can induce charges in a biological system in a molecular level and to develop clean and green energy harvesting solutions to charge portable electronic devices and biomedical applications in future.

**SB03.08.10**

**An All-in-One Fluorescent Supramolecular Bacterial Sensor Assisted by Transformation of Peptide Self-Assembly**

Youjin Jung\(^1\), Woo-jin Jeong\(^2\), Se-Hwan Choi\(^1\), Hye-soo Lee\(^1\) and Yong-beom Lim\(^1\); \(^1\)Yonsei University, Korea (the Republic of); \(^2\)University of Wisconsin–Madison, United States

An all-in-one fluorescent supramolecular bacterial sensor assisted by transformation of peptide self-assembly is reported.
The essential components of a sensor are receptors, signal converters and detectors. Here we propose an all-in-one bacterial biosensor in the form of supramolecular peptide assembly, which contains all three components by itself. The assembly consists of a double-layered octa-helical tetrameric coiled-coil structure. The outer surface of the assembly shows tetravalent helical bioreceptors for targeting bacteria and the inner core is composed of environment-sensitive fluorophores as detectors. At the connection between them are reversibly self-assembling peptides that play a role in signal transduction. The signal transduction exploits the reversible and non-covalent property of the self-assembled supramolecular system. The multivalent binding of bacteria activates supramolecular transformations, which are transduced into fluorescence changes. Our fluorescent supramolecular biosensors (fSBs) could selectively detect E. coli over other bacteria. Since the fSBs are not denatured by heating, they maintain their capability as a bacterial sensor even at high temperature (50 °C). Based on this research, a variety of responsive supramolecular sensors can be developed to detect diverse biomacromolecules and large biological objects.

SB03.08.11
Spray-Dried Microspheres of Starch as Enhanced Efficiency Fertilizer Materials Camila G. Chiaregato1,2 and Roselena Faez2,1; 1University of Sao Paulo, Brazil; 2Federal University of São Carlos, Brazil

By 2100, the population is expected to reach 11.2 billion people, and agriculture has the challenge to establish strategies to achieve sustainable production of food. Fertilizers are used to increase crop production by replacing the necessary nutrient for the plant and also are the major cause of contamination of underground water and rivers. About 30 to 50 % of the fertilizers applied are lost by lixiviation or volatilization, being necessary to use a higher quantity than the real need. The big question is how to increase fertilizer efficiency and crop yield without compromising natural resources? One of the answers is developing a material that controls the availability of fertilizer in the soil, a technology that enhanced efficiency fertilizer, reducing the loss, the amount of fertilizer applied and, consequently, production costs. To achieve this goal is relevant to use polymers from natural resources with wide availability, and potential to biodegrade, to act as a protection layer. Starch polymer fits all these characteristics and has a low cost. For this purpose, the aim of this work was developed microspheres of starch and micronutrients by spray drying technique. For starch gelatinization, 6 wt. % of food-grade corn starch was added in 100 mL in distilled water and heat in an oil bath at 97 °C during 30 min. After, the gelatinized starch was homogenized in a Turrax for 5 min with 10,000 rpm and during the atomization process kept in magnetic stirring. For starch atomization, we use a 2 - fluid nozzle (0.5 mm diameter) at 130 °C and aspiration rate of 10 % in a Mini spray drying (B290/Buchi) yielding 47 %. The X-ray diffraction pattern of native corn starch exhibited peaks at 15 °, 18 ° and 23 ° (20), which indicates A-type starch crystallinity. After the atomization, the microspheres showed an amorphous pattern, which is a consequence of the drying process. The decrease of nutrient release in water demonstrates the potentiality of spray-dried starch microspheres as an enhanced efficiency fertilizer.

SB03.08.12
Spray-Dried Microparticles Based on Chitosan and Cellulose Nanocrystal as Supporting Material for Controlled Release of NPK Fertilizer Lucas L. Messa1,2,3 and Roselena Faez2,1; 1University of Sào Paulo-USP, Brazil; 2University of São Carlos-UFSCar, Brazil; 3University of California, Davis, United States

The development of microparticles based on natural polymers has attracted great interest for numerous applications, mainly as the release of compounds. It can offer a longer diffusional path, which prolonged release. One of the most potential application of these systems of microparticles is in agriculture, where the main issue presented is the loss of fertilizers, like nitrogen (N), phosphorus (P) and potassium (K). Chitosan (CS) is a cationic polysaccharide frequently used for slow/controlled release due to its biodegradability and availability of functional groups (N-H, O-H) on its surface. Because of the reactivity of the protonated amino group (NH3+), CS is able to interact with anionic compounds such as phosphate ions. In addition, cellulose nanocrystal (CNC), which is produced from acid hydrolysis of native cellulose fibers, has negatively charged groups due to the insertion of sulfate groups from hydrolysis. These groups can bind many cationic ions, such as potassium and ammonium. This work focus on the preparation of spray-dried microparticles and the surface interactions between of both polymers (CS and CNC) and the NPK fertilizer as well. First, the CNC was prepared by acid sulfuric hydrolysis (64% wt., 50°C, 120 min) from sugarcane bagasse cellulose. Then, 4 formulations based on 100 mL of Cs (1 wt.%) and two different mass ratios of CNC (0.1 and 1.0 g) and NPK (2.7 and 16.2 g) to CS were dried on a Mini Spray Dryer B-290-BUCH (inlet temperature: 180°C, aspirator: 100%) using two-fluid (flow rate: 7 ml/min). Microparticles were compacted using a hydraulic press (6 ton, 25°C for 1 min) to produce materials in pellet form. All produced materials were characterized using FTIR, XRD, SEM and releasing tests were carried out to evaluate the CNC effect on release.
property of the composites. XRD confirmed the presence of NPK in the spray-dried microparticles. The interactions between chitosan polymer and ions from fertilizer were confirmed by FTIR results. The non-encapsulated NPK had the fastest release due to high solubility of the fertilizer in water. SEM results showed that CS concentration used in this work was not able to encapsulate the high content of NPK (16.2 g). The fertilizer encapsulated by composites with 0.1 wt.% of CNC showed a slower release profile as compared those with 1.0 wt.% of CNC. This suggests that part of the NPK remains not encapsulated in the presence of CNC high content and can be quickly released from the system. Our work demonstrates one application of CNC and chitosan to bind fertilizers into microparticles that would improve nutrient use efficiency.

SB03.08.13
Single-Cell Drop-Seq Techniques for Genomic Profiling of Microorganisms Abhiteja Konda1,1, Ryan Dohn2, Rebecca Back2, Pavani Vamshi Krishna Nittala2,1, Ralu Divan1, Supratik Guha1,2 and Anindita Basu1,2; 1Argonne National Laboratory, United States; 2The University of Chicago, United States

Single-cell genomics research has gained significant and rapidly growing interest due to its ability to characterize a population of cells at epigenomic, transcriptomic, or proteomic level with a single-cell resolution that is critical to understanding the genomic heterogeneity between individual cells comprising a population for its potential applications in industry and medicine. The existing single-cell techniques have mainly focused on multicellular, complex organisms such as primates, insects, rodents, and fish; however, understanding the heterogeneity in unicellular microbial organisms is important and will be critical in addressing some of the challenges in environment, medicine, and energy-related applications. This heterogeneity in microbes exists as a response to the ever-changing complex environment. Currently, there are no tools or technologies that allow the quantification of this variation. In the present work, a droplet-based approach is used to transcriptionally profile each microbial species at single-cell resolution and high throughput. Emphasis is laid on the lysis of the microbial cell wall which is one of the key challenges to overcome for the success of the project. A suite of different techniques (both physical and chemical) including the use of microelectromechanical systems [MEMS], laser ablation, acoustic waves, plasmon resonance either used independently or in combination are studied for the lysis of the cell wall. The single-cell lysates are then used as input for high-throughput single-cell RNA-Seq. This work will significantly enhance the current technologies and will enable generalized, cost-effective single-cell RNA sequencing in microbes at high throughput and therefore will be vital to advancing science from different fronts for applications in synthetic biology, environmental engineering, energy, and medicine.

SYMPOSIUM SB04

Hydrogel Materials—From Theory to Applications via 3D and 4D Printing
December 2 - December 6, 2019

Symposium Organizers
Namita Choudhury, RMIT University
Jurgen Groll, University of Wurzburg
Ferenc Horkay, National Institutes of Health
Marc In het Panhuis, University of Wollongong

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* Invited Paper
8:00 AM *SB04.01.01
Phase-Separating Biopolymer Conjugates in Designing Multicomponent Biomaterials Kristi L. Kiick; University of Delaware, United States

Microstructured hydrogels offer many opportunities in developing therapeutic matrices for guiding cell behavior. This presentation will outline our recent studies in formulating PEG- and (poly)peptide-based conjugates with nanoscale and microscale structures imparted by the controlled phase separation of multicomponent solutions. Resulting microstructured hydrogels can be manipulated on the basis of solution conditions and the composition of the polypeptide. The materials exhibit distinct microscale mechanical properties (1-15kPa) in ranges relevant for the development of synthetic pedicles for vascular grafts and high cytocompatibility over weeks in static and dynamic culture. Given our observations that the activation of fibroblasts and the differentiation of CD34+ stem cells can be directed in substrates with shear storage moduli in this range, our data suggest possible cell-materials platforms for modulating the activities of cells relevant in cardiovascular applications.

8:30 AM *SB04.01.02
3D-Extrusion Printing of Stable Constructs Composed of Polypeptide Hydrogels Robert Murphy and Andreas Heise; Royal College of Surgeons in Ireland, Ireland

The field of tissue engineering and regenerative medicine aims to regenerate damaged tissues rather than their replacement via the creation of well defined, surgically implantable biomaterial constructs. The development of defined three-dimensional (3D) architecture fabrication for tissue engineering has been a recent emergence within the field. In particular, 3D printing represents a promising rapid prototyping technology for the production of intricate bio-inspired scaffolds/constructs. The primary feedstock materials used are polymeric hydrogels, which possess ideal physicochemical properties for these rapid 3D patterning techniques. Hydrogels encompass the capability to augment native tissue due to their comparative 3D nano-architecture while holding the potential to act as a mimic of the extracellular environment. Recent work on 3D rapid prototyping with hydrogels has mainly focused on the use of natural polymers. Polysaccharides such as chitosan have been chemically functionalized and used as carriers within hydrogel inks. Recent reports also detail the fabrication of modified bio-native gelatin hydrogels which were 3D printed into cell laden constructs and self-healing structures respectively. More synthetic approaches have utilized poly(ethylene glycol) or acrylic monomer loaded inks. Despite these efforts, the limited number of suitable bio-inks has been identified as the major barrier to progress and the development of new advanced hydrogel applications.

We present a new family of copolypeptide based hydrogel ink capable of structural microfabrication using 3D extrusion printing. The material comprises an amphiphilic block or star copolymer structure which spontaneously form hydrogels through hydrophobic interaction. The chemical design allows the bulk phase of the hydrogel to remain intact after application of shear due to its self-recovery behavior. It is demonstrated that the composition of the materials is ideally suited for 3D printing; with scaffolds capable of maintaining structural cohesion after extrusion. Post extrusion UV-triggered fixation of the printed structures can be carried out resulting in stable hydrogel constructs. The constructs were found to be degradable, exhibited favorable release of encapsulated molecular cargo and did not affect the metabolic health of the commonly used fibroblastic cell line, Balb/3T3 cells. Moreover, the functionality of the amino acid building block allows the design of intrinsically antimicrobial constructs. In summary, the copolypeptide inks offer a new bioink platform that allow for rapid prototyping enabling the fabrication of defined intricate microstructures, providing a platform for complex scaffold development.

9:00 AM *SB04.01.03
3D Bio-Printed Platforms for Oral and Dental Diseases Stella Alimperti1,2; 1American Dental Association, United States; 2National Institute of Standards and Technology, United States

Traditional treatments for periodontal and dental diseases have severe limitations, including high-cost, non-efficient drug delivery, and aging. For example, patients who receive tooth and gum grafts are subject to lifelong side-effects,
such as increased rates of gum infections and oral malignancies. A solution to overcome these barriers is the integration of oral medicine and bioengineering within a single framework for potential translational and therapeutic purposes of dental diseases. Our lab focuses on identifying new biological targets involved in periodontal disease with the development of multidisciplinary tools, including organ-on-a-chip technologies, oral biology, and 3D printing technology. Our particular focus for today’s presentation is diabetes on oral health. Diabetes is a chronic, incurable disorder characterized by lack of resistance to insulin, leading to an excess of serum glucose, which negatively affects homeostasis of the oral epithelium [1,2]. Alterations or disruptions of the epithelial integrity can ultimately result in chronic inflammation and periodontal disease. We engineered a 3D platform to deconvolute the dynamic contribution of epithelium in diabetic periodontitis. The in-vitro disease epithelium model is a 3D printed microfluidic platform that is comprised of 3D cylindrical channel (diameter 160 µm) embedded within different stiffnesses (0.1kPa, 1kPa, 10kPa) of hydrogel solution of collagen I. Human oral keratinocytes (HOKs) were seeded and allowed to adhere through the collagen I wall. The epo-oral tube was exposed to 11 nmol/ml glucose to mimic diabetic conditions compared to control, 4 nmol/ml glucose under different stiffnesses. In addition, we introduced a pro-inflammatory stimulus into the 3D bio-printed platform, named lipopolysaccharides (LPS) (100 ng/ml) for 1hr. The diffusion of fluorescent dextran (70 kDa Texas Red, Thermo Fisher) (12.5 μg/mL) was imaged in real time with a confocal microscope (LSM 800, Carl Zeiss). The diffusive permeability coefficient ($P_d$) was calculated by measuring the flux of dextran into the collagen gel and fitting the resulting diffusion profiles to a dynamic mass conservation equation [3]. The $P_d$ was increased dramatically in LPS treated diabetic conditions compared to non-diabetic ones. Finally, LPS treatment increases FOXO1 translocation in diabetic HOKs. Collectively, the 3D bioengineered micro-platforms substantially provide insights on periodontitis area by developing sophisticated approaches, based on the 3D printing and organ-on-a-chip technology, avoiding the limitations of the 2D standard cell culture and enabling us to approach potential efficient treatments for periodontal diseases.

9:30 AM BREAK

10:00 AM *SB04.01.04
3D Printing of Transparent and Conductive Heterogeneous Hydrogel-Elastomer Systems Joost J. Vlassak; Harvard University, United States

Interest in stretchable electronics has grown significantly in recent years, driving a need for soft and stretchable materials that can sustain high strains and still fulfill their function in applications such as wearable sensors for health monitoring or feedback sensors in soft robotics. Many stretchable conductors exist including liquid metals, nanowires, and micro-cracked metals. Conventional strategies of incorporating hard components with soft elastomers to attain stretchability often lead to failure of the hard-soft material interface and limited stretchability. The use of gels as soft conductors, where ions are the charge carriers instead of electrons, represents an entirely different approach that has gained popularity recently. Their high stretchability, when combined with recent improvements in toughness and stiffness, enable their use as stretchable electrical conductors, capacitive strain sensors, and chemical/pH sensors. Gel-based ionic circuits thus represent a unique class of devices within stretchable electronics. Fabrication of stretchable electronics using hydrogels requires integrating hydrogels with stretchable dielectrics such as dielectric elastomers; a process thus far achieved primarily via the combination of several different manufacturing techniques. We have developed an extrusion printing technique capable of fabricating an ionic circuit that integrates a LiCl-doped poly(acrylamide) (PAAm) hydrogel with a poly(dimethylsiloxane) (PDMS) dielectric elastomer. By incorporating hygroscopic salts such as LiCl into the hydrogel, we are able to prepare an ionically conductive hydrogel with excellent water-retaining properties. For printing reliability, we have optimized the rheological properties of a high ionic-strength hydrogel precursor using a nonionic rheological modifier. We show that the adhesion between oxygen plasma-treated PDMS and hydrogel increases with time to reach a stable value of 15 J m$^{-2}$ after approximately six days. During that time, the contact angle of water on the PDMS interface remains constant at 30°, suggesting that hydrophobic recovery of plasma-treated PDMS is suppressed by the presence of the hydrogel. Furthermore, a thin viscous layer develops at the interface between PDMS and hydrogel, which results in energy dissipation upon debonding and which allows full recovery of the adhesion after debonding and rejoining. Finally, we demonstrate the viability of silane coupling agents to further enhance the adhesion between PDMS and hydrogel. By introducing a charge-neutral surfactant in the PDMS and adjusting silane concentrations in the PAAm, interfacial adhesion can be increased to the point that the system fails by cohesive failure within the hydrogel, achieving toughness values of up to 193 J m$^{-2}$ for a fully printed PAAm hydrogel-on-PDMS bilayer. This result suggests that an integration strategy with silane coupling agents may enable robust extrusion printing of a wide variety of hydrogel and silicone elastomer chemistries.
Stereolithographic 3D Printing of Self-Adhesive Double Network Hydrogels for Soft Actuators and Microfluidics

Thomas M. Valentin, Eric DuBois, Catherine E. Machnicki, Dhananjay Bhaskar, Francis R. Cui and Ian Y. Wong; Brown University, United States

Hydrogel building blocks that are stimuli-responsive and self-adhesive could be utilized as a simple “do-it-yourself” construction set for soft machines and microfluidic devices. However, conventional covalently-crosslinked hydrogels are unsuitable since they are as static materials with poor interfacial adhesion. Here, we demonstrate ion-responsive interchangeable parts based on composite hydrogels that incorporate both covalent and ionic crosslinking. We use light-directed 3D printing to covalently-crosslink poly(ethylene glycol) diacylate in the presence of anionic poly(acrylic acid) of much higher molecular weight. The addition of trivalent cations acts to crosslink the anionic polymer chains together. Using high cation concentrations drives strong crosslinking, which can result in dramatic hydrogel contraction. Mismatched contraction of layered ion-responsive and non-ion-responsive hydrogels can control bending and twisting actuation, which is utilized for a gripping device. Alternatively, moderate cation concentrations permit strong self-adhesion between hydrogel surfaces. LEGO-like hydrogel blocks with internal channels and external mechanical connectors can be stacked into complex microfluidic device geometries including serpentine micromixers and multilevel architectures. This approach enables “plug-and-play” hydrogel parts for ionic soft machines that mimic actuation, sensing, and fluid transport in living systems.

3D Printing of Biocompatible and Structurally Relevant Hydrogel Scaffolds for Articular Cartilage Tissue Engineering

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Osteoarthritis (OA) is a disease that affects more than 30 million adults in the US, posing a huge economical burden and adversely affecting people’s lifestyle. It is the hallmark of the degradation of Articular Cartilage (AC) lining moving joints, due to systemic, genetic, and injury related causes. One of the most prevalent types of OA is knee OA. Knee OA can cause enormous pain and discomfort and may lead to disability. No current single efficient treatment exists for knee OA. The disease is managed through pain killers, anti-inflammatory drugs, hyaluronic acid injections, and eventually a total knee replacement (TKR). Tissue Engineering (TE) offers an alternative route that is potentially capable of managing or treating OA while avoiding the limitations associated with OA’s traditional treatment routes. In TE, cells are seeded on a scaffold and grown in a bioreactor under a controlled environment in vitro. Ideally, the bioreactor is supplied with nutrients and built to mimic the mechanical shear stress, compression and oscillation pressures present in the knee. The product of interest of a TE approach is a functional AC tissue that mimics the native one in structure and function. AC has a unique structure that consists of three different zones (superficial, intermediate, and deep). Each zone is characterized by its own cellular and protein composition, fibrillar alignment, porosity and mechanical strengths. The variations in the zonal properties allow each zone to serve a specific AC function including lubrication and loadbearing. To our knowledge there is no current AC tissue engineered that mimics the native AC in structure and function. In a step towards replicating the AC unique zonal structure, we hypothesize that a structurally relevant scaffold that mimics the gradated anatomy of the native AC will guide the chondrocytes to create a native-mimicking tissue that can be used as an alternative to traditional cartilage grafts. Onto test our hypothesis, a biocompatible, biodegradable, and structurally relevant graded scaffolds in composition, porosity and mechanics will be fabricated using 3D printing and optimized via testing in a bioreactor for appropriate AC growth. Our scaffolds are hydrogels consisting of Gelatin (GEL), Gum Arabic (GA), and Sodium Alginate (SA) mixed in different concentrations and crosslinked by cooling, Calcium Chloride (CaCl2), 1-Ethyl-3-(3-dimethylaminopropyl)-carboidiimide (EDC) and N-Hydroxysuccinimide (NHS) respectively to achieve a mechanically stable structure. To print the scaffold, we have modified the commercial 3D bioprinter BioX from Cellink with a pressure amplifier and a home-made software control to achieve high printing pressure and time-efficient printing of scaffolds with different printing parameters. With that, we have been able to 3D print scaffolds with line width as fine as 250 µm using a 100 µm nozzle and a pressure of 700 kPa at room temperature using the hydrogel composed of (8.2% GA, 4.2% GEL, 8.2% SA). When bovine chondrocytes were cultured on the hydrogels for 14 days, they were viable. Biochemical assays confirmed that the cells with their pre-mature tissue expressed...
AC-specific biomarkers such as glycosaminoglycan (GAGs) and total collagen. To improve on our current findings, ongoing work aims at characterizing the ultimate tensile strength, elastic modulus, and hardness of the structural scaffolds using a universal testing machine. We hypothesize that the resulting AC tissue will have better native-mimicking AC structure and function when the mechanical properties of the scaffold mimics those of the native AC ECM properties. Ultimately in the future, the 3D printed structural scaffold combined with cell-laden hydrogels will be grown in a unique centrifugal bioreactor to create a mechanically and biologically native-mimicking AC tissue.

11:00 AM SB04.01.07
A Mechanically Enhanced Electroactive Hydrogel for 3D Printing Using a Multileg Long Chain Crosslinker
Yong-Woo Kang, Jaesung Woo, Hae-Ryung Lee and Jeong-Yun Sun; Seoul National University, Korea (the Republic of)

Electroactive hydrogels (EAHs) are receiving attention in soft robotics. 3D printing makes EAHs even more attractive, due to the diversification and elaboration of actuations. However, 3D printing needs a large amount of photoinitiator for faster printing, which makes the printed hydrogels so brittle that they cannot produce large scale 3D printing. Here, we developed a 3D printable EAH based on poly(3-sulfopropyl acrylate, potassium salt) (PSPA) using glycidyl methacrylated hyaluronic acid (GMHA) as a mechanically enhancing multileg long chain (MLLC) crosslinker. The MLLC crosslinking improved the stretchability of the PSPA-based hydrogel to 49% from 28%, while maintaining the same level of electroactivity. Additionally, the fracture toughness of the PSPA-based hydrogel remarkably increased from 11 J/m² to 40 J/m² with crosslinking by the MLLC. Using the mechanically enhanced EAH, i.e., the GMHA-PSPA EAH, the 3D printing of elaborate structures, e.g., ‘Leaning Tower of Pisa’ and a hand, and their electroactuation were successfully demonstrated.

11:15 AM SB04.01.08
3D Printing of Programmable Microbial Hydrogels
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Over the years, 3D printing technology has witnessed the development of numerous inks and bioinks for various applications. Bioinks are especially challenging as it requires biocompatibility, resembling microenvironment that favors cellular viability/adhesion, adequate mechanical properties and the capabilities for chemical/photochemical functionalization. Building on these characteristics and advances, herein, we present programmable living inks comprising of microbial hydrogels. Our innovative strategy provides unprecedented control on the characteristics of the ink as well as the ability to systematically regulate the microbes embedded in the 3D patterns.

11:30 AM SB04.01.09
Nanoscale Hydrogel 3D Printing with Focused Electron Beam
Andrei A. Kolmakov¹, Tanya Gupta¹², Glenn Holland¹, Evgheni Strelcov¹², Joshua Schumacher¹, Yang Yang¹², Mandy Esch¹ and Vladimir Aksyuk¹; ¹National Institute of Standards and Technology, United States; ²University of Maryland, United States

Additive manufacturing of hydrogel scaffolds has become the key technology for tissue engineering, soft robotics, biosensing, drug delivery and biomedical research in general. The progress in the field has been advanced via development of special polymerization initiators coupled with modern additive manufacturing techniques. The current state of the art 2-photon, and stereolithography curing techniques allow for 3D printing of submicron scale hydrogel features. Further advancement in printing time and resolution could be envisioned by using curing radiation with shorter wavelength and larger crosslinking cross-section. Despite of highly developed electron, ultraviolet and X-ray lithography of dry polymers to pattern nanoscopic features, 3D printing from liquid hydrogel precursor solutions is hard to realize due to vacuum incompatibility of liquid samples. In this work we resolve this “pressure gap” impediment and demonstrate a technique for in-liquid hydrogel 3D-sculpturing using fluidic enclosures equipped with electron transparent windows. The principle of the technique, details of the curing mechanism and factors affecting the ultimate feature size (resolution), are described and validated through the comparison of experiments and simulations. The potential of this technique is demonstrated on few selected examples such as live-cell encapsulation, synthesis of nanocomposite hydrogels and microfabrication of mesoscopic 3D-hydrogel structures.
Matrix Assisted 3D Printing of Cellulose Nanofiber Hydrogels Sungchul Shin and Jinho Hyun; Seoul National University, Korea (the Republic of)

In the matrix assisted 3D printing, rheological properties of materials are of importance for the formation of highly resolved structures. The concentration of hydrophobically modified-CNF (Hphob-CNF) and hydrophilic-CNF (Hphil-CNF) hydrogels was fixed at 1%, and petroleum jelly was mixed with liquid paraffin at a ratio of 3:1 for the 3D printing. The viscosity change of hydrogels and petroleum-jelly ink showed a shear thinning behaviour, which was an important parameter for the easy extrusion of ink in direct ink writing. The Hphob-CNF hydrogel continued to show a high colloidal stability without any stabilizer as the Hphil-CNF hydrogels showed. It is considered that the viscosity of CNF hydrogels is mainly determined by the aspect ratio of fibers, the number of ends and the branch of fibers rather than the surface property of high aspect ratio of nanofibers. The sol-gel transfer properties of Hphob-CNF matrix and Hphil-CNF ink exhibited elastic properties over a wide range of shear stress, making it very useful as a printing matrix and a printing ink. Channel forming petroleum-jelly ink also showed the elastic properties confirming the stability in printing. The applicability of the CNF hydrogels embedding microchannels will be introduced in the presentation.

Granular Hydrogels for Biomedical Applications Jason Burdick; University of Pennsylvania, United States

Hydrogels represent a class of biomaterials that have great promise for the repair of tissues, particularly due to our ability to engineer their biophysical and biochemical properties. Hydrogels can provide instructive signals through material properties alone (e.g., mechanics, degradation, structure) or through the delivery of therapeutics that can influence tissue morphogenesis and repair. In recent years, we have transitioned from traditional hydrogels to granular hydrogels that are comprised of smaller hydrogel units (i.e., microgels). Granular hydrogels have advantages in that they can be designed through heterogeneous microgels to introduce complexity to the material, they support cell invasion through the space between microgels, and they can be packed together to act as solids that can be easily extruded through a syringe.

Here, I will give examples of the design and use of granular hydrogels based on hyaluronic acid for use as injectable therapeutics, as well as in 3D printing. Microfluidic devices are used to fabricate the microgels using photoinitated thiol-ene reactions or radical polymerizations for intraparticle crosslinking where crosslinkers can be stable or responsive to local proteases. For cardiac therapeutics, we injected heterogeneous granular hydrogels into the myocardium and showed selective microgel degradation to release factors and introduce porosity for cellular ingrowth. In 3D printing, we jammed together microgels to form shear-thinning and self-healing hydrogels that could be printed either onto surfaces or within other hydrogels. These could be cell-laden or stabilized where necessary with secondary crosslinking. Most recently, we designed these granular hydrogels to be conductive, through an in situ metal reduction process of silver onto microgels and then jamming into solids with high conductivity due to increased surface area when compared to traditional hydrogels. The conductive granular hydrogels were shown to influence electrical tissue bridging in muscle defects and could be 3D printed into conductive lattices. Overall, the granular hydrogel design opens up new opportunities in the design of functional hydrogels in biomedical applications.
response to the implant and development of bacterial biofilms. A multifunctional surface coating that can address all these two issues concomitantly would significantly improve clinical outcomes. We hypothesized that polyarginine (PAR), a synthetic highly cationic polypeptide, can act on macrophages to control innate immune response because arginine is an important component of macrophage metabolism. Moreover, PAR is susceptible to act as an antimicrobial agent due to its positive charges. We developed a new polyelectrolyte multilayer film based on PAR and hyaluronic acid (HA). The layer-by-layer PAR/HA films have a strong inhibitory effect on the production of inflammatory cytokines released by human primary macrophages subpopulations [1]. This could reduce potential chronic inflammatory reaction following implantation. Next, we show that PAR/HA films were very effective to inhibit Gram-positive and Gram-negative pathogenic bacteria associated with infections of medical devices [2] [3]. We demonstrate that exclusively films constructed with poly(arginine) composed of 30 residues (PAR30) acquire a strong antimicrobial activity. Moreover, changing HA by another synthetic or natural polyanion did not provide any more antimicrobial activity. HA is a key component of the system and the mechanism behind this property has been elucidated. The cytocompatibility of the PAR/HA films was assessed with several cell types playing a major role in tissue regeneration. This system can also be fabricated in the form of hydrogel, useful to provide antibacterial properties to porous implants like surgical meshes. In this case, a precise controlled release can be achieved with strong efficiency over multi-infections. Recent developments to render these systems smart and responsive have also been made to obtain a release and activity only when bacteria are closed to the implants.


2:30 PM SB04.02.03
In Vitro Hair Shaft Generation from 3D Cell Aggregate for Hair Regenerative Medicine Rikuma Nakajima1, Akihiro Shimizu1, Tatsuto Kageyama1,2 and Junji Fukuda1,2; 1Graduate School of Engineering, Yokohama National University, Japan; 2Kanagawa Institute of Industrial Science and Technology (KISTEC), Japan

Hair loss is a common concern among numerous individuals. Hair regenerative medicine has recently been attracting attention as a promising treatment approach for hair loss. Hair follicle morphogenesis is triggered by interactions between epithelial and mesenchymal germ layers during embryogenesis, and various approaches for fabricating tissue grafts by recapitulating such interactions in vitro have been examined in the past decade. Since thousands of tissue grafts are necessary for a single patient, approaches for fabricating tissue grafts should be scalable. Herein, we fabricated a microwell array device with oxygen-permeable poly(dimethylsiloxane), wherein epithelial and mesenchymal cells spontaneously formed hair follicle germ (HFG)-like cell aggregates in 3 d of culture. This approach was scalable and >5,000 HFGs were prepared simultaneously by simply seeding the two types of cells and culturing them for 3 d in the device (T. Kageyama et al. Biomaterials, 154, 291-300, 2018). This approach is simple and robust. However, there are still certain issues, including further improvement of hair regeneration owing to the low hair regeneration efficiency when patients’ own cells are employed.

In this study, we propose an approach to screen HFGs based on their hair regeneration potential. HFGs generated herein produced hair shafts in vitro, which sprouted from the HFGs at 12 d of culture and reached ~200 µm in length at 23 d of culture. However, only less than 1% of HFGs (a few/300 HFGs) generated hair shafts. Thus, we optimized culture conditions and found that supplementation of an extracellular matrix hydrogel, Matrigel, significantly increased hair shaft generation. HFGs exposed to Matrigel generated hair shafts at 4 d of culture, which then ~1,400 µm in length at 17 d of culture. Moreover, the efficiency of regeneration was significantly increased (~90%, 275/300 HFGs). Scanning electron microscopy and transmission electron microscopy revealed that the hair shafts have typical morphological features including hair cortices, hair cuticles, melanosomes, and micro-fibrils. HFGs producing hair shafts at 6 d were selected and transplanted into the dorsal and scalp skin regions of nude mice. The hair generation efficiency was 85.4%, which was significantly greater than that of HFGs generated using our previous approach without pre-screening (i.e., 65.0%). The present approach may provide a better strategy for hair regenerative medicine.

2:45 PM SB04.02.04
Zapping Bacterial Infection with a Fast Setting Biodegradable Hydrogel Daniela Vieira, Samuel Angel, Edward Harvey and Geraldine Merle; McGill University, Canada

Wound infections have been a major challenge especially for military medicine. As the care of casualties continues to enhance survival rates, infectious complications will remain a major cause of morbidity. When bacteria biofilm sus
formed at the wound site, the infection is significantly more difficult to treat, increasing the healing time and the cost of the treatment. Conventional way of treatment is surgical debridement combined with antibiotics to prevent the growth of bacteria in and around wound before infection is established. Because of the misuse and overuse of antibiotics more than 50% of the bacteria are resistant to standard antibiotics. Bacterial resistance has become a serious global problem with a morbidity up to 45% in developing countries. Additionally, antibiotics often have serious negative effects on normal bodily functions. Given these challenging concerns, new strategies to treat bacterial infection are necessary. The use of antimicrobial peptides, polysaccharides and other antimicrobial components are an alternative. However, they are also hemolytic, toxic and easy to lose efficacy. Using electrical current (EC) to break down and destroy bacterial biofilms has been investigated for several years. Our concept is based on targeting the bacteria synergistically on various fronts. The impact of EC associated with antibacterial materials may be more significant. In this work, we designed a bioresorbable hydrogel free of antibiotics able to combat antibiotic resistance and help heal infected wounds. We synthesized an injectable biodegradable hydrogel based on silk fibroin (SF) and silver nanoparticles (Ag-NP) capable of fast setting, transporting EC and killing bacteria. SF solution was prepared following Rockwood protocol. This biocompatible and biodegradable natural polymer contains some tyrosine motifs, which reduce silver ions (Ag+) into Ag-NP with great toxicity against diverse bacteria. Sequentially, AgNO3 was added, mixed and exposed 24 h to incandescent light at room temperature. SF hydrogel and Ag-NPs exhibit an excellent conductivity of 1.2 S cm⁻¹, allowing the electrons to flow. Different conditions were performed to evaluate cytotoxicity and bacteria viability. First, as a control, just cell or bacteria (C/B). Second, C/B in contact with hydrogels (t= 60s). Third, C/B in contact with EC (1mA/60s). And finally, our approach, C/B in contact with the hydrogels combined with EC (1mA/60s). Hydrogels were removed right after from the medium. There is no toxicity on CHO mammalian cells treated with hydrogels or EC, separately or combined. In contrast to the effect in cells, the proposed work has a significant toxicity on E. Coli. Only hydrogels have no significant effect on bacterial killing, and further for EC, with 12.9% and 8.6% of death, respectively. However, the combined effect produced 77.8% of dead bacteria. In order to analyze these effects, Ag⁺ release, and ROS (oxygen species) generation was performed. Treatments with hydrogels and the combined effect presented similar Ag⁺ release, 21.94 ± 2.21 ppm and 19.59 ± 3.32 ppm, respectively. It is not the main cause of bacterial toxicity. However, for ROS generation, a difference of 50% was found between treatments, showing an interesting contribution of EC to produce ROS. Ag-NPs are able to generate ROS, and combined with EC, its ability increased, being more efficient. Furthermore, bacteria require extracellular electron acceptors to realize electron transport in its respiratory chain. Thereby, we believe these hydrogels have an electron extraction ability. It means, it may form a circuit to electron transfer, causing an extraction of electron from the bacteria membranes. Eventually, it causes membrane disruption and, consequently, the bacterial death. These results are promising and unprecedented in literature.

3:00 PM BREAK

3:30 PM *SB04.02.05
Bioinspired Elastin-Based Adhesives for Surgical Glue Applications Julie C. Liu; Purdue University, United States

A successful biomedical adhesive must be biocompatible, set in a wet environment, match the mechanical properties of the surrounding tissue, and have proper adhesive and cohesive properties. Current technologies do not meet these needs. We developed bioinspired protein-based adhesives that combine adhesion from DOPA residues found in mussel adhesive proteins with the mechanical properties of elastin, which can also coacervate in response to the environment. We demonstrated that these proteins are cytocompatible, provide the strongest bonds of any rationally designed protein when used completely underwater, and can be easily applied underwater because they coacervate in physiological conditions. Recently, we investigated different formulations and crosslinking chemistries in physiologically relevant environments by using pig skin substrates and curing in a warm, humid environment.

4:00 PM SB04.02.06
Bioinspired Self-Healing Protein Materials Abdon Pena-Francesch¹, Huilun Jung², Melik Demirel² and Metin Sitti¹; ¹Max Planck Institute for Intelligent Systems, Germany; ²The Pennsylvania State University, United States

Recent research efforts have focused on developing soft, flexible, compliant materials for medical robotics, biointerfacing, and biosensing applications, with properties matching those of biological tissue. Because of their intrinsic softness, these materials are susceptible to cut, puncture, scratch, and/or tear damage that compromises the
physical integrity of the device/interface. Soft self-healing materials offer a solution to this challenge and improve the long-term reliability, although many of the commonly explored self-healing chemistries are not biocompatible and are time-consuming (long healing times). To overcome these problems, we present biocompatible synthetic protein-based materials, inspired in squid proteins, that self-repair microscopic and macroscopic damage within seconds. The self-healing mechanism relies on the formation of reversible physical crosslinks in an elastomeric protein network. The healing process takes place in physiological conditions and the mechanical properties are recovered after healing. Furthermore, the protein material can be functionalized with biomolecules such as enzymes that maintain their activity after several healing cycles. These protein-based self-healing materials find applications as adaptive actuators for soft robotics, dependable biosensing platforms, and protective textiles against chemical and biological warfare agents.

4:15 PM SB04.02.09
pH Triggered Drug Release from Hydrogel Layers Integrated in Magnetically Controlled Microdevices
Roberto Bernasconi¹, Bradley Nelson², Salvador Panè², Marinella Levi¹, Filippo Rossi¹ and Luca Magagnin¹; ¹Politecnico di Milano, Italy; ²ETH Zürich, Switzerland

Two of the most crucial topics in modern medicine are medicines administration routes and their relative pharmacokinetics inside human body. The largest part of conventional drug delivery methodologies, like absorption through the gastrointestinal tract or intravenous injection, are generally based on the non-selective distribution of the active substance in the whole body, mediated by blood circulation. With these delivery methodologies, however, most of the drug reaches non-target parts of the body. This implies that higher dosages must be provided to reach the optimal concentration in the target organ, lowering administration efficacy and amplifying drug side-effects.

To overcome these problematic issues, advanced administration strategies based on targeted delivery have been recently developed [1]. More specifically, drugs are released in controlled amounts only in correspondence of the target organ. This approach requires a superior temporal and spatial control over release, which is challenging to achieve. A possible solution to control drug delivery timing can be the use of stimuli responsive polymers [2], which can release therapeutic drugs under the influence of an external stimulus (thermal, chemical, …). By employing this class of advanced materials, medicines can be released upon request and with controlled rates. Conversely, to allow spatial control, a possible key can be the use of magnetically controlled microrobots [3]. These microdevices are able to perform different tasks in-vivo, including for example cell transport [4] and medicine delivery applications [5]. For the latter, they can be covered with drug releasing materials and wirelessly guided inside human body to perform administration only in close proximity of the target organ. Moreover, magnetic field is harmless for humans, allowing a limited invasivity of the microrobots in conjunction with a great manipulation precision.

In this context, we describe the realization of magnetically guidable microdevices integrating a hydrogel layer specifically tailored to perform pH triggered drug release. The microdevices are characterized by a microporous structure, which increases hydrogel loading capability and that is obtained employing additive manufacturing. More specifically, we employ microstereolithography, a highly scalable and flexible 3D printing technique able to yield micrometric sized objects at relatively low cost. To allow magnetic actuation, a CoNiP layer is applied by mean of wet metallization on the 3D printed devices. The same technique is employed also to deposit a gold layer to make the surface biocompatible. Finally, the micropores are filled with an alginate hydrogel modified with click chemistry, in which the drug is binded to the biopolymer chains by mean of a pH cleavable bond. In this way, release takes place only when the device reaches the part of the body presenting the correct pH range. An example of possible application may be drug release in well-defined zones of the gastrointestinal apparatus, which is characterized by different pH levels according to the tract considered [6].


4:30 PM SB04.02.07
Piezoionics as a Mechanism for Sensing in Gels
Yuta Dobashi¹,², Yael Petel², Dickson Yao², Carl Michal² and
Hydrogels have been shown to be effective as transparent electrodes in pressure and touch sensors, forming “ionic skin”. Interestingly, the gels themselves also generate voltage when they are deformed. An ionic sensing effect has long been known in cartilage tissues in which counter ions that balance the charged collagen backbone are redistributed when pressure is applied. In this work, we propose a new mechanisms in which voltage arises from differential rates of ion motion within the gel when pressure gradients are applied. Fluid flow is generated within pores that are so small that ions experience additional drag. Some ions move more slowly than others, leading to voltage generation that is typically in the tens of millivolts.

In this work, we report on our investigation of pressure-induced ion redistribution and electric field generation arising due to differential cationic and anionic mobilities in solid polymer electrolytes. An organic phase solid polymer electrolyte was synthesized by a solution-casting technique using lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), propylene carbonate (PC) and Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). The PVDFHFP/PC/LiTFSI gels of varying concentrations (0.1 M ~ 3 M) were subjected to mechanoelectrical transduction tests and the magnitude of generated potentials were recorded. Subsequently, diffusion NMR (pulsed field gradient spin echo) was performed on the polymer electrolytes to determine the self diffusion coefficients of the lithium and TFSI ions. The results revealed that the signs of the voltages generated were largely determined by the ion of higher diffusivity. Subsequently, the mechanotransduction was numerically modelled by coupling Darcy’s flow velocity to the convective flux of the ions, and subsequently computing the Nernst Planck equation. The equation was modified such that for each transport coefficient (diffusion, convection, and electrophoretic), hindrance factors were imposed representing the slowing of each ionic species by the presence of the polymer matrix. The hindrance is relative to solvent flow through the pores in the case of convection, and relative to bulk solution in the case of diffusion. Using measured the ionic diffusion coefficients and the Darcian permeability as the inputs, and using the hindrance factors as fit parameters, the observed mechanotransduction effect is largely in agreement with measurements.

We further show that these sensors, which, like piezoelectrics, do not require any external power beyond the induced mechanical deformation, can readily be formed into sensor arrays. They produce sufficient voltage and current to stimulate nerve and muscle activation – a possible area of application.
We demonstrate that by optimising the chrysophenine doping levels, the actuation strain can be increased to 17%. This is far in excess of analogous systems, e.g., 2-hydroxyethylmethacrylate, ethylene glycol-dimethacrylate copolymers equilibrated in a 0.4% chrysophenine solution displayed photo-actuated strains of under 1% [6]. Moreover, regardless of the fibres’ cross-sectional area, the hydrogel could be stretched up to 4 times its initial length. In conclusion, we demonstrate the successful fabrication of single fibre photo-actuators which amplify the molecular interactions between chrysophenine and the tough PU-PAA IPN, achieving spatiotemporal independence and control.


SB04.03.02
Double Covalent Network—3D Printing of Customized, Complex Hydrogel with Hyper-Elastic, Self-Adhesive and Shape Memory Effect Lei Zhang; Northeastern University, United States

Double covalent network hydrogels have attracted extensive attention as an innovative material having both high-water content and extremely high mechanical strength. 3D printing has revolutionized the way products are developed and customized, as satisfied with the integration of the complex structure and multiple-functions. Here, based on the classical PAMPS/PAAm double network strategy, a new 3D printing method, combined with nanocomposites enhancing mechanism and self-polymerized dopamine modification, is presented for customizing the complex double covalent network architectures.

Double network gels are characterized by a special network structure consisting of two types of polymer components with opposite physical natures: the first component is abundantly cross-linked polyelectrolytes (rigid skeleton) and the second component comprises of poorly cross-linked neutral polymers (ductile substance). The synthesis orders and process are vital to realizing their excellent mechanical performances which comparable to that of rubbers and soft load-bearing bio-tissues. However, tough mechanical feature and the unique crosslinking process make double network gel interesting and challenging on the developing in customization of 3D architectures. Thus, this work reported a simple yet versatile method for establishing a fair balance between the dopamine polymerization and second covalent crosslinking network together with the doped-nanoparticles, which makes the double covalent network hydrogel into the customized, complex 3D architecture with hyper-elastic, self-adhesive, fatigue resistance and shape memory effect. This strategy could potentially expand double network gel’ application in fashion, medical devices, human tissue replacement and engineering.

SB04.03.03
Synthesis, Characterization and Antimicrobial Measurement of BSA Conjugated Silver Nanoparticle Filled Hydrogel Nanocomposite Berhanu Zewde, Olufolasade Atoyebi, Ayele Gugssaa and Dharmaraj Raghavan; Howard University, United States

Nanocomposite hydrogels is attracting significant interest due to their potential use in implants, drug delivery systems, and tissue design scaffolds. This paper reports about the synthesis of precursors (tetrazine-modified polyethylene glycol and norbornene-modified hyaluronic acid) to form crosslinked hydrogels and hydrogel nanocomposite. Click chemistry of precursors in combination with in situ encapsulation of preformed Bovine Serum Albumin (BSA) conjugated silver nanoparticles (Ag/BSA) yielded nanocomposite hydrogel. 1H-NMR of
norbornene-modified hyaluronic acid and tetrazine-modified polyethylene glycol showed characteristic peaks for the vinylic protons of the endo and exo configuration of norbornene and tetrazine unit as well as PEG chains of tetrazine-modified polyethylene glycol, respectively. The Ag/BSA nanoparticles in the nanocomposite, were well dispersed as revealed by SEM and TEM, and were 20-30 nm in size. By TGA analysis, the percent of silver in the nanocomposite was established to be 2%. The interaction between the nanoparticles and the hydrogel was demonstrated by studying the shift in OH peaks of hydrogel via FTIR, changes in binding energy of O1s peak in XPS and measuring the desorption of nanoparticles from the hydrogel nanocomposites of various crosslinked system by AAS. Unlike native hydrogel, the hydrogel nanocomposite showed good antibacterial activity against gram positive/gram negative bactericides, and the loading of nanoparticles had a strong bearing on the extent of antibacterial activity.

SB04.03.04
Self-Restorable Adhesive Hydrogels Synthesized Using Poly(N-vinylpyrrolidone) and Tannic Acid via Supramolecular Assembly

Myeong-gyun Nam1, Hyeon-Gyun Nam2, Ji-heung Kim1 and Piljin Yoo1;
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Supramolecular assembly and complexation is a powerful method to impart new functionalities to various organic compounds and is extensively used in biomedical, energy, and surface coating applications. Especially, when strong molecular interactions are exerted simultaneously, interacting molecules suffer the gelation by internal cohesive bonding, triggering a pseudo-crosslinking effect forming a supramolecular gel. Among various substances inducing supramolecular assembly, phenolic substances, e.g. 3,4-dihydroxy-L-phenylalanine (DOPA), are tremendously applied for adhesive materials owing to abundant hydroxyl groups driving supramolecular assembly via hydrogen bonding. However, in spite of the strong adhesive property of monomeric phenol, it is deficient to induce cohesive strength, resulting in rarely forming a supramolecular gel to secure its mechanical properties. Herein, to overcome this drawback, we realized a supramolecular coacervate hydrogel through simple mixing process of poly(N-vinylpyrrolidone) (PVP) and tannic acid (TA), resulting in internal cohesive interactions by virtue of the large molecular size of TA compared to monomeric phenols and enhanced molecular interactions triggered by a tremendous number of galloyl groups with a high density. Additionally, we tried to analyze the rheological and adhesive properties of PVP-TA coacervate hydrogels. Interestingly, on various substrates, remarkably high adhesive property is shown by PVP-TA hydrogel with abnormal self-healing property against extreme deformation. In detail, average adhesion strength of PVP-TA hydrogel shows 3.71 MPa on a glass substrate, which is 4 – 5 times stronger than that of conventional PVP.

SB04.03.05
A Novel Self-Healing Hydrogel with Stretchable, Conductive and Super-Adhesion

Yimeng Wang, Jing Peng and Maolin Zhai; Peking University, China

Multifunctional and adhesive hydrogels show excellent potential for multifarious applications, such as tissue adhesives, sealants, and implantable electronic devices, but most of them still suffer from poor reusable performance, high synthesis complexity, and low conductivity when facing to electronic device adhesives. Herein, based on a fully physical crosslinking network, a novel self-healing hydrogel (named GO,SPNB) with various ratios of graphene oxide (GO) to soluble starch and polyelectrolyte poly(sodium 4-vinylbenzenesulfonate-co-(3-(methacyroyloxy)ethyl)-N,N-dimethylbutan-1-aminium bromide) (PNaSS-co-MOBAB) was synthesized successfully by a simple one-pot γ-ray radiation-induced polymerization. Due to the multi-physical crosslinking network inside the hydrogels among GO, starch and PNaSS-co-MOBAB polymer, such as electrostatic interactions and hydrogen bonds, the resultant nanocomposite hydrogels exhibit fast automatic self-healing ability. In the meantime, the obtained hydrogels show super stretchable ability, non-toxicity, and ionic conductivity about 10.5 mS dm⁻¹. With high adhesive components such as soluble starch and acrylate derivatives inside, it was also endowed with super adhesion to various substrates, including solid materials and biological tissues. For example, the adhesion strength to the copper plates was about 60.5 MPa at room temperature, nearly one magnitude larger than other reversible adhesives that have been reported. Considering the facile preparation and all the advanced properties, the procedure provided here opens up a promising avenue to develop multifunctional hydrogel glues for design and fabrication of smart electronic device adhesives.
SB04.03.06
Design of Tunable Multicolor Fluorescent Materials as Strain Sensors Dong Zhang, Jie Zheng, Yanxian Zhang, Yonglan Liu, Shaowen Xie and Li Tang; The University of Akron, United States

Development of tunable multicolor fluorescent materials is important but challenging for fundamental research and practical applications. In this work, a series of trichromic (blue, green, and red), fluorescent polymers are synthesized by covalently copolymerizing spiropyran-based, naphthalimide-based, and pyrene-based monomer onto hydrophilic poly(acrylic acid-co-acrylamide) chains separately. Due to the dynamic fluorescence resonance energy transfer process between electron donors and acceptors, the tunable rainbow-color fluorescent polymer films and polymer solutions can be effectively fabricated by simply mixing and blending monochrome copolymers. Interestingly, utilizing the abundant carboxyl groups in the macromolecular chains, the thin fluorescent polymer films can also form physical hydrogels in a single step through carboxyl-Zn$^{2+}$ coordination. Furthermore, such dynamic physical cross-linked hydrogels could also be easily loaded onto complex electric driven devices, achieving organic combination of fluorescent hydrogels and actuators based on reversible sol-gel transition. Ultimately, we demonstrated a new strategy to enhance mechanical properties by embedding this mechanically weak fluorescent gel into a brittle alginate hydrogel shell via metal ion (Zn$^{2+}$ ion) diffusion induction mechanisms. We believe that our design principles and the resultant multicolor materials will broaden the design of next-generation fluorescent materials.

SB04.03.07
Stimuli Responsive Shape Recovery Hyaluronic Acid Hydrogel Using Ice-Template Eunsook Park and Haeshin Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Hyaluronic acid (HA), an essential component of the extracellular matrix, has been recognized as a promising building block in cell therapy and tissue engineering due to its excellent biocompatibility and biological properties. Furthermore, HA is versatile in functionalization with various crosslink-moieties and has been easily transformed into hydrogel via chemical and physical crosslinking for cell culture and transplantation. However, cross-linker and photoinitiator, used in the crosslinking reaction, cause chemical and radical induced cytotoxicity. Current catechol modified hyaluronic acid (HA-C) was reported as a novel candidate that overcame these limitation, showing low cytotoxicity and tissue adhesive properties. However, it was inevitable to use a high pH environment or oxidizing agent due to slow catechol oxidation rate. Moreover, the gel had low mechanical properties and was unable to maintain its shape.

In the study, we describe another technique to make mechanically robust HA-C gel using the ice template. When HA-C is frozen, the formation of ice promotes the oxidation of catechol by two mechanism: 1) the increase of the local concentration of HA-C in the unfrozen area, and 2) the increase of buffer pH with decreasing temperature. Initially, an injectable gel is formed but as freezing and thawing cycle are repeated, a solid-like free-standing gel is formed. When compressed, the water trapped in the pore squeezes out and the gels show compressibility due to large porous structure that is prepared by ice. However, when water feeding, the gel present rapid water uptake properties and repeatable water induced shape recovery. In addition to, the large pore structure of the gels improved the permeability of nutrients and cells and biocompatibility. These gels is best mimic bio-tissues (e.g. cartilage) with compressible properties and porous structure, and thus can be used promising building blocks in tissue engineering.

SB04.03.08
The Biocompatible Hydrogel Skin for Long-Term Used Catheter Yueying Yang, Yan Yu, Qing Ling, Jiaxin Wang, Le Lin, Jianfeng Zang and Xuanhe Zhao; 1Huazhong University of Science and Technology, China; 2Massachusetts Institute of Technology, United States

With the rapid development of global science and technology, the average life expectancy of human beings is generally extended, and the social problems caused by the aging of population are also increasing. Due to the rapid increase of diseases caused by aging, such as heart disease, high blood pressure, stroke, etc, the number of hospitalized patients increases rapidly, and the number of bedridden patients also increases continuously, accounting for 30% of hospitalized patients. The catheters used by bedridden patients for long periods of time need to be replaced on average once a week, however it greatly increases the risk of urinary tract infections. The existing catheters made of natural rubber, silicone rubber or PVC, which has high friction coefficient, render patients uncomfortable. Since the external environment is connected with the human body through the catheter, the risk of patients’ infection is increased. In our study, we coat the hydrogel skins on inner and outer surfaces of the Catheter,
the hydrogel skins exhibit tissue-like softness and provide superior low-friction, antifouling, anti-bacterial, to the catheter. In addition, we demonstrate the new catheter’s features through animal experiment.

**SB04.03.09**  
**Fabrication of Photo-Curable Polyurethane-Acrylate for 3D Printing Based on Viscosity and UV Curing Time**  
WonBin Lim and PilHo Huh; Pusan National University, Korea (the Republic of)

Nowadays, 3D printers have been undergone much attention in all fields of industry. The photo-curing resins which ranging from rigid to flexible, are successfully prepared using the synthesis of Polyurethane-Acrylate. It will be used for according to the application through the measurement of flexural strength and hardness. The intrinsic viscosity of the photo-curable monomer and polymer is measured to target the molecular weight of the material. The photo-curing polymer is produced through physical or chemical reaction, and the curing time and physical properties of the material are adjusted according to the purpose. It can be controlled the ratio of the photo initiator and polymer. For example, Thermoplastic polyurethane (TPU) series based on polyethylene glycol(PEG) as a polyol and hexamethylene diisocyanate (HDI) as an isocyanate were synthesized as a function of molecular weight formulation. After that, PU-acryl will be synthesized by attaching hydroxyethyl-methacrylate(HEMA) and used for DLP 3D printing by controlling the content ratio of photo-initiator and addition multifunctional acrylate.

**SB04.03.10**  
**3D-Printed Microbe and Consortia Hydrogels for on Demand Bioproduction and Preservation**  
Trevor Johnston¹, Shuo-Fu Yuan², James Wagner², Xiunan Yi², Abhijit Saha¹, Alshakim Nelson¹ and Hal Alper²,*; ¹University of Washington, United States; ²The University of Texas at Austin, United States

Living materials are composites of polymers and living cells wherein the function of the material is derived from the residing cells. Here, we describe a 3D-printed hydrogel-based system for harnessing the bioactivity of embedded microbes for on-demand small molecule and peptide production in mono-culture and microbial consortia systems. This platform bypasses the challenges of multi-organism consortia by spatially organizing organisms into hydrogel inks to precisely control the final consortium composition and dynamics without the need for synthetic control. Furthermore, we demonstrate that these hydrogels provide protection from preservation techniques (including lyophilization) and can sustain active metabolic function for over 1 year of repeated use. We demonstrate the utility of this approach (compared to traditional liquid-based culturing) for four chemicals and peptide antibiotics using through both mono-cultures and cross-feeding and parallel consortia of yeast and E. coli. In all cases, the printed hydrogel ink’s efficiency in repeated production phases, both pre- and post-preservation, outperformed liquid culture. We envision this technology being a step forward in the ease of use of complex designed biological systems for the expanded, on-demand production of a variety of high-value compounds.

**SB04.03.11**  
**A Supramolecular Hydrogel for Spatial-Temporal Release of Auxin to Promote Plant Root Growth**  
Yao X. Chen; Nankai University, China

So far, synthetic auxins other than indole-3-acetic acid (IAA) have been widely used in both scientific studies and agricultural and horticultural practices. The synthetic auxin 1-naphthalene acetic acid (NAA) is popular because of its relative stability and its lipophilicity, which allows it to freely enter the plant cell. However, because of the rapid diffusion of NAA in agarose hydrogel, the most commonly used technique for physically encapsulating NAA in an agarose hydrogel or hydrogel beads cannot fulfill the need for the spatial release of NAA for plant research. It remains a challenge to develop materials for the spatial-temporal release of auxin for research use. In this study, we demonstrated the effectiveness of an auxin-based hydrogelator linked by a hydrolysable ester bond. Hydrogel I, formed by the gelator (NAA-G’FFY) linked with an ester bond, was able to release 1-naphthaleneacetic acid (NAA), whereas hydrogel II, formed by the gelator without an ester bond (NAA-GFFY), was not. By mixing NAA-G’FFY with Fmoc-GFFY to form a two-component hydrogel, the spatial and temporal release of NAA was achieved, promoting on-site auxin responses including primary root elongation and lateral root formation in the model plant Arabidopsis thaliana. The strategy of using a hydrolysable ester bond to connect drug molecules and self-assembling peptides could lead to the development of supramolecular hydrogels with more controllable drug release profiles.

In summary, we demonstrated that an auxin-based supramolecular hydrogel connected by a hydrolysable ester bond has a good capacity to slowly release NAA into the environment, while the control connected by an amide bond...
cannot release NAA. The spatial and temporal release of NAA could be a useful new tool in the study of auxin-induced plant growth and development.

**SB04.03.12**  
**β-Galactosidase Instructed Supramolecular Hydrogelation for Selective Identification and Removal of Senescent Cells**  
Tengyan Xu; Nankai University, China

Cellular senescence is a natural process to prevent the proliferation of damaged or stressed cells, and it is also believed to be beneficial in wound healing. However, senescent cells tend to accumulate upon persistent damage or during aging, which impairs tissue functions and accelerates aging. Recent studies indicate that the clearance of senescent cells can delay features of aging and counteract the loss of tissue hemeostasis after chemotherapy or chronic damage. It is therefore very important to develop strategies for selective identification and removal of senescent cells.

In this work, we introduced a novel strategy of β-galactosidase (β-Gal) instructed peptide self-assembly to selectively form nanofibers and hydrogels in senescent cells. We demonstrated that the in situ formed nanofibers could alleviate endothelial cell senescence by reducing P53, P21, and P16INK4a expression levels. We also demonstrated that our strategy could selectively remove senescent endothelial cells by inducing cell apoptosis, with an increase in the BAX/BCL-2 ratio and caspase-3 expression. Our study reports the first example of enzyme instructed self-assembly (EISA) by a sugar hydrolase, which may lead to the development of supramolecular nanomaterials for the diagnosis and treatment of many diseases, such as cancer, and for other applications, such as wound healing and senescence.

As a result, this is the first example of supramolecular hydrogel formation triggered by a sugar hydrolase. Sugar hydrolases play important roles in many diseases, and we envision great promise for the diagnosis and treatment of these diseases by sugar hydrolase-controlled supramolecular nanomaterials.

**SB04.03.13**  
**Supramolecular Nanofibers of Drug-Peptide Amphiphile and Affibody Abolish HER2+ Tumor Growth**  
Chunhui Liang; Nankai University, China

Antibody-based medicines and nanomedicines are very promising for cancer therapy due to the high specificity and efficacy of antibodies. However, antibody-drug conjugates (ADCs) and antibody-modified nanomaterials frequently suffer from low drug loading and loss of functions due to the covalent modification of the antibody.

We herein reported on a novel and versatile strategy to prepare supramolecular nanomaterials by the co-assembly of an affibody (antiHER2) and drug-peptide amphiphiles. During the enzyme-instructed self-assembly (EISA) process, the drug-peptide amphiphile could co-assemble with the affibody, resulting in supramolecular nanofibers in hydrogels. The drug loading in the supramolecular nanofibers was high (>30 wt%), and the stability of antiHER2 was significantly improved in the nanofibers at 37 °C (>15 days in vitro). The supramolecular nanofibers exhibited high affinity for HER2+ cancer cells and could be efficiently taken up by these cells. In a mouse tumor model, our supramolecular nanofibers abolished HER2+ NCI-N87 tumor growth due to the good accumulation and retention of nanofibers in tumor.

We demonstrated a novel and versatile method to prepare nanomedicines composed of drug-peptide amphiphiles and antibodies/affibodies by the EISA process. Compared with general ADCs that had very low drug loading, our system possessed much higher drug loading (31.6 and 30.2 wt% of CRB in co-assembled nanofibers with 10 and 15 wt% of affibody). The stability of the affibody could be significantly improved in our supramolecular nanofibers. More importantly, the in vitro and in vivo results indicated the excellent performance of our supramolecular nanomedicines, which possessed good targeting and therapeutic effects for cancer diagnostics and therapy. We also envision the generation of more supramolecular nanomedicines for the diagnostics and treatment of important diseases.

**SB04.03.14**  
**Spiral-Shaped Stimuli-Responsive Hydrogel Actuator for Controlling Compression and Expansion**  
Koki Yoshida and Hiroaki Onoe; Keio University, Japan

Stimuli-responsive hydrogels swell and shrink corresponding to external stimuli such as temperature, pH, light, and chemical compounds. These characteristics are attractive for soft actuators including artificial muscles, biomimetic robotics, and microfluidic components. Current challenges of hydrogel actuators are controlling their displacement...
and deformation direction, since bulk stimuli-responsive hydrogels only swell/shrink isotropically, as determined by the nature of the hydrogel materials. To overcome this challenge, various types of double-layered hydrogel actuator have been developed to controlling deformation direction, however controlling displacement of the stimuli-responsive hydrogel materials has not been achieved.

Here we present spiral-shaped stimuli-responsive hydrogel actuator for controlling deformation direction (compression/expansion). The magnification of deformation and controlling the deformation direction by shrink/swell characteristics can be enhanced just by the shape of spirals without any molecular modification of materials.

Simulation of actuation of the spiral-shaped actuator:
We use finite element simulation (COMSOL) for simulating the actuation of the spiral-shaped actuator. We consider the spiral-actuator with a diameter of gel $D_{gel} = 300 \, \mu m$ and a diameter of spring $D_{spring} = 1000 \, \mu m$. We apply a shrinkage ration of stimuli-responsive hydrogel $\alpha = 0.6$ which determined by measuring a shrinking ration of the stimuli-responsive hydrogel. The Double-layered spiral-shaped actuator behaved as axial compression with winding up. In contrast, when patterned stimuli-responsive hydrogel in the outside of spiral-shaped actuator, spiral-shaped actuator behaved as an axial expansion with winding down.

Fabrication of spiral-shaped stimuli-responsive hydrogel actuator:
We prepared a bevel-tip capillary by cutting a perfluoroalkoxy (PFA) microtube (inner diameter: 200 $\mu m$) at the tip angle to $\sim 20^\circ$. The tube was set horizontally to the liquid surface. By using bevel-tip capillary, a continuous flow of mixed sodium alginate and poly(N-isopropylacrylamide-co-acrylicacid) pre-gel solution was extruded in CaCl2 solution, resulting in spontaneous formation a spiral-shaped hydrogel with a wide range of gradient pitches via buoyancy force. We used double-layer laminar flow for the formation of double-layered spiral-shaped hydrogel composed of stimuli-responsive part and non-responsive part. The resulting spiral-shaped hydrogel has double-layered structures and different pitches.

Results of spiral-shaped actuation:
We applied stimuli to the spiral-shaped actuators in CaCl2 solution by heating at 50°C. The double-layered spiral actuator shrank with large compression. The double-layered spiral actuator was mainly compressed in an axial direction. These results indicate that the spiral structure enhances the magnification of shrinkage of stimuli-responsive hydrogels. Furthermore, expansion of a spiral actuator in the axial direction was achieved by using a double-layered spiral actuator whose boundary between the two layers was parallel to the axial direction of the spiral (outside: stimuli-responsive hydrogel). These results showed that shrinkage of the stimuli-responsive hydrogel was converted to large expansion movement in the axial direction. Therefore, these results indicated that the deformation direction can be controlled by patterning the stimuli-responsive hydrogel.

Conclusion: Compression and expansion motions of spiral-shaped actuator were magnified by forming a spiral shape, which was corresponding to the simulation results. Therefore, it is expected that various multiple complex actuation could be realized by other complex compartmentalization and encapsulating functional materials. The success of multiple complex movements and magnifying the deformation would open new avenues to various microscale biochemical applications such as autonomous soft robots and drug release systems.

SB04.03.15
Aldenronate-Functionalized Poly(2-oxazoline)s with Tunable Affinity for Calcium Cations Maria J. Sanchez Fernandez1,2; 1Radboudumc, Netherlands; 2Radboud University, Netherlands

A library of poly(2-oxazoline)s functionalized with controllable amounts of alendronate, hydroxyl and carboxylic acid side groups was successfully synthesized to create novel polymers with tunable affinity for calcium cations. The affinity of alendronate-containing polymers for calcium cations was quantified using isothermal titration calorimetry. Thermodynamic measurements revealed that the Ca$^{2+}$ binding affinity of these polymers increased linearly with the amount of alendronate functionalization, up to values ($K_{Ca^{2+}} = 2.4 \times 10^5 \, M^{-1}$) that were about 120-fold higher than those for previously reported polymers. The calcium-binding capacity of alendronate-functionalized poly(2-oxazoline)s was exploited to form robust hydrogel networks cross-linked using reversible physical bonds. Oscillatory rheology showed that these hydrogels recovered more than 100% of their initial storage modulus after severe network destruction. The versatile synthesis of alendronate-functionalized polymers and their strong and tunable affinity for calcium cations render these polymers promising candidates for various biomedical applications.
SESSION SB04.04/SB01.04: Joint Session: 3D/4D Printing of Stimuli-Sensitive Materials
Session Chairs: Marc In het Panhuis and Andreas Lendlein
Tuesday Morning, December 3, 2019
Hynes, Level 3, Ballroom A

8:00 AM *SB04.04.01/SB01.04.01
Gels for Bioprinting—Finding, Functionalising, Formulating, Printing and Characterising Gordon Wallace; University of Wollongong, Australia

The ability to create 3D printed structures containing living cells is providing a route to the creation of "living" systems that might be useful for bench top drug testing or implantables that facilitate tissue regeneration.

However, the realisation of a useful printed structure based on hydrogels is not a simple task. While we can build on the extensive knowledge that has accrued through cell-gel interaction studies to date, there are a number of dimensions that add to the challenge.

Central to these is that the gel containing the cells must undergo a reasonably rapid phase transformation. In addition, with some applications multiple cells and other bioactive entities need to be strategically distributed in 3 dimensions. Sterilisation of the components and/or the final structure is also of critical importance and finally knowing what we have created without destroying it remains a challenge.

Returning to the start of this process we encounter perhaps the most neglected aspect - most of the emerging hydrogels finding use in bioprinting are naturally occurring. So where do we find them - how do we ensure a reliable high quality source?

8:30 AM SB04.04.02/SB01.04.02
Novel Hybrid Approach to 3D-Print Graphene/Polymer Composites Xuechen Shen, Taylor J. Morrison, Hani E. Naguib and Tianhao Chen; University of Toronto, Canada

Current 3D printing uses a wide range of plastic, metal, and ceramic materials, with no significant effort to integrate these techniques for multi-material fabrication. We previously developed a novel method to deposit non-viscous ink through a stable continuous jet formed by gearing-enhanced peristaltic pumping. This ink deposition technique was used to deposit graphene oxide (GO) ink in a binder jetting (BJ) process to fabricate GO/polyvinyl alcohol composites. In this technique, ink particles are accelerated to speeds of 2-10ms\(^{-1}\) to overcome surface tension forces tending towards pendant drop formation. Gearing is applied to achieve mechanical advantage (MA)<1, enabling high pump velocity. Motor acceleration made up for the lost torque. In recognizing that gearing could be used to increase torque with MA>1, we realized the potential to perform Direct Ink Writing (DIW) using our ink deposition system. To this end, we DIW-printed viscous graphene/nanocellulose inks. We also recognized that DIW and BJ shared similar layer change, material transport, and gantry motions, allowing the 2 techniques to be implemented in the same system. We designed and built the hybrid 3D printer, implementing transmission to switch gearing ratios. The hybrid printer was demonstrated to print Graphene/polymer composites using both DIW and BJ printing modes.

8:45 AM SB04.04.03/SB01.04.03
Three-Dimensional Printing with Silica Cages Jen-Yu Huang\(^1\), Tangi Aubert\(^1,2\), Ulrich Wiesner\(^1\) and Tobias Hanrath\(^1\); \(^1\)Cornell University, United States; \(^2\)Ghent University, Belgium

Material scientists have now developed an extensive library of nano-sized building blocks, offering a vast panel of properties (optic, magnetic, plasmonic, catalytic, etc.). Nevertheless, combining these building blocks for the realization of multifunctional materials while controlling their structure from the nano- to the micro- and all the way to the macroscale still remains an open challenge in order to fully exploit their potential. In parallel, new material processing techniques such as 3D printing technologies are emerging for the fabrication of macroscopic highly engineered parts and devices. In this work, newly discovered silica nanocages are combined with digital light processing 3D printing technique for the rapid fabrication of mesoporous parts with arbitrary shapes and tunable internal structures. Complementary strategies are then deployed for the implementation and deliberate positioning of various functionalities throughout 3D printed objects with high control on the microstructure and macroscopic
architecture of the superstructures. This approach paves the road for innovative device concepts and designs, that will benefit from the unique properties of nanomaterials and from the micro- and macroscale manufacturing capability of 3D printers.

9:00 AM SB04.04.04/SB01.04.04
Magnetically Navigable 3D Printed Multifunctional Microdevices for Water Quality Control Roberto Bernasconi¹, Elena Carrara¹, Marcus Hoop², Fajer Mushtaq², Bradley Nelson², Salvador Panè³, Caterina Credi¹, Marinella Levi¹ and Luca Magagnin¹; ¹Politecnico di Milano, Italy; ²ETH Zürich, Switzerland

Water contamination, either chemical or biological, is one of the main problems for public healthcare in many parts of the world. Contaminated water is a source of a great number of diseases caused by pathogens or by chemical agents. Many techniques are available to improve water quality, but in many cases these methods are not entirely environmentally friendly. Current research efforts are directed toward the use of harmless substances and safer methods. From the pathogens control point of view, silver is one of the most used non-antibiotic agents. Regarding chemical pollutants elimination, one of the most promising techniques is photodegradation mediated by titania (TiO₂). This material photocatalytically generates reactive radicals able to oxidize pollutants upon exposure to an electromagnetic radiation. Functional layers of silver and titania can therefore be used to provide efficient water remediation.

An interesting approach consists in manufacturing multifunctional materials that exhibit both antimicrobial and photocatalytic activities. A fabrication technique able to yield this type of materials is electrolytic codeposition of particles with metals or alloys [1]. For example, thanks to this wet deposition technique, a matrix of silver with embedded titania particles can be easily obtained. The final composite layer exhibits both antibacterial and photoactive properties. Water cleaning possibilities can be further expanded if the antibacterial and the photodegradation action is performed by microdevices covered with silver/titania composites. An example of such devices are the so-called microrobots [2], which can be wirelessly guided using magnetic field and placed exactly where the water decontamination action is needed. Examples of microrobots presenting photocatalytic [3] or antimicrobial activity [4] are available in literature, but none of them combines these two actions on the same device.

The aim of this work is the realization of cylindrical shaped microrobots combining biokilling and photodegradation thanks to the presence of a bifunctional composite on their surface. Such microrobots are produced using 3D printing, more specifically microstereolithography, and are subsequently metallized using wet techniques. Two functional layers are applied on the surface of the 3D printed device: a CoNiP magnetic alloy and an Ag/TiO₂ composite. The first makes possible the movement of the device under the influence of an external magnetic field, while the latter imparts the biocidal/catalytic activity to the device. We demonstrate that these devices exhibit antimicrobial activity toward methicillin resistant Staphylococcus aureus bacteria. Moreover, from the pollutants removal point of view, we prove that they can efficiently photodegrade a model molecule like rhodamine B when exposed to ultraviolet radiation.


9:15 AM SB04.04.05/SB01.04.05
Macroscale Double Networks—A Universal Method for Improving the Strength and Toughness of Soft Materials Daniel R. King, Tsuyoshi Okumura, Riku Takahashi and Jian Ping Gong; Hokkaido University, Japan

The double network concept has been revolutionary in its ability to turn soft, brittle hydrogels into tough, robust materials with mechanical properties that match the best synthetic elastomers. Double network hydrogels consist of two interpenetrating networks, where each network has a specific mechanical response: the “first network” acts as a sacrificial network, consisting of a rigid, extended network, and the “second network” is a globally percolated, stretchable network. When a double network hydrogel is stretched, covalent bonds of the first network break, dissipating energy; this process continues with increasing strain, until the sacrificial network is completely broken and the second network ruptures. The goal of this research is to demonstrate that the “sacrificial bond concept” is
applicable at length-scales beyond the molecular scale. We aim to incorporate this design concept universally for application in structural and medical devices.

Like double network hydrogels, our system consists of a rigid “first network,” 3d printed polyurethane/polyacrylate grids, embedded in a soft and stretchable “second network,” silicone rubber. We found that when the strength of the matrix exceeds the strength of the grid, local fracture occurs in the grid, and stretching is isolated to the rubber in the fractured region. As stretching increases, the force increases, and when the local force exceeds the global strength of the grid, fracture will occur elsewhere in the composite. This process continues sequentially throughout the sample until all grid fracture sites are exhausted, and the matrix ruptures. By tuning the stiffness of the grid, we can independently control the yield strength and fracture strain of the composite, until a point where the grid strength exceeds the matrix strength, and the multiple fracture process no longer occurs.

We also systematically studied the interfacial interactions between the matrix and the reinforcing grid. Both interfacial adhesion as well as topological interlocking are important towards developing a robust composite. By adhesive interactions alone, only minimal fracture of the reinforcing phase occurs; topological interlocking is required to maximize fracture. Based on this result, we systematically change the grid size to modify the number of fracture events. In the optimized form, an increase in work of extension of ~50% over the neat matrix was achieved, representing a ~70% toughening efficiency versus the calculated maximum toughness. These results demonstrate that macroscale double networks can dramatically increase the toughness of soft materials.

9:30 AM *SB04.04.06/SB01.04.06
4D Printing Thermoplastic Polyurethane Hydrogel-Elastomer Trilayers for Structural Applications Richard S. Trask; University of Bristol, United Kingdom

Hydrogels represent a class of engineering materials that have great promise for integration within the human body; particularly by optimising and functionally grading their biophysical and biochemical properties. The ability to construct complex architectures through 3D printing is now common place but introducing the ability to transform a planar architecture into a new configuration once manufactured opens up the potential to minimise manufacturing complexity but maximising the design potential. This presentation will detail our latest design thinking utilising a multifunctional materials design methodology and 4D printing research for producing a diverse range of complex architectures utilising thermoplastic and hydrogel trilayer constructs. This unique methodology permits the viable construction of dynamically robust and complex bilayer and trilayer origami architectures for a new generation of active structures. In our study the resulting creations transform from flat 2D parts to 3D structures through submersion in water and return to their original configuration through dehydration. This technique uses commercially available materials and printers to enable a controlled and predictable actuation method that is more accessible and affordable than previous examples of hydration triggered 4D printing. We show the ability to create tessellated origami patterns, such as the Miura-ori origami fold pattern and the waterbomb configuration; the latter being a design that has not previously been realised with 4D printing. These new designs demonstrate how the integration of multiple trilayers into a single 3D print enables through-thickness control of actuation resulting in the formation of active structures with complexity beyond what has previously been achieved with 4D printing. The research will now be extended by the generation of curved-layer morphing origami architectures (i.e. individual layers with variable z-component actuation) to enable selective structural buckling; the generation of tubular bilayer/trilayer architectures; and, the generation of sequential actuation through the addition of porogens (i.e. dissolvable particles used to create porous hydrogel structures) such that the rate and magnitude of actuation can be further programmed in the design phase.

10:00 AM BREAK

10:30 AM *SB04.04.07/SB01.04.07
Extreme Hydrogel Technology Xuanhe Zhao; Massachusetts Institute of Technology, United States

While human tissues and organs are mostly soft, wet and bioactive; machines are commonly hard, dry and biologically inert. Bridging human-machine interfaces is of imminent importance in addressing grand societal challenges in health, security, sustainability, education, and joy of living. However, interfacing human and machines is extremely challenging due to their fundamentally contradictory properties. At MIT Zhao Lab, we propose to harness “extreme hydrogel technology” to form long-term, high-efficacy, compatible and seamless interfaces
between humans and machines. In this talk, I will first discuss the fundamental mechanisms to design extreme properties for hydrogels, including extremely tough, resilient, adhesive and anti-fatigue, for long-term robust human-machine interfaces. Then I will discuss a set of novel hydrogel technologies, including i). hydrogel bioelectronics capable of electro-opto-fluidic interrogating single neurons and continuously monitoring gastric physiological conditions over the long term; ii). tissue double-sided tapes that give instant strong adhesion of wet tissues and devices. I will conclude the talk with a perspective on future human-machine convergence enabled by extreme hydrogel technology.

11:00 AM *SB04.04.08/SB01.04.08
Smart Hydrogels from Mechanistic Design to Practical Applications Jie Zheng; University of Akron, United States

Synthetic polymer hydrogels as soft-wet materials, consisting of three-dimensional cross-linked networks and a large amount of water (50–90%), possess many unique properties such as swelling/deswelling, stimuli-responsiveness, shock absorption, and low sliding friction, making them as potential excellent biomimetics for substitution of soft living materials. However, conventional hydrogels often suffer from weak mechanical properties, which greatly limit their extensive uses for many other applications. In this talk, we will present different design strategies to prepare tough and multifunctional hydrogels with unconventional polymer network architectures and extraordinary properties. Guided by our design principle, we will demonstrate different hydrogels with high mechanical properties, self-healing, actuation, antifouling, and/or wound healing to mimic cartilages, artificial muscles, and mussel-inspired glues. In parallel, molecular simulations will be presented to given atomic-details of structure-properties relationship. Finally, several unique aspects for future development of tough hydrogels will be suggested.

11:30 AM SB04.04.09/SB01.04.09
Design and Understanding Dynamic Hydrogel with Hydrazone Crosslinks for 3D Printing Junzhe Lou, Sean Friedowitz, Christopher Lindsay, Sarah C. Heilshorn, Jian Qin and Yan Xia; Stanford University, United States

Dynamically crosslinked hydrogels received increasing interest for their adaptive mechanical behaviors under stress and deformation and wide applications for cell scaffolding and delivery. We present a new concept of modulating the dynamics of hydrogel systems crosslinked by hydrazone bonds via a biocompatible organic catalyst. The catalyst accelerates the exchange kinetics of hydrazone bonds for over two orders of magnitude, resulting in identical network structure with widely tunable viscoelastic behavior. The catalyst control of network dynamics enabled quantitative and unambiguous correlation between the network parameters and mechanical properties of dynamic polymer networks, which can be generalized to provide design principles to engineer their viscoelastic properties. We also applied this system for 3D bio-printing to modulate the dynamic properties of hydrogels at different time points of application to have both high injectability and high stability. The incorporated catalyst enhanced the exchange of dynamic crosslinks to achieve high injectability during printing process, but rapidly diffused away from the hydrogel after ejection to retard the exchange and improve the long-term stability for cell culture.

11:45 AM SB04.04.10/SB01.04.10
Chemical Pumps for Soft Autonomous Robots Junsoo Kim¹, Kai Luo² and Zhigang Suo¹; ¹Harvard University, United States; ²Beijing Institute of Technology, China

Soft robots can be untethered by carrying a chemical fuel of pneumatic actuators. However, it has a fundamental design restriction; the fuel pressure should be higher than the actuator pressure to transport the fuel. Given that the fuel part occupies most of the volume, the robot becomes pressurized as much as the actuating pressure and requires stiffer materials for the fuel part, making entire robots stiffer. Here, inspired by the pit in plants, we decouple the pressures of the fuel part and the actuator while providing a fuel against the pressure gradient by introducing an isolator between them, thereby liberating from the design constraint. This isolator consists of a hydrophilic nanoporous membrane made of a hydrogel and a micro-porous wall made of a nylon mesh, that correspond to the pit membrane and the cellulose wall at the pit respectively. The mechanical integrity of the structure according to the geometry is studied by finite-element analysis to establish a design rule and the pneumatic power is extensively characterized experimentally with various parameters. Finally, the isolator is implanted to the conceptual soft robots.
to demonstrate the merits of the isolator.

SESSION SB04.05: Actuators
Session Chairs: Namita Choudhury and Jurgen Groll
Tuesday Afternoon, December 3, 2019
Hynes, Level 3, Room 302

1:30 PM *SB04.05.01
Function-Function Relationships in Multifunctional Soft Actuators Andreas Lendlein\(^1,2\); \(^1\)Helmholtz-Zentrum Geesthacht, Germany; \(^2\)University of Potsdam, Germany

The limitation of classical shape-memory polymers of a stimuli-induced one time shape shift was overcome with the realization of shape-memory polymer actuators (SMPA). SMPA are soft actuators, which can repetitively change their shape reversibly controlled by temperature under stress-free conditions. They possess the unique feature of re-programmability of their actuation capability related to shape changing geometry and switching temperature. The thermally controlled reversible actuation can occur many times [1,2]. Structure-function relationships for SMPA can be derived from datasets, which are generated by comprehensive characterization of the effects caused by systematically varying structural parameters on different length scales. Motivated by potential application, e.g. in the field of robotics or healthcare technologies require additional functions such as self-repair, magnetic controllability or degradability. Besides integrating these different functions in one material system, creation of targeted function-function relations are a major challenge. Orthogonal multifunctionality is realized when several functions can be addressed almost independently from each other. An example for orthogonal functions are soft actuators equipped with a self-healing capability [3]. Sequentially coupled functions enable linking functions according to a domino effect. Sequential multifunctionality relies on a series of functions, where the effect (output) of one function is the input of the next function. The coupling of a stimulus conversion from magnetic to thermal with an actuation capability will be presented as a prominent example [4].

References

2:00 PM *SB04.05.02
Hydrogels and Other Ionic Conductors in ‘Piezo-Ionic’ Sensors, Actuators and Electrochemical Devices John D. Madden\(^1,2,3\), Yuta Dobashi\(^1,2\), Mirza S. Sarwar\(^1,2\), Dickson Yao\(^1,2\), Saeedeh Ebrahimi Talakoo\(^1,2\), Claire Preston\(^1,2\), Ngoc Tan Nguyen\(^1,3\), Justin K. Wyss\(^1,3\), Bertille Dupont\(^1,2\), Yael Petel\(^1\), Carl Michal\(^1\), Cédric Plesse\(^4\), Giao T. Nguyen\(^5\), Frédéric Vidal\(^1\), Eric Cattan\(^1\), Sébastien Grondel\(^1\), David Shepherd\(^1\) and Geoffrey M. Spinks\(^1\); \(^1\)University of British Columbia, Canada; \(^2\)Faculty of Applied Science and Engineering, University of Toronto, Canada; \(^3\)École Polytechnique de Montréal, Canada; \(^4\)Institut Énergie Matière NANO (IEMN-CNRS), France; \(^5\)Université de Cergy-Pontoise, France

Ionic conductors offer exciting device possibilities, particularly with the advent of highly extensible and easily synthesized hydrogels. Following on from recent work on hydrogel “ionic skin”, ‘piezo-ionic’ sensors and ionic artificial muscle, we present example ionic devices, including stretchable and transparent capacitive sensor arrays, pressure sensors that generate currents upon stretching, actuators that bend or contract when ions are inserted, as well as stretchable electrochrome elements and batteries.

Hydrogels and other ionic conductors offer advantages over metals and semiconductors in being intrinsically stretchable and non-absorbing of visible light. Their moderate to low moduli and non-linear mechanical properties can match those of tissue, and make them of interest for use in human interfacing devices. On the other hand, ions are much less mobile than electrons, ionic conductors don’t have bandgaps, and, unlike electrons and holes, anions and cations don’t recombine. The materials are typically wet, and properties can depend significantly on dimensions, pH and temperature. Given these drawbacks, how can we make practical use of ionic conductors?
In order to avoid being limited by the low mobility of ions, we can take two approaches. One is to implement gels and other ionic conductors in devices that consume very little current – such as capacitive sensor arrays. Even in low current devices, dropping temperatures can dramatically and unacceptably increase resistance, so a careful consideration of RC charging time is important in the design. Another approach to avoid being limited by low mobility is to make the transit distances short. We present bending actuators that can operate hundreds of hertz. Relative speed of ion motion is important in ‘piezo-ionic’ sensors, where application of a pressure gradient leads to differential rates of ion motion between positive and negative ions – and the generation of current. NMR and electromechanical measurements suggest that in hydrogels ions move more slowly than solvent, perhaps hindered by the polymer structure. The small voltages that result are sufficient to stimulate nerves.

Electrochemical devices combine electronic and ionic conductors – for example in batteries, electrochromics and ionic diodes. In such cases, the electrode material is not as stretchable as the hydrogel. We present a symmetric conducting polymer-based electrochromic element that can stretch and change colour, and battery that is robust under extension.

If ionic devices dry out, they will slow or stop. One approach to avoid drying is to use salts that dramatically reduce vapour pressure – but this can come at the cost of conductivity. We instead demonstrate the use of non-volatile ionic liquids to keep a capacitive sensor array working for years without encapsulation. Alternatively, low vapour transmission rate elastomers can keep fast actuators and stretchable batteries functional for months or even years without preventing bending.

2:30 PM SB04.05.03
Electrically Controlled Gel Actuator Using Liquid Metal Spring Ken Matsubara and Hiroki Ota; Yokohama National University, Japan

This report demonstrates an electrically controlled gel actuator by a three-dimensional(3D) helical structure with liquid metal. Previously, core-shell hydrogel microsprings was fabricated using a double bevel-tip nozzle. In this study, liquid metal as conductive material was injected into core part of microspring, which formed liquid metal spring which has 3D helical structure. A rod of a temperature responsive gel was inserted into the center of the liquid metal spring in order to an actuator. Current was applied to the spring to heat the entire actuator. The rod of temperature responsive gel was warmed up, and shrinks together with the spring. As a result, we succeeded in control the actuation of the gel by the liquid metal spring by 16%. Spring structures might be used in a wide range of fields taking advantage of energy absorption and storage. Our gel actuators present an important advancement towards development in several fields including soft robots, microactuators, drug delivery systems (DDS).

Background: Poly(N-isopropylacrylamide) [PNIPAM] is a temperature-responsive polymer that has lower critical solution temperature (LCST) at 32°C. PNIPAM gel exposed to an environment at higher than LCST changes hydrophilic to hydrophobic so that the water is discharged, and its volume decreases eventually. In several fields such as soft robotics and DDS, this characteristics is taken advantage of. However, in terms of an actuator using a temperature responsive gel, they require temperature change in entire environment, which make control of an individual actuator difficult. To improve this individual controllability, we propose a gel actuator that combines a heater using a liquid metal coil which is ultra soft, and a temperature responsive gel. In addition, the coil made of liquid metal has little change in cross-sectional area during the deformation, which leads stability of the resistance change. This helical shape overcomes the problem of changing parameters due to deformation that often occurs in soft actuators and stretchable sensors, and provide electrical control of gel actuation.

Fabrication: In order to create helical structure of gel by imbalance of crosslinking due to inclination of the nozzle, sodium alginate was poured from a bevel-tip nozzle into an aqueous solution of calcium chloride. Core-shell hydrogel helical structure was made by double nozzles held by a 3D printed nozzle joint. In this study, polyvinyl alcohol was used as a core part, and sodium alginate as a shell part. Then, the polyvinyl alcohol was extruded with liquid metal (Galinstan). Eventually, a spiral structure of Galinstan was established. Temperature responsive gel was molded by 3D printer. Then, the rod of the gel was inserted to the liquid metal microspring. Gel actuator with liquid metal coil was established.

Results: Characteristics of liquid metal microspring was investigated. Modules of microsprings filled with liquids metal in core parts were 0.33 N/m. we measured resistance change as a function of elongation of the straight and spiral wiring. The resistance of a straight wiring of the liquid metal increased to 140% by 100 % tension. On the other hand, a spiral wiring of the liquid metal increased to only 1.2%. Therefore, we accomplished the liquid metal
spiral wiring which maintained stable resistance in DC during harsh deformation of a circuit in this study. Furthermore, electrically controlled gel actuation was demonstrated. The gel actuator was heated by supplying 1.4W of power to liquid metal coil. As a result, it contracted 16% in 15 minutes. In summary, we succeeded in producing an actuator that can be controlled by electricity.

2:45 PM SB04.05.04
Design with Supramolecular Hydrogels Hector Lopez Hernandez and Eric A. Appel; Stanford University, United States

Supramolecular hydrogels are appealing for biological applications such as drug delivery, 3D printing bio-inks, and cell therapies. These applications create a diverse set of material requirements which are met by exploiting the broad tunability of the hydrogel’s material properties through modifications to the composition, crosslinking moieties, concentration, and molecular weight. The effects of these variables on the material properties can be complex and difficult to characterize. In addition, the vast parameter space makes it difficult to rationally design the hydrogels for specific applications.

Herein we present the complex rheological and diffusive behavior for supramolecular polymer-nanoparticle hydrogels, comprising hydroxypropyl methylcellulose and poly(ethylene glycol)-b-poly(lactic acid) nanoparticles, from the perspective of designing an injectable controlled release drug-delivery platform. The hydrogel’s associative gel formation dynamics and the strong non-Newtonian rheological behavior, including yield stress fluid behavior and shear-thinning, are presented as a function of variations in the formulation of the polymer-nanoparticle hydrogels. Diffusion, measured by fluorescence recovery after photobleaching (FRAP), is presented to demonstrate the correlation between the mechanical properties of the hydrogels and the transport within the hydrogel. It is shown that formulations created to expand the timescale of release may result in an inadvertent effect of increasing the viscosity and yield stress of the hydrogels, precluding injectability. We also present a design-oriented approach, developed from our systematic rheological and diffusive characterization, which allows for visualizing the effects of each formulation knob on intrinsic material properties and behavior. Furthermore, this approach allows for the generalization of the hydrogel platform and provides a means for engineering formulations for a more diverse set of applications beyond injectable therapeutics, such as 3D printing.

3:00 PM BREAK

3:30 PM *SB04.05.05
Design of Novel Homocomposite and Hierarchically Structured Hydrogels for 3D Printing Orlin D. Velev; North Carolina State University, United States

This talk will present two interrelated approaches to making novel classes of extrudable and responsive hydrogel materials based on special suspensions and multiphasic compositions. The first one uses a method called 3D printing with Homocomposite Thixotropic Paste (HTP). This method was originally developed in our group for 3D printing of ultrasoft silicone structures. The extrudable HTPs are “capillary gels” made of particles and binding liquid with the same chemical composition. At a certain volume fraction the pre-gelled particles jam and make a two-phase thixotropic homocomposite paste. Once this paste is extruded, the gelation of the liquid medium results in a homogeneous and cohesive single-component hydrogel. Its remarkable flexibility and extensivity are based on the strong cohesion of the particles and identical cured liquid. The HTP compositions allow for easy doping with magnetic nanoparticles to make them field-responsive. The mechanical properties of the homocomposite material can be enhanced further by using particles with special morphology and interactions. In the second part of the talk, we will show how the HTP-3DP method was enhanced by using a new class of hierarchically structured soft particles. The morphology of these “dendricolloid” particles is similar to molecular-scale polymer dendrimers, but is two orders of magnitude larger in scale. They are formed as a result of a new process of polymer precipitation in turbulently sheared liquid. The dendricolloids have very large excluded volume, while their nanofiber corona possesses the highly adhesive abilities of the nanofiber-padded gecko legs. The dendricolloids form strong gels at very low volume fractions. They produce even sturdier homocomposite and heterocomposite hydrogels when their medium is molecularly gelled on its own. The investigation of the interactions-structure-property relationship of such HTP 3D printed materials could enable the making of numerous hydrogel architectures with excellent mechanical properties and programmed response and actuation.
4:00 PM SB04.05.06
A Photothermal Responsive Actuator with Self-Monitoring Strain Sensing Capability  Chiao-Yueh Lo, Cheolgyu Kim and Ximin He; University of California, Los Angeles, United States

Soft robots, with their attractive living organism-like compliance and flexibility, have motivated the development of new active materials capable of neuromuscular behaviors. In spite of many new soft sensors and soft actuators, self-sensing materials that can monitor their own motions are highly desirable but proven challenging to realize. In this paper, we present a photothermally-responsive electrically conductive soft material that can serve as a strain sensor and a self-monitorable photothermal actuator, simultaneously owning two key functions essential to artificial muscle materials. This material is a nanostructured conductive hydrogel based on an interpenetrating network of theromoresponsive hydrogel and conducting polymer with enhanced stretchability and responding speed. A variety of complex photo-driven anisotropic locomotion of the homogeneous composite hydrogels can be precisely remotely controlled by near-infrared (NIR) laser illumination. The strain produced from the controlled motion is sensed by the actuator itself in real time. The photothermal response and electrical conductivity allow the hydrogel acts as a photo-triggered switcher. With this unprecedented capability of sensing the magnitude of the strain that the actuator produces, the robust, stretchable, and ultra-sensitive conductive hydrogels will lead to the next-generation soft robots with self-diagnostic feedback-controlled, higher level of autonomy.

4:15 PM SB04.05.07
Mechanical Characterization of Graded Hydrogel/Polymer Interfaces to Assess Robustness  Andrew A. Tomaschke, Archish Muralidharan, Stephanie J. Bryant, Robert McLeod and Virginia L. Ferguson; University of Colorado Boulder, United States

As our understanding of tissue engineering for cartilage repair has progressed, so has the complexity of scaffolds designed to repair cartilage defects. Early scaffold designs focused on getting cells into the defect using a soft, biocompatible materials like Pluronic and Polyglycolic acid [1]. When outcomes proved undesirable due to inability of soft hydrogels to bear physiological loads, researchers designed scaffolds to mimic the properties of the native tissue [2]. Unfortunately, these stiff scaffolds were highly cross-linked and as a result, had diffusional limitations that limited the ability of the cells to proliferate and create new tissue. Thus, recent approaches now utilize a composite design [3]. These use a stiff polymer skeleton to control strain under externally applied loads and match the stiffness of surrounding tissues when implanted and a soft hydrogel cellular niche for cells to grow and proliferate. For this combined approach to be effective, it relies on the attachment of the soft cellular niche to the stiff skeleton in order to transmit the proper strains to the seeded cells.

Briefly, our approach includes a 3D stereolithography (SLA) manufactured, stiff PEGDA:PETMP structure (target modulus = ~1 MPa) that is infilled with a soft (~50 kPa), PEG-norborene hydrogel. The stiff structure bears load and controls strain, whereas the soft infilling hydrogel can be tailored [4,5] to serve as a cellular niche. To mitigate potential interfacial failure between the stiff structure and soft hydrogel, we have created a graded interface by creating a shell of 13% converted stiff material around a 100% converted core and infiltrating the 13% converted PEGDA:PETMP with PEG-norborene.

Preliminary testing of sharp versus graded interface materials showed that the graded interface more effectively resisted fracture when loaded in tension. However, this analysis lacks context of how specific property gradients (i.e., via spatial control of conversion) can be designed to minimize interfacial failure between the two materials. Thus, this work presents a direct assessment of the material property gradients spanning sharp and a range of graded interfaces. Using nanoindentation testing, the distribution of mechanical properties across the interfaces are characterized. These measures will be used to help explain the role of fracture across gradient conversion interfaces between two dissimilar materials. This work is designed to both validate our existing approach for interface design and serve as a guide to others seeking to utilize composite, SLA-printed scaffolds in their work.


engineering gel structural changes to facilitate cartilaginous tissue production." Biotechnology and bioengineering 86.7 (2004): 747-755.


4:30 PM SB04.05.08
From Aqueous Graphene Dispersions to Smart Soft Materials Ester Vazquez; UCLM, Spain

The synthesis of different hybrid hydrogels by in situ radical polymerization in the presence of graphene derivatives, is one of the followed approaches to attain three-dimensional nanocomposite scaffolds. The role of the nanomaterial within the polymer network is primarily intended for the reinforcing (i.e. increasing the stiffness and toughness). However, we have shown that the presence of graphene can also enhance features such as biocompatibility, smart behavior based on responsiveness to external stimuli, sensing, or self-healing ability, giving rise to truly hybrid composites.

The preparation of these soft materials requires the production of large amounts of graphene derivatives in water, and for this reason, ball milling approaches developed in our labs, have proven a method of choice for the preparation of graphene starting dispersions. Moreover, aqueous graphene suspensions can be rapidly frozen and, subsequently, lyophilized giving rise to a very soft and low-density black powder which can be readily dispersed in water and in organic monomers allowing the preparation of the hybrid hydrogels.

4:45 PM SB04.05.09
Artificial Phototropism and Artificial Phototaxis Based on Light-Sensitive Hydrogels Yusen Zhao, Xiaoshi Qian and Ximin He; University of California, Los Angeles, United States

Many living organisms track light sources and adaptively stop their movement when the tracking is achieved. This phenomenon, known as phototropism, occurs as plants self-orient to face the sun perpendicularly throughout the day. While many smart materials exhibit nastic behaviors in response to external stimuli, no synthetic material can intrinsically detect and accurately track the direction of stimuli, i.e., exhibit tropistic behaviors. Other than the phototropism in dynamic equilibrium state, oscillations are also widely found in living organisms to generate propulsion-based locomotion often driven by constant ambient conditions, such as phototactic movements.

However, most man-made oscillations require non-constant energy input and cannot perform environment-dictated movement. Here we report an artificial phototropic and an artificial phototactic system by using the same light-sensitive hydrogel system, respectively, termed sunflower-like biomimetic omnidirectional tracker (SunBOT) and soft swimming robot (OsciBOT). The SunBOT can instantaneously aim to incident light in three-dimensional space over broad ambient temperatures. Phototropism successfully enabled plant-like maximization of energy harvesting through SunBOT-based omnidirectional solar vapor generation, achieving up to 400% energy harvesting enhancement over non-tropic materials by maintaining normal to oblique illuminations. OsciBOT showcases agile life-like omnidirectional oscillatory motion in entire 3D space with near-infinite degrees of freedom. The large force generated by the powerful and long-lasting oscillation of OsciBOT can effectively self-propel away from light source, showing high-speed and controllable phototactic locomotion. The artificial phototaxis opens broad opportunities in maneuverable marine automated systems, miniaturized transportation, and solar sails.
Molecular self-assembly is a key direction in current nanotechnology based material science fields. In this approach, the physical properties of the formed assemblies are directed by the inherent characteristics of the specific building blocks used. Molecular co-assembly at varied stoichiometry substantially increases the structural and functional diversity of the formed assemblies, thus allowing tuning of both their architecture as well as their physical properties.

In particular, building blocks of short peptides and amino acids can form ordered assemblies such as nanotubes, nanospheres and 3D-hydrogels. These assemblies were shown to have unique mechanical, optical, piezoelectric and semiconductive properties. Yet, the control over the physical properties of the structure has remained challenging. For example, controlling nanotube length in solution is difficult, due to the inherent sequential self-assembly mechanism. Another example is the control of 3D-hydrogel scaffold’s physical properties, including mechanical strength, degradation profile and injectability, which are important for tissue engineering applications.

Here, in line with polymer chemistry paradigms, we applied a supramolecular polymer co-assembly methodology to modulate the physical properties of peptide nanotubes and hydrogel scaffolds. Utilizing this approach with peptide nanotubes, we achieved narrow nanotube length distribution by adjusting the molecular ratio between the two building blocks; the diphenylalanine assembly unit and its end-capped analogue. In addition, applying a co-assembly approach on hydrogel forming peptides resulted in a synergistic modulation of the mechanical properties, forming extraordinary rigid hydrogels. Furthermore, we designed organic-inorganic scaffold for bone tissue regeneration.

This work provides a conceptual framework for the utilization of co-assembly strategies to push the limits of nanostructures physical properties obtained through self-assembly.

References
8:30 AM *SB04.06.03
Biophysics of Complex N-glycan Shields on HIV Pseudovirus Preethi Chandran; Howard University, United States

The surface of cells and pathogens is coated with a layer of carbohydrates called glycans. Majority of glycans on secreted and membrane proteins is produced by the N-glycosylation pathway and are known as N-glycans. N glycans have either (i) core and distal branches of mannose sugars (high-mannose type) or (ii) core of three mannose sugars followed by distal branches of non-mannose sugars that end in sialic acid (complex type). Our goal is to understand in the inherent biophysical design in the choice and placement of the complex N-glycan sugars. Single sugar biophysics obtained with force spectroscopy was integrated to composite N-glycan biophysics by systematically increasing the complexity of sugar presentation in monolayer-monolayer to virus-monolayer to virus-virus experiments. In all systems, there were consistent long-ranged, charge-mediated, and materially 'tough' self-adhesions originating from sialic acid residues. On the other hand there were more short-ranged, hydrogen-bonding mediated, and materially 'brittle' self-adhesions originating from mannose residues. The two sugars did not cross-interact and neither did most other sugars in the glycan shield. Correspondingly in solution, mannose-stabilized gold nanoparticle tightly coated viruses, but sialic-stabilized gold nanoparticle particles aggregated and precipitated viruses. Moreover, the sugar interactions in the glycan shield gave rise to a rate-dependence, with both the virus glycan shield and virus itself being penetrated at low rates but only compressed at high rates. The findings imply that biological surfaces would have different interfacial properties and aggregation propensities based on the sugar composition of the surfaces and the solvent shear.

9:00 AM SB04.06.04
Vascularized Bone Grafts Prepared with Hydrogel Micro-Dispenser and 3D Mesh Printing Hikaru Akieda, Tatsuto Kageyama, Yohei Noda, Shoji Maruo and Junji Fukuda; Graduate School of Engineering, Yokohama National University, Japan

Large bone defects are serious complications typically caused by extensive trauma, tumors, infections, and congenital musculoskeletal disorders. Current approaches to treat bone defects include autograft and allograft transplantation. However, limited availability of grafts, infections, and immune rejection hinder the widespread application of these approaches. Recently, tissue engineered bone grafts using osteogenic cells and/or osteoconductive materials have emerged as a promising approach for treating large bone defects. However, their therapeutic use remains limited due to the significant time required for ossification and remodeling of large grafts after transplantation. To shorten the required time, pre-vascularization of grafts may be critical, because vasculature delivers not only oxygen and nutrients, but also osteogenic cells for bone formation and subsequent remodeling. In this study, we propose an approach for fabricating vascularized bone grafts containing osteoblasts, bone matrix, and complex vasculature. A unique aspect of our approach is that we first prepare collagen-rich cell aggregates, named bone beads, through the spontaneous constriction of cell-encapsulating collagen drops during a 24 h culture. This spontaneous formation of bone beads facilitated large scale bone bead preparation using a micro-dispenser system. This approach allowed the spotting of 10,000 collagen microgels in 10 minutes. After gelation at 37 °C for 30 min, constructs were collected, suspended in culture medium, and seeded onto a non-cell adhesive dish or spinner flask bioreactor. Interestingly, cells in bone beads showed better osteogenic differentiation, including osteogenic marker expression and bone matrix secretion, compared with conventional spheroid culture after 2 weeks in an osteogenic differentiation medium. We further optimized the stirring rate of the spinner flask bioreactor to maximize osteogenic differentiation of cells in bone beads. In particular, bone matrix secretion was significantly increased by increasing the stirring rate from 0 to 250 rpm. To fabricate vascularized bone grafts, a few hundred bone beads were cultured for 14 days. They were then suspended intermixed with vascular endothelial cells and seeded into non-cell-adhesive flat-bottom dishes. After 1 day of culture, these constructs were stacked into a cell culture insert for 2 days of further culturing. Endothelial cells formed luminal structures in the spaces between bone beads. Fabricated vascularized bone grafts were transplanted into 4-mm-diameter cranial bone defects in nude mice, and bone regeneration efficiency was evaluated by micro computed tomography. Five weeks after transplantation, vascularized bone grafts achieved 83% coverage of the bone defect area, which is significantly greater than that achieved using other approaches, such as the use of beta tricalcium phosphate (β-TCP) powder. Moreover, histological analysis showed newly formed bone at
transplanted sites. Finally, to hold bone beads in place at bone defect sites, we tailor-made β-TCP meshes using a 3D printer. Transplantation of bone-bead-loaded β-TCP meshes showed higher bone regeneration at bone defect sites than transplantation of β-TCP mesh alone. This simple approach using a micro-dispenser and a 3D printer may provide a promising strategy for advancing bone regenerative medicine.

9:15 AM SB04.06.05
Fabrication of Universal Thermoresponsive Cell Culture Platform—Toward a New Horizon in Tissue Engineering Andrew Choi1, Kyoung Duck Seo2, Hyungjun Yoon1, Seon Jin Han1 and Dong Sung Kim1;
1POSTECH, Korea (the Republic of); 2Wonkwang University, Korea (the Republic of)

Over the course of years, a cascade of studies has engaged in enhancing the health of mankind scrutinized diverse biomaterials (metals, ceramics, polymers, hydrogels, and etc.) for the development of novel and innovative cell culture platforms. And inevitably continued expansion in material selectivity of cell culture platform enabled the creation of diverse cell culture platforms with increased functionalities. One of the most intriguing functional cell culture platforms utilizes the thermoresponsive hydrogel, poly(N-isopropylacrylamide (PNIPAAm), which possesses a prominent behavior of reversibly altering its physicochemical characteristics in response to change in temperature; and consequently, enables the harvest of cell sheets in a scale of $10^2$ mm by altering the ambient condition of temperature above/below low critical solution temperature (LSCT) of 32 °C without any use of chemical treatment. However, its common fabrication method (grafting method) currently confronts several issues due to the instability of grafted polymer chains on the substrate. Depends on the type of the substrate that polymer chains are being grafted and the fabrication methods that are being utilized to graft polymer chains, thermally triggered intermolecular interactions of the grafted polymer chains were found to be all different. And therefore, it is still arduous to achieve stable adhesion behavior of the cells on the fabricated cell culture platform and the inherently constrained geometry of the harvested cell sheet limits the range of its utilization. While the realization of various methods of adopting PNIPAAm on cell culture platform is continuously being pursued to attain in vivo-like heterogeneous or vascularized cell sheets, there are clear fundamental issues in the current ‘form’ of PNIPAAm cell culture platform that hamper maximizing the potential of cell sheet engineering.

In this study, we tailored the polymer network of conventional PNIPAAm through the modification of its substance composition and for the first time introduce a thermoresponsive cell culture platform composed only in a ‘bulk’ form of a PNIPAAm hydrogel having an MPa-scale Young’s modulus. While the initial surface roughness of the bulk PNIPAAm could be modulated by altering the cross-linker concentration, the value of the roughness was found to be changing from nm- to μm-scale above/below the LCST. Through the proper adjustment in the concentration of the cross-linker inside of the bulk PNIPAAm, a stable attachment and easy detachment of diverse cells were allowed. During the incubation of cell lines (C2C12 and NIH3T3) at a temperature condition of 37 °C, all cells were able to be attached on the prepared PNIPAAm cell culture platform with the roughness value of below ~50 nm. On the other hand, the primary cells were found to be only attached on a surface with the roughness value of below ~30 nm during the incubation at the same condition. Moreover, in the act of detaching cell sheet via incubating them at a temperature condition of 20 °C, the cell sheets consists of cell lines were fully detached from the surface with the roughness value of ~10 μm or higher, whereas the cell sheets consists of primary cells were detached from the surface with a roughness of ~19 μm or higher. Based on such behavior of the diverse cells on prepared PNIPAAm cell culture platform, this study successfully optimized the surface roughness value and suggested a universal thermoresponsive cell culture platform which allows the harvest of all types of cell sheets consists of cell lines (C2C12 and NIH3T3) or primary cells (human umbilical vein endothelial cells and keratinocytes). We believe this novel universal cell culture platform could play a powerful and versatile role in igniting a spark to the advancement of cell sheet engineering.

9:30 AM BREAK

10:00 AM SB04.06.06
The Visco-Elasticity of 2D Protein Networks—Implication for Stem Cell Expansion at Liquid-Liquid Interfaces Julien Gautrot, Dexu Kong and Lihui Peng; Queen Mary, University of London, United Kingdom

The mechanical behaviour of the extracellular matrix has an important impact on cell phenotype. Despite the importance of mechanotransduction in regulating a wide range of phenotypes, we recently reported the surprising observation that cells (keratinocytes and mesenchymal stem cells) can adhere, spread and proliferate at the surface
of liquids. This observation is particularly surprising as the reinforcement of cell adhesion is thought to require a solid elastic or viscoelastic substrate that can resist cell-mediated contractile forces. Our work has evidenced the formation of protein nanosheets, self-assembled at the liquid-liquid interface, displaying strong mechanical properties that can provide a sufficient mechanical scaffold to promote cell adhesion and expansion. We showed that this is sufficient to regulate stem cell phenotype. However, the parameters controlling the self-assembly and the mechanical properties of protein nanosheets remain poorly understood. In this work we investigate the assembly of polymers and proteins at liquid-liquid interfaces, and the impact of pro-surfactants with a wide range of chemistries. We identify structural features that control the visco-elastic properties of the resulting nanosheets and regulate associated cell phenotype. In this work, we show the importance of parameters such as pH and concentration on protein self-assembly and the impact it has on interfacial mechanics. Importantly, we demonstrate the impact that pro-surfactant-protein interactions play on regulating the assembly and the interfacial mechanical properties of the corresponding interfaces.

ACKNOWLEDGEMENTS
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REFERENCES

10:30 AM SB04.06.07
Thermoresponsive Hydrogel Scaffolds with Cysteine Pendant Groups Show Enhanced Mucoadhesion Ninad S. Kanetkar and Adam K. Ekenseair; Northeastern University, United States

Introduction: Inflammatory Bowel Disease (IBD) affects 1.9 million people in the United States. Current treatments demand invasive surgery and lifelong immunosuppression that lead to poor quality of life. Systemic stem cell delivery has been shown to regenerate damaged tissues, however cell viability and therefore effectiveness remain suboptimal. In situ forming biomaterial scaffolds can overcome this limitation by sustaining non-invasively delivered cell populations for a longer duration. Poly(N-isopropylacrylamide) (pNiPAAm) is a polymer that forms a gel above a Lower Critical Solution Temperature (LCST) of 32°C due to a shift in the balance between hydrophobic and hydrophilic interactions. pNiPAAm copolymers have been investigated as in situ forming scaffolds due to the proximity of its LCST to body temperature. Previous research has established the ability of p(NiPAAm–co-Glycidyl Methacrylate (GMA)) thermogelling macromer (TGM) to be delivered to the intestine via an airbrush spray and sustain encapsulated cells. Here, cysteine pendant groups were introduced on the polymer to covalently bind to the intestinal mucus, a hydrogel composed of cysteine rich proteins called mucins. This work investigated the kinetics of cysteine conjugation, crosslinking, viability of encapsulated cells, and the impact on mucoadhesion.

Materials and Methods: TGM was obtained by copolymerization of pNiPAAm and GMA in a 10:1 mole ratio. Cys-TGM was obtained by reacting 0.1 equivalents of Cysteine with a 10% TGM solution at room temperature. DSC, GPC, NMR spectroscopy, and rheometry were used for characterization. Mucoadhesion was determined by the pull-off force required to separate two pieces of porcine intestine bound with the polymer.

Results & Discussion: The progress of cysteine conjugation was followed over time using DSC. The peak LCST of Cys-TGM increased from 30.24 to 32.05, and can be attributed to the increased hydrogen bonding in Cys-TGM, requiring higher energy to undergo a coil-globule transition to form a gel. Whereas TGM exhibited fully reversible thermogellation, Cys-TGM formed crosslinked gels which remained insoluble upon cooling below LCST. This network formation was accelerated when the gels were kept in a thermogelled state over several hours as confirmed.
by the net movement of the polymer from sol phase to gel phase. This indicated network formation, which reached a critical point at 4 hours of incubation and was complete after 6 hours. Cysteine conjugated TGM showed superior adhesive strength compared to unmodified TGM and a significant increase compared to a mucus-only control. LIVE/DEAD staining showed cells encapsulated in unmodified TGM initially showed higher death in comparison with the cysteine containing gels. Gels with 30% equivalent cysteine showed similar low death compared to 50% equivalent cysteine gels but showed a higher migratory behavior as opposed to clustered proliferation.

Conclusions: Cysteine modified thermogelling polymers were synthesized, characterized and tested in the context of applicability as an intestinal scaffold. Cysteine-mediated disulfide bond formation was shown to be a promising pathway to enhance scaffold mucoadhesion. Cysteine modification did not hinder the viability of encapsulated cells cultured over a long term.

References:

10:45 AM SB04.06.08
In Situ Formation of Cell-Containing Hydrogel Sheets Conformal to Full-Thickness Burn Wounds Richard Y. Cheng1, Gertraud Eylert1,2, Jean-Michel Gariepy1, Sijin He1, Marc Jeschke1,2 and Axel Guenther1; 1University of Toronto, Canada; 2Sunnybrook Research Institute, Canada

The current standard of care for treating patients with severe large area burns involves the direct application of a bilayered matrix consisting of a silicone layer for immediate wound coverage and a crosslinked collagen layer as a scaffold for host cell migration. Cell repopulation remains a challenge especially as acellular scaffolds rely on the recruitment of host cells. While emerging treatment options including the delivery of allogeneic or autologous cells via spraying or injection have demonstrated improved wound healing, the consistent delivery of cellularized biomaterials conformal to wound topologies remains a challenge.

Here, we report a handheld instrument for the in-situ formation of cell-containing biomaterial sheets conformal to a burn wound. The mesenchymal stem cell (MSC)-containing, fibrin-based bioink and thrombin crosslinker solutions are delivered through on-board syringe pumps to a microfluidic printhead with internal bifurcated channels. A skin precursor sheet of consistent thickness covered with the crosslinker is obtained at the exit. Wound-conformal delivery of MSC-laden biomaterial sheets was achieved by translating the printhead along the wound surface by a soft silicone wheel, while a two-axis gimbal design allowed it to adapt to the wound topology. We observed that the addition of 1% hyaluronic acid (HA) provided desirable shear-thinning behavior of the bioink (1.2 Pa*s at shear rate 1/s, 0.35 Pa*s at shear rate 100/s), resulting in 83% of the starting thickness to be maintained for deposition surfaces with inclination angles of 45 degrees. Furthermore, these fibrin-HA hydrogels maintained high biocompatibility with the co-delivered MSCs (>94%), in addition to long-term preservation of 3D morphology and cell proliferation as shown with Hoechst/Phalloidin+ immunostaining over one week. To demonstrate the clinical utility of this approach, we uniformly distributed 1x10^6 MSCs/ml of the fibrin-HA hydrogel on a porcine 5cm x 5cm full-thickness burn wound model and quantified a 1.4-fold improvement of macroscopic re-epithelialization speed, a 1.3-fold increase in collagen density in the dermal layer, and a 2.5-fold reduction in CD11b+ inflammatory cell activity after 28 days compared to burn only controls, as observed via microscopic analysis of H&E histological stains. Taken together, these results highlight the utility of in-situ delivering cell-containing bioinks conformal to physiological surfaces, while promoting cell viability and migration to accelerate wound healing in full-thickness burns.

11:00 AM SB04.06.09
Cell-Friendly, Low-Cost and Fast Assembled Orthopaedic Treatment Using Hybrid Polycaprolactone/Alginate Hydrogel 'Bone Bricks' for Refugees Fengyuan Liu; University of Manchester, United Kingdom

Physical, sensory or intellectual impairments affect one in every five refugees, a further one in seven is affected by a chronic disease and one in 20 suffers from injury. A 2016 Handicap International report stated that 53% of injuries were due to the use of explosive weapons, among this 47% of refugees had fractures or complex fractures and this
includes open fractures of lower and upper limbs. Orthopaedic surgical intervention is a priority after blast injuries to align broken bones/fixate, treat infection and implement solutions for the associated bone loss. However, often the only feasible treatment for these injuries is limb amputation. Amputation has associated complications including heart attack, slow wound healing and infection.

This project aims to create a medical implant allowing for non-union bone loss of 10-20 cm in the lower limb able to induce bone regeneration. The research is built on the current treatment of external fixation but with the addition of an engineered internal prosthetic implant to improve patient outcomes, avoid painful limb lengthening and reduce recovery time. The patient specific prosthetic is achieved by constructing the prosthetic implant from modular pieces, “bone bricks”. The bone bricks, are hybrid scaffolds consisting of different biocompatible and biodegradable materials and infection prevention hydrogel, manufactured using multi-head extrusion-based 3D printing technique, come in a pallet of shapes and sizes and fit together in a “lego like” way to form the prosthesis. The prosthesis and paste will prevent infection, promote bone regeneration creating a mechanically stable bone union. The external fixator offers a comfortable support for patients and a strong stimulation to facilitate bone ingrowth.

This paper reports preliminary results using polycaprolactone/alginate hydrogels scaffolds. Scaffolds are extensively characterised in terms of morphology, physical, chemical and biological properties, and the results show that these scaffolds are suitable candidates to treat large bone defects enabling limb salvage as an alternative to amputation, avoiding painful limb lengthening and improving recovery time/functional patient outcomes.

11:15 AM SB04.06.10
Novel Hydrophilic/Hydrophobic Thermo-Responsive Platforms from Citric Acid Crosslinked Methylcellulose Hydrogels Lorenzo Bonetti1, Luigi De Nardo2, Fabio Variola1 and Silvia Fari1,2; 1Politecnico di Milano, Italy; 2National Interuniversity Consortium of Materials Science and Technology (INSTM), Italy; 3University of Ottawa, Canada

Methylcellulose (MC) hydrogels undergo sol-gel reversible transition upon temperature changes. At temperatures higher than their lower critical solution temperature (LCST) they are in a gel, hydrophobic state. Conversely, at T < LCST they are in a sol, hydrophilic state [1]. These hydrogels lend themselves to smart system applications, exploiting the body temperature as a trigger to activate their sol-gel transition [1,2]. However, one of the limiting factors of MC hydrogels consists in their reduced stability and mechanical properties [3]. The purpose of our research is to explore a novel method to crosslink MC hydrogels in order to increase their mechanical properties while preserving their smart behavior.

A crosslinking strategy based on the employment of citric acid (CA) was developed. The thermal response of the gels was studied by using a Design of Experiment approach, analyzing the effect of three independent variables, namely CA concentration [1-5% w/w], crosslinking time [1-15 min], and crosslinking temperature [165-190 °C] on the swelling rate of the hydrogels. This approach allowed to identify three crosslinking conditions (low, medium, high) while avoiding a trial-and-error approach. The resulting crosslinked hydrogels were characterized by a physico-chemical, mechanical and in vitro biological point of view.

Swelling tests in water revealed the effectiveness of CA crosslinking in modulating the water uptake of MC hydrogels. The crosslinking density [4] increased from (0.19 ± 0.02)*10^{-4} to (2.58 ± 0.65)*10^{-4} mol cm^{-3} for low and high crosslinking conditions, respectively. FTIR analysis and acid-base titrations confirmed the efficacy of CA in controlling the crosslinking degree of the hydrogels [5]. Specifically, carboxylic esters increased from 0.05 ± 2.74 to 42.25 ± 3.71 mmol/100 g for low and high crosslinking conditions, respectively. The extent of hydrophilic/hydrophobic transition was assessed by swelling tests in solvents with different polarities (water and 70% 2-propanol solution) and at different temperatures (4, 25, 37 and 50 °C) [6]. These tests showed that both low and medium crosslinking conditions preserved the smart behavior of MC hydrogels. Ongoing studies aim at assessing temperature-induced chemical and nanomechanical variations assessed by Raman spectroscopy and Atomic Force Microscopy. In vitro biological characterization proved the absence of any cytotoxic effect induced by CA or by the crosslinking procedure when extracts were put in contact with L929 cells for 24 h.

The obtained results pave the way for the development of MC smart hydrogels with tunable properties, with potential innovative implications in the field of smart systems, e.g. for drug delivery.

11:30 AM SB04.06.11
Room-Temperature Formed PEDOT:PSS Hydrogels Enable Injectable, Soft and Healable Organic Bioelectronics

Yihang Chen, Shiming Zhang and Ali Khademhosseini; University of California, Los Angeles, United States

There is an increasing need to develop conducting hydrogels for bioelectronic applications. In particular, PEDOT:PSS hydrogels have gained significant focus due to their excellent biocompatibility and stability [1]. However, injectable PEDOT:PSS hydrogels have not yet been reported. Such syringe-injectable hydrogels are highly desirable for minimally invasive biomedical therapeutics [2]. Here, we demonstrate an approach to enable injectable PEDOT:PSS hydrogels by using room-temperature crosslinked PEDOT:PSS hydrogels (RT-PEDOT:PSS hydrogels). These RT-PEDOT:PSS hydrogels formed spontaneously after syringe-injection, without the need of any thermal treatments. We further demonstrate that these RT-PEDOT:PSS hydrogels can be used for soft and self-healable bioelectronics.


11:45 AM SB04.06.12
Shining a Light on Mechanotransduction—Photo-Patterned Hydrogels for Tissue Engineering

Phillip Chivers1,2, Simon J. Webb1, Paul G. Genever2 and David K. Smith2; 1University of Manchester, United Kingdom; 2University of York, United Kingdom

The high demand for transplant tissue is a major health concern worldwide. A shortage of donors combined with poor long-term outcomes post-transplant has seen tissue engineering emerge as an alternative therapy. Using a patient’s own stem cells to regenerate lost or damaged tissue could reduce pressure on transplant waiting lists and avoid issues of organ rejection. However, for laboratory research to be translated into clinical applications, the development of biomaterials which stimulate the formation of specific tissues is essential.1

In recent years, hydrogels have become leading candidates as scaffolds for controlled cell growth. Despite this, there is a dearth of literature exploring the applications of low-molecular-weight gels (LMWG) in this field.2 These materials, which self-assemble through non-covalent interactions, are often dynamic – able to modulate their structure and properties in response to their external environment. Such responsive materials have great potential for complex control of stem cell fate through the delivery of spatiotemporally defined cues.

We report the use of LMWG-containing materials for the spatial control of mesenchymal stem cell (MSC) behavior. By combining DBS-CONHNH2 (a LMWG) with a photo-curable polymer gel (PEGDM), we were able to modify the stiffness of the gels with spatial control by exposing specific regions to UV irradiation.3 MSCs grown on stiffer gels were significantly more likely to differentiate into bone cells than those cultured on soft gels. Furthermore, MSCs at each side of an interface between soft and stiff gel showed significantly different behavior, illustrating the potential of these patterned materials to direct stem cell growth. Studies into the controlled release and diffusion of model compounds and biomolecules indicate that these heterogeneously structured materials could be used for spatially-defined presentation of other stem cell directing factors in the future.

Temporal changes in gel stiffness can be used to impart a further level of control over MSC behavior. We are currently developing a family of hydrogels which modulate their mechanical properties through a reversible photoreaction. Using these materials, we aim to understand and exploit the influence of stem cell mechanical memory to develop next-generation biomaterials.

References
SESSION SB04.07: Fundamentals and Applications I
Session Chairs: Namita Choudhury and Jurgen Groll
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Room 302

1:30 PM *SB04.07.01
Failure and Fracture of Hydrogels and Hydrogel Composites Michelle L. Oyen; East Carolina University, United States

Hydrogels have gained recent attention for biomedical applications due to their large water content, which imparts biocompatibility. However, their mechanical properties can be limiting. There has been significant recent interest in the strength and fracture toughness of hydrogel materials in addition to their stiffness and time-dependent behavior. Hydrogels can fail in a brittle manner even though they are extremely compliant. In this work, the failure and fracture of hydrogels is examined using a range of mechanical test methods, including compression, tension, mode I fracture and mode III tearing. Spheres of commercially-available sodium polyacrylate were tested to failure in compression as a function of loading rate. The spheres exhibited virtually no load relaxation when compressed to small fixed displacements. The distributions of strength values obtained were examined in a particle fracture framework previously developed for brittle ceramics. Mode I and mode III fracture experiments were conducted for single-component hydrogels and for hydrogel composites reinforced by nanofibers. Even though the fibers were themselves also hydrogels, the composite toughness values were two orders of magnitude greater than those for the component gels. Strength and toughness of composite hydrogels approached values seen in natural soft biological tissues, indicating that a biomimetic approach to microstructure relates to increasing material properties of hydrogels, making them suited for use as tissue engineering scaffolds in demanding load-bearing applications such as articular cartilage in the joint.

2:00 PM *SB04.07.02
Coarse-Grained Model of the Influence of Solvation on the Properties of Electrolyte, Nanoparticle and Polyelectrolyte Solutions Jack F. Douglas; National Institute of Standards and Technology, United States

The aqueous solvation of ions, highly charged nanoparticles and polymers, and the resultant non-trivial interactions between these solvated species, is a ubiquitous, but poorly understood phenomenon that underpins many biological and manufacturing processes. This solvation phenomenon is investigated based on simple, but explicit, model of the solvent that accounts for the high cohesive interaction strength of water based on the constraint that the solvent reproduces the critical temperature of pure water, while the strength of the van der Waals ion-solvent interactions between the ions and the solvent are fixed by the experimentally observed enthalpy of solvation. We find that this coarse-grained model of aqueous ionic solutions reproduces observed trends of the viscosity of water and water diffusivity with specific salt types, along with observed trends in the density, compressibility and surface tension of aqueous solutions. The application of this model to highly charged particles and polyelectrolytes, leads to new phenomena associated with nanoparticle and polymer solvation that are not observed when the solvent is treated as a continuum. In particular, while the counter-ions dissolve into the solvent as in the case of a continuum solvent, they continue to dynamically associate, leading to the formation of a diffuse “polarizable” cloud of counter-ions around the polymers and nanoparticles. We find that the fluctuations of the ions of opposite charge, which are modulated by competitive counterion and polymer/particle solvation, can lead to strong attractive interactions between charged species having a common sign. We argue that these solvation-induced interactions are crucial for understanding the widespread observations of supramolecular assembly in highly charged polyelectrolyte and colloidal solutions in the context of viscoelastic solutions and gels of proteins, and many other naturally occurring polyelectrolytes, and in common charged colloidal viscoelastic materials such as soils, setting concrete, etc. Further development of this type of model for hydrogels, and many other aqueous solution applications, requires improvements in the modeling of ion-ion interactions and van der Waals solvent-polymer or nanoparticle interactions that become large when the

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3 Chivers, P. R. A; Smith, D. K. Chem. Sci. 2017, 8, 7218-7227
salt concentration becomes large. Further validation studies of the coarse-grained model for transport coefficients such as ion diffusivity, etc. are also required.

2:30 PM BREAK

3:30 PM SB04.07.03
Behavior of Polyelectrolyte Gels in Concentrated Solutions of Highly Soluble Salts Jessica Sargent1, John A. Howarter1, Kendra A. Erk1, Mitchell Brezina1 and Xunkai Chen1,2; 1Purdue University, United States; 2University of California, Berkeley, United States

Hydrogels composed of lightly crosslinked poly(sodium acrylate-co-acrylamide) (P(ANa-AM)) have been investigated as responsive materials for a wide range of applications. This polyelectrolyte network is highly hydrophilic and sensitive to changes in the pH and ionic strength of its environment. Above a pH of ~5, the sodium acrylate moieties dissociate to produce negative charges along the polymer chain, which increases the gel’s swelling capacity due to a further increase in the osmotic pressure difference between the gel interior and the surrounding aqueous solution. However, if the solution in which the gel is submerged contains free cations (e.g., dissolved salt ions), these ions interact with the charged polymer molecules and reduce the gel’s swelling capacity and, consequently, transport properties. P(ANa-AM) gels have been applied in many biological applications and consumer products, and they are also a prime candidate for controlled release agents in internally cured high-performance concrete. The effects of biologically-relevant saline solutions on the swelling properties of these gels have been thoroughly investigated, but little has been reported regarding the performance of P(ANa-AM) gels in concentrated saline solutions (e.g., 10 mM to greater than 1 M) or after cyclical swelling and deswelling in saline solutions. In particular, it is expected that the effect of crystal formation of monovalent and multivalent salts within the gels from these concentrated solutions will have significant impacts on hydrogel behavior as well as offer new avenues for tailoring gel compositions for applications such as controlled crystal growth and recyclable hydrogel materials.

This research probes the effects of concentration, valency, and crystallization of highly soluble salts (e.g., sodium chloride and calcium chloride) on fundamental hydrogel properties including swelling capacity, mesh size, and free volume. In so doing, we seek to develop an enhanced understanding of structure-property-performance relationships in these materials that can contribute to the informed design of responsive hydrogel materials for targeted environments. This work focuses specifically on polymer compositions of 17% and 83% sodium acrylate with 0.5 and 2.0% crosslinker due to their relevance to recent research in high-performance concrete. Investigation utilizes a combination of characterization techniques that span multiple length scales in order to correlate macroscopic changes in performance with the molecular-scale interactions that induce these changes. Specifically, we incorporate bulk measurements (e.g., gravimetric swelling tests), optical analysis, and spectroscopy experiments including x-ray scattering and positron annihilation to elucidate the structural relationships between hydrogel composition (e.g., amount of charged monomer units and crosslink junctions in the network) and effects of high ionic concentrations in solution. X-ray scattering (XRD and SAXS) and positron annihilation lifetime spectroscopy (PALS) are complimentary spectroscopy techniques that allow us to probe both the size and distribution of electron-dense regions (i.e., salt crystals, collapsed polymer coils, and crosslink junctions) via x-ray scattering and the relative abundance and size of void spaces between network components (i.e., free volume) through positron annihilation. Combining these techniques with larger-scale measurements of changes in the gels’ swelling behavior, we aim to provide a complete picture of P(ANa-AM) hydrogel performance in high salinity environments.

3:45 PM SB04.07.04
Modeling Tetra-PEG Hydrogels with Degradable Crosslinks Vaibhav A. Palkar, Chandan K. Choudhury and Olga Kuksenok; Clemson University, United States

Soft materials with controllably degradable crosslinks constitute an important component of active stimuli responsive platforms for numerous applications. As one example, fast photo-cleavage of crosslinks has enabled the development of a soft material allowing user-directed growth of neural networks. Apart from light, other stimuli such as heat and ultrasound can also be utilized for controlled degradation. Herein, we develop a Dissipative Particle Dynamics (DPD) simulation framework aimed at modeling tetra-arm polyethylene glycol (tetra-PEG) hydrogels with transient crosslinking. This framework allows single parameter control over the crosslink degradation rate. Further, we develop a correspondence of our DPD framework with continuum level modeling and isolate phantom
and affine network conditions with respect to our model hydrogel network. Our results show a good correspondence with prior experimental studies on tetra-PEG gels showing crossover from phantom to affine network models for these systems with an increase in crosslink density. We then focus on adsorption of tetra-PEG nanogels at oil-water interface and on dynamics of confined films of these gels. We show that the cleavage of crosslinks leads to the controlled spreading of nanogels at the interface and to degradation-induced buckling of constrained films.

4:00 PM SB04.07.05
Ideal Dynamic Covalent Hydrogels for Thermal Stabilization of Biologics Bruno Marco Dufort and Mark W. Tibbitt; ETH Zürich, Switzerland

Recent research in the design and engineering of polymer networks has introduced a new class of hydrogels based on dynamic covalent chemistry, which combines the mechanical properties of both physically and chemically cross-linked materials. Dynamic covalent hydrogels enable the formation of responsive, mouldable, and self-healing materials, as the bonds in the network can break and reform in response to external stimuli [1]. These unique properties are being leveraging in many biomedical applications, such as in responsive drug delivery systems, dynamic scaffolds for cell culture and more recently in our work on the thermal stabilisation of biologics. The macroscale properties of these hydrogels, however, depend on the specific chemistry of the cross-link binding pairs as well as the network topology. Successful application of dynamic covalent gels therefore requires a robust understanding of how these factors influence each other and the emergent properties of the network.

In this work, we related the viscoelastic properties of dynamic covalent networks, measured by dynamic mechanical analysis, to the microscopic behaviour of the reversible junctions, through kinetic NMR studies. Boronic ester-based hydrogels were used as model dynamic covalent gels, since their viscoelastic properties can be tuned over several orders of magnitude by tailoring the chemistry of the acid-diol binding pair or by changing network pH [2]. Oscillatory shear rheometry revealed that these materials behave as ideal dynamic covalent networks, exhibiting both rubber elastic behaviour and time-dependent mechanical properties, which can be modelled by a single Maxwell element with a spring and a dashpot in series. Uniquely, the viscoelasticity in these materials could be linked to the microscopic behaviour at the junctions via 2D ¹H NMR exchange spectroscopy (EXSY), as the relaxation behaviour in these materials at different pH scale with the reaction rates of the diols with the boronic acids. This work, which links dynamics of the junction chemistry in a reversible network to its bulk behaviour, is being used to develop physical models that relate binding pair thermodynamics and kinetics to macroscale properties in order to enable the rational design of hydrogel systems.

In addition, we are applying the knowledge gained from these fundamental studies to the development of a platform material with utility in 3D printing, injectable drug delivery, and for the thermal stabilisation of biologics. We present here new results on the thermal stability of a broad range of biologics; leveraging the ability of these dynamic covalent gels to enable encapsulation, stabilisation, and triggered release of cargo. The ability to protect biologics from thermal stress with a simple material solution presents a useful approach to mitigate the cost and risk associated with reliance on a continuous cold chain for biologic transport and storage.


4:15 PM SB04.07.06
Structural and Conformational Properties of Bottlebrush Polyelectrolyte Solutions Alexandros Chremos¹, Jack F. Douglas² and Ferenc Horkay¹; ¹National Institutes of Health, United States; ²National Institute of Standards and Technology, United States

Bottlebrush polyelectrolyte solutions have great significance in biology, e.g., aggrecan is a major proteoglycan in the articular cartilage, and exhibit great potential in drug delivery applications, however, there is little theoretical understanding of their behavior compared to their linear polyelectrolyte solutions. We made a comparative investigation of linear and bottlebrush polyelectrolyte solutions with the use of molecular dynamics simulations. In particular, we utilize a previously developed polyelectrolyte coarse-grained bead-spring model that includes an explicit treatment of the charged species and solvent to probe the conformational properties of polyelectrolyte linear and bottlebrush polyelectrolytes at different polymer and salt concentrations. Specifically, we calculate the polymer hydrodynamic radius and radius of gyration along with its eigenvalues. Moreover, we calculate the structure factor
and determine the scaling of the location of the polyelectrolyte peak with polymer concentration. Overall, our findings are in agreement with small angle neutron scattering (SANS), dynamic light scattering (DLS) and osmotic pressure measurements. These complementary experimental and computational techniques probe different length and time scales providing a comprehensive picture of the essential properties of bottlebrush polyelectrolytes.

4:30 PM SB04.07.07
Light-Induced Shape-Morphing Hydrogels—Dynamic Motion and Programmable Assembly Hyunki Kim, Todd Emrick and Ryan C. Hayward; University of Massachusetts Amherst, United States

Small organisms living on the surface of water often rely on the modulation of capillary forces to propel themselves on demand. For example, springtails move at the air-water interface by simply adjusting their posture, which in turn modulates capillary forces. This results in the aggregation of the springtails and migration of individuals between aggregates. Inspired by nature, we developed a dynamic soft material that mimics the behavior of on-demand attraction and repulsion and displays programmable assembly patterns and non-equilibrium capillary motion.[1] Our synthesis of shape-morphing hydrogels used in situ patterned growth of Au nanoparticles (NPs) embedded within temperature-responsive hydrogel films. The patterns of Au NPs yielded spatially non-uniform heating under illumination, and therefore light-induced differential swelling and wrinkling of the hydrogel films. As a result, the three-phase contact line at the air-water-hydrogel interface was distorted dynamically to generate capillary attraction and repulsion. The geometry of these hydrogel nanocomposite films was designed to generate specific wrinkling patterns and resulting configurations of the hydrogel assemblies. Time-varying patterns of illumination led to reconfiguration of the assemblies, allowing them to be ‘annealed’ to reach low-energy structures. Furthermore, an appropriately chosen static pattern of illumination and geometry of the hydrogel actuator induced sustained rotation and translation. This approach provides synthetic tools to control objects in time and space with implications for the design of hydrogel nanocomposite materials and soft robots.

Reference:

4:45 PM SB04.07.08
Muscle-Like Fatigue-Resistant Hydrogels by Mechanical Training Ji Liu1,2, Shaoting Lin2, Xinyue Liu2 and Xuanhe Zhao2; 1Southern University of Science and Technology, China; 2Massachusetts Institute of Technology, United States

Skeletal muscles possess the combinational properties of high fatigue resistances (1,000 J/m²), high strengths (1 MPa), low Young’s moduli (100 kPa), and high water contents (70 – 80 wt%), which have not been achieved in synthetic hydrogels. The muscle-like properties are highly desirable for hydrogels’ nascent applications in load-bearing artificial tissues and soft devices. Here, we propose a strategy of mechanical training to achieve the aligned nanofibrillar architectures of skeletal muscles in synthetic hydrogels, resulting in the combinational muscle-like properties for the first time.1 These properties are obtained through the training-induced alignment of nanofibrils, without additional chemical modifications or additives. In situ confocal microscopy of the hydrogels’ fracturing processes reveals that the fatigue resistance results from the crack pinning by the aligned nanofibrils, which require much higher energy to fracture than the amorphous polymer chains. This strategy is particularly applicable for three-dimensionally printed microstructures of hydrogels, in which we can achieve isotropically fatigue-resistant, strong yet compliant properties.

Reference
SB04.08.01
Synthesis of Photo-Activating Acryl-Polyurethane Containing Multifunctional Monomer for High Strength and Biocompatible 3D Printing Materials Jihong Bae and PilHo Huh; Pusan National University, Korea (the Republic of)

A UV curable acryl-polyurethane is successfully prepared by a combination of poly(tetramethylene ether) glycol (PTMG) and 1,4-butandiol (1,4-BD) as polyols, 4,4’-methylene bis(phenylisocyanate) (MDI) as an isocyanate, pentaerythritol triacrylate and triethyleneglycol dimethacrylate (TEGDMA) as multifunctional monomers and benzophenone was used to photoinitiator for UV curing to optimize the physical property of the 3D structure. The crosslinking step of acryl-polyurethane elastomers were processed using the exposure to 385~405nm UV radiation. The structure of the resulting acryl-polyurethane was evaluated by fourier transform infrared spectroscopy (FT-IR), gel permeation chromatography (GPC). The tunable UV absorbance of acryl-polyurethane was adjusted through the material design. The mechanical properties such as tensile strength, elongation and modulus were evaluated by universal testing machine. And flexural strength and hardness were measured by durometer and ISO test machine. The surface resolution-quality of the 3D structure was analyzed by field emission scanning electron microscope (FESEM).

SB04.08.02
Stability-Enhanced Chitosan-Catechol 3D Bioink by Diatom Frustule Silica Jeehee Lee and Haeshin Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

This study shows the availability of a 3D bioink enhanced by diatom frustules. Diatoms are photosynthetic, aquatic creatures with a skeleton called frustule, mainly composed of silica. Many materials for 3D printing require a liquid to solid transition so that stimuli such as temperature, or UV curing were employed. However, this method is difficult to use in bio printing, which requires printing with live cells. Although there are many conventional biocompatible materials, it should be fulfill requirements: injectable, adhesive to the each layer, and maintainable without spreading after printing. Chitosan-catechol, mussel-inspired adhesive, is a 3D bioink that catechol is conjugated to chitosan, which contains an amine group that plays a synergistic role in adhesion with catechol. Chitosan-catechol is the representative adhesive that best mimics the adhesion of mussel byssus. Rapid complex formation of chitosan catechol with serum proteins is known to be able to form 3D structures. Thus, it is also possible to use it as a bio ink for rapid liquid printing, which is next generation 3D printing, not to be stacked layer by layer. However, while having a good system, the formed chitosan-catechol 3D composites have poor stability after injection and weak mechanical strength after gelation. There have been attempts to overcome this with addition of vanadium, but there are still other issues to address such as in terms of price and in vivo safety as well as performance.

In this study, we significantly enhanced the stability of the bio ink by simply mixing silica microparticles with a charged nanoporous structure. As a model system, we used Melosira nummuloides, because they are relatively bulky at ~ 50 μm in diameter, and numerous nanopores are exposed to the surface, which is likely to increase the chance to form entanglements of the bio-ink polymer to the silica surface. The results showed that the addition of Melosira nummuloides greatly increased the post - injection stability of chitosan-catechol bioink, and confirmed increased storage and loss modulus values and shear thinning rheological properties. Through the Universal Testing Machine data, it was confirmed that it has stronger mechanical tensile strength. In addition, it is verified that cells were viable on this bio ink. By using these properties, it is possible that diatom frustule-reinforced chitosan-catechol bioink can be used for printing directly in the body.

SB04.08.03
Silk Fibroin Based Antimicrobial Hydrogel for Wound Infection Treatment Wenlong Li1,2,3 and Xiaodong Chen1,2,3; 1NTU Institute for Health Technologies, Singapore; 2Innovative Centre for Flexible Devices (iFLEX), Singapore; 3Max Planck-NTU Institute for Artificial Senses, Singapore

Pathogen infection into human beings is a worldwide problem. With the global crisis of multi-drug resistance in bacteria, it is becoming an emerging urgent task in the fighting of bacteria related infections. Wound infection is one
of the easiest ways for pathogen transmission if no proper treatment is engaged. As such, the development of antimicrobial biomaterial is of great importance to interface with pathogenic microorganism. Silk fibroin, a natural protein produced from *Bombyx mori*, can be a promising candidate due to their biocompatibility, biodegradability, low immunogenicity, and tuneable mechanical properties. However, silk fibroin-based hydrogel biomaterial is not bacteria resistant, and its Young’s modulus is not comparative with human skin, hindering its application for infection treatment. Here, we present a facile self-assembly process to prepare silk fibroin hydrogel with the antimicrobial property. Dialyzed silk fibroin is co-assembled with Fmoc-protected amino acids. This procedure has very fast gelation kinetics (within two minutes), which is faster than most of the currently applied silk fibroin gelation methods. It was found that increasing Fmoc-Leu-OH (Fmoc-L) and silk fibroin concentration increased the gelation kinetics. From FTIR study, Fmoc-L transformed silk fibroin secondary structure from random coil to β-sheet. It indicates Fmoc-L promoted β-sheet formation in silk fibroin. This is probably due to the amphiphilic property of Fmoc-L, causing a capping effect on silk fibroin protein. The antimicrobial activity of hydrogel was evaluated by agar plate spreading and LIVE/DEAD staining, which showed that the hydrogel is very effective at killing *B. subtilis* with 108 CFU/mL. In addition, the mechanical property of the antimicrobial hydrogel can be tuned with other PAAm hydrogel co-gelation, making it wearable on the skin. Our results suggest a novel biomaterial candidate for wound treatment on human skin.

SB04.08.04

**Static and Dynamic Properties of Aggrecan Assemblies** Ferenc Horkay¹, Peter Basser¹, Erik Geissler² and Anne-Marie Hecht²; ¹National Institutes of Health, United States; ²Universite Grenoble Alpes, France

Aggrecan is a bottlebrush shaped high molecular weight proteoglycan. It consists of an extended protein core to which many chondroitin sulfate and keratan sulfate (linear sulfated polysaccharide) chains are attached. This array forms a bottlebrush structure. Aggrecan’s primary biological role is to provide the osmotic properties for cartilage. In the presence of hyaluronic acid (HA) aggrecan molecules self-assemble into a supramolecular structure with as many as 100 macromonomers bound to a HA molecule. The aggrecan-HA complexes govern the load bearing properties of cartilage.

Small angle neutron scattering (SANS), dynamic light scattering (DLS) and osmotic pressure measurements were made on near physiological solutions of aggrecan and aggrecan-HA complexes. SANS reveals that the supramolecular structure of aggrecan assemblies is only marginally affected by the HA molecules. DLS indicates that the dynamic response of the aggrecan-HA complex is slower than that of the corresponding aggrecan solution. The relaxation rates measured by dynamic light scattering is proportional to $q^3$, which is the signature of internal modes in large loosely connected assemblies of smaller units, such as individual aggrecan molecules. This is reflected in the hydrodynamic radius, $R_H$, whose apparent value varies inversely with $q$. With increasing aggrecan concentration $R_H$ increases, which is a consequence of the steric hindrance due to densification of the aggrecan aggregates. HA slows the relaxation rate in agreement with an increase of the friction coefficient owing to the rearrangement of the aggrecan molecules along the HA chain. However, addition of calcium chloride slightly increases the relaxation rate of the correlation function. Osmotic pressure measurements quantify the effects of HA and calcium chloride on the osmotic modulus, which defines the compressive resistance of aggrecan assemblies.

SB04.08.05

**Development of an Ingestible pH Sensitive Actuator for Edible Devices via One-Pot Synthesis** Alex Keller, Holly Warren and Marc In het Panhuis; University of Wollongong, Australia

Edible devices are an emergent technology which seek to provide researchers and health professionals with tools to monitor the GI tract without the traditional risks of retention as they are constructed from edible materials.

To this effect an ingestible actuator was developed using non-toxic poly(acrylic acid) and calcium hydroxide. Poly acrylic acid and poly(acrylic acid)/calcium hydroxide hydrogels displayed compressive stresses of 0.08 ± 0.02 MPa and 0.10 ± 0.03 MPa, respectively and swelling ratios of 61 ± 3 and 45 ± 2, respectively. However, on exposure to simulated gastric fluid (pH 1.2) for 1 hour the polyacrylic acid hydrogels were destroyed whereas the poly(acrylic acid)/calcium hydroxide hydrogels displayed a compressive stress of 0.16 ± 0.04 MPa and a swelling ratio of 12 ± 2. Furthermore, the poly(acrylic acid)/Calcium hydroxide hydrogels displayed a volume change to 17% ± 2% of it’s original volume.
This demonstrates the ability that the calcium hydroxide provides in preserving the polyacrylic acid in acidic environments such as gastric fluid and that this neutralisation reaction results in a volume change of the hydrogel. In addition to this, the poly(acrylic acid)/calcium hydroxide hydrogels exhibited reversible actuation on submerging in 0.1 M sodium citrate for 2 hours. The poly(acrylic acid)/calcium hydroxide hydrogels where able to restore their compressive stress to $0.19 \pm 0.06$ MPa, swelling ratio to $26 \pm 2$ and volume to $56\% \pm 3\%$ of its original volume.

This work offers new oppurtunities for researchers to further the state of the art for a variety of fields such as drug delivery, 4D printed materials, soft robotics and edible devices.

**SB04.08.06**  
**Strain Sensors Based on Conducting Tough Hydrogels** Matthias Kuenzel, Matthew McRae and Marc In het Panhuis; University of Wollongong, Australia

A simple model system towards an impedance-probing strain sensor based on conducting tough hydrogels is demonstrated.

An easy-to-make poly(acrylamide) (pAAm) hydrogel, cross-linked with N,N-methylene-bis(acrylamide) (MBAAm) was prepared and contacted with carbon fibres for electrical impedance analysis. The conductivity of these LiCl salt-containing hydrogel was determined to be $114 \pm 10$ mS/cm.

Upon stretching the hydrogel samples to their fourfold initial length, the impedance response increased according to a power law. This was used to establish a sensing equation for the relation between the resistive component of the impedance signal and the applied mechanical strain under tension.

Functional capacitance strain sensing devices were constructed the salt-containing hydrogels, carbon ribbons and a dielectric elastomer. The sensors were tested under cyclic loading/unloading. The measured capacitance value of the sensor was found to be linearly dependent on the extension ratio.

Our results contribute to the development of highly stretchable and soft strain sensors for the application in soft robotics or tissue engineering.

**SB04.08.07**  
**Living Electrodes from Green Algae in Hydrogels** Mohammed Al-Mossawi$^{1,1}$, Holly Warren$^{1,1}$, Paul J. Molino$^{1}$, Paul Calvert$^{2}$ and Marc In het Panhuis$^{1,1}$; $^{1}$University of Wollongong, Australia; $^{2}$New Mexico Institute of Mining and Technology, United States

Hydrogels are attracting great interest due to their unique material properties, which have found potential applications in a range of disciplines such as fuel cells, membrane electrode assemblies, neural interfaces and other biomedical applications. A relatively new direction is to combine soft (hydrogel) electrically conducting materials with living entities to create living electrodes.

In this presentation, living electrodes have been prepared by embedding green algae Chlorella Vulgaris within a hydrogel consisting of alginate and cross-linked with a salt charge carrier. We have established various immobilisation techniques to allow high-density algae cultivation. We demonstrate that the algae cells were capable of growing within alginate hydrogels for more than 28 days. Mechanical, rheological, electrical and biological properties of the living electrodes were assessed to investigate the impact of algae growth.

These living (algae-hydrogel) electrode materials are an important stepping stone towards the future development of living electrodes for biomedical and tissue engineering applications.

**SB04.08.08**  
**Decellularized Extracellular Matrix for In Situ Cell Encapsulation for Tissue Engineering** Seth Edwards, Jason Brown and Kyung Jae Jeong; University of New Hampshire, United States

Extracellular matrix (ECM) provides the ideal microenvironment for various tissue specific cellular functions including adhesion, migration, proliferation and differentiation. Using decellularized ECM (D-ECM) as a tissue
engineering scaffold has been proposed to take advantage of the chemical and physical information it retains for the growth of tissue-specific cells, in addition to retention of physical strength of the original tissue. However, introduction of cellular components into D-ECM scaffolds involves injection of cells, significantly damaging the D-ECM structure and resulting in a poor distribution of cells within the ECM. Thus, scaffolds of this nature are unfit for traditional cellular encapsulation. Alternatively, D-ECM can be milled and digested into a solution, and crosslinked to form a homogeneous hydrogel. Although this method enables in situ cell encapsulation, the mechanical properties of the resulting hydrogel are poor due to the low concentration of soluble D-ECM (~2%), and encapsulated cells are trapped in the polymer mesh of the hydrogel, which inhibits cell adhesion, spreading, and proliferation. In addition, the digestion of D-ECM results in a partial loss of molecules important to ECM function, and destroys the 3D microenvironment of the original ECM, which has been shown to be important in promoting proper cell and tissue function. Here, we propose a new method of producing D-ECM hydrogel, by assembling and curing D-ECM ‘microparticles’, allowing for in situ cell encapsulation. Using porcine corneal stroma as a model tissue, D-ECM is first mechanically milled into microparticles by cryomilling, and upon suspension in physiological buffer, particles are chemically crosslinked by microbial transglutaminase (mTG). Due to a high solids concentration, the resulting hydrogel has improved mechanical strength when compared to homogeneous D-ECM hydrogel. Additionally, the macroporous structure allows for a more optimal growing surface for encapsulated cells when compared to homogeneous D-ECM hydrogel, and the negation of a digestion step allows for the partial retention of the original ECM microstructure. This proposed change in methodology introduces a new avenue of research for using D-ECM as a biomimetic scaffold, and can be applied to other relevant tissues.

**SB04.08.09**

Wenwen Huang¹,²; ¹The Zhejiang University-University of Edinburgh Institute, Zhejiang University School of Medicine, Zhejiang University, China; ²The 2nd Affiliated Hospital, Zhejiang University School of Medicine, Zhejiang University, China

Fine-tuned programmable shape changing biomaterials are crucial for a variety of task-specific applications ranging from health care to sustainable novel devices. Biocompatible smart actuators with multifunctions and complicated architectures fabricated from natural materials remains a challenge. To generate tailored bio-polymeric materials with predictive functional outcomes, exploiting designs from nature while morphing them towards non-natural systems offers an important strategy. Elastin is a major structural protein abundant in the extracellular matrix, providing reversible extensibility and elastic recoil to the skin, elastic cartilage and blood vessels. The dynamic elastomeric systems based on elastin proteins have gained increasing attention due to their great potential for controlled release and actuating systems. In current research, an integrated modeling-experimental approach were used to rationally design and fabricate stimuli responsive and shape changing silk-elastin-like protein (SELP) hydrogels, which response to environmental stimuli, such as thermal, pH and enzymatic triggers. New stimuli-responsive bilayer hydrogel actuators were also fabricated based on genetically engineered SELP in composite laminate arrangements with cellulose nanofibers (CNF). These hybrid devices were designed to respond to dual stimuli, temperature and ionic strength, around body temperature and salt concentration of 0.5 M to 5 M. The sensitivity of these actuators support intricate morphological transformations in SELP/CNF bilayer designs where pre-patterned control of the materials assembly provides options for diverse applications for these devices. These studies provided further insight into the sequence-function relationship of SELP and bio-actuator design, and therefore accelerated the development of stimuli-responsive biomaterials.

**SB04.08.10**

**Responsive Peptide-Based Supramolecular Hydrogels Constructed by Self-Immolative Chemistry**  
Zheng Debin; Nankai University, China

Peptide-based supramolecular hydrogels that are stimuli-responsive under aqueous conditions have many potential biological applications, including drug delivery and sensing. Herein, we reported a series of responsive peptide-based supramolecular hydrogels that respond to glutathione (GSH), nitric oxide (NO) and hydrogen sulfide (H2S), which are biologically important signaling molecules. The responsive hydrogelators were designed by “self-immolative” chemistry and constructed by using self-immolative groups to modify short peptides. The self-immolative capping group could be removed in the presence of a corresponding trigger, thus causing gel–sol phase
transitions. The potential of our responsive hydrogels for drug release was also demonstrated in this study. We developed several responsive supramolecular hydrogels using self-immolative chemistry. The short peptide, GFFY, was modified with self-immolative aromatic groups to yield supramolecular hydrogelators that could form hydrogels. In the presence of small molecules capable of removing the aromatic groups from the peptide, the hydrogels changed to solution.

The potential of our hydrogels in sensing and drug delivery was demonstrated in principle. The hydrogelators were biocompatible to LO2 cells. Our study provided novel responsive hydrogels that responded to biologically important small molecules and could be applied in drug delivery and sensing.

SB04.08.11
Rationally Designed Self-Healable Planar Supercapacitor for Driving an Integrated UV/NO2 Multifunctional Sesonor Minsu Kim and Jeong Sook Ha;1 KU-KIST graduate school, Korea (the Republic of); 2Korea University, Korea (the Republic of)

Recently, there have been extensive efforts to develop self-healable electronics with reliability which can spontaneously restore electrochemical as well as mechanical properties after damages due to external impact or continuous usage. In this work, we report a rationally designed self-healable planar supercapacitor for driving an integrated UV/NO2 multifunctional sensor. As a good self-healable electrolyte in both air-ambient and watery conditions, PVA/Borax/Agarose hydrogel with NaN03 was used. The dynamic network of PVA–Borate provides the hydrogel with ultrafast self-healing property, and the agarose network provides an additional mechanical strength and stability. Bisected hydrogel electrolyte restores 96% of tensile stress and 98% of ionic conductivity after simple physical contact for 30 s without external stimuli. Gold nanosheets and multi-walled carbon nanotubes (MWNTs) transferred on to a PVA/Agarose substrate by vacuum filtration was used as self-healing electrodes. A multifunctional sensor was fabricated by vacuum filtration of MWNTs and Zinc oxide nanowires to detect both UV and NO2. The fabricated self-healable supercapacitor exhibits areal capacitance of 68.7 mF cm-2 at 1 mA cm-2, maximum energy density of 6.1 μWh cm-2, and maximum power density of 1.4 mW cm-2. The supercapacitor maintained 87% of initial capacitance and the UV/NO2 sensor also kept its sensing ability after 5 repetitive healing cycles. Using the stored energy of the supercapacitor, both UV and 10 ppm of NO2 gas could be detected for sufficiently long time. This work demonstrates a high potential of our self-healable planar supercapacitor as an integrated energy storage device in application to high performance self-healable sensor system.

SB04.08.12
Mineralization-Assisted Additive Manufacturing of Alginate Shubhanga Ballal, Qiaochu Li, Niels Holten-Andersen and Seth A. Cazzell; Massachusetts Institute of Technology, United States

We investigate a novel approach to additive manufacturing using a mineralized alginate hydrogel. By coupling the polymerization of alginate in the presence of calcium ions with the reaction of calcium ions and carbonate ions, the hydrogel is mineralized. This alters the mechanical properties of the hydrogel, making it more suitable as a structural material that can be printed. We explore how the ion concentrations and reaction times affect the properties of the resultant hydrogel. We also determine optimal methods for extruding the gel so that it may be used to form larger structures.

SB04.08.13
3D Printing of Anisotropic Hydrogels with Bioinspired Motion Hakan Arslan, Amirali Nojoomi, Junha Jeon and Kyungsuk Yum; University of Texas, United States

Motion in biological organisms often relies on the functional arrangement of anisotropic tissues that linearly expand and contract in response to external signals. However, a general approach that can implement such anisotropic behavior into synthetic soft materials and thereby produce complex motions seen in biological organisms remains a challenge. Here, we present a bioinspired approach that uses temperature-responsive linear hydrogel actuators, analogous to biological linear contractile elements, as building blocks to create three-dimensional (3D) structures with programmed motions. This approach relies on a generalizable 3D printing method for building 3D structures of hydrogels using a fugitive carrier with shear-thinning properties. This study demonstrates that the metric incompatibility of an orthogonally growing bilayer structure induces a saddle-like shape change, which can be further exploited to produce various bioinspired motions from bending to twisting. The orthogonally growing bilayer structure undergoes a transition from a stretching-dominated motion to a bending-dominated motion during its shape
transformation. The modular nature of this approach, together with the flexibility of additive manufacturing, enables the fabrication of multimodular 3D structures with complex motions through the assembly of multiple functional components, which in turn consist of simple linear contractile elements.

SB04.08.14
Molecular Dynamics Simulations of Nanocomposite Hydrogels with Nanoplatelet Clay Fillers Shoumik Saha, Miriam Rafailovich and Dilip Gersappe; SUNY-Stony Brook, United States

Nanocomposite hydrogels are physical gels formed from a mixture of hydrophilic polymer chains and nanoparticles. They have enhanced properties and can retain higher amounts of water. Despite the large number of experimental studies on this topic, little is known about the mechanism of formation and structure of these gels. Here, we use molecular dynamics simulations to study structure formation in physically associating nanocomposite hydrogels. Nanofillers were modeled as rigid bodies of disk-like shapes and physical crosslinks were simulated by introducing a short-range attraction between the nanofillers and polymer chain ends. The structure, dynamics and mechanics of these polymer gels were studied as a function of nanofiller volume fraction. We model gels both with a single polymer, as well as a binary mixture of polymers to study the effects of polymer chain interaction and assembly on structure formation and gelation of these systems. Our results show that assembly between the nanoparticles is an important determinant of the final properties of the gel. This assembly is mediated by the types and interactions of the polymer used. Our simulations are able to determine local structural information and can determine conditions under which the strength of the hydrogel is optimal.

SB04.08.15
Systematic Characterization of 3D-Printed Polycaprolactone/ Poly (Ethylene Oxide)/ Hydroxyapatite (HA) Scaffolds For Biomedical Devices and Bone Tissue Engineering—Influence of Material Composition and Structure Design Bin Zhang1,2, Alesander Nguyen, Jie Huang and Roger Narayan; 1University College London, United Kingdom; 2University of North Carolina at Chapel Hill and North Carolina State University, United States

This works aims at guiding systematic experimental characterization for the design of 3D printed scaffolds for bone tissue applications, focusing on direct ink writing with a biocomposite of polycaprolactone (PCL), poly (ethylene oxide) (PEO) and hydroxyapatite (HA). Firstly, the effect of the material composition (HA concentration in the range from 55 to 85% w/w) on the PCL/PEO/HA ink rheology properties we studied. Secondly, the impact of the ink compositions on the 3D printed scaffold mechanical properties were systematically investigated. Thirdly, different concentrations of vancomycin drug (5%, 10%, and 15% w/w) have been successfully loaded on the PCL/PEO/HA scaffold, and drug release profile was investigated. Work is continuing to characterize the PCL/PEO/HA scaffolds in anti-microbial properties and tissue regeneration in biological models to develop a 3D multifunctional composite scaffolds by changing scaffold material, structures, and mechanical properties. The biocomposite scaffold fabricated in this study has the potential for the application of tissue replacement.

SB04.08.16
Additive Manufacturing of Bovine Serum Albumin-Based Hydrogels and Bioplastics Patrick Smith, Benjaporn Narupai, Jonathan Tsui, Sayami C. Millik, Ryan Shafranek, Deok-Ho Kim and Alshakim Nelson; University of Washington, United States

Bio-sourced and biodegradable polymers for additive manufacturing could enable the rapid fabrication of parts for a broad spectrum of applications ranging from healthcare to aerospace. However, a limited number of these materials are suitable for vat photopolymerization processes. Herein, we report a two-step additive manufacturing process to fabricate robust protein-based constructs using a commercially available laser-based SLA printer. Methacrylated bovine serum albumin (MA-BSA) was synthesized and formulated into aqueous resins that were used to print complex 3D objects with a resolution comparable to a commercially available resin. The MA-BSA resins were characterized by rheometry to determine the viscosity and the cure rate, as both of these parameters can ultimately be used to predict the printability of the resin. In the first step of patterning these materials, the MA-BSA resin was 3D printed, and in the second step, the printed construct was thermally cured to denature the globular protein and increase the intermolecular noncovalent interactions. Thus, the final 3D printed part was comprised of both chemical and physical cross-links. Compression studies of hydrated and dehydrated constructs demonstrated a broad range of compressive strengths and Young’s moduli that could be further modulated by adjusting the type and amount of co-monomer. The printed hydrogel constructs demonstrated good cell viability (> 95%) after a 21-day culture period.
These MA-BSA resins are expected to be compatible with other vat photopolymerization techniques including digital light projection (DLP) and continuous liquid interface production (CLIP).

SB04.08.17
Cucurbit[8]uril-Mediated Supramolecular Graphene Hydrogel Vijay K. Rana and Oren A. Scherman; University of Cambridge, United Kingdom

Once graphene (GR) is incorporated into polymer matrices, the resultant composites show enhanced mechanical, thermal, electrical and biological properties. However, the scalable production of uniformly distributed graphene-based composite materials remains a sizable challenge. While GR-polymer nanocomposites can be manufactured at large scale, processing limitations result in poor control over the homogeneity of hydrophobic GR sheets in the matrices. Such processes often result in difficulties controlling stability and avoiding aggregation, therefore eliminating benefits that might have otherwise arisen from the nanoscopic dimensions of GR.

Here, we report an exfoliated and stabilized GR dispersion in water. Bicationic viologen derivative was used to exfoliate and stabilize partially reduced/defected/oxidized graphene sheets in water. Finally, cucurbit[8]uril (CB[8])-mediated host-guest chemistry was used to obtain supramolecular hybrid hydrogels consisting of uniformly distributed, low amounts of graphene with guest-functionalized macromolecules. The obtained GR-hydrogels show superior bioelectrical properties over identical systems produced without CB[8]. Utilizing such supramolecular interactions with biologically-derived macromolecules is a promising approach to stabilize graphene in water and avoid oxidative chemistry.

SB04.08.18
Optimizing Thermal and Mechanical Properties of Poly(Lactic Acid) / Polypropylene / Graphene Nanocomposite Polymer Blends in Fused Deposition Modeling Systems Yu-Chung Lin1, Larry J. Huang2, Richard Li3, Addison Liu4, Nikita Salunke5, Yuval Shmueli1, Miriam Rafailovich1 and Steve Nitodas1; 1Stony Brook University, The State University of New York, United States; 2Wilton High School, United States; 3Conestoga High School, United States; 4Unionville High School, United States; 5Evergreen Valley High School, United States

The Fused deposition modeling (FDM) process is highly non-equilibrated and often has inadequate thermal retention, posing problems which can be addressed via binary blending. This work explores a binary polymer blend of polylactic acid (PLA) and isotactic polypropylene (iPP) with added graphene nanoplatelets (GNPs). Mechanical testing revealed that in comparison to a control sample of pure PLA, the addition of only 1% iPP resulted in a 66% increase in toughness, and a further increase to 2.5% resulted in an increase of only 16%. Further increase above 5% decreased the toughness by 45%. These results correlated with SEM and HD optical microscopy where the filament/filament interfaces were still visible in the pure PLA sample, while they appeared completely fused in the sample with 1% iPP. Water contact angle goniometry showed an increase from 66 degrees on the pure PLA sample to 88 degrees, the value of pure iPP, on the samples containing only 1% iPP. These results indicate that an iPP shell had formed at the filament surface, which is consistent with the segregation of iPP whose surface tension is significantly lower than that of PLA. The glass transition of iPP, also being lower than that of PLA, enables interdiffusion between filaments, leading to complete obliteration of the interface and enhanced mechanical properties. Blends of iPP/PLA containing 5% GNP were also produced and drawn into filaments. While SEM imaging indicated nearly complete alignment of the GNPs along the extrusion direction, partial sequestration of the particles in the iPP shell and internal phase segregated regions were also evident. Infrared imaging (FLIR A300) of samples in contact with a well-defined heat flux indicated an increase of 159% over the pure PLA control sample with the addition of 5% GNP. Addition of 5% GNP, with 2.5% and 5% iPP yielded an increase of 272% and 245% respectively, indicating greater thermal conduction efficiency when graphene platelets are confined in the iPP domains.

SB04.08.19
Thermoresponsive Triblock Copolymers for 3D Printing of Hydrogels Kusuma Betha Cahaya Imani and Jinhwan Yoon; Pusan National University, Korea (the Republic of)

Pluronic is a highly biocompatible and thermoresponsive triblock copolymer consists of hydrophobic poly(propylene oxide) (PPO) as the center block and hydrophilic poly(ethylene oxide) (PEO) as the side blocks. Because of its amphiphilic nature, pluronic possess the ability to form spherical micelles within aqueous solution above its critical micelle temperature (CMT). This phenomenon is driven by the decrease of PPO block’s solubility,
forming a core for the micelles. This reverse thermoresponsive characteristic allows pluronic to have shear thinning property, which can be utilized as an ink for extrusion 3D printing. The quick shear thinning behavior is useful to prevent the ink from flowing upon its deposition on a substrate and retain the desired shape. In this study, we combined pluronic F127 ((PEO)_{99}-(PPO)_{65}-(PEO)_{99}) with methacrylate groups into pluronic F-dimethacrylate (FDMA) as an ink to prepare hydrogels with extrusion-based 3D printing. The methacrylate groups are added to maintain the 3D printed structure after immersion in water by photopolymerization, forming crosslinking that prevent pluronic from dissolving out. In addition, we also manipulated the hydrogels toughness and conductivity by incorporation of ionic bonding and conductive materials. The synthesis of FDMA is simple and it has the prospect for further studies in various fields such as soft robotics and tissue engineering as artificial human organs.

SB04.08.20
Toughening of Polysaccharide Hydrogels for Biomedical Applications Muhammad R. Hossen and Michael Mason; University of Maine, United States

Polysaccharide hydrogels are excellent candidates for biomedical applications such as drug delivery, wound dressing and tissue engineering. For each of these applications, mechanical robustness of the gels, specifically in an aqueous environment, is crucial. Polysaccharide gels are commonly formed by fiber entanglement and hydrogen bonding. Water molecules can disrupt the hydrogen bonding and causes disentanglement of the fibers. Therefore, these gels lose their stiffness and structural integrity in water. Here we describe a new approach for generating wet stable and mechanically stiff semi-interpenetrating (IPN) composite hydrogels through the addition and photo-crosslinking of methacrylate functionalized carboxymethyl cellulose (MetCMC) in the polysaccharide matrices. Physical and mechanical properties such as wet stability, swelling, shrinkage, and stiffness of the gels were studied to test their suitability towards biomedical applications. Data supporting the superior mechanical properties and biocompatibility of the chemically cross-linked wet stable polysaccharide hydrogels will be presented.

SB04.08.21
Poly(ethylene glycol) diacrylate (PEGDA) Degradation Studies for Tissue Engineering Applications Ozlem Yasar and Deldrys Gomez Reynoso; City University of New York, United States

Tissue engineering targets to study the organ regeneration as an alternative approach to the organ transportation. Organ regeneration can only be done successfully, if cells are seeded on the building blocks that are known as scaffolds. Scaffolds help cells to grow in 3-D, as cells migrate within the scaffolds. In this research, Poly(ethylene glycol) diacrylate (PEGDA) was chosen to fabricate the engineered scaffolds. PEGDA is a photo-curable solution and it can be mixed with different chemical solutions to work with the different percentages of PEGDA. In this research, degradation rate of PEGDA was studied. First of all, three sets of cylindrical PEGDA samples with the height of 14 mm and diameter of 14 mm were fabricated by using the 20%, 40%, 60%, 80% and 100% of PEGDA. All of the cylindrical samples were weighted before the degradation tests. Then, first PEGDA sets were immersed into the limonene solution for four hours and they were weighted in every hour. Their dimensions were also measured in every hour. After that, the second set of PEGDA samples were immersed into the water and both weight and dimension measurements were also done in every hour for four hours. At the end, the third PEGDA samples were immersed into the 99% ethyl alcohol and their weight and dimensions were measured in every hour. Our results indicate that, as the PEGDA percentage increases, its degradation rate decreases. Also, PEGDA degrades away the most in the 99% ethyl alcohol more than limonene and water. Our research to study the degradation rate of PEGDA will extend to the use of hot-stir plate to study investigate the temperature affect.

SB04.08.22
Designing of Three-Dimensional Hybrid Scaffolds for Tissue Regeneration Olga Urbanek-Swiderska and Dorota Kolbuk; Institute of Fundamental Technological Research PAS, Poland

Application of electrospun nonwovens is limited due to its two-dimensional (2D) architecture. Hybrid scaffolds consisting of electrospun fibres and other 3D techniques are formed to overcome this problem. Those scaffolds are able to combine advantages of both materials’ forms [1]. Electrospun nanofibers mimic the biopolymer network of native tissue very well and provide significant surface area for attaching bioactive components for local stimulation of cellular activity. On the other hand, hydrogels and its freeze-dried forms provide 3D architecture. An example of 3D tissue are bones cavities, occurring in the result of disease or injuries. For this purpose fibres may be coated with
hydroxyapatite, in order to stimulate osteoblasts proliferation and activity [2]. The aim of this research was to develop 3D hybrid scaffold from the electrospun fibres and hydrogel. Poly(lactic-co-glicolide)(PLGA) fibres were formed via electrospinning technique and subjected to ultrasounds in order to increase the nonwoven dimensions. Additionally, this procedure was used to cover one group of the nonwovens with hydroxyapatite (nHAp). Finally, fibres were immersed in gelatine solution, crosslinked and subjected to both, materials characteristic and \textit{in vitro} biological tests.

The contribution of fibres to hydrogel mass after lyophilisation was 50/50 w/w. SEM imaging confirmed presence and homogeneously distributed PLGA and PLGA-nHAp coated fibres in the pore walls. FTIR, EDS analysis as well as WAXS measurement confirmed presence of nHAp crystal in the scaffolds, its distribution and structure. DSC analysis revealed no significant changes in glass transition temperature nor melting temperature of PLGA. The weight loss of 3D scaffolds was conducted per one month. During the first week of incubation the weight loss was ca. 5%. Moreover, the mechanical tests and \textit{in vitro} tests were conducted. The biological tests confirmed constant proliferation of cells in the analysed time points, as well as proper cell morphology and spreading on the scaffold surface.

Summarizing, presented technique is an effective method of 3D hybrid scaffolds preparation, based on ECM mimicking electrospun fibres.

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A new facile synthesis of white light-emitting, multifunctional, water-soluble, metal-free, non-toxic, highly photostable, bio-active Protein Quantum Dot (ProQDot) hydrogels is reported here. These advanced functional nanoparticles consist of cross-linked bovine serum albumin (BSA) and graphene quantum dots (GQDs). The ProQDots contain blue, green and red dye conjugated GQDs, which are intern crosslinked with BSA to form white emitting hydrogels. These are bio-degradable and highly photostable when compared to organic and inorganic dyes. This bio-hydrogels are further characterized by XRD, CD, FT-IR, DLS, Raman, UV-Visible, TEM, SEM, confocal laser microscopy, photoluminescence spectroscopy, and gel electrophoresis techniques. This robust ProQDots with a variety of surface-functionalities with unique optical properties has led to promising applications in bioimaging, cellular biology, and drug delivery studies. Furthermore, as prepared ProQDot hydrogels can be used to study neuronal intracellular processes for in vivo observation of cell trafficking, tumor targeting, bio-sensing, CRISPR-Cas, and immunohistochemistry (IHC) applications.

SB04.08.26
Biorprinting Autologous Dermal Equivalent Organotypics Juyi Li1, Michael Cottone1, Philip Cottone1, Olias Christie1, Vivian Su1, Zahin Huq1, Michael Gozelski1, Sampson Berlinski1, Kimberly Lu1, Adeel Azim1, Christopher Chan2, Teresa Duong1, Saba Gulzar4, Clara Doyung Lee3, Stella Lessler4, Somya Mehta2, Katherine Tian2, Marcia Simon1 and Miriam Rafailovich1; 1Stony Brook University, The State University of New York, United States; 2Hicksville High School, United States; 3St. Anthony’s High School, United States; 4New Hyde Park Memorial High School, United States; 5Daegu International School, Korea (the Republic of); 6Yeshivah of Flatbush Joel Braverman High School, United States; 7Ward Melville High School, United States

Rheinwald and Green were pioneers in the development of cell culture methods later incorporated into the protocol for production of organotypic cultures. The technique, as described by [1], dermal fibroblasts are first spread as sheets encapsulated in a collagen matrix, then keratinocytes, expanded using immortalized 3T3 cells are spread on top at a high density. This technique proved very successful since it used autologous cells to minimize rejection, and the use of 3T3 cells allowed for rapid expansion of epithelial cells. In order to further increase the utility of these dermal equivalents, inclusion of vascularization is desirable. Production of the organotypics via bioprinting would greatly facilitate attainment of this goal, since the flat sheets could be replaced by patterned layers where vascularization could be initiated through insertion of angiogenic hydrogel segments. Here we first report on the production of the autologous organotypic following the protocol of Carlson [1] adapted for printing with a Cell Ink bioprinter. The first layer of fibroblasts embedded in collagen and second layer of keratinocytes were either printed with a 0.2mm nozzle or simply poured to make four different conditions of skin equivalents. The organotypics were evaluated by H&E staining and compared with those produced by the standard sheet deposition method. The results indicated that even though the structures had high integrity and good interlayer adhesion, the keratinocytes layer was significantly thinner in the printed samples. Ancillary experiments to determine the effect of nozzle shear showed no influence on the ability of fibroblasts to contract collagen, but a small yet significant reduction in colony formation by the keratinocytes was observed. Further testing will be performed to determine if this is a consequence of the larger keratinocyte cell printing density or the lower viscosity of printing solution. Overlaying the secondary pattern structures for vascular initiation may induce further shear, and the impact on the skin structures will be presented.


SB04.08.27
In Situ Simultaneous Time Resolved X-Ray Scattering and Thermal Imaging and of Isotactic Polypropylene Homopolymer and Graphene Nanocomposites During Fused Filament Deposition Printing Miriam H. Rafailovich1, Yuval Shmueli1, Yu-Chung Lin1, Sungsk Lee2, Mikhail Zherenkov3, Rina Tannenbaum1, Dilip Gersappe1 and Gad Marom4; 1Stony Brook University, The State University of New York, United States; 2Argonne National Laboratory, United States; 3Brookhaven National Laboratory, United States; 4The Hebrew University of Jerusalem, Israel

Fused filament deposition (FDM) is a common 3D printing technique, in which a thermoplastic polymer is melted and extruded in specific forms according to the user input file. In contrast to bulk fabrication methods, the FDM printing occurs under conditions which are far from equilibrium, and produce rapidly fluctuating thermal and
mechanical gradients, which have temporal as well as spatial variations that can impact crystallization and ultimately filament fusion and sample integrity. In order to image these gradients directly, and understand the structure property relationships during the FDM process, we have designed an apparatus which can be placed directly in an X-ray scattering beamline to simultaneously profile, with micron spatial resolution, temperature, and SAXS, MAXS and WAXS spectra. Here we describe results obtained with isotactic polypropylene (iPP) and iPP/graphene nanocomposite filaments. The homopolymer filaments were amorphous when they emerged from the nozzle, but crystallization, of a shish-kebab structure occurred within 12 seconds initially at the outer edge of the filament (shell) and propagating in time towards the center. When the second filament was printed, the core continued to crystalize, but crystallinity in the shell disappeared, which was attributed to chain relaxation to relieve stress across the interfacial region. Three-point-bending measurements of the flexural modulii showed no significant difference between molded and printed samples, consistent with SEM images which showed complete internal fusion of the filaments. The shish kebab structures were not present when more than 1% GNPs were included. Orientation of the graphene along the flow direction as well as redistribution of the platelets towards the center of the filament was observed, which correlated with large directional enhancement of the thermal and electrical conductivities of the printed samples. The depletion of GNP from the shell region correlated with SEM images of cryo-fractured segments. The enhanced thermal retention in this region enabled chain diffusion across the filament interfaces, consistent with the good mechanical performance of the composites.

**SB04.08.28**

**Enhancing the Flame Retardancy of Biodegradable Poly(vinyl alcohol) Hydrogels with Resorcinol Bis(diphenyl phosphate) Coated Starch**

Yuan Xue1, Jalaj Mehta2, Lauren Stiefel3 and Miriam Rafailovich1; 1Stony Brook University, United States; 2Hauppauge High School, United States; 3Yeshiva University High School for Girls, United States

Flame retardant components are necessities to a firefighter’s protective gear, such that more eco-friendly advancements in this technology have become more pertinent in an effort to better ensure the safety of both firefighters and victims in fire. Conventionally, flame retardants have been created from only slightly biodegradable superabsorbent polymers with extremely high water content. Generally these superabsorbent polymers are derived from acrylic acid and acrylamide and unless these are oligomers it is likely that they are not biodegradable. In lieu of these facts the primary goal of this research was to synthesize a biodegradable hydrogel flame retardant that is as efficient as its less environmentally friendly equivalents.

To create the hydrogel samples we used a cyclic freezing and defrosting procedure consisting of 24 hours in a -20 degree Celsius freezer and then 1 hour of defrosting at room temperature 3 times for each set of samples. We derived from the FTIR results that hydrogen bonds were present in the PVA and RDP-PVA, and learned that the gels were mainly shear-thinning through the rheological studies. Overall samples with PVA as the hydrogel base with RDP-coated starch performed the best in terms of the completeness of the char layer formed. The temperature of the skin sample under the hydrogel were kept being below 65°C during burning test. Additionally the flame retardant hydrogel displayed clear shear-thinning. Thermal protective performance (TPP) tests were performed to evaluate heat transmission through the FR hydrogel when exposed to a continuous heat source, and result compared to the Stoll Curve which represent the heat level for causing second-degree burn. The TPP test result showed that the poly(vinyl alcohol) flame retardant hydrogel provided a prolonged protection time.
Biofabrication is a specific area within the field of tissue engineering which takes advantage of rapid manufacturing (RM) techniques to generate 3D structures which mimic the natural extracellular matrix (ECM). A popular material in this respect is gelatin, as it is a cost-effective collagen derivative, which is the major constituent of the natural ECM. The material is characterized by an upper critical solution temperature making the material soluble at physiological conditions. To tackle this problem, the present work focusses on different gelatin functionalization strategies which enable covalent stabilization of 3D gelatin structures [1, 2].

In a second part, synthetic (multifunctional) acrylate-endcapped, urethane-based precursors will be discussed with exceptional solid state crosslinking behaviour compared to conventional hydrogels [3].

Several polymer processing techniques will be covered including conventional 3D printing using the Bioscaffolder 3.1, two-photon polymerization (see Fig.) and electrospinning starting from crosslinkable hydrogels. A number of biomedical applications will be tackled including adipose tissue engineering [4], vascularization [5], ocular applications [6], etc. The results show that chemistry is a valuable tool to tailor the properties of hydrogels towards processing while preserving the material biocompatibility.


8:30 AM *SB04.09.02
Adaptable Hydrogels as Custom Bioinks Sarah C. Heilshorn; Stanford University, United States

Despite the rise of 3D printing of thermoplastics both in industry and the general public, a key limitation preventing the widespread use of cell-based 3D printing is the lack of suitable bioinks that are cell-compatible and have the required properties for printing. Current commonly used biomaterials have distinct limitations when used as a bioink including difficulty maintaining a homogeneous cell suspension, avoiding cell damage during extrusion, customizing the printed matrix properties to facilitate cell-matrix interactions, and printing within a bath to prevent cell dehydration while preserving high print resolution. We have designed a new family of tunable biomaterials specifically designed for cell-based 3D printing. These hydrogel-based bioinks are produced from blends of engineered recombinant proteins and peptide-modified, naturally occurring biopolymers such as alginate and hyaluronic acid. These materials undergo two-stages of crosslinking: (i) weak, peptide-based, self-assembly to homogeneously encapsulate cells in a shear-thinning hydrogel within the ink cartridge and (ii) stimuli-responsive crosslinking post-printing to rapidly stabilize the construct. Benefits of this two-stage crosslinking strategy include the prevention of cell sedimentation within the ink cartridge, mechanical shielding of the cell membrane from damaging extrusion forces during printing, rapid post-print self-assembly within an aqueous bath that prevents cell dehydration, and fine-tuning of the printed scaffold mechanical properties for optimal cell-matrix interactions.

9:00 AM SB04.09.03
Laser Direct Writing of Multi-Metal Microstructures in Hydrogel—From Core-Shell Nanoparticle Formation to Spatially-Selective Plasmon Absorption Manan Machida1, Takuro Niidome2, Hiroaki Onoe1, Alexander Heisterkamp1,3,4 and Mitsuhiro Terakawa1; 1Keio University, Japan; 2Kumamoto University, Japan; 3Gottfried Wilhelm Leibniz University Hannover, Germany; 4Laser Zentrum Hannover, Germany

For development of hydrogels to novel biomedical devices such as wearable or implantable devices, it has been desired to provide hydrogels with specific optical, electrical, or mechanical properties. Since metallic micro- and nanostructures exhibit unique properties depending on the size, shape, and material of the structures, further high-functional flexible devices can be realized if the metal structures are able to be fabricated spatial selectively inside a hydrogel. We demonstrated spatially-targeted fabrication of metal microstructures in poly(ethylene glycol) diacrylate (PEGDA) hydrogel by using femtosecond laser, in which multi-photon photoreduction of metal ions occurs in the tightly focused space of the laser pulses. The metal microstructures were fabricated along a predefined trajectory by using computer-aided laser scanning. We fabricated gold, silver, and gold/silver bimetallic structures coexisting in the same hydrogel in a stepwise manner by taking advantage of the hydrogel’s ionic permeability. Red
and yellow colors were observed for the fabricated gold and silver microstructures, respectively, which are attributed to the plasmonic resonances of the respective metal nanoparticles. Moreover, the absorbance peak of the fabricated bimetallic structures shifted from those of the single metal structures. EDX analysis revealed that the fabricated bimetallic structures consist of core-shell nanoparticles. Our technique allows to create arbitrary three-dimensional (3D) dissimilar metal microstructures, which provides the site-selective optical properties within the same supporting hydrogel that can be applied for various applications including optically-driven actuators and sensing applications.

9:15 AM SB04.09.04
Visualizing Morphogenesis through Instability Formation in 4D Printing Dong Wu, Jiaqi Song and Mutian Hua; University of California, Los Angeles, United States

Heterogeneous growth in a myriad of biological systems can lead to the formation of distinct morphologies during the species’ maturation processes. We demonstrate that the distinct longitudinal buckling observed in pumpkins can be reproduced using 4D printing of stimuli responsive materials, taking advantage of digital light processing (DLP) 3D printing and stimulus-responsive materials. The mechanical mismatch between the different printed regions results in buckling instability on the surface. The initiation and formation of buckles are governed by the ratio of core/shell radius and the difference in swelling ratio and stiffness of the core and shell. For a thin shell, the buckles are more likely to occur, which is corresponding to the phenomenon that buckling initiates at the top few layers. The number of buckling increases from 4 to 44 as the swelling ratio of the shell decreases. Furthermore, the rigid core not only acts as a source of confinement laterally, but it also sets a boundary at its ends, exerting compressive stress and inducing buckling formation along the shell layer. This heterogeneous structure with controllable buckling geometrically and structurally behaves much like the plant’s fruits.

9:30 AM SB04.09.05
3D Bioprinting Vascularized Hydrogel Constructs for Cancer Models Murat Guvendiren and Chya-Yan Liaw; New Jersey Institute of Technology, United States

3D bioprinting is an emerging manufacturing approach to fabricate (cell-laden) hydrogel constructs with embedded microchannels, which are potentially useful for fundamental studies to understand vascularization and angiogenesis, and for developing organ-on-a-chip devices for disease modeling. In this work, we developed a novel bioprinting approach to print a sacrificial ink within photocurable matrix hydrogels. Micro-channels are formed when sacrificial hydrogel is dissolved post-printing. Our approach differs from commonly utilized extrusion-based free-from printing approaches, as it doesn't require a support bath or a shear thinning behavior for the matrix hydrogel to enable needle motion. To achieve this, a photocurable hydrogel is printed layer-by-layer as usual, but each layer is exposed to light briefly (seconds) to create partially crosslinked, self-supporting layer. At a desired thickness, immediately after the layer is printed, prior to partial crosslinking step, sacrificial hydrogel is directly printed within this viscous uncrosslinked layer. The layer is then exposed to light to confine and support the sacrificial hydrogel. After fully crosslinking the system, sacrificial hydrogel is washed away, forming a channel. This approach allows bioprinting of cells with the matrix material and seeding of cells into channels after the sacrificial ink is removed. To further utilize our approach, we developed a photocurable bioink formulation enabling cell-mediated degradation, allowing cells to remodel their surrounding microenvironment. We fabricated a perfusable hydrogel device using these bioinks to investigate the behavior of cancer cells within vascularized 3D hydrogel microenvironment.

9:45 AM SB04.09.06
3D Printed Hydrogel-Based Electrical Impedance Tomography Sensor for In Situ Monitoring of Deformation Zhijie Zhu, Hyun Soo Park and Michael C. McAlpine; University of Minnesota Twin Cities, United States

The ability to directly print soft, compliant biomedical devices and sensors on the skin and inside the body could enable revolutionary advances in portable healing, wound monitoring, and traumatic shock reduction. Previously, we have shown the ability to directly 3D print functional materials on moving freeform surfaces, in which the rigid-body motion of the target surface can be tracked via a closed-loop feedback control system. Specifically, we were able to directly 3D print a functional electronic circuit directly on a moving hand, using the printer nozzle to “tattoo” electronics. Here, the capability of this adaptive 3D printing system is expanded for the first time to track the deformation of target surfaces, such as expansion and contraction of soft tissues. We demonstrate that the motions and time-variant geometries of the target surface can be estimated on-the-fly and in a closed loop fashion via
machine learning from a data set of 3D scans and a real-time visual tracking system. Using this approach, a unique and conformal ionic hydrogel sensor was directly printed on a ‘breathing’ swine lung in vitro under respiration-induced deformation. The ionic hydrogel sensor is compliant to the soft tissue surface and can monitor the tissue deformation utilizing electrical impedance tomography, which provides a spatial mapping of the deformation. This adaptive 3D printing method for the direct fabrication of soft, stretchable sensors on deforming surfaces may enhance robot-assisted medical treatments and minimally-invasive procedures with additive manufacturing capabilities, enabling autonomous, direct printing of wearable electronics and biological materials on and inside the human body.

10:00 AM BREAK

10:30 AM SB04.09.07
Ultrashort Self-Assembling Peptides for Robotic 3D Cell Bioprinting under Physiological Conditions
Hepi Hari Susapto, Kowther Kahin, Zainab Khan, Salwa Alshehri, Sherin Abdelrahman, Jordy Homing Lam, Xin Gao and Charlotte Hauser; King Abdullah University of Science and Technology, Saudi Arabia

3D bioprinters have received considerable attention in latest studies, primarily owing to their customization and flexibility that provide an advantage over traditional lab-grown organ development. By printing with a bioink, productivity and efficacy are enhanced while accelerating medical procedures like organ transplantation. Many different natural bioinks have also been studied for their potential application in 3D bioprinting, such as matrigel, collagen, and alginate, all of which are obtained from non-human sources. Because of their complex and variable composition, these natural bioinks are not suitable for controlled modifications. Complications in controlling these materials’ physiological variables (e.g. pH and salt concentration) also pose challenges in mimicking the extracellular matrix (ECM). Their batch-to-batch fluctuations can also have a significant impact on the sustainability and immunogenicity of the bioprinted 3D structures, which are among the drawbacks of using these bioinks for tissue/organ growth or downstream clinical applications. In addition, 3D molds based on polymers are a prerequisite for the manufacturing of 3D structures using natural bioinks. This introduces more difficulties for complex molds as they are not easily constructed. The issues associated with natural bioinks can be solved by harnessing a synthetic peptide material that can self-assemble to form 3D nanofibrous scaffolds, in addition to other benefits, such as control over composition and ease of chemical modifications. In this study, we have developed an in situ bioprinting technique that enables the printing of cells under true physiological conditions using ultrashort self-assembling peptides as bioinks. Previously, we designed a set of ultrashort peptide bioinks that demonstrated adequate mechanical strength, rigidity, and shape fidelity on glass substrates. To understand more about the self-assembly process of these peptides, the morphology, secondary structure and viscoelastic property of self-assembled peptide nanostructures were further characterized, in addition to molecular dynamics simulations of these peptides in water to study fiber formation at the atomic scale. The 3D structure of these assembled peptides were then determined using NMR spectroscopy to support the simulation result. An extruder was engineered to be compatible with the peptide-based hydrogel and installed for improved printing by a 3D bioprinting robotic arm. We believe that as we print under truly physiological conditions, our unique in situ 3D bioprinting technique offers benefits over current bioprinting methods. The bioprinting methods that makes use of UV-treatment, chemical crosslinking, and viscous bioinks that result in stress to the cells can also be avoided with our method. Furthermore, the self-assembled peptide bioinks prove to be durable, readily printable, and offer great biocompatibility with tested cell lines including human dermal fibroblast cells and human mesenchymal stem cells. From the results, the cell proliferation in printed peptide hydrogels after 14 days and 21 days of culture was higher than that of alginate gelatin. RNA sequencing was also conducted to compare the difference in gene expression patterns in HDFn cells cultured in 2D, 3D bioprinted in IVZK and alginate-gelatin (AG) bioinks. We further demonstrate that various nanomaterials can easily be synthesized or incorporated into the 3D bioprinted peptide scaffolds that create a new opportunity for functionalized 3D scaffolds for a wide range of applications, including tissue engineering and regenerative medicine.

10:45 AM SB04.09.08
Biodegradable Thermoplastic Elastomers as 3D-Printed Nerve Guidance Channels for Peripheral Nerve Repair
Yang Hu1, Robert Newman1 and Adam K. Ekenseair1,2,3; 1Northeastern University, United States; 2The University of Texas at Austin, United States; 3University of Arkansas–Fayetteville, United States

The peripheral nervous system (PNS) is a complicated and extensive network of nerves that are the means by which
the brain and spinal cord control the rest of the body. The PNS is fragile and can be easily damaged by injuries or trauma. Surgical treatment is the only remedy currently available, with the gold standard for defects greater than 8 mm being autologous nerve grafts; however, only around 40% of the 1.8 million US PNS patients each year regain normal function. In addition, nerve grafts have been particularly ineffective at repairing critical-size nerve defects (>3 cm). Scaffold-based strategies where a tubular nerve guidance channel (NGC) is used to bridge the nerve defect have been promoted as a potential alternative that could avoid the additional surgeries and associated donor site morbidity involved in the harvest of nerve grafts. Clinicians have thus increased the use of NGCs combined with current surgical therapeutics. However, current NGCs lack patient-specific tunability and are only approved for small-gap (<3 cm) injuries by the U.S. Food and Drug Administration (FDA). Current research efforts are focused on creating more complex NGCs that can support the regeneration of critical-size defects.

In this context, our research seeks to use additive manufacturing technologies to create bioactive and cellular NGCs on demand for the repair of critical-size nerve defects. Recently, 3D printing has been increasingly used in research and medical therapeutics for rational, computer-aided design of biomaterial-based scaffolds with complex architecture. Furthermore, printing with co-axial extruders can enable the direct printing of layered tubular structures for use as NGCs. The NGCs should contain an outer flexible shell that seeks to mimic the mechanical properties of the surrounding biological tissue and enable diffusion of nutrients to support encapsulated cells. The use of biodegradable block copolymers with both hydrophilic and relative hydrophobic functions can provide a flexible, partially-hydrated, biocompatible and bioresorbable NGC shell.

In this study, A-B-A type triblock copolymers of PLLA-PEG-PLLA were synthesized using varied ratios of PEG and PLLA. The resulting block copolymers were characterized with gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR) to determine molecular weight, polymer structure, and thermal behavior. In addition, equilibrium water content, degradation rates, mechanical properties, and cell response were all evaluated and correlated to the polymer structure.

11:00 AM SB04.09.09
3D-Bioprinting of Spatially Organized Bacterial Microcosmoi Using Chaotic Flows Carlos F. Ceballos-González1, Edna J. Bolivar-Monsalve1, Carolina Chávez-Madero1,2, Everardo González-González1, Juan Yee-de León3, Christian C. Mendoza-Buenrostro1, Yu S. Zhang1,2, Mario M. Alvarez1,1 and Grissel Trujillo-deSantiago1,1; 1Tecnológico de Monterrey, Mexico; 2Harvard Medical School, United States; 3Delee Corp., United States

Cells do not work alone but as collaborative micro-societies. Cells in human tissues are spatially organized, and these deposition patterns may have significant effects on their functionality. In the case of bacteria, spatial distribution (micro-biogeography) has also been suggested as a determinant of their behavior. Unfortunately, current microbiological techniques, which are more focused on the culture of single bacterial strains or well-mixed bacterial communities, fail to reproduce the micro-geography of polybacterial societies. Moreover, printing spatially-controlled scaffolds at high resolution is currently challenging.

We developed a simple 3D-printing technique (chaotic bioprinting) that produces alginate-based and agar-based fibers at rates of ~1.0 m min⁻¹ and exhibiting finely-ordered internal lamellar microstructures with resolutions of ~4 μm. This straightforward approach allows us to place various bacterial strains in these constructs to analyze how their spatial distribution may affect their social behavior and/or survival abilities. We illustrate the use of chaotic bioprinting protocols to create fine-scale bacterial microcosmoi. For instance, we fabricated lamellar arrays of two different bacterial types (i.e., two *Escherichia coli* strains, each one producing a different fluorescent protein or containing different antibiotic resistance plasmids). We demonstrate that these biological microsystems can exhibit a competitive dominance or cooperation as a function of culture time, the development of hypoxic regions, and the degree of interface shared between the microcolonies.

Chaotic bioprinting enables the printing of cell-laden constructs with fine-scale deposition patterns. We envision that this technique will contribute to the development of more complex poly-bacterial microcosmoi, such as gut-microbiota models.

11:15 AM SB04.09.10
A 3D Bioprinted Brain-Like Co-Culture Network towards Modeling Neural Cell Interactions Yasamin
Reproducing the remarkable features of the multi-cellular three-dimensional (3D) environment of the brain in vitro, such as 3D cell-cell interactions, is considered a crucial step in creating reliable drug testing platforms for a variety of brain diseases. More specifically, the intercellular interactions between neural cells is a key factor to regulate brain functions and ensure health homeostasis. Recent advances in microfabrication and biomanufacturing techniques such as 3D bioprinting has opened new doors to create microscale 3D platforms to study 3D cell-cell interactions and mimic the structural and functional behavior of tissues in vitro. Here, a 3D brain-like co-culture construct is developed using multi-material embedded 3D bioprinting technology to study the neuron-glial interactions. Specifically, free-standing neuron-laden 3D structures are fabricated in a self-healing glia-laden support bath, resembling a brain-like tissue with neural fibers and glia-neuron interactions. The biomaterials were engineered to provide tunable soft tissue stiffness while allowing the creation of 3D geometries and complex networks. Moreover, the biomaterials showed excellent support for neural stem cell differentiation and glial cell spreading. Additionally, the differentiated neurons in the printed fibers exhibited glutamate synthesis capabilities, proving that the engineered brain-like tissue constructs can recapitulate neurotransmitter interactions, namely the glutamate-glutamine cycle. Eventually, the engineered brain-like co-culture constructs can prove useful for studying the levels of glutamate in the diseased brain and provide a reliable and highly reproducible in vitro platform for neurological drug screening and brain disease modeling.
employed the unusual multi-stimuli responsiveness of RMPs to create patterned surfaces,\textsuperscript{9} responsive interfaces\textsuperscript{10} and tunable co-assembled hydrogels.\textsuperscript{11} We have developed a directed self-assembly approach for colloidal synthesis of RMP-mediated size-controlled metallic nano-particles, nano-clusters\textsuperscript{12,13} and colloidal catalyst ink based electrocatalyst layer\textsuperscript{14} in aqueous medium under mild condition. Overall, the research has revealed the potential of the IDPs to pave the way for the design of novel biomaterials and nano-bio conjugates.

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2:00 PM *SB04.10.02
Architectured Conductive Hydrogel Sensors with High Sensitivity Jun Fu; Chinese Academy of Sciences, China

Ultrastretchable conductive materials are promising for electronic skin, human-machine interfaces, human activity monitors, and wearable devices. Currently, most strain sensors are comprised of elastomer matrix with metal particles/liquid, carbon materials, or conductive polymers. Conductive polymer hydrogels have recently been recognized promising for applications in pressure and strain sensors. The high stretchability and toughness are advantageous over those based on elastomers. Either electro-conductivity or ion conductivity could be achieved by appropriate design and synthesis of the network structures. So far, most conductive hydrogels are based on composites with a large amount of conductors, which is unfavorable for the linearity. Moreover, besides the high conductivity of the hydrogels, the sensitivity and performance of hydrogel sensors rely on the structural design of the sensors.

This talk introduces, ultrastretchable and tough hydrogels with electronic or ionic conductivities. Ionically conductive hydrogels comprised of zwitterionic chains interpenetrating freeze-thawed PVA network show adhesiveness to many substrates including glass, steel, polymer, and skin. The zwitterionic moieties in the network not only provide ion conductivity, but also serve as electrostatic crosslinks to toughen the hydrogels. Moreover, the strong electrostatic dipoles in the zwitterionic units enables robust adhesion to a variety of substrates from skin to polymer, glass and metals, which is beneficial for wearable devices. The hydrogels show outstanding strain and pressure sensing performance.

Electronic conductive hydrogels comprised of interpenetrating network of polyaniline (PANi) and poly(acrylamide-co-2-hydroxyethylene methacrylate) hydrogel show very high stretchability and toughness. The hydrogels show a very low threshold PANi content (0.5wt/vol%) to reach a plateau conductivity. A conductive network percolation is assumed in the hydrogel. At the percolation point, the hydrogels show a linear dependence on and high sensitivity to subtle tensile strains. The ultrastretchable and conductive hydrogels have been used to monitor subtle movements of joints and wrist pulse, which suggest important applications in implantable and wearable devices.

To prepare hydrogel sensors with very high sensitivity, conductive hydrogel arrays with well designed architectures have been fabricated by using 3D printing of hydrogel precursors followed by polymerization. The shape of each hydrogel unit can be well defined. Theoretical calculations and experimental results show that the sensitivity is highly related to the geometry of the hydrogels. Array sensors have been fabricated to detect pressures and pulse of 10 Pa and below.

Such hydrogel sensors and arrays are promising for wearable devices and implantable sensors.
2:30 PM BREAK

3:00 PM *SB04.10.03
Programmed Deformations of Composite Hydrogels into Multi-Stable Configurations Chen Yu Li, Zhi Jian Wang and Ziliang Wu; Zhejiang University, China

It is well-known that nature utilizes controlled deformation strategies to produce complex three-dimensional (3D) shapes of plant organs. Inspired by the natural activated systems, the realization of 3D shapes of artificial materials by programmed deformations has recently attracted great interest as a delightful concept and a practical technology with promising applications in biomedical devices, soft robotics, and flexible electronics. One fundamental task is to exploit new deformation modes and reveal the deformation mechanism. Shape transformations of intelligent materials are realized by switching the environmental conditions. However, it's challenging to form multi-stable morphing structures under the same condition. We present here a photolithographic method to pattern one responsive polymer in a non-responsive hydrogel sheet with well-designed gradient structures. Under external stimuli, the swelling mismatch results in the built-up of internal stress and thus programmed deformations of the composite hydrogel. Owing to the bi-stable nature of buckling deformation, i.e. the hydrogel sheet with in-plane gradient buckles upward or downward with almost equal possibility, the integrated composite hydrogel with multiple units of in-plane gradient structure has multiple distinct configurations. We will report both experimental and simulation results to demonstrate that various stable configurations can be obtained in one composite hydrogel under the same condition by controlling the buckling direction of each unit by a selective pre-swelling step. This concept and strategy should be applicable for other intelligent materials and merit their applications in diverse areas.

3:30 PM SB04.10.04
Expanding Gelation Conditions in Metal-Coordinated Hydrogels Seth A. Cazzell and Niels Holten-Andersen; Massachusetts Institute of Technology, United States

Polymer networks with dynamic physical crosslinks have generate widespread interest as tunable and responsive viscoelastic materials. A subclass of these materials containing multi-component, or complimentary, crosslinks, such as host-guest interactions and metal-coordination, are limited by their ability to percolate under stoichiometric imbalances of their crosslink components. Here we present a method to relax this stoichiometric requirement through the use of a third component, a dynamic, free competitor. This approach to expand the conditions that result in gelation is demonstrated experimentally with metal-coordinated hydrogels, and simulations are used to show the thermodynamic criteria that are necessary to expand the previously understood tight stoichiometric tolerance for gelation. This work can then be generally applied to advance engineering of the broadening class of polymer materials with dynamic crosslinks.

3:45 PM SB04.10.05
Molecular Understanding of Bond Dissociation Kinetics in Metal-Coordination Transient Hydrogels Using Simulation and Experiment Eesha Khare, Markus J. Buehler and Niels Holten-Andersen; Massachusetts Institute of Technology, United States

Metal-coordination hydrogels represent a new class of advanced materials for biomedical, composites, and structural applications. The dynamic properties enabled by this bonding are useful for the development of hydrogels in drug delivery, tissue scaffolds, and wound-healing, where tunable viscoelastic properties are critical in determining biological response. Metal-coordination bonds are reversible and tunable, unlike more static ionic or covalent chemical crosslinks commonly employed in hydrogels that permanently break upon fracture. As they have the capacity to break and reform after rupture, metal-coordination bonds can act as sacrificial bonds that help increase the fracture toughness of a material. Such sacrificial bonds are also important molecular motifs in biological systems where metal-mediated bonds play significant roles in protein folding and unfolding, rupture, and shock absorbance in many biological tissues such as mussel threads and other marine organisms. In fact, incorporating sacrificial metal bonding in hydrogels enables us to achieve transient mechanical properties which can be dynamically tuned over several time scales. Despite the emergence of new, dynamic properties enabled by metal-coordination chemistry, a fundamental understanding of the relationship between the chemistry, effective bond properties, and overarching macroscale mechanical properties of such systems is yet to be developed.

The development of histidine-divalent metal-coordination hydrogels presents a good model system with which to
study the role of metal coordination in the mechanics of hydrogels (Grindy et al., 2015). In this system, 4-arm polyethylene glycol (PEG) is end-functionalized with histidine derivatives that can coordinate with divalent metal cations (Zn²⁺, Ni²⁺, Cu²⁺) to form transient crosslinked gels. The kinetics of metal-coordination bonding to produce dynamic viscoelastic properties can be tuned through simple levers such as pH, temperature, and chemistry. This study couples multiscale computational modeling with experiment to characterize the molecular bonding landscape and kinetics of histidine functionalized PEG hydrogels. Density functional theory (DFT) and molecular dynamics (MD) are used to characterize the equilibrium bonding configuration and optical properties of the metal cations with the histidine ligand. The energy landscape of this bond is probed through metadynamics calculations and MD. Simulation results are compared with rheological and spectroscopic experimental characterizations of the hydrogels. Based on insights gained into the role of ligand-metal binding, coordination of surrounding ligands, and polymer physics from these calculations and experiments, this work proposes key design criteria for how this new class of metal-coordination chemistry hydrogels can be advanced for biological and environmental applications with dynamic, self-healing properties.

4:00 PM SB04.10.06
Bottom-Up Assembled Hierarchical Bacterial Network of Chronical Stability Pu Deng, Andrew Y. Xu and Xiaocheng Jiang; Tufts University, United States

Bioprinting is a method to create ex-vivo replicates of biosystems through precise three-dimensional (3-D) assembly of basic biocomponents into hierarchical structures with rationally designed functionalities. In the context of energy and environmental science, bacteria are widely exploited as self-sustainable biocatalysts to build systems that are capable of processing complex biochemical reactions and bioenergy transduction with superb efficiency and specificity at low-cost, mild reaction conditions. Ion crosslinked alginate is a popular supporting material for bacteria printing due to its fast and reliable gelation, structural similarities to the polysaccharide in native biofilms, and sufficient porosity for effective nutrients/metabolites transport. The lifetime of alginate supported bioprints, however, is quite limited, as a result from weak and reversible ion-alginate bonds, which initiate the leakage of encapsulated bacteria and eventually leads to the complete failure of the printed structures. To ultimately overcome this challenge, in this work, we modulated the alginate structure to strengthen the intermolecular interactions and improve the structural integrities of the bio-printed bacteria networks. Additionally, reduced graphene oxide (rGO) was introduced into this bacteria-alginate matrix, which further enhances the long-term stabilities through strong rGO-alginate interactions. These approaches result in the significant increase in the lifetime of bio-printed bacteria networks as the concentrations of the escaped/floating bacteria were reduced by 400% after 24 hours of culture. Based on this platform, we designed and constructed a 3-D living filter for toxic ions remediation using *S. loihica* encapsulated alginate microfibers as one-dimensional building blocks. Additionally, by tuning the composition and microstructure from bottom up, the degradability, bacteria loading density, and mass transport efficiency can be customized to meet the requirements of various wastewater conditions. The current work provides important insight about the fundamentals of bio-printing design and process and could open up new opportunities toward the creation of chronically stable biosystems with predictable and versatile functions encoded.

4:15 PM SB04.10.07
Anisotropic Hydrogels by Magnetically-Oriented Nanoclay Suspensions SungHo Yook and Mukerrem Cakmak; Purdue University, United States

With the presence of nanoparticles in a 3D hydrogel network, nanocomposite polymer hydrogels can exhibit additional functional properties in mechanical strength, swelling kinetics, and transparency. The nanostructure of nanocomposite hydrogels is generally isotropic because the nanoparticles entrapped within the 3D hydrogel network are randomly dispersed. However, the anisotropic features in hydrogels are often necessary to mimic anisotropic hierarchical structures in nature organism or to develop soft materials with directional mechanical/optical/thermal properties. In this study, anisotropic nanocomposite hydrogels were achieved by orienting nanoclay in a hydrogel network. The aqueous suspension of nontronite nanoclays, which are sensitive to magnetic fields due to high contents of ferric ions (Fe³⁺), were oriented in various strength of the magnetic field and then the final morphology was fixed by the synthesis of the hydrogel. The nanostructure of the anisotropic hydrogels was characterized by measuring birefringence, 2D Small Angle X-ray Scattering (SAXS), and transmission. The magnetic field-induced birefringence of anisotropic hydrogels increased with the applied magnetic field strength in a range between 0 to 9 Telsa in all different concentrations (0.05 wt%, 0.1 wt%, 0.2 wt%, and 0.4 wt%) as the orientation degree of nanoclay particles increased. The birefringence was also proportionally increased with nanoclay concentrations from
0.05 wt% to 0.2 wt%, but it significantly decreased at 0.4 wt% concentration. Furthermore, 2D SAXS revealed that the long axis of nontronite platelets was oriented parallel to the applied magnetic field direction. With 2D SAXS patterns, the orientation order parameter was calculated at different magnetic field strength and concentrations. At 0.1 wt% nanoclay concentration, the orientation order parameter increased up to 0.67 as applied magnetic field strength increased. The samples prepared in 9 Tesla showed high orientation order parameter in all different concentrations. The field-induced birefringence and orientation order parameter showed a linear correlation over the magnetic field strength range from 0 Tesla to 9 Tesla. The anisotropic hydrogels also showed the 7% and 8% increase in optical transmission to applied magnetic field direction at 0.1 wt% and 0.2 wt% concentrations.

**4:30 PM SB04.10.08**

**Printable Ag-Based Conductive Composites** Yunsik Ohm, Chengfeng Pan, Michael Ford, Xiaonan Huang and Carmel Majidi; Carnegie Mellon University, United States

Conductive and stretchable materials are important components in soft electronics and sensors that are used for emerging applications in soft robotics and wearable physiological monitoring. Compared with other stretchable conductors composed of different types of polymers, conductive hydrogels are promising candidates for soft electrode materials due to their mechanical compliance, which is similar to biological tissues (0.5-500 kPa) such as human skin; compatibility with aqueous environment due to high water content; and inherent ability to adhere to other materials. However, most conducting polymer-based hydrogels are ionic conductors, so they are not able to deliver direct current (DC) but instead support alternating current (AC). Here, we introduce a novel and facile method for making a soft (<1 MPa), highly stretchable (>200% strain), and electrically conductive (>10$^3$ S/cm) hydrogel composite that can be functional in water and conductive enough to transmit digital signals. The composite is composed of micron-sized silver (Ag) flakes (2-5 micrometers) distributed over an alginate-acrylamide based hydrogel matrix. The mixture of silver flakes and alginate-acrylamide hydrogel is not electrically conductive immediately after curing; however, it can achieve electrical conductance while maintaining its soft and deformable nature by controlling the amount of water inside the composite through drying. During the drying process, evaporating water enables the formation of a percolating network of silver flakes within the hydrogel matrix, which makes the conductive gel electrically conductive (maximum initial conductivity ~90000 S/cm). Moreover, the inherent mechanical properties of the hydrogel are preserved (e.g. maximum strain limit ~250% while maintaining electrical conductivity). We demonstrate the utility of the conductive hydrogel ink by powering a soft swimming eel that can swim with the help of bi-stable SMA actuators. We will also present a stencil-printed stretchable circuit in which several surface mounted LEDs are continuously powered through use of the conductive hydrogel ink. The stretchable and conductive hydrogel ink that we present here represents a new route to controlling conductivity in conductive hydrogel.

**4:45 PM SB04.10.09**

**Mussel Inspired Tough Double Network Hydrogel as Shapeable Adhesive** Xiaohan Wang, Yisheng Xu and Xuhong Guo; East China University of Science and Technology, China

Hydrogels with excellent adhesive and mechanical properties have attracted extensive attractions due to its application prospects in various fields such as wound dressing, electronic skin and wearable devices. However, few has successfully prepared “tough and sticky” hydrogel with desirable and tunable performance. In this work, dopa modified hyaluronic acid (HA-dopa) was firstly introduced to the double network (DN) system, which greatly improved the mechanical and adhesive performance of the original HA-Acrylamide (AAm) DN hydrogel. By modulating external parameters such as pH and Fe$^{3+}$ concentration of the precursor solution, the overall property of the hydrogel could be well-tuned. Moreover, a non-monotonic dependence of the HA-dopa content on mechanical and adhesive enhancement could be clearly observed. Based on this phenomenon, we proposed a new mechanism that the catechol moiety within HA-dopa played a different role and served as chemical crosslinker to reinforce the hydrogel, leading to a more compact network and improved overall performance. Therefore, as an effective approach to enhance the adhesive and mechanical property of hydrogel, this mussel-inspired practice would provide valuable insight into designing functional hydrogel and elastomer for various applications.
Biomimetic Cartilage Model Exhibiting Matrix “Prestress”

Peter Basser; National Institutes of Health, United States

A critical feature of extracellular matrix (ECM), in general, and cartilage tissue, in particular, is the prestress that develops within the tissue matrix. Cartilage is a composite medium whose proteoglycan (PG) components imbibe water, while its confining collagen matrix resists PG swelling. This balance of forces results in a significant matrix prestress—on the order of four atmospheres—under no external load. Our group recently developed a composite polymeric medium consisting of poly-acrylic acid (PAA) microgel assemblies (mimicking the PG phase) dispersed within a PVA gel network (mimicking the collagen matrix). This hydrogel composite exhibits remarkable load bearing ability, and key quantitative and qualitative material behaviors observed in human cartilage specimen. The osmotic modulus of this aggregate gel system provides an eloquent measure of its load bearing ability.

Transport into Stiff Gel-Like Deformable Articular Cartilage for Drug Delivery

Alan Grodzinsky; Massachusetts Institute of Technology, United States

Traumatic joint injury in individuals at any age can initiate cartilage and subchondral bone degeneration in the presence of elevated levels of inflammatory cytokines, leading to post-traumatic osteoarthritis (PTOA). There are currently no disease modifying drugs for osteoarthritis or PTOA, and a major challenge is the ability to achieve sustained levels of potential therapeutics inside a target tissue such as cartilage, with no side effects, after intra-articular delivery. We use in vitro organ culture models to study the beneficial effects of combination therapeutics (e.g., glucocorticoids, growth factors) to inhibit matrix degradation and cell apoptosis in cartilage. These experiments are performed with isolated cartilage explants, intact osteochondral plugs or osteochondral plugs in the presence of synovium explants (the latter known to release inflammatory proteins). To simulate a traumatic joint injury, the cartilage is also subjected to an initial acute impact compressive load. Parallel in vitro and animal studies are aimed at approaches to targeted tissue drug delivery. In particular, charge based intra-cartilage delivery of glucocorticoids and/or growth factors has been enabled using cationic nanoparticles including Avidin and supercharged green fluorescent proteins. In studies of cartilage degradation and repair, it is important to assess the mechanical function of newly synthesized tissue and constituent matrix molecules at the molecular scale. We have therefore developed and used an AFM-based wide-bandwidth rheology system to measure the dynamic nanomechanical behavior of normal and degraded cartilage as well as end-grafted aggrecan brush layers over the frequency ranges relevant to impact injuries. The effects of mechanical loading on cartilage degradation and repair is also under study, as it is very important to clinical rehabilitation.

Direct Visualization of Functional Crosslinkers in Swollen PNiPAm Based Microgels

Apostolos Karanastasis¹, Gopal Kenath¹, Yongdeng Zhang², Mark D. Lessard², Joerg Bewersdorf² and Chaitanya Ullal¹; ¹Rensselaer Polytechnic Institute, United States; ²Yale, United States

The spatial distribution of cross-links in bulk gels and colloidal gel particles impacts their mechanical and transport properties. Here we report on the spatial distribution of dye tagged crosslinkers of colloidal PNIPAM microgels revealed by super-resolution microscopy at the level of individual particles as well as at the ensemble level. Using a W-4PiMSMN microscope we demonstrate the presence of higher crosslink nanodomains within the already dense cores of the microgels. Additionally, we show that the average probability density profile, extracted from super resolution, can be used to extract quantitative relative reaction rate constants. We prove this by coupling the localization probability density profile with the temporal volumetric evolution of the particles to accurately predict the consumption of the dye tagged species with time. These predicted consumption curves are fit to accepted kinetic models for precipitation polymerization of microgels to extract relative rate constants for the functional cross-linker to n-isopropylacrylamide and N,N’-methylene-bis-acrylamide.

Tailoring hydrogels and their properties for customized applications is a highly interesting task in tissue engineering to develop biomimetic materials for biomedical applications. Thereby, crosslinking processes are commonly used since the degree of crosslinking precisely determines the material properties. Among the diverse techniques of crosslinking, high-energy electron treatment is a highly advantageous method, which allows reagent-free tuning of structural and mechanical features of hydrogels while chemical structure and cytocompatibility are excellently maintained.[1]

Within this contribution, we will introduce electron beam treatment and we will show the high potential to tailor precisely biological hydrogel properties. In particular, we will show how electron beam treatment effectively tunes network structure and viscoelastic properties of biological hydrogels such as collagen. In addition, we will demonstrate their excellently maintained chemical structure and cytocompatibility. With this, our research describes a promising reagent-free method to tailor precisely hydrogel properties for prospective biomedical applications.


10:00 AM BREAK

10:30 AM *SB04.11.05
Electrical “Suturing” of Polyelectrolyte Hydrogels to Reseal Cut or Damaged Tissues Srinivasa Raghavan; University of Maryland, United States

This talk will present studies from our lab on the electrically induced adhesion of hydrogels and beads made from polyelectrolytes. When a rectangular strip of a cationic gel (connected to an anode) is contacted for just a few seconds with a strip of anionic gel (connected to a cathode) under a voltage of ~ 10 V, the two gel strips form a strong adhesive bond. When the polarity of the electrodes is reversed, the phenomenon is reversed, i.e., the gels can be easily detached.

While the above phenomenon of ‘electro-adhesion’ has been reported before for hydrogels, we show that it is much more general and widespread. Specifically, we can substitute either of the above gels with a spherical bead made using charged biopolymers such as chitosan or alginate. The same electro-adhesion works to join beads to gels, or two beads to each other. In turn, electro-adhesion can be applied for the pick-up and drop-off of soft cargo, and for the sorting of beads. Most interestingly, the same phenomenon also works with certain animal tissues. That is, many tissues are anionic, and we show that cationic gels can be electro-adhered to them. We thereby demonstrate that cuts or tears in tissues can be electro-sealed using beads or gel strips. As an extreme case, two severed pieces of a tube can be stuck back together using a gel strip that spans both cut segments; this is thereby an example of a needleless suture using only hydrogels and an electric field.

11:00 AM *SB04.11.06
Gelation Control in Polysaccharides Juan D. Londono¹, Kyle Kim², Natnael Behabtu² and Laura Clinger¹; ¹DuPont, United States; ²DuPont Biomaterials, United States

Polysaccharides are derived from renewable resources, supporting trends to reduce the consumption of plastics made from petrochemicals. Polysaccharides consist of sugar units linked by glycosidic bonds. Seemingly small variations in the glycosidic bond often result in dramatic changes in properties [e.g. hydrophobic cellulose β-(1→4) vs hydrophilic starch α-(1→4)]. There is, in addition, the possibility of mixed linkages and complex architectures, from linear to highly branched. Finally, polysaccharides may be derivatized, with the potential of changing properties entirely. Polysaccharides therefore provide a wide platform from which polymers with diverse properties can be obtained. Due to their versatility, these polymers are ubiquitous in nature and industry. Industrial polysaccharides are widely used as viscosity modifiers, food texturants and in oil recovery applications. The major source of industrial polysaccharides is the natural world. For example, carrageenans are a family of sulphated polysaccharides that are widely used as gelling agents and stabilizers in dairy, beverages, confectionery and meat applications. Carrageenans show a thermo-reversible disorder-to-order transition that is key for its gelling
and stabilization. Although carrageenans have a long history of use, it remains unclear which physical states different carrageenans have and which intrinsic and extrinsic factors influence their physical state. Polysaccharide viscosity depends on a structural hierarchy spanning a multitude of length scales, and a suite of analytical techniques are needed to understand the secondary, tertiary and quaternary structure of these materials. Characterization of this hierarchy from x-ray scattering, rheology, microscopy and size-exclusion chromatography are presented for carrageenan. Furthermore, polysaccharides harvested from the natural world entail issues of variability, heterogeneity, purity, and reliability. There is therefore the need for structural control at the molecular, nano and mesoscales, to improve industrial use of these polymers.

Another polysaccharide, α-(1→3)-D-Glucan (glucan), is mainly found in the cell wall of micro-organisms. A linear form of glucan can be obtained from fungi and yeasts while some bacteria produce branched glucan chains in human saliva where a connection to dental caries has been suggested. Several patents [1] and recent literature [2] have shown that the glucan polymer can be synthesized enzymatically with good yield. There are strong parallels between the glucan colloidal material as obtained from enzymatic polymerization and the hierarchical structures found in other conventional materials like fumed silica and carbon black. Indeed, both glucan and carrageenan hold promise for viscosity modification applications such as 3D printing with the added benefit that natural polysaccharides are both renewable and biodegradable. In addition, glucan is consistent in purity and quality since it is enzymatically derived.

J O’Brien, DuPont, USP 7,000,000, January 19, 2000; and similar patents dating since 2000.
S Puanglek et al.; Scientific Reports, 6:30479, DOI: 10.1038/srep30479, 29 July 2016.

11:30 AM SB04.11.07
A Simple Way to Synthesize a Protective ‘Skin’ around a Hydrogel Sai Nikhil Subraveti and Srinivasa Raghavan; University of Maryland, College Park, United States

In nature, various structures such as fruits and vegetables have a water-rich core that is covered by a hydrophobic layer, i.e., the skin. The skin creates a barrier for chemicals from the external environment to enter the core; at the same time, the skin also ensures that the water in the core is preserved and not lost by evaporation. Currently, for many applications involving hydrogels, especially in areas such as soft-robotics or bio-electronic interfaces, it would be advantageous if a hydrogel could be encased in a skin-like material. However, forming such a skin is challenging because it would need to be a hydrophobic material with a distinct chemistry from the hydrophilic gel core. Here, we present a simple solution to this problem, which allows any hydrogel of arbitrary composition and geometry to be encased in a hydrophobic ‘skin’. Our synthesis technique involves an inside-out polymerization, where one component of the polymerization (such as an initiator) is present only in the hydrogel core while other components (such as monomers) are present only in the external medium. Accordingly, a skin, i.e., a thin polymeric layer, grows outward from the core, and the entire process can be completed in a few minutes. We show that the presence of the skin prevents the hydrogel from swelling in water and also from drying in air. Likewise, hydrophilic solutes in the hydrogel core are prevented by the skin from leaking out into the external solution. The properties of the skin are all tunable, including its thickness, its mechanical properties, and its permeability. The ability to grow such a skin readily around any given hydrogel is likely to prove useful in numerous applications.

11:45 AM SB04.11.08
Tearing a Hydrogel of Complex Rheology Ruobing Bai1, Baohong Chen2, Jiawei Yang2 and Zhigang Suo2; 1California Institute of Technology, United States; 2Harvard University, United States

Tough hydrogels of many chemical compositions are being discovered, and are opening new applications in medicine and engineering. To aid this rapid and worldwide development, it is urgent to study these hydrogels at the interface between mechanics and chemistry. A tough hydrogel often deforms inelastically over a large volume of the sample used in a fracture experiment. The rheology of the hydrogel depends on chemistry, and is usually complex, which complicates the crack behavior. In this talk, we study a hydrogel that has two interpenetrating networks: a polyacrylamide network of covalent crosslinks, and an alginate network of ionic (calcium) crosslinks. When the hydrogel is stretched, the polyacrylamide network remains intact, but the alginate network partially unzips. We tear a thin layer of the hydrogel at speed $v$ and measure the energy release rate $G$. The $v$-$G$ curve depends on the thickness of the hydrogel for thin hydrogels, and is independent of the thickness of the hydrogel for thick hydrogels. The energy release rate approaches a threshold, below which the tear speed vanishes. The threshold depends on the concentration of calcium. The threshold may also depend on the thickness when the thickness is comparable to the
size of inelastic zone. The threshold determined by slow tear differs from the threshold determined by cyclic fatigue. We discuss these experimental findings in terms of the mechanics of tear and the chemistry of the hydrogel.

SESSION SB04.12: 3D and 4D Printing II
Session Chairs: Ferenc Horkay and Marc In het Panhuis
Friday Afternoon, December 6, 2019
Hynes, Level 3, Room 302

1:30 PM SB04.12.01
Spatially Patterned Magnetic Hydrogels for Responsive Cell Culture Applications Dermot Brougham\(^1\), Patricia Monks\(^2\), Jacek Wychowaniec\(^1\), Shane Clerkin\(^3\), John Crean\(^3\), Kevin McCarthy\(^3\), Andreas Heise\(^2\) and Brian Rodriguez\(^3\); \(^1\)School of Chemistry, University College Dublin, Ireland; \(^2\)Royal College of Surgeons in Ireland, Ireland; \(^3\)University College Dublin, Ireland

Responsive functional soft nanocomposite materials remain a significant focus of scientific effort worldwide due in part to their applications in biomedicine ranging from cancer treatment to biomolecule/drug delivery\(^4\) through to cell supports. Their responses to electric and/or magnetic fields, temperature, salts, pH, and light can be engineered through precise physicochemical modifications across multiple length scales and also by spatial patterning using 3D printing technologies\(^2\). Magnetic nanoparticles (MNPs) and also their clusters are used in the biomedical field in a wide range of applications from cancer treatment to MRI imaging\(^3\). The combination of MNPs and established 3D printable polymeric hydrogel formulations can provide multifunctional and stimuli-sensitive nanocomposite delivery systems with spatial-, temporal- and dosage-controlled release properties. We are interested in exploring these possibilities for tissue engineering applications.

A multi-head 3D printer was successfully built and modified to allow extrusion of Pluronic F127 hydrogels and composite gels including F127 and PEG-diacrylate with parameters of moderate temperature and pressure that would support cell viability. Magnetic nanoparticles were synthesised, stabilized and incorporated homogenously; oscillatory rheology measurements confirmed the viscoelastic properties with storage modulus values in the \(\sim 20 \text{ kPa}\) range providing ideal materials for 3D printing well-defined architectures with high fidelity for both magnetic and non-magnetic streams. The hybrid inks showed complete shear- and temperature-recoverability/reversibility to their initial state, confirming that at particle concentrations that enable magnetic responses the necessary printability is not lost. Various complex structures were printed with high resolution (~100 micron) with independent magnetic and non-magnetic patterned components and these were shown to be reproducible and robust and they could be cured in situ at magnetically responsive particle concentrations to retain the fidelity of printed features. Biocompatibility of the printed hybrid hydrogels for various cell lines including stem cells was demonstrated.

For AC-magnetic field responsiveness, high resolution IR thermography confirmed that incorporated magnetic nanoparticles retain sufficient magnetic response to provide spatial temperature gradients for cell stimulus and for stimulus-responsive release. The advantages of spatial patterning of thermally active components will be described. Applications of DC-magnetic fields to physical stimulation of patterned magnetic gels will also be presented.


ACKNOWLEDGMENTS
The authors acknowledge support from Science Foundation Ireland (16/IA/4584 and 13/IA/1840).
Living organisms use spatially controlled expansion and contraction of soft tissues to achieve complex three-dimensional (3D) morphologies and movements and thereby functions. However, replicating such features in man-made materials remains a challenge. Here we present a method named digital light 4D printing (DL4P) that encodes 2D hydrogels with spatially and temporally controlled growth (expansion and contraction) to create 3D structures with programmed morphologies and motions. This approach uses temperature-responsive hydrogels with locally programmable degrees and rates of swelling and shrinking. This method simultaneously prints multiple 3D structures with custom design from a single precursor in a one-step process within 60 s and is thus highly scalable. We suggest simple yet versatile design rules and the concept of modularity for creating complex 3D structures and a theoretical model for predicting their motions. We reveal that the spatially nonuniform rates of swelling and shrinking of growth-induced 3D structures determine their dynamic shape changes. We demonstrate shape-morphing 3D structures with diverse morphologies, including bioinspired structures with programmed sequential motions. This approach could potentially transform the way we design and fabricate soft engineering systems, such as soft robots, soft actuators, and 3D tissue structures.

Stem cell therapies have emerged as a promising method for treating injuries and diseases in regenerative medicine, but delivering stem cells often requires invasive techniques and results in heterogeneous injections and poor cell retention at the injection site. Traditional cell delivery methods using liquid injections or surgical implants have limited the efficacy of these treatments. We have designed a novel injectable polymer-nanoparticle based hydrogel for effective delivery of human mesenchymal stem cells. This supramolecular hydrogel supported by dynamic hydrophobic interactions is capable of longterm 3D cell maintenance and retains injected cells for up to 10 days, twice as long as traditional delivery with liquid PBS injections. We uncover the fundamental hydrogel mechanical properties that enhance the entire cell delivery process. Through both in vitro and in vivo experiments, we demonstrate a scalable, synthetic, and biodegradable hydrogel with tunable mechanical properties that enables effective cell delivery. This shear-thinning and self-healing polymer-nanoparticle hydrogel also presents valuable opportunities in designing novel inks for applications in 3D bioprinting.

Shape-morphing structured materials have the ability to transform a range of applications, from deployable systems and dynamic optics to soft robotics and frequency shifting antennae. Despite numerous advances, the integrated design and fabrication of shape-shifting structures that morph into complex three-dimensional (3D) shapes remains a challenge, owing to the difficulty of controlling the underlying metric tensor in space and time. Here, we exploited a combination of multiple materials, geometry, and 4D printing to create structured lattices that overcome this problem. We first produced printable inks composed of elastomeric matrices with tunable cross-link density and anisotropic fillers to control the material elastic modulus ($E$) and actuation capability via coefficient of thermal expansion ($\alpha$). We then printed curved bilayer ribs in the form of lattice structures, in which the geometry of each rib is individually programmed to achieve local control over the metric tensor. Using multiplexed bilayer ribs composed of four materials, we can independently control extrinsic curvature and thereby encode a wide range of three-dimensional shape changes in response to temperature. As exemplars, we designed and printed flat lattices that morph into frequency-shifting antennae and a human face that demonstrate functionality and geometric complexity, respectively. Our inverse design and multi-material 4D printing method can be readily extended to other stimuli-responsive materials and different 2D and 3D cell designs to create scalable, reversible, shape-shifting structures with unprecedented complexity.
Peptide/Graphene Hybrid Hydrogels as Potential 3D Injectable Cell Delivery Vehicle for Intervertebral Disc Repair
Cosimo Ligorio, Jacek Wychowaniec, Aravind Vijayaraghavan, Judith Hoyland and Alberto Saiani;
University of Manchester, United Kingdom

Cell-based therapies in particular have shown significant promise in tissue engineering with one key challenge being the delivery and retention of cells. As a result, significant efforts have been made in the past decade to design injectable biomaterials to host and deliver cells at injury sites. A recent strategy that has emerged for the design of increasingly functional hydrogels is the incorporation of nanofillers in order to exploit their specific properties to either modify the performance of the hydrogel or add functionality. The emergence of carbon nanomaterials in particular has provided great opportunity for the use of graphene derivatives (GDs) in biomedical applications. The key challenge when designing hybrid materials is the understanding of the molecular interactions between the matrix (peptide nanofibers) and the nanofiller (here GDs) and how these affect the final properties of the bulk material. For the purpose of this work, three gelling β-sheet-forming, self-assembling peptides with varying physiochemical properties and five GDs with varying surface chemistries were chosen to formulate novel hybrid hydrogels. First the peptide hydrogels and the GDs were characterized; subsequently, the molecular interaction between peptides nanofibers and GDs were probed before formulating and mechanically characterizing the hybrid hydrogels. We show how the interplay between electrostatic interactions, which can be attractive or repulsive, and hydrophobic (and π−π in the case of peptide containing phenylalanine) interactions, which are always attractive, play a key role on the final properties of the hybrid hydrogels. The shear modulus of the hybrid hydrogels is shown to be related to the strength of fiber adhesion to the flakes, the overall hydrophobicity of the peptides, as well as the type of fibrillar network formed. This work clearly shows how interactions between peptides and GDs can be used to tailor the mechanical properties of the resulting hydrogels, allowing the incorporation of GD nanofillers in a controlled way and opening the possibility to exploit their intrinsic properties to design novel hybrid peptide hydrogels for biomedical applications. [J. Wychowaniec et al. Biomacromolecules 2018, 19, 2731−2741]

Intervertebral disc (IVD) degeneration, a major cause of back pain, is a particularly relevant example where a minimally-invasive cellular therapy (injectable hydrogel) could bring significant benefits specifically at the early stages of the disease, when a cell-driven process starts in the gelatinous core of the IVD, the nucleus pulposus (NP). Based the knowledge gained above we explored the use of graphene oxide (GO) as nano-filler for the reinforcement of FEFKFEFK (β-sheet forming self-assembling peptide) hydrogels. We confirmed the presence of strong interactions between FEFKFEFK and GO flakes with the peptide coating and forming short thin fibrils on the surface of the flakes. These strong interactions were found to affect the bulk properties of hybrid hydrogels. At pH 4 electrostatic interactions between the peptide fibres and the peptide-coated GO flakes are thought to govern the final bulk properties of the hydrogels while at pH 7, after conditioning with cell culture media, electrostatic interactions are removed leaving the hydrophobic interactions to govern hydrogel final properties. The GO-F820 hybrid hydrogel, with mechanical properties similar to the NP, was shown to promote high cell viability and retained cell metabolic activity in 3D over the 7 days of culture and therefore shown to harbour significant potential as an injectable hydrogel scaffold for the in-vivo delivery of NP cells. [C. Ligorio et al. Acta Biomaterialia in press DOI: 10.1016/j.actbio.2019.05.004 ]

Exploring the Future of Hydrogel Systems in Preserving 3D Mechanical Integrity of Cell-Extra Cellular Matrix(ECM) Mixtures within Biofabricated Assemblies
Raymond Oliver and Chawisa Deesomboon;
Northumbria University, United Kingdom

In the UK, 1 in 111 people have a disfigurement of the face. Each year, 1 in 44 people require surgical reconstruction due to facial deformity from congenital disease, cancer resection, burns, paralysis or inflammatory skin diseases. Current surgical reconstruction involves restoring facial defects including bone, cartilage, muscle and skin with the patients own tissue from elsewhere in the body where possible. Often tissue is limited to restore the defect and there are drawbacks including donor site morbidity, long term pain and surgical risks. Thus, there is a compelling and urgent need to find a new solution to restoring facial tissues for example, which transends the current surgical approach.

As we advance our knowledge of biocompatible and responsive material systems and beneficial cell biology, we
have an opportunity to accelerate viable outcomes in regenerative medicine for human repair. It is generally accepted that in designing an appropriate and proper scaffold biomaterial, one must try to translate the mechanical characteristic features of the target tissue into the mechanical features of the desired fabricated construct. For example, hard tissue regeneration requires strengths of $O[10-1500 \text{ MPa}]$, while soft tissue strengths are typically located between $O[0.4 – 300 \text{ MPa}]$.

As part of the overall solution, we are investigating how best to preserve the mechanical integrity of the scaffold which contributes significantly to the overall success of the intervention. Using 3,4D additive biofabrication through precision extrusion, we have observed that mechanical integrity can be enhanced as indicated through evidence based characterisation and measurement and that the important role that hydrogels can play not only in control of the mechanical properties but also over biological and sensory effects. Our paper will discuss some of the results of our studies using both polysaccharide and alginate based hydrogel systems can enhance cell – ECM viability for human repair.

3:30 PM SB04.12.07
Electrochemical 4D Printing of Bimetallic Objects Xiaolong Chen; University of Cambridge, United Kingdom

3D printing (additive manufacturing) is drawing more attention as a flexible manufacturing technology. In particular, Selective Laser Sintering (SLS) is a metal-based additive manufacturing technique that has been widely applied in medical, aerospace and motorsport applications. However, the essential parts of SLS system, such as high-power laser nozzle and metals powders, have high capital cost associated with the safety risks, which limit its wider application. In addition, most of the existing metal 3D printing systems can only print in a single material, which lack design flexibility. Concurrently, interest in 4D printed structures, which can react to environmental stimuli such as temperature, light, electrical and strain, is also growing due to the potential of creating objects with passive mechanisms and self-morphing characters. However, most 4D printed structures currently use polymer-based or hydrogel-based materials, which limits their mechanical strength and operating temperature.

Here, I present a novel multi-metal electrochemical 3D printer that can fabricate copper-nickel bimetallic with different architectures. Due to the mismatch in the thermal expansion coefficients, the mechanical deformation of printed bimetallic structures was programmed at temperatures up to 300 °C enabling tailored high-temperature responsive behaviour. Using a combination of scanning electron microscopy, optical microscopy, energy dispersive X-ray spectroscopy, X-ray computed tomography and electrical measurements, the morphologies of the printed structures were investigated. Moreover, electrochemical deposition of these metals create polycrystalline structures, achieving electrical conductivities that lie between that of nanocrystalline copper ($5.41 \times 10^6 \text{ S/m}$) and nickel ($8.2 \times 10^6 \text{ S/m}$). A tightly formed metal-metal boundary can be achieved, reducing delamination problems observed in other multi-material printing approaches. However, non-uniform convex cross-sections are created due to current density vibration. The work also explores different bimetallic structural designs and how modifications of this can generate different programmable structures with examples being a self-assembled “ICL”.

The author believes that this technique has broad and high impact applications due to the ability to process a range of materials and alloys, which can produce high temperature 4D structure and more importantly opens possibility for creating more intelligent structures and sensors at low cost and high safety. Other advantages include the fact that this process can be both additive and subtractive through reversal of potential, allowing for recycling of components through electrochemical dissolution.

3:45 PM SB04.12.08
Patterned Hygroscopic Control of Four-Dimensional Prints of Silk Fibroin Protein Xuan Mu and David L. Kaplan; Tufts University, United States

Four-dimensional (4D) printing of shape-morphing hydrogels is generally realized through patterning composite materials with contrasting properties (e.g., rigid vs. soft, responsive vs. non-responsive) or through control of crosslink density within photo-curable polymers. Here, we demonstrate a new strategy to print shape-morphing monolithic structures of silk fibroin protein by exploiting molecular assembly to pattern hygroscopicity. Hygroscopicity results in materials that expand and shrink upon absorption and removal of water, respectively, which has been found in natural and synthetic materials including paper, polycarbonate, wood, nylon as well as silk. Macroscopic deformation results from changes of hydrogen bonds between/within molecular chains and the transport of water molecules through nano- and micro-scale porous morphology. We used well-dispersed silk fibroin solution (~30 wt%) regenerated from B. mori. cocoons as the printing ink, which was then printed in layer-by-layer fashion on plain glass slides immersed in an aqueous inorganic salt bath. The bath was rationally designed to direct
the assembly of silk fibroin molecules into hierarchical structures from beta-sheet crystals to nano-fibrils, to micro-filaments and then to 3D macro-prints. The phase transition of the protein ink from liquid to water-insoluble solid was accompanied by the removal of water into the salt bath; while water removal at the bottom/first layer (adjacent to the water-impermeable glass slide) was more difficult than later layers that are fully exposed to the aqueous bath. The residual water influenced the crystallinity and porous morphology of the assembled structures. FTIR and SEM identified the bottom layer with ~48% beta-sheet and micro-pores (~10 micrometer diameter) in contrast to 41% and nano-pores (~10 nm) for the later layers. There is a significant difference in the magnitude of hygroscopic strain of the filaments from the different layers. We employed the mismatch of the strain to transform a planar print into a range of Gaussian curvatures including positive (cone), zero (cylinder) and negative (saddle). Furthermore, full control over the transformation of planar two-layer rectangles into 3D helices was demonstrated, where the pitch and radius of the helix was dictated by filament interval and angle. In order to predict the transformations of the printed structures, a finite element analysis model was developed to simulate large hygroscopic strains under humidity changes using experimentally obtained hygroscopic coefficients and hyperelastic properties of silk fibroin. The numerical simulations were in good agreement with the experimental results, supporting the proposed mechanism of patterned hygroscopic control. The versatile and programmable transformations, as well as the simulations, should enable a range of biomedical applications and provide key insights into 4D printing of other hygroscopic materials.

**SYMPOSIUM SB05**

Light-Matter Interactions at the Interface with Living Cells, Tissues and Organisms
December 2 - December 4, 2019

**Symposium Organizers**
Guglielmo Lanzani, Italian Inst of Technology
Bozhi Tian, University of Chicago
Brian Timko, Tufts University
Elizabeth von Hauff, Vrije University

* Invited Paper

SESSION SB05.01: Fundamentals of Light-Matter Interaction in Biology I
Session Chairs: Guglielmo Lanzani, Jing Tang and Brian Timko
Monday Morning, December 2, 2019
Hynes, Level 3, Room 303

8:00 AM SB05.01.01
Non-Genetic Projection-Specific Modulation of Neuronal Activity Huiliang Wang, Lief Fenno, Yun-Sheng Chen, Christina Kim, Charu Ramakrishnan, Masatoshi Inoue, Sam Gambhir and Karl Deisseroth; Stanford University, United States

Developments in optogenetics and virology have demonstrated that modulating the neural activity of specific projections in the brain is capable of rescuing behavioral deficits, including those relevant to depression, autism and anxiety. This approach requires genetic modification of neurons via viral transduction of transducers of visible light, and thus light penetration depth is limited by the scattering of visible light (although fiberoptic interfaces can overcome this challenge). Additional channels for modulating neural activity would be valuable, ideally minimally-invasive. Here, we developed a non-genetic, nanoparticle-based approach to achieve projection-specific modulation of neural activity in freely behaving mice. First, we observed that gold nanorods were rapidly endocytosed into cultured neurons after just a few minutes of incubation. Transmission electron microscopy images illustrate that gold...
nanorods are located both inside and outside the endosome. Second, we showed that the endocytosed gold nanorods were transported retrogradely and anterogradely along axons, with average speed of 0.2 μm/s (1.7 cm/day). Third, we demonstrated the effectiveness of photothermal inhibition of neural activity with axon-transported gold nanorods, illustrating the concept of projection-specific modulation of neural activity in vitro, and also demonstrated biocompatibility of gold nanorods in neurons after one-week incubation and photothermal neural modulation. Finally, we observed the neural uptake and axonal transport of gold nanorods in vivo, as well as the effectiveness of neural modulation in mouse behavior. Overall, this nanoparticle-based methodology demonstrates a promising approach to non-genetic, projection-specific modulation of neural activity.

8:15 AM SB05.01.02
Luciferase-Chlorin e6 Conjugates for Bioluminescent Photodynamic Therapy Sarah Forward1, Hao Yan2, Kwon-Hyeon Kim2, Anokhi Kashiparekh1, Sheldon J. Kwok3,1 and Seok-Hyun Yun1,2,3; 1Massachusetts General Hospital, United States; 2Harvard Medical School, United States; 3Massachusetts Institute of Technology, United States

Bioluminescence (BL) has the potential to serve as a new “light” source to activate photosensitizers. Since excitation energy is delivered chemically, this approach can overcome the light-penetration problems of conventional photodynamic therapy (PDT) in deep tissue. We have developed novel RLuc8-Ce6 conjugates, which generate bioluminescence resonance energy transfer (BRET) from RLuc8, a Renilla luciferase mutant, to Chlorin e6 (Ce6), a photosensitizer, upon binding with methoxy-e-coelenterazine (meCTZ) substrates. A high BRET efficiency was achieved by optimizing the molecular ratio and spacing, as well as the spectral overlap. We also developed a protocol based on membrane fusion liposomes to deliver the protein constructs effectively into cells and obtained promising therapeutic effects of BL-PDT in a mouse model of metastatic, triple-negative breast cancer.

8:30 AM *SB05.01.03
Optical Stimulation of Excitable Tissues by Optocapacitance Francisco Bezanilla1,2 and Joao Carvalho-de-Souza3; 1The University of Chicago, United States; 2Universidad de Valparaíso, Chile; 3University of Arizona, United States

The technique of optocapacitance is a non-genetic way used to initiate action potentials in excitable tissues with light. The principle is simple: the current $I_c$ flowing to the cell membrane capacitance $C$ is given by $I_c = \frac{C}{dV/dt} + \frac{(V-V_s)dC/dt}{dV/dt}$, where $V$ is the membrane potential and $V_s$ is the net surface potential. Membrane capacitance increases with an increase in temperature, therefore a fast increase in temperature will induce a term that, under conditions of current clamp, it depolarizes the membrane which opens sodium channels thus initiating an action potential. The energy required to excite a neuron decreases as the pulse is made shorter. This is because the induced current depends on the rate of change of the temperature and not the temperature change. Therefore a long pulse does not contribute to the capacitive current thus becoming wasted energy. Experimentally, maximum efficiency is obtained with microsecond pulse durations (1). There are several ways to achieve this fast increase in temperature. An infrared pulse will increase the membrane temperature but the disadvantages are poor tissue penetration and increase of the tissue temperature (2). A more localized approach is to use light-to-heat energy transducers located in close proximity to the cell membrane. Gold nanoparticles, that have the advantage of surface plasmon resonance absorption, have been successfully used as such transducers to deliver just enough heat energy to quickly change membrane temperature of the neuronal membrane for the initiation of an action potential (3). In addition, gold nanoparticles can also be functionalized to get bound to a particular cell using antibodies (3) or specifically to the cell membrane using cholesterol (4). Other materials such as graphite particles, carbon nanotubes and mesoporous silicon (5) are also very good light-to-heat transducers that we have used to excite neurons. The technique has been applied to cultured dorsal root ganglion cells or to tissues such as brain slices (3) or isolated retina.


9:00 AM SB05.01.04
Functional Interaction between Light-sensitive Conjugated Polymer and Cytochrome C for Active Control of Intracellular Signalling Ilaria Abdel Aziz1,2, Francesco Roggiani3, Marco Malferrari1, Gabriele Tullii3, Stefania Rapino3 and Maria Rosa Antognazza1; 1Istituto Italiano di Tecnologia, Italy; 2Politecnico di Milano, Italy; 3Università di Bologna, Italy; 4National Research Council, Italy

Light modulation of cell activity is an active field of research: the possibility of coupling low invasiveness and high resolution assisted the transition from a passive, diagnostic element to an active modulator of cellular physiology. The lack of natural absorbers led to the development of tools able to transduce the optical signal into a biologically readable one, typically through a combination of photo-thermal, photo-electrochemical and photo-capacitive effects. In this framework, organic materials, and in particular poly-thiophene based materials, demonstrated to be reliable for both \textit{in vitro} and \textit{in vivo} use [Feyen et al, 2016, Lodola et al, 2017, Zucchetti et al, 2016, Bossio et al, 2018].

In this work, we prove the behaviour of Poly-3-hexyl thiophene (P3HT) as active modulator of redox metabolic signalling. We first demonstrate that the photocatalytic activity of P3HT in aqueous environment is spatially and temporally confined to the illuminated area by means of Scanning ElectroChemical Microscopy (SECM). To study the possible interactions with the photoexcited polymer, in view of \textit{in vitro} application, we focus our attention on two possible acceptor moieties present in the cell cytosol, namely cytochrome C and oxygen, being their energetic levels well aligned with those of P3HT. The former is a transmembrane protein located across the mitochondrial membrane, being one of the components of the cellular respiration cycle. Its biological relevance is thus associated with the metabolic functions of the cell. By coupling electrochemical and spectro-electrochemical methods, we demonstrate for the first time that a direct, photoinduced electron transfer does occur between P3HT and cytochrome C in extracellular, aqueous environment.

Our results shed light on a technique for active redox modulation of cell metabolism, through on demand, light-activated smart organic interfaces.

9:15 AM SB05.01.05
Controlling Capacitive and Faradaic Charge Transport Processes in Organic Photoelectrodes for Optoelectronic Biointerfaces Tobias Cramer1, Eric D. Glowacki2, Beatrice Fraboni1 and Vedran Derek2; 1University of Bologna, Italy; 2Linköping University, Sweden

Optoelectronic wireless stimulation of cells and tissue is evolving as an inherently less invasive alternative to wired microelectrodes. Wireless stimulation is enabled by photoelectrodes that harvest the light excitation in a semiconducting layer and transduce it to a stimulating ionic current sufficiently strong to depolarize attached neurons thus allowing for optical triggering of action potentials. Organic semiconductors offer a range of important advantages for photoelectrodes such as biocompatibility and the possibility to process them on flexible plastic substrates.\textsuperscript{1} In addition organic semiconductors can show an exceptional electrochemical stability in water and do not require a dielectric to separate the cell-containing electrolyte. As a result a high capacitive coupling is achieved between the semiconductor and the electrolyte. It is exploited in organic photocapacitors to stimulate efficiently retinal cells.\textsuperscript{2} However, the absence of a dielectric can allow for direct charge transfer into the liquid causing faradaic currents and potentially cytotoxic reactive electrochemical species. Therefore the optimization of organic semiconductor based photoelectrodes requests the detailed understanding of the materials and device properties that impact on these different routes of ionic current generation.

Here we address the problem in organic photoelectrodes based on a planar p/n junction containing phthalocyanine (H2PC) and N,N’-dimethyl perylenetetracarboxylic diimide (PTCDI).\textsuperscript{2} We combine the detailed characterization of photoelectrochemical currents with spectroscopic measurements and impedance spectroscopy. The data allows to establish a model that predicts quantitatively faradaic or capacitive current transients based on material properties and layer thicknesses. We find that most crucial to avoid faradaic processes are the semiconductor energy levels as well a precise tuning of electric fields present at the semiconductor liquid interface.

10:30 AM *SB05.01.06
Nanowire Templated Three-Dimensional Fuzzy Graphene for Remote Photothermal Stimulation of Cells
Tzahi Cohen-Karni; Carnegie Mellon University, United States

Electrical stimulation of tissue and ultimately individual cells has not only played an essential role in our understanding of the structure and function of excitable tissue but continues to serve as the basis for a variety of therapeutic interventions for the treatment of disorders ranging from cardiac arrhythmias to Parkinson’s disease. Advances in technology have attempted to overcome barriers associated with the spatial resolution (i.e., who and where to stimulate) and the invasiveness of the process. Optogenetics has revolutionized the way we can record and affect the electrophysiology of cells and tissue, using light as the input/output (I/O) interface. Though optogenetics has developed at a great pace and is making profound scientific contributions, the core of the technique requires genetic modifications of the cells or organism. This presents challenges both in terms of achieving targeted gene expression and the potential deleterious consequences of the expression of foreign proteins, which have implications on clinical translation to humans and regulatory approval. We report our developed breakthrough hybrid-nanomaterial synthesis process to enable minimally invasive, remote and non-genetic light-induced control of targeted cell activity with high spatial-temporal resolution. We combine one-dimensional (1D) nanowires (NWs) and two-dimensional (2D) graphene flakes grown out-of-plane with tailor-made physical properties for highly controlled photostimulation. Our non-genetic NW templated 3D fuzzy graphene (NT-3DFG) platform adds a powerful toolset to the basic scientists studying cell signaling within and between tissues, obviating the need for slow and expensive breeding protocols and/or the screening of viral serotypes to enable the use of light to control cell activity. As we continue to struggle to understand the cells and circuits involved in health and disease, our approach to controlling cell excitability has the potential to accelerate knowledge generation as well as the identification of novel therapeutic targets. Last, this platform can be adapted to address challenges in tissue engineering, i.e. the much-needed non-genetic stimulation control of engineered tissues. By controlled delivery of the NT-3DFG we will be able to locally and selectively control cellular activity with high spatial and temporal resolution of 3D tissues.

10:00 AM BREAK

10:30 AM *SB05.01.07
Photonic Upconversion in Organic Nanoparticles via Cooperative Energy Pooling Sean E. Shaheen1, Cody W. Sharp1 and Garry Rumbles2,1; 1University of Colorado-Boulder, United States; 2National Renewable Energy Laboratory, United States

Organic nanoparticles provide a platform for two-photon microscopy and theranostics that has highly tunable spectroscopic properties and versatile biocompatibility pathways. Here we demonstrate two-photon absorption and subsequent photon upconversion in organic nanoparticles that utilize a three-body resonant energy transfer known as cooperative energy pooling (CEP). CEP is based on the sensitization of two-photon absorbing chromophores with low-energy antennae molecules in the surrounding environment. It relies on the simultaneous transfer of two singlet excitons, initially generated on the sensitizers, to a single high-energy exciton state on an acceptor. This provides for a vast increase in the effective two-photon absorption cross-section of the acceptor by placing real, as opposed to virtual, states at the low-energy resonance. It relaxes the requirement of coincident photons normally needed for two-photon absorption by temporarily storing the energy of one photon in a singlet exciton state. It also circumvents the need for intersystem-crossing events that occur in triplet-triplet annihilation (TTA) upconversion and therefore allows for the possibility of high energetic efficiency and short, nanosecond timescales for the upconversion process. Here we synthesize organic nanoparticles of sensitizer-acceptor mixtures with diameters on the order of 100 nm and with zeta potentials of approximately -50 mV. These carry out photon upconversion from red to blue light with energetic efficiencies of ~77% and on timescales of a few nanoseconds. We discuss the photophysical process, its efficiency, and its intensity dependence, and we suggest strategies for utilizing the concept in biological applications.

11:00 AM SB05.01.08
The Photosynthetic Reaction Center Encapsulated in Micro and Nano Containers Based Upon Melalin-like
Polymers Massimo Trotta1, Danilo Vona2, Gabriella Buscemi2,1, Stefania Cicco1, Roberta Ragni2, Angela Agostiano2,1, Francesco Milano1, Marco Lo Presti2 and Gianluca M. Farinola2; 1Consiglio Nazionale delle Ricerche, Italy; 2Università degli Studi di Bari Aldo Moro, Italy

The photosynthetic enzyme reaction center (RC) is the photochemical core of the photosynthetic bacterium *Rhodobacter sphaeroides*, a bacterium able to grow using light as sole energy source. The RC is a transmembrane protein composed by three subunits and nine cofactors involved in a cascade of electron transfer reactions that, upon the absorption of a photon, produce a hole-electron couple. The electrical charges generated within the enzyme are roughly 3 nanometers apart from each other and have a lifetime that can last from tenths to few seconds. The generation of such nanocapacitor has a conversion photons to electrons efficiency close to unity, making this biological transduction appealing in principle for bioelectronics applications. [1] This biological macromolecule are also amenable for the assembly of organic-biological hybrids with improved enzymatic photoconversion ability. [2-4]

Such photoconverters, either bare or as biohybrids, require an optimised interface with electrode surfaces for their applications [5]. Recently polydopamine (PDA), a self-assembling melanin-like bioinspired polymer, has been exploited to attach and protect enzyme into metal-organic frameworks (MOF) [4] and graphene nanosheets [5] on devices substantially maintaining their activities.

We present here PDA nanoparticles containing the photosynthetic RC able to confine the photoenzyme that retains unaltered the photoactivity, i.e. the capability to generate nanocondensers. The RC has been encased into PDA particles of different size from the micrometer to the nanometer, the smaller being characterised by a bright yellow luminescence. These PDA nanocontainers have an intrinsic n type semiconductive [6] making these organic RC containing nanocapsules highly interesting for bioelectronics purpose.

This work was funded by European Commission through the EU project 800926 - HyPhOE (Hybrid Electronics based on Photosynthetic Organisms)


11:15 AM SB05.01.09

Photoactivated Bismuth Vanadate for Light-Induced Disassembly of Alzheimer's β-amylloid Aggregates

Kayoung Kim, Saehg Ha Lee, Da Som Choi and Chan Beum Park; KAIST, Korea (the Republic of)

Bismuth vanadate (BiVO₄) is a promising n-type semiconductor due to its superior photoelectrocatalytic performance, chemical stability, cost-effectiveness. Despite its beneficial advantages along with non-toxicity and biocompatibility, there are few studies for a biomedical application of BiVO₄. Here, we report a BiVO₄’s newly discovered capability to dissociate the β-amylloid (Aβ) aggregates associated with Alzheimer’s disease (AD) under illumination. An accumulation of β-sheet-rich amyloid aggregates in the brain is a major pathological hallmark of AD. The extremely high stability of amyloid structures makes it challenging to disassemble Aβ aggregates, which sparks the need for the development of new agents for breaking the pre-existing amyloid aggregates and alleviating Aβ-induced toxicity. The use of photoactive materials in medical application is an attractive strategy because of the temporal, spatial controllability, reduced side effects. The development of optogenetic technologies has opened up a new possibility of light-assisted treatment of AD by delivering light energy directly into the brain, which motivated us to develop a new photo-active anti-Aβ neurotoxin agent for localized therapy of AD. In this study, we have verified that nanoporous BiVO₄ photoelectrode can effectively break long Aβ aggregates into non-toxic, small-sized,
and soluble Aβ species under the illumination of a white light-emitting diode and applied bias. According to our photochemical and microscopic analyses, photoexcited BiVO₄ photoelectrode under anodic bias generates oxidative stress, such as superoxide ions and hydrogen peroxide, which play a significant role of oxidizing Aβ peptides and irreversible disassembling the Aβ aggregates. The efficacy of photoelectrocatalytic disaggregation against Aβ assemblies was enhanced by doping Mo ions into BiVO₄ photoelectrode by improving electron-transport properties of BiVO₄. Furthermore, we have demonstrated that both pristine and Mo-doped BiVO₄ photoelectrodes are biocompatible and effective in reducing Aβ-induced cytotoxicity. Our work shows the potential of the visible light-active, nanoporous BiVO₄ photoelectrode-based platforms for dissociating the neurotoxic, highly stable self-assembled ß-sheet-rich aggregates using light energy.

11:30 AM *SB05.01.10
Photonic Structures with Diatoms Microalgae and Molecular Fluorophores Gianluca M. Farinola; University degli Studi-Bari Aldo Moro, Italy

Diatoms are a large and prolific class of single cell photosynthetic microalgae, whose mesoporous biomineralized silica shells (frustules) encase the organic protoplasm [1]. Frustules exhibit interesting properties such as high surface area, mechanical resistance and mesoporosity, which make them appealing materials for applications in photonics, sensing, optoelectronics and biomedicine [2]. In particular, due to their quasi-periodic 3D hierarchical patterns of pores on both the nano- and microscale, frustules can act as natural photonic crystals.

We have demonstrated that in vivo incorporation of organic molecular emitters into frustules through diatoms’ silica biomineralization represents an efficient biotechnological route to new photonic materials whose properties result from the combination of the frustule hierarchical nanostructure with the luminescence of incorporated emitting molecules [3]. The in vivo incorporation approach has been also exploited by our group to generate porous biosilica nanostructures doped with organometallic iridium emitters [4]. More recently, we have also demonstrated that the in vivo incorporation of tailored light harvesting organic antennas into diatom cells can be a suitable method to enhance the algal photosynthesis, leading to increased diatoms growth rate and biomass production. In particular, our study points out that the combination of tailored photoactive molecules with diatoms microalgae can either represent a profitable strategy to get novel biohybrid photonic materials or be a straightforward non-genetic approach to enhance algal growth and biomass production.

2:00 PM *SB05.02.02
Living Electronic Biocomposites Guillermo Bazan, Samantha McCuskey and Yude Su; University of California, Santa Barbara, United States

Composites, in which two or more material elements are brought together to provide properties unattainable by single component alternatives, have a long historical record dating back to ancient times. Few of them have included a living microbial community as a key design element. Here, we describe the use of a self-doped conjugated polyelectrolyte, namely CPE-K, in combination with Shewanella oneidensis to generate gels that can produce biologically-derived currents. CPE-K is a key ingredient due to its ability to dope via protonation reactions and the stability of the resulting polarons under biologically relevant conditions, i.e. buffered aqueous media. Moreover, CPE-K forms gels that exhibit both ionic and electrical conductivity and permit the diffusion of nutrients/waste to/from microorganisms entrapped within the gel network. One finds that the biocomposite gels can generate more than two orders of magnitude greater biocurrent density, when compared to a standard Shewanella oneidensis biofilm formed atop gold electrodes. Such an increase reflects the increase in dimensionality of the biotic/abiotic interface from two to three. We will also provide characterization of the device characteristics and will discuss the vitality of the microbial community within the gels.

2:30 PM SB05.02.03
3D Human Eye Model Using Soft and Rigid Materials Simon Regal, Roger Delattre, Thierry Djenizian and Marc Ramuz; Ecole des Mines de Saint-Etienne, France

We present here the development of a physical human eye model – based on hybrid soft/rigid materials - in order to create a test bench reproducing the optical eye properties.

We have developed phantom eye tissues in order to mimic the different parts like the sclera or the ciliary body as finely as possible regarding the optical properties. As a matter of fact, these parts are crucial in order to mimic human eye but often neglected in the literature. For the development of these models, we used the optical parameters (absorption and scattering coefficients; and refractive index) extracted from an experimental study carried out on porcine eyes – which are close to human one. Moreover, we present a soft actuated model of the iris where the aperture ranges from 1 mm to 8 mm. Finally, all the different parts are put together to obtain a device mimicking exactly the optical properties of an eye. Our work encompasses eye optical simulation, soft material for fabrication and characterization of the eye phantom model.

Light stimuli are used in the medical field to treat diseases as glaucoma based on infrared light or used blue light to treat circadian sleep disorders. The models developed in this study allow us a better understanding of the amount of light that propagates inside the eye.

2:45 PM SB05.02.04
Wireless Organic Electronic Ion Pumps Driven by Photovoltaics Marie Jakesova, Theresia Arbring Sjöström, Vedran Derek, David J. Poxson, Magnus Berggren, Eric D. Glowacki and Daniel T. Simon; LiU, Sweden

Organic electronic ion pumps (OEIP) are an emerging bioelectronic medicine technology for on-demand delivery of pharmacologically-active species. While electrical control is advantageous for providing precise spatial, temporal, and quantitative delivery, it necessitates wiring, which complicates implantation. Herein we demonstrate integration on a flexible carrier of an OEIP with a photovoltaic driver which can be addressed by red light within the tissue transparency window. Organic thin-film bilayer photovoltaic pixels are arranged in series and tandem to provide the 2-5 V necessary for operating the high-resistance electrophoretic ion pumps. We demonstrate light-stimulated transport of protons as well as acetylcholine. The end result of our work is a thin and flexible integrated wireless device platform for targeted drug delivery.

3:00 PM BREAK

3:30 PM *SB05.02.05
Soft Electronic Devices for High Resolution Neuro-Technology Yael Hanein; Tel Aviv University, Israel
Stimulating and recording the electrical activity of neurons and muscles is a major scientific and technological challenge. Although this field dates back centuries, it still remains at the forefront of contemporary investigations, in particular owing to the exploding interest in brain machine interfaces and electronics skin technology. Our investigations in recent years focus on developing and characterizing highly efficient nanomaterial based platforms for superior electronic interfacing with the human body. In particular, we focus on artificial vision and skin electronics for recording emotions. Artificial vision in particular is a very active field with many researchers and companies are trying to restore vision to blind patients through specially designed electronic devices. We recently implemented and validated ex-vivo, two novel systems: The first consists of photosensitive pixels made of a three-dimensional matrix of carbon nanotubes (CNTs) decorated very densely with quantum dots (QDs) or nano rods (NRs) (referred to also as quantum rods (QRs)). Light is absorbed and converted into a transient electrical dipole by the QRs/CNTs system. The use of a three-dimensional matrix as well as an optimized selection of QRs, their surface coating, and conjugation procedure contributes to the superior properties of our films. The second system consists of organic pigments. These materials offer superior photo response and most importantly can be readily implemented on flexible materials. Compared with other photo-sensitive artificial retinal platforms the two systems we have developed so far are marked by several clear advantages. Foremost is low stimulation threshold. Second is their biocompatibility, chemical stability and mechanical flexibility rendering the devices improved stability in the tissue. Implementing some insights gained in our artificial retina project into the realm of skin electronics, we developed a new skin electromyography system to open entirely new and exciting opportunities in recording facial emotions, in neuro-modulation application and in bio-feedback based on EMG.

4:00 PM *SB05.02.06
Charge Accumulation Spectroscopy of Solid-Liquid Interfaces in Organic Bioelectronic Devices Yu Zhang¹, Jonathan Rivnay² and Ni Zhao¹; ¹Chinese University of Hong Kong, Hong Kong; ²Northwestern University, United States

Organic electronics has recently emerged as a powerful technology platform for bio-sensing applications. In many applications, the organic devices are operated in direct contact with an aqueous environment, thus resulting in strong coupling between charge transport in the organic solid and water dipoles, ions and cells in the liquid. These interactions, although dictate the sensing performance, are not well understood. In particular, how these interactions are influenced by the structural and morphological properties of the organic materials remains unknown. In terms of sensing mechanisms, many devices make use of only the electrical responses of organic semiconductors, while the optical signatures of these materials, which are very sensitive to their surroundings, have not been utilized.

In this talk, I will introduce how charge accumulation spectroscopy (CAS) can be applied with other characterization techniques to study the structure-charge transport property relations at the water-solid interfaces. In the first example, we exploit water-gated organic field-effect transistor as the testing platform to investigate the structure-dependent localization of polaronic charge carriers at the organic semiconductor-liquid interface. Our results reveal that the degree of charge delocalization is reduced drastically when the charge carriers are moved from the bulk semiconductor to the semiconductor-water interface, suggesting the existence of a highly disordered surface layer in contact with water. It is also found that the charge delocalization could be further reduced by intercalation of chloride ions (from saline solution) in the semiconductor surface layer. This study suggests that the spectroscopic signatures of polaronic charge carriers could be a sensitive probe to detect the structure-dependent charge localization at organic solid-liquid interfaces. In the second example we combine electrochemical quartz crystal microbalance (EQCM) with CAS to study the ion-to-electron conversion efficiency and water uptake properties of the active layer of organic electrochemical transistors (OECTs). Two material systems, namely PEDOT:PSS (representing depletion-mode OECT) and p(g2T-TT)(representing accumulation-mode OECT), are investigated. We found that the ion-to-electron conversion efficiency of both p(g2T-TT) and cross-linked PEDOT:PSS is close to one at low voltage, indicating highly efficient doping and de-doping processes; while the coupling tends to be weaker at higher voltages, suggesting reduction in the doping efficacy at high ion concentrations. The study also reveal that the PEDOT:PSS layer with low or no cross-linkers exhibits low ion-to-electron conversion efficiency, which is likely associated with the high density of trap states for cations. By simultaneously measuring the mechanical, electrical and optical properties of the polymeric active layer, we are also able to estimate the water hydration numbers of the injected ions. The result suggests that due to the hydrosopic nature of the PSS phase, the PEDOT:PSS film becomes increasingly viscous and hydrated upon ion injection at high operation voltages.

4:30 PM SB05.02.07
NIR Responsive Composite Materials for Stem Cell Behaviors Study Yixiao Zhang, Sy-Tsong D. Chueng,
Photo-crosslinking hydrogels have been vastly utilized as scaffolds for tissue engineering and regenerative medicine. Albeit, ultraviolet and visible light, which has been shown strongly intervene with biological systems, are currently utilized as major excitation sources for hydrogel photo-crosslinking methods. Moreover, these excitation wavelengths are highly limited for in vivo applications because of the compromised spatial resolution and penetration depth. Alternatively, near-infrared (NIR) lights with minimal cellular and tissue interactions become a better candidate. Given the significance of NIR light in next-generation photo-crosslinking hydrogel for regenerative medicine and tissue engineering, a NIR-mediated photo-crosslinking and post-gelation modification method is on demand. Recently, with the swift development of upconversion nanoparticle (UCNP), emerging efforts have been made to drive various photoreactions with NIR light, for instance photo-cleavage, photo-isomerizations, photo-click reaction, and photo-polymerization. In terms of hydrogel crosslinking, the incorporation of NIR light as external stimulus is limited to photothermal crosslinking. The photothermally induced crosslinking mechanism requires high intensity NIR light for generating chemical reactions, where significant heating effect is inevitable. In theory, a NIR photo-crosslinking mechanism without utilizing heat as energy source will be more desirable for biomedical applications. Interestingly, photochemically activated initiator is rarely explored for NIR based hydrogel crosslinking systems.

This study demonstrates NIR-mediated photo-crosslinking (NmPC) of functionalized 4-arm-PEG with small molecule cross-linker, in which the interaction between NIR (980nm) excitation and UCNPs activate a photo initiator, resulting in stimulated photo-click reaction to form hydrogel. In order to utilize NIR excitation more efficiently, multi-shelled UCNPs were synthesized according to a reported procedure. As the efficient NIR (980nm) to visible (520nm-540nm) converter, the multi-shelled size increase was confirmed with TEM (30-60nm) and a 19 times luminescence enhancement was confirmed with luminescence spectroscopy. From rheometry characterization, the NIR mediated hydrogel cross-over point ($G'' = G'$) was found to be 43 seconds under 15 W/cm² 980nm laser intensity and Young’s moduli was found to be 1.9 kPa. Typical porous hydrogel structures were confirmed with SEM and HIM. Adipose-derived Mesenchymal Stem Cells (ADMSCs) were seeded on NmPC hydrogel with different surface binding ligand (RGD) density, showing great cellular viability and different spreading behaviors. Based on the hydrogel mechanical property, different chondrogenic behaviors were observed depending on different surface RGD functionalization, where low density (2mM) shows better chondrogenic markers expression comparing to high density (10mM) and conventional tissue culture polystyrene (TCPS). Interestingly, a proof-of-concept demonstration of NIR-mediated hydrogel printing was succeeded using same hydrogel precursor composition and focused 980nm laser beam.

By utilizing the upconversion effect of UCNPs to convert NIR light into visible emission, 4-arm-PEG chains could be crosslinked through photo-click reaction mediated by the photo initiator. To generate a 2D culture environment for ADMSCs differentiation, various concentrations of RGD ligands were functionalized on the hydrogel surface using NIR light. Low density RGD surface functionalization showed better chondrogenic differentiation comparing to high density and TCPS. With further improvement on the efficiency of upconversion process and better photo-initiator for the photo-click reaction, this hydrogel system can be a powerful approach for in vivo hydrogel property manipulation, cell/protein delivery, and tissue engineering applications.

4:45 PM SB05.02.08
Synthesizing Tunable Artificial Color—A Combined Approach Sunanda Sharma, Bianca C. Datta, Christoph Bader, Sara L. Wilson and Neri Oxman; Massachusetts Institute of Technology, United States

In living systems, color is generated in three main ways - through bioluminescence, as seen in dinoflagellates; through pigments that absorb and reflect light, such as in human skin; or through specific structures that combine light interference and diffraction, such as in peacock feathers. The latter two phenomena do not involve light emission, but rather interact with light to yield an impressive range of colors. Many structural colors also involve the use of pigments, including melanins, that are patterned to geometrically interact with light and thereby enhance the phenomenon. Melanins are a group of organic pigments widely found across the kingdoms of life and are best known for their protective qualities against ultraviolet radiation. Eumelanin, responsible for light brown to black coloration, forms melanosomes in several types of bird feathers, which consequently organize to form structural color with and without iridescence, while simultaneously protecting from UV light, dissipating heat, and minimizing misdirected scattering.

This useful combination of protective and tunable characteristics has long been pursued across the fields of biochemistry and materials science. There has been great interest in controlled synthesis of color using pigment-
related structural color, as the applications of such biocompatible and visually dramatic materials in products such as passive displays, inks, or cosmetics, become more evident. Only a handful of methods have thus far been published, the most prominent of which involve the use of high refractive index melanin or melanin-like materials as the shell layers or core of silica or polystyrene particles. Other methods include incorporation of polydopamine or synthetic melanin into photonic crystals, or thin films. In all of these approaches, the focus has largely been on incorporating eumelanin or a similar synthetic analog such as polydopamine. However, there are other types of pigments, such as pheomelanin or carotenoids, that may also be involved in structural color in Nature. In contrast to eumelanin, these pigments absorb at different spectra and thus may expand the toolbox of synthetic, protective, and biocompatible structural colors. Furthermore, combinations of pigments within multi-layer structures that utilize materials with both high and low refractive indices can create additional complexity with regard to light interaction, pointing towards optical assemblies that yield greater precision, efficiency, reflectance, and finer tunability.

Here we explore the incorporation of mixtures of synthetic eumelanin, pheomelanin, and carotenoids in multiple layers of synthesized particles to yield combination pigment-structural colors. We will examine criteria such as multi-layer shell coating, stacking of close-packed layers of pigment-incorporated particles, shell thickness, and shell composition, and heterogeneity of structures. Properties such as reflectance, absorption, packing, layer interfaces, and global architectures will be studied using a variety of methods, including spectrophotometry, scanning and transmission electron microscopy, light microscopy, and angular spectroscopy. In doing so, we hope to provide a path towards the utilization of the impressive protective properties and functions of natural pigments and their synthetic analogs in the study of structural color, resulting in multi-functional, biocompatible, and scalable coloration.

SESSION SB05.03: Poster Session I: Light-Matter Interactions for Biological Applications I
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB05.03.01
High Sensitivity, High Multiplexity Biosensor Based on Graphene-Enhanced Raman Spectroscopy
Shengxi Huang, Alexander Silver and Dongqiang Han; The Pennsylvania State University, United States

Graphene is a two-dimensional (2D) material consisting of a single sheet of sp2 hybridized carbon atoms laced in a hexagonal lattice, with potentially wide usage as a Raman enhancement substrate, also termed graphene-enhanced Raman scattering (GERS), making it ideal for sensing applications. GERS improves upon traditional surface-enhanced Raman scattering (SERS), combining its high sensitivity and spectral fingerprinting of molecules, and the unique advantages of graphene including simple processing, superior uniformity and low cost. This enables fast and highly sensitive detection of a wide variety of analytes. Accordingly, GERS has been investigated for a wide variety of molecule sensing applications. In the field of molecule sensing, biomolecule detection is an important branch and plays significant roles in biomedical research and medical diagnosis. While GERS have witnessed great success in the sensing of small organic molecules, its potential in biomolecule sensing is yet to be discovered. In this work, we report our pioneer investigations in using GERS for biomolecule detection, including various types of proteins. The unique molecular selection rules in GERS of small molecules still apply for proteins. In addition, we revealed several structures in proteins that enable strong GERS signals. Furthermore, the application of GERS for tissue imaging show unprecedentedly high signal-to-noise ratio, high spatial resolution, rapid measurement and multiplexed data obtained. We further demonstrate the effectiveness of GERS-based hyperspectral imaging as a novel tool for disease diagnosis. Our work unveiled the tremendous potential of GERS in biomedical studies and opened a new path of biosensing using GERS,

SB05.03.02
Mechanism of Plasmonically Enhanced Selective Virus Inactivation
Ramprasath Rajagopal, Mina Nazari, Min Xi, Netania Marc, Suryaram Gummuluru, Mi Hong, Björn M. Reinhard, Lawrence Ziegler and Shyamsunder Erramilli; Boston University, United States

Efficient Plasmon enhanced photonic pan-microbial pathogen inactivation was demonstrated under conditions that
allow for shockwave generation and E-field mediated cavitation. We report ultra-fast transient absorption of gold nanoparticles to explore the microscopic mechanism of shockwave generation. We use 800nm, 100fs pulses with a repetition rate of 1KHz generated with chirped pulse amplification as the pump beam and a white light continuum derived from the pump beam incident on a sapphire plate as the probe beam. Transient absorption spectra were obtained by chopping the pump beam at 500Hz with lock-in detection. Systematic studies of probe wavelength, intensity, and nanoparticle morphology to test the proposed mechanism of inactivation. Our work demonstrates the potential of plasmonic nanomaterials for pan-pathogen inactivation without targeting.

SB05.03.03

Hybrid Donor Acceptor Polymer Particles (HDAPPs) Comprised of Oligomer and High Molecular Weight PCPDTBSe for Near-Infrared Fluorescence Imaging and Photothermal Ablation of Cancer

Santu Sarkar, Elizabeth G. Graham, Christopher M. MacNeill, Bryce D. McCarthy, Aron M. Mohs, Sneha Kelkar and Nicole Levi-Polyachenko; Wake Forest University of School of Medi, United States

Near infra-red (NIR) light mediated photothermal therapy (PTT) has emerged as an excellent therapeutic method to ablate cancer due to its outstanding benefits of noninvasiveness, high specificity and high tissue transparency. Along with therapeutic treatment, diagnosis of tumors is equally vital for the visualization of the tumor and approaching therapeutic activity of remotely activated nanoparticles. Among several imaging modalities, NIR fluorescence imaging is an excellent technique due to its high sensitivity, low scattering, portability and safety. Recently, conjugated polymer nanoparticles have successfully employed as biological imaging agents and more recently evolved for photothermal therapy.

Our lab has recently demonstrated that the donor acceptor based conjugated polymer poly[4,4-bis(2-ethylhexyl)-cyclopenta[2,1-b;3,4-b']dithiophene-2,6-diy-alt-2,1,3-benzoselenadiazole-4,7-diy] (PCPDTBSe) is an excellent photothermal therapy agent but the oligomer of PCPDTBSe as fluorescent material has not yet been explored. Oligo PCPDTBSe showed emission in the NIR region (800 nm) upon excitation at 550 nm. The NIR fluorescence of the oligomer was explored for cellular imaging along with photothermal therapy when combined with the high molecular weight (hMW) segment of PCPDTBSe in 2:1 (oligo: hMW) ratio to form hybrid donor acceptor polymer particles (HDAPPs). Oligo NPs and hMW NPs were also prepared from oligomer and hMW of PCPDTBSe respectively by similar method for comparison. HDAPPs showed absorption maxima at 550 nm and 760 nm in UV-visible spectroscopy due to the presence of oligomer and hMW PCPDTBSe respectively, along with a new peak at 650 nm because of combined absorption. HDAPPs displayed a huge stokes shift of 264 nm with emission maxima at 810 nm upon excitation at 550 nm, producing 0.077 quantum yield. The hydrodynamic diameter of HDAPPs was found 65 nm, whereas oligo NPs and hMW showed 107 nm and 94 nm respectively. Upon 808 nm laser (3W) irradiation, 100 µg/ml hMW NPs produced temperature increase to 45°C, whereas equal concentration of HDAPPs produced temperature increment to 40°C; which is an unexpected phenomenon as HDAPPs contain only 1/3 of the heat generating hMW PCPDTBSe. HDAPPs were photostable with minimal decrease in fluorescence intensity through consecutive heating cycles. No significant decrease in heat generation capacity or fluorescence ability of HDAPPs was found despite of autoclaving for sterilization. HDAPPs incubated with non-tumorigenic MCF10A breast cells and triple negative MDA-MB-231 breast cancer cells displayed no cytotoxicity up to 100 µg/ml in the absence of NIR exposure. HDAPPs were clearly visible in the cytoplasm around the perinuclear region of MDA-MB-231 cell lines in Fluorescence microscopy. Upon 808 nm laser (3W) irradiation, MDA-MB-231 cells incubated with 40 µg/ml HDAPPs produced 35% cell viability whereas 100% cell killing was observed with 100 µg/ml HDAPPs. These results demonstrate that HDAPPs are a novel theranostic photothermal agent composed of two different molecular weights of PCPDTBSe for imaging as well as ablation of cancer cells.

SB05.03.04

Refractive Index Determination of Fabricated Squid Chromatophore Pigment Thin Films via Ellipsometry

Sean R. Dinneen1, Camille A. Martin2, Amrita Kumar2, Yassine Ait-El-Aoud1, Michael Okamoto1, Leila Deravi2 and Richard M. Osgood1; 1Combat Capabilities Development Command - Soldier Center, United States; 2Northeastern University, United States

We further our understanding of the optical properties of squid chromatophore pigment in order to interrogate its utility as a functional optical coating. Cephalopods (which include octopuses, cuttlefish, and squid) have evolved to create one of the most complex photonic systems. Using hierarchical layers of optical organs, these animals can change the color patterns of their skin within milliseconds. A majority of their bulk coloration is facilitated by pigmentary organs known as chromatophores, which can expand many times their size in surface area. The pigment
responsible for this color has been identified as a mixture of xanthommatin and decarboxylated xanthommatin in previous studies, and its refractive index has been measured in both the solution phase and aerosol phase. The indices of refraction of the pigments are needed for essential analysis and modeling of the chromatophore organs in order to understand how the cephalopod accomplishes its unique color and pattern changes for camouflage. To examine these optical properties in the solid state, we fabricated thin films using extracted squid chromatophore pigment mixed with polyvinyl alcohol (PVA) in a 50/50 mixture by weight. The pigment/polymer solution was spin-coated onto silicon substrates achieving a range of thicknesses (200 – 700 nm) by controlling the spin speed. The polymer aids in the homogenous distribution of pigment throughout the film by eliminating aggregation and crystallization. This method has resulted in improved ellipsometry measurements, which require very smooth films, and thus can model the pigment’s refractive index from visible wavelengths up to 3 microns. Using the procedures in this study, we demonstrate increased control of thin-film fabrication methods of extracted pigments, and a greater understanding of their optical utility within the animal, for photonic devices, or coatings.

**SB05.03.05**

**Membrane Environment Enables Ultrafast Isomerisation of Amphiphilic Azobenzene**

Giuseppe M. Paternò¹, Vito Vurro¹, Francesco Lodola¹², E. Colombo¹, Simone Cimò¹, Matteo Bramini¹², D. Fazzi², Cosimo D’Andrea¹, F. Benfenati¹², C. Bertarelli³ and Guglielmo Lanzani¹³; ¹Istituto Italiano di Tecnologia, Italy; ²IRCCS Ospedale Policlinico San Martino, Italy; ³Politecnico di Milano, Italy; ⁴University of Cologne, Germany

Optogenetics and covalent approaches to bio conjugation allow to achieve large and effective cell photo-stimulation, yet these are invasive methods that might encounter severe limitations on the way towards clinical applications in photopharmacology. The non-covalent affinity of photoresponsive molecules to biotargets represents an attractive alternative. Here, we show that an amphiphilic azobenzene photochromic molecule, fully locked in water, recovers its photo switching dynamics once screened by the plasma phospholipid system. According to our steady state and time resolved spectroscopic investigations the photophysical scenario in different media is dramatically different. In molecular aggregates formed in water the isomerization reaction is hindered while the radiative deactivation is enhanced by an excimer type transition. Once protected by a lipid bilayer, either in artificial micelles or in the cell membrane, the photochromic molecules reacquire their photoisomerisation capacity. Together with the natural affinity for the plasma membrane, this suggests a potential in cell opto-stimulation. We demonstrate in vitro the reversible modulation of the membrane potential via illumination with visible light. These data represent a new rationale for designing photoresponsive systems that operate via simple non-covalent affinity to biotargets and can be of importance for future applications in photopharmacology.

**SB05.03.06**

**A Soft, Conformable, Free-Form OLED for Skin-Attachable Phototherapeutics**

Yongmin Jeon¹, Hye-Ryung Choi², Seungyeop Choi¹, Kyoung-Chan Park² and Kyung Cheol Choi¹; ¹Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of); ²Seoul National University Bundang Hospital (SNUBH), Korea (the Republic of)

Realizing soft, conformable, free-form opto-bioelectronic devices is of great interest in the wearable and bio-compatible medical device industries [1-2]. To achieve superior wearable and bio-compatible photomedical devices, high-performance and highly reliable free-form optoelectronic devices should be manufactured to accommodate a wide range of soft materials and shapes. In addition, a conformable surface light source should be directly attached to the skin to achieve a high-performance therapeutic effect. However, most studies have reported limited opto-bioelectronic devices that can only be fabricated on specific materials and shapes, or have relatively low performance and reliability. Even wearable photomedical device studies are mostly non-contact approaches based on point light sources, which are not flexible. Few studies on skin-attachable phototherapeutics based on ultimately soft, conformable, free-form optoelectronic devices have been reported.

In this study, we report soft, conformable, free-form OLEDs that can be attached to the skin for effective phototherapeutics. Ultra-thin free-form OLEDs (10 μm) are sandwiched by an attachable barrier and can be transferred to any soft, conformable material, including the skin. The attachable barrier is made of a nano-laminate film composed of three dyads of ZnO, Al₂O₃, and SiO₂ polymer to have high barrier performance (1.2 x 10⁻⁸ g/m²/day) and reliability to prevent a phase transition to boehmite even in moisture such as sweat [3]. Therefore, free-form OLEDs transferred to any soft material such as the skin and textiles showed high performance (>20mW/cm², 80 cd/A), low voltage (<10V), folding reliability, long operation reliability (>100h), and washing
reliability. When these free-form OLEDs were applied to real human skin keratinocytes and fibroblasts, cell proliferation was stimulated (>25%) and cell migration was effectively enhanced (>30%). Also, when the free-form OLED was attached to the rats' skin wound, the skin area was increased (>10%) and re-epithelialization was improved (>20%). In conclusion, it is expected to be applicable to various skin-attachable phototherapeutics based on high-performance, high-reliability, bio-compatible free-form OLEDs.


8:00 AM SB05.04/SB02.04/SB07.03: Joint Session: Bioelectronics
Session Chairs: Mohammad Reza Abidian, Ritchie Chen, Sahika Inal and Bozhi Tian
Tuesday Morning, December 3, 2019
Hynes, Level 3, Ballroom B

Graphene Based Health Monitoring Dmitry Kireev and Deji Akinwande; The University of Texas at Austin, United States

The modern healthcare and biomedical systems show a clear trend towards personalized, predictive, and preventive medicine. Development of the concept, commonly known as mobile health (mHealth), means that a huge shift in the paradigms of medical device architectures is to be expected in the near future thanks to the increased portability of medical devices as well as increase in number of specific mobile-based apps. An ideal wearable device should possess a set of important requirements, such as (i) low cost of fabrication, (ii) being conformable and compatible with human skin, and (iii) multifunctionality. The latter is of special importance if the goal is to build not just a single specific device, but to rather develop a technology and basis for scalable fabrication of devices that are capable to detect a plurality of vital signals (HR, EEG, ECG, hydration, galvanic response, etc.).

In order to develop the universal technology that meets all three requirements mentioned above, we propose to utilize graphene in combination with epidermal technology. The conventional epidermal biosensors are based on metal and silicon based thin films that are patterned into special structures for softness and stretchability and embedded into soft biocompatible polymers. The choice of two-dimensional materials is the most natural due to their ultra-thinness, allowing extreme flexibility, transparency, and conformability to almost any rough surface, including skin [1]. Graphene based passive electrodes have been successfully used to epidermal sensing of electrocardiograms (ECG), electromyogram (EOG), electroencephalogram (EEG), skin temperature, and skin hydration [1], [2]. It is important to emphasize that the research work is based on large-area CVD-grown graphene, allowing us to develop low-cost, wearable, and fully conformable to skin devices. Furthermore, large area fabrication gives an ultimate promise for future devices fully based on 2D materials to be available on market. In terms of possible applications, the proposed technology can be easily expanded towards other fields of healthcare biosensing, such as in vivo electrophysiology, UV exposure sensing, pressure sensing, or even towards building electronic skin, and prosthetics.


8:15 AM SB05.04/SB02.04/SB07.03.02
Multifunctional Fiber Based Neural Probes with Integrated Neurotransmitter Detection Atharva Sahasrabudhe1,4, Tural Khudiyev1, Tomo Tanaka2, Kyoungsuk Jin1, Marc-Joseph Antonini1,3, Andres Canales1, Yoel Fink1,3, Kartish Manthiram1 and Polina Anikeeva1,3; 1Massachusetts Institute of Technology, United States; 2NEC Corporation, Japan; 3Harvard-MIT Division of Health Science and Technology, United States
One of the major challenges in deciphering the fundamental principles of cognition is the lack of appropriate tools for seamless interfacing with neurons across all their signaling modalities. Gaining holistic understanding of neural circuits and their control of behavior requires invention of neural probes that can simultaneously record and modulate electro-chemical activity of neurons while evoking minimal inflammatory response for periods ranging from minutes to years. Multifunctional fibers have recently emerged as a promising platform for integrating multiple functional elements to probe and control neural activity that also minimizes the foreign body response.

In my presentation, I will describe our efforts in further expanding the multifunctionality of polymer-based fiber probes by incorporating an electrochemical sensor that enables real-time tracking of neurotransmitter dynamics in behaving animals. This is achieved by introducing a carbon nanotube (CNT) based electrocatalytic electrode within the multifunctional fiber-based probes during their fabrication via thermal drawing process. The resulting devices can be implanted chronically and perform electrical recording and stimulation of neurons, light delivery through waveguides for optogenetics, drug and gene delivery via microfluidic channels, and voltammetry via the CNT electrodes for dynamic detection of dopamine. We envision that these multimodal, miniature, and mechanically compliant probes will facilitate understanding of the neurophysiological underpinnings of dopamine-dependent behaviors including reward, addiction, and motor control.

8:30 AM *SB05.04.03/SB02.04.03/SB07.03.03
OPEN SLOT

9:00 AM *SB05.04.04/SB02.04.04/SB07.03.04
Chronic Recordings from Behaving Animals Using Microwire-CMOS Technology Nicholas Melosh; Stanford University, United States

Mammalian brains consist of billions of neurons operating at millisecond time scales, which current recording techniques only capture a tiny fraction. Recent advances in CMOS device design have led to high-recording quality planar probes, with diminishing sizes to ameliorate the extent of tissue damage. Matching these powerful silicon electronics to the inherently three dimensional architecture of the brain has remained challenging however, as devices are constrained to the planar two dimensional surfaces required for silicon processing. Here we describe a chronic interface using arrays of microwires read out by CMOS-based devices with a low-tissue damage, and controllable, three dimensional distribution of recording sites. The core concept is using a bundle of insulated microwires mated to a large-scale CMOS microelectrode array, such as found in modern camera chips or displays. We show recent results on the mechanics and tissue damage from microwire insertion scales strongly with wire diameter. Microwires with <25µm diameters are shown to have minimal to no vascular disruption or bleeding, as opposed to more conventional 75 to 100 µm devices. These microwires are then arranged into bundles to control the spatial arrangement and three dimensional structure of the distal (neuronal) end, while providing a robust parallel contact plane on the proximal side which is interfaced to a planar pixel array. The modular nature of the design enables a wide array of microwire types and size to be mated to a variety of different CMOS chips, making the same fundamental platform scalable from a few hundred electrodes to tens of thousands. We thus link the rapid progress and power of commercial multiplexing, digitisation and data acquisition hardware together with a bio-compatible, flexible and sensitive neural interface array. We present recent massively parallel recording using mouse and rat models, showing both spiking activity from single neurons and local field potentials within both chronic and acute settings.

9:30 AM *SB05.04.05/SB02.04.05/SB07.03.05
Membrane Curvature at the Interface between the Cell Membrane and Nanoscale Electrodes Bianxiao Cui; Stanford University, United States

The interaction between the cell membrane and the measuring electrode is crucial for crucial for sensitive measurement of cell electric activities. We are interested in exploring nanotechnology and novel materials to improve the membrane-electrode coupling efficiency. Recently, we and other groups show that vertical nanopillars protruding from a flat surface support cell survival and can be used as subcellular sensors to probe biological processes in live cells. The nanopillar electrodes deform plasma membrane inwards and induce membrane curvature when the cell engulfs them, leading to a reduction of the membrane-electrode gap distance and a higher sealing resistance. As an electrode sensor, nanoelectrodes offer several advantages such as high sensitivity, subcellular
spatial resolution, and precise control of the sensor geometry. Furthermore, we found that the high membrane curvature induced by nanoscale electrodes significantly affects the distribution of curvature-sensitive proteins and stimulates several cellular processes in live cells. Our studies show a strong interplay between biological cells and nanoscale topography, which is an essential consideration for future development of interfacing devices.

10:00 AM BREAK

10:30 AM *SB05.04.06/SB02.04.06/SB07.03.06
Engineering Skin-Like Soft Electrical Interface with Biological Systems Zhenan Bao; Stanford University, United States

In this talk, I will discuss several projects related to engineering conductive materials and developing fabrication methods to allow electronics with effective electrical interfaces with biological systems, through tuning their electrical as well as mechanical properties. The end result is a soft electrical interface that has both low interfacial impedance as well as match mechanical properties with biological tissue. Several applications of such electronics will be presented.

11:00 AM *SB05.04.07/SB02.04.07/SB07.03.07
Soft Materials in Wireless Closed-Loop Neuromodulation Systems for Treating Organ Dysfunction John A. Rogers; Northwestern University, United States

Bioelectronic medicines targeted at the peripheral nervous system have the potential to address a wide variety of diseases, from diabetes to bladder dysfunction. The foundational concepts have existed for decades but implementation has been limited and fraught with persistent challenges, including lack in target specificity, nerve interface biofouling, and inability to acquire real time physiologic signals for conditional delivery of corrective stimuli, leading to excess and unnecessary stimulation. Here we present a set of materials, a treatment strategy and supporting technology platform that address many of these challenges, using bladder control as model system. Specifically, we report capabilities for continuous monitoring of bladder function using an ultralow modulus, stretchable strain gauge to measure dimensional changes, real-time data analytics to identify pathological behavior based on the resulting data, and automated, closed-loop optogenetic neuromodulation of bladder sensory afferents to normalize bladder function in the context of acute cystitis, with generic applicability to many other organ systems and conditions.

11:30 AM *SB05.04.08/SB02.04.08/SB07.03.08
Miniature, Wireless Bioelectronics by Harvesting Energy from Magnetic Fields Jacob T. Robinson; Rice University, United States

Miniature, wireless bioelectronic devices enable less invasive surgical implantation and the ability to target tiny nerves or brain areas. However, as these neural stimulators become smaller, we must engineer new ways to deliver power. Conventional power deliver relies on long wires to deliver power from an implanted battery or subcutaneous antenna. These leads can limit device placement and cause device failure due to lead breakage or infection. Conventional wireless power delivery through biological tissue is difficult when devices are miniaturized and placed deep in the body. Here we show that magnetic materials can effectively harvest energy from magnetic fields and power millimeter-sized bioelectronics. These materials show excellent power densities even as the devices are made small allowing them to be fully implanted and wirelessly powered. We demonstrate that these mm-sized wireless devices can be used to power different types of conventional stimulation electrodes when implanted in rabbits, pigs, and freely moving rats. Furthermore, these miniature electrical stimulators can be adapted to power many individually addressable stimulation channels while still maintaining a small overall device footprint.
A fundamental goal of Neuroscience is to understand how the activity of specific neuronal circuits mediates behavior. Determining which aspects of neural activity are used by downstream circuits to guide behavior requires to manipulate activity while simultaneously monitoring behavioral readout. Holographic optical stimulation is an emerging toolbox for distributed control of spatiotemporal neuronal activity, which could shed new light on its direct link to behavior, by precisely manipulating the neural code while monitoring behavioral readout and neural responses.

I will describe new models, tools and experiments that together lead to recent advances in several fundamental technical aspects of optical neural interfacing and applications of such systems towards producing behaviorally relevant neural activity. First, I will focus on surprising new insights at the level of membrane biophysics that enable predictive modeling of both photo-thermal and optogenetic light-tissue effects. I will then describe our efforts to precisely probe neural circuits using rapid two-photon optogenetic stimulation and imaging with cellular resolution and ms-timescale temporal precision. Using high-energy lasers and rapid spatial light modulation we stimulate dozens of neurons deep (>250 µm) in brain tissue at a high rate. Our new system allows to generate and precisely manipulate artificial sensory responses. This approach has a broad range of potential applications in dissecting the activity codes that guide behavior across different modalities.

Recently, there is a growing interest in techniques for regulating the activity of nerve cells using light. The optical stimulation method has a higher spatiotemporal resolution than the electrical stimulation, and it is easy to implement multiple stimuli using multiple wavelengths. Although optogenetics, which is based on light-sensitive ion channels and pumps, has been widely used as an experimental tool owing to high cell specificity, the necessity of carrying out genetic manipulation is a limitation in terms of translation to clinical situation. To overcome this, nongenetic optical stimulation has been actively studied, and photothermal stimulation is one of them.

Photothermal stimulation is a method of modulating neuronal activity by applying heat to nerve cells via a substance that converts light into heat. Plasmmonic nanomaterials were used as transducers to induce photothermal effects. Among those nanomaterials, gold nanorods (GNRs) have been studied extensively in the field of nanomedicine on photothermal therapy because GNRs selectively absorb near infrared (NIR) rays and are highly efficient in converting light energy into thermal energy. Our group has been developing NIR sensitive GNR platform to suppress the neuronal activity, and investigated the inhibitory effect of photothermal stimulation on neuronal activity on in vitro neural activity.

In this presentation, I will present a GNR-based platform for locally applying photothermal stimulation to specific areas or cells of the network on a planar microelectrode array chip. In order to create a local heating pattern in tens of micrometer scale, two approaches were taken: patterning GNR particles onto the chip surface, or patterning the light. We applied inkjet printing technique to make high-quality GNR patterns in large area, and optimized the surface interaction with GNR ink droplets using a layer-by-layer technique. In order to pattern NIR light to the micrometer level, optical system was designed to achieve sufficient optical power density at a single cell size. We grew in vitro neural networks on microelectrode arrays to investigate the effect of local photothermal stimulation by multichannel spike recordings. When local photothermal stimulation was applied to a part of the network, the synchronized activity of the network was reduced and the degree of connectivity was changed. In the case of single cell-level photothermal stimulation, inhibition and rebound of action potential were observed. Comparing the optical power required for electrical activity inhibition, the action potential was instantaneously suppressed by using a very small level of optical power for single cell stimulation.

This study was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (NRF-2018R1A2A1A05022604).
Microalgae are extremely important photosynthetic organisms for both their environmental functions (e.g. CO$_2$ fixation and O$_2$ production) and industrial applications (e.g. food, drugs and bio-fuel production). In order to increase biomass production it is, indeed, of fundamental importance to increase the efficiency of microalgae photosynthesis. This approach fits perfectly into a circular economy scheme, in fact many waste products from industrial processes (e.g. CO$_2$, wastewater, sludge and agro-waste) can be used to feed photosynthetic processes to produce biomass. Among microalgae, diatoms constitute a major group that have found many industrial applications from biomedicine to photonics and they are particularly interesting for their hierarchically organized porous biosilica shells.

One possible strategy to enhance photosynthesis consists of filling the spectral gap in the light absorption of microalgae pigments (e.g. chlorophylls and carotenoids). The basic idea of this approach consists in introducing photoactive components which absorb light in the uncovered solar spectral regions and they transfer the collected energy to the photosynthetic units of the microalgae. Genetically engineered approaches can be exploited but, unfortunately, these tools in microalgae are still limited to few species.

In this work we demonstrate a new non-genetic approach to artificially increase the photosynthetic efficiency of *Thalassiosira weissflogii* diatoms by adding exogenous antennae cyanine molecules (Cy5) as a staining dye. In particular we observe that Cy5 is rapidly incorporated into the chloroplast of the microalgae without being toxic, increasing diatoms cell growth and photosynthetic oxygen production upon illumination. Cy5 dye was chosen as a possible FRET donor for chlorophyll a (acceptor) because of the following characteristics: (i) low toxicity, (ii) absorption/emission features and (iii) molecular structure.

By means of confocal microscopy we observe that Cy5 is localized in the shell and chloroplasts of the diatoms, where they can be still detected after 8 days. The incorporation of the dye is likely favored by the charged functional groups on the cyanine molecule which causes the electrostatic interaction between cyanine and cell membrane. Time-resolved fluorescence spectroscopy shows a decrease in the Cy5 excited state lifetime which is consistent with a resonant energy transfer (FRET) process between Cy5 (donor) and Chl a (acceptor). The quenching effect, and hence energy transfer, reaches a maximum after about 24 hours and, then, it gradually decreases never reaching the initial value after 6 days. In order to confirm the role of Cy5 as an enhancer of photosynthesis, photosynthetic activity was measured in the presence and absence of Cy5. The presence of Cy5 increases Pmax (maximum photosynthetic activity) by 49% compared to the control. In order to exclude that the increased productivity could be ascribed to any sort of Cy5 metabolism independent from light we repeated the measurement in the dark, observing no significant difference in cell density. This proves that only the simultaneous presence of Cy5 and light causes the diatoms growth increase. Finally it is worth stressing that the algae population is healthy for the whole experiment, and no toxic reactions or adverse effects in general have been observed.

In conclusion, in this work we demonstrated a novel method to increase *in vivo* photosynthetic activity in diatoms by...
adding Cy5 as exogenous antennae molecules. This route represents a convenient alternative to genetic modifications. This approach may be in principle extended to other photosynthetic organisms and it lays the foundations for the bio-photonic engineering of algal production by using photoactive molecules and it can impact on algae production technology, for instance extending the active volume of bioreactors and thus enhancing the yield.

3:00 PM BREAK

3:30 PM *SB05.05.05
Design Nanophotonics Interface for Photoacoustic Brain Stimulation Chen Yang; Boston University, United States

Implantable nanophotonics devices and injectable nanomaterials with new functions interfacing with neural systems enables new techniques to fire neurons. High spatial resolution and deep penetration in brain provided by NIR light opens up potential to overcome fundamental limitation of other photo or magnetic driven neural modulation techniques. Specifically, we will report our recent progresses on photoacoustic devices and nanotransducers for successful in vitro and in vivo neuro stimulation. In the first application, we designed and developed a miniaturized fiber with the fiber tip with two layer coating: a diffusion layer and an expansion layer with nanocomposites to produce high intensity and controlled frequency of localized ultrasound when excited with nanosecond laser light. In vitro and in vivo neuron stimulation was successfully achieved with a laser duration of 20 millisecond. Neural stimulation in motor cortex of intact awaken mouse brains confirmed the photoacoustic stimulation was localized with a high spatial resolution of 500 microns and not through indirect auditory stimulation. Additionally, to enable non-invasive and MRI compatible neurostimulation, we developed a semiconducting polymer based nanotransducer, which generate ultrasound upon excitation of NIR II nanosecond laser light and perform stimulation when binding to neuron membrane. In vitro photoacoustic neuron stimulation with a successful rate of 80% is achieved with a laser duration of 3 millisecond. Different neuron response were demonstrated through controlling the binding between nanotransducers and neuron membrane.

4:00 PM *SB05.05.06
See Infrared through Upconversion Nanoparticles Gang Han; University of Massachusetts Medical School, United States

Near Infrared light responsive photon upconversion nanoparticles possess a unique optical mechanism where long wavelength low-energy photons can be converted to high-energy emissions at the shorter wavelengths. They are highly promising for in vitro and in vivo optical imaging and therapy due to such special optical properties. Recently, upconversion nanoparticles (UCNPs) have stood out as a fascinating emerging tool in numerous biological and material applications. In this talk, I will first present new developments regarding engineering UCNPs towards wireless optogenetic applications in neuroscience and immunotherapy. Secondly, I will present our more recent development of an ocular injectable photoreceptor-binding upconversion nanoparticles that can create the mammalian infrared imaging vision in their naked eyes.

4:30 PM SB05.05.07
Light-Sensitive Conjugated Polymers Optically Control the Fate of Endothelial Progenitor Cells Francesco Lodola¹, Vittorio Rosti², Gabriele Tullii³, Andrea Desii³, Laura Tapella³, Paolo Catarsi³, Dmitry Lim³, Francesco Moccia⁴ and Maria Rosa Antognazza³; ¹Istituto Italiano di Tecnologia, Italy; ²IRCCS Policlinico San Matteo Foundation, Italy; ³Università del Piemonte Orientale "Amedeo Avogadro", Italy; ⁴University of Pavia, Italy

Direct control of cells homing to damaged myocardium after an ischemic insult is an overarching goal in the cardiac repair field because this will allow to prime the re-activation of the injured myocardium and vasculature. Here we propose a novel strategy to gain optical control of Endothelial Progenitor Cell (EPC) fate, avoiding the drawbacks associated with current approaches, mainly based on cell therapy and electro-mechanical stimulation. Our strategy is based on the combination of light sensitive conjugated polymers (CPs), used as photo-actuators, with the advantages offered by optical stimulation. At variance with cell therapy and electro-mechanical stimulation, light modulation offers unprecedented spatial and temporal resolution, permitting lower invasiveness and higher selectivity, and it allows to provide either excitation/inhibition of the cell activity. We focus on Endothelial Colony
Forming Cells (ECFCs), which represent the only known EPCs subset truly belonging to the endothelial lineage showing robust in vitro proliferation and overwhelming vessel formation in vivo. We demonstrate that polymer-mediated optical excitation is able to induce a robust enhancement of cells proliferation and lumen formation in vitro. Moreover, we identify the pathways leading to this effective enhancement in ECFCs network formation, as due to light induced activation of transient receptor potential vanilloid channels. Altogether our results represent a novel effective application of semiconducting polymer-based optical modulation to induce angiogenesis in vitro. More in general, this work represents, to the best of our knowledge, the first report on use of CP for optical modulation of the cell fate, with important perspectives in cell-based therapy and regenerative medicine.

4:45 PM SB05.05.08
Nanowire Arrays for Artificial Retina Jing Tang; Stanford University, United States

The restoration of light response with complex spatiotemporal features in retinal degenerative diseases towards retinal prosthesis has proven to be a considerable challenge over the past decades. Herein, inspired by the structure and function of photoreceptors in retinas, we develop artificial photoreceptors based on gold nanoparticle-decorated titania nanowire arrays, for restoration of visual responses in the blind mice with degenerated photoreceptors. Green, blue and near UV light responses in the retinal ganglion cells (RGCs) are restored with a spatial resolution better than 100 µm. ON responses in RGCs are blocked by glutamatergic antagonists, suggesting functional preservation of the remaining retinal circuits. Moreover, neurons in the primary visual cortex respond to light after subretinal implant of nanowire arrays. Improvement in pupillary light reflex suggests the behavioral recovery of light sensitivity. Our study will shed light on the development of a new generation of optoelectronic toolkits for subretinal prosthetic devices.

SESSION SB05.06: Materials and Systems for Advanced Imaging and Sensing
Session Chairs: Tzahi Cohen-Karni, Brian Timko and Elizabeth von Hauff
Wednesday Morning, December 4, 2019
Hynes, Level 3, Room 303

8:15 AM SB05.06.01
Engineering and Characterization of Polymer Colloidal Nanoparticles for Retinal Prosthesis Jonathan Barsotti, Guglielmo Lanzani and Giovanni Manfredi; Istituto Italiano di Tecnologia, Italy

Hybrid interfaces composed by organic semiconductors in contact with living tissues are appealing for the controlled photo-stimulation of tissue cells in both in-vivo and in-vitro applications. Organic optoelectronic materials, such as light sensitive and conjugated polymers, provide an easy processable, biocompatible and tunable tool for the development of bio-devices and prosthesis able to restore vision. Planar organic prosthesis based on a thin film of poly(3-hexylthiophene) (P3HT) have been proven to be successful in inducing vision recovery in rat model affected by retinitis pigmentosa.

Considering such a promising result, we decided to investigate P3HT nanoparticles (NPs). According to preliminary results, P3HT NPs succeeded in restoring vision acuity in blind rats. However, despite the encouraging results, the mechanisms at the basis of the retinal organic prosthesis functioning is still not well understood.

In this work, we investigate the photophysical properties of light sensitive core-shell nanoparticle in which one component is P3HT. Different core materials were selected (among which: ITO, TiO2 and Au) in order to have core-shell systems with different optoelectronic properties, permitting to investigate the cores effect on the organic NPs prosthesis.

Core-shell NPs provides a ground for investigating the photoexcitation mechanism and eventually controlling it by engineering ad hoc interfaces where energy level alignment can be predicted. NPs are a versatile system able to be widespread in the whole treated tissue. Moreover, NPS properties, such as tissue selectivity, light sensitivity, elasticity, etc. can be tuned, providing a versatile tool for the comprehension and improvement of the interaction between the prosthesis and the biological tissue.

8:30 AM *SB05.06.02
**Laser Particles as Novel Bioimaging Agents** Nicola Martino\textsuperscript{1,2}; \textsuperscript{1}Massachusetts General Hospital, United States; \textsuperscript{2}Harvard Medical School, United States

The emerging understanding of cellular heterogeneity in complex biological systems has necessitated new tools for large-scale, single-cell analysis. Single-cell molecular analyses have led to identification of new cell types and discovery of novel targets for diagnosis and therapy. Despite these advances, a major challenge is the ability to tag and discriminate individual cells, and track them over time or over the course of different measurements. Current fluorescence-based approaches are fundamentally limited in multiplexing ability due to typical fluorophores emission linewidths, between 30-100 nm.

We have recently developed a novel class of imaging probes, called \textit{laser particles} (LPs), with massive multiplexing capability and optimized properties for cell tagging applications. Our LPs are made of silica-coated semiconductor optical microcavities in a microdisk geometry, with ~2 μm diameter and 400 nm thickness. Upon optical pumping with a 1064 laser, the LPs generate single narrowband emission peaks (<0.5 nm) ranging from 1170 to 1580 nm, enabling massive spectral multiplexing. The LPs are readily internalized into cells to act as unique optical barcodes, where they occupy only ~0.1% of the cell volume.

In this contribution, I will present our results regarding the fabrication and characterization of these LPs, their stability and biocompatibility in biological environments and the use of these probes for wavelength-multiplexed cell tagging and imaging. I will demonstrate real-time tracking of thousands of individual cells in a 3D tumor spheroid invasion assay over several days showing different behavioral phenotypes.

**9:00 AM SB05.06.03**

**Optomechanical Microdisks for Biological Sensing** Eduardo Gil Santos\textsuperscript{1}, Jose Jaime Ruz\textsuperscript{1}, Oscar Malvar\textsuperscript{1}, Daniel Ramos\textsuperscript{1}, Sergio García-López\textsuperscript{1}, Priscila Kosaka\textsuperscript{1}, Aristide Lenaître\textsuperscript{2}, Ivan Favero\textsuperscript{3}, Montserrat Calleja\textsuperscript{1} and Javier Tamayo\textsuperscript{1}; \textsuperscript{1}Instituto de Micro y Nanotecnología (IMN-CNM, CSIC), Spain; \textsuperscript{2}Laboratoire de Photonique et Nanostructures, France; \textsuperscript{3}Université Paris Diderot, France

The field of Optomechanics has made impressive advances in the last decades, covering a broad range of applications going from ultrasensitive sensing to fundamental quantum studies. The use of optomechanical devices for biosensing has acquired crescent interest in the last years, being semiconductor microdisks one of the most promising platform on this field. Semiconductor microdisks support both, optical and mechanical modes, which possess extraordinary properties. Optically, semiconductor microdisks support the so called whispery gallery modes (WGMs), where the light circulates around the disk periphery. WGMs combine submycron optical mode volume and low optical dissipation, reaching optical quality factor above $10^5$. From the mechanical point of view, they support a family of modes, the radial breathing modes (RBM), which present extremely high mechanical frequencies (> GHz) and low energy losses in liquids. These assets, together with their remarkably low masses (in the pg range), provide them with extremely low mass sensitivities and high speed, notably, while immersed in liquid [1]. Moreover, semiconductor microdisks can be integrated in collective configurations, thus, improving their sensing efficiency while keeping their individual capabilities [2].

Optomechanical microdisks allows to simultaneously monitor optical and mechanical modes, which provides them with access to the optical and mechanical properties of the given analyte. This dual sensing approach is fully innovative and significantly improves the sensor reliability and robustness. We have first applied this novel method on the detection of environmental changes, particularly temperature and humidity. We demonstrated that the method allows to decoupled humidity and temperature effects with extraordinary precision, which place them as excellent sensors for this purpose. Notably, in this work we show the first application of optomechanical devices as biological sensors. We have developed a novel deposition method which allow us to precisely locate individual, alive and intact bacteria in our sensors. By simultaneous detecting changes in their mechanical and optical modes, we probe that microdisks allows to determine the mechanical properties (rigidity, viscosity and mass) and the optical properties (index of refraction, optical absorption coefficient and size) of \textit{Staphylococcus Epidermidis} bacteria. Importantly, besides their capabilities to sense the analyte optical and mechanical properties, we also proven that optomechanical microdisks can detect the intrinsic mechanical resonances of the bacteria. This concept has been never realized even proposed before. By coupling the mechanical modes of the sensor with the ones of the analyte, the coupled system supports detectable collective mechanical modes, which provide precise information about the analyte modes. Importantly, coupling between the sensor and the analyte modes require having close resonance frequencies. It is important to note that the detection of analyte mechanical modes provides extremely high sensitivity on the determination of the morphology and mechanical properties of the analytes. In addition, the
method allows to track in real-time the mechanical resonance frequency of the bacterium, which significantly increases the responsivity of the system to analyte changes. The proposed method radically departs from the classical paradigm for sensing the mass and stiffness of analytes with micromechanical resonators. This novel concept opens the door for studying biological interactions at the most fundamental level.

References

9:15 AM SB05.06.04
Trans-Membrane Fluorescence Enhancement by Carbon Dots—Ionic Interactions and Energy Transfer
Stefanie D. Pritzl1, Fernando Pschunder2, Florian Ehrat1, Santanu Bhattacharyya1, Theobald Lohmüller1, Maria A. Huergo2 and Jochen Feldmann1; 1Ludwig-Maximilians-Universität (LMU), Germany; 2Universidad Nacional de La Plata - CONICET, Argentina

We present how trans-membrane energy transfer and ionic interactions can be controlled across the bilayer membrane of large unilamellar vesicles. A system has been designed, where hydrophobic carbon dots (CDs) are embedded in the lipophilic part of lipid bilayers, while fluorescein molecules are covalently bound to the hydrophilic lipid heads [1]. The CDs are built of polycyclic aromatic hydrocarbon domains [2] that form biocompatible nanoparticles (~1.0 - 1.5 nm) with high photochemical stability. The spectral overlap between the CD emission and the fluorescein absorption spectra allows to establish trans-membrane Förster resonance energy transfer (FRET). We observe energy transfer efficiencies of 51% for a separation distance of ~4 nm between the donor CDs and the acceptor dyes, which is in good agreement with the bilayer geometry. Furthermore, we find that ionic interactions between the positively charged CDs and the anionic fluorescein let them conjoin within the vesicle membrane. This co-localization of both components does not only facilitate energy transfer, but also results in photoluminescence enhancement of the membrane bound dyes, which is beneficial for imaging applications and microscopy studies of membrane systems. Overall, this capability of balancing energy transfer and ionic interactions within a model membrane represents a general strategy to investigate trans-membrane related processes such as ion transport and changes of the membrane potential with high spatiotemporal control and resolution.

References:

9:30 AM *SB05.06.05
3D Nanostructures for Biosensing in Living Cells Francesco de Angelis; Istituto Italiano di Tecnologia, Italy

The ability to interact with neuronal cells and to monitor their status plays a pivotal role in neuroscience, pharmacology and cell biology. In the last years, we deeply investigated both theoretically and experimentally the interactions of 3D nanostructured surface sensors with living cells such human neurons and cardiomyocytes [1]-[2]. The aim is to make an effective interface between the intracellular compartment and different class of nano-sensors including optical sensors, electrodes and nano-needles for intracellular delivery or sampling [3]. We developed a method based on plasmonic generation of nano-shockwaves [4] for opening transient nanopores into the cell membrane that is in close proximity with the plasmonic nanosensor. After the membrane poration the tip of the sensor is in direct contact with the intracellular compartment thus enabling intracellular investigations which include Raman traces of biomolecules [5]-[6], electrical recording of action potentials [7], and controlled delivery of single nanoparticles into selected cells [8]. However, for these applications have a real impact in the fields of Biology and Medicine it is necessary to make them available on the market, i.e. in the hands of biologist and researchers working in those fields. To this aim, we introduced the concept of planar meta-electrodes [9], namely a nanostructured surface that can work as electrode, a broad band plasmonic antenna, and optimal cellular interface. We show that meta-electrodes combined with commercial CMOS technology enable high quality intracellular electrical signals on the large network scale of human neuron and cardiomyocytes. Due to its robustness and easiness of use, we expect
the method will be rapidly adopted by the scientific community and by pharmaceutical companies. In fact, the field suffers the lack of reliable approaches for pharmacological screening of drugs devoted to the central nervous system. Also, we will take this opportunity to give a short overview of different types of optical and plasmonic biosensors we are currently developing. The latter includes single molecule Raman Sensors, DNA detection, and Protein sequencing.

References

10:00 AM BREAK

10:30 AM *SB05.06.06
Biological Imaging of Chemical Bonds—Next Frontier of Light Microscopy Wei Min and Yuan Yang; Columbia University, United States

Innovations in light microscopy have revolutionized the way researchers study biological systems. Although fluorescence microscopy is currently the method of choice for cellular imaging, it faces several fundamental limitations such as the rather bulky fluorescent tags, color barrier for multiplex imaging, and limited ability for probing in vivo metabolism. To address these challenges, I will present three coherent Raman imaging strategies, respectively. First, we devised a Bioorthogonal Chemical Imaging platform suited for probing small bio-molecules. This scheme couples the emerging stimulated Raman scattering (SRS) microscopy with tiny vibrational probes. Exciting biomedical applications such as imaging fatty acid metabolism, glucose uptake and metabolism, drug trafficking, protein synthesis, DNA replication, and tumor metabolism will be presented. Second, we invented a super-multiplex optical imaging technique. We developed electronic pre-resonance SRS microscopy with high sensitivity. Chemically, we created vibrational palettes consisting of novel dyes. This super-multiplex optical imaging approach promises to facilitate untangling intricate interactions in complex biological systems, and can also find broad applications in photonics and biotechnology. Third, we introduced a platform that combines deuterium oxide (D2O) probing with SRS microscopy (DO-SRS) to image in situ metabolic activities in animals. Enzymatic incorporation of D2O-derived deuterium into macromolecules generates carbon-deuterium (C-D) bonds, which track biosynthesis in tissues in situ. Within the broad vibrational spectra of C-D bonds, we discovered lipid-, protein-, and DNA-specific Raman shifts with macromolecular selectivity. DO-SRS, being noninvasive and universally applicable, can be adapted to a broad range of biological systems to study development, tissue homeostasis, aging, and tumor heterogeneity.

11:00 AM SB05.06.07
Oxygen Monitor to Study Vascularization of Medical Devices Avid Najdahmadi¹, Rachel Gurlin¹, Mellonie Zhang,² John Weidling,¹ Sean White¹, Bhupinder Shergill², Jonathan Lakey¹ and Elliot Botvinick¹; ¹University of California Irvine, United States; ²University of California, Davis, United States

Subcutaneous medical devices designed for cell therapy can be advanced by a prevascularization phase that
proceeds the transplantation of tissue into the device. This approach holds promise to replace whole organ transplantation with thin vascularized devices hosting only the necessary supporting cells. We have developed a noninvasive optical technology to study the vascularization into such medical devices. In our technique, oxygen partial pressure within a device is monitored by Oxygen Sensitive Tubes (OSTs), comprising oxygen permeable silicone tubes coated on their inner surface with a porphyrin oxygen-sensitive dye. OSTs were placed within a PDMS device and transplanted into athymic nude mice. An optical probe placed on the skin excites the OSTs with a pulse of light and detects the luminescent lifetime of emitted light. The lifetime is uniquely related to oxygen partial pressure. Further, we developed a Dynamic Inhalation Gas Test (DIGT) to determine the oxygen transport rate between the microvasculature and the device. DIGT works by monitoring oxygen partial pressure during a step change in the inhaled gas oxygen content. We report changing DIGT oxygen dynamics from a series of experiments spanning eight weeks. Our study shows DIGT dynamics are unique to each implant, suggesting the important role of the host tissue response in the availability of oxygen over time.

11:15 AM SB05.06.08
Wavelength Modulation of Fluorescent Nanosensors for High SNR Operation in Thick Tissue Volodymyr Koman, Naveed Bakh, Freddy Nguyen, Daichi Kozawa, Michael A. Lee and Michael Strano; Massachusetts Institute of Technology, United States

Fluorescent sensors directly probe chemical kinetics in remote locations, transmitting the signal wirelessly to the observer. However, many biological organisms suffer from the limited penetration depth of light, obstructing the sensor use. Here, we present wavelength modulation spectroscopy (WMS) that improves the signal to noise ratio (SNR) in thick tissues by 100x. This allows the detection of near-infrared signals from sensors implanted at depths of up to 4.5 cm in chicken breast tissues. Additionally, WMS can eliminate the need of reference measurements, as it self-corrects for mechanical artefacts caused by tissue movements. WMS is enabled by the modulating the excitation wavelength across 50 nm in 0.2 s and measuring the changes in emission, which allows us to separate autofluorescent and fluorescent components of the response based on the period of modulation. We demonstrate the application of WMS on common near-infrared sensors, such as carbon nanotubes and ICG. We applied WMS to improve the SNR in sensing H2O2, riboflavin, and ascorbic acid in vivo. This technique may find a variety of uses in diagnostics, real-time therapeutics, and biochemical studies.

11:30 AM SB05.06.09
Towards Rapid, All-Optical Pathogen Identification Using Raman Spectroscopy and Machine-Learning Amr A. Saleh, Chi-Sing Ho, Neal Jean, Loza Tadesse, Niaz Banaei, Stefano Ermon and Jennifer A. Dionne; Stanford University, United States

Rapid, accurate identification of pathogens and their antibiotic susceptibility/resistance are essential to improve patient prognosis, slow the spread of infectious diseases, contain epidemics, and mitigate the misuse of antibiotics. Unfortunately, the gold standard for bacterial identification and antibiotic susceptibility testing (AST) still rely on century-old culturing methods that typically takes few weeks to run. In this work, we introduce a novel platform that combines Raman scattering spectroscopy with machine-learning to enable the identification of individual pathogens solely through their Raman signatures. Notably, cellular membranes have a unique molecular composition that give rise to a characteristic Raman signature that can be used for cellular identification. However, practical implementation of Raman-based identification has been hindered by the reproducibility of Raman measurements at the single cell level. To overcome this challenge and allow for accurate single-cell classification using Raman spectroscopy, we developed a machine-learning classification algorithm. Particularly, we developed a convolutional neural network (CNN) trained on Raman spectra from individual pathogens. Our CNN architecture consists of 25 one-dimensional (1D) convolutional layers and residual connections - instead of two-dimensional images, it takes one-dimensional spectra as input. Our training dataset consists of 60,000 single-cell spectra from 30 bacterial and yeast isolates representing over 94% of all bacterial infections treated at Stanford Hospital. The training data we used was acquired at a rate of 1 s per individual cell, corresponding to a signal-to-noise ratio (SNR) of 4.1 - roughly an order of magnitude lower than typical reported bacterial spectra. Using this dataset, we show that the average pathogen strain-level classification accuracy achieved is 93.8%. When these strains are grouped based on their empiric antibiotic treatment, the classification accuracy increases to more than 99% for the treatment group classification. To further enable studying the changes in the Raman signatures of pathogens upon exposure to external stimuli such as antibiotics while improving the signal-to-noise ratio, we implemented a liquid chamber
where mixtures of pathogens and gold nanorods were prepared. Using a palette of gold nanorods with resonances ranging from 650nm to 920nm and a 785nm excitation laser, we show that significant enhancement in the Raman signatures of both E. Coli (Gram-negative) and Staphylococcus (Gram-positive) can be achieved. Interestingly, the obtained enhancements are achieved using two different nanorod sizes for the two tested species; while nanorods with shorter resonant wavelengths result in a more pronounced enhancement for Gram-negative E. Coli, longer-wavelength resonant nanorods produce the largest enhancement for the Gram-positive Staphylococcus. This is due to the tendency of nanorod aggregation with the Gram-negative E. Coli, due to the bacterial and nanorod surface charge interaction, causing the nanorod frequencies to red-shift. Our results lay the foundation for a fast, all-optical pathogen identification and antibiotic susceptibility classification beyond the conventional slow culture methods.

11:45 AM SB05.06.10
Hybrid Plasmonic/Photonic Crystals for Optical Detection of Bacterial Contaminants Giuseppe M. Paternò¹, Liliana Moscardi¹,², Stefano Donini¹, Davide Ariodanti², Ilka Kriegel³, Emilio Parisini¹, Guglielmo Lanzani¹,² and Francesco Scotognella¹,²; ¹Istituto Italiano di Tecnologia, Italy; ²Politecnico di Milano, Italy; ³Materiali e Ingegneria Chimica "Giulio Natta", Italy; ⁴Istituto Italiano di Tecnologia (IIT), Italy

Photonic crystals (PhCs) have been largely employed as detection/sensing devices in recent years, since the photonic stop-band can be tuned by applying a number of external stimuli, such as chemical¹, thermal² and mechanical triggers³. In this context, we have recently proposed porous 1D photonic structures exhibiting electro-optical tunability, due to the incorporation of optoelectronically-active plasmonic nanoparticles in the photonic structures.⁴–⁶ Here, we show that a hybrid plasmonic/photonic crystal consisting of a thin layer of bioactive plasmonic material (i.e. silver) deposited on top a 1D PhC can detect one of the most common bacterial contaminant, namely Escherichia coli. We speculate that the change in the plasmon charge density brought about by metal/bacterium interaction results in a variation of the plasmon resonance which, in turns, translates in a shift of the photonic structural color.

References
As a result, there is still a need to develop methods capable of monitoring ENM-cell interactions in a quantitative fashion, independent of specific surface modifications. Addressing these concerns, here we show how scatter enhanced phase contrast (SEPC) microscopy, a dual light source microscopy technique, can serve as a generalized label-free approach for monitoring nanoparticle uptake and transport dynamics. By avoiding fluorescent labels, SEPC allows for a rational exploration of the surface properties of nanomaterials in their native state. We demonstrate this experimentally, showing that SEPC works for a variety of metal and metal oxides, including Au, Ag, TiO2, CeO2, Al2O3, and Fe2O3 nanoparticles. Additionally, we show that when combined with microcontact printing, a technique which can be used to control cell morphology, we are able to normalize dynamics across multiple cells, enabling a quantitative study of ensemble nanoparticle uptake (n= ~480 particle trajectories). Using this approach, we observed that particles began as evenly distributed across the cell surface but became clustered in the perinuclear region after a short duration, indicating the bulk of ENM transport occurs within the first 30 minutes of exposure. These studies also suggested further spatial heterogeneities in ENM dynamics, revealing three distinct regions of particle transport across the cell, with particles moving faster near the edge of the cell and slowing down as they approach the nucleus. Overall, this indicated that membrane dynamics play an important role in regulating initial particle flow, while intracellular vesicular transport dictates intermediate dynamics. Collectively, this ensemble approach to studying transport dynamics has important implications for designing next-generation ENM-based drug delivery systems and in better understanding the uptake of existing materials.

SB05.07.02
Three-Dimensional Quantitative Characterization of Migrating Cells Revealed by Optical Diffraction Tomography Yongkeun Park, Ariel J. Lee, Herve Hugonnet and Wei Sun Park; KAIST, Korea (the Republic of)

The wound-healing assay is one of the most useful methods for the study of collective cell migration and cell-to-cell interaction. Furthermore, it provides an inexpensive and easy tool for therapeutics, by observing the effect of various chemical treatments on wound healing speed. Numerous studies have observed some novel mechanical and molecular interactions between the cells during the healing process using this assay. Nonetheless, most are remaining at the stage of two-dimensional analysis such as gap closure rate, direct counting of cells or individual cell tracking, although it clearly involves a complex three-dimensional (3D) process. There are limitations when viewing the healing mechanism in 2-dimension. People do not have a full understanding of collective cell migration yet. The 3-dimensional (3D) properties of cells like thickness or velocity vector during the process present a new perspective to understand how cells near and away from the boundary migrate and interact with the neighboring cells. Here, we utilized non-labeling 3D long-term imaging and developed analysis tools for the wound healing assay.

Optical diffraction tomography (ODT) is an effective tool for imaging low-scattering samples like cells by utilizing intrinsic physical information in the sample without labeling. Based on laser interferometry, it reconstructs a three-dimensional refractive index tomogram of live cells or tissue, from multiple 2D measurements of optical field images of the sample illuminated from various angles. ODT provides label-free and quantitative phase imaging capability. Especially in terms of the experimental complexity or availability, its label-free imaging ability without difficulties such as photobleaching has an incomparable strength in monitoring the healing process for an extended period of time. A wide enough field of view for analysis can be covered by using a stitching algorithm. Thus, ODT with the aid of the stitching algorithm is an excellent fit for imaging the expanded area of wound healing model for an extended period of time in 3D.

To investigate dynamic 3D motions of cells in a wound-healing assay, we have systematically controlled the ODT imaging system and a motorized sample stage in a synchronized manner. We have measured a large area of a sample (up to 1 mm x 1 mm) with a high resolution (down to 110 nm and 360 nm in the lateral and axial spatial resolution, respectively) at a high frame rate (up to 3-5 tomograms per second for a specific field of view 81 μm x 81 μm). We studied both the overall shape and the subcellular structures of individual cells in a time-lapse manner. Several quantifiable 3D properties such as the thickness of cells or condensation level of the nuclei chromatin in groups of cells with different chemical treatments are explored by employing the system. Especially, an examination of RI distribution in the nucleus of cells revealed different chromatin condensation level near the boundary and the inner regions of cells. This provides a new tool to study and monitor the wound healing mechanism and how the chemical treatments affect cells.

Our 3D non-labeling imaging and analyzing techniques of wound healing will deliver a significant impact on the pharmaceutical industry. Quantitative 3D analysis for migrating cells’ behavior during the wound healing allows a unique chance to study and analyze with precision the wound healing mechanisms. Studying more complex 3D wound healing models utilizing this technique will be the subsequent step which may give us a fundamental
understanding of the in-vivo wound healing process.

SYMPOSIUM SB06

TUTORIAL: Molecules and Materials in Mechanobiology
December 1 - December 1, 2019

* Invited Paper

TUTORIAL
Molecules and Materials in Mechanobiology

Sunday Afternoon, December 1, 2019
Hynes, Level 2, Room 201

This tutorial aims at reviewing the fundamentals and applications of mechanobiology in the context of materials science. A comprehensive overview from the cellular principles to biomaterials will be given.

Recent developments in Materials Science and Biology have made it possible to investigate cell-matrix interactions in relation to mechanics. Therefore, the tutorial "Materials in Mechanobiology" presents the principles of mechanobiology in relation to materials science. The course includes an introduction into mechanobiology (1:30-3:00 pm), followed by a discussion of biofunctionalized materials that are relevant for controlling cells by environmental cues (3:30-5:00 pm).

The objective of the tutorial is to introduce materials scientists into this highly interdisciplinary, lively field of research.

1:30 PM
Molecules of Mechanotransduction Medha M. Pathak, University of California Irvine

The 1st half of the tutorial will review the most recent progress on mechanobiology. A particular focus will be on mechanotransduction, the process by which mechanical cues from the extracellular environment are transduced into biochemical signals, which in turn control physiological processes. The methods that allow cells to actively probe their environment, i.e. intracellular forces, will also be explained. Central to mechanisms of force sensing and transduction are mechanically-activated ion channels. The tutorial will provide an in-depth introduction to these molecules and their interaction with the cytoskeleton. Overall, this part of the tutorial will give a comprehensive introduction into the biological background that needs to be considered when designing materials for mechanobiology.

3:00 PM BREAK

3:30 PM
Strategies to Control Cellular Environmental Cues One at a Time or Combined Together Virgile Viasnoff, National University of Singapore and Centre National de la Recherche Scientifique
The 2nd half of the tutorial will cover biofunctionalized materials for investigating how cells respond to environmental cues. Such materials can have different features, ranging from specific matrix materials, specific geometry, to topography. These materials have high potential for controlling cells in a variety of applications, including tissue engineering. Therefore this tutorial will discuss methods to generate biofunctionalized materials that have well-defined ligand patterns, specific rheological properties, and well-controlled topography at the micro- and nanoscale. A highly timely aspect will be the presentation of methods to dynamically control such material properties over space and time.

SYMPOSIUM SB06

Bringing Mechanobiology to Materials—From Molecular Understanding to Biological Design
December 2 - December 4, 2019

Symposium Organizers
Jennifer Curtis, Georgia Institute of Technology
Matthew Paszek, Cornell University
Kate Poole, University of New South Wales
Christine Selhuber-Unkel, University of Kiel

Symposium Support
Bronze
TA Instruments

* Invited Paper

SESSION SB06.01: Cells as Mechanosensory Living Materials I
Session Chairs: Christine Selhuber-Unkel and Ana-Sucana Smith
Monday Morning, December 2, 2019
Hynes, Level 2, Room 201

8:30 AM *SB06.01.01
Sensing Local Strains in the Cytoskeleton via LIM Domains Patrick Oakes; Loyola University Chicago Stritch School of Medicine, United States

The actin cytoskeleton plays a fundamental role in giving cells their shape and mediating interactions between the cell and the extracellular environment. Specifically, actin filaments transmit the forces generated in the cytoskeleton by myosin motors to the extracellular matrix. It has been shown previously that proteins that contain multiple LIM domains (e.g. zyxin, paxillin, etc…) specifically recognize sites of strain in the cytoskeleton and localize to stress fiber tears. Using these proteins as markers in conjunction with an optogenetic approach to induce local contractions in the cytoskeleton, we have recently shown that strain in actin filaments is distributed non-uniformly. We find that in addition to random failures in the network, strain in the actin cytoskeleton preferentially concentrates at the interface between focal adhesions and stress fibers. We also surprisingly find that these proteins localize to sites of potential compression. Here we use the LIM family protein testin to explore these mechanisms of mechanosensing behavior. Using a combination of laser ablations and optogenetics, we find that full length testin localizes to the cytosol and is not mechanosensitive. Truncations of the protein that include just its three LIM domains (LIM1-3), however, localize to focal adhesions and sites of strain. Stress fibers that are fully severed show no recruitment of the LIM1-3 construct, suggesting that LIM domain proteins recognize a change in the conformation of actin, and not just free barbed ends. Further truncation constructs reveal that the first LIM domain is required for mechanosensitivity. Finally, using various phosphomutants, we find that we can drive testin to localize at adhesions, but that only a subset of them retain their mechanosensitivity. Together these results indicate a potential role for
phosphorylation in regulating the conformation of testin, thereby controlling its mechanosensitivity and its ability to recognize local strain in actin filaments.

9:00 AM SB06.01.02
Mechanical Manipulation of Tandem Repeats of Biological Motifs—One Molecule at a Time Jaba Mitra1,2 and Taekjip Ha2; 1University of Illinois at Urbana-Champaign, United States; 2Johns Hopkins University, United States

Tandem repeat motifs are ubiquitous across the central dogma of biology and regulate a variety of physiological processes including gene regulation, membrane functionalization etc. For example, in eukaryotic cells, the ends of linear chromosomes are capped by 50-200 nt long telomeric DNA, consisting of tandem hexanucleotide guanine (G)-rich repeats. Four of such telomeric, G-rich motifs can spontaneously associate and fold into thermodynamically stable structures, known as G-Quadruplexes (GQs). Interplay between mechanical forces and structural transformations is fundamental to several biological processes, such as, transcription, replication, cellular locomotion etc. We integrated the unique abilities of single molecule fluorescence and optical traps to demonstrate unprecedented heterogeneity in GQs, with at least six interconvertible species which differ in mechanical responses, but are largely resistant to unfolding by cellular motor proteins associated with transcription, replication etc. Additionally, our studies revealed direct mechanical regulation of a GQ-core in presence of unassociated G-rich motifs. The extreme conformational and mechanical diversity of GQs may induce differential protein binding in cells and serve as cornerstones for engineering novel anti-cancer therapeutics. The conformational versatility of G repeats have been harnessed for development of molecular tools called “light-up” aptamers used for visualization and localization of RNA in cells. We evaluated the mechanical stabilities of two classes of such RNA aptamers, known as Mango and Spinach. Our results illustrated that despite a common GQ core, the aptamers have characteristic mechanical signature and in general, with respect to Mango, Spinach is mechanically weaker and susceptible to unraveling via helicases and polymerases. Thus, the RNA aptamers can be leveraged as molecular platforms for simultaneous visualization and prediction of forces involved in transcription. We next extended our assay to demonstrate linear spring-like mechanical response of a malarial circumsporozoite protein (CSP). CSP being a surface protein, this facilitates gliding motility of the sporozoites in the host. Moreover, the repeat peptides can be used for engineering cellular tension sensors which are sensitive to forces between 1 and > 30 pN.

9:15 AM SB06.01.03
Biologically Inspired, Cell–Selective Release of Aptamer–Trapped Growth Factors by Traction Forces Benjamin Almquist; Imperial College London, United States

Biomaterial scaffolds that are designed to incorporate dynamic, spatiotemporal information have the potential to interface with cells and tissues to direct behavior. Here, I will describe a bioinspired, programmable nanotechnology–based platform that harnesses cellular traction forces to activate growth factors, eliminating the need for exogenous triggers (e.g., light), spatially diffuse triggers (e.g., enzymes, pH changes), or passive activation (e.g., hydrolysis)1. Flexible aptamer technology is used to create modular, synthetic mimics of the Large Latent Complex that restrains transforming growth factor–β1 (TGF–β1). I will show that this nanotechnology–based approach works with multiple growth factors, integrates with both 2D and 3D substrates and scaffolds, and enables fundamentally new capabilities such as selective activation of growth factors by differing cell types (e.g., activation by smooth muscle cells but not fibroblasts).


9:30 AM *SB06.01.04
Watching Cellular Mechanotransduction—Piezo1 Activation by Cellular Traction Forces Kyle L. Ellefsen1, Jesse R. Holt2, Alice C. Chang1, Jamison L. Nourse2, Janahan Arulmoli2, Armen Mekhdjian1, Hamid Abuwarda2, Francesco Tombola1, Lisa A. Flanagan2, Alexander Dunn2, Ian Parker1 and Medha M. Pathak2; 1University of California, United States; 2University of California, Irvine, United States; 3Stanford University, United States

A major unanswered question in biology is how mechanical forces are generated, detected and transduced by cells to impact biochemical and genetic programs. Our work is aimed at uncovering the mechanical principles at play in cells and tissues using novel molecular, imaging and bioengineering tools. Here we present insights gleaned from
non-invasive approaches to measure and manipulate mechanical cues in native cellular conditions. We find that the mechanically-activated ion channel Piezo1 transduces cell-generated traction forces to regulate lineage choice of neural stem cells. We show that actomyosin-based cellular traction forces generate spatially-restricted Piezo1 Ca2+ flickers in the absence of externally-applied mechanical forces. Although Piezo1 channels diffuse readily in the plasma membrane and are widely distributed across the cell, their Ca2+ flicker activity is enriched in regions proximal to force-producing adhesions. The mechanical force that activates Piezo1 arises from Myosin II phosphorylation by Myosin Light Chain Kinase. We propose that Piezo1 Ca2+ flickers allow spatial segregation of mechanotransduction events, and that mobility allows channel molecules to efficiently respond to local mechanical stimuli.

10:00 AM BREAK

10:30 AM *SB06.01.05
From Microdishes to Microniches—Controlling Single Cell Apico-Basal Polarity and Lumenogenesis Virgile Viasnoff1,2, Yue Zhang1, Richard deMets1 and Celine Stoecklin1; 1National University of Singapore, Singapore; 2Centre National de la Recherche Scientifique, France

The key influence of the microenvironment on cell behavior and fate is increasingly recognized. It follows that new techniques to control the 3D environment around cells are essential to understand the processes by which cells probe and respond to the cues received by their microniches. Here, we present an approach that allows transforming microwells into artificial microniches where the chemical coating, the rheological properties and the topographical properties can be differentially controlled on the top, sides and bottom of the wells and assembled in a combinatorial way. This technique is also compatible with high and super resolution imaging that allows probing the dynamics of cell cytoskeleton and regulatory proteins with unprecedented resolution down to the single molecule level in 3D. We exemplify how these bone fide artificial microniches can be used to induce full apico-basal polarization of single epithelial cells as well as to control intercellular stresses driving the anisotropic growth of intercellular lumens. We will detail our recent studies on the role of mechanical forces in the development of bile canaliculi in liver and explain our minimal organ approach.

11:00 AM *SB06.01.06
Mechanism in Collective Organizations of Living Cells Joachim P. Spatz and Oskar Staufer; Max Planck Institute for Medical Research, Germany

Regulating the emergence of leading individuals is a central problem to collectively migrating biological entities. For example, leaders in the mobile animal groups arise through collective decision making of the followers. However, the fundamental control of leader selection remains unclear in the physiologically relevant collective migration of epithelial cells. Here we present that the selective emergence of leader cells at the epithelial wound-margin depends on the dynamics of the follower cells and is spatially limited by the length-scale of collective force transduction. Owing to the dynamic heterogeneity of the monolayer, cells behind the prospective leaders manifest locally increased traction and monolayer stresses much before these leaders display any phenotypic traits. Once formed, the territory of a leader can extend only to the length up-to which cells can pull on their neighbors. These findings provide a novel mechanobiological-insight into the hierarchy in cell collectives during epithelial wound healing.

Lit.: A molecular mechanotransduction pathway regulates collective migration of epithelial cells; Nature Cell Biology 2015; DOI 10.1038/NCB3115
Sequential bottom-up assembly of mechanically stabilized synthetic cells by microfluidics; Nature Materials 2018; DOI 10.1038/NMAT5005
Mechanical interactions among followers determine the emergence of leaders in migrating epithelial cell collectives, Nature Communication 2018; DOI 10.1038/S41467-018-05927-6

11:30 AM *SB06.01.07
Soft Tissue Mechanics Result from Fibrous Networks Confined by Close-Packed Cells Anne van Oosten1,2, Xingyu Chen1, Vivek Shenoy1,1 and Paul A. Janmey1; 1University of Pennsylvania, United States; 2Leiden University, Netherlands

Crosslinked semi-flexible polymer networks are ubiquitous to both the internal cytoskeleton and the extracellular
matrix. The viscoelasticity of these networks is therefore presumed to dominate tissue mechanics. However, the responses of soft tissues and semiflexible polymer gels to uniaxial loading differ from each other in many respects. Tissues stiffen in compression but not in extension, whereas semiflexible polymer networks soften in compression and stiffen in extension. In shear deformation, semiflexible polymer gels stiffen with increasing strain, but tissues do not. Tissue rheology emerges from an interplay between strain-stiffening polymer networks and volume-conserving cells within them. Polymer networks that soften in compression but stiffen in extension, can be converted to materials that stiffen in compression, but not in extension, by including within the network either cells or inert particles to restrict the relaxation modes of the fibrous networks that surround them.

SESSION SB06.02: Cell Adhesion and Mechanics
Session Chairs: Christine Selhuber-Unkel and Britta Trappmann
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 201

1:30 PM SB06.02.01
Single-Molecule Measurements of Force Transmission by Integrin Heterodimers in Living Cells Alexander Dunn; Stanford University, United States

Integrins are heterodimeric transmembrane adhesion proteins that link the cytoskeleton to the extracellular matrix (ECM), and hence play a central role in the construction of complex, multicellular tissues. Although integrins are required for both cellular traction generation and for sensing mechanical cues such as substrate rigidity, the magnitude of the forces born by integrin heterodimers was unclear. We used FRET-based molecular tension sensors to determine the magnitude and origins of the forces experienced by individual integrins in living cells. We found that this distribution was highly skewed, with the majority of integrins bearing loads of ~2 pN, while a small subpopulation experienced forces >11 pN. Further experiments revealed that this distribution was controlled in a modular manner: integrin heterodimer usage controlled the number and stability of cellular connections to the ECM, while the proteins that link integrins to the cytoskeleton regulated the distribution of loads borne by individual integrin complexes. These and other observations support a general model for how cells create the regulated and dynamic adhesion complexes that are a defining feature of multicellular life.

2:00 PM SB06.02.02
Multiscale Modeling of the Facet Capsule Ligament—Size Effects and Problem Size Reduction through Generalized Boundary Conditions Jacob Merson and Catalin Picu; Rensselaer Polytechnic Institute, United States

A Multiscale approach (similar to the FE2 method) is developed to investigate the mechanics of the facet capsule ligament (FCL). The multiscale analysis technique allows for discrete micromechanical representations of the collagen tissue, coupled to a macroscale model which can use geometries obtained from segmented image stacks of biologically relevant domains. These complex biological geometries are coupled with other data sets, such as initial network orientation fields, to obtain models which can output biologically relevant mechanics information such as network orientation trajectories and local stresses not accessible by direct measurement. One of the challenges with the multiscale analysis is choosing an adequate sized representative volume element (RVE) at the microscale. This talk will discuss size effects on the RVE fiber network, and tools which can be used to ameliorate the large RVE sizes which are needed.

2:15 PM SB06.02.03
Towards Non-Optical, Label-Free Measurements of Particle and Cell Stiffness in Flow Charles Dhong1 and Darren J. Lipomi2; 1University of Delaware, United States; 2University of California, San Diego, United States

The mechanical properties of cells, such as cell stiffness, are important biomarkers in both clinical applications (e.g. detecting circulating tumor cells) and fundamental biological studies. Despite the importance of cell stiffness in mechanobiology, there are relatively few facile techniques that have the temporal resolution for basic research, or
the throughput required for clinical applications. Limitations of current technologies is that they rely on optical equipment, which can be bulky and expensive, or indirect measurements of force, such as calcium labeling. Here, we describe a new technique for monitoring the properties of particles and cells within an elastic, microfluidic channel. As a particle flows inside the channel, it deforms the walls in a characteristic manner. This fluid-induced deformation (i.e., elastohydrodynamics) is measured by using ultra-sensitive piezoresistive strain sensors. By transducing the wall deformation into voltage, we are able to monitor analytes within the channel without the use of any optical equipment. We discuss our validation of using elastohydrodynamic phenomena to monitor analytes and the future directions for the platform.

2:30 PM *SB06.02.04
Local Catalytic Effects in Adherent Membranes Ana-Sucana Smith; FAU Erlangen-Nürnberg, Germany

A number of cell functions rely on the formation of macromolecular platforms in the plasma membrane. While the functional role of these assemblies has been intensively investigated over the years, little is known about the mechanisms underlying their formation. In this presentation, several possible pathways will be discussed, including the role of the membrane elasticity, composition fluctuations, and the interactions with the cytoskeleton. Furthermore, cooperative attachments of proteins with different length, flexibility and affinities will be explored, allowing the development of a hypothesis regarding the simultaneous repellent and catalytic roles of the glycocalyx in the formation of membrane-associated macromolecular assemblies.

3:00 PM BREAK

SESSION SB06.03: Tools to Study Mechanotransduction
Session Chairs: Matthew Paszek and Medha Pathak
Monday Afternoon, December 2, 2019
Hynes, Level 2, Room 201

3:30 PM *SB06.03.01
Synthetic Extracellular Matrices to Study Mechanotransduction in 3D Britta Trappmann; Max Planck Institute for Molecular Biomedicine, Germany

Cell fate decisions are influenced by many cues, which together constitute the cell microenvironment. One critical regulator is the extracellular matrix (ECM), which varies not only in composition, but also in physical properties such as stiffness. The impact of matrix stiffness on cell spreading and differentiation has been studied intensively on 2D surfaces using synthetic hydrogels, but very little is known about stiffness sensing within more complex 3D matrices. Here, a major hurdle is to isolate the role of ECM stiffness from other matrix properties, in particular degradability. If cells are fully encapsulated, changes in bulk stiffness also influence the amount of matrix crosslinks that a cell has to cleave in order to spread and interact with its surroundings, impacting cell shape and function. Here, we have developed a sugar-based hydrogel system that offers independent control over mechanical properties, adhesive ligand density and matrix degradation rates. The material can be processed under physiologic conditions rendering it suitable for cell encapsulation. Matrix metalloproteinase (MMP) cleavable peptides as crosslinking units enable cellular matrix remodeling and variation of their sequence gives access to a range of degradation rates. Using this system, we study the impact of matrix stiffness and degradability on cell spreading, mesenchymal stem cell differentiation and angiogenic sprouting. In particular, we demonstrate that matrix degradability, mechanics and adhesivity jointly control the multicellularity of 3D endothelial cell invasion.

4:00 PM SB06.03.02
A Sensitive Tool for Probing Cellular Mechanics—Tracking Longitudinal Rotation with a Kinked-Silicon Nanowire Youjin Lee, David Wu, Yuxing Peng and Bozhi Tian; The University of Chicago, United States

A technique for tracking the longitudinal rotation of nanoscale objects has the potential to serve as a powerful
experimental tool to researchers across a variety of fields. Longitudinal rotation (i.e. rolling about a long axis) is a subtle movement that requires less free space than other types of movements such as translation and lateral rotation. Therefore, longitudinal rotation is particularly sensitive to small forces and does not significantly alter the local environment. This is especially true for long cylindrical objects since they require no additional space to rotate along their long axis. As such, tracking the longitudinal rotation of nanowires can serve as a sensitive and minimally perturbing method to probe forces in nanoscale environments. In this work, we present a simple and versatile method of tracking longitudinal rotation using a kinked silicon nanowire. By imaging the changes in the length of the kinked nanowire’s arm projected on the detection plane, we can measure the nanowire’s longitudinal rotation. To precisely measure the projected length of the nanowire’s arm, we developed a sub-pixel particle detection algorithm. To improve efficiency in the data processing pipeline, we incorporated a statistical procedure (principal component analysis) to automate the detection process. We applied this method to study the longitudinal rotation of nanowires in the presence and absence of endothelial cells. We found that nanowire rotational dynamics were significantly affected by the nanowire’s environment. While the free-floating nanowires underwent consistent and fast sub-diffusive rotation, the cell-interacting nanowires exhibited a greater variety of behaviors, including slow sub-diffusive random rotation and super-diffusive unidirectional rotation. The nanowires underwent this type of unidirectional rotation when the cell actively extended its boundary to cover the nanowire or when the cell contracted significantly. Our ability to detect cellular behavior via conspicuous changes in the nanowire’s longitudinal rotation showcases the sensitivity of this technique. Furthermore, the detection algorithm and the statistical method developed for this work can be applied to tracking the movements of other nanoscale objects with various geometries.

4:15 PM SB06.03.03
NIR-Actuated Composites to Perturb and Profile Mechano-Chemical Cell Signaling Nicholas Vishnosky and Rachel Steinhardt; Syracuse University, United States

Mechanical and chemical signals from the extracellular milieu are crucial to cell differentiation, morphology, and function. New materials are needed that can send precise, multivariate cues on cellular length- and timescales. For this purpose we are synthesizing novel near-IR actuators and incorporating them in new composite materials. The resultant biocompatible structures can change modulus and 3D morphology in response to tissue-penetrating wavelengths of light on multiple length scales, and we are now incorporating protein and drug functionalities onto the materials' surface. We are currently tailoring these composite materials for use as venous stents and stem cell differentiation scaffolds.

4:30 PM *SB06.03.04
A Materials Approach to Studying Forces, Form and Function in Cells and Tissues Christopher Chen1,2; 1Boston University, United States; 2Harvard University, United States

A long recognized tenet of biological systems is that structure gives rise to function. Mechanical force in contrast has emerged only recently as a critical dimension that links form and function, providing the central effector to sculpt the body plan during morphogenesis, as well as a mechanism for cells to sense and respond to local changes in tissue structure and mechanics. Despite the realization that forces, form, and function permeate all living systems, we as a research community sorely lack methods to control the mechanics of the environment, the spatial organization of cells, or the architecture of cell-matrix and cell-cell interfaces, which collectively define the boundary conditions for how forces are transmitted into cells. Here, I will describe our efforts to design and build physical microenvironments that explicitly manipulate and monitor the physical (structural and mechanical) interactions between cells and their surroundings. Using these approaches, we demonstrate that mechanical forces generated either internally by the cytoskeleton or externally regulate cell, matrix, and tissue structure, signaling, and function, and begun to use these insights to build in vitro organotypic models of the cardiovascular system that mimic native tissue functions. I will use our studies to illustrate how deeper insights into the structure-function links are critical to our ability to engineer stem cells to recapitulate differentiated function, and how engineered systems ultimately could have a major impact on biomedical research.
SB06.04.01
Towards the Development of a Macroscopic, Biohybrid, Hydrogel-Based Actuator Christine Arndt, Mohammadreza Taale, Florian Ceynowa, Fabian Schuett, Rainer Adelung and Christine Selhuber-Unkel; Kiel University, Germany

Biohybrid soft robotics is an emerging field of research that offers new concepts for the current challenges of soft robotics. This includes the ability to self-heal, soft touches and miniaturization possibilities, as well as situational and autonomous adaptations. Here, living beings have an unprecedented variety of possibilities to manipulate and interact with objects and the combination of elements from soft robotics with living cells opens up new opportunities. As an example, skeletal muscle cells can be used to actuate biohybrid, hydrogel-based actuators but they require electrical stimulation in order to contract. However, most currently used biomaterials, e.g. in cardiac tissue engineering, lack electrical conductivity and appropriate mechanical properties. Both parameters are important for regulating skeletal muscle cell behavior. In this work, we present conductive and structured hydrogel scaffolds where the conductivity is achieved by incorporating reduced graphene oxide or carbon nanotubes in the material. Further, the stiffness of the scaffolds can be tailored to match the stiffness of native muscle tissue. MTT-assays have shown that the scaffolds have no negative impact on the cell viability. Apart from this, the samples are biofunctionalized with collagen to enhance cell adhesion. The presented work illustrates the potential of conductive and structured hydrogels as a first step towards the development of a biohybrid, hydrogel-based actuator.

SB06.04.02
Detachment of the Biomolecule Bindings between the Microtubules and Kinesins Kenta Hatazawa1, Ryuzo Kawamura2, Masahiro Nakamura1 and Takayuki Hoshino1; 1Hirosaki University, Japan; 2Saitama University, Japan

Microtubule (MT)-kinesin gliding systems are known as the biomolecules to cause cell motility cytokinesis and cellular transport [1]. Previously, we reported the local detaching control of a living cell from the SiN membrane and investigated spatio-temporal distributions of intracellular elastic strain as mechanical strain microscopy by using a fine virtual cathode (VC) on the VC display [2]. In addition, to examine the biomolecules control using the VC display [3], we reported the pause of the target gliding MTs [4]. In the same way as the former report, we considered that the pause mechanics of the gliding MTs are caused by detachments between the biomolecules (= MTs and kinesins) bindings. In this report, we examined to cause the detachments between the target MT and kinesins on the VC. As the results, some target MTs were confirmed to move to the directions different from the each MTs axial direction by applying the VC. These results showed that the MTs detached from the kinesins and showed the detach between the biomolecules can be controlled on the VC. In summary, the detachments of the biomolecules binding forces include the mechanical function could provide the novel tool to molecule mechanobiology.

References

SB06.04.03
Behavior and Phenotype of Cancer Cells in Response to Varied Mechanical Environment in 3D Hydrogel Models Cultured In Vitro Tayler Laycox, Riley Aspinwall, Ian Schmidt and Jason W. Nichol; Endicott College, United States

Cells of all types react in response to changes in their mechanical environment typically to return their surroundings to homeostatic conditions. In cancer cells this response is varied in ways which also vary based on the cancer type or even the phenotype within one type of cancer. These are some of the reasons why mechanical stiffness and the extracellular matrix (ECM) play key roles in tumor formation/progression and cancer cell phenotype. Cancer cells originating from different tissues, possessing different stiffnesses, will respond to their environment differently,
which could yield important information in better understanding cancer cell physiology. Gelatin methacrylate (GelMA) is a UV-crosslinkable hydrogel that has been shown to be effective in the 2D and 3D culturing of cells in a wide variety of applications including cancer models. Cells can easily bind to GelMA 2D surfaces and within 3D structures, and can proliferate, elongate, and remodel their surroundings due to the presence of natural binding and enzymatic degradation sites in the gelatin backbone. GelMA is a highly elastic material with tunable mechanical stiffness through variation of gel concentration and degree of methacrylation. It has been established that normal breast tissue has a compressive modulus of roughly 200 Pa, whereas precancerous regions have a modulus of roughly 600 Pa and cancerous regions can be as high as 1-2 kPa. Analogous studies are underway to create similar stiffness ranges for other cancer types such as prostate, as well as to control stem cell differentiation via similar principles. The major aims in these studies were to create robust GelMA hydrogels in the 3 mechanical ranges (normal, precancerous, tumor) for breast and other tissues, and once validated to investigate the differences in behavior, morphology and gene expression of cancer cells encapsulated in these hydrogels. Validation studies with NIH 3T3 cells determined the parameters and conditions (exposure time, lamp power, photoinitiator concentration) where cells could be 3D encapsulated with a high degree of early viability that was maintained for 1-2+ weeks. Preliminary results suggest evidence that different cancer cell types react differently to varied levels of mechanical stiffness. Further experiments will aim to further elucidate these effects and the factors driving these phenomena through RNA isolation and analysis using NextGen sequencing.

SB06.04.04
The Signaling Response of Artificial Neurons Made from Chemical Oscillators James Sheehy and Seth Fraden; Brandeis University, United States

Rhythmic movements in biology are abundant, across a number of length scales from the beating of a heart to digestion, locomotion, and breathing. These simple yet vital functions are controlled by patterns of signals created by a series of neurons, known as central pattern generators. Neurons within these central pattern generators are capable of robustly maintaining these complex oscillations without the benefit of inputs from higher brain functions, yet they are also able to modify their oscillatory behavior in response to stimuli. The Belousov-Zhabotinsky reaction is a fluid which acts as a chemical oscillator, which obeys reaction-diffusion dynamics. This chemical oscillator periodically oxidizes and reduces, causing a periodically spike in voltage. Using microfluidic techniques, we can embed pockets of this chemical oscillator within a gel network which allows us to control the connections between these pockets. It has been shown that using this technique, we can create artificial central pattern generators. In this work, we will investigate how individual artificial neurons respond to changes in local environment in order to examine how these artificial neurons change their behavior in response to changes in stimuli. Additionally, we will examine the communication between pairs of these artificial neurons in order to understand how the interactions give rise to robust complex patterns.

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SB06.04.05
Characterizing Hetero-Oligomers from Amyloid-Beta and Alpha-Synuclein with AFM Eun Ji Shin and Joon Won Park; Pohang University of Science and Technology, Korea (the Republic of)

A large proportion of patients with Alzheimer's disease or Parkinson's disease may have symptoms of both diseases at the same time. Such diseases overlapping Alzheimer’s disease and Parkinson’s disease have been attempted to explain with the hetero-oligomer hypothesis associated with Amyloid-beta (Aβ) peptides and Alpha-synuclein (α-syn) peptides. However, neither presence nor structure of the hetero-oligomers have not been clarified. Herein, we have investigated surface structure of protein oligomers at the single peptide level. We employed Atomic Force Microscopy (AFM) with a liquid cell to characterize the hetero-oligomers generated in vitro. In particular, a probe tethering an antibody recognizing the N-terminal of Aβ and another probe tethering N-terminal of α-syn were prepared, and one-to-one interaction was realized through utilizing dendron coating of the probes before the conjugation with the antibodies. High resolution force maps of the oligomers were obtained with thus-prepared AFM probes. It revealed that specific unbinding events with respect to two different antibodies were observed within an oligomer,
and such coexistence of specific pixels was persistent for all sizes under investigation. Because homo-oligomers were not observed at all, it can be said that formation of the hetero-oligomers is strongly favored. It is intriguing to note that the percentage of positive pixels for the hetero-oligomer is higher than that for the homo-oligomer, suggesting a different mode of aggregation for the hetero-peptide oligomerization. We suggest that this approach is useful for understanding the overlap of neurodegenerative brain disorders.

References

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SB06.04.06
Designed Liquid Crystalline Polypeptide Fibres
James MacDonald1, Hannah Leese2,1, Karan Bali1, Paul Freemont1 and Milo Shaffer1,1; 1Imperial College London, United Kingdom; 2University of Bath, United Kingdom

Significant progress has been made in the de novo design of protein-based biomaterials at the atomic-level.1 But, to date, there has not been a significant advance in the de novo design of macroscopic biomaterials that match the extraordinary mechanical properties of some natural materials such as silk. Self-organising materials are commonly observed in biological systems and the ability to control this self-organising behaviour in optimally designed systems opens up new approaches for the creation of advanced materials. Synthetic biology provides the tool to build artificial proteins that can be ideal precursors for such advanced materials as their structure can be controlled at the atomic level and synthesised with monodispersed precision. In this work, we show that de novo synthetic proteins spontaneously display liquid crystalline behaviour at critical concentrations. These liquid crystalline synthetic proteins were successfully wet-spun into aligned tough continuous fibres without disruption of the protein back-bone.


SB06.04.07
Cortex Dominates Bacillus subtilis Spore’s Water-Responsive Behaviors
Zhi-Lun Liu, Haozhen Wang and Xi Chen; The City University of New York, United States

Water-responsive (WR) materials that swell and shrink in response to changes in relative humidity (RH) show a great potential as building blocks for developing better actuators and artificial muscles. Bacillus (B.) subtilis spore has demonstrated a WR energy density of ~10 MJ m⁻³ that is significantly higher than that of reported actuator materials. However, the origin of such a powerful actuation of spores remains unclear. Here, we present that cortex layers within spore exhibit dramatic water-responsiveness that could dominate spores’ WR actuation. We isolated cortex from B. subtilis spores and found that its WR strain and stiffness reach ~38.7 % and 1 GPa, respectively, which suggests a WR energy density of 74.9 MJ m⁻³. To correlate WR properties of cortex to that of spores, we characterized the distribution of cortex within spores by 3D reconstructing serial cross-sectional images of spores obtained from an FIB-SEM. We have analyzed 85 spore samples and found cortex’s average thickness and volume ratio to be 122.4 nm and 52.4 %, respectively. These results, together with the measured WR strain and energy density, suggest that spores’ water-responsiveness is largely contributed by its cortex layer rather than other components. Our finding of the extreme water-responsiveness of spores’ cortex also provides insight to its important functions in spores’ biological processes.

SB06.04.08
Understanding the Molecular Mechanism of Cartilage Degradation and Cation Channel Activity
Deng Li,
Biomechanical forces play a critical role in our body. Collagenous tissues such as cartilage and bone are smart materials that can adapt their properties in response to mechanical forces through altering their structures from the molecular level up. They are able to convert mechanical forces into biochemical signals that control many biological and pathological processes such as wound healing and tissue remodeling. However, how collagenous tissues convert the biomechanical forces into signaling that regulates the cells during tissue development and remodeling remains unclear.

Here we employed a bottom-up computational approach to investigate the joint mechanobiology from two aspects: the molecular mechanisms of the extracellular matrix degradation and the molecular mechanisms of how point mutations affect the constitutive activity of transmembrane cation channel. We find that specific residues in the vicinity of the catalytic site play crucial roles in forming a stable binding pose in cartilage, which is vital for cartilage degradation. Our results also show that point mutations alter the molecular structure of the transmembrane protein and thus affect the channel size, which is one of the essential factors that alter the constitutive activity of the channel. Understanding the molecular mechanisms from the molecular level is crucial for the development of novel skeletal regenerative medicine or preventative strategies for related diseases.

SB06.04.09
Nanofibrils as Basic Building Blocks of Natural Spider Silk Qijue Wang, Chloe Walsh, Dinidu Perera and Hannes C. Schniepp; College of William and Mary, United States

As one of the most exciting biomaterials nature has to offer, spider silk has long fascinated researchers in various disciplines because of its both superior mechanical properties and biocompatibility. In order to replicate these properties in synthetic materials, an accurate and detailed structural description of silk is necessary. Though protein nanofibrils have been proposed to be the key structural element in natural silk fibers, experimental evidence about their existence, dimension, and structure is insufficient. Many important details of these nanofibrils, including their formation and spatial organization within a silk thread, are still missing.

Recently, we showed that the ribbon-like silk of the brown recluse spider is entirely composed of 20-nm thin nanofibrils using atomic force microscopy (AFM) and scanning electron microscopy (SEM). This is the first time that the fibrillar percentage and the complete structure down to the nanofibril level can be determined experimentally for any spider silk. First-ever evidence of individual isolated spider silk nanofibrils was also obtained. We also studied fibers from other spider species and observed nanofibrils with similar morphologies. Hence, we suggest that nanofibrils are the dominating structural element in all silk fibers. Consequently, the formation of nanofibrils will also be important in novel synthetic materials inspired by spider silk. For the first time, we achieved in-vitro self-assembly of nanofibrils from the native silk dope of the golden silk orb-weaver spider (*Nephila clavipes*), one of the most studied species. In the presence of shear, silk protein molecules form individual 20-nm thin nanofibrils longer than 1 mm, similar with what we have observed in natural silk fibers. This unprecedented observation suggests an intrinsic tendency to form a linear fibrillar structure for the silk molecules. Furthermore, based on our spectroscopy study about the protein secondary structures within spider silk, and with the help of force modulation microscopy (FMM), we can characterize the mechanical behaviors of these nanofibrils at the molecular level.

Thus, our exhaustive investigation of silk nanofibrils from multiple angles points to nanofibrils as the basic and necessary building blocks of all silk fibers. This puts a complete structural description for natural silk materials within reach, and benefits efforts to develop protein- and polymer-based high-performance materials and biocompatible medical devices.

SB06.04.10
Influence of Different Mechanical Conditions on Cell Behavior Sandra Sindt, Yasmeen El-Rayyes, Galen Ream and Christine Selhuber-Unkel; Kiel University, Germany

In nature, cells are exposed to various environmental conditions that can influence their behavior. How chemical cues influence cell behavior has been studied for decades, whereas the sensing and reaction of cells to external mechanical stimuli still contains a vast number of open questions.

A very well-known aspect, however, is that integrin-based adhesion clusters can grow upon externally applied shear forces. Furthermore, many cell types respond to the stiffness of their underlying substrate, and it has even been
shown that cells can feel a stiff substrate underneath a soft material layer if the soft layer is thin. For example, mesenchymal stem cells sense an underlying hard substrate if the thickness of the soft layer is below 5 µm. This ability of cells to feel through soft material layers is essential in the design and application of implants, particularly in soft environments like the brain. Hence, the understanding of the underlying principles of these mechanosensory cell mechanisms is vital for biomedical research. In addition, the manipulation of cells with mechanical stimuli has great potential for biomedical applications.

However, external mechanical cues might affect single cells and cells in ensembles in different ways as cells in collective ensembles have the ability to distribute the applied stress over several cells via, for example, rearrangement processes. Consequently, they can bear mechanical stress better than single cells. To investigate how single cells and collective cell ensembles react to external stress, we built a setup to induce different mechanical stimuli. We will here present results on how such induced mechanical stimuli influence the cell behavior of cell ensembles and furthermore show how the thickness of soft layers affects the adhesion of single cells.

SB06.04.11
Rapid Magnetic Printing of 3D Cell Structures Sarah Mishriki1, Abdel Rahman Abdel Fattah1,2, Tobias Kammann1,2, Srivatsa Aithal1, Rakesh Sahu1, Fei Geng1 and Ishwar K. Puri1,1; 1McMaster University, Canada; 2KU Leuven, Belgium; 3Friedrich-Schiller-University, Germany

The demand for tissues and organs is unmet by the current supply. Engineering solutions are desired to create 3D cell structures to help fulfill this need. Using a unique bottom-up approach, we can rapidly form 3D cell assemblies by exploiting the diamagnetic property of cells. Most mammalian cells are weakly attracted to a magnet. This is also true of their culture medium, which is an aqueous solution of proteins, sugars, and nutrients to maintain their growth. The addition of a paramagnetic salt hydrate, such as gadopentetic acid (Gd-DTPA), transforms the culture medium to become paramagnetic. This establishes a difference between the magnetic susceptibility of cells and their liquid counterpart. The presence of a magnetic field gradient displaces the suspended cells towards regions of relatively lower magnetic field in the direction of where H is the magnetic field. This movement of cells followed by the movement of the culture medium seeds the formation of 3D cell cluster in a contactless, label-free manner within hours. Using this method, 3D cell structures can be formed on an ultra-low attachment surface, and 2.5D cell structures on a tissue-culture treated surface. The presence of a co-culture introduces new printing abilities and cell morphologies. This engineering solution has the potential to overcome limitations in bioprinting to expedite efforts in drug discovery, tissue engineering and regenerative medicine.

SB06.04.12
Design of Novel Scaffolds for Effective Healing of Bone Fractures Using Topology Optimization Based on Mechano-Biological Model, Angiogenesis and Scaffold Degradation Mervenaz Sahin1, Mehmet Serhat Aydin1 and Gullu Kiziltas Sendur1,2; 1Sabanci University, Turkey; 2Sabanci University Nanotechnology Research and Application Center, Turkey

Bone repair is known to be a complex process affected by many parameters such as fracture size. 3D composite porous tissue scaffolds loaded with bioactive molecules and cells are being developed to offer a better solution for bone fracture healing. Accordingly, an ideal bone tissue scaffold should provide the following functions: a. mechanical support for the growth and functioning of new tissue, b. adequate porosity and permeability for nutrients and oxygen supply, waste removal and growth factors release, c. suitable surface for cell attachment, differentiation and growth, and d. controlled degradation. Therefore, an optimal bone tissue scaffold should have a multi-functional structure with desired mechanical, biological and chemical properties. However, it is still unclear what kind of properties optional bone scaffolds should provide leading to effective tissue repair. Thus, there is a critical need to find methods suitable for designing novel bone scaffolds and the investigation of structure-function relationships for optimal tissue regeneration. Existing experimental studies are usually very time and cost ineffective.

Most of the computational design studies in literature that target ideal scaffold geometries with desired functional properties do not account for dynamic effects within the scaffold-tissue-cell environment. Among these, topology optimization based studies offer promise to design novel architectures of bone tissue scaffolds1 but mostly have neglected the dynamic mechano-biological nature of regenerative healing2. Unlike topology optimization, scaffold design studies based on parametric size optimization3 and mechano-biological regeneration models offer limited design freedom, hence resulting designs are not necessarily the best candidates to ensure effective healing.
Moreover, angiogenesis - a critical part of the regeneration process- and scaffold degradation are not considered in any of these studies together despite their known coupled effect in healing. To address these limitations, we propose, for the first time, a computational framework to design the optimal microstructure of scaffolds that maximize bone formation considering mechano-biology, angiogenesis and scaffold degradation simultaneously. Thus, our model includes the following 4 parts in an integrated fashion: 1. Mechano-biological model describing tissue differentiation, 2. Angiogenesis, 3. Topology optimization targeting maximum bone formation, and 4. Time dependent degradation of the bone scaffold.

The proposed computational design framework is developed in a MATLAB GUI as an integration of above computational modules with a FEA software, namely COMSOL Multiphysics, a SIMP based topology optimization method and a random walk approach for angiogenesis modeling. The computationally designed scaffolds are compared with existing designs and fabricated based on a recently introduced phase separation technique. Morphological and mechanical characterization techniques will be performed to validate bone regeneration performance of designed bone tissue scaffolds. Integration of the proposed computational framework to existing experimental studies should pave the way for more efficient and low-cost solutions in bone tissue engineering.

**Keywords:** Tissue engineering, bone tissue scaffold, topology optimization, mechano-biology, angiogenesis, scaffold degradation.

**References**


**SB06.04.13**

**Modulation of Chemical Reactivity by Strong Coupling to Molecular Vibrations**

Wonmi Ahn, Igor Vurgaftman, Adam Dunkelberger, Jeffrey Owrsutsky and Blake S. Simpkins; 1Excet Inc., United States; 2U.S. Naval Research Laboratory, United States

Quantum emitters placed in resonant optical cavities have shown modified spontaneous emission rates and frequency when they are coupled in the weak coupling regime. In the so-called strong coupling regime, however, the coupled oscillators, i.e., emitters and optical modes, exchange energies inextricably, creating new hybrid states called polaritons. Recently, this half-light half-matter quasi-state has been demonstrated in a system where molecular vibrations are coherently coupled to optical cavity modes. In this talk, we will demonstrate our recent results on the vibrational strong coupling, with a particular focus on its ability to modify chemical reactivity. We monitor transmission spectra of the Fabry-Pérot microcavity filled with species that cause a simple addition reaction. Both reactants and products have strong molecular vibrations that couple to the optical cavity modes, resulting in quantifiable vacuum Rabi splittings. We examine the reaction rates in and out of the cavity to elucidate the influence of vibrational strong coupling on the chemical reactivity. Our results will extend the potential of cavity-modified material properties, which will have important implications for controlling chemical reactivity and biological activity by light.
Cells sense their environment by transducing mechanical stimuli into biochemical signals. Commonly used tools to study cell mechanosensing provide limited spatial and force resolution. To overcome this limitation, we recently reported a novel platform for monitoring cell forces, which was based on nanowires functionalized with ligands for cell immunoreceptors, and used this platform to explore mechanosensitivity of Natural Killer (NK) cells [1]. We found that nanowires stimulate cell contraction, and, by assessing the nanowire deflection, detected forces of down to 10 pN applied by cells. Furthermore, we found that the combination of (i) nanowire topography and (ii) activating produced enhanced activation of NK cells. Thus, we proposed a mechanosensing mechanism of NK cells, by which they integrate biochemical and mechanical stimuli into a decision-making machinery analogous to AND logic gate, whose output is the immune activation. This mechanosensing platform allowed unprecedented integration of biochemical and mechanical cues at the nanometric length-scale. Still, this platform lacked the ability to control another important signaling aspect – the spatial distribution and clustering of extracellular ligands. Indeed, in the physiological immune synapse, ligand-receptor pairs form highly regulated nanometric clusters, whose exact role is still obscure. On the contrary, in our reported nanowire-platforms the activating ligands were immobilized all over the nanowires surface, providing continuous medium for biochemical stimulation of NK cells.

Motivated to investigate the role spatial ligand clustering in cell mechanosensation, we engineered a new nanowire-based platform for mechanical stimulation of NK cells, in which extracellular ligands are spatially confined within specific regions on nanowires. To that end, we grew Si nanowires from Au catalytic nanoparticles, and selectively functionalized the Au nanowire tips, whose size was about 30-50 nm, with biotinylated thiols, to which we conjugated biotinylated anti-NKP30 (activating ligands for NK cells) via neutravidin bridge. We verified that the functionalization is specific to the nanowire tips using fluorescent imaging of the attached avidin. We then stimulated primary NK cells onto the functionalized nanowires, which we grew either as a continuous array, or as ordered separated clusters with a diameter of 5 microns. Interestingly, we detected two sub-populations within the cells stimulated on the clustered nanowires. The first sub-population consisted of cells on the surface among the nanowire clusters. These cells had elongated shape, and expressed very low degree of activation, as assessed by the expression of degranulation marker CD107a. The second sub-population consisted of cells laying on the top of the nanowire clusters. These cells showed high circularity, low spreading area, and enhanced degree of activation, most probably due to the combination of (i) the high compliance of nanowires to the mechanical forces applied by the cells and (ii) the contact formed by the cell with the antigen-functionalized nanowire tips. These newly results confirmed the importance the integration of the mechanical and chemical cues in the immune signaling.

Furthermore, the demonstrated nanowire platform for the cell stimulation presented two new, unprecedented features. On the molecular level, it allows and exquisite control over spatial positioning and clustering of extracellular ligands on the nanowires. On the cell level, it allows three-dimensional spatio-mechano-chemical guidance of the cell motility and immune activity, and paves the way to numerous studies aimed at understanding the integration of mechanical and biochemical signals in cells.

altering actomyosin contractility. Altogether, these findings demonstrate a key role for matrix plasticity in MSC biology and spreading, and we anticipate this will have ramifications in the design of biomaterials to control cell function and fate and in numerous biological contexts where matrix properties are altered.

SESSION SB06.06: Responsive Biomaterials
Session Chairs: Christine Selhuber-Unkel and Michael Timmermann
Tuesday Morning, December 3, 2019
Hynes, Level 2, Room 201

8:30 AM *SB06.06.01
Photoresponsive Materials for Resolving Mechanobiology in Collective Cell Migration Jun Nakanishi; National Institute for Materials Science, Japan

Collective cell migration is the migration of cells in a group rather than individually. It plays a pivotal role not only in physiological processes, including morphogenesis, wound healing, and immune responses, but also in pathological ones, such as cancer invasion, metastasis, and tissue fibrosis. In addition to such involvements in various biological reactions, collective migration draws interests of researchers as it includes emergent collective characteristics that cannot be expected from simple summation of multiple single cells. For example, at the leading edges of migrating epithelial cell sheets, boundary cells are divided into actively migrating “leader cells” with frequent extension of lamellipodia and “follower cells” following the leaders. Also, some of cell collective exhibit autonomous group rotation with preferential asymmetry (left or right). All of these phenomena indicate that surrounding cells are not mere physical hindrance, rather those cells chemically and mechanically communicate with each other and against their extracellular matrices (ECMs) to function as an active soft matter. To decipher such complex regulation mechanisms of collective phenotypes from the reductionism viewpoint, our group is developing photoactivatable substrates based on photocleavable poly(ethylene glycol), where collective migration can be analyzed spatiotemporally under controlled chemical, mechanical, and geometrical cues (1-3). In this presentation, I will represent some of our recent progresses in the development and applications of the photoactivatable substrates, with special focus on the impact of chemical and mechanical cues on leader cell formation. I will also represent our new photoresponsive materials that can be used for analyzing collective behaviors on dissipative matrices.

[Reference]

9:00 AM SB06.06.02
Dynamic, Reversible Control of Biomaterial Properties Using DNA Nicholas Stephanopoulos; Arizona State University, United States

The ability to dynamically control the mechanical properties of biomaterials is critical for regenerative medicine applications. For example, matrix stiffness controls the differentiation of stem cells, or the metastasis of cancer cells. However, most methods for tuning the mechanical properties of 3D hydrogels are not reversible, or involve potentially harmful stimuli like UV light. Here we use DNA as a programmable crosslinker to reversibly change the stiffness of gelatin hydrogels. We modified DNA with a methacrylate moiety, allowing it to be crosslinked along with methacrylated gelatin (GelMA). By tuning the amount of pre-formed DNA crosslinks relative to GelMA, we were able to tune the stiffness of the hydrogels obtained from 0.5 – 2 kPa, as measured by an AFM-based method. The crosslinkers contained single-stranded toehold sequences, allowing them to be broken by adding fully complementary displacement strands. The stiffness of the formed hydrogels could be tuned through the amount of
displacement strand added, and the process was reversible: adding more crosslinker restored the stiffness to the original value. We explored various crosslinker lengths, designs, and geometries (including branched and more rigid multi-helical DNA tiles), demonstrating the straightforward tunability of DNA. The use of GelMA allows for photopatterning of hydrogels into micron-sized patterns, and cells could be incorporated into the materials and responded to the reversible changes in stiffness. DNA-based crosslinking also enables spatial patterning of stiffness, and will allow for incorporation of multiple ligands in a programmable manner to impart the gels with bioactivity. We will also outline chemical strategies for incorporating DNA into other biomaterial scaffolds, such as hyaluronic acid or PEG, demonstrating the versatility of our approach. We envision that DNA-based control of stiffness will allow for programmable and reversible control of hydrogel properties, and lead to advanced biomaterials for regenerative medicine, tissue engineering, and fundamental biological studies.

9:15 AM SB06.06.03
Design and Development of Mechanobiological Gels That Can Control Mechanical Property Takeshi Ueki¹, Ryota Tamate¹, Aya Akimoto², Ryo Yoshida² and Jun Nakanishi¹; ¹National Institute for Materials Science, Japan; ²The University of Tokyo, Japan

Mechanical environment around cells, not only physiological chemistry surrounding cells, strongly affects cell behaviors such as spreading, proliferation, and differentiation. Here, we describe a novel platform of cell culture scaffold that possesses tunable mechanical property. The design strategy for the materials includes self-assembly of block copolymers, photo-responsiveness, and solvent engineering of polymer gels. We show a 3D cell scaffold gel as one example that can change stress relaxation surrounding cells on demand. The gel is made by self-assembly of a well-defined coumarin containing ABA triblock copolymer. We demonstrated that the cell spreading embedded the 3D scaffold dynamically changes corresponding stress relaxation of gels.

9:30 AM *SB06.06.04
Building with Cells—Exploiting Mechanobiology to Use Living Cells as an Engineering Material Kevin Kit Parker; Harvard University, United States

Some engineers build with steel, copper, polymer composites, and wood. Bioengineers build with cells and because these cells are alive, they have a vote in our successes or failures. Our team has spent the last 15 years understanding how cells build themselves, how tissues assemble themselves, and the emergence of structure-function relationships in organs. These hierarchal organizations span from nanometer to meter length scale and have provided insight, and useful tools for drug discovery, toxicology, food, and regenerative medicine. This presentation will discuss how we have tried to understand the architecture and function of biological pumps, both in marine lifeforms and human organs, to understand the fundamental design principles that allow cells to serve as engineering materials.

10:00 AM BREAK

SESSION SB06.07: Bioinspired and Biofunctional Materials
Session Chairs: Cornelia Lee-Thedieck and Angela Pitenis
Tuesday Morning, December 3, 2019
Hynes, Level 2, Room 201

10:30 AM *SB06.07.01
Bioinspired Materials for Deconstructing Matrix Structure-Cell Function Relationships Kristopher Kilian; University of New South Wales, Australia

The extracellular matrix surrounding cells in tissue is a dynamic composite material, where the presentation of biophysical and biochemical information directs functional bioactivities. We are interested in how the properties of the extracellular matrix guides tissue form and function and have developed a suite of engineered extracellular matrices to probe matrix structure-cell function relationships. Microengineered hydrogels that control tissue geometry, mechanics and composition have served to model how the microenvironment may exert an influence on
The Adaptive Behavior of Cells as Archetype for Novel Strain-Stiffening Structures

Cells have developed several mechanisms to protect themselves from physical damage. One of these mechanisms is the cell's ability to form stress-fibers as a response to mechanical deformation. This can for example be observed in epithelial cells that form stress-fibers to withstand the cyclic deformation of a blood vessel. Stress-fibers are cross-linked bundles of actin-filaments that show a higher stiffness than the underlying unlinked filaments. This ability to actively increase the stiffness as a response to deformation was the archetype for the development of our innovative strain-stiffening structures. A material behaves strain-stiffening if its stiffness is increased with increasing deformation. This behavior is desired for engineering applications like damping systems or shock absorbers where all requirements are met with already available materials. But these materials have disadvantages that make them unsuitable for special applications like novel orthotic devices or artificial blood vessels. The stiffening is either not reversible, highly dependent on the rate of deformation, can only be achieved with special materials or only occurs when the material is compressed. By taking advantage of the strain-stiffening mechanism we observed in cells, we were able to come up with structures that do not show any of these disadvantages. Our structures contain parallel slats, as a resemblance of cytoskeletal fibers, that touch each other upon deformation. This mimics the cross-linking of cytoskeletal fibers. The touching of the slats also leads to a change of mechanical properties of the entire material and its stiffness is increased. This effect is completely reversible, does not depend on the rate of deformation and every elastic material can be brought into the developed geometry. By variations of the geometry and the underlying material we are able to finely tune the mechanical properties of the structure and define, if the stiffening occurs upon compression or elongation. The influence of several geometrical factors on the strain-stiffening behavior was determined via finite element simulations and tensile tests. With the help of our novel strain-stiffening structures more comfortable orthotic devices and more compliant artificial blood vessels are now in development.

Stiff and Responsive Hybrid Bacterial Assemblies through Covalent Crosslinking of Nanoparticles to Engineered Bacterial S-Layer Proteins

Engineered Living Materials (ELMs) that incorporate genetically modified cells to actively adjust the expression and organization of biomacromolecules are excellent candidates for applications in bioelectronics, biosensing, enzyme biocatalysis, and smart materials. Here we report a new strategy to create an ELM using *Caulobacter crescentus*. The surface layer (S-layer) protein of *C. crescentus* has been engineered to display a 2D array of functional peptide, *i.e.* SpyTag, over the entire cell body. A layer of closely packed nanoparticles is attached to the recombinant protein lattice through formation of SpyCatcher-SpyTag iso-peptide bond. The functionalized bacterial cells are further crosslinked into hierarchically ordered 3D assemblies. Stiffness of the self-assembled bacterial assemblies increases more than 30 times compared to non-crosslinked case. Cleavage of a disulfide bond inserted between SpyCatcher and the nanoparticles results melting of the bacterial assemblies, indicating the specific covalent linkage between S-layer proteins and nanoparticles is responsible for the enhanced mechanical properties. In the presence of excess nanoparticles, the crosslinked bacterial assemblies can autonomically self-regenerate after being damaged due to the continuous growth of *C. crescentus* cells and the expression of new S-layer proteins. Furthermore, the bacterial that coated with magnetic nanoparticles can form cohesive assemblies guided by external magnetic field, and the shape of the assemblies maintains when the magnetic field is removed due to the crosslinking. The ubiquity of S-layers in almost all archaea and many bacteria indicates the current crosslinking method could be applied to other microbe systems to create new ELMs with tunable mechanical properties.
Lipid vesicles are aqueous volumes surrounded by a bilayer of lipid molecules, which are amphiphilic molecules with their head groups facing water and tail groups facing oil. These vesicles are simple models that mimic cell membranes and can be used for drug delivery. Similarly, block copolymers are amphiphilic molecules that form vesicles by themselves or when mixed with lipids. Like lipid vesicles, polymer vesicles can also be used for cell membrane mimicry and drug delivery. One interesting type of lipid/polymer vesicle is the asymmetric vesicle, in which its bilayer is composed of two dissimilar lipid monolayers or a lipid monolayer and a polymer monolayer. Importantly, all eukaryotic cell membranes exhibit this type of asymmetry and asymmetry is also proposed to enhance mechanical properties of the membrane. Here, we use microfluidics to fabricate mono disperse and highly controllable asymmetric vesicles, which unlike the conventional methods that often end up with highly poly disperse samples. To achieve this, asymmetric vesicles are produced using water/oil1/oil2/water emulsions in a glass capillary device, with different lipids/polymers immersed in two different volatile oil phases. Using the asymmetric vesicles, we are trying to measure how mechanical properties are affected by this asymmetry and also how to improve the degree of asymmetry in our vesicles even more. In future, we envision asymmetric lipid/polymer vesicles could open a new door in the field of drug delivery.

Mechanophores are force sensitive molecules that undergo productive chemical transformations under a mechanical force including color change, small molecule release, and cross-linking. Mechanophore reactivity depends on the intrinsic molecular structure as well as the extrinsic environment of the mechanophore. This presentation summarizes the extrinsic, force-focusing effects of mechanochemical activation at an interface. New methodologies are developed to characterize interfacial mechanochemical transformations for two different color-changing mechanophores. Maleimide–anthracene (MA) mechanophores covalently anchored at a fused silica–polymer interface are activated using laser-induced stress waves. In contrast to activation in solution or bulk polymers, whereby a proportional increase in mechanophore activity is observed with applied stress, interfacial activation occurs collectively with spallation of the polymer film. MA mechanophores located at the interface between poly-(glycidyl methacrylate) (PGMA) polymer brushes and Si wafer surfaces were also activated locally using atomic force microscopy (AFM) probes. In a separate set of experiments, the reaction of spiropyran (SP) mechanophores is demonstrated at nanoparticle/polymer interfaces. A new SP mechanophore containing a pentene and alkyl bromide group at each pulling point was designed and synthesized for functionalization of silica nanoparticles. The mechanical activity of the SP functionalized at the interface between silica particles and a polymer matrix is compared with that of SP linked directly into bulk polymers. As anticipated, the interfacial mechanophores exhibit more efficient mechanical activation under tensile loading.

Nature has effectively revised engineering designs of elastomeric biopolymers through years of evolutionary history. In this work, we examine the molecular and multiscale mechanisms of elasticity of biopolymers exhibiting...
exceptional elasticity in vivo to deduce design principles and mechanisms that can be used to develop novel elastic biopolymers for medical and engineering applications. We consider two examples from nature: resilin, a biopolymer found in insect cuticles and elastin, a key component within the extracellular matrix of elastic tissues in mammals. We use molecular models to compare effects of sequence and structural hierarchy, hydration, librational effects and temperature on elasticity. Through this comparison, we identify unifying principles that can be used for rational design of elastomeric biopolymers.

2:15 PM SB06.08.03
Morphogenic Patterning in Synthetic Polymers Evan M. Lloyd1,2, Adam Feinberg1,2, Philippe Geubelle1,2, Nancy R. Sottos1,2 and Jeffrey Moore1,2; 1University of Illinois at Urbana-Champaign, United States; 2Beckman Institute for Advanced Science and Technology, United States

Complexity in biological systems spontaneously emerges from an initial state of symmetry through coupled reaction and diffusion, a process known as morphogenesis. In this work, we explore the coupled reaction and thermal diffusion inherent to frontal ring-opening metathesis polymerization (FROMP) of dicyclopentadiene (DCPD) as a synthetic mimic to biological morphogenesis. Propagation instabilities arise from an initial state of symmetry and generate patterns of thermal fluctuations on multiple length scales. Incorporation of thermo-active small molecules enables spontaneous patterning of the optical, chemical, and mechanical properties of structural thermosets. Material stiffness and glass transition temperatures were found to vary by up to two-fold and 30 °C, respectively. Control over patterns by tuning reaction and diffusion rates will also be discussed.

2:30 PM *SB06.08.04
Embodied Intelligence and Energy in Autonomous Matter Rob Shepherd; Cornell University, United States

Embodied Intelligence is the principle that describes autonomous mechanical responses to external environmental inputs (e.g., stress causes strain). This concept has been explored in depth previously and has resulted in a variety of compliant mechanisms and smart materials that combine, for example, the functions of structure and actuation. Energy (e.g., Chemical, Mechanical, Electrical, Optical) sources can also be put to multifunctional use; for example, a lead-acid battery being used a counterweight in a forklift. A more principled approach to Embodied Energy, however, does not presently exist. This talk will, for the first time, introduce this concept and focus on specific examples of forming these energy sources at a finer scale, into structural and other functional components and composite materials that provide benefits in the form of reduced SWaP tradeoffs. Examples of how these energetic composites and their chemo-electro-opto-mechanical responses can be tuned to perform work autonomously or in cooperation with higher level sensing and control for augmenting, supplementing, or replacing some robotic systems, including morphing structures, will be presented, and identification of gaps and future needs will also be discussed.

3:00 PM BREAK

3:30 PM *SB06.09.01
Cells, Gels and Shear—Designing Soft Materials for Biomedicine Angela Pitenis; University of California, Santa Barbara, United States

Epithelial cells are the body’s front-line defenders against foreign objects and environmental challenges and could be considered the biological equivalent of surface engineers. These cells continuously secrete high water content mucin gels to protect approximately 400 square meters of underlying cells, tissues, and organs from damage. Surfaces involving intentional and frequent sliding contact – such as the cornea, the digestive and reproductive...
tracts, and many distal interfaces for organs and tissues – adopt a stratified epithelial tissue approach. Epithelial cells are sophisticated sensors of mechanical stresses; friction and the resulting direct contact shear stresses have been shown to increase gene expression of pro-inflammatory cytokines and pro-apoptotic markers in vitro. In this work, a suite of experiments was performed under acute and chronic conditions to explore the onset and progression of apoptosis in corneal epithelial cell monolayers using in situ fluorescence microscopy and a custom-built microtribometer with aqueous gel probes. Recent results suggest that the onset of apoptosis occurs near physiological shear stresses (<100 Pa), although direct contact pressures in the absence of sliding did not initiate apoptosis, even at contact pressures approaching 3,000 Pa. These findings may help inform future designs of soft implants to mitigate friction-induced inflammation.

4:00 PM SB06.09.02
Mechanically Tunable Structured Hydrogels and Their Impact on Cells Katharina Siemsen¹, Chanh Hu Trinh¹, Florian Ceynowa¹, Rainer Adelung¹, Jan Lammerding² and Christine Selhuber-Unkel³; ¹Kiel University, Germany; ²Cornell University, United States

The mechanical properties of different mammal tissues vary within the body. Starting with the structural components of the body like bones with a Young’s modulus of several hundreds of kPa down to soft tissue like the brain with a Young’s modulus of 1 kPa and below.¹ This knowledge is important for the development of synthetic material for biomedical applications. It is assumed, that a mismatch between implant material and tissue can lead to scar tissue formation and tissue remodeling. Consequently, the understanding and investigation of the link between the mechanical properties and the structure of an implant material and the tissue response are essential. Another critical point is that cells in the body are often situated in a 3D structured and porous environment. Therefore, it is important to mimic such environments in implant materials to investigate questions such as how single cells migrate through different 3D constrictions and the consequences on the cells.

A step towards studying these questions is the use of a synthetic and 3D structured material, which closely mimics the natural tissue and its environment with similar hydration and mechanical properties. We developed a 3D environment consisting of a polyacrylamide hydrogel with interconnected and hollow microchannels.² It enables to vary the Young’s modulus by changing the chemical composition of the crosslinker to match elasticity values within a certain (soft) tissue regime up to 120 kPa.

Using such materials, we are investigating different hydrogel stiffness (1 kPa – 50 kPa) and the consequences of compliant and incompliant material mechanics towards cell behavior in 3D environments. With the possibility of using different adhesion ligands for the biofunctionalization such as collagen or fibronectin, we are able to specifically induce cell adhesion of different cell types. These cell types include pathogenic species, such as Acanthamoebae castellanii, for which we can use the hydrogel microchannels as biomedical capture device. Another possibility is the usage of cells with a preference to soft tissue surroundings such as fibrosarcoma cells, which act as an excellent robust role model for cells of the soft tissue region.

In conclusion, we show an artificial 3D interconnected environment with designed Young’s moduli and our investigation towards the influences on the cellular behavior of fibrosarcoma cells such as adhesion and migration on and within interconnected microchannels.


4:15 PM SB06.09.03
Hyper-Activation of Cellular Rigidity Sensing Pathways by the Surface Tension of Biomedical Silicones Zhu Cheng, Carolyn Shurer, Samuel Schmidt, Vivek Gupta, Grace Chuang, Jin Su, Amanda Watkins, Jason Spector, Chung-Yuen Hui, Heidi Reesink and Matthew Paszek; Cornell University, United States

Silicone gels are commonly used for the encapsulation and construction of implantable medical devices. Viscous silicone “oils” are also commonly used for lubrication of current-generation pre-fillable syringes, which are known to expel silicone oil droplets into patients during administration of aqueous drug formulations. While silicones are generally viewed as relatively inert to the cellular milieu, they can mediate a variety of inflammatory responses and other deleterious effects, but the mechanisms underlying the bioactivity of silicones remain unresolved. Cells physically interrogate their extracellular environment to make decisions related to cell proliferation, migration
and other critical processes. In addition to biochemical signals, physical properties of the extracellular matrix, including its stiffness, are key regulators for cell behaviors. Typically, on stiff substrates, cells display large spreading areas, assemble robust integrin-based adhesion complexes, whereas on soft substrates these functions are suppressed. However, cell behaviors that defy expectations based on substrate rigidity alone have been observed.

Here, we report that silicone liquids and gels have high surface stresses that can strongly resist deformation at cellular length scales. We demonstrate that cells interacting with soft materials with high surface tension primarily sense and respond to surface tension and not the bulk elastic moduli of the materials. Our results are consistent with theory that predicts that solid surface tension can dominate over elasticity at cellular length scales. On silicone materials with appreciable surface tension, cells assemble robust adhesion complexes and cytoskeleton stress fibers, spread over large areas, upregulate canonical integrin-based signal transduction, proliferate and migrate efficiently. Grown directly on the interior materials of silicone breast implants, cells are well spread and show nuclear localization of gene transcriptional factor YAP. In 3D culture models, liquid silicone droplets support robust cellular adhesion and the formation of multinucleated monocyte derived cell masses that recapitulate phenotypic aspects of granuloma formation in the foreign body response.

Together, our results indicate that material surface tension is a cellular stimulant that should be considered in application of silicones for biomedical purposes.

4:30 PM *SB06.09.04
Mechanobiology in the Hematopoietic Stem Cell Niche Cornelia Lee-Thedieck; Leibniz University Hannover, Germany

The hematopoietic stem cell (HSC) niche in the bone marrow is a unique microenvironment, which controls HSC maintenance and differentiation throughout the entire lifespan. HSCs are the source of all blood cells that are produced in billions on a daily basis. The niche is the only place, where HSCs can expand while keeping their stem cell properties. Thus, recreating the HSC niche in the lab for producing HSCs for clinical applications is an intriguing research objective that is pursued since the 1960s, when HSC transplantation became a life-saving treatment option for patients with hematological diseases. In this endeavor, researchers have concentrated for a long time on the influence of biological and chemical factors that are naturally found in the niche on HSCs. Only during the last decade, the importance of physical parameters – including 3D architecture, nanostructure and mechanical stimuli – became evident. We and others could show in vitro that human hematopoietic stem and progenitor cells are mechanosensitive and we proposed a model, how mechanical properties in the HSC niche might change and thus influence HSC behavior under different physiological conditions. Nevertheless, most in vitro experiments to test the mechanosensitive responses of cells still rely on hydrogels, in which the crosslinking degree is modulated to tune the mechanical properties of the resulting polymer network. Changing the crosslinking degree, however, does not only change the E modulus of hydrogels, but also their porosity, hydrophilicity or other parameters at the same time, which makes it impossible to conclude on the influence of one particular parameter from these experiments. To overcome this challenge, we developed a new platform-technology allowing to investigate mechanotransduction in a hydrogel-independent way. In a proof-of-principle study we could show that this platform allows to decouple mechanical from biochemical properties of biomolecules and thus to investigate the influence of both parameters on cells independently from each other. The results of these studies will help us to gain a fundamental understanding of the role of mechanobiology in the HSC niche, which might be an important step towards the goal of an artificial niche for HSC production for clinical applications.
Cell invasion into the surrounding matrix from non-vascularized primary tumors is the main mechanism by which cancer cells migrate to nearby blood vessels and metastasize to eventually form secondary tumors. This process is mediated by an intricate coupling between intracellular and extracellular forces that depend on the stiffness of the surrounding stroma and the alignment of matrix fibers. A multiscale model is used to elucidate the two-way feedback loop between stress-dependent cell contractility and matrix fiber realignment and strain stiffening, which enables the cells to polarize and enhance their contractility to break free from the tumor and invade into the matrix. Importantly, our model can be used to explain how morphological and structural changes in the tumor microenvironment, such as elevated rigidity and fiber alignment prior to cell invasion, are prognostic of the malignant phenotype. The model also predicts how the alignment of matrix fibers can recruit macrophages, which are among the first responders of the innate immune system following organ injury and are crucial for repair, resolution, and re-establishing homeostasis of damaged tissue. I will discuss how the deformation of the nucleus during migration can lead to changes in the spatial organization of chromosomes and their intermingling which can result in genetic mutations and genomic instability. I will also discuss how targeting extracellular matrix mechanics, by preventing or reversing tissue stiffening or interrupting the cellular response in cancer and fibrosis, is a therapeutic approach with clinical potential.

**BIO:** Vivek Shenoy is the Eduardo D. Glandt President’s Distinguished Professor in the School of Engineering and Applied Sciences at the University of Pennsylvania. Dr. Shenoy’s research focuses on developing theoretical concepts and numerical methods to understand the basic principles that control the behavior of both engineering and biological systems. He has used rigorous analytical methods and multiscale modeling techniques, ranging from atomistic density functional theory to continuum methods, to gain physical insight into a myriad of problems in materials science and biomechanics. Dr. Shenoy's honors include a National Science Foundation CAREER Award (2000), the Richard and Edna Solomon Assistant Professorship (2002-2005) and the Rosenbaum Visiting Fellowship from the Isaac Newton Institute of Mathematical Science, University of Cambridge and the Heilmeier award for excellence in faculty research (2019). He is the principal investigator and director of the NSF-funded Science and Technology Center for Engineering Mechanobiology established in 2016. He also serves the editor of the Biophysical Journal and is a fellow of the American Institute for Medical and Biological Engineering.

**9:00 AM *SB06.10.02/SB09.08.02**

**Biomechanical Imaging of Cancer Cells and Tumor Development in 3D**

*Ming Guo; Massachusetts Institute of Technology, United States*

Sculpting of structure and function of three-dimensional multicellular tissues depend critically on the spatial and temporal coordination of cellular physical properties. Yet the organizational principles that govern these events, and their disruption in disease, remain poorly understood. Here, I will introduce our recent progress performing biomechanical imaging to quantify cell and extracellular matrix (ECM) mechanics, as well as their mechanical interaction. By integrating confocal microscopy with optical tweezers, we have developed a platform to map in three dimensions the spatial and temporal evolution of positions, motions, and physical characteristics of individual cells throughout a growing mammary cancer organoid model. Compared with cells in the organoid core, cells at the organoid periphery and the invasive front are found to be systematically softer, larger and more dynamic. These mechanical changes are shown to arise from supracellular fluid flow through gap junctions, suppression of which delays transition to an invasive phenotype. Together, these findings highlight the role of spatiotemporal coordination of cellular physical properties in tissue organization and disease progression.

**9:30 AM SB06.10.03/SB09.08.03**

**3D Traction Force Microscopy of Multicellular Invasion in Biomimetic Silk-Collagen Hydrogels**

*Susan E. Leggett¹, Mohak Patel¹, Thomas M. Valentin¹, Christian Franck² and Ian Y. Wong¹; ¹Brown University, United States; ²University of Wisconsin–Madison, United States*

Epithelial tumors exhibit dysregulated cell-cell and cell-matrix adhesions as they invade into the surrounding extracellular matrix. In particular, the epithelial-mesenchymal transition (EMT) is associated with weakened cell-cell adhesions and strengthened cell-matrix adhesions, resulting in multicellular dissemination. Traction force microscopy enables new insights into the cell-generated forces that mediate these behaviors, but has primarily been
applied to individual cells in 3D. Here, we elucidate the collective tractions of multicellular clusters in 3D matrix after induction of the EMT master regulator Snail. We find that multicellular clusters exhibit characteristic spatial signatures that can be used for mechanophenotypic profiling. In particular, EMT results in highly localized “hotspots” of strong cell-matrix adhesion, associated with high contractility and front / back polarization. We further show that chemotherapeutics and targeted inhibitors can perturb clusters towards more epithelial or mesenchymal-like mechanophenotype. We envision that this 3D culture assay will enable high content preclinical screening of targeted anticancer compounds as well as to predict the clinical response of human patient samples.

9:45 AM SB06.10.04/SB09.08.04
Unjamming and Collective Migration in MCF10A Series of Breast Cancer Cell Lines Jae Hun Kim and Jeffrey Fredberg; Harvard University, United States

Carcinoma cells tend to migrate in collective strands, ducts, sheets or clusters (Friedl, & Gilmour, Nat. Rev. Mol. Cell. Bio. 2009). To migrate collectively, the epithelial collective has been argued to overcome geometric constraints attributable to cell jamming (Atia et al., Nat. Phys. 2018). If so, then the greater is the degree of cellular jamming, then the more would be the extent to which each individual cell becomes caged by its neighbors, and therefore, the less rapidly it would be able to migrate (Park et al., Nat Mat. 2015). The jamming hypothesis, however, has never been tested in the context of cancer cell invasiveness. Using classical in vitro cultures of six breast cancer models, here we investigate structural signatures of jamming, dynamical signatures of jamming, and the relationship between them. In order of increasing invasiveness, the cell lines examined included MCF10A, MCF10A.vector; MCF10A.14-3-3z; MCF10.Erb2, MCF10AT; and MCF10CA1a. Across all models tested, cell shape and shape variability from cell-to-cell conformed well to structural signatures of cell layer jamming. In all cases but one, migratory dynamics changed roughly in concert with expectations based on structural signatures –as the strength of structural signatures of unjamming increased, the rapidity of migratory dynamics tended to progressively increased. The exception was the case of MCF10CA1a, wherein structure signified a moderately jammed state whereas migratory dynamics were excessively rapid and therefore discordant with structure. Closer examination of migratory dynamics of MCF10CA1a showed anomalously large migratory persistence, but the mechanism of discordance in this case remains unclear. A hallmark of cancer is multiple dimension of heterogeneity. Nevertheless, each of the diverse cases examined here reveals that cell jamming imposes an overriding geometric constraint.

10:00 AM BREAK

10:30 AM *SB06.10.05/SB09.08.05
Mechanical Forces, the Microenvironment and Metastasis of 3D Microtumors Joe Tien¹, Celeste Nelson² and Bryan A. Nerger²; ¹Boston University, United States; ²Princeton University, United States

Progression to metastatic breast cancer requires cancer cells to invade from a solid tumor into the surrounding stroma and escape into a lymphatic or blood vessel. To understand the biophysical and biochemical parameters that define the kinetics of invasion and escape, we engineered a three-dimensional model of human breast microtumors embedded within native extracellular matrix. We previously found that interstitial fluid pressure (IFP) determines the invasive response of human breast microtumors: specifically, interstitial hypertension (i.e., elevated IFP) prevents invasion, whereas interstitial hypotension (i.e., lowered IFP) promotes invasion. We have now used this system to examine the effects of matrix density, proteolysis, proliferation, and IFP on the kinetics of tumor cell escape into an empty cavity. Our data suggest that the physical microenvironment of a tumor dictates the rates of two early steps in the metastatic cascade, namely, invasion of the surrounding interstitium and escape into an open space. These physical features dictate whether escape results from a ballistic or diffusive invasion process. Furthermore, acute changes in interstitial pressure can suppress tumor cell escape after invasion has already occurred. Our results point to the possibility of using physical therapies to delay or prevent metastatic progression in breast cancer.

11:00 AM *SB06.10.06/SB09.08.06
Engineered Microfluidic Environments to Study the Role of Nuclear Mechanobiology in Cancer Progression Jan Lammerding; Cornell University, United States
Cancer metastasis, i.e., the spreading of cells from the primary tumor to distant organs, is responsible for more than 80% of all cancer deaths. During cancer cell invasion and metastasis, tumor cells migrate through interstitial spaces and transendothelial openings substantially smaller than the diameter of the cell. Recent research has made it apparent that cells migrating in such confined three-dimensional (3D) environments face substantially physical challenges. In particular, the cell nucleus is the largest and stiffest organelle, making nuclear deformation a rate-limiting factor in the passage of cells through confined 3D environments. We have used micro- and nano-fabrication approaches to generate microfluidic devices that closely mimic the physical constraints of physiological interstitial environments, while providing precise control over the constriction geometry and enabling live-cell imaging at high spatial and temporal resolution. Using these devices, we demonstrated the importance of available pore size and nuclear deformability on the ability of cells to move through 3D environments. We combined these devices with fluorescent reporters for nuclear envelope rupture and DNA damage to assess the functional consequences of the physical forces exerted on the nucleus during confined migration. In addition, we developed a microfluidic micropipette aspiration device to rapidly measure nuclear stiffness in large numbers of cells. We found that highly metastatic breast cancer cells had decreased levels of the nuclear envelope proteins lamin A/C, which determine nuclear deformability, compared to less aggressive tumor cells, and that the increased nuclear deformability promoted migration through tight spaces. Increasing expression of lamin A in breast cancer cells with normally low levels of lamin A/C significantly impaired their invasive properties, while depletion of lamin A/C increased invasive potential through micron-scale microfluidic constrictions and dense collagen matrices. Importantly, analysis of human breast tumor tissue microarrays showed that low levels of lamin A/C correlated with reduced disease-free survival, demonstrating the clinical relevance of our findings. Taken together, these studies indicate that downregulation of lamin A/C could promote both cancer cell invasion and metastasis in breast cancer while highlighting the appeal of engineered materials and microenvironments to study tumor cell mechanobiology. Insights gained from this work could improve prognostic approaches; ultimately, targeting regulator pathways associated with altered lamin expression may offer novel therapeutic avenues to control metastatic disease in breast cancer.

11:30 AM *SB06.10.07/SB09.08.07
The National Cancer Institute’s Support for the Interface of Bio/Nano Materials with Cancer Research Nas Zahir; National Cancer Institute, United States

The U.S. National Cancer Institute (NCI) leads, conducts, and supports cancer research across the nation to advance scientific knowledge and help people live longer, healthier lives. Many advancements in cancer research in areas of progression, metastasis, and treatment response have been enabled by the development of innovative technologies, including novel biomaterials, microfluidics, and biomimetic engineered technologies. Several programs at the NCI have helped foster cancer technology development in these areas as well as the overall convergence of approaches and perspectives from the physical sciences and engineering into cancer research. Over the past decade, the NCI has supported the NCI Physical Sciences – Oncology Network (PS-ON), which is comprised of nearly 30 transdisciplinary teams that integrate physical sciences perspectives with cancer research to complement and expand on our current understanding of cancer across many biological length- and time-scales. Thematic areas under investigation in the PS-ON include transcriptional dynamics and genomic architecture, modeling evolutionary dynamics of treatment response, cancer mechanobiology and the physical microenvironment, and multi-scale computational modeling approaches to integrate data across length scales. PS-ON investigators and those in the affiliated Cancer Tissue Engineering Collaborative (TEC) research program are utilizing biomaterials and biofabrication for experimental model systems of cancer that recapitulate the tumor microenvironment and tumor-stromal interactions. There is also sophisticated incorporation of bioreactors and microfluidic culture to mimic perfusion, lymphatics, interstitial pressure, and molecular gradients. Other research initiatives supported by the NCI to promote convergent, cross-disciplinary research that include projects incorporating novel biomaterials are the Cancer Systems Biology Consortium (CSBC) and the Innovative Molecular Analysis Technologies (IMAT). The NCI demonstrates its interest in supporting materials science and engineering in cancer research by investment in these areas through investigator-initiated research and the targeted programs. The continued investigation of the physical dynamics of cancer and incorporation of novel biomaterials and biomimetic engineered technologies will be important, focusing on understanding the complex and dynamic multiscale interactions of the tumor, host, and immune system. Innovative technology development will continue to be critical for unprecedented measurements and discoveries in cancer research.
SESSION SB06.11/SB09.09: Joint Session: Cancer Cell—ECM Interactions
Session Chairs: Sidi Bencherif, Matthew Paszek, John Slater and Nas Zahir
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Room 304

1:30 PM *SB06.11.01/SB09.09.01
Nuclear Rupture at High Curvature and High Rates Upsets DNA Repair to Affect Cell Cycle, Differentiation and Genome Variation Dennis E. Discher; University of Pennsylvania, United States


2:00 PM *SB06.11.02/SB09.09.02
The Dynamic and Reciprocal Relationship between Tissue Tension and Pro Tumor Immunity Valerie Weaver; University of California, San Francisco, United States

Tumors show increased tissue level forces and a present with a chronically stiffened extracellular matrix (ECM), and transformed cells exhibit a perturbed oncogene-stimulated and ECM-tuned mechanophenotype. We have been studying how these aberrant cell and tissue level forces promote malignant transformation and drive tumor metastasis, and how they modulate tumor recurrence and treatment resistance in breast and pancreatic cancer and glioblastoma. We use two and three dimensional culture models with tuned extracellular matrix stiffness, as well as transgenic and syngeneic mouse models, human PDX models and human biospecimens, in which ECM crosslinking and stiffness and integrin mechanosignaling can be quantified and modified. Our studies have thus far revealed that the ECM in all tumors is progressively remodeled and stiffened by stromal fibroblasts and that this occurs prior to malignant transformation. We determined that ECM remodeling and stiffening is mediated very early during malignancy by stromal fibroblasts that are activated by factors including TGFb that are secreted by infiltrating pro-inflammatory macrophages. The stromal-fibroblast stiffened ECM disrupts tissue organization, promotes cell growth and survival and drives cell invasion. A chronically stiffened tissue stroma drives angiogenesis, and activates STAT3 to induce key cytokines and chemokines that promote pro-tumor immunity to foster tumor growth and dissemination and impede tumor treatment. The stiffened ECM also drives an epithelial to mesenchymal transition and primes the metastatic niche to foster metastasis. I will discuss the dynamic and reciprocal interplay between tissue tension and innate and acquired immunity and how this can not only force tumor aggression and metastasis but may also initiate tumor progression.
Hydrogels, highly hydrated cross-linked polymer networks, have emerged as powerful synthetic analogs of extracellular matrices for basic cell studies as well as promising biomaterials for regenerative medicine applications. A critical advantage of these synthetic matrices over natural networks is that the biophysical and biochemical properties of the material can be tuned with high control and precision. For example, bioactive functionalities, such as cell adhesive sequences and growth factors, can be incorporated in precise densities. We have engineered poly(ethylene glycol) [PEG]-maleimide hydrogels that support improved pancreatic islet engraftment, vascularization and function in diabetic models. Two biomaterial strategies will be discussed. We have developed proteolytically degradable synthetic hydrogels, functionalized with vasculogenic factors, engineered to deliver islet grafts to extrahepatic transplant sites via in situ gelation. These hydrogels induce differences in vascularization and innate immune responses among subcutaneous, small bowel mesentery, and epididymal fat pad transplant sites with improved vascularization and reduced inflammation at the epididymal fat pad site. This biomaterial-based strategy improves the survival, engraftment, and function of a single pancreatic donor islet mass graft compared to the current clinical intraportal delivery technique. In a second application, we have developed a localized immunomodulation strategy using hydrogels presenting an apoptotic form of Fas ligand (SA-FasL) that results in prolonged survival of allogeneic islet grafts in diabetic mice. A short course of rapamycin treatment boosts the immunomodulatory efficacy of SA-FasL-hydrogels, resulting in acceptance and function of allografts over 200 days. Survivors generate normal systemic responses to donor antigens, implying immune privilege of the graft, and have increased T-regulatory cells in the graft. Current studies focus on evaluating this immunomodulatory strategy in a large animal model of type 1 diabetes. This localized immunomodulatory biomaterial-enabled approach may provide an alternative to chronic immunosuppression for clinical islet transplantation.

Viscoelasticity and Cancer

It has long been recognized that tissue mechanical properties are altered in cancer, and this can serve as the basis for early diagnosis. While the impact of changes in tissue stiffness has been the focus of research to date, the role of tissue viscoelasticity has not been widely explored. We have developed hydrogels which allow for independent control over elastic moduli and stress relaxation/creep, and can mimic the fibrillar architecture of native collagenous matrices. These material systems are being utilized in 3D cell culture models of cancer and immunotherapy, and demonstrate that the gene expression of various cell types present in tumors, including cancer cells, mesenchymal cells, and immune cells is profoundly impacted by the viscoelastic properties of their matrix.

Integrin-Specific Hydrogels Direct Mesenchymal Stem Cell Immunomodulation and Bone Regeneration

Mesenchymal stem cells (MSCs) are a promising cell source for regenerative medicine applications due to their ability to self-renew, capacity for multipotent differentiation and secretion of a diverse array of cytokines and growth factors (the MSC secretome). These cells are frequently utilized in conjunction with biomaterial scaffolds designed to encourage cellular retention and direct the cells’ regenerative properties. However, hydrogel carriers have not yet yielded significant results in the clinic in part due to a lack of understanding of how hydrogel biophysical and biochemical properties impact cellular function. Although many synthetic hydrogels incorporate short peptides (e.g. RGD) to support integrin-mediated cell adhesion, the impact of hydrogel adhesive properties on transplanted cell function remains unknown.

We engineered integrin-specific hydrogels for the delivery of MSCs by tethering either the ubiquitous RGD cell adhesion motif or the type-1 collagen derived GFOGER adhesion motif into synthetic poly(ethylene) glycol (PEG)-
based hydrogels. Integrin-specificity was confirmed using blocking antibodies and a custom spinning disk platform in which cells attached to hydrogel disks are exposed to well-defined hydrodynamic shear forces allowing for sensitive measurements of the force required to detach the cell from the substrate. The effects of integrin-specific adhesive peptide presentation on MSC secretome and MSC-macrophage interactions were evaluated in vitro using Luminex multiplex technology. Finally, integrin-specific hydrogel directed MSC bone tissue regeneration was assessed over the course of 8 weeks in a critical size radial bone defect in an NSG mouse model.

Spinning disk analysis shows that cell adhesion to hydrogels presenting the adhesive peptides RGD and GFOGER are specific to αvβ3/β1 and α2 integrins respectively. Luminex data shows that the secretome of MSCs encapsulated in integrin-specific hydrogels cluster distinctly based on peptide and secretion of IL-6, IL-8, and VEGF is increased in GFOGER functionalized gels compared to RGD and non-adhesive controls. Further, in a co-culture assay, we show that macrophage cytokine secretion is differentially modulated by MSCs encapsulated in integrin-specific hydrogels, including an increase in IL-10 secretion by macrophages interacting with GFOGER encapsulated MSCs. Finally, MSCs delivered in GFOGER functionalized hydrogels significantly enhance repair of critical size bone defects in vivo compared to RGD and non-adhesive controls. Taken together, our results demonstrate that integrin specificity can be engineered into synthetic hydrogel systems resulting in modulation of the MSC secretome, differential MSC-macrophage interactions and improved tissue healing.

SESSION SB06.12: Poster Session II: Bringing Mechanobiology to Materials—From Molecular Understanding to Biological Design II
Wednesday Afternoon, December 4, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB06.12.01
Elucidating the Effects of Direct Physical Contact between Dental Pulp Stem Cells Cultivated on Polybutadiene with Different Stiffness on Proliferation and Differentiation Behaviors
Yihan Shen1, Zijian Ma2, Ya-Chen Chuang3,4, Jessica Hofflich3, Miriam Rafailovich3 and Marcia Simon3; 1St. Andrew's School, United States; 2Tianjin Nankai High School, China; 3Stony Brook University, United States; 4ThINC Facility, Advanced Energy Center, United States

Dental Pulp Stem Cells (DPSCs) have demonstrated immense potential for therapeutic purposes due to their easy accessibility as well as their capacity for self-renewal. Nonetheless, despite the increasing body of knowledge of stem cell transplantation, achieving specificity in cell responses remains challenging. In our previous study, we have shown that monodispersed Polybutadiene (PB) forms a convenient biocompatible scaffold to which cells can adhere without additional coatings. DPSCs plated on these PB substrates were able to adjust their moduli in response to the film thickness. However, a threshold at 2.3 MPa was observed after 28 days such that large amounts of biomineralized deposits would be produced if the substrate moduli were higher than this value. In this work we investigated how direct cell-cell contact of DPSCs cultured on PB substrates with different thicknesses (20nm and 200nm), representing hard and soft substrate mechanics effects, respectively, impacts differentiation pathways. The substrates were designated into 3 groups: contact group, non-contact group, and control group. Cell moduli and morphology were investigated by Atomic Force Microscopy and Confocal Laser Scanning Microscopy, respectively, after the first week of culture. Reverse Transcriptase Polymerase Chain Reaction was performed for selected gene markers: Alkaline Phosphatase (ALP), Runx-related transcription factor (Runx), and late markers, Dentin Sialophosphoprotein (DSP) and Osteocalcin (OCN). The latter served as indicators of odontogenic and osteogenic differentiation. In addition, microarray was conducted to explore whether genetic expressions were affected by cell contacts. Finally, biomineralization images were captured on day 28 using Scanning Electron Microscopy. Our experimental results signify that DPSCs on substrates with different mechanics can alter their behaviors through direct cell-cell contact. No biomineralization was found on either hard or soft substrates when cells physically contact; however, differentiated and non-differentiated cells were
capable of coexisting within a single culture when they did not contact across different substrates, where the phenotype was governed by the substrate mechanics. This study explored the influence of purely mechanical heterogeneity and the significance of cell communication, which are important for applying printed scaffolds as dentin/tooth regenerative biomaterials and promoting stem cell-based treatments.

SB06.12.02
Bio-Inspired and Bio-Mimetic Self-Assembled Materials Sharon Gilead and Ehud Gaizt; Tel Aviv University, Israel

Bio-inspired nanotechnology aspires to harness natural compounds, their chemical derivatives and formed supramolecular structures for various technological applications. In recent years, a key direction in the electronics and electro-optics technologies involves the transition from inorganic to organic components, including organic light emitting diodes (OLED), thus paving the way towards flexible and wearable electronic and light emitting devices. Bio-inspired organic materials may be the next-generation of organic optoelectronic devices based on self-organization principles, which allow facile synthesis, eco-friendliness, resistance to oxidation and no need for heavy metal doping.

We and others, have taken a reductionist approach to form new materials based on self-assembled peptide structures. We were the first to demonstrate that ultrashort peptides can form well-ordered nanostructures such as nanotubes and nanospheres. Specifically, the diphenylalanine peptide (FF) self-assemblies have been shown to display intriguing features, including mechanical, optical, semiconductive and piezoelectric properties. We thoroughly characterized mechanisms that facilitate peptide self- and co-assembly and the structural basis for the resulting physical properties. Several studies have explored the piezoelectric properties of the FF peptide. In the presence of an external electric field, vertically aligned FF microrod arrays can be organized on a substrate, resulting in enhanced piezoelectric response.

Here we show the ability of FF and other similar peptide assemblies to be used in various electronics and optics application as new bioorganic materials. FF assemblies and derivatives can act as an active optical waveguiding material, allowing locally excited states to propagate along the axis of the assemblies. In addition, Fmoc capped building blocks exhibit remarkable optical properties, such as quantum confinement and fluorescence. In addition, We based on our reductionist approach, to expand our search for minimal building blocks towards single amino acids as well as other metabolites such as nucleobases, demonstrating their self-assembly into various ordered structures. Doing this we are enlarging our library of biological building blocks which bear the potential to be novel bio-inspired supramolecular materials for optics and electronic applications.

SB06.12.03
Investigating Substrate Mechanics Effects in Combination with TiO2 Thin Layer Coated by Atomic Layer Deposition (ALD) for Dental Pulp Stem Cell Proliferation and Differentiation Megha Gopal1, Jessica Hofflich2, Ya-Chen Chuang2,2 and Miriam Rafailovich2; 1New Hyde Park Memorial High School, United States; 2Stony Brook University, The State University of New York, United States

Dental Pulp Stem Cells (DPSC) provide a valuable and enticing avenue for the field of regenerative medicine. Previously, we determined that DPSC cultured on monodispersed polybutadiene (PB), a biologically compatible substrate without additional coating, induced high levels of biomineralization in surfaces with a modulus over 2.3 MPa. [1] Similarly, titanium surfaces have been noticed to support osseointegration in dental implants. [2] In this study, we introduce a new method to deposit a 2–3 nm layer of titanium dioxide by Atomic Layer Deposition (ALD) on PB substrates to investigate DPSC behavior and differentiation lineages in an environment where surface chemistry has changed but substrate modulus remains the same.

ALD was employed to deposit TiO2 on thin (20 nm) and thick (200 nm) PB substrates, which respectively formed hard and soft substrate mechanics effects. All substrates were cultured with human DPSC, with data samples taken weekly. At first week, population doubling time determined that ALD had no major effect on cell proliferation while confocal images showed similar actin density and length of DPSC on all hard and soft PB substrates, suggesting that the TiO2 nanolayer has minimal effect on cell behaviors in the initial period. At the later stage of differentiation, biomineralization was characterized by SEM/EDS and Ramen spectroscopy, with templated, mineralized deposits observed only on ALD coated both hard and soft PB substrates. Osteocalcin (OCN) antibody staining observed by confocal also showed that ALD coating substrates favored OCN protein, suggesting that TiO2 ALD coating promotes differentiation and biomineralization on soft PB substrates where no mineralized deposits and upregulation of OCN was found. On the other hand, on hard PB substrates, even though biomineralization and differentiation
were found on both with and without ALD coating substrates, templated mineralized deposits and more evenly spread OCN protein were observed on ALD coating hard substrates, while particle-like deposits without fibers templated were presented on hard PB substrates without coating, suggesting that surface chemistry of TiO₂ coating by ALD may alter DPSC behaviors and differentiation pathway. This ALD method provides a potential application to coat a nanolayer on titanium on any biomaterial to further promote stem cells differentiation and proliferation.

We acknowledge support from the Louis Morin Charitable Trust and the NYS Department of Economic Development.


SB06.12.04
Shape Memory Cell Culture Platform for Mechanobiology Koichiro Uto and Mitsuhiro Ebara; National Institute for Materials Science, Japan

It is well-known that biomimetic microenvironments play an important role in governing cell function and fate. Conventionally, researchers utilize tissue culture plastic for cell culture; however, there are large and obvious differences in the biochemical and mechano-structural properties of cellular surroundings in vitro (plastic dish) and in our body. In addition, the native cellular environment incorporates several dynamic cell stimulatory factors beyond static biochemical and mechano-structural cues. To understand and bridge these gaps between in vitro and in vivo cell culture, a new research field known as ‘mechanobiology’ has emerged. Though today we have a greater understanding of the mechanobiological cellular phenomena in static systems, we have yet to fully explore the effects of ‘dynamic stimulation’ on cell behavior.

To recapitulate the complex microenvironment inside the body, spatio-temporal biomaterials have emerged as powerful tools to probe and direct active changes in cell function. In this presentation, I will briefly introduce our established dynamic cell culture platforms with ‘shape memory’ abilities. In order to evaluate the potential for cultured cells to respond to dynamic changes in their in vitro microenvironment as they do in vivo, we studied the effects of controllable anisotropic topographies on cell function. Given the importance of dynamic cues in regulating cell behaviors, investigation of such dynamic topography may have important implications to advance cellular manipulation and performance in vitro, as well as improving our understanding of cellular development in response to dynamic biophysical cues.

SB06.12.05
Engineering Tubular Structured Epithelial Organoids by Directed Tissue Assembly Yan Yan Shery Huang, Ye Liu, Joo-Hyeon Lee, Catherine Dabrowska and Iek Man Lei; University of Cambridge, United Kingdom

Epithelial organoids cultured in appropriate 3D conditions typically develop a microscopic, cystic structure lined with a polarized epithelium. Despite their great potential in research and therapy, epithelial organoids grow in heterogeneous sizes, and are too small to display physiologically relevant performance and applications. Here, we show directed assembly of mouse tracheal basal stem cell organoids towards geometrically-defined, lumenized constructs. We demonstrate perfusion of the macroscopic organoid construct; and the transplantation of the construct devoid of a carrier matrix, in a de-epithelialized explant model. Drawing parallel to liquid droplet interaction, we provide hypothesis on how epithelial organoid assembling can be achieved in a more efficient and predictable manner, of which principles could be extended to other organoid types developed form epithelial stem cells. The guided self-assembly system presented here opens up the possibility for engineering size-relevant, geometrically defined epithelial structures towards broad applications in biomimetic organoid-devices and tissue engineering.
**SYMPOSIUM SB07**

Bioelectrical Interfaces  
December 2 - December 6, 2019

**Symposium Organizers**  
Tzahi Cohen-Karni, Carnegie Mellon University  
Anastasia Elias, University of Alberta  
Sahika Inal, King Abdullah University of Science and Technology  
Christoph Tondera, BIOTEC, TU-Dresden

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* Invited Paper

**SESSION SB07.01: Flexible Bioelectronics I**  
Session Chairs: Tzahi Cohen-Karni, Anastasia Elias, Sahika Inal and Christoph Tondera  
Monday Morning, December 2, 2019  
Hynes, Level 3, Ballroom B

**8:00 AM SB07.01.01**  
**Non-Dissolvable Silk—From Hydrated Films to Bionic Links**  
Anoop Patil1,1 and Nitish Thakor1,1,2;  
1National University of Singapore, Singapore;  
2Johns Hopkins University, United States

**SUMMARY AND MOTIVATION** - This paper presents non-dissolvable silk fibroin in the form of highly-bendable and flexible films, housing ultrathin electrodes and conductive traces to enable soft bionic links. These links are wrapped around challenging nerve geometries and laminated onto planar cortical surfaces, assisting in the electrical recording of neural activity from the target tissue surfaces. Various materials tests and functional demonstrations in an anesthetized animal model illustrate the suitability of non-dissolvable silk as a candidate material for use in water-stable electrical sensing devices for *in vivo* applications.

**ADVANCES OVER PREVIOUS WORKS** - Silk, due to its excellent biocompatibility, has largely facilitated the development of resorbable devices meant to function *in vivo* for a limited amount of time. Even though there have been research studies on the sustainability of pristine silk in an animal model, use of non-dissolvable silk films in the design of fully functional bionic links has not been reported.

**METHODS** - A silk substrate housing the gold electrode sites was integrated with a patterned silk film to yield a silk link. EIS measurement was carried out in an electrochemical workstation. The functional validation of the silk link was carried out in a rat model. The silk links were deployed on the sciatic nerve and the cortex *in vivo* using a medical grade adhesive. *In vitro* material tests were carried out in a saline medium using an accelerated soak model.

**RESULTS** –
1. **Impedance:** The electrode sites of the nerve links provided an impedance of ~2.1 kΩ (1 kHz), and ~22 kΩ (at 1 kHz) in case of cortical links. The impedance values were found to be consistent across different samples ($Z=1.9±0.2$ kΩ at 1 kHz; n=6 sites, nerve link; $21 ± 1.21$ kΩ at 1 kHz, n=12 sites, cortical link).
2. **Flexibility:** The silk links could be bent around a silicone tube (~600 µm Ø) without inducing any cracks or delamination. Impedance measurements prior to and post wrapping showed negligible differences.
3. **In vitro recording:** The silk links could record minute sinusoidal signals (0.5-7 kHz), fed into the saline medium from a signal source.
4. **Young’s modulus:** The Young’s modulus of hydrated non-dissolvable silk films used as substrates and insulation layers was ~6-8 MPa; n=3.
5. **Affinity to wet surface:** The hydrated silk films used in the bionic links showed affinity to the wet surfaces and conformed well with the slimy surfaces of the sciatic nerve and the cortex *in vivo*.
6. **Biocompatibility Test:** Silk films did not exhibit any toxicity to neuronal cells including rat primary Schwann cells, DRG neurons, and hNSC. The films showed excellent cell-material interactions and good bioactivity with
7. *In vivo recording:* The sciatic nerve was electrically stimulated, and the corresponding evoked action potentials recorded by the distally placed silk links measured ~320 µV (E#1) and ~170 µV (E#2) in an experiment trial (60 µs pulse, 600 µA). The electrocorticogram (ECoG) recording capability of the silk link was demonstrated using a rat transient ischemia (TIA) model. ECoG recordings (evoked through forepaw stimulation) prior to induction of stroke served as the baseline and recordings post induction provided functional validation of the silk link. Suppression of the ECoG activity observed post induction of stroke was captured cleanly by the silk link.

**CONCLUDING OPINION** - The materials and methods described here provide the basis for excellently biocompatible sensor links on ultrathin non-dissolvable silk that offers robust conformal lamination onto tissue surfaces *in vivo*. Upcoming research studies will focus on building a well-tested and validated soft neurotechnology toolbox that can offer a library of materials to design tissue-compliant interfaces that are well-accepted by the biological milieu. Non-dissolvable silk, given its excellent biocompatibility, transparency, flexibility, and robustness is a value-add to such a toolbox.

8:15 AM SB07.01.02

**Transparent Single Layer Graphene Electrodes for Electroretinogram Recordings** Jose de la Cruz¹, Diep Nguyen², Serge Picaud², Clement Hebert¹ and Jose Antonio Garrido¹,²; ¹Catalan Institute of Nanoscience and Nanotechnology, Spain; ²Institut de la Vision, France; ³ICREA, Spain

Graphene has proved to be an outstanding material for the fabrication of biocompatible electrodes and microelectrode arrays (MEA). Motivated by their high sensitivity, low noise, scalability and stability in aqueous electrolyte, graphene-based MEA have been used for the detection of relevant molecules and biomolecules as well as electrical cell signals, either in vivo or in vitro. Using these new technology developments we are now able to shed new light onto several diseases and pathologies. One particular field in which this technology can be useful is electroretinography (ERG). This technique involves placing an electrode on the cornea, flashing the eye with light and recording the electrical signal produced by the retina. Usually, a metal electrode bended in a loop or a contact lens with attached wires are used. These types of electrodes mainly present two problems: discomfort produced by the used rigid materials and the difficulty to measure signals from the whole cornea, since their opacity would block the light meant to stimulate the retina. Therefore, electrodes combining flexibility and transparency could provide a solution for ERG measurements. In this work we present the fabrication and characterization of such devices based on single layer graphene technology, as well as their use on two different applications.

On the one hand we use single layer graphene electrodes to diagnose retinitis pigmentosa on a P23H rat model. Retinitis pigmentosa is a degenerative disease that causes the loss of photoreceptor cells on the retina producing night blindness and a progressive loss of the visual field. The graphene electrode, despite its small size, performs very well, enabling the diagnosis of the disease as good as its bulkier, more uncomfortable gold counterpart. Furthermore, the graphene device shows better resolution when dealing with the high frequency components of the ERG signals.

On the other hand, we use this technology to gain insight on the spatial distribution of electrical signals across the retina. With a flexible and transparent graphene MEA we can measure individual signals on different locations of the cornea without blocking the light used to elicit the retinal response. These measurements can shed new light on how the electrical signals are produced and propagated inside the eye. Using these devices, we have detected differences on the signal recorded on the centre of the cornea compared to that coming from the edges. Altogether, SLG electrodes provide an outstanding solution to perform ERG. Graphene transparency, flexibility and biocompatibility allow us to fabricate devices that can compete with the current state of the art ERG electrodes.

Acknowledgements:

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8:30 AM *SB07.01.03

**Biocompatible Nanomesh Electronics for Wearables and *In Vitro* Characterizations** Takao Someya¹,²,
Stretchable thin-film electronics are expected to open up a new class of applications ranging from wearable electronics for health-monitoring and human-machine interfaces, implantable electronics, and in vitro characterization. In this talk, we will review recent progress and outlook of hypoallergenic electronic sensor that can be worn on the skin continuously for a week without discomfort. The elastic electrode constructed of breathable nanoscale meshes holds promise for the development of noninvasive on-skin devices that can monitor a person's health such as electrocardiogram and skin moisture levels continuously over a long period. Then, similar nanomesh sensors is applied to in vitro characterization. These can monitor the field potential of cardiomyocytes on gel, while enabling them to move dynamically without interference.

9:00 AM SB07.01.04
Porous and Elastomeric Resistive Pressure Sensors for Wearable Devices Dan Li, Sophie Shi, Hyun-Joong Chung and Anastasia L. Elias; University of Alberta, Canada

Human skin is excellent at detecting pressures over a wide range of values, from the light movement of air against its surface (< 1 kPa) to the load of heavy weights (> 10 kPa). An electronic analog to skin (e-skin) is highly desirable, both to provide closed-loop (tactile) feedback for robotic limbs and to enable wearable devices for human health monitoring (e.g. detecting pulse). Towards the development of e-skin, numerous thin film-based pressure sensors have been demonstrated in the literature; these devices are typically designed to undergo changes in either resistance or capacitance in response to pressure, transducing a mechanical force into an electrical signal. In such devices, different microstructures or porous structures may be leveraged to control the physical deformation of the sensing material that occurs in response to the applied force.

Here, we demonstrate a simple, non-lithographic method for fabricating resistive pressure sensors with a broad range of working pressures (up to 40 kPa) and a low limit of detection. The device is soft, compact and conformable, with a thickness of around 300 microns. One advantage of this device design is that all electrical contact is made at the interface between the two layers; therefore very small changes in pressure can be measured, resulting in a low limit of detection (20 Pa). As the applied pressure increases, the pores themselves can deform drastically and form new contacts between the layers. This sensor has a sandwich structure comprised of metallized top and bottom sheets of porous polydimethylsiloxane (PDMS), fabricated using a simple templating method. In this method, a spin-coated layer of PDMS is pressed onto a layer of powder. The PDMS is then cured and the template is subsequently dissolved. To metallize the structures, the inner faces of each of these porous layers are coated with a layer of conductive silver nanowires, which coats the surface of the pores. The Ag nanowires layers are initially in light contact, and the device undergoes a change in resistance when pressure is applied perpendicular to the plane of the sheets.

In this work, we investigate how the properties of the porous layers affect both the mechanical properties and the response of the device by varying both pore size and elastomer stiffness. The stiffness of the elastomer was tuned by varying the ratio of base to crosslinker in the material (5:1, 10:1, and 15:1); as the fraction of crosslinker in elastomer increased, the response time of the sensor was found to decrease. To vary pore size, three different powder templates were utilized: KCl, NaCl, and sugar, with typical diameters of 60-80 µm, 150-200 µm, and 400-550 µm, respectively. The sensor fabricated with a KCl template (which had the smallest pores) and 10:1 PDMS demonstrated the best performance, with a sensitivity of 14.1 kPa⁻¹ (up to 3.5 kPa), 4.8 kPa⁻¹ (up to 10 kPa), 1.84 kPa⁻¹ (up to 40 kPa) and no performance degradation over 1000 loading and unloading cycles.

Wearable electronic applications of these devices, including pulse measurement, facial movements, and sound tracking, are demonstrated in this work. Overall the combination of non-lithographically-defined pores and solution-processed Ag nanowires yields a simple to fabricate device which exhibits high sensitivity and a low limit of detection. In addition to providing tactile feedback to robotic limbs, such devices may have applications in intrinsically stretchable bioelectronics.

9:15 AM SB07.01.05
Fully Printed Silver Nanowire-Based Biosensor for Point-of-Care Measurement of Prothrombin Time Brittani
Heart failure is a critical public health issue affecting tens of millions of people each year. One paradigm that has revolutionized treatment plans is the continuous flow Ventricular Assist Device (VAD). However, due to the thrombogenic nature of the VAD, complications associated with bleeding events and thrombosis require the patients to take blood thinners, which limit the overall quality-of-life and survival of implanted patients. When on a continuous regiment of blood thinners, VAD patients require frequent monitoring to ensure that prothrombin time (and the corresponding international normalized ratio, INR) is within a clinically acceptable range. Currently, the standard of care requires outpatient testing of prothrombin time (PT) every 1–4 weeks. This is time-consuming and burdensome to patients and healthcare systems, and furthermore recent studies indicate that patients may benefit from more frequent testing intervals. An affordable, point-of-care test (POCT) coagulometer for home monitoring of PT would fill these needs.

In this work, a fully printed point-of-care test (POCT) for the measurement of PT using electrical transduction is demonstrated. In order to create a low-cost device, an inexpensive testing platform was designed, which consists of a printed silver nanowire thin-film resistor to provide high electrode surface area and to set the baseline impedance signal. The nanowires had diameters of 30-50 nm and lengths of 2-6 µm and were synthesized using the polyol method. After all rinsing steps, the silver nanowire concentration was measured using atomic absorption spectroscopy (AAS) and then concentrated in water at 10 mg mL⁻¹. The resultant Ag nanowire inks were printed using an aerosol jet printer under ultrasonic atomization, forming thin films with a resistance in the range of 50–200 Ω. Interrogation of whole blood modulates the impedance of the Ag nanowire film, with the impedance maximum corresponding to the PT. Measured using electrochemical impedance spectroscopy (EIS), the operating frequency was found to be optimal at 15kHz, at which a stable and reproducible clotting time response was obtained. The functionality of the device was demonstrated in whole blood derived from both animal and human subjects. Devices were printed on both glass and polyimide, establishing the ability to measure identical clotting times even on a flexible substrate under strain / bending. These results lay the groundwork for fully printed impedimetric coagulometers that could address the unmet need for a low-cost, robust POCT to improve outcomes for VAD patients by straightforward monitoring of PT/INR.

9:30 AM *SB07.01.06
Reflectance Oximetry Enabled by Flexible Organic Array of Printed Devices
Yasser Khan, Donggeon Han, Adrien Pierre, Jonathan Ting, Ana Claudia Arias and Anju Toor; University of California, Berkeley, United States

The optical method to determine oxygen saturation in blood is limited to only tissues that can be transilluminated. The status quo provides a single-point measurement and lacks 2D oxygenation mapping capability. We have demonstrated a flexible and printed sensor array composed of organic light-emitting diodes and organic photodiodes, which senses reflected light from tissue to determine the oxygen saturation. We use the reflectance oximeter array beyond the conventional sensing locations. The sensor is implemented to measure oxygen saturation on the forehead with 1.1% mean error and to create 2D oxygenation maps of adult forearms under pressure-cuff–induced ischemia. In addition, we present mathematical models to determine oxygenation in the presence and absence of a pulsatile arterial blood signal. The mechanical flexibility, 2D oxygenation mapping capability, and the ability to place the sensor in various locations make the reflectance oximeter array promising for medical sensing applications such as monitoring of real-time chronic medical conditions as well as postsurgery recovery management of tissues, organs, and wounds.

10:00 AM BREAK

10:30 AM *SB07.01.07
Wireless E-Tattoos Chargeable On-the-Go
Nanshu Lu; The University of Texas at Austin, United States

Soft, noninvasive and multifunctional epidermal electronics (a.k.a. e-tattoos) have demonstrated many exciting applications in mobile health, human-machine interface (HMI) and so on. However, e-tattoos are only practically useful when they are low cost and wireless. Previously, our group has invented a dry and digital manufacturing approach named the “cut-and-paste” method for the rapid prototyping of e-tattoos using a paper/vinyl cutter plotter [1]. This method has been demonstrated to work for thin film metals [1, 2], various polymer sheets [1, 3], ceramics
As the quality of life increases, people’s interest in better healthcare grows, and their demand for customized healthcare devices for individuals increases. Accordingly, there is an increasing interest in wearable devices that can be worn on the body and detect biological signals in real time. Thus, many researchers have intensively studied to develop skin-attachable electronics without any physical inconvenience in daily life. These wearable electronics vitally need not only bio-signal sensing devices but also data storage components to manage a user’s health condition in real time. Therefore, nonvolatile memory is a key part of these customized healthcare wearable devices. Among various nonvolatile memories, a resistive random-access memory (RRAM) is attracting attention as a next-generation nonvolatile memory device because of its advantages of high-speed switching, low power consumption, low manufacturing cost, etc. However, in order to apply RRAMs to skin-attachable wearable devices, problems such as ultra-lightweight, unbreakable, and free-form design must be resolved. To overcome these problems, organic-based RRAMs can be an attractive candidate with advantages such as flexibility, simple process, and so on. However, these organic-based RRAMs are difficult to apply to skin-attachable devices due to their sensitivity to the external environmental factors. In particular, moisture could cause degradation of an organic thin film and fatally affect the memory operations of organic-based RRAMs. Therefore, resolving issues such as degradation of the electrical performance of organic-based RRAMs due to external moisture before implementing...
for skin-attachable wearable devices become an important factor. In this study, we demonstrate a novel organic material, nitrocellulose (NC), as a switching layer of RRAM for the first time that meets the requirements of the skin-attachable wearable devices. NC is obtained by nitriding cellulose and can be formed at low temperature through a simple solution process. To fabricate NC based RRAMs, we deposited NC by solution process on the p+Si wafer, and top electrode, Al/Au, was deposited by the thermal evaporator. Fabricated NC based RRAMs shows bipolar switching behavior for current-voltage (I-V) characteristic. The 'Set' voltage, which is converted from a high resistance state (HRS) to a low resistance state (LRS), is about 2.5 V, and the 'Reset' voltage, which is converted from LRS to HRS, is -1.5 V. NC based RRAM shows a resistance switching window of 10² and maintains switching operations after 100 cycles of consecutive endurance tests. Data retention results show reliable data storage performance of up to 10⁴ seconds under constant voltage stress of 0.3 V. As one of the previous researches of organic-based RRAMs proposes, the switching operation in organic-based RRAMs using the easily oxidizable metal electrode is attributed to the formed native oxide layer between the organic layer and the metal electrode. Likewise, as Al is one of the easily oxidized metals when it is used as a top electrode of NC based RRAMs, it is easily oxidized by the oxygen functional groups present in NC. Thus, We can deduce that NC based RRAMs show the switching operation by the formed native Al oxide. We found a new layer was formed between Al and NC by high-resolution transmission electron microscopy (HR-TEM) images. In addition, an energy dispersive X-ray spectrometer (EDS) mapping and an X-ray depth photoelectron spectroscopy (XPS depth) analysis confirmed that the newly formed layer is Al oxide. Additionally, NC based RRAMs show robust memory operations even after dipping in deionized water (DI water) for 24 hours due to the high moisture stability of the nitrocellulose. Finally, this RRAM is fabricated on polyimide (PI) to demonstrate the applicability of flexible memory suitable for skin-attachable wearable devices.

11:15 AM *SB07.01.10
Bouncing Balls and Inflating Balloons—Exploiting Rubbers Nature Ingrid M. Graz; Johannes Kepler Universität Linz, Austria

Rubber’s inherently dissipative nature and its extreme elastic properties make it the material of choice for children’s toys such as bouncing balls and air-filled balloons. This talk takes inspiration from these toys to understand materials properties and design soft actuators: Bouncing balls help exploring the dissipative properties for damping structures inspired by fruit while balloon shaped actuators inspired by plants enable fast and strong actuators. Potential applications include design guidelines for protective structures in two and three dimensions such as cushioning e-skin complete with stretchable sensors and soft actuators for exoskeletons.

SESSION SB07.02: Materials for Bioelectronics
Session Chairs: Tzahi Cohen-Karni, Anastasia Elias, Sahika Inal and Christoph Tondera
Monday Afternoon, December 2, 2019
Hynes, Level 3, Ballroom B

1:30 PM SB07.02.01
Fabrication of Ready-to-Wear Resistive Strain Sensors by Electroless-Nickel Immersion Gold Deposition on Nitrile Butadiene Gloves for Hand Gesture Mapping Sara Mechael, Yunyun Wu, Yiting Chen and Tricia B. Carmichael; University of Windsor, Canada

Wearable electronics enable an intimate experience between users and their devices. In contrast to conventional large, rigid-body electronics, wearables conform to the human body even during routine motion. Wearable electronics can be applied to strain sensing, contributing to fields such as physiotherapy, virtual reality gaming, and robotics. Current efforts to prototype soft strain sensors often disregard the integration of the sensor onto a wearable platform, instead using temporary mounting techniques such as taping or gluing onto skin or articles of clothing. While these methods enable characterization of the strain sensors, they are not suitable for practical wearability. Here, we present an alternative method for the fabrication of wearable strain sensors by creating ready-to-wear prototypes by fabricating stretchable metal strain sensors on the surfaces of commercially available wearable nitrile butadiene rubber (NBR) gloves. In this presentation, we discuss the fabrication method, which uses a stencil mask to pattern a spray-coated latex resist, followed by electroless-nickel immersion-gold deposition selectively within the
regions unprotected by the resist. We discuss the surface morphology, resolution of the patterning technique, electrical performance, and durability of these strain sensors. We also demonstrate the versatility of this ready-to-wear strain sensor as a low-cost, lightweight, fitted glove sensor in relation to gesture monitoring in an American Sign Language translator and remote control of a soft robotic hand that mirrors the gestures made by the glove user.

1:45 PM SB07.02.02
Organic Electronics for Self-Powered ECG Signal Acquisition Patches Georgios Spyropoulos, Zifang Zhao, Jennifer Gelinas and Dion Khodagholy; Columbia University, United States

In the near future, wearable electronics that can serve as devices for point of care diagnostics, brain machine interfaces, and therapeutic responsive stimulation may not only facilitate health monitoring and disease diagnosis, but on-the-spot treatment and intervention. Low cost energy storage, flexibility, and capacity for internal functionality are ideal characteristics that those devices should exhibit.

In this project, we demonstrate a thin, flexible self-powered epidermal electronic device that provides an efficient interface for high quality electrophysiological signal acquisition. This medical patch-like device is built on a micrometer thick parylene substrate with microfabricated gold interconnects and consists of three main parts; i) a biological interface, ii) a microcontroller/bluetooth module, and iii) a flexible battery. Because of its conformability, it can be attached as a patch on different human body areas. To determine the configuration and material composition for optimal signal acquisition, we microfabricated various designs with gold interconnects that lead to several biological interfaces. Gold electrode contacts coated with conductive poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) enriched with D-sorbitol or PEDOT:PSS based anisotropic layers enable low impedance, adhesive interfaces with high spatial resolution. Additionally, internal ion gated organic electrochemical transistor (IGT)-based interfaces were tested to acquire locally amplified physiological signals. The signals are sent to a microcontroller with high speed data acquisition for processing and storage. The heart of the device is a battery based on an electrolyte sandwiched between a composite film of highly conductive PEDOT:PSS and an aluminum electrode, serving as cathode and anode respectively. The battery shows an average cell discharge voltage of 0.5V and can provide specific energy of at least ~15 Whkg⁻¹, which can operate our system continuously for at least 40 hours.

The resulting optimal patch was attached on human subjects to obtain high quality electrocardiogram (ECG). Detection algorithms run by our devices can locate ST segment abnormalities that indicate coronary ischemia. Our findings communicate concrete steps towards subtle wearable bioelectronics systems and medical care devices that can record and potentially intervene with the electrophysiological signal of human body.

2:00 PM *SB07.02.03
Development of Semiconducting Polymers for Electrochemical Transistors for Organic Bioelectronic Applications Iain McCulloch; King Abdullah University of Science and Technology, Saudi Arabia

Organic electrochemical transistors (OECTs) have been shown to be promising devices for amplification of electrical signals and selective sensing of ions and biologically important molecules in an aqueous environment, and thus have potential to be utilised in bioelectronic applications. The sensitivity, selectivity and intensity of the response of this device is determined by the organic semiconducting polymer employed as the active layer. Until now, most OECTs have been fabricated with commercially available conducting poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) as the active layer, and therefore operated in depletion mode with limited modulation. This work presents the design of new organic semiconducting materials which demonstrate significant improvements in OECT performance, through operation in accumulation mode, with high transconductance and low operating voltage, combined with good operational stability.

We discuss here the design, synthesis and performance of novel intrinsic semiconducting polymers for efficient accumulation mode OECT devices. Key aspects such as ion and charge transport in the bulk semiconductor and operational voltage and stability of the devices are addressed in order to elucidate important structure-property relationships. A range of new semiconducting polymers, designed to exhibit facile electrochemical doping of either holes or electrons, facilitate ion penetration and migration, as well as have aqueous compatibility are reported. Electrochemical stability will also be discussed. Optimisation of a series of polymer parameters including electrochemical doping, charge carrier mobility and capacitance are discussed. This approach leads to the design of polymers that can outperform state-of-the-art PEDOT:PSS based depletion mode devices with peak
transconductances above 20 mS, peak currents in the mA regime, on/off ratios above 105 and excellent switching times below 1 ms. In addition, we demonstrate that polymers with sufficiently high electron affinities and low ionisation potentials can achieve charge carrier ambipolarity, with both p and n-type device operation.

2:30 PM SB07.02.04
Fully Rubbery Electronics and Biointegrated Devices Cunjiang Yu; University of Houston, United States

While human organs and tissues are mostly soft; conventional electronics are hard. Seamlessly merging electronics with human is of imminent importance in addressing grand societal challenges in health and joy of living. However, the main challenge lies in the huge mechanical mismatch between the current form of rigid electronics and the soft curvy nature of biology. Here, I will present a new form of electronics, namely “rubbery electronics and bioelectronics”, with skin-like softness and stretchability, which is constructed all based upon elastic rubbery electronic materials. These rubbery electronic materials are structured in the format of composites, which can be scalably manufactured from common and commercial available materials without dedicated and complicated synthesis. Specifically, we build nanofibril organic semiconductor and metallic nanowires percolated in the elastomeric polymer matrix in a composite format for the rubbery semiconductors and conductors, respectively. Employing these rubbery electronic materials, we have achieved fully rubber format devices, including transistors and sensors, logic gates, active matrices, elastic sensory skin systems, and biointegrated devices, etc. I will showcase a few examples including artificial skins, biomedical implants, and wearable applications.

2:45 PM SB07.02.05
Reversible Electronic Solid-Gel Switching of a Conjugated Polymer, from Electroactive Filters to Drug Delivery Devices Johannes Gladisch¹, Sarbani Ghosh¹, Alexander Giovannitti², Maximilian Moser², Igor Zozoulenko³, Iain McCulloch³, Magnus Berggren¹ and Eleni Stavrinidou¹; ¹Linköping University, Sweden; ²Imperial College London, United Kingdom; ³King Abdullah University of Science and Technology, Saudi Arabia

Conjugated polymer films can transform electrical energy into volume changes when included in electrochemical devices via the exchange of ions and solvent. So far, this volumetric change has been limited to 40% and 100% for reversible and irreversible systems, respectively, thus restricting potential applications of this technology. We report a thiophene based conjugated polymer that reversibly expands by about 300% upon addressing, relative to its previous contracted state, while the first irreversible actuation can achieve values ranging from 1000-10000%, depending on the voltage applied. From experimental and theoretical studies, we find that this large and reversible volumetric switching is due to reorganization of the polymer during swelling as it transforms between a solid-state phase and a gel, still maintaining percolation for conductivity. The polymer was utilized as an electroactive cladding to reduce the void sizes of a porous carbon filter electrode by 85% and for controlled delivery of large biomolecules.

3:00 PM BREAK

3:30 PM SB07.02.06
Perovskite Nickelates as Biological and Brain Interfaces Hai-Tian Zhang, Yifei Sun and Shriram Ramanathan; Purdue University, United States

Bioelectrical interfaces between biological systems and electronic devices are crucial in understanding physiological pathways, monitoring onset of diseases at early stages, and transferring information across brain-machine interfaces. Simultaneous transduction of ionic-electronic signals would be of particular interest in this context since ionic transmitters are the means of information transfer in biological media while traditional electronics utilize electrons or holes. In this presentation, we propose strongly correlated oxides (mainly focused on perovskite nickelate) as a potential candidate for this purpose.¹,² We show that perovskite nickelates can be doped with small ions such as H⁺ and Na⁺ and show large amplified response in their electrical resistance through the Mott metal-insulator transition. The capability of reversibly accepting small ions and converting ionic signal to electrical signals renders perovskite nickelate a strong candidate for bioelectrical and haptic interface applications. We will present case studies of mouse brain interfacing with nickelate devices to record neurotransmitter release. We will also discuss the structural as well as electronic mechanisms leading to experimental observations based on X-ray absorption techniques and first-principle calculation studies. Collaborative contributions will be pointed out in the presentation.
New Semiconducting Materials for Organic Bioelectronic Application Christian Nielsen; Queen Mary University, United Kingdom

The emerging research field of organic bioelectronics has developed rapidly over the last few years and elegant examples of biomedically important applications including for example in-vivo drug delivery and neural interfacing have been demonstrated.

The organic electrochemical transistor (OECT), capable of transducing small ionic fluxes into electronic signals in an aqueous environment, is an ideal device to utilise in bioelectronic applications. To date, nearly all OECTs have been fabricated with commercially available PEDOT:PSS, heavily limiting the variability in performance. We have previously shown that tailor-made semiconducting polymers are fully capable of matching the performance of PEDOT:PSS. To capitalise on this discovery and the versatility of the organic chemistry toolbox, further materials development is needed. In my talk I will discuss our recent work in this area covering examples of both molecular and polymeric semiconducting materials and their performance in bioelectronic devices.

Designing Polymer Mixed Conductors for Applications in Bioelectronics Jonathan Rivnay; Northwestern University, United States

Direct measurement and stimulation of ionic, biomolecular, cellular, and tissue-scale activity is a staple of bioelectronic diagnosis and/or therapy. Such bi-directional interfacing can be enhanced by a unique set of properties imparted by organic electronic materials. These materials, based on conjugated polymers, can be adapted for use in biological settings and show significant molecular-level interaction with their local environment, readily swell, and provide soft, seamless mechanical matching with tissue. At the same time, their swelling and mixed conduction allows for enhanced ionic-electronic coupling for transduction of biosignals. These properties serve to enable new capabilities in bioelectronics. In the first part of my talk I will focus on the design of polymer bioelectronic materials for enhanced electrophysiological sensors based on electrochemical transistors. Synthetic design and processing can yield stable and high performance mixed conductors with high volumetric capacity, high transconductance, and steep subthreshold switching characteristics for low power sensing. Rising areas in stability and circuit integration are highlighted. I will then discuss the unique form factors enabled by polymer electronics, and their applications in regenerative engineering, including the development of thermo-responsive conductive hydrogel composites with osteoinductive characteristics. New materials design will continue to fill critical need gaps for challenging problems in bio-electronic interfacing.

Role of the Cation in Electrochemical Doping of p-Type, Accumulation Mode Polymers for Bioelectronics Lucas Flagg, Jonathan W. Onorato, Christine Luscombe and David S. Ginger; University of Washington, United States

Mixed ionic/electronic conductors have demonstrated importance for a number of applications including bioelectronics, neuromorphic computing, and energy storage. Of particular interest are organic electrochemical transistors (OECTs), which have multiple uses for biosensing, but also provide a valuable platform for studying the fundamental properties of mixed conducting materials. The current understanding of the doping mechanism for p-type, accumulation mode OECTs is that the application of a negative gate bias causes the injection of anions into the polymer film along with a corresponding accumulation of holes. However, the highest performing materials demonstrate extensive swelling in the presence of electrolyte, suggesting that there is some intrinsic cation uptake prior to electrochemical biasing. Here we carefully examine the role of the cation on the doping mechanism of poly(3-[(2-(2-methoxyethoxy)ethoxy)methyl]thiophene-2,5-diyli) (P3MEEMT), a high performing OECT active layer material with glycolated side chains. We study the mass of the polymer film at different doping levels using
Electrochemical Quartz Crystal Microbalance (EQCM) and find significant mass loss during the initial stages of doping for smaller cations. We confirm the initial presence and the subsequent expulsion of cations from the polymer film by Glow Discharge Optical Emission Spectroscopy (GDOES). From these measurements we propose the following doping mechanism for this polymer: 1) initial diffusion of electrolyte (cation and anions) into the film, 2) cation expulsion and hole accumulation upon applying a gate bias, 3) anion insertion and further hole accumulation. Lastly, we show that the cation expulsion step does not exist when very large cations are used, presumably because large cations cannot diffusively enter the film initially. These findings help clarify the doping mechanism in the highest performing mixed ionic/electronic conductors and demonstrate that OECT operation depends not only on the anion, but also the cation, paving the way to further improvements.

4:45 PM SB07.02.10
Energetic Control of Redox–Active Polymers towards Safe Organic Bioelectronic Materials
Alexander Giovannitti1,2, Reem Rashid3, Bryan Paulsen3, Jenny Nelson1, Alberto Salleo2, Iain McCulloch1 and Jonathan Rivnay2; 1Imperial College London, United Kingdom; 2Stanford University, United States; 3Northwestern University, United States

In this study, we draw attention to electrochemical side–reactions of redox–active polymers for organic electrochemical transistors (OECTs)1. We find that electron–rich polymers such as PEDOT:PSS1 or pg2T-TT2 can undergo oxygen reduction reactions (ORRs) and form hydrogen peroxide (H2O2) as a side product. H2O2 is an oxidant that can cause harm to biological systems and devices. Hydrogen peroxide production occurs through an electron transfer from the electron–rich conjugated polymer to molecular oxygen dissolved in the electrolyte, with the ionization potential (IP) of the redox-active polymer determining whether or not the reaction occurs spontaneously under ambient conditions.

To prevent this side–reaction from taking place during device operation, we designed a redox–active polymer with an IP > 4.9 eV. The polymer is a donor–acceptor type copolymer with polar side chains, specially designed to achieve a high redox-stability in aqueous electrolytes. OECTs were fabricated and tested where we observe a turn on voltage at –0.4 V (vs Ag/AgCl), a peak transconductance of 200 S/cm (at VG = –0.7 V), and good device stability with no sign of H2O2 formation during device operation. This study elucidates the interaction of redox-active conjugated polymers and molecular oxygen which has previously been overlooked with potentially critical issues for operating electrochemical devices in oxygen containing aqueous electrolytes (biological environments).


8:00 AM SB07.03.01/SB02.04.01/SB05.04.01
Graphene Based Health Monitoring
Dmitry Kireev and Deji Akinwande; The University of Texas at Austin, United States

The modern healthcare and biomedical systems show a clear trend towards personalized, predictive, and preventive medicine. Development of the concept, commonly known as mobile health (mHealth), means that a huge shift in the paradigms of medical device architectures is to be expected in the near future thanks to the increased portability of medical devices as well as increase in number of specific mobile-based apps. An ideal wearable device should possess a set of important requirements, such as (i) low cost of fabrication, (ii) being conformable and compatible with human skin, and (iii) multifunctionality. The latter is of special importance if the goal is to build not just a single specific device, but to rather develop a technology and basis for scalable fabrication of devices that are capable to detect a plurality of vital signals (HR, EEG, ECG, hydration, galvanic response, etc.). In order to develop the universal technology that meets all three requirements mentioned above, we propose to
utilize graphene in combination with epidermal technology. The conventional epidermal biosensors are based on metal and silicon based thin films that are patterned into special structures for softness and stretchability and embedded into soft biocompatible polymers. The choice of two-dimensional materials is the most natural due to their ultra-thinness, allowing extreme flexibility, transparency, and conformability to almost any rough surface, including skin [1]. Graphene based passive electrodes have been successfully used to epidermal sensing of electrocardiograms (ECG), electromyogram (EOG), electroencephalogram (EEG), skin temperature, and skin hydration [1], [2]. It is important to emphasize that the research work is based on large-area CVD-grown graphene, allowing us to develop low-cost, wearable, and fully conformable to skin devices. Furthermore, large area fabrication gives an ultimate promise for future devices fully based on 2D materials to be available on market. In terms of possible applications, the proposed technology can be easily expanded towards other fields of healthcare biosensing, such as in vivo electrophysiology, UV exposure sensing, pressure sensing, or even towards building electronic skin, and prosthetics.


8:15 AM SB07.03.02/SB02.04.02/SB05.04.02
Multifunctional Fiber Based Neural Probes with Integrated Neurotransmitter Detection Atharva Sahasrabudhe1,1, Tural Khudiyev1, Tomo Tanaka1,2, Kyoungsuk Jin1, Marc-Joseph Antonini1,1,3, Andres Canales1, Yoel Fink1,1, Karthish Manthiram1 and Polina Anikeeva1,1,1; 1Massachusetts Institute of Technology, United States; 2NEC Corporation, Japan; 3Harvard-MIT Division of Health Science and Technology, United States

One of the major challenges in deciphering the fundamental principles of cognition is the lack of appropriate tools for seamless interfacing with neurons across all their signaling modalities. Gaining holistic understanding of neural circuits and their control of behavior requires invention of neural probes that can simultaneously record and modulate electro-chemical activity of neurons while evoking minimal inflammatory response for periods ranging from minutes to years. Multifunctional fibers have recently emerged as a promising platform for integrating multiple functional elements to probe and control neural activity that also minimizes the foreign body response.

In my presentation, I will describe our efforts in further expanding the multifunctional activity of polymer-based fiber probes by incorporating an electrochemical sensor that enables real-time tracking of neurotransmitter dynamics in behaving animals. This is achieved by introducing a carbon nanotube (CNT) based electrocatalytic electrode within the multifunctional fiber-based probes during their fabrication via thermal drawing process. The resulting devices can be implanted chronically and perform electrical recording and stimulation of neurons, light delivery through waveguides for optogenetics, drug and gene delivery via microfluidic channels, and voltammetry via the CNT electrodes for dynamic detection of dopamine. We envision that these multimodal, miniature, and mechanically compliant probes will facilitate understanding of the neurophysiological underpinnings of dopamine-dependent behaviors including reward, addiction, and motor control.

8:30 AM *SB07.03.03/SB02.04.03/SB05.04.03
OPEN SLOT

9:00 AM *SB07.03.04/SB02.04.04/SB05.04.04
Chronic Recordings from Behaving Animals Using Microwire-CMOS Technology Nicholas Melosh; Stanford University, United States

Mammalian brains consist of billions of neurons operating at millisecond time scales, which current recording techniques only capture a tiny fraction. Recent advances in CMOS device design have led to high-recording quality planar probes, with diminishing sizes to ameliorate the extent of tissue damage. Matching these powerful silicon electronics to the inherently three dimensional architecture of the brain has remained challenging however, as devices are constrained to the planar two dimensional surfaces required for silicon processing. Here we describe a chronic interface using arrays of microwires read out by CMOS-based devices with a low-tissue damage, and controllable, three dimensional distribution of recording sites. The core concept is using a bundle of insulated microwires mated to a large-scale CMOS microelectrode array, such as found in modern camera chips or displays.
We show recent results on the mechanics and tissue damage from microwire insertion scales strongly with wire diameter. Microwires with <25µm diameters are shown to have minimal to no vascular disruption or bleeding, as opposed to more conventional 75 to 100 µm devices. These microwires are then arranged into bundles to control the spatial arrangement and three dimensional structure of the distal (neuronal) end, while providing a robust parallel contact plane on the proximal side which is interfaced to a planar pixel array. The modular nature of the design enables a wide array of microwire types and size to be mated to a variety of different CMOS chips, making the same fundamental platform scalable from a few hundred electrodes to tens of thousands. We thus link the rapid progress and power of commercial multiplexing, digitisation and data acquisition hardware together with a bio-compatible, flexible and sensitive neural interface array. We present recent massively parallel recording using mouse and rat models, showing both spiking activity from single neurons and local field potentials within both chronic and acute settings.

9:30 AM *SB07.03.05/SB02.04.05/SB05.04.05
Membrane Curvature at the Interface between the Cell Membrane and Nanoscale Electrodes Bianxiao Cui; Stanford University, United States

The interaction between the cell membrane and the measuring electrode is crucial for sensitive measurement of cell electric activities. We are interested in exploring nanotechnology and novel materials to improve the membrane-electrode coupling efficiency. Recently, we and other groups show that vertical nanopillars protruding from a flat surface support cell survival and can be used as subcellular sensors to probe biological processes in live cells. The nanopillar electrodes deform plasma membrane inwards and induce membrane curvature when the cell engulfs them, leading to a reduction of the membrane-electrode gap distance and a higher sealing resistance. As an electrode sensor, nanoelectrodes offer several advantages such as high sensitivity, subcellular spatial resolution, and precise control of the sensor geometry. Furthermore, we found that the high membrane curvature induced by nanoscale electrodes significantly affects the distribution of curvature-sensitive proteins and stimulates several cellular processes in live cells. Our studies show a strong interplay between biological cells and nanoscale topography, which is an essential consideration for future development of interfacing devices.

10:00 AM BREAK

10:30 AM *SB07.03.06/SB02.04.06/SB05.04.06
Engineering Skin-Like Soft Electrical Interface with Biological Systems Zhenan Bao; Stanford University, United States

In this talk, I will discuss several projects related to engineering conductive materials and developing fabrication methods to allow electronics with effective electrical interfaces with biological systems, through tuning their electrical as well as mechanical properties. The end result is a soft electrical interface that has both low interfacial impedance as well as match mechanical properties with biological tissue. Several applications of such electronics will be presented.

11:00 AM *SB07.03.07/SB02.04.07/SB05.04.07
Soft Materials in Wireless Closed-Loop Neuromodulation Systems for Treating Organ Dysfunction John A. Rogers; Northwestern University, United States

Bioelectronic medicines targeted at the peripheral nervous system have the potential to address a wide variety of diseases, from diabetes to bladder dysfunction. The foundational concepts have existed for decades but implementation has been limited and fraught with persistent challenges, including lack in target specificity, nerve interface biofouling, and inability to acquire real time physiologic signals for conditional delivery of corrective stimuli, leading to excess and unnecessary stimulation. Here we present a set of materials, a treatment strategy and supporting technology platform that address many of these challenges, using bladder control as model system. Specifically, we report capabilities for continuous monitoring of bladder function using an ultralow modulus, stretchable strain gauge to measure dimensional changes, real-time data analytics to identify pathological behavior based on the resulting data, and automated, closed-loop optogenetic neuromodulation of bladder sensory afferents to normalize bladder function in the context of acute cystitis, with generic applicability to many other organ systems and conditions.
Miniature, wireless bioelectronic devices enable less invasive surgical implantation and the ability to target tiny nerves or brain areas. However, as these neural stimulators become smaller, we must engineer new ways to deliver power. Conventional power delivery relies on long wires to deliver power from an implanted battery or subcutaneous antenna. These leads can limit device placement and cause device failure due to lead breakage or infection. Conventional wireless power delivery through biological tissue is difficult when devices are miniaturized and placed deep in the body. Here we show that magnetic materials can effectively harvest energy from magnetic fields and power millimeter-sized bioelectronics. These materials show excellent power densities even as the devices are made small allowing them to be fully implanted and wirelessly powered. We demonstrate that these mm-sized wireless devices can be used to power different types of conventional stimulation electrodes when implanted in rabbits, pigs, and freely moving rats. Furthermore, these miniature electrical stimulators can be adapted to power many individually addressable stimulation channels while still maintaining a small overall device footprint.

1:30 PM *SB07.04.01
Optically-Triggered Dynamics at the Semiconductor-Cell Interfaces Bozhi Tian; University of Chicago, United States

Optically-controlled non-genetic biological modulation represents a promising approach for the fundamental study of biological circuits and the clinical treatment of disorders. Among existing material candidates that can transduce light energy into biologically-relevant cues, silicon and silicon carbide are particularly advantageous due to its highly tunable electrical and optical properties, ease of fabrication into multiple forms, and biocompatibility. In this talk, I will present some of the latest research in our lab, including the use of intracellular silicon for biophysical studies in cardiac system, and doped silicon carbide for several types of biological modulation. I will also present a few new directions where many other soft materials can be incorporated for bioelectronics studies.

2:00 PM *SB07.04.02
Organic Optoelectronic Biointerfaces—Photocapacitive and Photofaradaic Effects Marie Jakesova, Vedran Derek, Malin Silverà Ejneby, Ludovico Migliaccio, Maciej Gryszel and Eric D. Glowacki; Linkoping University, Sweden

We report on development of ultrathin optoelectronic devices for stimulating biophysical processes. All of these devices rely on near infrared irradiation in the tissue transparency window to actuate nanoscale organic semiconductor components. Our flagship technology is the photocapacitor – a device that mimics biphasic current-pulse neurostimulation and thus transduces an optical signal into directly-evoked action potentials in neurons. The devices operate in the tissue transparency window of the near-infrared, where light can penetrate deeply through skin and bone. The motivation is to provide a wireless and minimalistic implant which can perform the duty of standard implantable electrodes, but without the wiring. The devices we fabricate are not only wireless, but also 100-1000 times thinner than most existing technologies. Making implants have as small as possible mechanical footprint improves the efficacy of bioelectronic medical treatments by minimizing the risk for inflammation and making surgical implantation less invasive. On the other hand, the other block of our research efforts is directed at devices which, when stimulated with light, deliver controlled amounts of reactive oxygen species (mostly peroxide). We aim to study the effects of photoelectrochemically-generated peroxides on physiological processes, with the hope of developing novel therapeutic approaches to neurodegenerative diseases.
Bioresorbable Pressure Sensors Protected with Thermally Grown Silicon Dioxide for the Monitoring of Chronic Diseases and Healing Processes Jiho Shin; Massachusetts Institute of Technology, United States

Measurements of pressure in organ systems such as the brain, eyes, bladder and blood vessels form an essential diagnostic basis for the assessment of patient health and progression of diseases such as traumatic brain injury, hydrocephalus (intracranial pressure), glaucoma (intraocular pressure) and hypertension (blood pressure). Therefore, the capacity for precise, continuous monitoring of pressure can be critically important in defining treatment protocols that decrease the rate of morbidity and increase the pace of recovery. Conventional sensor technologies designed for this purpose are available in the form of accurate, implantable devices that must be surgically extracted following clinical use. These procedures are costly and they expose the patient to additional risks of complications. The devices can also serve as a nidus for infection and immune-mediated inflammatory responses. Emerging classes of bioresorbable electronic sensor systems have the potential to address these disadvantages. Here, all of the constituent materials dissolve in biofluids over well-defined periods of time, with biologically benign endproducts. Although recently reported bioresorbable pressure sensors have comparable sensitivity and accuracy to those of conventional, nonresorbable analogues, they offer stable operation over a period of only several days, which is insufficient for many applications. Extending this operational lifetime to several weeks demands solutions to daunting challenges in materials science and device design that follow directly from the requirement that the systems must ultimately dissolve completely, at a molecular level, without adverse effect. This difficulty is inherent to all classes of implantable, bioresorbable systems because immersion in biofluids immediately initiates processes of bioresorption. The most effective method to prolong their lifetimes relies on passive encapsulating layers that delay the time at which biofluids come into contact with the active materials. Bioresorbable polymers such as silk fibroin, poly(L-lactide) and poly(lactic-co-glycolic acid) (PLGA) are attractive for such purposes, but their hydrophilic nature leads to swelling and water permeation, thereby causing premature fracture, buckling and/or dissolution of the underlying materials. Inorganic alternatives such as silicon dioxide, silicon nitride and various metal oxides formed by chemical or physical vapour deposition offer exceptionally slow rates of dissolution, but the extreme difficulties in forming coatings without micro- or nanocracks, pinholes or other defects limit their practical utility.

Here, we demonstrate materials, device structures and fabrication methods for bioresorbable pressure sensors that rely on thermally grown layers of silicon dioxide on device-grade silicon wafers as biofluid barriers with defect-free, materials-level perfection over large areas. Overall fabrication involves bonding of a pair of silicon-on-insulator wafers using adhesion layers of amorphous silica formed by calcination of poly(dimethylsiloxane) (PDMS), followed by elimination of the handle wafers. Data on the biodistribution of dissolved silicon in mice at five weeks following implantation of intracranial sensors formed in this manner, together with assessments of the haematology (complete blood count), blood chemistry and MRI compatibility, confirm their biodegradability and clinical utility. Measurements of intracranial pressures in rats over 25 days illustrate high accuracy and low drift, with an overall performance that compares favourably to that of non-resorbable clinical standards. The results not only establish routes to bioresorbable pressure monitoring technologies that meet requirements for clinical use, but they also serve as a generalizable platform for broad classes of bioresorbable electronic devices that can offer stable operating characteristics over long periods of time.


2:45 PM SB07.04.04
Temporary Tattoo Electrodes in Magnetoencephalography Application Laura M. Ferrari1,2, Usein Ismailov3, Jean-Michel Badier4, Francesco Greco5 and Esma Ismailova3; 1Istituto Italiano di Tecnologia, Italy; 2Scuola Superiore Sant’Anna, Italy; 3École des Mines de Saint-Étienne, France; 4Aix-Marseille Université, France; 5Institute of Solid State Physics, Graz University of Technology, Austria

Recently, ultraconformable TTEs have been adopted in the recording of many electrophysiological signals (1,2). Medical standard wet electrodes are routinely used in electrophysiology thanks to their high signal quality. On the other hand, these electrodes exhibited many disadvantages which impose severe restrictions especially in electroencephalography applications. The major issues are related to their limited time stability, due to gel drying, and to their cumbersome nature. In order to provide an alternative technology in the broad field of brain recordings, we investigated the TTEs capabilities in electroencephalography (EEG) applications and their compatibility with the
magnetoencephalography (MEG). While EEG records the variations of the electrical field generated by cortical pyramidal neurons, the MEG senses modification in the magnetic field, induced by changes of the electric field generated by the same population of neurons. These two techniques are frequently used in combination, thanks to their high temporal resolution. The simultaneous EEG/MEG assessment is essential in the understanding of dynamic cognitive processes and in focal epilepsy diagnostics. The MEG instrumentation is very sensitive to electromagnetic variations. Besides the use of a proper shielded room, also dedicated electrodes are usually adopted to perform EEG/MEG recordings. As an example, ferromagnetic materials are forbidden in order to avoid the generation of magnetic artefacts. Furthermore the vertical profiles of the electrodes has to be minimized to allow an efficient coupling with the MEG sensor. In order to meet these requirements, we exploited TTEs as metal-free and ultra-thin sensors to efficiently combine EEG/MEG recordings. Indeed the fabrication method developed allows the production of sensors that are all made of polymers and with an overall thickness < 1-2 µm. We firstly validated TTEs in EEG application with the recording of alpha waves, the most known and studied brain rhythm. TTEs were also compared with Ag/AgCl electrodes, through Power Spectral Density (PSD) assessment, showing a good match over the whole signal spectrum. Then, the participant, with TTEs laminated on his head, was placed under the MEG apparatus. We were able to record neural activity at different frequencies without any high-density magnetic flux appearance in the electrode’s proximity. The EEG and MEG recordings were performed simultaneously showing well visible alpha waves. To the best of our knowledge, this is the first demonstration of dry organic electrodes performance in joint EEG/MEG assessment.


3:00 PM BREAK

SESSION SB07.05: Flexible Bioelectronics II
Session Chairs: Tzahi Cohen-Karni, Anastasia Elias, Sahika Inal and Christoph Tondera
Tuesday Afternoon, December 3, 2019
Hynes, Level 3, Ballroom B

3:30 PM SB07.05.01
Wearable Organic Electrochemical Transistors for Biomarker Detections Feng Yan; Hong Kong Polytechnic University, China

Wearable biosensing technologies have emerged as an alternative tool for the personalized healthcare management. Compared to the conventional wearable biosensors, organic electrochemical transistor (OECT) -based biosensors can be more sensitive due to the merits of in-situ amplification and ion-to-electron conversion. OECTs have been successfully used in the following applications. (1) The glucose level in sweat can be real-time and wirelessly monitored and analyzed by OECT sensors remotely controlled by a mobile phone (2) Label-free RNA detection has been realized using flexible OECTs based on the interaction between RNA molecules and the organic semiconductor channels. The devices can selectively detect RNA cancer biomarkers down to the concentration of 1 pM. (3) Fabric OECTs are successfully prepared on Nylon fibers and integrated into wearable systems for monitoring glucose and uric acid levels with high sensitivity. All the results clearly indicate that OECT biosensors can be an excellent platform for wearable healthcare monitoring. The wearable biosensing technology has many advantages, such as simple apparatus, quick detection, short waiting time, and versatility for different wearable scenarios, which could revolutionize the current wearable technologies in individual disease diagnosis and health monitoring applications.

3:45 PM SB07.05.02
A Flexible Bioelectronic pH Sensor with Enhanced Sensitivity Based on an Organic ElectroChemical Transistor Erika Scavetta, Federica Mariani, Isacco Gualandi, Beatrice Fraboni and Marta Tessarolo; University of Bologna, Italy
Real-time, non-invasive pH monitoring of biofluids such as human sweat is currently attracting a great deal of interest for accessing information from our body. However, such emerging bioelectronic application poses several constraints to existing sensing technologies, as configurational versatility and ultra-sensitivity stand out as essential requirements. In this scenario, organic electrochemical transistors (OECTs) are promising electronic platforms that can interface the biological domain providing intrinsic signal amplification and they can be exploited as sensing devices without the need of a freestanding reference electrode.

In this contribution, we show the optimisation of pH responsive materials, able to successfully convert a pH chemical signal into an electrical one, which are exploited to modify the gate electrode of the OECT. The semiconducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) was electrochemically doped with pH dyes (Bromothymol Blue or Methyl Orange) and the PEDOT:dye composites were thoroughly investigated by electrochemical and spectroscopic analyses. It was demonstrated that the transduction mechanism of the proposed materials originates from the pH-dependent change of the dyes’ electronic charge. Due to its electrostatic interaction with the polymer backbone, this phenomenon affects the doping level of the semiconducting polymer. The PEDOT:dye composites were employed as sensing element in an OECT configuration to obtain a device that can reliably detect pH variations in the range 1-9 with super-Nernstian sensitivity, taking advantage on the amplification offered by the transistor. Finally, thanks to the OECT major advantages with respect to conventional electrochemical sensors, we assessed the sensor adaptability to a plastic substrate. With our flexible sensor, we were able to estimate the pH of an artificial sweat sample with a standard deviation equal to 0.06 pH units within a medically relevant range.[1] Moreover, the pH sensor was realized on sterile bandage and integrated into a smart patch. With the help of a simple, textile microfluidic system, we made our device compatible with wearable applications and continuum, small-volume sampling of biofluids.


4:00 PM SB07.05.03
Multifunctional Inkjet-Printed Cutaneous MXene Electrodes Abdulelah Saleh, Shofarul Wustoni, Eloise Bihar, Yizhou Zhang, Husam N. Alshareef and Sahika Inal; King Abdullah University of Science and Technology, Saudi Arabia

Skin electronics are rapidly advancing due to the increased interest in wearable electronics, which allows monitoring of various biosignals. Ti$_3$C$_2$ MXene is a promising 2D conducting material for applications in skin electronics. It is biocompatible, easily processable in many solvents, including water, and is highly conductive. Ti$_3$C$_2$ MXene also makes an excellent candidate ink for inkjet printing. However, Ti$_3$C$_2$ MXene has only been shown so far to be printed in organic solvents and alcohols. While these inks are easily processable, they are toxic and introduce difficulties when scaling up, which is the main advantage of printed electronics. Here we report the first inkjet printable aqueous Ti$_3$C$_2$ MXene ink. The films printed thereof that were conductive at even one layer and deposited on various substrates. Ti$_3$C$_2$ MXene films were printed on a conductive flexible substrate to develop a multifunctional sensor that can record ECG signals while detecting Na$^+$ ions and cytokine biomarkers.

4:15 PM SB07.05.04
Patterning Soft and Stretchable Liquid Metal Electrodes for Biological Interfaces Ishan D. Joshipura$^{1,2}$, Collin B. Eaker$^2$, Hudson Ayers$^2$ and Michael Dickey$^2$; $^1$Lawrence Livermore National Laboratory, United States; $^2$North Carolina State University, United States

This work presents approaches to pattern gallium (Ga)-based liquid metal alloys to form ‘softer than skin’ electrodes for biological interfaces. These soft and fluidic conductors exhibit low toxicity, maintain electrical performance under tension and torsion, and are self-healing. Thus, combining Ga alloys with soft materials can form robust biocompatible electrical interfaces. These metals can also integrate with microfluidic platforms for fundamental biological studies (i.e., organ-on-chip). This work reports methods to rapidly (~secs) form liquid metal electrodes onto or within a wide range of materials, including soft polymers, at ambient conditions (i.e., room temperature, atmospheric pressures), and outside clean-room settings. One approach utilizes the adhesion of the native surface oxide of Ga to simply ‘paint-on’ liquid metal electrodes. This oxide ‘skin’ (~3 nm) can serve as a stretchable and self-healing dielectric for capacitive sensing (~0.1 μF/cm$^2$) and ultra low-voltage electrowetting (0 to 2 V). Alternatively, injecting liquid metal into molds placed against rough surfaces enables patterning of liquid metals into arbitrary designs. Because the interface with the rough surface is non-wetting, the mold can peel off to form open-
to-air electrical contacts. As a result, this technique forms open surface patterns of conductive traces of liquid metal that can interface directly with biological tissues, be transferred onto other substrates, or encapsulated by other materials.


4. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. IM Release Number: LLNL-ABS-762385

4:30 PM SB07.05.05

**Flexible and Transparent Reduced Graphene Oxide Strain Gauges with Extremely High Gauge Factor**

Joe Neilson and Brian Derby; University of Manchester, United Kingdom

Flexible and transparent strain gauges are of interest for applications such as: e-skins, wearable sensors, voice recognition, and haptic sensing. Development of sensors with high displacement sensitivity which are flexible and transparent remains a challenge. Here, we present the simple and efficient assembly of highly sensitive, flexible and transparent resistive strain sensors formed from sheets of reduced graphene oxide (RGO) assembled at the interface between immiscible solvents.

Previous work on graphene based strain sensors relied on the percolation of electrical current through a network of overlapping graphene flakes deposited on a flexible substrate. As the substrate is strained the stiffer graphene flakes slide past each other and change the resistivity of the network leading to stable and repeatable strain gauges with gauge factors (GF) in the range 100 – 300. [1,2] Thin film sensors with gauge factors around 1000 have been fabricated that exploit networks of cracks that form in thin conductive films, these have GF of around 1000 but the conductive films are opaque to light. [3,4]

In this work, nanoflakes of electrochemically exfoliated graphene oxide (EGO)[5] were assembled at the interface of immiscible solvents to generate an ultrathin film of EGO. By initiating gradients of interfacial tension at the liquid/liquid interface, the EGO film is placed in compression and this generates efficient packing and flake edge contact without significant flake overlap. The ultrathin film was transferred onto flexible and transparent substrates of polydimethyl siloxane and the resulting thin film is a monolayer of EGO flakes with minimal overlap and predominantly edge to edge contact between flakes. The packing density of the transferred films is high (92 %). After chemical reduction, the resulting RGO thin films were highly transparent (transmittance 88 % at 550 nm) and conductive (10000 S/m).

The thin films of RGO on flexible substrate were analysed for their mechanosensing capabilities. To our knowledge, the gauge factor of the strain gauges is the highest reported for graphene oxide based sensors (>2000 over 2% strain). The extremely high gauge factor is enabled by the formation of nanoscale cracks perpendicular to the direction of strain which cause disconnection and reconnection of the RGO film.

References


4:45 PM SB07.05.06

**Breathable, Single-Crystalline Electronic Skin**

Hanwool Yeon, Yeongin Kim, Jaekang Song, Wei Kong, Jiho Shin, Kuan Qiao, Sungkyu Kim, Jaeyong Lee, Sanghoon Bae, Peng Lin and Jeehwan Kim; Massachusetts Institute of Technology, United States

Electronic skin patch represents one of the mainstream innovations in human/Internet of Things (IoTs) interfaces technologies, enabling communication of bio-information obtained from the skin to computing machines. For the long-term communication without damping of the device performance during an extraction of the body information
as well as transmission of the data, an interface-stable, conformal contact of the electronic patch on the skin has been developed. Surprisingly, amid this sweeping trend, human skin has been treated mostly as a curvilinear surface for mounting electronic patches to monitor health of internal organs and neglects to recognize how these may affect the biological functions of the skin. Skin is the outmost and the largest organ covering the entire body surface, protecting inner organs from various external hazards and perspiration through the skin pores are essential for preserving the homeostasis of the human body via temperature regulation and water retention. However, non-breathable electronic skin induces degradation of physical properties of skin, more importantly, deterioration of barrier functionality against viruses will lead to secondary infections and complications with physiological problems. Therefore, the electronic skin patch should possess open-spaces that do not block sweat and maintain a perspiration for long-term health monitoring with securing homeostasis of the skin. Here we introduce a platform of breathable electronic skin that can permeable to sweat as well as vapors, showing ~100% breathability on the skin, via a sweat pore-inspired through-holes on thin-film electric modules and skin-like, soft patch. We have engineered through-hole structures by forming ‘dumbbell’ patterns that include kirigami patterns (auxetic fractal cuts) at the patches with drilling the circular holes at the sharp edges of fractal cuts. Such kirigami fractal cuts enhance conformability of the patches on the skin by increasing biaxial expandability while rounded hinges of the cuts prevent stress-localization-induced crack. Dumbbell patterns also drive skin-like elastic modulus of patches, resulting in an imperceptible lamination onto the skin. More importantly, dumbbell hole patterns form open-space onto sweat pore, enabling sweat penetration through the electronic skin in addition to the vapor, thereby long-term attachment without sweat trapping at skin/patch interface. Additionally, such dumbbell-patterned patch system exhibits excellent mechanical endurance (1,000,000 fatigue cycles with 5% strain cyclic loadings). With this precisely engineered skin patches and interconnects, we have developed the method to heterointegrate single-crystalline freestanding semiconductors on them to maximize the sensitivity of the electronic skin. As a sample case for an ultrasensitive sensor, we have integrated 200-nm-thick single-crystalline GaN freestanding membranes on our advanced skin patch. GaN has been selected as it is bio-compatible while its piezoelectric properties can be maximized when it is free from substrate clamping. Thus, high quality GaN epitaxial films are prepared by remote epitaxial growth on graphene-coated GaN wafers followed by mechanical exfoliation from graphene surface. GaN sensor arrays exhibit ultrahigh strain sensitivity with ~5000 of gauge factor (GF) and 0.001% of strain sensing limit without a signal amplifier. This enables monitoring a nanometer-scale mechanical deformation of stratum corneum that contains clinical information such as dehydration and skin complications, unravelling a kinetics of natural skin movement. Our breathable electronic skin system with freestanding single-crystalline sensors lay foundation for developing ultrasensitive electronic skins for monitoring various biomarkers from human body by applying variety of single-crystalline functional materials as active parts in the breathable electronic skins.

SESSION SB07.06: Poster Session I: Bioelectronics I
Session Chairs: Tzahi Cohen-Karni, Anastasia Elias, Sahika Inal and Christoph Tondera
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB07.06.01
3D Graphene Integration with Skeletal Muscle Yongdeok Kim, Gelson Pagan-Diaz, Judy Suh and Rashid Bashir; University of Illinois, United States

Graphene has been spotlighted as a promising nanomaterials for biological applications such as bioelectronics, imaging, drug delivery, and tissue engineering because of its unique and outstanding optical, electrical, mechanical, and biological characteristics. Especially, regenerative properties of graphene and its derivatives let them broadly used for tissue engineering and regenerative medicine area. Among its tissue applications, it is very interesting for skeletal muscle with graphene because it can effect on the adhesion, proliferation, and myogenesis. Skeletal muscles, serving the primary actuator in animals, have been used for biohybrid actuators in the soft robotics field. Integration of a three dimensional (3D) engineered skeletal muscle embedded in extracellular matrix (ECM) with 3D printed hydrogel skeleton ranging from mm to cm scale enabled a locomotion from electrical or optical stimulation for walking or pumping functions. If the biohybrid machine can integrate with electronics, it can be very synergetic
for various functions with electrical applications such as electrical actuation control and sensing.

In this regard, the integration of the conductive graphene electrode with a 3D skeletal muscle tissue has a great potential for electrical applications of biological systems due to its biocompatibility and significant electrical properties. However, its applications for skeletal muscle have been limited on 2D cultured cellular system not for 3D due to the 2D nature of graphene. Although 3D structured graphene systems as a tissue scaffold have been reported using 3D printing or dry spinning with graphene derivatives such as reduced graphene oxide or graphene oxide, they have limited electrical conductivity due to the presence of insulating polymer. In addition, the reduced graphene oxide has a worse uniformity compared with chemical vapor deposition (CVD) synthesized graphene. Several previous work has been reported for the 3D integration using CVD grown graphene using a thin poly (methyl methacrylate) (PMMA) as a supportive layer. However, the PMMA based wet transfer is limited for the biological application due to its cytotoxicity. Although the PMMA layer was removed after graphene transfer, it is difficult to remove the layer perfectly and the remained residue can be problematic for biological applications.

Here, we report a novel 3D graphene transfer method using a poly (ethyelne glycol) diacrylate (PEGDA) supportive layer and its integration with 3D skeletal muscle ring. A softer PEGDA layer enabled the conformal integration of graphene with a millimeter scaled 3D printed PEGDA pillars. The softer PEGDA supportive layer which has a 10^5 times lower Young’s modulus compared with PMMA made a conformal integration with 3D printed pillars, followed by integrated with the muscle ring. Considering the PEG is an FDA approved biocompatible material, it can be a good candidate for 3D biological application with electronics. The 3D integrated graphene on the 3D printed pillars was characterized using Raman spectroscopy and electrical conductivity was measured. As an electrical application with 3D electrode integrated tissue system, the 3D muscle ring on the integrated structure was actuated by electrically with different voltages and frequencies through the transferred graphene which contacts to muscle ring. We believe that it can be a potential integration platform of electronics with 3D in-vitro tissue for electrical applications in the soft robotics or tissue-on-a-chip areas.

SB07.06.02
Biodegradable Polycarbonate IonGels for Electrophysiology Measurements Luca Porcarelli1, Alexander Y. Yuen1, Roberto H. Aguirresarobe1, Ana Sanchez-Sanchez2, Isabel Del Agua1, Usein Ismailov3, George G. Malliarias2, David Mecerreyes1, Esma Ismailova1 and Haritz Sardon1; 1University of the Basque Country, Spain; 2University of Cambridge, United Kingdom; 3Ecole Nationale Supérieure des Mines, France

In recent years, polymer matrices loaded with ionic liquids - namely iongels - have emerged as promising materials for long-term cutaneous electrophysiology. Iongels display high ionic conductivity, negligible vapor pressure and can be designed on demand. Despite the attractive properties, the availability of biocompatible and biodegradable iongels remains scarce. In this work, biodegradable polycarbonate-based iongels were prepared by organo-catalyzed ring-opening polymerization of N-substituted cyclic carbonate monomers in the presence of imidazolium lactate ionic liquid. Our iongels were able to incorporate up to 30 wt% of ionic liquid without compromising the mechanical properties. The ionic conductivity of these iongels increased with the amount of free ionic liquid, up to 5×10^-4 S cm^-1. Additionally, we showed that the polycarbonate matrix of the iongel can undergo hydrolytic bond cleavage, returning non-toxic degradation products. The iongels reduced the impedance of gold electrodes placed on the skin, and were used to record physiologic signals with accuracy levels similar to that of commercial Ag/AgCl electrodes. The low toxicity and biodegradability of polycarbonate-based iongels make these materials highly attractive for cutaneous electrophysiology applications.

SB07.06.03
Highly Flexible Multi-Modal Capacitive Pressure Sensors Responsive over Wide Pressure Range for Artificial Skin Haechang Lee1, Hanul Moon2 and Seunghyup Yoo1; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2Stanford University, United States

Human skin recognizes the information of shape and texture of various objects by sensing tactile and pressure changes in space over a wide dynamic range. In order to mimic such functionalities, artificial skin should not only be sensitive in low pressure range (e.g. tactile stimulation and measure of artery pulse, etc.) but also should be able to detect mid-to-high pressure change. In addition, it is desired to be thin enough to be applicable to various objects. For this reason, film-type pressure sensors using a variety of materials and structures have been widely studied in recent years. However, it has been challenging to realize a wide pressure sensing range and high flexibility at the
same time, because there is a trade-off relationship between wide range and thickness of the pressure sensors. Furthermore, the problem becomes more severe when one tries to realize a multi-modal sensor having high sensitivity in low pressure region as well.

In this study, we propose a flexible capacitive pressure sensor based on topographically patterned arrays of concaved ionic gels as a dielectric layer whose capacitance is responsive to applied pressure, which are positioned in between two substrates having electrodes. The ionic gel film is electrically suitable for high sensitivity due to ultra-high capacitance based on electric double layers, and it is also promising in terms of mechanical properties as a pressure sensing material because it has low Young’s modulus similar to that of rubber. By structuring the surface of the ionic gel film with concave shape of several micro-meter scale to utilize compression of air confined between the structure and an electrode, linear response to large pressure range of over 100 kPa has been obtained. In addition, the complete pressure sensor can be highly flexible because the thickness of the ionic gel film can be reduced near or even below 10 μm. By using an appropriate surface structure of ionic gel film, the sensor shows distinctive responses to low and high pressure regions, respectively, thus demonstrating a multimodal sensing capability for both tactile and pressure signals.

With the overall thickness of the proposed pressure sensor being as low as ca. 15 μm, it exhibits a high degree of mechanical flexibility. Together with this, multi-modal sensing capability, the proposed pressure sensors are expected to be highly beneficial as a key element for artificial skin, which can be important in human-machine interfaces and healthcare products for disabled people.

**SB07.06.04**

**Spatial Modulation of Hydrogel Stiffness for Soft and Integrated Wearable Electronics** Hao Liu¹, Moxiao Li¹, Pengpeng Jia¹, Tian J. Lu², Fei Li¹ and Feng Xu¹; ¹Xi’an Jiaotong University, China; ²Nanjing University of Aeronautics and Astronautics, China

One major conundrum that impedes the development and application of the emerging soft and stretchable electronics lies in the integration of electronic components with soft substrates for rational combination of various device functionalities into a single wearable state, since the rigid, nondeformable electronics tend to detach from the deformable substrate under mechanical loadings like stretch. Modulating the stiffness of soft materials in a spatially controllable manner provides a promising solution to this rigid-soft coupling challenge, by shielding the local strain of rigid components while maintaining the stretchable property of soft substrates. Hydrogels with superb biocompatibility and skin-like mechanical features are ideal candidates to interface human body and electronic functionalities for the cutting-edge wearable uses, where there exists a major challenge of spatially modulating stiffness of hydrogel to meet the application demands.

In the present work, we develop a facile and straightforward scheme to spatially modulate hydrogel stiffness through local stiffening of the hydrogel. Locally stiffened patterns on hydrogel featuring highly increased stiffness compared to that of the raw hydrogel can be easily achieved via additional crosslinking the hydrogel. For example, the polyacrylamide-alginate (PAAm-alginate) hydrogel demonstrated here is locally stiffened through additional crosslinking with multi-valent ions in specifically designed areas. The local stiffness of hydrogel can be controllably adjusted by tuning ion concentration and the time of additional crosslinking, providing one order of magnitude enhancement of hydrogel stiffness. The locally stiffened hydrogel shows excellent strain shielding efficacy with only ~12% actual strain observed in the stiffened area, relative to a 100% strain applied to the whole hydrogel substrate. With this strategy, rigid electronic components can be directly mounted onto the locally stiffened sites on hydrogel to isolate strains as induced by substrate stretch. We further develop a hydrogel-based multifunctional integrated electronic device and its satisfactory performance in monitoring temperature, UV exposure and EMG signals unveils the brilliant prospect for advanced wearable healthcare applications.

**SB07.06.06**

**Ultra-Efficient and Highly Water-Insensitive Self-Healing Sensing Platforms** Muhammad Khatib; Technion-Israel Institute of Technology, Israel

Imparting self-healing capabilities into soft electronic devices and sensors has been of outmost importance for increasing long-term reliability and sustainability. Though some advances have been made in this endeavor, the use of self-healing electronics in environment of wet and/or (under)water has been most challenging. Herein, we report
on a new self-healing thermoplastic elastomer having high stretchability and mechanical strength that can reach 1000% and ~ 6 MPa, respectively. The elastomer exhibits high (>90%) self-healing efficiency in harsh humidity and/or (under)water conditions without the assistance of any external physical and/or chemical triggers. Flexible electronic devices, chemical and electrochemical sensing platforms were demonstrated to operate in extreme wet or underwater conditions (e.g., salty sea water). Moreover, the healing process eliminates significant electrical leakages that would have been caused by structural damages. The healing process can reach ~90% efficiency, in terms of mechanical strength, within ~ 24 hr even after multiple harsh mechanical scratches or cuts. These highly-efficient and self-healing properties would serve as a shuttling pad for extending the use of flexible electronics outside lab applications and for widening the spectrum into wide variety of wet (implants) and sub-marine applications.

**SB07.06.07**

**Conductive, Self-Healing Interfaces** Antonio Riu¹, Gabriel Gaal¹, Carlos Avila-Avendano², Anerise Barros², Mônica J. Andrade², Varlei Rodrigues¹, Manuel Quevedo-Lopez² and Ray Baughman²; ¹Universidade Estudal de Campinas, Brazil; ²The University of Texas at Dallas, United States

Soft and healable structures mimicking biological systems have received great attention due to their applications in flexible electronics, soft robotics and bioelectronics. The layer-by-layer technique is a simplified, elegant way to form nanostructures having molecular level thickness control, and homogeneous dispersions of materials for the formation of multifunctional nanocomposites. Thereafter, poly(ethyleneimine) (PEI) and poly(acrylic acid) (PAA) LbL matrices have been extensively explored in this task due to its intrinsic self-healing ability when in contact with water at ambient conditions. Here, we studied the incorporation of conductive materials (metallic nanoparticles, PEDOT:PSS and reduced graphene oxides) in the (PEI/PAA) LbL matrix in order to check a balance between healing and electrical properties. The main motivation has been the fact that the increase in the electrical conduction of the composites implies in a decrease in the healing ability. Electrical and mechanical characterizations were performed in distinct molecular architectures, with multiple healing cycles verified in one case that presented high electrical transport.

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**SB07.06.08**

**Self-Healable Organic Electrochemical Transistor with High Transconductance, Fast Response and Long-Term Stability for Robust Bioelectronics** Wei Lin Leong, Jieun Ko, Xihu Wu and Abhijith Surendran; Nanyang Technological University, Singapore

Organic electrochemical transistors (OECTs) are highly attractive for applications ranging from circuit elements, neuromorphic devices to transducers for biological sensing and the archetypal channel material is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), PEDOT:PSS. The operation of OECTs involves the doping and dedoping of a conjugated polymer due to ion intercalation under the application of a gate voltage. The major challenges in developing self-healable conjugated polymers for organic electrochemical transistors (OECTs) lie in maintaining good mixed electronic/ionic transport and the need for fast restoration to the original electronic and structural properties after the self-healing process.

Herein, we demonstrate ionic liquid doped PEDOT:PSS that shows good mechanical properties, robust towards physical deformation and further capable of showing high transconductance, fast transient response and high device stability over 3600 switching cycles.[1] Next, we provide the first report of an all solid state OECT that is self-healable and possess good electrical performance, by utilizing a matrix of PEDOT:PSS and non-ionic surfactant as channel, and ion conducting poly(vinyl alcohol) hydrogel as a quasi-solid-state polymer electrolyte. The fabricated OECT exhibits high transconductance (maximum 54 mS), on/off current ratio of ~1.5×10³, fast response time of 6.8 ms and good operational stability after 68 days of storage. Simultaneously, the OECT showed remarkable self-healing and ion-sensing behaviors and recovered ~95% of its ion sensitivity after healing. These findings will contribute to the development of high performing and robust OECTs for wearable bioelectronic devices.

Sheet-Type Instrumentation Amplifier Integrated with Bio-Conformable Organic CMOS Circuit and Thin-Film Resistors
Masahiro Sugiyama1,2,3, Takafumi Uemura1,3, Masaya Kondo1,2,3, Mihoko Akiyama1, Naoko Namba3, Yumi Inoue1, Shusuke Yoshimoto1, Tepppei Araki1,2,3, Yuki Noda1 and Tsuyoshi Sekitani1,2,3; 1The Institute of Scientific and Industrial Research, Japan; 2Osaka University, Japan; 3Advanced Photonics and Biosensing Open Innovation Laboratory, National Institute of Advanced Industrial Science and Technology (AIST), Japan

In this study, we have developed a sheet-type biosignal voltage amplifier integrated with fully flexible electronic components. The biosignal amplifier comprises from thin-film resistors and CMOS circuits with organic thin-film transistors (OTFTs). All electronic components were integrated on a single 1-μm-thick polymeric foil, therefore showing high mechanical flexibility and conformability to attach on a soft human skin surface. The sheet-type amplifier shows high signal gain over 55 dB that can be tunable by the resistance control of feedback thin-film resistors. The use of such flexible voltage amplifier would play a significant role as an analog-front-end of wearable bioelectrical interfaces for processing human physiological activities.

Flexible and bio-conformable organic circuits are expected to build active electronic components of wearable medical and healthcare applications. In this sense, various kinds of fabrication processes and materials have been intensively studied to realize high performance OTFTs[1,2]. However, electronic circuits with OTFTs such as voltage amplifier are not still satisfactory to condition weak biological information with high signal integrity due to the substantial electrical variations in OTFTs and the lack of flexible passive components such as resistors and/or capacitors with high yield.

The developed circuit is based on an instrumentation amplifier with integration of organic CMOS operational amplifier circuits and film metal resistors. The organic operational amplifier comprises from p-type and n-type OTFTs, and exhibits the high amplification gain of 2,185 ± 272 with the low supply voltage below 3 V. Parylene dielectrics with the surface modification of thermally-evaporated triptycene layer were used for the gate dielectrics, enabling field-effect mobility of 0.68 cm²/Vs for p-type OTFTs and 0.12 cm²/Vs for n-type OTFTs. Thin-film resistors were realized by the 3-nm-thick and 14 μm-wide nichrome layers with the sheet resistance of 765 Ω/square. We also implemented compensation techniques on the organic circuit utilizing top-gate structures to reduce the electrical variations in the amplifier, enabling low input offset voltage ~ 0 V.


Printed, Ultrathin and Transparent Organic Electrochemical Transistors via Selective Wetting and Thermal Lamination for Soft Bioelectrical Interfaces
Ashuya Takemoto1,2,3, Teppei Araki1,2,3, Yuki Noda1, Takafumi Uemura1,3 and Tsuyoshi Sekitani1,2,3; 1ISIR, Osaka University, Japan; 2Graduate School of Engineering, Osaka University, Japan; 3Advanced Photonics and Biosensing Open Innovation Laboratory, National Institute of Advance Industrial Science and Technology (AIST), Japan

This work reports on ultrathin and transparent organic electrochemical transistors (OECTs) fabricated with printing technologies of selective wetting and thermal lamination. The printed OECTs exhibit high transconductance of gm = ~0.97 mS, high stability to diluted-water washing (~8.7% change in gm), and mechanical durability to crumpling. Furthermore, the biosignal amplification using the printed OECTs can be demonstrated. These features of printability, high gain, washability, and flexibility would be suitable for disposable and soft bioelectrical interfaces. OECTs are attracting interest as ideal bioelectrical interfaces because of many advantages such as low-voltage operation, high transconductance, and biocompatibility [1–3]. Recently, the OECTs have been constructed in ultrathin design with 2–4 µm thickness and used as soft bioelectrical interfaces to evaluate brain and heart activities [2, 3]. Until now, the ultrathin OECTs have required the complicated fabrication process such as photolithography, but they could be more cost-effective by manufacturing with low-cost and high-throughput printing technologies. However, the ultrathin OECTs are still limited to inert gold electrodes prepared with thermal vacuum evaporation, because O2 plasma process to prepare through holes in OECTs encapsulation layers can easily dysfunction most printable electrodes such as metal nanomaterials, nanocarbons, and conductive polymers.

Here, this work introduces the thermal lamination process for encapsulation of printed ultrathin OECTs. First in the fabrication, transparent silver-nanowires (AgNWs) electrodes and PEDOT:PSS active layers are printed by using a selective-wetting method with hydrophilic/hydrophobic surface patterns. Then, for the encapsulation, a parylene film with through holes is thermally laminated onto a base parylene film with AgNWs and PEDOT:PSS. This thermal lamination allows us for the low gate-leakage current, and for the narrow ion-electron interaction sites (=
channel areas with ~100 µm width) between PEDOT:PSS and electrolytes. The completed OECTs achieve stable low-voltage operation < 0.6 V with negligible changes in \( g_m \) after diluted-water washing (~8.7% change) and under white-light illumination (~0.35% change). Furthermore, the OECTs exhibit high transconductance of \( g_m = \sim 0.97 \) mS, comparable to OECTs fabricated with inert gold electrodes [2, 3], and mechanical durability to crumpling (~25% change) due to the ultrathin design with total 2 µm thick. This presentation will show the detailed information on the printing technologies, the OECTs properties, and biosignal (ie. EEG, ECG) amplification demonstration.


SB07.06.14
Building High-Performance FETs at DNA-CNT Interface Mengyu Zhao1, Kexin Wang1, Ming Zheng2 and Wei Sun1; 1Peking University, China; 2National Institute of Standards and Technology, United States

Building high-performance field-effect transistors (FETs) is the foundation towards using CNTs in future high-performance logic circuits, flexible sensors and diagnostic platforms. In particular, aligned CNT arrays with both parallel orientation and evenly small spacings promote on-state performance and accelerate on-off switching. Conventional thin-film approaches produce inter-CNT spacings down to 2 nm, on the cost of wide orientation and crossing CNT junctions, which lead to large subthreshold swing (slow on/off switching) around 500 mV/dec.

Self-assembled biomolecular templates, especially DNA, exhibit complex in silico designed morphologies and atomic-precise dimensions. Using biomolecule-templated fabrication, CNT FETs have been constructed with prescribed CNT orientations. However, surface charges and metal ions within biomolecular templates surround the assembled CNTs, which screen the gate modulation and increase the scattering of charge carriers. As results, the biomolecule-templated FETs typically exhibit one order of magnitude worse on-state performance and on/off switching compared to those fabricated from non-biomolecule approaches.

We here develop a general strategy in constructing high-performance FETs at biomolecule (DNA)-CNT interface. CNTs aligned onto self-assembled DNA templates exhibit uniform inter-CNT spacing down to 8 nm. Next, we explore the impact of DNA at the FET channel area. Within a top-gated PMOS FET, high-concentration DNAs negatively shift the threshold voltage, and increase the doping level at n-region. Furthermore, we invent a method that eliminate DNA templates without affecting the CNT alignment after DNA removal. Using this method, we finally construct multi-channel CNT FETs with record-high transport performance in biomolecule-templated FETs (10 folds better than previous records). Both high on-state conductance (exceeding 0.3 mS/um) and fast on/off switching (less than 150 mV/dec) have been simultaneously demonstrated within a same FET, which is still challenging via conventional thin-film-based approaches.

More generally, current strategy could be used to construct diverse devices at biology-electronics interface, including bio-compatible or bio-implantable optoelectronics and multiplexed sensors. It could also be used to construct 3D device architectures over wafer scale, thus building a bridge between precise biomolecular self-assembly and high-performance electronics.

SB07.06.15
Highly Stretchable Organic Electrochemical Transistors Yang Li1, Shiming Zhang2 and Fabio Cicoira1; 1Polytechnique Montréal, Canada; 2University of California, Los Angeles, United States

Organic electrochemical transistors (OECTs) become suitable candidates for biological interfacing and logic circuitry applications due to the synthetic tunability, facile fabrication, and bio-compatibility. Our group has demonstrated stretchable OECTs can be stretched up to 30% strain while maintaining identical transistor characteristics via optimizing the processing conditions during device fabrication. However, some circumstances, such as heart beating monitoring, require electronics to withstand larger strain comparing with wearable electronics on the skin (30% strain). In this talk, we show that the addition of polyethylene glycol (PEG) can greatly enhance the stretchability of conducting polymer films on the elastomer. With the formation of microcracks at a pre-set strain, the conducting polymer can maintain a stable current during high strain stretching cycles. As a result, the OECTs using highly stretchable conducting polymers as the channel material can keep the same performance during
stretching even at strain higher than 30%. This work paves the way for OECTs applications as conformable biosensors or bio-electronics which need to endure high strain, such as heartbeat monitoring.

References

SB07.06.16
Transfer-Printing PEDOT:PSS Films with Hydrogels Haonan Ling, Shiming Zhang, Ali Khademhosseini and Martin Hartel; University of California, Los Angeles, United States

The use of conducting polymer PEDOT:PSS for the development of flexible organic bioelectronic devices, such as organic electrochemical transistors (OECTs), is growing fast [1] [2]. However, direct manipulation of PEDOT:PSS thin films on flexible substrates remains challenging [1] [3]. Transfer printing films from glass to flexible substrates offers an alternative solution. In this communication, we report that PEDOT:PSS thin films on glass substrates, once mixed with surfactants such as dodecylbenzene sulfonic acid (DBSA), can be delaminated with hydrogels and thereafter transferred to flexible substrates without any further treatments. The proposed method allows easy, fast, and reliable transfer of patterned PEDOT:PSS thin films from glass substrates to various soft substrates, facilitating their application for soft organic bioelectronics. We take advantage of this method and demonstrate a skin-attachable OECT prototype, which is relevant for conformable, lightweight, and wearable biosensing.


SB07.06.17
Ultra-Low Fouling PCB Layer on PEDOT:PSS Based Organic Electrochemical Transistor for Sensitive Ion Detection in Human Serum Shin-Ya E. Chen, Erjin Zheng and Qiuming Yu; University of Washington, United States

Organic Electrochemical Transistor (OECT) is a voltage to current transducer with high transconductance (~1 mS) and low operating voltage (< 1 Volt). These features make OECT a good candidate as biosensor. Instead of typical solid dielectric material used in Organic Field Effect Transistor (OFET), electrolyte is used to couple gate and channel in OECT. In particular, ions which injected from electrolyte to channel will either dope or de-dope the channel conducting polymer (CP) and modulate the bulk conductivity of channel. The ion injection lies in the center of all OECT applications. If ions can’t diffuse into CP channel, the OECT will operate as an electrolyte-gated OFET with smaller transconductance. To date, the most common used CP material in OECT is Poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) (PEDOT:PSS) due to its high conductivity and solution processability. PEDOT:PSS based OECT had been used for cation detection as well as detecting metabolites and protein biomarker concentration in Phosphate-buffered Saline (PBS) solution. However, when tackling with human serum or plasma, albumin and other proteins will non-specifically attach onto channel CP surface. This may hinder the ion injection and cause the false detection results for PEDOT:PSS based OECT biosensor.

In this work, we covalently link a roughly 30 nm thick copolymer with carboxybeteaine functional group on top of PEDOT:PSS based OECT device. We then investigate the device ion sensing ability after the surface is exposed to 5 Wt% Bovine Serum Albumin (BSA) solution or human serum. The copolymer used is PCB(30%), poly(Carboxybeteaine acrylamide (CBAA) -co- n-buty methacrylate (BMA) -co- N-(4-benzoylphenyl) acrylamide (BPAA)), with CBAA, BMA and BPAA at 7:2:1 ratio. While in contact with aqueous solution, the carboxybeteaine functional group will flip onto surface and prevent the non-specific adsorption. The BMA functional group helps the copolymer to attach onto the surface while the BPAA functional group reacts with alkyl backbone of CP after UV
Biocompatible microbatteries have a high potential as energy sources for a wide range of applications—electronic medical implants, health monitoring devices, and environmental sensors. One concrete example of the application of such microbatteries is in ingestible electronic devices. These devices can be employed for regular monitoring of vital body functions such as core body temperature, pH level, for controlled drug release, and for checking of medication adherence. Presently, ingestible electronic devices are usually powered by relatively large batteries that often contain toxic materials. As a consequence, the whole battery necessitates encapsulation to avoid any leakage of potentially harmful substances into the body, but this also makes the devices difficult to swallow and increases the risk of retention inside the body. Moreover, fabrication of the batteries is mainly based on conventional, macroscale techniques and therefore possesses only limited prospects for miniaturization and mass production. Previously, we developed a primary biocompatible microbattery that was entirely realized by conventional microfabrication techniques. However, the thin film electrodes (thickness about 2–3 µm) had only limited capacities of about 0.5–0.8 µA h, enabling operating times of about 10–25 minutes.

To overcome these limitations and to increase the capacities, we have developed microbatteries that can be realized by a combination of conventional microfabrication and direct printing of the active materials using functional inks. The device consists of two main parts: a Si microreservoir that is filled with the electrolyte (gastric acid) once the device is swallowed, and the microbattery itself. The Si microreservoir was fabricated by dry etching in Si, which was then bonded to a glass wafer that contained the microbattery. For the fabrication of the cathode and anode, Au thin films were first deposited as current collectors (nominal size 0.7 × 3.2 mm²), using standard photolithography followed by sputtering. The anode ink consisted of Zn powder that was mixed with ethyl cellulose as binder and acetylene black to increase the conductivity, while Ag/AgCl ink was used for the cathode. Both Ag/AgCl cathodes and Zn anodes were printed directly on the current collectors using a custom-made 3D printing system, allowing electrode thicknesses of the order of 100–150 µm. The performance of the microbatteries was assessed by galvanostatic testing in simulated gastric fluid (pH 1.2) at current levels ranging from 2 to 10 µA. Compared to the sputtered thin film electrodes, the printed electrodes enabled increasing the capacities to about 10 µA h. It is expected that by optimizing the ink composition, especially the content of the active materials, that the capacities can be increased further. The combination of established microfabrication techniques with direct printing is expected to enable more complex microbattery architectures, allowing customized and easier-to-integrate energy sources in future electronic devices aimed at medical and environmental sensing applications.

**SB07.06.18**

**Microbatteries for Ingestible Electronic Devices Realized by Combining Conventional Microfabrication with Direct Printing**  
Sven Stauss, Ryuichi Miyazaki, Yoshiyuki Gambe and Itaru Honma; Tohoku University, Japan

Biocompatible microbatteries have a high potential as energy sources for a wide range of applications—electronic medical implants, health monitoring devices, and environmental sensors. One concrete example of the application of such microbatteries is in ingestible electronic devices. These devices can be employed for regular monitoring of vital body functions such as core body temperature, pH level, for controlled drug release, and for checking of medication adherence. Presently, ingestible electronic devices are usually powered by relatively large batteries that often contain toxic materials. As a consequence, the whole battery necessitates encapsulation to avoid any leakage of potentially harmful substances into the body, but this also makes the devices difficult to swallow and increases the risk of retention inside the body. Moreover, fabrication of the batteries is mainly based on conventional, macroscale techniques and therefore possesses only limited prospects for miniaturization and mass production. Previously, we developed a primary biocompatible microbattery that was entirely realized by conventional microfabrication techniques. However, the thin film electrodes (thickness about 2–3 µm) had only limited capacities of about 0.5–0.8 µA h, enabling operating times of about 10–25 minutes.

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Recent advances in soft electronics have enabled a class of bio-integrated sensors that combine advanced sensing functionality with skin-compliant form factors that reduces contact resistances and motion artifacts. Research efforts have yielded a range of biophysical and biochemical sensors for measurements of motion, electrophysiology, sweat biomarkers, temperature and several other clinically relevant quantities.

Here, we demonstrate the use of arrays of thermal sensors and actuators to map out heat transfer through soft tissue and extract properties such as thermal conductivity, thermal diffusivity and volumetric heat capacity. The low thermal masses and contact resistances of these sensors are uniquely suited to making these precise, quantitative thermal measurements to extract depth-dependent tissue properties as they correlate to vascular perfusion, skin hydration and overall activity level. We will discuss three broad areas where we have made significant recent progress:

1. **Measurements of skin thermal transport properties for a range of clinical conditions:** The thermal transport properties of skin are determined by its constituent materials, including vasculature and free and bound water molecules. These constituents change in response to activity levels and changes in ambient thermal conditions, a critical mechanism for thermoregulation. We present materials, mechanics and thermal transport considerations to map out heat transfer as a correlate for each of the above, with systematic validations in the form of benchtop studies, finite element analyses and on-body testing. These sensors can also be used to map directional, anisotropic thermal transfer in the presence of flow through large blood vessels or implanted catheters. We discuss the potential of these materials advances to in the creation of a class of wearable flow sensors to fundamentally improve the care and treatment of patients suffering from hydrocephalus, a neurological condition caused by the buildup of cerebrospinal fluid in the ventricles of the brain.

2. **Fully implantable flow sensors to map vascular changes through peripheral nerves:** The peripheral nervous system represents a large research area for materials scientists and neuroscientists alike, presenting challenges due the mechanical mismatch between soft, deformable nerves and traditional rigid, metallic recording electrodes. Here, we discuss our recent work in creating a class of soft, tissue-compliant nerve ‘cuffs’ formed via a novel buckling process of pre-strained elastomer bilayers, that are instrumented with the thermal characterization electronics discussed above. These sensors are capable of measuring blood perfusion through peripheral nerves in a manner that can be correlated with overall nerve health.

3. **Wireless powering and data transfer schemes:** Wireless power and data transfer are critical for the deployment of these sensors for continuous, real-time monitoring. We discuss two paradigms for wireless operation that offer the advantages of soft, tissue-compliant materials, while allowing for high-precision data transfer and completely wireless powering. The first involves the use of near-field communication (NFC) while the second involves Bluetooth-low energy (BLE) protocols. We demonstrate the utility of these materials integration schemes for measurements of skin hydration and flow.

**SB07.06.20**

**A Novel, Flexible and Ultra-Thin Pressure Sensor for Concentric Tube Manipulators in Intra-Ventricular Neurosurgery Robotic Tools** Tianhao Chen, Zia Saadatnia and Hani E. Naguib; University of Toronto, Canada

In minimally invasive endoscopic intraventricular surgeries, very small robotic surgical tools such as a grasper and cutter can be designed and miniaturized to a size of less than 2 mm while maintaining its dexterity and force required to resect brain tumors without open-skull surgery. However, due to remote control the robotic systems, there are very limited haptics namely tactile and kinesthetic information being received by the surgeons, leading to loss of control over tissue and causing unexpected slippage and trauma. This study presents the design of a small and highly sensitive smart material-based sensor being integrated to the tool shaft, known as the concentric tube manipulators, to provide instrument-tissue interaction force feedback for this tool. A 100 μm-ultrathin layer of micropatterned resistive carbon-filled polyvinylidene fluoride (PVDF) conductive polymer is wrapped spirally around the 2 mm-diameter concentric tube for static and quasi-static force sensing. A layer of interdigitated electrodes, connecting with a high-frequency, real time data acquisition (DAQ) system, is designed to achieve pressure readings with both directional and locational information. These pressure readings are visual pressure profile displays generated based on concentric tube-brain tissue contact mechanics with assumption of cylinder-sphere contact model. Optimizations are performed on the size, pitch and shape of the microstructures as well as the...
width and spacing of the electrodes to improve sensitivity with reduced hysteresis. The finalized design can sense a pressure from as low as 0.55 kPa to 5.5 kPa with an accuracy of 93%. The sensor demonstrates excellent proportionality between the acquired signal and force applied with 91% consistency under small loads while retaining its flexibility, biocompatibility and sterilizability. The sensor will also enhance more intuitive force feedback for surgeons to use the dexterous neurosurgical tool, ensuring the safety and quality of operations for minimally invasive surgeries involving brain tumor and epilepsy practice.

SB07.06.21
Epidermal Electronics as a P300-Based Wireless Brain-Computer Interface Joohwan Shin and Tae-il Kim; Sungkyunkwan University, Korea (the Republic of)

Progress in highly conformal epidermal electronics led electrophysiology recording based on dry electrodes which breakthrough critical problems such as low skin-electrode impedance and motion artifact issues. These astonishing advances give a new opportunity to Brain-Computer Interface (BCI) which is using non-invasive electroencephalography (EEG) recording. Nevertheless, researches so far have just reported electrical and mechanical performance of electrode or suggested elementary exemplification about recording EEG. Here, we introduce a comprehensive wireless BCI system which can be used in daily life such as driving situation, based on depth study about Event-Related Potential (ERP) and tattoo-like epidermal electrode. P300, which is one of the main components of ERP, is considerably used in BCI application and occurred from brain when a person recognizes unexpected stimulus. In this study, P300 wave was thoroughly analyzed from 10 different subjects, three different oddball paradigm tests, both epidermal and conventional electrode simultaneously and motion induced situations to ensure compatibility of epidermal electronics and P300-based BCI. In addition, we present device structures and fabrications, electrical and artifact characteristics of epidermal electrode, epidermal electrode positioning strategy, skin mounting methods, P300 wave recording procedures, and design of miniaturization FPCB chip to measure EEG and communicate wirelessly. As a proof-of-concept, mobile RC car was used as target platform and we compared braking distance between BCI based autonomous driving car and manually controlled driving car in the emergency situations.

SB07.06.22
Correlating Electromechanical Patterns with Hand Gestures Based on Cytoadhesion-Inspired Hybrid Electrodes Pingqiang Cai, Jing Yu and Xiaodong Chen; Nanyang Technological University, Singapore

Hand gesture recognition based on muscle activity monitoring has been implemented in robust human-machine interactions, bionic prosthetics, and prognosis of neuromuscular disorders. Muscle activities involve myoelectrical trigger of motor neurons at neuromuscular junctions and the mechanical actuation of muscle fibers. Monitoring the functionality of either single event has been fulfilled with various electromyogram electrodes or skin-mountable strain sensors. However, the patterns of myoelectrical triggers and mechanical shortening of myofibers can be different spatiotemporally, intrinsically arising from the excitation-contraction coupling process. Hence, the fidelity of interpretation muscle activities by retrieving either single event is disputed. There is an unmet demand on establishing the electromechanical coupling of the myoelectrical triggers and mechanical responses in muscle for the high-fidelity hand gesture recognition. To address this, we developed the hybrid electrode to spatiotemporally couple the surface electromyogram (sEMG) signals and the mechanical strain of local skin. By resembling the transmembrane architecture of cytoadhesion, the electrode utilized discrete “adhesion plaques” to mechanically and electrically integrate the microcracked metallic nanofilms for strain sensing at a gauge factor, and the ionic gel with low contact impedance for sEMG collection at a high signal-to-noise ratio. By establishing the electromechanical patterns of forearm muscle contraction, the electrode was able to distinguish loose and tight fist clenching, as well as the flexion of different fingers. In addition, the electrode was able to orthogonally recognize the hand gesture dynamics, which could be transferred to robotic hands for recapitulating human grip gestures with varying dynamics.

SB07.06.23
A Wireless-Powered, Biosensing Soft Contact Lens Taiki Takamatsu, Lu Chen, Te Xiao, Lunjie Hu, Shujie Fang and Takeo Miyake; Waseda University, Japan

Smart contact lenses—contact lenses with built-in electronics—are a next-generation wearable product with capabilities beyond simple vision correction. Since the electrical lenses are in continuous contact with the eyeball
surface, they have three main applications: (i) biomedical sensing of tears to monitor health conditions, (ii) wearable displays for augmented reality (AR), and (iii) actively regulating eye accommodation to ensure perfect vision. Thus, a smart contact lens has substantially greater functionality than an electrical eyeglass. Here we demonstrate electrochemically (EC) printing a wireless-powered circuit onto a moist, soft contact lens. EC printing involves adding a conductive polymer at the interface between a metal contact and a hydrogel-based contact lens, resulting in strong adhesion of the circuit to the lens without losing high power transfer efficiency (50%) from an eyeglass transmitter to the printed receiver lens. Our wireless powered system is combined with an AC/DC rectifier circuit for a single LED display and for electrochromic filter applications.

SB07.06.24
An Eco-Friendly and Flexible pH Sensor for Chronic Wounds Monitoring Manni Yang and Kwang-leong Choy; University College London, United Kingdom

Different from normal wounds, chronic wounds often have a large and deep wound area and patients often experience long-term suffering from inflammation and bacterial infection. In chronic wounds healing process, pH is a key parameter, indicating the state of bacterial infections. For a healthy skin, the typical pH is 5.5-6.5, while in chronic wounds, the pH can be above 8 due to the by-products created by bacteria in the process of cell proliferation. In order to treat wound promptly and effectively, pH monitoring requires multiple measurements from the wound area with high spatial resolutions. However, current wound sensors are mostly in solid forms and cannot detect in different depth of wound area comprehensively, while some flexible sensors are costly and with some chemical-based fabrication methods or materials that could be potentially harmful in human body. Herein we proposed an eco-friendly fabrication of, flexible and highly sensitive pH sensor for chronic wounds based on bio-derived materials. The resulting composite sensor has near Nernst limit pH sensitivity in the pH range from 4-10, with low Young’s modulus, and also has a long-term sensitivity lasting for at least 24 hours. This renders its applications in flexible bio-sensors and smart wound dressings.

SB07.06.25
Novel Optical Polymers and Patterning Technologies for Flexible Bio-Optoelectronics Komal Kampasi, Jenny Zhou, Alicia Calonico Soto, Vu Nguyen, Susant Patra and Razi Haque; Lawrence Livermore National Laboratory, United States

Advanced nano-science and patterning technologies are constantly evolving to meet the ever-growing expectations for improved flexible optical MEMS. In this work, for the first time to our knowledge, we compare state-of-art commercially available photo-definable optical polymers, namely Ormoclear FX and Ormocomp (hybrid polymers called ormocers), IP-Dip (UV resin) and Epocore (an improved SU8-like epoxy) and explore their suitability for design of flexible bio-optoelectronics. We demonstrate micro- and nano-technologies to pattern optical films on polymer substrates and evaluate their characteristics such as optical transmission and clarity, in vivo lifetime and resistance to photodamage.

Flexible optical materials can be used for applications ranging from waveguide circuits in optical interconnects to micro-lens for CCD/CMOS imagers to optical sensors in bioimplants and wearables. The advantages of polymers include lightweight, flexibility, thin film formation at lower temperatures and wide range of molecular designs. Unlike semiconductor material growth and deposition approaches which are carried out at higher temperatures, polymers can be spun at room temperature and cured at relatively lower temperatures to achieve wide range of thicknesses. With the aid of computational models, polymer molecular formations can be synthesized to tune in optimal physical properties like elasticity, tensile strength and so forth. However, common drawbacks of polymers are narrow range of controllable optical properties such as transmittance, transparency, durability and high moisture absorption. Recently, nano-hybridization of polymers with metallic or inorganic nano-particles has been proposed as a promising technique to overcome polymers’ drawbacks without reducing their inherent advantages. Our results show that hybrid polymers Ormoclear FX and Ormocomp are indeed most flexible (1-1.2 GPa Young’s modulus) with highest transmissivity in visible and near infrared spectrum, high optical transparency and good photodamage resistance. These characteristics make ormocers most preferable for polymer optics including long-term biomedical applications such as waveguiding and imaging. Epocore and IP-Dip are comparable to polyimide and parylene in flexibility (~3GPa of Young’s modulus) but exhibit lower optical transmission in UV/near-UV range with average optical clarity. All polymers withstand a 6-month equivalent accelerated saline soak with only 2-6% decrease in transmissivity over 300-800nm spectral range demonstrating appreciable resistance to in vivo degradation. The results conclude that unique polymer characteristics combined with compatible patterning technologies can be
applied to target different optoelectronic applications. While nanoscribe printing (with IP-Dip and Ormocomp) was found suitable for high precision 3D printing of microstructures like diffractive optical elements, optical bonds and hollow guides; 2D microfabrication (with Ormoclear FX and Epocore) was better suited for reliable design of continuous and longer optical structures such as waveguides.

SB07.06.26

Xanthommatin-Based Electrochromic Displays Inspired by Squid Skin

Amrita Kumar¹,² and Leila Deravi¹;
¹Northeastern University, United States; ²University of Connecticut, United States

Color is a signature visual feature in nature; however, the ability to trigger color change in the presence of different environmental stimuli is unique to only a handful of species in the animal kingdom. We exploit the natural color changing properties of the predominant pigment in arthropods and cephalopods - xanthommatin (Xa) - and describe its utility as a new broad-spectrum electrochromic material. To accomplish this goal, we explored the spectroelectrochemical properties of Xa adsorbed to an indium-doped tin oxide (ITO) coated substrate chemically modified with poly (3,4-ethylene dioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS). We identified a synergistic role between PEDOT:PSS and Xa that contributed to its absorption profile which could be modulated across multiple cycles. This bio pigment was encapsulated into polymeric material and investigated color tunability in response to pH and electrochemical reaction. Enhanced visible through SWIR scattering makes this nano material as a potential candidate for IR colorant.

SB07.06.27

Synthesis and Characterization of Phosphonated PEDOT—A Novel, Water-Processable Conjugated Polyelectrolyte

Jonathan A. Hopkins, Kristina Fidanovski, Lorenzo Travaglini and Damia Mawad; University of New South Wales, Australia

Conjugated polymers have great potential as flexible, electroactive materials for cell stimulation, but their application is often hindered by their limited processability in non-toxic solvents. A promising solution lies in conjugated polyelectrolytes (CPEs) bearing ionizable pendant groups; these materials are processable in water and exhibit “self-doping” behaviour without the need for external dopants or dispersants. We report the synthesis and characterization of a novel CPE, poly(ethylenedioxythiophene) doped with ionizable phosphonate groups (PEDOT-Phos), which is soluble in several solvents including deionized water, phosphate-buffered saline, and dimethylformamide. Raman spectroscopy confirms the presence of both the conjugated PEDOT backbone and the phosphonate pendant groups. The polymer undergoes changes in ultraviolet-visible light absorption and photoluminescence spectra as a function of pH, indicating polaron formation. This pH-dependence is attributed to the tunable ionization behaviour of the phosphonate pendant groups. The polymer is readily processed directly from aqueous solution into semi-crystalline films, which exhibit strong visible-light photoluminescence and reversible redox behaviour. The morphology of cast films can be controlled by modifying the casting solvent and performing thermal annealing. With its intriguing optoelectronic properties and easy processing from aqueous media, PEDOT-Phos has significant potential as a novel, electroactive substrate material for bioelectronic devices.

SB07.06.28

Flexible Biomimetic Polymer Thin Films for High Resolution Temperature Measurement

Tae Hyun Kim, Zhun Zhou, Vincenzo Costanza, Luca Bonanomi, Linghui Wang and Chiara Daraio; Caltech, United States

Flexible thermal sensing devices have shown great potential towards many biomedical applications and robotic/machine interfaces in which direct conformal measurement over complicated geometry is necessary. However, conventional inorganic materials widely used to fabricate the sensory element either inherently lacks flexibility and sensitivity, or often requires high temperature processing steps which complicates their integration with flexible plastic substrates. Recently, we have demonstrated that organic thin films composed of plant-derived polysaccharide, pectin, can detect temperature changes with more than two order of magnitude higher sensitivity compared to those state-of-art temperature sensing layers. However, the characteristics of these natural products are complex and their properties can vary widely. In addition, pectin films exhibit poor mechanical properties over repeated stress and bending solicitations. Here we report a multifunctional polymer scaffold inspired by pectin. The chemical structure and mechanical properties of the polymer are tailored to retain the thermal response with flexible functionality. Through impedance characterization as a function of temperature, we show that the ionic conductivity within the polymer film is strongly related to temperature and demonstrate its ultra-high temperature responsivity.
and reproducibility that also allows device scalability for large scale integration.

**SB07.06.29**
**Functional Polythiophene Deposition and Biocompatibility with SH-SY5Y Neuroblastoma** Peter Sitarik, David C. Martin, Quintin Baugh, Samadhan Nagane and Yuhang Wu; University of Delaware, United States

We have been investigating the electrochemical deposition of functionalized polythiophenes around neural cells with the goal of creating stable, directly biointegrated electronic devices. Our previous efforts have primarily focused on the well-studied 3,4-ethylenedioxythiophene monomer (EDOT). While the corresponding polymer (PEDOT) has shown considerable potential, its highly hydrophobic character leads to issues when depositing it around living cells. Here, we discuss recent efforts to examine the potential of an EDOT monomer with a pendant carboxylic acid moiety (EDOT-acid). We have examined the cell viability of EDOT-acid relative to EDOT and have found that EDOT-acid solutions are much more cytocompatible. We have also seen variations in the growth mechanisms when P(EDOT-acid) is deposited around living cells. P(EDOT-acid) grows in a manner that is more attached directly to the cell surfaces, rather than to the electrodes as seen with PEDOT. Most recently, we have been examining the deposition of a bifunctional monomer that combines EDOT with dopamine, creating what we call EDOT-dopamide. P(EDOT-dopamide) polymers can also be grown electrochemically and show low impedances over a broad frequency range. The morphological, physical and chemical characterization of these materials with optical and electron microscopy, spectroscopy, and other techniques will be discussed and compared with PEDOT.

**SB07.06.30**

Although peripheral nerves possess the inherent ability to regenerate, nerve transections require surgical intervention to optimize functional recovery. While small gaps (≤5 mm) may be directly coapted without tension, larger gaps may require interposition grafting with nerve auto- or allografts or conduits to provide tension-free mechanical support, axon guidance, and protection from fibrous tissue ingrowth. Conduits avoid the substantial disadvantages of autografts, i.e. a second surgical site, donor site morbidity, limited availability, high treatment cost, but current FDA approved devices are limited to use in defects ≤30 mm. Cadaveric nerve allografts are used only for defects ≤70 mm due to the limited regenerative capacity of neurons through such grafts. Thus, autografts remain the gold standard and outcomes remain suboptimal with only 50% of patients with mixed nerve injuries regaining meaningful motor and sensory function, and less than 15% regaining full functionality.

Nerve guidance scaffolds (NGS), in which piezoelectric nanoparticles (PNPs) are homogeneously distributed enable the possibility of fractionated stimulation of the PNPs using ultrasound (US) to aid speed and quality of regeneration over several weeks and months. Innovative are the application of a straightforward, benign processing technique, freeze casting, to the manufacture of multifunctional scaffolds from a novel PNP composite. The freeze-cast scaffold architecture emulates that of the natural tissue and, through composition and processing parameters, can be custom-designed in its structural, mechanical, and piezoelectric properties. Presented will be a summary of key experimental and modeling results, and correlations obtained during the design, manufacture and testing of the piezoelectric NGS, from the poling of the PNP to enhance their piezoelectric conversion to their structural and piezoelectric characterization, and finally in vitro and in vivo testing. The results suggest that piezoelectric scaffolds and their US stimulation offer a very promising approach for neuroregenerative devices with comparative ease of translation into clinical application.

**SESSION SB07.07/SB08.06: Joint Session: Neural Interfaces**
Session Chairs: Mohammad Reza Abidian and Tzahi Cohen-Karni
Wednesday Morning, December 4, 2019
Hynes, Level 3, Ballroom B

8:30 AM *SB07.07.01/SB08.06.01*
Are Conducting Polymer Electrodes Capacitive or Faradaic? George G. Malliaras; University of Cambridge, United Kingdom

Organic electrochemical devices, which use conjugated polymers in contact with an electrolyte, have applications in bioelectronics, energy storage, electrocatalysis, and sensors. Their operation relies on the oxidation (electron loss) or reduction (electron gain) of the polymer, which are traditionally described as Faradaic processes that transfer charge. However, recent evidence from various devices based on poly(3,4-ethylenedioxythiophene) chemically doped with poly(styrene sulfonate) (PEDOT:PSS) is consistent with a purely capacitive process that stores charge. To clarify whether PEDOT:PSS is an exception or the rule and determine which processes are capacitive and which are Faradaic, solid-state physics methodology developed to understand the operation of organic light-emitting diodes can be used. Such studies can pave the way for device optimization.

9:00 AM *SB07.07.02/SB08.06.02
Fiber-Based and Nanomagnetic Neural Interfaces Polina Anikeeva; Massachusetts Institute of Technology, United States

Within 1.3L of human brain billions of neurons connected by trillions of synapses are continuously exchanging signals. These signals govern the inner workings of the nervous system, and the aberrations in communication between neurons and other cells within the brain are manifested as the neurological and mental conditions that increasingly affect our aging society. While clinically available devices lack the finesse of the neural circuits and drugs often come with unwanted side effects, our team leverages the principles of optoelectronics and magnetism to develop tools matching the signaling complexity of the nervous system and cause minimal disruption to natural physiological function.

My talk will discuss how multimaterial fiber technology can be leveraged to produce compliant and miniature devices capable of electrical and optical recording and stimulation of neural activity, and delivery and sensing of neurochemicals. I will further highlight how multimaterial fibers can be employed for neural repair following traumatic injury as well as the potential candidates for artificial muscles with future applications in prosthetics. The second half of my talk will focus on using iron-containing nanomaterials as transducers of magnetic fields to biologically relevant stimuli such as heat and force. By tuning magnetic nanomaterials properties in conjunction with magnetic field conditions, it is possible to independently control multiple heat- or force-dependent biological processes. Finally, iron-containing nanomaterials can be used to aid minimally-invasive delivery of neurochemicals via magnetothermal and electrocatalytic means.

9:30 AM *SB07.07.03/SB08.06.03
Microfabricated, Conformable Auditory Brainstem Implants—Materials and Technology Advances towards Clinical Translational Nicolas Vachicouras¹, Christina Tringides², Osama Tarabichi³, Vivek Kanumuri³, Yohann Thenaisie¹, Florian Fallegger¹, Chris Brown³, Daniel Lee³ and Stephanie P. Lacour¹; ¹Ecole Polytechnique Federale de Lausanne, Switzerland; ²Harvard University, United States; ³Massachusetts Eye and Ear Infirmary, United States

The auditory brainstem implant (ABI) is a neuroprosthesis that provides sound awareness to deaf individuals who are not candidates for the cochlear implant. The ABI electrically stimulates the surface of the cochlear nucleus (CN) in the brainstem. The complex anatomy and physiology of the CN together with the poor spatial selectivity of electrical stimulation and inherent stiffness of contemporary implants lead to only modest auditory outcomes in ABI users.

We propose a soft conformable ABI electrode array to improve the biomechanical match of the man-made implant to the curved CN surface. The conformable implant provides stable positioning of the implant in vivo and enables higher selectivity of electrical stimulation. The soft neurotechnology leverages miniaturization, high performance thin-film materials, and engineered mechanical compliance to produce implants compatible with the demanding ABI surgical insertion and conformability to the curvature of the brainstem. We developed elastic micro-structured multilayers, a soft electrode coating, and transient surgical features that allowed the fabrication of a scalable ABI from miniaturized mouse implants to human-size arrays.

This talk will report on the microfabrication and scaling process, mechanical and electrochemical characterization of the compliant ABIs. The soft electrode specifications are very similar to those measured in clinical ABIs with average impedance at 1 kHz of 5.78 ± 0.62 kΩ (electrodes of 0.385 mm² surface area). In a mouse model, we show that soft neurotechnology can be implemented to reliably activate auditory neurons in vivo for up to 4 weeks, a mandatory step before evaluating longer, chronic use of the technology. In a human cadaveric model, we
demonstrate that the soft ABI is robust to surgical manipulation and insertion into the lateral recess of the IVth ventricle, and displays improved electrochemical performance compared to current clinical devices.

10:00 AM BREAK

10:30 AM SB07.07.04/SB08.06.04
Conductive Hydrogel-Coated Cochlear Implants Improve Electrical Performance In Vivo
Ulises A. Aregueta Robles1, Mario Huynh2, Ashley Dalrymple2, Bryony Nayagam3, James Fallon2, Rob Shepherd2, Rylie Green4 and Laura Poole-Warren1; 1UNSW Sydney, Australia; 2Bionics Institute, Australia; 3The University of Melbourne, Australia; 4Imperial College London, United Kingdom

Aim: This study aimed to compare the chronic in vivo charge transfer properties of conductive hydrogel (CH) coated cochlear implant (CI) electrodes to traditional platinum (Pt) CI electrodes.

Background: CIs can improve quality of life in profoundly deaf people by restoring sound perception. Ideally, bionic devices should safely operate for a lifetime; however, host responses such as protein adsorption, inflammation and fibrosis can impact electrode impedance. These host responses can lead to inefficient stimulation and formation of toxic byproducts. CH coatings, based on poly(vinyl alcohol) (PVA) anti-fouling polymers modified with conductive polymers (CPs), can provide enhanced electrical properties, superior to those of traditional Pt electrodes. This technology can be directly coated onto metallic substrate of state-of-the-art bionic devices1. This study tested the hypothesis that PVA conductive hydrogels can enhance safe charge injection and improve the quality of neural recordings.

Methods: CIs with 4 electrodes specifically designed for the rat cochlea were implanted for up to 5 weeks. The CH coating was fabricated using PVA hydrogel modified with 20 taurine groups for electrical doping and 5 methacrylate groups for crosslinking. The CP poly(ethylene dioxythiophene) (PEDOT) was galvanostatically grown through the hydrogel and arrays were ethylene oxide-sterilized (ETO) prior to implantation. Electrochemical impedance (EI), charge injection limits (CIL) and charge storage capacity (CSC) of electrodes was compared before and after implantation using a 3-electrode cell (vs Ag/AgCl). Sprague Dawley rats were unilaterally implanted with CH coated or uncoated Pt CIs. The animals were chronically stimulated using charge balanced biphasic pulses for ~20 hrs/week over the implantation period. To evaluate electrode performance in vivo, voltage transient impedance was measured 5 days/week, and EI, CIL and CSC was also recorded over the implantation period. Explanted electrodes were imaged using scanning electron microscopy (SEM) for evaluation of the CH attachment and for signs of Pt oxidation.

Results: Before implantation, EI of CH coated electrodes over a frequency range of 10Hz-50kHz was more than 3 times lower than uncoated Pt implants. CSC and CIL of CH-coated electrodes was over one and two orders of magnitude higher than Pt electrodes, respectively. During implantation periods, common ground impedance of CH-coated electrodes increased from ~4kW in the first week, and stabilized thereafter at ~6kW. In contrast, the impedance of Pt electrodes was approximately double that of CH immediately after surgery at ~8kW and after 2 weeks at ~13kW. Following implantation electrochemical impedance was maintained at close to pre-implantation levels in CH coated electrodes, which was significantly lower than in Pt. CSC and CIL decreased by ~40% and ~60% in CH coated electrodes following implantation, but both were still ~10 times higher than the Pt CSC and CIL. Preliminary observations of SEM images (n=2) showed that the CH coat remained attached to the cochlear implant throughout studies. However, further histological analysis will assess potential CH residues in cochlear tissue. Following removal of CH no signs of Pt oxidation were observed.

Conclusion: CH-coated cochlear arrays maintained enhanced electrical properties during and after implantation. These results support the potential of CH as an advanced electrode coating for cochlear implants with superior electrochemical performance than Pt electrodes.


10:45 AM *SB07.07.05/SB08.06.05
Towards Seamless Neural Implants/Tissue Integration
Xinyan T. Cui; University of Pittsburgh, United States
Microelectronic devices placed in the nervous system present tremendous potentials for mapping neural circuits and treating neurological disorders. Currently, these devices often experience failures in part due to the electrical, mechanical, and biochemical, mismatch between the artificial device and neural tissue. Quantitative histology and 2 photon imaging have revealed neuronal damage and degeneration, inflammatory gliosis, blood brain barrier leakage and oxidative stress at the site of implants which may compromise the intended recording/stimulation/neurochemical sensing function. We use several biomaterial strategies to minimize these mismatches in order to achieve seamless and stable device-tissue interface. First, various conducting polymer based nanocomposites have been investigated as electrode coatings and facilitate the signal transduction/charge transfer between the ionically conductive tissue and the electrical device. Nanostructuring is employed to improve the adhesion, stability and charge injection and drug delivery capability of the conducting polymers to meet the material challenges in chronic interface. Secondly, to minimize the mechanical mismatch at the device-brain tissue interface, novel soft and elastomeric electrode materials have been developed with Young’s modulus approaching that of neural tissue (less than 1 MPa). Soft implants demonstrated reduced inflammatory tissue response in both CNS and PNS compared to stiff implants of similar geometry and surface chemistry. Thirdly, bioactive approaches are being developed to modulate the biological responses. One approach is to modify the implant surface with biomolecules or biomimics. Surface immobilization with these bioactive molecules significantly improved neuronal health and inhibited the inflammatory tissue response around the implants. Alternatively, therapeutics that control inflammation, neurodegeneration and oxidative stress have been delivered systemically or locally. These bioactive approaches have demonstrated significant benefit in neural recording quality and longevity. The ultimate solution to a seamless device/tissue interface may be a combinatorial approach that takes advantage of multiple biomimetic strategies discussed above and beyond.

11:15 AM SB07.07.07/SB08.06.07
Design and Fabrication of Tissue-Mimicked Parylene C Based Neural Microelectrode Arrays Yu-Chih Chiu and Pochun Chen; National Taipei University of Technology, Taiwan

In recent years, implantable bioelectronics has raised huge interest, especially for neural diseases. Among them, devices with a nerve guidance to guide neuron growth can enhance neural regeneration for traumatic peripheral nerve injury. However, the commonly used nerve conduit cannot provide a spatiotemporal regulation and in-situ monitoring for localized neurons. Accordingly, in this study, an implantable neural device that is built with microelectrode arrays on transparent and flexible substrate was developed to enhance cell growth through applying electrical stimulation and neural signals recording in a tissue-mimicked microenvironment. A new type of flexible substrate, nanoporous Parylene C, was designed and fabricated to exhibit tissue-mimic structural and mechanical properties. The microelectrode array, iridium oxide electrode for both neural stimulation and recording, was pre-deposited on a water-soluble sacrificial layer of poly acrylic acid (PAA) prior to the transfer print process. Such transfer printed tissue-mimic neural microelectrode array enabled conformable adhesion on a curvilinear nerve surface and electrical signals transduction from the microelectrode site, which is expected to provide higher performance of peripheral nerve regeneration. In addition, we characterized and evaluated the microelectrode array of iridium oxide film, including charge storage capacity, charge injection capability, and electrochemical impedance.

11:30 AM SB07.07.08/SB08.06.08
Conductive and Tissue-Adhesive Interfaces for Bioelectronics Jue Deng1, Hyunwoo Yuk1, Chuanfei Guo2 and Xuanhe Zhao3; 1Massachusetts Institute of Technology, United States; 2Southern University of Science and Technology, China

Various bioelectronic devices have attracted broad attentions and they inevitably require stable integration with biological tissues to ensure their reliable functions without compromising their electrical performance. Due to the intrinsic wet, dynamic, and deformable nature of biological tissues, the poor combination and the potential tissue damages during integration is undoubtedly interfered with the accuracy and reliability of electrical communication between biological tissues and bioelectronics. Here, we present a new family of conductive tissue-adhesive (CTA) interface capable of offering a general strategy for integrating various bioelectronics with wet and dynamic tissues to develop stable electrical communication between them seamlessly and instantly. The soft, stretchable, patternable and biocompatible CTA interface can adhere diverse materials of electronics and different biological tissues, as well as provides stable electrical properties in wet physiological environment and under deformation \textit{ex vivo} and \textit{in vivo}.
The study provides a new powerful platform for diverse bioelectronics to address the long-standing challenges in human-machine interface.

SESSION SB07.08: Bioelectronics III
Session Chairs: Tzahi Cohen-Karni, Anastasia Elias, Sahika Inal and Christoph Tondera
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Ballroom B

1:30 PM SB07.08.01
Nanoscale Solid-State Glucose Fuel Cell for Energy Harvesting in the Human Body Philipp Simons¹, Marco A. Gysel¹,², Steven A. Schenk¹,³, Kierstin P. Torres¹ and Jennifer L. Rupp¹,¹; ¹Massachusetts Institute of Technology, United States; ²ETH Zürich, Switzerland; ³EPFL, Switzerland

Efficiently powering the next generation of highly miniaturized bio-sensors, implantable drug delivery systems and bio-electronic devices for the human body defines a new era of medicine to track, support and operate body functions. Here, glucose fuel cells have seen a renaissance in recent years as an implantable power source harvesting energy from readily available fuels in the human blood stream.¹ Compared to existing implantable batteries, glucose fuel cells do not require frequent replacement surgery, due to the abundance and perpetual availability of glucose inside the human body. However, state-of-the-art glucose fuel cells are primarily based on polymer electrolytes being relatively bulky, suffer from long-term stability issues and exhibit low power densities. Here, we innovate a miniaturized glucose fuel cell, which is fully composed of solid state materials based on thin film processing.² This all-solid-state glucose fuel cell can be scaled down to the sub-micrometer range for unprecedented miniaturization and is built on a Si-chip using standard semiconductor fabrication methods suitable for integrated and direct powering of bio-electronic devices and implants. Through the use of abiotic catalysts instead of conventional biological catalysts such as enzymes and microbes, long term stability and increased power density are in perspective. Free-standing fuel cell membranes based on a proton conducting oxide on Si-chips were assembled using a microfabrication route with standard semiconductor processing techniques. Oxide thin films were prepared via pulsed laser deposition.³ The anode is in contact with glucose in phosphate buffered saline solution to mimic blood, whereas the cathode is in contact with oxygen. Performance characterizations were carried out via electrochemical impedance spectroscopy and galvanostatic polarization curve measurements. During this presentation we will present that the proposed cell is electrochemically active and reproducibly functions as the first all-solid-state glucose fuel cell with a roughly 100-fold lowered thickness of the device (only 250 nm) compared to polymer-based glucose fuel cells. In addition, we will present our recent efforts in developing a new, cheap and scalable route of fabricating our newly invented glucose fuel cell using spray pyrolysis.

References

1:45 PM SB07.08.02

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), PEDOT:PSS, has been regarded as one of the most successful semiconductor polymers for organic electrochemical transistors (OECTs) due to their solution-processability and aqueous stability. The ability to operate in aqueous environments make OECTs excellent candidates for a variety of applications, especially in the area of sensing. Incorporation of plasticizers or pre-treatment, such as ethylene glycol or sulfuric acid, have been done to boost the electrical performance of PEDOT:PSS-based OECTs by changing the PEDOT domain, crystallinity and nanostructure. In our previous work, we have introduced ionic-liquids in PEDOT:PSS induced a highly ordering molecular packing, and enable good
device characteristics, including high transconductance, controllable operating window and fast response time with long-term stability. Here, we expand our work further to study the various ionic liquids in PEDOT:PSS and their effects in the structural realignments of PEDOT and therefore on OECT performance. In addition, we demonstrate a facile patterning method via spray-coating to fabricate ionic liquid doped PEDOT:PSS-based OECTs, instead of the conventional complicated photolithography process, with great electrical performance and excellent device stability. More importantly, this facile technique makes it possible to fabricate high-performance OECTs on diverse substrates such as biodegradable flexible substrates based on ethyl-cellulose and natural leaf, wearable type substrate based on the commercial adhesive bandage, and deformable elastic substrate based on polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) elastomer. Using these substrates, the fabricated OECTs maintained high electrical performance with a transconductance of $\sim 3.7 - 7.4$ mS at $V_G = 0$ V. Overall, the results indicate that the spray-deposition technique provides a convenient route to prepare high performing OECT channels and exhibits great prospects in various ubiquitous electronics and bio-integrated organic electronics, such as flexible, conformal biological sensors and foldable wearable integrated circuits.

Reference

2:00 PM *SB07.08.03
Distributed Recording and Delivery of Biochemical Compounds at High Spatiotemporal Resolution and Selectivity Magnus Berggren, Daniel T. Simon, Eleni Stavrinidou, Isak Engquist and Goran Gustafsson; Linkoping University, Sweden

The tight coupling between ions and electronic charges, along with several unique physical and chemical features, makes the conducting polymers a unique material platform in bridging the signaling gap between biology and technology. Here, different organic bioelectronic sensor and delivery devices will be reported that can operate as distributed and autarchic nodes within a body area network. The resulting system, the BioComLab, can be applied to the human body and has been explored in different healthcare-relevant settings. The BodyComLab technology has been developed to enable fast diagnostics, decision-making and delivery of targeted compounds.

2:30 PM BREAK

3:30 PM SB07.08.04
Stretchable and Transparent EEG Sensor Based on Metal Nanowire and Dry Bioelectrode Teppei Araki, Takafumi Uemura, Shusuke Yoshimoto, Yuki Noda, Shintaro Izumi and Tsuyoshi Sekitani; Osaka University, Japan

A stretchable and transparent sensor enables to monitor electroencephalogram (EEG) with less psychological stress. Here, an Au-plated Ag nanowire (AgNW/Au) is reported to enhance properties of a conductive track in the sensor on conductivity, stretchability, and electrochemical durability without the loss of transparency. With a newly-developed dry bioelectrode, the sensor wirelessly records EEG with low noise less than 1 microvolt and can contribute to diagnose brain disorders in relaxed state. Recently, stretchable and transparent conductive electrodes (stretchable TCE) including conductive tracks have been demonstrated to be applicable in biosensors. [1] The softness, as being closely equal to biological body, steps forward to long lasting therapeutic.[2,3] However, there is a challenge on recording small biopotential such as EEG having amplitude of 1–100 microvolt using stretchable TCE. Signal to noise ratio is impacted from an exogenous noise that is usually related high skin-electrode contact impedance. Here, conductive materials that show biocompatibility meeting the ISO standards and exhibit low skin contact impedance less than 50 kilo-ohm are reported and integrated in a stretchable and transparent sensor. AgNW/Au-based TCE shows an improved sheet resistance by 20–30% and stretchability up to 100 cycles between 0–60% strains although pristine AgNW-based TCE could not achieve them. No severe change of electrical resistance is also confirmed under accelerated test by high current on AgNW/Au-based TCE in the presence of water. Meanwhile, a stretchable and transparent adhesive as the dry bioelectrode is developed based on anisotropic conduction mechanism in order to reduce cross-talk. Finally, EEG is successfully recorded under wireless communication with low noise during continuous 12 h usage of the developed sensor. The technologies that lead to the development of the stretchable and transparent sensor will provide a new way for long therapeutic system.
Recent advances in medical technologies have enabled a new generation of implantable devices to treat neurological disorders, restore and repair lost functions, and to modulate neural circuitry to control mood and behavior. Tapping into the nervous system to monitor its state and achieve the desired output, however, requires understanding the fundamental neural processes underlying function, behavior, and disease. The rapid development of neural microelectrodes operating in close proximity with neural circuits, has enabled mapping and modulating neural dynamics at fine spatial and temporal scales. Yet, establishing a stable, safe, long-term functional interface between these man-made artificial components and the host neural tissue, still remains an unsolved challenge. Furthermore, while the brain naturally operates across multiple domains, neural microelectrodes can only transduce either electrical, chemical or optical signals, thus completely missing the interplay between the different signaling modalities.

Nanostructured materials are uniquely positioned to address these challenges because they combine high electrical conductivity with intrinsically high mass-specific surface area and mechanical flexibility. Furthermore, they can interact with biological systems on a molecular scale and can be processed into thin films with tunable optical properties, thus opening new and exciting opportunities for neuroelectronic interfaces. In this talk I will present the ongoing work in my lab leveraging the unique properties of nanostructured materials, such as nanocarbons and MXenes, to engineer novel devices for neural recording and stimulation at high spatial and temporal resolution, as well as for integrating multiple mapping modalities within the same platform. I will also present examples of applications in animal models of neurologic disorders and discuss the potential for future translation of these technologies in the clinical domain.

With the development of low power neuromorphic systems, novel paradigms based on combining artificial intelligence (AI) and machine learning with local adaptive biological systems can be envisioned. This could have applications in a variety of smart “trainable” devices, notably in adaptive prosthetics. However, to achieve a feedback mechanism between the biological systems and AI, a neuromorphic memory must act as an adaptive mechanism that is responsive to biological systems and can close the loop. In this talk, I will bridge the gap between artificial and biological synapses by creating a neurotransmitter-sensitive organic neuromorphic device. We combine microfabricated neuromorphic devices in a microfluidic channel to form a neuromorphic-neurotransmitter biohybrid interface. Voltage pulses at the pre-synaptic electrode drive the oxidation of the excitatory neurotransmitter dopamine (DA), leading to both a short-term potentiation of the channel from ionic drift as well as a long-term potentiation due to the chemical reaction with dopamine at the biohybrid interface. This demonstrates the direct translation of dopamine secreted by PC12 neuron-like cells to a change in memory state in artificial synapses. These results are opening the pathway to combine artificial neural networks with biological systems and develop biohybrid and bidirectional closed-loop sensing platforms.

Synaptic devices that can emulate biological neuron functionality and be reliably programmed to a continuum of resistance states at low energy cost are highly desirable for neuromorphic computing. Despite recent progress in demonstrating neuromorphic arrays using conventional inorganic resistive memories, no architecture to date can...
operate with comparable efficiencies to that of the human brain due to limitations at the device level. State-of-the-art filament-forming metal oxides (FFMOs) and phase change memory (PCM) based synaptic devices still suffer from excessive write-noise and device non-linearities, preventing massively parallel information processing at a comparable efficiency to that of the human brain. We show that polymer-based devices relying on mixed ionic-electronic conduction are highly promising to address these challenges [1].

To demonstrate this, we have developed a new class of polymer-based devices which can be linearly and symmetrically programmed over 100× distinct states by low voltage pulses (<1 V) at low power (<1 pJ per write) while retaining low write noise. Reversible switching in our devices relies on controlled insertion/extraction of ions into a transistor-like channel, similar to the synaptic cleft in the brain, whereas device non-volatility is enabled by a supercapacitor-like architecture. Our devices can be reliably programmed using <1 μs pulses and endure >10⁸ write-read events without notable deterioration in device performance, thus exceeding the endurance of conventional FLASH memories, subject to oxide stresses. This shows that polymer-based devices can meet the stringent speed, endurance and linearity requirements necessary for efficient neuromorphic computing.

As a proof of concept integration into synaptic arrays, we have combined our polymer-based device with an inorganic diffusive memristor, serving as an access device. Using this two-device combination as an addressable memory cell, we built prototype 3×3 organic/inorganic neuromorphic arrays [1]. The linear switching characteristics of our polymer-based devices allowed the arrays to be programmed in parallel, resulting in an n² latency advantage compared to conventional crossbar memories, where n is the array size. Architectural simulations predict that a scaled 1024×1024 organic/inorganic synaptic array would have an energy, latency and area advantages of 476×, 16× and 9.5×, respectively, compared to an optimized 8-bit static random-access memory (SRAM) accelerator, highlighting the yet untapped potential of polymer-based synaptic devices for brain-like computing.


SESSION SB07.09: Poster Session II: Bioelectronics II
Session Chairs: Tzahi Cohen-Karni, Anastasia Elias, Sahika Inal and Christoph Tondera
Wednesday Afternoon, December 4, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB07.09.01
Ferritin as a 3D Bioelectronic Material Sudipta Bera and Rupa Mukhopadhyay; Indian Association for the Cultivation of Science, India

Ferritin is an intracellular iron-storage protein that maintains iron balance by storing and releasing iron in response to physiological need. It is present in almost all living organisms, which means that it is an environment-friendly material and is easily available. It is a stable protein that remains functional in both solution and solid phases in a wide range of temperatures (up to 85 °C) and pH 4.0–9.0. It sustains its electronic integrity in solid-state condition for a long period of time (about one year). Ferritin has a unique spherical structure, having an 8 nm semiconducting iron oxy-hydroxide core. Ferritin has been suggested for use in wide ranging device applications - the nano-battery, FET, and memory device. Ferritin appears to be a versatile protein as its electron transport properties can be tuned and it can be anchored onto a solid substrate (silicon, Au, Al, ITO, HOPG, glass etc.) as per device requirement by various means of chemisorption and physisorption. In this presentation, the suitability of ferritin as a 3D bio-electronic material is discussed. It is first ensured that the native ferritin and the different reconstituted ferritins along with apoferritin show their electron accessibility and statistically distinct band gap characteristics in the monolayer configuration on heavily doped silicon substrate by using conductive atomic force microscopy and spectroscopy (C-AFM and C-AFS) [1]. Here, ferritin has been treated as an insulator-conductor composite as the core modification results in a change in overall electronic state of the ferritin. The successful tuning of band gap of the different metal core reconstituted ferritins indicate that band gap engineering is possible in case of ferritins which is quite useful in synthetic semiconductor technology. The success with ferritin-monolayer-based bioelectronics on silicon surface prompted us to prepare a purely proteinaceous iron-loaded holoferritin multilayer
using layer-by-layer electrostatic deposition of successive cationized and native ferritin layers. This ferritin multilayer is found to be capable of long-range electron transport in solid-state configuration - the maximum range being ~40 nm for vertical transport (across the multilayer) as observed in a C-AFS study and ~40 μm for lateral transport (along the multilayer) as observed by an interdigitated electrode-based measurement [2]. The ferritin multilayer is largely an electronically homogeneous material as found in a KP-AFM study, and it shows less substrate influence than the monolayer configuration. Importantly, the holoferritin multilayer exhibits Z-electronic confinement with a high exciton radius of 45 nm [2]. This is one of the longest exciton radii reported so far. This is also the first report of electronic confinement inside any biomaterial. The bulk electron transport capacity of the ferritin multilayer as presented here indicates its potential for use as a component in futuristic molecular 3D circuit.

References:


**SB07.09.02**

**Bio-Sourced Eumelanin Pigments—Charge Transport Properties and Beyond**

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Organic electronic materials have been widely investigated as a valid complement to conventional electronic technologies, owing to their mechanical properties and large area printability. Green electronics recently opened new research avenues to use bio-sourced, biocompatible (possibly biodegradable) materials to limit the environmental impact of the electronics sector. Within bio-sourced carbon-based materials, eumelanin, a black-brown conjugated biopigment, emerged as an excellent candidate for green electronics. A rapid interest grew around eumelanin due to its fascinating physicochemical properties (e.g. broadband optical absorption, metal-ion chelation, mixed ionic/electronic conductivity and biocompatibility). The conjugated sp² backbone of eumelanin suggests that it would be a naturally occurring semiconductor. The amorphous semiconductor model (ASM) was proposed for the first time in the 70s after the reports on resistive switching behavior in wet melanin pellets. Recent investigations on the role of adsorbed water on eumelanin charge carrier transport challenged the ASM by proposing mixed electronic/protonic and proton membrane models. None of the current models can provide a comprehensive understanding of the charge carrier transport properties of eumelanin.

In this work we fabricated wet and dry sepia melanin pellets included between Cu and stainless-steel electrodes. We report for the first time the electrical response of dry eumelanin pellets. As opposed to previous studies that indicated dry eumelanin as an insulating material, dry pellets switch. Surprisingly, the electrical response of dry pellets features a quasi-linear, metallic-like behaviour. On the other hand, wet pellets show a reversible and reproducible resistive switching, in agreement with McGinness et al. Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), X-Ray Photoemission Spectroscopy (XPS) and Raman Spectroscopy did not reveal neither the formation of metallic filaments bridging the electrodes nor a phase transformation (i.e. amorphous to graphitic carbon) possibly induced by Joule heating. We can, therefore, exclude the formation of metallic filaments or graphitic carbon in the interpretation of the electrical response. These findings suggest that dry pellets would be predominant electronic conductors. Our results show that despite huge effort, certain fundamental aspects of eumelanin’s transport physics need to be radically reconsidered and confirm the tremendous potential of the biopigments for green electronics and bioelectronics.

References

SB07.09.03
Mesoscale Structure-Ionic Transport Relationship of Eumelanin
Zhen Tian1, Wonseok Hwang2 and Young Jo Kim1; 1University of New Hampshire, United States; 2University of Maryland, United States

Recent advances in biodegradable electronics exhibit a huge potential to transform the conventional implantable biomedical devices into transient ones by obviating many challenges associated with chronic implants. Biocompatible/biodegradable packaging materials, naturally-sourced electronic components, or biodegradable charge storages would be the ideal building block to fabricate these types of devices. Recent researches have shown that eumelanin pigments can be served as promising electrode materials due to the exceptional biodegradability, the ease of processing, and the capability of binding various cations. Coordination bonding with cations can be formed mostly with semiquinone radicals that are induced by comproportionation reaction of indoles. These electrochemical properties are largely dependent upon the chemical functional groups as well as the structural characteristics. Eumelanins are mainly composed of the aggregated network of oligomers that include two subunits of 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA) in various ratios. These subunits are randomly crosslinked into planar protomolecules by Pmel17 proteins that are further p-stacked to form spherical nanostructures. The protomolecules of natural eumelanins have been known as the unique structural feature that cannot be observed in the synthetic counterparts synthesized from the template free autoxidation. Despite numerous efforts with a wide range of techniques, little has been known about the macromolecular topography that links the configuration of two subunits. Furthermore, the structural effect on charge transport is still elusive due to the disordered nature during melanogenesis. We report herein the presence of the meso-scale protomolecule structures of natural eumelanins using x-ray scattering, electrochemical techniques and spectroscopic analysis. Increased understanding of structure-property relationship can provide insight into the template-assisted self-assembly in melanosome. In addition, controlling the charge transport would be advantageous to design the device quality bioinspired materials as well as the high performance energy storage devices for biodegradable transient biomedical electronics.

SB07.09.04
Biological Model Membranes Supported on Electroactive Polymer Devices for Measuring Protein Ion Channel Activities
Han-Yuan Liu1, Anna-Maria Pappa2, Charalampos Pitsalidis2, Quentin Thiburse1, Surajit Ghosh1, Alberto Salleo3, Roisin Owens1 and Susan Daniel1; 1Cornell University, United States; 2University of Cambridge, United Kingdom; 3Stanford University, United States

The effective treatment of pain remains a challenge as current therapeutics still lack desired levels of efficacy and tolerability. Around 80 protein ion channels have strong links to pain sensation, but only a small number of these channels have been successfully drugged for pain management. One reason for the bottleneck in discovery is the inadequacy of conventional platforms for drug discovery that monitors modulation in ion channel activity. Current methods require a skilled hand, yet are still very laborious, time-consuming, and low throughput. There is an urgent need to develop faster, authentic, and high throughput assays that give direct and quantitative information on ion channel function, drug interactions, and insight on the efficacy of a developed therapy. The platform presented here features a biomimetic membrane that provides an authentic lipid environment, native cell membrane material to support the natural transmembrane ion channel function, and a sensor made from an electroactive polymer surface upon which the biomembrane is supported. Of focus here is the ATP-gated P2X family ion channels. These protein ion channels are considered important therapeutic targets for multiple pain modalities including neuropathic, inflammatory, and chronic pain states. This biomembrane sensor is capable of reading and transducing ion channel activity as it depends on the availability of ATP. Critically, this platform captures these essential features: 1) it preserves native plasma membrane, protein orientation, fluidity, and activity; 2) is robust and long-lasting; and 3) is compatible with high throughput expansion. Given the considerable amount of research focus and development on identifying drug targets and engineering new drugs for the treatment of pain,
this new biosensing platform may prove to be a useful new approach for ion channel research and drug screening.

SB07.09.05
A Versatile Zwitterionic Conjugated Polyelectrolyte Platform for Bioelectronics Gang Cheng; University of Illinois at Chicago, United States

Implantable bioelectronics has drawn huge attention in recent years since they can monitor the levels of biomarker(s) continuously. For example, the implantable glucose sensor is highly desired for diabetic people. Implantable sensors were used to monitor electrical signal and bio-analytes in the brain and they can be coupled with implantable drug delivery system for controlled release of drugs. The performance and lifetime of implantable sensors are significantly influenced by interfacial phenomena at the interface of the sensor/biological system, including biofouling, foreign body reaction, loss of structural integrity, and infection. In electrochemical bioelectronics, bioelectrodes are a core component for the delivery of charge and recording of an electrical signal. Conventional electrodes are fabricated from platinum and gold, which require surface modification to increase their integration with biological tissue and minimize foreign body encapsulation at the electrode/tissue interface. As emerging biomaterials, conjugated polymers have attracted significant interests for bioelectronics; however, traditional conjugated polymers, which were originally designed for non-biological applications, lack biocompatibility, functionality to conjugate biomolecules, tunable mechanical properties and antimicrobial properties to prevent infection. In the past five years, we have developed a versatile zwitterionic conjugated polyelectrolyte (CP) platform to address key challenges of conjugated polymers for biomedical applications. Zwitterionic CPs, consisting of conjugated backbones and multifunctional zwitterionic side chains, integrate all essential functions and tunable properties into one material at monomer level. Zwitterionic materials gain tunable conducting, optical and antimicrobial properties through conjugated backbones. Low-biocompatible conjugated polymers obtain outstanding biocompatibility, controllable antifouling properties, enhanced ionic conductivity, sensitivity to environmental stimuli, functionality for bioconjugation and tunable mechanical properties via zwitterionic side chains. In this presentation, I will show you why and how we designed the zwitterionic conjugated polyelectrolytes and how we synthesized and characterized this versatile platform. In the end, I will show you how we used this zwitterionic CP platform to improve the performance of bioelectronics using the glucose sensor as an example.

SB07.09.06
Quantification of Nanoparticles Surface Grafted Groups by Electrokinetic Sonic Amplitude, ESA Alexander M. Renner, Markus B. Schütz, Daniel Moog, Thomas Fischer and Sanjay Mathur; Institute of Inorganic Chemistry, Germany

In recent years, nanotechnology developed into a promising field in cancer research by using various kind of magnetic nanoparticles such as magnetite (Fe3O4) in early diagnosis and prompt treatment of cancer. In this context, nanomaterials loaded with different biomolecules and imaging agents contribute to the improved delivery of drug at the target site and minimizing its exposure to the healthy tissues. At this point, active surface chemistry is considered essential for the specific uptake of nanoparticles to the cancer cells. Nevertheless, surface grafted molecules and their quantification is an immense challenge in nanoparticle surface modification but indispensable in regard of their possible medical applications. Nearly all known quantification methods of surface-bound molecules including direct and indirect methods are affected by their size, surface consistency, composition or charge distributions of particles, resulting in scattering of measurement results. To fill up this knowledge gap, we present a novel quantification method in which freely accessible hydroxide groups located on the surface of SiO2 particles, utilizing the electrokinetic sonic amplitude (ESA) effect supported by simultaneous conductivity measurements. ESA techniques itself became one of the most innovative methods for analyzing particle-ligand interactions. The zeta potential of charged particles located in an alternating electric field is calculated from the resulting sound wave, opening insights into the surface chemistry of nanoparticles. Furthermore, the degree of surface functionalization of phase-pure quasi-cubic hematite (Fe2O3) particles with a zeta potential value of +50 mV was monitored through their reaction with 10-undecynoic acid and citric acid as ligand molecules, paving a profound approach of ligand quantification. Thereby, all results highlight the usage of ESA techniques by its high potential as quantification method in nanoparticle surface modification.

SB07.09.07
Translocation Properties of Analytes through Asymmetric Nanopores Chenyu Wen, Shuangshuang Zeng, Shiyu
Nanopore sensing technology has been developed for detection of various biomolecules such as DNA, RNA, proteins, and metabolites in order to exploit the single-molecule discrimination capability of a nanopore. Succinct device structure, easy fabrication process, and simple electrical readout facility are additional features for this technology [1]. Solid-state nanopores are usually formed in a solid-state membrane such as SiNx, SiO2, graphene, MoS2, etc., to benefit from the mechanical robustness and fabrication compatibility with traditional semiconductor processes. As such, they offer great potential for low-cost, large-scale, high-throughput sensing applications [2, 3].

Here, we present a novel asymmetric nanopore with a truncated-pyramid shape (TPP) realized in silicon-on-insulator wafers. This unique pore structure facilitates the formation of electroosmotic vortex in the nanopore and offers a unique platform to study the interaction between analytes and the pore through the corresponding apparent translocation behaviors.

In general, two forces simultaneously act on an analyte in an electric field formed inside a nanopore under external bias voltage. They are electrophoresis force, \( F_{\text{ele}} = Eq \), and viscosity drag force by electroosmotic flow, referred to as electroosmotic force, \( F_{\text{EOF}} = 6\pi \eta vr \). where, \( E \) is electric field intensity, \( q \) charge on the analyte, \( \eta \) electrolyte viscosity, \( r \) analyte radius, \( v \) velocity of the analyte. The direction and intensity of the two forces determine the translocation direction, which are further influenced by carried charge on the analyte, surface charge density of the pore sidewall, size and shape of the nanopore, concentration and pH of the electrolyte, etc. [4].

In our experiments, DNA and protein IgG1 are selected to perform the translocation in TPPs. DNA is a long strand and heavily charged. Therefore, the electrophoresis force is expected to dominate the translocation. IgG1 is disk-like with low density of charge. Thus, the electroosmotic force dominates. In addition, by varying pH, the polarity and amounts of charge for a protein can change, which may lead to alternation of direction and intensity of the electrophoresis force. Changing pH can also tune the surface charge density of the pore sidewall, which can further influence the velocity of electroosmotic flow, as well as the size and intensity of the aforementioned electroosmotic vortex. Hence, the electroosmotic force is affected. Comprehensively considering the effects of many related factors, reflected as the competition between \( F_{\text{ele}} \) and \( F_{\text{EOF}} \), the translocation behavior of analytes can be understood. By clarifying the kinetic mechanism of analyte translocation, it paves the way to practices of versatile applications of nanopore sensing.


**SB07.09.08**

**Parallelized Single-Molecule Translocations in Arrayed Silicon Nanopores Coated with a Lipid Bilayer**

Shiyu Li, Shuangshuang Zeng, Zhen Zhang, Klas Hjort and Shi-Li Zhang; Uppsala University, Sweden

Solid-state nanopores have been recognized as a versatile tool for single-molecule detection with high sensitivity. They have been extensively studied for analysis by nanopore translocation of biomolecules, such as DNA, RNA, and proteins. As a complement to the electrical sensing readout, optical sensing of labeled molecules on a solid-state nanopore array can notably enhance the sensing capacity with high throughput. However, the widely used silicon nitride (SiN\(_x\)) nanopore produces significant photoluminescence (PL) background under blue-green laser illumination, which can severely limit, e.g., multicolor sensing for DNA barcode discrimination. In addition, the occasionally occurring irreversible DNA clogging in a solid-state nanopore, because of DNA molecules interacting with the nanopore channel wall during translocation, can seriously affect the sensing efficacy and accuracy. To address these problems, we have developed an optical sensing system dedicated to nanopore arrays fabricated in a free-standing silicon membrane with its surface functionalized by lipid bilayer coating.

A silicon nanopore array with pores of sub-20 nm diameter is fabricated in a silicon-on-insulator wafer using electron beam lithography in combination with anisotropic etching. The 55 nm thick free-standing silicon membrane shows negligible PL emission in the 550 to 800 nm spectral range under blue-green laser illumination, which greatly improves the optical signal-to-background ratio for single-molecule detection in comparison with standard SiN\(_x\) devices. The formation of a lipid bilayer on the nanopore walls is successful as inferred by monitoring in situ the homogenous fluorescence emitted from a labeled lipid bilayer. As a demonstration, we perform the optical sensing measurements with a conventional wide-field microscope to detect the translocation of fluorophore-labeled DNA strands (120 kbp). With the low background PL of the silicon membrane, the optical signal of individual DNA
translocation events is more clearly identified than when using similarly processed SiN, nanopore devices. Moreover, the coated fluidic lipid bilayer provides a nonstick surface to minimize the non-specific interaction of DNA molecules with the silicon pore walls. The results show that the DNA clogging is substantially reduced in the lipid bilayer coated nanopores as compared to uncoated nanopores. These results demonstrate that using silicon nanopores coated by a lipid bilayer is a promising strategy to realizing massively-parallel single-molecule optical detection.

SB07.09.09
**Percolated Metal Films on Graphene and Hexagonal Boron Nitride for Biocompatible Piezoresistive Sensors**
Armando Urbina, Darren J. Lipomi and Julian Ramirez; University of California, San Diego, United States

This talk describes how single layer graphene functionalized with thin metal films was functionalized to form piezoresistive (increasing resistance with strain) sensors capable of resolving 10ppm strain. Our group has demonstrated the strong bio-compatibility, substrate flexibility, and exceptional piezoresistive capability of graphene/gold films by monitoring contractions of stem-cell derived human cardiomyocyte cells and fabricating wearable heart rate sensors. These sensors exhibit a dynamic range of 9% strain with a sensitivity of 10ppm. By utilizing image analysis software, the relationship between fractional metal film coverage and thermal coefficient of resistivity (TCR) was studied. A sensor with near-zero TCR was created, mounted on flexible tape, and affixed to a subject’s wrist for non-invasive heart rate monitoring. While these composite films have demonstrated notable mechanical and electrical properties, the mechanisms for piezoresistance have not been thoroughly studied. To understand the mechanisms for strain sensing, graphene was replaced with hexagonal boron nitride (hBN). This semiconducting 2D material has gained interest in recent years due to its near insulator bandgap and exceptional chemical stability. Image analysis of ultra-thin gold films on hBN and graphene demonstrate the effect of the 2D scaffold on the metal film morphology (i.e. surface coverage and density of discrete islands). In replacing graphene with hBN, thus removing the conduction path through the 2D scaffold, the piezoresistance of percolated gold films could be compared to intrinsic graphene and graphene decorated with gold. Electromechanical characterization of strain sensor devices comprising these composite films determined the morphologies with highest strain sensitivity. By optimizing the gold film morphology that gives the highest piezoresistive sensitivity, we were able to fabricate piezoresistive sensors capable of resolving 1ppm strain.

SB07.09.10
**Kirigami Engineering of Transparent Conductor for Highly Stretchable Electronic Skin Applications**
Phillip Won¹, Jung Jae Park¹, Inho Ha¹, Seongguen Han¹, Sukjoon Hong² and Seunghwan Ko¹; ¹Seoul National University, Korea (the Republic of); ²Hanyang University, Korea (the Republic of)

Recent research progress of relieving the discomfort between electronics and human body involves serpentine designs, ultra-thin films and extraordinary properties of nanomaterials. However, these strategies addressed thus far each face own limitation for achieving desired form of electronic-skin (E-skin) applications. Evenly-matched mechanical properties anywhere on the body and imperceptibility of electronics are two essentially required characteristics for E-skin devices. Yet accomplishing these two main properties simultaneously is still very challenging. Hence, we propose a novel fabrication method borrowing an idea from kirigami, Japanese ancient cutting art, to pattern highly conductive and transparent electrode into diverse shapes of stretchable electronics with multi-variable configurability for E-skin applications. These kirigami engineered patterns impart tunable elasticity to the electrodes, which can be stretched over 400% tensile strain with strain-invariant electrical property and show excellent strain reversibility even after 10,000 cycles of 400% stretching while exhibiting high optical transparency (more than 80%). The transparent kirigami electrodes with customizable elasticity pave the way of offering facile construction and providing appropriate geometries for achieving multi-functional transparent and wearable electronic skin applications. The versatility of this work is demonstrated by ultra-stretchable transparent kirigami heater for personal thermal management and conformal transparent kirigami electrophysiology (EP) sensor for continuous health monitoring of human body conditions. Finally, by integrating E-skin sensors with a quadrotor drone, we have successfully demonstrated human-machine interface using our stretchable transparent kirigami electrodes.

SB07.09.11
**Stretchability of PMMA-Supported CVD Graphene and of Its Electrical Contacts**
Hongwoo Jang, Zhaohe Dai,
The remarkable mechanical robustness and excellent electrical/thermal properties make graphene a strong candidate for future flexible, stretchable and bio-integrated electronics. In practice, many soft electronics such as the graphene electronic tattoos (GETs) demand the chemical vapor deposited (CVD) graphene to be supported by a deformable substrate. Moreover, various conductive overlayers need to directly laminate on graphene to make electrical contacts. In such cases, the overall device performance relies dominantly on the substrates and the interfaces, especially when subjected to deformations. To investigate the mechanical reliability of CVD graphene in these situations, we fabricated CVD monolayer graphene supported by 300-nm-thick poly(-methyl methacrylate) (PMMA) substrate and also placed gold/polyethylene terephthalate (Au/PET) and graphene/PMMA (Gr/PMMA) overlayers on graphene. The stretchability of the Gr/PMMA and the overlayer-Gr/PMMA interface was characterized by electrical resistance change during uniaxial tensile tests. Combined with semi-
in situ microstructure and Raman investigation, we identified four deformation/fracture stages of Gr/PMMA – elastic deformation, microcracking in graphene, macrocracking in PMMA, and full rupture. While microcracks emerged in graphene at very small strain (~0.9%), electrical conductivity of the Gr/PMMA specimen remained up to tensile strains of ~14.5%. In contrast, 100-nm-thick Au film supported by the same PMMA substrate fully ruptured after tensile strains of ~1%. When laminating Au/PET and Gr/PMMA over Gr/PMMA, we found that the Au/PET-Gr/PMMA interface is very vulnerable but the Gr/PMMA-Gr/PMMA interface behaves very similar to intact Gr/PMMA electromechanically. The present experimental study provides fundamental insight into the fracture and interface behaviors of polymer-supported graphene, which is critical for designing future graphene-based soft electronics.

SB07.09.12

Wearable and Transparent Strain and Temperature Sensors Based on Patterned Ag Nanowire Networks for Health Monitoring Seung-Rok Kim and Jin-Woo Park; Yonsei University, Korea (the Republic of)

Healthcare monitoring devices assess the state of a person by detecting the physiological signals such as heart beat, respiration rate, and temperature measured directly or in relation to the deformation and vibrations of the human body. The body deformation strains provide useful information about the body movement, which helps people optimize their performance in sports and physical activities as well as provide warnings to avoid serious injuries especially in athletes and the elderly population. The body temperature is one of the most important vital signal since it reflects the overall health condition of a person. An abnormal rise or drop in body temperature may indicate infections and/or diseases in a patient. However, conventional rigid physiological measuring devices could not achieve complete and efficient contacts with the skin of the human body without the use of additional interfacing gels due their non-deformable configuration that also limits the mobility of the patient. Hence, many researchers have struggled to make these physiological sensors into conformable and stretchable wearable devices as part of non-invasive diagnostic system that enables remote and continuous healthcare monitoring outside the clinical settings. In this work, we fabricated both capacitive strain sensors patterning Ag nanowire networks (AgNWs) and capacitive temperature sensor using pyroelectric polymer P(VDF-TrFE) as dielectric material. The AgNWs were patterned using capillary force lithography (CFL) method and were embedded onto the surface of the elastomeric polydimethylsiloxane (PDMS) substrate. The strain sensor was patterned as the interdigitated shape, while the temperature sensor was patterned as the serpentine shape. The interdigitated capacitive strain sensor (ICSS) had a -2 gauge factor (GF) at 30% strain (ε), which is much higher than the sensitivity of conventional parallel plate-type capacitive strain sensors. The ICSS had no hysteresis behavior up to ε of 15% and showed stable ε sensing performance during the repeated stretching test at ε of 10% for 1000 cycles. Furthermore, there was no crosstalk between the ε and pressure sensing in the AgNW-based ICSS, which was found to be insensitive to externally applied pressure. The ICSS was then used to detect the finger and wrist muscle motions of the human body in order to simulate its application to large and small ε sensing. The pyroelectric capacitive temperature sensor (PCTS) had 0.23 %/°C sensitivity in the range of 25 to 40°C. This sensitivity was maintained under mechanical stretching under 10% strain although the initial value of the strain is changed. Using those strain sensor and temperature sensor, we could successfully measure the physiological breathing rate and body temperature.

SB07.09.13

Laser Direct Writing of Electrically Conductive Structures with Anisotropic Sensitivity to Strain on an Elastic Polymer Shuichiro Hayashi, Yasutaka Nakajima and Mitsuhiro Terakawa; Keio University, Japan

Electronic devices with high degrees of flexibility have been attracting considerable amount of attention, owing to
their potential novel applications such as electronics skins, wearable textiles, and real-time health monitors. Flexible electronic devices have been demonstrated by combining electrically conductive materials, including metals and carbon-based materials, with flexible substrates, such as polydimethylsiloxane (PDMS), polyimide (PI), and natural rubber. Various fabrication techniques have been developed to fabricate such composite structures for flexible devices applications, such as transfer printing techniques, lithography techniques, as well as laser-based techniques. Recently, our group reported the fabrication of electrically conductive structures composed of crystalline silicon carbide (β-SiC) directly on the surface of PDMS by femtosecond-laser-based-modification of PDMS. The degradation of PDMS into β-SiC is hypothesized to be a result of photolysis, due to the high laser energy, as well as thermal degradation, due to the thermal effects resulting from the high repetition rate. To investigate the potential of the fabricated structures for future flexible device applications, the effects of strain on the electrical conductance of the fabricated structures were investigated in the present study. Electrically conductive structures, 8 mm x 3 mm, were patterned on the surface of a PDMS thin-film by focusing laser pulses onto the surface and raster scanning the beam over the surface. Two types of structures were individually fabricated by different raster scanning directions, longitudinal scanning and transverse scanning, respectively. Both structures were bent in the longitudinal direction, and the structures showed changes in electrical conductance with bending. However, the structures showed different sensitivity to bending, i.e. the change in electrical conductance with bending was significantly less for the structures fabricated with transverse scanning, indicating anisotropic directional sensitivity to strain. SEM observations revealed the generation of micro-cracks on the surface when the structures were bent parallel to the laser scanning direction, while significantly less generation of micro-cracks when the structures were bent perpendicular to the laser scanning direction. The changes in electrical conductance of the fabricated structures could be attributable to the formation of such cracks on the surface. The findings of this study indicate that the structures fabricated by femtosecond-laser-based direct modification of PDMS can be applied for strain sensing, and could allow for a simple one-step method to fabricate directional strain sensors. Furthermore, by focusing the femtosecond pulses into bulk PDMS, arbitrary 3D electrically conductive structures could be directly written inside PDMS via multiphoton process.

SB07.09.14

Laser Micro-Patterning of Graphene Oxide Functionalized Silk Fibroin

Cleber Mendonça¹, Kelly Paula¹, Moliria Santos¹, Murilo Facure², Marcelo Andrade¹, Francineide Araújo¹, Daniel Correa¹ and Sidney Ribeiro³;
¹University of Sao Paulo, Brazil; ²Embrapa Instrumentação, Brazil; ³University of São Paulo State–UNESP, Brazil

Graphene-based materials have been attracting a great deal of attention as candidates for a variety of applications, from electronics to biology, thanks to its unique set of properties. Therefore, patterning graphene-based materials is of foremost relevance for the development of devices. Novel transferring/printing methods have been developed for fabricating high-resolution patterns, such as direct laser writing (DLW), as alternatives to standard lithographic processes. In this direction, Laser Induced Forward Transfer (LIFT) has been attracting considerable attention because it allows patterning different materials, from metals to polymers, to distinct types of substrates. In the LIFT technique, a laser pulse with enough intensity is focused onto the donor material, which is ejected towards the receiver substrate, allowing the production of micro-scale patterns.

In this work, we used fs-LIFT to fabricated graphene oxide functionalized silk fibroin micrometric patterns on a glass substrate. In such structures, graphene oxide is dispersed in silk fibroin, which is a natural biopolymer that has numerous applications due to its excellent biocompatibility, chemical stability, and mechanical properties. Scanning electron and atomic force microscopy results revealed a localized, controllable and reproducible deposition, with lines widths on the order of 1 µm, when the proper parameters are employed. Furthermore, Raman spectroscopy reveals the reduction of graphene oxide upon fs-LIFT, which is in agreement with the observed increase in the electrical conductivity of the transferred material. It is worth mentioning that femtosecond pulses offer advantages to LIFT in terms of resolution and transferring of intact material, thanks to the reduced thermal effects and minimal collateral damage resulting from the nonlinear light-matter interaction. Such results offer novel perspectives on the use of graphene/biopolymer composites for the development of electronic and biomedical devices.

SB07.09.15

Three-Dimensional Structuring of Block Copolymers on Flexible Substrates Using Wrinkle Confinement

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Patterning three-dimensional (3D) architectures into elastomeric substrates can advance development of stretchable bioelectronics, sensors, and data storage devices. Block copolymer (BCP) self-assembly under topographical confinement has shown promise in generating 3D nanostructures down to sub-10 nm scale. Experimental efforts in directed BCP assembly, however, have focused on using hard pre-patterned substrates that require top-down processing, which limits scalability for large-area patterning. Also, the fabrication steps involving BCP film casting and thermal/solvent annealing typically deform polymeric substrates and damage complex 3D geometries. Here we present an all-soft templated assembly of PS-b-PDMS BCPs using polymeric nanowrinkle confinement. We precisely structured BCPs in highly aligned, densely packed arrays on the wrinkled substrate. We also selectively tuned the BCP alignment parallel or perpendicular to the wrinkle orientation by manipulating the pre-strain. Furthermore, self-consistent field theory modeling revealed that wrinkle curvature and surface affinity drove the aligning behavior. Controlled BCP structuring was demonstrated with complex wrinkle geometry, various copolymer molecular weights, and functional skin layers such as graphene and gold. This integration of BCP patterning with flexible 3D architectures will serve useful in lithographic applications for nano-bio interfaces and next-generation soft electronics.

SB07.09.16
Simple 3D Printing-Based-Fabrication of Micromixer Chips for Detecting Hemagglutination Sunwoong Lee¹, DongIl Won² and SungWook Nam¹; ¹Kyung-Pook National University School of Medicine, Korea (the Republic of); ²Kyung-pook National University Hospital, Korea (the Republic of)

3D printing technology has an importance for manufacturing microfluidic chip since it offers high-resolution complex structures. We designed a micromixer chip in which liquid solutions are mixed for detecting hemagglutination. To fabricate the chip, we prepared a mold structure by employing digital light processing (DLP), one of the most popular 3D printing methods. Upon the 3D printed mold, polydimethylsiloxane (PDMS) fluidic device was prepared, which was with another PDMS layer. The assembled micromixer chip consists of multi-level geometry: The first level has meander channels for liquid solution guiding, and the second one has microwell structures to capture blood cell droplets. Inside the micromixer chip, blood cells were initially loaded and captured in the microwells, followed by being mixed with the subsequently loaded antibody solutions, either anti-A or anti-B solutions. As a result, we identified a mixing between blood cell droplets and antibody solutions. In particular, hemagglutination behaviors were identified inside the micromixer chip, which was further characterized by conventional colorimetric microplate-readers. Interestingly, once the hemagglutination occurs, the mixed solution has transparent regions in between the dispersed aggregates of blood cells and antibody solutions. Therefore, the measured absorbance value, optical density (OD), through the channel was significantly decreased. Our method provides an insight for 3D printing technology to be coupled with the existing the benchtop analysis tools.

SB07.09.17
Fibrous Elastomer for Bio-Integrated Epidermal Electronics Matthew S. Brown, Melissa Mendoza, Gretchen Mahler and Ahyeon Koh; The State University of New York at Binghamton, United States

Although research in bio-integrated electronics has been advancing at a rapid pace, the substrates of these systems haven’t been fully optimized for their developed applications (e.g., on-skin, cardiac, and neural lamination). Current wearable electronics rely on impenetrable, non-porous platforms that obstruct the natural diffusive and convective fluid flow and gas transfer, which consequently increase inflammation, contributes to device delamination, and sensor inaccuracies. Furthermore, the microspatial mechanical mismatch at the interface between flexible electronics and soft biological tissue continuously evokes shear stress and thus further exacerbates biomedical complications. To solve critical challenges in soft bioelectronics, we have developed a device capable of being fully breathable, an open-mesh structural design with comparable mechanics to the epidermis (e.g., elastic modulus = 10–500 kPa, 30% ≥ strain). Polydimethylsiloxane (PDMS), a common substrate material because of its soft mechanics and ability to be used in soft lithography makes it a desirable material for breathable electronics. Here, we developed an elastomorphic network of PDMS fibers by utilizing coaxial electrospinning, where a non-spinnable material, PDMS was encapsulated with a spinnable polymer of polyvinylpyrrolidone (PVP). Coaxial electrospinning was capable of producing a core-shell structure of PDMS-PVP fibers. Post electrospinning the PVP encapsulation was able to be fully removed through submergence in ethanol, leaving behind a fibrous network of PDMS micro sized fibers. The fibrous mesh presented
a fiber diameter (1.99 ± 0.56 µm) and mechanically biomimicry structure similar to native tissue, with a viscoelastic response, nonlinear region, and a soft elastic modulus response (129.07 ± 14.85 kPa) comparable to the epidermis. Furthermore, performing mechanical testing under wet conditions the fibrous mat was capable of exhibiting dynamic properties, a more prominent non-linear region, and viscoelastic effect. The water was capable of expanding the fiber pores and decrease the fiber-fiber interaction. To establish biocompatibility, human keratinocyte (HaCaT) immortalized cells were seeded in static culture over a film of PDMS and the PDMS fibrous mesh. The fibrous PDMS demonstrated greater cell viability and proliferation in comparison to the PDMS film. In application, this PDMS fibrous mat can be utilized for implantable biomedical devices where cell integration is required. Furthermore, through soft lithography techniques, microfabricated sensors were capable of fully bonding to the PDMS micromesh and conformally laminating onto the skin while enabling biopotential (e.g. electrocardiogram (ECG)) measurement. Applying this elastomeric mesh platform to stretchable electronics can attribute to the development of the next class of wearable electronics for innovation in chronic health diagnostics, multifunctional sensing, and a more quantitative understanding of dynamic physiochemical biological microenvironments.

SB07.09.18
Fabrication and Use of PDMS Based MEA with Porous Platinum Electrodes as a Multimodal Tool in Neuroscience Aline F. Renz1, Christopher Lewis2, Jihyun Lee3, Klas Tybrandt4, Maciej Brzezinski1, Mouna Cheraka1, Fritjof Helmchen2 and Janos Vörös1; 1ETH Zurich, Switzerland; 2University of Zurich, Switzerland; 3Linköping University, Sweden

Stretchable electronics for seamless implant integration attracted increased attention in the last years, by overcoming the mechanical miss-match between implant and soft organic tissues such as the brain. Enhancement of the implant-tissue interface to both reduce the foreign body response as well as achieve improved electrode properties has been the main focus of many new devices. However, with the increased focus on non-invasive techniques such as in vivo optical recordings, new challenges arise to incorporate temporal and spatial resolution in future brain monitoring implants. Especially for basic neuroscience, where the interplay between single neurons and complete neuronal networks are crucial to understand origins of diseases such as Parkinson and Epilepsy. Here, we present the combination of optical and electrical recording using PDMS based electronic implants to gain scattering free optical recordings through this transparent base material. The highly porous platinum electrodes allow for electrical recording with high temporal resolution while the PDMS insulator is sufficiently transparent for 2-photon imaging of neural activity with single cell resolution. We were able to generate multimodal neuronal recordings in living animals in first proof-of-concept experiments. By fabricating PDMS based electronic implants with a newly generated protocol, new designs, sizes and unconventional shapes can be incorporated within a short time frame and show distinct electrical performance for electrode sizes between 30-100 µm. This approach shows promising results for the versatile use of PDMS based implants for complex brain activity recordings.

SB07.09.19
Characterization of Electrochemically Coated Pt-Ir Microelectrode Arrays Elena della Valle, Elissa J. Welle and James D. Weiland; University of Michigan, United States

Next-generation brain-machine interfaces may use thin-film metals or non-metallic materials (e.g. carbon) for electrical connection to the brain. However, thin-films are not robust to electrical stimulation and carbon is not a low impedance material. Thus, improving the electrical and mechanical stability of neural microelectrodes is a major challenge facing chronic brain interfaces. Electrochemical deposition of a rough, robust material onto an electrode surface is a promising technique that increases real surface area, which facilitates charge transfer, while maintaining geometric area for targeted recording from and stimulation of small neural populations. In this study, a Pt-Ir alloy is electrodeposited on two different multi-electrode arrays to investigate the impedance, durability and morphology at both the surface and within the film. Polymide electrodes array consisted of a 4 µm base and top layer of polymide 2611, a middle layer of a metal stack of 20/80/400 nm of Ti-Pt-Au, respectively. Standard photolithography was used to define 17 circular gold electrodes with a diameter ranging from 30 to 200 µm. Carbon fiber arrays consist of 8 fibers (~8 µm diameter) of 2 or 5 mm length, coated with parylene-C [1, 2]. Pt-Ir was deposited using a potential cycling technique following the process in Petrossians et al. that utilizes sonication to improve the surface coating rate [3]. Electrode impedance was measured with the electrochemical impedance spectroscopy (EIS) method. EIS consistently was decreased after coating, for example a carbon fiber probe showed decreases in impedance modulus of 96 % @10 Hz, 89 % @1 kHz and 10 % @ 1 MHz. The surface morphology of the Pt-Ir coated electrodes was
characterized using both scanning and transmission electron microscopy (SEM, TEM). The chemical composition analysis was then acquired with the energy-dispersive X-ray spectroscopy (EDS) on both microscopy systems. An average percentage of 65 – 35 % of Pt-Ir composition was measured in selected regions up to 10 x 7 µm² and up to 200 x 200 µm² for the carbon fiber probes and gold probes, respectively. Further, inspection of images, delineating Pt and Ir with false colors, show uniformity with respect to distribution of Pt and Ir across the electrode surface. To analyze the interface between the base electrode and the Pt-Ir coating, a focused ion beam (FIB) was used to cut a thin region of the interface to be examined at the TEM. It was then possible to establish the coating thickness and the distribution of the Pt-Ir molecules on the coating surface using EDS analysis. The FIB cut performed on one carbon fiber showed a ~400 nm thick and well homogenous Pt-Ir coating closely adherent to the carbon fiber surface.

A heated soak test was performed on the carbon fibers arrays to mimic an in vivo environment by immersing the fiber tips in PBS by 1mm at 50 °C for 36 days. Some probes electrically failed after 10 days, but still showed the Pt-Ir coating on the surface, indicating a connector failure. Other fibers displayed an impedance increase of 8 % after 36 days.

Overall, from the electrochemical characterization, a low electrode impedance has been achieved while having a homogenous and well distributed Pt-Ir coating on two different material testing arrays. Further analysis will be performed to characterize the stability of the coated arrays by the means of electrical pulsing tests.

Patel et al., Journal of neural engineering, 2016
Patel et al., Journal of neural engineering, 2015

Dr. James D. Weiland has a commercial interest in Pt-Ir electrode materials.

SB07.09.20
Mediating Interfacial Electron Transfer with Biologically Reduced Graphene Oxide Yixin Zhang and Xiaocheng Jiang; Tufts University, United States

Biological electron transfer represents critical processes upon which many essential biological functions depend. Its seamless integration with artificial electronics offers tremendous potential in various engineering applications including biosensing, biocomputing, and bioenergy conversion. The effective coupling at their interface, however, remains challenging, the active redox centers involved in biological electron transfer are typically buried inside the insulating protein matrix, creating large contact resistance with inorganic electrodes. To overcome this challenge, we explored a bottom-up, bio-synthetic strategy to actively “wire” these redox centers to the electronics. In this approach, graphene oxide (GO) were exploited as the solid-state electron acceptors, which can be reduced by G. sulfurreducens as a result of extracellular electron transfer through their membrane cytochrome C (cytCs). Since EET can only occur within the tunnelling distance of cytCs, reduced graphene oxide (rGO) can naturally link the redox centers of cytCs to the external electrodes to facilitate the interfacial charge transport. Through this strategy, the contact resistance at the biofilm-electrode interface can be effectively reduced by 90%, which enables unambiguous characterization of the inherent DC and AC transport across the electroactive biofilm independent of the contact barrier. The current work represents a strategically new approach to seamlessly interface the charge transfer between biological and artificial electronic systems, which is expected to open-up new opportunities for tackling the fundamentals and implications of biological charge transfer.

SB07.09.21
Biocompatible Microneedle Array Dry Electrodes for Bioelectric Potentials Measurement in Organic-Electronic Wearable Health Monitoring Applications Marco V. Alban, Haechang Lee, Hanul Moon and Seunghyup Yoo; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Dry electrodes are an important component of organic-electronic wearable devices for future human-centric Internet of Things (IOT) applications such as health monitoring and diagnostic; measuring brain, heart, and muscle bio potentials can allow early diagnosis of diseases relating to these organs as well as prevention, treatment, and therapy. In addition, they may provide means to monitor auxiliary brain-related information when used, for example, together with OLED-based photo biomodulation (PBM) devices that activate brain activity by light; as well as in electrical impedance tomography (EIT), an emerging imaging technology used to detect brain injury and stroke.
Likewise, they may allow one to realize a wearable device combining both electrocardiogram (ECG) and
photoplethysmography (PPG), the latter of which can be realized with OLEDs and organic photodiodes. Similarly,
they can be part of human-machine interfaces (HMI) used to control organic fiber strands for muscle-like actuators.
If realized, such devices will deliver continuously measured vital information beyond only heart rate in a way that
diminishes any disturbances on everyday life.

Existing clinical-use electrodes have limited wearable and external use capabilities due to the use of gels, a long
time to set up the electrodes, and lack of comfort. Dry electrodes have shown to improve on these issues, but still
lack the signal quality of gel electrodes required for accurate and relevant measurements. Some research has been
done on dry electrodes based on soft polymers with different structures on the surface, and covered by metallic
layers and nanowires, as well as carbon nanotubes among other conductive materials; these approaches are
successful in measuring bio potentials but are often bulky and show high electrode-skin impedance compared to gel
electrodes, this directs to a lower signal performance.

In this study, we propose microneedle array dry electrodes that demonstrate decreased electrode-skin impedance
compared with current dry electrodes in a flexible substrate and able to be fitted on wearable devices; as well as
comparable characteristics to gel electrodes. The proposed electrodes were fabricated using a biocompatible
conductive-filled polymer on top of an also biocompatible flexible substrate, reducing skin irritation and increasing
the comfort of the electrode. By constructing the electrode with a microneedle array structure, we provide a better
contact over hairy skin and an enhanced conformality to different places on the body, ensuring the reduction of the
electrode-skin impedance while keeping the electrode comfortable to wear due to the absence of skin preparation.
The proposed electrodes are characterized by impedance and signal quality; to be compared with clinical-use gold
cup electrodes, and Ag/AgCl standard-use electrodes. The impedance of the electrodes is measured using impedance
spectrometry over typical bio potential frequencies in a two-electrode configuration; and the signal quality is
determined by recording EEG, ECG, and EMG, to later calculate the signal-to-noise ratio (SNR) of the recorded
data. We believe the proposed electrodes can be used on wearable health monitoring applications requiring long-
term measurement, comfort, and high performance, and can do the groundwork for future Internet of Humans
devices, such as active electrodes for remote health data monitoring.

SB07.09.22
Ischemia-on-a-Chip Model with Integrated Extra- and Intra-Cellular Bioelectronic Interfaces for Monitoring
Cardiac Electrophysiology under Acute Hypoxic Stress Olurotimi A. Bolonduro1, Haitao Liu1, Akshita Rao1,
Breanna Duffy1, Lauren D. Black1,2 and Brian Timko1; 1Tufts University, United States; 2Sackler School for
Graduate Biomedical Sciences, United States

Cardiovascular disease is the leading cause of death in the US, accounting for 630,00 deaths in the US each year.
Ischemic stresses substantially alter cardiac electrophysiology, yet there are few tools that enable multiplexed, real-
time studies of cardiac function under controlled ischemia-like conditions. Such a platform would have substantial
implications for disease modeling and drug screening. Herein, we present an integrated microfluidic and
bioelectronic platform that exposed cultured HL-1 cells to controlled hypoxic stresses while simultaneously
providing extra- or intracellular electrophysiological readouts from up to 16 distinct recording sites. Planar device
arrays provided extracellular readouts which allowed for construction of isochronal maps and calculation of signal
propagation velocities. Vertical nanopillar arrays entered the cytosol following localized electroporation, enabling
direct readouts of the intracellular action potential.

Immunohistochemical analysis of HIF-1a expression demonstrated that HL-1 cells became hypoxic upon exposure
to deoxygenated media (1.0 – 1.3% O2). During a five-hour window of hypoxia HL-1 cells exhibited episodes of
tachycardia followed by bradycardia and arrhythmia. During that same window the action potential shortened from
4.89 ±1.54 to 1.68 ±3.34 ms (APD50). Normal cardiac function resumed after exposure to normoxic medium. Our
microfluidic platform enabled rapid modulation of media profiles to achieve acute hypoxic stresses similar to those
present during a cardiac infarct. Our ability to simultaneously read electrophysiological activity—including
intracellular action potentials—provides information not readily achievable using other electrophysiological
techniques. The noninvasive nature of our platform enables a wide range of long-term studies, including hypoxic
conditioning or chronic hypoxia and is also amenable to more complex biological systems including 3D tissue
models. Ultimately, these advances could provide new insights into the role of hypoxia in cardiac function.
SB07.09.23
Addressing the Stability Limitations of Miniaturized Ion Sensors Using a Thin Protective Film Deposited by a Non-Vacuum Low-Cost Technique Antonio R. Ruiz Gonzalez and Kwang-leong Choy; University College London, United Kingdom

The measurement of electrolytes has a high value in the clinical routine. Ions are present in all body fluids with variable concentrations and are involved in multiple pathologies such as heart failures and chronic kidney disease. In the case of dissolved potassium, although a high concentration in the blood (hyperkalemia) is relatively uncommon in the general population, it is one of the most frequent acute electrolyte abnormalities. In recent years, the integration of thin films technologies in this field has allowed the development of highly sensitive biosensors with ultra-low limits of detection for the assessment of metals in liquid samples. However, despite the current efforts in the miniaturization of sensitive devices and their integration into portable systems, only a limited number of successful examples used commercially can be found. This fact can be attributed to a high cost involved in their production and the sustained degradation of the electrodes over time, which causes a signal drift in the measurements. Thus, there is an unmet necessity for the development of low-cost and robust sensors for the real-time monitoring of analyte concentrations in patients to allow the early detection and diagnosis of diseases. This work reports a thin film ion-selective sensor for the evaluation of potassium ions in aqueous samples. As an alternative for this fabrication method, aerosol assisted chemical vapor deposition (AACVD), was applied due to cost-effectivity and fine control over the film deposition. Such a technique does not require vacuum and is suitable for the coating of large surface areas and structures with complex geometries. This approach allowed the fabrication of highly homogeneous surfaces with well-defined microstructures onto 50 nm thin gold layers. The degradative processes of the ubiquitously employed poly(vinyl chloride) membranes in contact with a biological solution were studied, including the polymer leaching process, mechanical desorption of nanoparticles and chemical degradation over time. A rational design of a protective coating based on an organosilicon material in combination with cellulose to improve the long-term stability of the sensors was then carried out, showing an improvement in the performance after 5 weeks. The antifouling properties of such coating were assessed using a cutting-edge quartz microbalance sensor, allowing the quantification of the adsorbed proteins in the nanogram range. A correlation between the microstructural properties of the films with the surface energy and biomolecules adhesion was then found and used to optimize the protective film.

SB07.09.24
The Virus Bioresistor—Wiring Virus Particles for the Direct, Label-Free Detection of Target Proteins Apurva Bhasin; University of California Irvine, United States

Advances in organic bioelectronics have urged to bridge the gap between interfacial compatibility and electrical charge transfer. Establishing communication between the electronic device and bio-entities surfaces the challenge of complexity involved in translating a biological event into an electronic signal. The goal of this project is to learn how to electrically communicate with virus particles. The virus particles of interest are M13 bacteriophage that have been engineered to recognize and bind a protein disease marker. This capability will provide the basis for a new type of biosensor in which M13 bacteriophage (or “phage”) supplant antibodies for the detection of protein disease markers in bodily fluids, such as urine.

It is demonstrated that M13 phage particles (dimensions 6 nm (w) x 1 mm (l)) can be wired into an electrical circuit by first embedding them in an electronically conductive polymer composed of poly(3,4-ethylene dioxythiophene) or PEDOT. This virus-PEDOT composite material, which is prepared by electrodeposition, acts as a resistor, and its resistance is increased when the entrained virus particles recognize and bind a target protein. The virus-PEDOT material provides a convenient means for electrically communicating with virus particles which are electrically insulating. An increase in resistance of the virus-PEDOT material signals the presence of the target protein and the amplitude of the resistance change allows its concentration in the contacting solution to be measured.

More information is obtained by measuring an electrical impedance spectrum for the virus-bioresistor (VBR), across a frequency range from 1 Hz to 40 kHz. These semi-circular Nyquist plots can be interpreted in terms of an equivalent circuit with three circuit elements: A channel resistance (RVBR), a solution resistance (RSOL) and an interfacial capacitance (CVBR). Information on target binding is extracted from RVBR that increases upon target recognition and binding, producing a signal DRVBR.

The VBR concept is tested on a model system in which a dynamic range of 7.5 nM – 900 nM human serum albumin (HSA, 66kDa) is detected in phosphate buffer solution. The high DRVBR (>200 W) induced by HSA binding capacitates the sensor to achieve a coefficient of variation <15% for a total of 20 devices tested for 7 different
protein concentrations. The reliability of signals is testified by the control experiments; followed by real-time sensing measurements. The VBR does not employ a redox probe or reagents for signal amplification. The Nyquist plot also allows the electrical resistance of the solution, R_{soln} to be deconvoluted from the electrical resistance of the virus-PEDOT channel which contains information about the target concentration. This means that the VBR is able to detect and measure the concentration of a target protein irrespective of the salt concentration of the solution, and this capability will be demonstrated.

Higher sensitivity for the VBR can be achieved by reducing the conductivity of the PEDOT-PSS base layer in order to force maximum current through an ultra-thin (<80 nm) virus-composite channel. This modification enabled picomolar detection of a 22kDa cancer biomarker, DJ-1 in synthetic urine. The signal produced by the modified VBR for 10 pM DJ-1 is 50 – 60 W, compared to the 5 W signal generated by the controls accounting for non-specific binding. The new VBR with the inherited ability to distinguish between the R_{soln} and R_{VBR}, produces maximum signal 500-600 W for DJ-1 in synthetic urine which has a total concentration of 160 mM. VBRs are characterized by extreme sensor-to-sensor reproducibility of 2-9% across the entire binding curve for DJ-1. Response time for sensing of 1.0 min. is also demonstrated. The mechanism of VBR transduction will also be discussed.

**SB07.09.25**

**Electrical Detection of Antibiotic Resistant Bacteria in Graphene Field Effect Transistors**

Narendra Kumar¹, Wenjian Wang¹, Juan C. Ortiz-Marquez¹, Matthew Catalano¹, Mason Gray¹, Kitadai Hikari², Xi Ling², Tim van Opijnen¹, Jianmin Gao¹ and Kenneth Burch¹; ¹Boston College, United States; ²Boston University, United States

Antibiotic resistance is one of the most serious threats to global health and food security. Misuse and over-prescription of antibiotics accelerates the promotion of resistant bacteria. To prevent and control this process, the development of new diagnostics which can specifically test for the specific bacterial strain is an urgent need. Graphene field effect transistor (GFET) based label free biosensors have shown great promise due to their highly sensitive Dirac voltage to any chemical/biological modification that occurs on the channel, fast response time, and flexibility to different substrates, which make them capable to be utilized for point of care diagnostics. In this study, the specific probes were synthesized, which are selective to clinical bacterial strains of Staphylococcus aureus (Sa) and Acinetobacter baumannii (Ab). The GFET devices fabricated using CVD monolayer graphene transferred over SiO2/Si substrates were functionalized with these probes in the single step process via non-covalent binding using π-π interaction with the graphene surface. In the talk I will discuss the various controls employed to ensure the selectivity of our probes. In addition, I will discuss device fabrication and measurement protocols to reduce the concentration required. These results point to the utility of gFET sensors for future point of care devices to rapidly detect bacteria strain and resistance.

**SB07.09.26**

**High-sensitive and Fast Detection of C-Reactive Protein and Troponin Biomarkers Using Liquid-Gated Single Silicon Nanowire Biosensors**

Yurii Kutovyi¹, Jie Li¹, Ihor Zadorozhnyi¹, Hanna Hlukhova¹, Nazarii Boichuk¹, Dmytro Yehorov¹, Marcus Menger² and Svetlana Vitusevich¹; ¹Forschungszentrum Jülich, Germany; ²Fraunhofer Institute for Cell Therapy and Immunology, Germany

Fast, precise, and reliable detection of cardiac biomarkers is essentially important for early diagnosis and prognosis of cardiovascular diseases, the most common life-threatening illnesses. However, the current commercially available diagnostic methods either lack of the sensitivity needed for the proper detection of cardiac biomarkers at the very early disease development stage or still suffer from the long-term process of enzymatic labeling. In this work, we designed and fabricated liquid-gated single silicon nanowire field-effect transistors (NW FETs) for label-free sensing of cardiac biomolecules. We demonstrate selective and direct detection of C-reactive protein (CRP) and cardiac troponin I (cTnI) proteins as gold standard biomarkers for prediction and detection of cardiovascular diseases at the early stage. A detailed electrical characterization of fabricated nanosensors, as well as the proof-of-principle experiments such as pH response, were performed before sensing measurements. Sensor characteristics reflect high working stability and nearly ideal Nernstian sensitivity confirming the high-quality of fabricated structures. High specific recognition elements like aptamers and antibodies were immobilized on functionalized nanowire surfaces. A novel attachment approach was shown by using dibenzocyclooctyne (DBCO)-linked aptamers for cardiac troponin to azide-functionalized nanowire surface. The approach has several advantages: fast covalent and directed attachment of aptamers to the azide-terminated surface of nanowires, efficient linkage and high-yield covering of nanowire surface with cTnI-specific aptamers. In particular, the DBCO-linked aptamers do not react with amines or hydroxyls presented in most of the biomolecules, which makes functionalization of nanowires more
efficient and specific. After covalent immobilization of cTnI-specific aptamers and CRP-specific antibodies on the silicon nanowires surface, the highly sensitive and fast electrical detection was performed. A 1 fg/ml detection limit concentration was achieved for both CRP and cTnI biomolecules. The target biomolecules on the Si NW surface are confirmed by atomic force microscopy (AFM) characterization. Moreover, application of nanowire structures with different sizes allowed us to detect biomarkers in a wide concentration range (from 1 fg/ml to 1 µg/ml). This range covers the dynamic concentration range of CRP and cTnI biomarkers release during the early disease stage and progression. Thus, we demonstrate that our specifically functionalized silicon NW FET biosensors integrated with polydimethylsiloxane (PDMS) microfluidic channels can be effectively used as highly sensitive diagnostic tools for early prediction and prevention of cardiovascular diseases.

SB07.09.27
Polymeric Nanofilter-Based Bioelectrical Interface for Potentiometric Small-Biomolecule Recognition Shoichi Nishitani and Toshiya Sakata; The University of Tokyo, Japan

Small biomolecules are often recognized as significant biomarker candidates in the field of in vitro diagnostics. In this study, we propose a novel concept of a biointerface, a polymeric nanofilter, for the potentiometric detection of small biomolecules using an extended-Au-gate field-effect transistor (EG-Au-FET). A Au electrode has the potential capability to detect various small biomolecules with high sensitivity at nM levels on the basis of a surface redox reaction, but it exhibits no selective response to such biomolecules. Therefore, a suitable polymeric nanofilter is designed and modified on the Au electrode, so that a small target biomolecule reaches the Au surface, resulting in an electrical signal, whereas low-molecular-weight interferences not approaching the Au surface are captured in the polymeric nanofilter. The polymeric nanofilter is composed of two layers. The first layer is electrografted as an anchor layer by a cyclic voltammetry method [1]. Then a filtering layer is precisely polymerized as the second layer by a photo-mediated surface-initiated atom transfer radical polymerization method [2]. As a model case, serotonin, a well-known stress marker, is detected by filtering a series of stress markers including catecholamine-related small biomarkers using the polymeric nanofilter-grafted EG-Au-FET on the basis of the following mechanism. The phenylboronic acid (PBA) that copolymerizes with the polymeric nanofilter captures catecholamines through diol binding, whereas serotonin reaches the Au surface through the filter layer. The polymeric nanofilter can also effectively prevent the interaction between biomacromolecules, such as amylase and human-serum albumin, and the Au electrode. A platform based on a polymeric nanofilter-grafted EG-Au-FET biosensor is suitable for the ultrasensitive and specific detection of a small biomolecule in biological samples such as tears and sweat, which include small amounts of low-molecular-weight interferences, which generate nonspecific electrical signals.


SB07.09.28
Investigation of Normal Cell and Cancer Cell Attachment and the Effects of Ganoderma Lucidum Using Electric Impedance Sensing Technique Steffi Kong, Alejandra Martinez and Maddy Behravan; Converse College, United States

This research focuses on analyzing the attachment of normal cells (HaCAT) and cancerous cells (A431), and the effects of Ganoderma Lucidum (reishi) treatment on the attachment of HaCAT and A431 cells. Cell attachment is an important property of the cell membrane; cells are held together through direct membrane contact and adhesion to the extracellular matrix. Cell attachment is essential to maintain tissue structure. Cells with poor attachment can detach and enter into the body’s fluid stream, which in cancer results in metastasis. It has been shown by researchers that reishi is commonly used as a nutritional supplement and is known to improve immunity. There have been previous reports that there has been an increase in the rate of apoptosis of cancer cells after being treated with reishi. In this study, attachment of HaCAT and A431 cells has been investigated using an impedance sensing system. An impedance sensing system is used to characterize the cell membrane attachment quantitatively. This technique is noninvasive and allows for observation and analysis of various aspects of cell behavior, particularly attachment and spreading in real time. An impedance sensing system measures changes in impedance with respect to an applied alternating current (AC) in real-time. Cell attachment and the epithelial layer formation limit current flow between the basal membrane and the cell. The attachment of HaCAT cells and A431 cells, and the influence of reishi with various dosages of 0.005, 0.01, 0.02 g/mL on these cells has been examined. The impedance analysis will be used to compare the attachment and the spreading rate of HaCAT cells and A431 cells, and the effect of reishi on the
epithelial cell layer. The initial set of data shows that the impedance of HaCAT cells and A431 cells increases with time; cell attachment and spreading impedes current flow. There is a significant difference between the impedances of normal cells and cancer cells detected over time. The time dependent response of HaCAT and A431 cells shows a characteristic behavior and reveals junction formation of these epithelial cells. The impedance of HaCAT and A431 cells continued to increase after 24 hours. The effect of reishi on cell attachment of HaCAT and A431 cells will be compared. The first series of reishi treatment reduced cell attachment of A431 cells. Various dosages of reishi could potentially slow down the rate of cancer cell attachment. Further experimental analysis could reveal the possible therapeutic or unwanted side effects due to reishi, a widely used supplement.

SB07.09.29
OPEN SLOT

SB07.09.30
Low-Cost Implantable Transient Electronic Memory Devices for Patients Using Magnetic Resonance Imaging Akshita Mishra, Henam Sylvia Devi and Madhusudan Singh; Indian Institute of Technology Delhi, India

Electronic implants in the human body present safety challenges when exposed strong external magnetic fields, such as those encountered in magnetic resonance imaging (MRI). Metallic and other conductive interconnects, being ubiquitous in electronic devices, including memories, are susceptible to displacement forces and torques that can result in potentially lethal projectile effects. The Food and Drug Administration (FDA) provides guidance on listing implants as MR safe/unsafe/conditional under ASTM F2503-13. Cancer patients, who may need real-time monitoring of tumor growth offered by implants, as well as MRI scans for charting the progress of the therapy, are sometimes forced to accept less than ideal choices in their treatment as they often make poor candidates for repeated extractive surgeries needed to extract the implants. The cost of implanted electronic devices presents another challenge. In this work, we have developed an exemplar biocompatible memory device that is biodegradable at a specific pH. Cleaned commercial thermal silicon dioxide (500 nm) wafers (University Wafers) were drop cast with ~100 µl of polyvinyl alcohol (PVA), and then heated at 80°C for 30 minutes (thickness ~600nm). Bottom contacts of the device were next grown using shadow masks using successive DC sputtering (Cr ~200Å) and thermal evaporation (Au ~300Å) at 4 x 10^-6 Torr (Angstrom Engineering). A titania sol was synthesized using the sol-gel method, and spin-coated (spin NXG-P2) was next deposited as the active layer. Top contacts (Ag ~500Å) were thermally deposited to complete the metal-insulator-metal structure. Current-voltage characteristics of the device were acquired using a Keithley 4200-SCS semiconductor parameter analyzer in dual sweep mode with a grounded bottom electrode. Pristine devices were assumed to be in a high resistive state (HRS, off). On the application of bias voltage [-8, 5] V, the device switches to low resistive states (LRS, on) and exhibits a repeatable pinched hysteresis loop. Retention measurements were carried out at a constant readout voltage (0.01 V) to obtain the retention ratio (R_wt/R_off) of (~10^6). After the device characterization, these devices were dipped in three different media: acidic (pH=3), neutral (pH=7) and basic (pH=9). The devices were found to completely vanish (visual inspection) due to PVA dissolution in 15 min, 150 min, and 90 min respectively. As titania, silver and gold are all biocompatible materials, and present in minute quantities in the device, the dissolution of such devices over 150 minutes in neutral blood (modeled with pH ~7.4) presents few health challenges. Further, it was found that PVA films were easily removable from the silica substrate through peeling, thus enabling the use of the flexible memory device directly in the human body. Operationally, such biologically transient devices could be used to monitor patient vitals and permitted to completely dissolve prior to any MRI scans, without any extractive surgery with its deleterious health effects. Owing to the low cost of the implant, a patient can be injected with the device as many times as necessary during treatment.

SB07.09.31
Device Physics and Transient Behavior of Microfluidic Ion Pumps Shao-Tuan Chen, Christopher Proctor and George G. Malliaras; University of Cambridge, United Kingdom

Targeted drug delivery devices have flourished in recent years due to their superior biocompatibility and lower possibility of side effects compared to systematic drug treatments. Following recent advances of microfluidic ion pumps (µFIPs) [1,2], it has been demonstrated that drugs can be delivered to targeted cells with temporal and spatial precision with applied electric field.

In the µFIP, drugs are electrophoretically pumped from the microfluidic reservoir through an ion exchange
membrane into the targeted area. The ion exchange membrane bears fixed charges in the polymer matrix, which allow the membrane to selectively transport oppositely charged ions while blocking ions with the same charge. Hence, µFIP can actively deliver the drug of interest when electric field is applied while preventing passive drug diffusion when device is switched off.

An ideal µFIP should have a perfectly selective membrane and passive leakage should be minimal. Parameters such as device geometry, fixed charge concentration in the membrane and initial drug concentration in the microfluidic reservoir would all affect the efficiency and performance of µFIP.

Having fundamental knowledge and accurate quantitative models therefore are crucial to the design and optimization of such implantable medical devices. As the range of applications for µFIP continue to expand, there is an urgent need for deeper understanding of their device physics.

Here we report a numerical model for µFIP platforms. The transient behavior of µFIP during operation is described by time-dependent governing equations for the ionic/electronic coupled model. We identified three performance indices to characterize the device performance, namely, the pumping efficiency, amount of drug transported, and the ON/OFF ratio. Performance contour plots for these three indices were obtained by varying two parameters—initial drug concentration in the microfluidic reservoir and fixed charge concentration in the membrane, both by three orders of magnitude.

The parameter space covered in this study encompasses a concentration range far wider than those commonly found in membrane materials and drug molecules used today, thereby giving a comprehensive view of the device performance of µFIPs and possible new avenues for material development and design optimization for such devices.

The model is able to describe both steady state and transient behavior of the ionic and electronic transport across the ion exchange membrane over a wide range of parameter space. Dynamic phenomena, such as electric double layer relaxation within the conducting polymer coated at the electrodes and concentration polarization at the electrolyte-membrane interface, are also captured by the time-dependent numerical model.

The results from this study allow us to design advanced µFIP platforms and push forward the development of targeted drug delivery devices for higher efficiency and extend its range of applications.

References:


SB07.09.32 Design of a Sensor Platform Using Bacterial Outer Membranes on Organic Electrochemical Surfaces

Antibiotic resistance is a growing global health concern in part due to changes in membrane properties and composition of Gram-negative bacteria that affect antibiotic efficacy. The alteration in membrane properties of Gram-negative bacteria influences response to antibiotics and mediates resistance; consequently, the antibiotic is unable to control or kill these bacterial strains, instead, they survive and multiply in the presence of an antibiotic. Therefore, understanding the interactions between bacteria membrane and antibiotics and the transport across the membrane is important for elucidating membrane properties that can be used for the design of novel antimicrobial drugs. The outer membranes of Gram-negative bacteria containing protein and complex lipopolysaccharides that helps to protect them from external harsh conditions. To study outer membrane-antibiotic interactions, we created an electrochemical sensing platform based on a surface-supported planar bacterial outer membrane on an optically transparent conducting polymer surface poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). The bilayer platform is fabricated using outer membrane vesicles (OMVs) of different clinically-relevant Gram-negative
bacteria in order to incorporate native lipids, membrane proteins and liposaccharides to the supported bilayer. The supported bilayer formation and their fluidity are characterized using Fluorescence Recovery After Photobleaching (FRAP) technique, which also enables measurement of the diffusion coefficient using fluorescently labelled molecules/phospholipids. The change in electrical properties of surface-supported bacteria membrane during formation and their interaction with disrupting compounds have been monitored by electrochemical impedance spectroscopy (EIS). The optical transparency and conducting properties of the polymer allowed us to monitor the bilayer formation by both microscopic techniques and changes in ion flux by electrical readout. This sensor platform introduces a method containing biologically-complex membranes to the study of antimicrobial drug testing, a much-needed intermediate between very simple bilayer platforms and whole cell readouts.

SB07.09.33
Electrocaloric (EC) Solid-State Heat Pump without Involvement of Moving Parts Farrukh Najmi, Lorenzo Cremaschi, Wenxian Shen and Zhongyang Cheng; Auburn University, United States

One of the challenges in the development of Electrocaloric (EC) based solid state cooling device/heat pump is the involvement of moving parts – either active material or regenerator needs to be moved to extract energy from source (hot end) and releasing it to the sink (cold end). This not only reduces the efficiency but also adds the complexities in the device design limiting its exploitation in small scale applications. In this study, a two-layered solid-state heat pump is being devised in which the EC layers have been sandwiched between source and sink and the heat is pumped from source to sink in a complete silent operation (no moving parts). An electric field cycle is applied on the EC layers alternatively in such a way that it creates a temperature gradient to achieve a directional heat flow in a system of bodies (Sink/ECs/Source) which are otherwise in thermal equilibrium. This transient heat conduction problem has been solved analytically and gives promising results specially for interfaces having lower contacting coefficients. This technique can offer viable solutions to address the cooling issues in high power electronics and other portable medical applications.

SB07.09.34
Defect-Induced Magnetism in Copper(I) Oxide as a Biocidal Tool Yinying Hua, Brian Lejeune, Xiaoyu Zhang and Laura Lewis; Northeastern University, United States

Antimicrobial materials that are less susceptible to evolved resistances are one approach for combatting the rise in antibiotic resistance, which is a growing concern for public health [1]. Metallic materials have been widely used as a biocidal tool since ancient time and copper-based materials are a key component because of their observed ability to generate radicals and cause cell membrane damage. According to reports which discussed the antibacterial activities of elemental copper, copper(II) oxide and copper(I) oxide [2], Cu(I) and metallic Cu show higher antibacterial activity than Cu(II) state, although the mechanism remains unclear. At the same time, it is known that lattice defects in transition-metal oxides donate local charges that can enhance catalytic properties [3]. To test the hypothesis that lattice defects, such as oxide sublattice vacancies, underlie the noted biocidal activity of Cu$_2$O, initial studies of the relationship between degree of lattice damage and defect concentration in this material were undertaken.

The structural and the electronic states, as revealed by magnetic characterization, were assessed in Cu$_2$O powders (Alfa Aesar, < 200 mesh powder) that were subjected to cryo-milling for up to two hours. Decreases in the cubic $a$-lattice parameter, the unit cell volume $V$ and an increase in both the Pauli paramagnetic and the Curie-Weiss susceptibilities with an increase of cryo-milling time were observed. These observations, which are consistent with changes in the defect state of the lattice, will be correlated with the potential catalytic state of the processed material. Clarification of these structure/property correlations demonstrates the relationship between the lattice defects and the potential catalytic state, which may be a promising way to tailor the antibacterial activity of Cu$_2$O.

Acknowledgement: This research was conducted under the auspices of Northeastern University.


SB07.09.35
Carbon Composites with Improved Properties of for Wearable Electronics Ji-Young Hwang\textsuperscript{1,2}; \textsuperscript{1}Korea University, Korea (the Republic of); \textsuperscript{2}Korea Institute of Carbon Convergence Technology, Korea (the Republic of)

Wearable electronics has progressed dramatically and has opened the prospective future, including electric circuits, flexible displays, stretchable energy storages, electronic skins, wearable devices, \textit{etc}. For flexibility and elasticity are hardly a matter, these have to be surmounted beyond convergence of state-of-the-art technologies. Here, we developed simple and cost-effective fabrication method of nanohybrid composites with carbon nanotubes (CNTs) and polydimethylsiloxane (PDMS) elastomer for improving its electrical and mechanical properties for wearable electronics. CNT/PDMS composites provide high flexibility, elasticity, and electrical conductivity itself and are also biocompatible and mechanically stable. The CNT/PDMS composites are demonstrated to create functional materials that are used for effective bio-signal monitoring of brain, heart, and muscle signals, as well as devices with incorporated integrated flexible circuits. This simple and cost-effective fabrication method provides a promising process and material for various applications of flexible, stretchable and wearable electronic devices, particularly considering the growing global interests in wearable healthcare monitoring system.

SB07.09.36
Fabrication of Nanopore Ion Transistor via Conformal Metal-Film Deposition of Gate-Electrode Structure Kwanjung Kim\textsuperscript{1}, Sunwoong Lee\textsuperscript{1}, Seung-Min Han\textsuperscript{2}, Soo-Hyun Kim\textsuperscript{2} and Sung-Wook Nam\textsuperscript{1}; \textsuperscript{1}Kyungpook National University, Korea (the Republic of); \textsuperscript{2}Yeungnam University, Korea (the Republic of)

Electrofluidics is an emerging technology of combining electronics and nanofluidics. One important device in electrofluidics is an ion transistor in which the ionic current through a nanopore is regulated by gate voltage bias. Here, we suggest a fabrication method of nanopore ion transistors by introducing focused ion beam (FIB) and atomic layer deposition (ALD). We deposited 100 nm-thick silicon-nitrite layers on both sides of silicon wafer by low-pressure chemical vapour deposition (LPCVD). We fabricated rectangular patterns by photolithography followed by reactive ion etching (RIE) on the backside of the wafer. Anisotropic silicon etching by KOH was performed. The front side of the chip was patterned by photolithography followed by Ti/Au deposition for the fabrication of electrode structures. We drilled 50 ~ 100 nm pores in the Si\textsubscript{3}N\textsubscript{4} membrane by FIB. By the ALD process, we deposited highly-conformal metal film, either Platinum (Pt) or Ruthenium (Ru) to shrink nanopores by a self limiting process. We expect that the gate modulation of ionic current through the nanopore is efficiently controlled by the gate-surrounding structures.

SB07.09.38
Detection of IL-10 Cytokine on Roll-to-Roll Nanoimprinted Au Localized Surface Plasmon Resonance Chip Assisted by Au Nanoparticle Seung Hee Baek, Hyun Woo Song, Moon Kyu Kwak, Hye Jin Lee and Sung-Wook Nam; Kyungpook National University, Korea (the Republic of)

Localized surface plasmon resonance (LSPR) is a highly sensitive platform for detecting biomolecules including protein, nucleotide, and vesicle. Although LSPR signal is easily taken by ultraviolet-visible (UV-Vis) spectroscopy, the shift of LSPR peak by the attachment of target molecules is small, which makes it challenging the precise evaluation of the peak shift. Here, we report an Au LSPR sensor platform in which the Au nanoparticle assists the precise evaluation of LSPR peak shift by offering a stable reference peak in UV-Vis spectroscopy. For LSPR sensor fabrication, we employed a roll-to-roll nanoimprint process to create nanograting structures on polyethylene (PET) film. By angled deposition of Au, we demonstrated double-bent Au structures which have strong LSPR peak at \textasciitilde 740 nm. Upon the Au structures, we introduced IL-10 capture antibody to Au LSPR chip by using cross-linking chemistry. Afterward, we loaded IL-10 target protein for specific adsorption to the IL-10 capture antibody. To form a sandwich assay platform assisted by Au nanoparticle, we conjugated Au nanocube (AuNC) with IL-10 detecting antibody and induced it to bind with IL-10 capture antibody/IL-10 complex specifically. We note that AuNC has a stable peak at \textasciitilde 530 nm in the solution state. By using the characteristic peak of AuNC as a reference, we estimated the red shift of the LSPR peak of Au strip structures with high accuracy, which is caused by the formation of IL-10 capture antibody/IL-10/IL-10 detection antibody sandwich assay. We expect that the Au nanoparticle assisted LSPR sensor platform can be used as diagnostic tools for detecting various biomarkers.

SB07.09.39
Characterization of Proton Conducting Materials Manping Jia, John A. Selberg and Marco Rolandi; University of California, Santa Cruz, United States
Proton conduction is important in many natural phenomena including oxidative phosphorylation, enzyme reaction, and is extensively studied and developed in bioelectronic technologies and renewable energy, like actuators, sensors, and fuel cells. Recently, with the rapid development of bioelectronics, efforts are expended on developing proton conducting materials to bridge the gap of the biological system and electrical devices. Natural biomolecules, like peptides, glycosaminoglycans, DNA, etc., show great potential to be proton conducting materials because of their intrinsic biological function and biocompatibility. The sulfate group in glycosaminoglycans, amino acid residues in peptides, and the helix structure of two hydrogen-bonded complementary strands of DNA, provide good environments for proton transfer. Here we compare the results of AC electrochemical impedance spectroscopy (EIS) on several proton-conducting natural materials with the DC data obtained with Pd/PdHx proton-conducting electrodes and show that the two techniques are consistent with each other.

SB07.09.40
Enhancing Diabetic Wound Healing with Therapeutic- and Cell-Loaded Alginate Bandages

Sahar Rahmani1,1, Georgios Theocharidis1,2, Evan Thompson1, Selena Zhang1, Konstantinos Kounas2, Ting-Yu Shih1,1, Aristidis Veves1,1,2 and David J. Mooney1,1; 1Harvard University, United States; 2Beth Israel Deaconess Medical Center, United States

An estimated 285 million adults suffered from diabetes mellitus worldwide in 2010, a number that is expected to exponentially grow. Approximately 15% of diabetics develop diabetic foot ulcers (DFU) and one-in-five are estimated to suffer from a lower extremity amputation in their lifetime. While a number of methods have been developed for wound healing, most are not applicable for DFUs due to their unique pathophysiology, especially their impaired immune response during the wound healing process. In healthy patients, macrophages have an integral part in homeostasis and tissue repair and orchestrate the wound healing process through various mechanisms. Unfortunately, a decrease in the number of macrophages is observed in diabetic wounds, and those present tend to be pro-inflammatory (M1s) instead of pro-healing and/or anti-inflammatory macrophages (M2a/c, respectively). As a result, the wound healing progression is delayed, or prevented, which can lead to non-healing wounds and amputations.

To address this challenge, we hypothesized that increasing the number of macrophages at the wound site and redirecting them to a more pro-healing state can enhance healing in diabetic wounds. To this end, we have developed alginate, cryogel bandages to deliver various factors to wounds. The hydrogel bandages can be manufactured on a large scale as off-the-shelf products and be loaded with therapeutics (cells or factors) during or after the manufacturing process.

Using this bandage system, bone marrow derived macrophages were polarized to inflammatory or healing states, loaded into bandages, delivered to diabetic wounds in a murine model of type 2 diabetes, and the wound size was monitored over a 10-day period. Additionally, the wounds’ cellular components were analyzed by immune-histochemistry and immunofluorescence. Wounds treated with macrophage had smaller wound sizes as compared to the empty bandages. Normalized wound size at Day 10 was 23, 18, 22, 19, and 14% of the original wound size for wounds treated with empty bandages, non-polarized (M0), M1, M2a, and M2c macrophages, respectively. Furthermore, wounds treated with M2c loaded bandages were significantly more healed than those treated with M1 loaded macrophages. These results confirmed our hypothesis that the addition of macrophages, especially anti-inflammatory macrophages, to the wound site can enhance healing in diabetic wounds.

Currently, we are exploring the use of therapeutic-loaded bandages for the recruitment of macrophages to the wound site (MCP-1) and their polarization to the pro-healing state (IL-4 and IL-10) to aid in the healing process. This approach can be advantageous over the delivery of cells in several aspects, including processing time, cost, patient compliance, and feasibility. Depending on the therapeutics’ properties such as surface charge, molecular weight, and heparin binding affinities, we have fabricated bandages with different material compositions to create a prolonged therapeutic release profile for each factor that can be tuned-in to range from a few hours to days and weeks. Using these bandages, we have demonstrated that more immune cells, specially macrophages, are recruited to the wound site as compared to traditional bandages. Here, MCP-1 loaded bandages were placed on wounds over a 3-day period and the cell types and numbers present in the wound were analyzed via flow cytometry. A significantly higher number of macrophages were recruited to the wound site in samples treated with MCP-1 loaded bandages as compared to traditional bandages (approximately four times more). Our next step is to assess the capability of bandages loaded with IL-4 and IL-10 to polarize the local macrophages to the M2 state and, thereby, enhance wound healing. Such bandage systems can potentially provide significant improvement in the lives of diabetic patients by using their body’s own immune system to directly address their impaired healing mechanism.
SESSION SB07.10: 3D Printing and Tissue Engineering
Session Chairs: Tzahi Cohen-Karni, Anastasia Elias, Sahika Inal and Christoph Tondera
Thursday Morning, December 5, 2019
Hynes, Level 3, Ballroom B

8:30 AM *SB07.10.01
Engineering Personalized Tissue Implants—From 3D Printing to Bionic Organs  Tal Dvir; Tel Aviv University, Israel

In this talk I will describe cutting-edge technologies for engineering functional tissues and organs, focusing on the design of new biomaterials mimicking the natural microenvironment, or releasing biofactors to promote stem cell recruitment and tissue protection. In addition, I will discuss the development of patient-specific materials and 3D-printing of personalized vascularized tissues and organs. Finally, I will show a new direction in tissue engineering, where, micro and nanoelectronics are integrated within engineered tissues to form cyborg tissues.

9:00 AM SB07.10.02
Bioelectronics with Food—Celery, Vegemite and Jelly  Rhiannon Morris, Charles Hamilton, Alex Keller, Holly Warren and Marc In het Panhuis; University of Wollongong, Australia

Bioelectronics from edible materials (e.g. food) can be defined as the design of circuits and devices that incorporate edible materials into electronic components and/or uses edible materials to perform the function of electronic components.

I will discuss the (bio-)electronic behaviour of three different types of common food products, i.e. breakfast spreads (Vegemite, Marmite), a vegetable (celery) and a desert (jelly).

The characteristic breakfast spreads Vegemite and Marmite were 3D printed into edible circuitry onto bread substrates. We demonstrated the importance of characterising the rheological behaviour of the food products in retaining the structural integrity of the printed materials (e.g. pyramids on bread). The electrical conductivity (20 +/- 3 mS/cm) of Vegemite and Marmite was used to 3D print edible circuits on “breadboards.”

The edible gelatin product Jell-O (or Aeroplane Jelly) was turned into an electrode structure via the inclusion of table salt during preparation of the hydrogel material. It was shown that the resulting hydrogels prepared using a one-pot synthesis method displayed suitable conductivity values (190 +/- 20 mS/cm) at high water content (70% by weight).

Celery is a marshland plant that has been cultivated as a vegetable. We show that its vascular system (xylem) can be used to facilitate the uptake of the conducting polymer, poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) PEDOT:PSS. Our results indicate that PEDOT:PSS is an ideal candidate for enhancing the electrical behavior of the biological system, i.e. celery. The celery-PEDOT:PSS bioelectrical system exhibit conductivity value of 500 +/- 30 mS/cm, suitable to function as components in electrical devices.

9:15 AM SB07.10.03
Morphing Electronics for Growing Tissue  Jinxing Li, Yuxin Liu and Zhenan Bao; Stanford University, United States

Bioelectronics for modulating nervous system, such as the vagus nerve stimulator, demonstrate great promise in treating various neurological diseases. However, their fixed sizes and shapes cannot accommodate the rapid tissue growth and negatively influence normal developmental functions. For infants, children and adolescents, once the implanted devices are ‘outgrown’, additional surgeries are usually needed for device removal, followed by replacement. These tedious processes inevitably lead to repeated intervention and elevated complication rates. Although stretchable electronics with high elasticity is ideal for repeated motion and volumetric expansion of
In this work, we demonstrated an innovative method of rapid in-situ fabrication of conductive-bacterial-composite on carbon electrodes. The conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) was electrochemically polymerized by 3D printing the monomer precursor directly onto the surface of electrode submerged in an aqueous suspension of *Shewanella oneidensis* wild type MR1, creating an electrochemically active biocomposite within 35 min. Using cyclic voltammetry (CV), the biocomposite showed enhanced bio-electrochemical activities, opening up new avenues to the development of bioenergy harvester, biosensor and biomedical device. Ever since the discovery of conductive polymers, their electroactive properties have been extensively examined by researchers and engineers alike. Particularly, the biocompatible conductive polymers have been given significant attention in recent years as a promising bridge between biology and electronics. Applications as microbial fuel cell (MFC), water-quality sensor, glucose sensor, or body-machine interface have shown great potentials in the fields of energy harvesting technology, biosensing, bioelectronics and health care. Bioelectrochemical systems (BES) utilizing conductive polymer and electroactive bacteria biocomposite to directly transduce biological processes to electrical signals are of unique interest as their immediate application in bioenergy harvesting and biosensing. Comparing to the natural biofilms, the electrochemically active biocomposite offers distinctive advantages as enhanced extracellular electron transfer (EET) rate, denser cell attachment onto the electrode, higher signal-to-noise ratio, and more controllable and versatile composite constitution and functions. Yet, current conductive biocomposite formation procedures such as polymer coating over bacteria cells and electrode surface, cell absorption onto polymer matrix, or cell immobilization by polymerization often involve prolonged cell exposure to cytotoxic chemicals, species-specific procedures, or complicated experimental process and setup. Thus, a more rapid, non-specific and simple biocomposite fabrication method is urgently needed to fully unleash the full potential of conductive-polymer-based BES. Using 3D printing, we present a novel, rapid and simple method to fabricate conductive biocomposite by
The electropolymerization was conducted with plenary 3-electrode electrochemical cells containing *S. oneidensis* in M9 medium in room environment. While a constant potential (1V versus Ag/AgCl) was applied to the carbon working electrode (WE) by a potentiostat in chronoamperometry (CA) mode, 10mM EDOT (in M9 medium) was patterned over the WE surface by a 3D printer. Cells attached to the WE were entrapped by the in-situ synthesized PEO-DT whereas their exposure to the cytotoxic monomer was minimized. The dimension of the conductive biocomposite can be controlled by the printing pattern and number of repeated iterates. A settling time of 10 min between each print and iterate repeat of 3 times were selected in this work.

10:00 AM BREAK

SESSION SB07.11: Tissue Engineering

Session Chairs: Tzahi Cohen-Karni, Anastasia Elias, Sahika Inal and Christoph Tondera

Thursday Morning, December 5, 2019
Hynes, Level 3, Ballroom B

10:30 AM SB07.11.01

Three-Dimensional Printing of Conducting Polymer Baoyang Lu1,2, Hyunwoo Yuk1, Jingkun Xu2 and Xuanhe Zhao1; 1Massachusetts Institute of Technology, United States; 2Jiangxi Science & Technology Normal University, China

Three-dimensional (3D) printing is one of the most transformative technologies in modern manufacturing that offers unprecedented capabilities of programmable, rapid, and flexible fabrication of materials. Despite their unique benefits and growing importance, conducting polymers have yet remained as an inaccessible class of materials for 3D printing. Here we introduce a 3D printable high-performance conducting polymer based on poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) to take full advantage of advanced 3D printing. Superior 3D printability of the conducting polymer ink enables high resolution (over 30 µm), high aspect ratio (over 20), and reproducible fabrication of conducting polymer in microscale, seamlessly integrable with multi-material printing with other 3D printable materials such as insulating elastomers. The 3D printed conducting polymer structures can readily be converted into highly conductive and flexible pure PEDOT:PSS both in dry and hydrogel states. Both of the 3D printed PEDOT:PSS films and hydrogels exhibit interesting properties that are desirable for optoelectronic and bioelectronic applications, such as high electrical conductivity, low Young's modulus, superior mechanical, electrical and electrochemical stability in wet physiological environments. We further demonstrate various functional applications of the 3D printable conducting polymer including a high-density flexible electronic circuit and a soft neural probe capable of *in vivo* single-unit recording, all fabricated by 3D printing. This work not only widens the choice of materials for 3D printing but also provides a promising new fabrication strategy for a broad range of applications in flexible electronics, wearable devices, and bioelectronics.

10:45 AM SB07.11.02

Modularized Field-Effect Transistor Biosensors Xiaochuan Dai1,2, Richard Vo1 and Xiaocheng Jiang1; 1Tufts University, United States; 2Massachusetts Institute of Technology, United States

Field-effect transistors (FETs), when functionalized with bioactive receptors (such as antibodies or enzymes), represent a unique platform for real time, specific, label-free transduction of biochemical signals with unprecedented sensitivity and spatiotemporal resolution. However, direct functionalization of bio-receptor on FETs places limitations on reprogrammability, sensor regeneration and sensitive bio-receptor handling. Here we demonstrate a modularized design of FET biosensors with separate recognition module and transducer module, which are capable of reversible assembly and disassembly. Successful detection of penicillin down to 0.25 mM was achieved by integrating penicillinase-encoded hydrogel module onto graphene FETs, demonstrating effective signal transduction across the interface. Moreover, sequential integration of urease- and penicillinase-encoded modules on the same FET device allows us to reprogram sensing modality without cross-contamination. Except for the variation of bio-receptor encoding, the modular design also fosters sophisticated modulation of the biophysical/biochemical microenvironment in the recognition modules for controllable diffusion dynamics. Specifically, the tuning of
hydrogel porosity with polyethylene glycol and gelatin enables the selective detection of poly-L-lysine (MW 150-300 kDa). Recognition modules designed with standardized interfacing geometry towards transducer modules have also been shown to be capable of being mass fabricated by 3D printing and batch photopolymerization, demonstrating potential for low cost, ease of storage, multiplexing and great customizability for personalized biosensor arrays. This generic concept presents a unique integration strategy for modularized bioelectronics and could impact broadly hybrid device development.

11:00 AM SB07.11.03
From 2D to 3D Material—New Strategies for Cell-Chip Coupling in Bioelectronics Francesca Santoro; Istituto Italiano di Tecnologia, Italy

The interface between biological cells and non-biological materials has profound influences on cellular activities, chronic tissue responses, and ultimately the success of medical implants and bioelectronic devices. For instance, electroactive materials in contact with cells can have very different composition, surface topography and dimensionality. Dimensionality defines the possibility to have planar (2D), pseudo-3D (planar with nanomicropatterned surface) and 3D conductive materials (i.e. scaffolds) in bioelectronic devices. Their success for both in vivo and in vitro applications lies in the effective coupling/adhesion of cells/tissues with the device’s surface. In fact, the tight contact between the cellular membrane and the electrode surface massively affects the quality of the recorded signals or ultimately the stimulation efficiency of a device. However, it is largely unexplored how the patterning and ultimately the dimensionality of bioelectrodes are enhancing the cell-chip coupling.

Here, we explore how the transition from planar to pseudo-3D nanopatterned materials (i.e. conductive vertical nanostructures, nanogrooves, nanofibers) have introduced a new strategy of integrating with biological cells. Although a spontaneous penetration does not occur, adhesion process are extremely distinct when bioelectronics devices are engineering with those patterned materials. These materials have been further exploited towards fully 3D dimensional solutions, moving closer to complex 3D architectures which could directly resemble tissue-like architectures. In this way, cells recognize the bioelectrodes as being embedded in their own matrix and thus fully integrate with the device.

11:30 AM SB07.11.04
A Novel 3D In Vitro Model of the Human Gut-Microbiome Axis—A Bioelectronics Approach Chrysanthi-Maria Moysidou, Charalampos Pitsalidis, Janire Saez and Roisin Owens; CEB, University of Cambridge, United Kingdom

The human gut microbiome plays an essential role in health and disease. Gastrointestinal disease phenotypes (e.g. coeliac disease (CeD), colorectal cancer), have been linked with an impaired gut microbiome, while increasing evidence suggests that microbiome alteration effects extend beyond the gut, reaching other organs, and particularly, the brain. However, the cross-talk interactions of the ‘gut-brain-microbiome axis’ remain a mystery, mainly due to the lack of a human clinical model. Over the last decade, organ-on-chip technology has arisen as powerful alternative to animal models for studying human (patho-)physiology. Integration of this technology with organic electronics can be particularly favourable for delivering robust, biomimetic models, with in-line, multiparametric monitoring.

Here, we report the first version of an in vitro intestinal model integrated with a novel 3D bioelectronic device (i.e. Tubistor), based on scaffolds made from the conducting polymer poly(3,4-ethylenedioxythiphene)poly(styrenesulfonate) (PEDOT:PSS). To emulate the intestinal epithelial barrier we established co-cultures of enterocytes, along with fibroblasts which are used for their ability to secrete extracellular matrix and render the surface of the scaffolds more appealing for cell adhesion. This co-culture system is generated inside Tubistors, both under static and flow conditions, where PEDOT:PSS scaffolds serve both as cell host and as the active material for monitoring cell integrity and activity. During a 25-day growth period, we continuously monitor the model electrically and at the end of this period, these data are cross-validated with traditional optical assays (i.e., Scanning Electron Microscopy and immunofluorescence staining). The soft, tissue-like nature of PEDOT:PSS scaffolds provides a favourable microenvironment for tissue growth and differentiation, exhibiting typical in-vivo-like characteristics of the native tissue (e.g. brush border formation, tight junction and mucin expression). To generate a complete gut-microbiome model, we are currently working on co-culturing bacterial cells – representative of the human microbiome - with our intestinal model.

We anticipate that this bioelectronic platform will serve as a powerful tool for studying host-microbiome
interactions, as well as a diagnostic tool for personalised medicine applications.

**11:45 AM SB07.11.05**
**High Aspect Ratio Semiconducting Polymer Pillars for 3D Cell Cultures**
Gabriele Tullii1, Federica Giona2, Francesco Lodola1, Silvio Bonfadini1, Caterina Bossio1, Andrea Desii3, Luigino Criante1, Carlo Sala1, Maria Cecilia Pasini3, Chiara Verpelli2, Francesco Galeotti3 and Maria Rosa Antognazza1; 1Istituto Italiano di Tecnologia, Italy; 2University of Milan, Italy; 3Consiglio Nazionale delle Ricerche, Italy

Hybrid interfaces between living cells and nano/micro-structured scaffolds have been extensively investigated over the latest decades, due to their huge application potential in biotechnology, spanning from regenerative medicine and stem cells therapies to localized drug delivery, from biosensing and tissue engineering to neural computing. In particular, 3D scaffolds based on organic conductors have recently gained increasing interest, due to the combination of excellent biocompatibility properties with versatile fabrication techniques and good electrical conductivity. In this scenario, however, architectures based on semiconducting polymers, endowed with responsivity to visible light as an additional interesting feature, have never been considered.

Here, we originally develop a push-coating technique to realize high aspect ratio (HAR) polymeric pillars, based on polystyrene. The organic semiconducting structures show optimal biocompatibility and allow for the realization of soft, three-dimensional cell cultures, as tested with both primary neurons and cell line models. HEK-293 cells cultured on top of polymer pillars display a remarkable change in the cell morphology. Interestingly, we observe a sizable enhancement of the cell membrane capacitance as due to the cell membrane thinning in correspondence of the pillars’ top surface. Importantly, however, this does not negatively affect cells proliferation. Electrophysiology properties and synapses number of primary neurons are also very well preserved.

HAR semiconducting polymer pillars represent the first necessary step towards the realization of 3D, electro-optically responsive organic structures. In perspective, they may find interesting applications as soft, photoactive elements for cell activity sensing and modulation.

**SESSION SB07.12: Biosensors**
Session Chairs: Tzahi Cohen-Karni, Anastasia Elias, Sahika Inal and Christoph Tondera
Thursday Afternoon, December 5, 2019
Hynes, Level 3, Ballroom B

**1:30 PM *SB07.12.01**
**Ultimately Sensitive Bioelectronic Sensor by Materials and Device Structures Design**
Luisa Torsi1,2, Rosaria Anna Piccia1,2, Kyriaki Manoli1, Lucia Sarcina1, Eleonora Macchia1,2, Davide Blasi2, Nicola Cioffi1,2, Gerardo Palazzo1,2, Gaetano Scamarcio4,5, Cinzia Di Franco6, Ronald Österbacka3 and Fabrizio Torricelli6; 1University of Bari Aldo Moro, Italy; 2Centre for Colloid and Surface Science - CSGI, Italy; 3Åbo Akademi University, Finland; 4Università degli Studi di Bari Aldo Moro, Italy; 5CNR - Istituto di Fotonica e Nanotecnologie, Italy; 6Università degli studi di Brescia, Italy

Organic bioelectronic sensors are gaining momentum as they can combine high performance sensing level with flexible and stretchable large-area processable materials. This opens to potentially highly powerful biomarkers sensing systems for point-of-care health monitoring and diagnostics. Prominent to detect biochemical recognition events are the Electrolyte-Gated Organic Field-Effect Transistors (EGOFETs) and Organic ElectroChemical Transistors (OECTs) as they are easy to fabricate and operate. Relevantly, the EGOFETs have been recently shown capable of label-free single-molecule detections even in blood serum.

This lecture aims to provide a critical perspective through a selected overview of the literature on both EGOFETs and OECTs organic bioelectronic sensors. Attention is paid to correctly attribute them to the potentiometric and amperometric categories which is important to set the right conditions for quantification purposes. Moreover, to deepen the understanding of the sensing mechanisms, also with the support of unpublished data, focus is put on two among the most critical aspects, namely: the capacitance interplay in EGOFETs and the role of faradaic currents in OECTs. The final aim is to provide a general rational encompassing both EGOFETs and OECTs sensors, to improve materials and devices design taking full advantage of the processes that enhance the sensing response enabling the
extremely high-performance level resulting in ultimate sensitivity, selectivity and fast response.

2:00 PM SB07.12.02
Ultrasensitive Detection of Nucleic Acids Using Deformed Graphene Channel Field Effect Biosensors Michael Hwang, Mohammad Heiranian, Yerim Kim, Yuhang Jing, Seungyong You, Vahid Faramarzi, Juyoung Leem, Amir Taqieddin, Arend M. van der Zande, SungWoo Nam, Narayana R. Aluru and Rashid Bashir; UIUC, United States

Field effect transistor-based electrical biosensors are capable of label-free detection of nucleic acids and proteins by measuring the intrinsic charge of these biomolecules. However, the ultimate detection limit of these sensors is determined by the Debye screening from counter ions in solution, the proximity of the biomolecules to the surface of the sensor, and the operating conditions of the transistor sensor. Here, we use field effect transistors with a deformed monolayer graphene channel for the detection of DNA molecules and DNA/RNA hybridization. We find that these devices with even millimeter scale long channels show an ultra-high sensitivity detection in buffer and human serum sample down to 20 aM in 50 µL, which is equivalent to ~600 DNA/RNA molecules. Molecular dynamic simulations reveal that the nanoscale deformations can result in the formation of ‘electrical hot spots’ in the sensing channel which reduce the charge screening at the concave regions allowing improved detection of the molecular charge. These hot spots also exclude mobile charges, thus exhibiting a high local potential due to the charge of the DNA/RNA. In addition, the deformed monolayer graphene could exhibit a band-gap allowing an exponential change in the source-drain current due to a small number of unscreened biomolecular charges at those hot spots. Collectively, these phenomena can allow for ultrasensitive electronic biomolecular detection in millimeter scale structures, opening the way to many applications in biology and medicine.

2:15 PM SB07.12.03
Aerosol Jet Printed Organic Electrochemical Transistors with NHC Functionalized Gate for Biosensing Applications Jiaxin Fan, Alexandra Predy, Darren R. Majak, Krystyn Dubicki, Florence Williams and Manisha Gupta; University of Alberta, Canada

In the past decades, wearable biosensors have attracted a great amount of attention due to the increasing demands for affordable, non-invasive, and continuous monitoring of physiological parameters for disease prevention, early medical diagnostics, and personalized medicine. These rapid diagnostic biosensing devices should be sensitive, robust, and compact. They do not require conventional clinical laboratory infrastructures to perform the tests, which potentially contributes to reducing healthcare service costs. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS) based organic electrochemical transistors (OECTs) have been demonstrated to have great potentials for customizable biosensors due to their simple device structure, great material stability, capability to operate in aqueous environment with low operation voltage, and most importantly high transconductance (g_m).[1–3] Devices with high g_m show high sensitivities and transduce biological and chemical signals into electrical signals with high signal to noise ratio (SNR). Functionalization is essential for improving the sensing selectivity and sensitivity, which involves modifying the channel and/or gate surface of OECT with functional groups and linking the desired biomolecules. N-heterocyclic carbene (NHC) forms extremely strong bonds with transition metals and has been demonstrated as surface-ligands on different metal surfaces, which can be used as linkers for the conjugation of needed biological recognition elements.[4]

In this study, we have integrated NHC modified Pt wire as the gate for 3D printed OECTs. The OECTs were printed by Optomec Aerosol Jet 5X system on both rigid and flexible substrates with silver source and drain electrodes, PEDOT:PSS channel, and UV-curable polydimethylsiloxane (PDMS) as the passivation layer. All materials used for OECT printing are commercially available. The printed OECTs exhibit high g_m of 30.63 mS (L = 104 µm, W/L = 4, d = 570 nm) tested with 100 mM NaCl electrolyte and Ag/AgCl gate. A distinctive shift in the transfer characteristic was observed when measuring with the NHC modified Pt gate compared to the pristine Pt wire gate. This is due to the work function change of the Pt wire with NHC functionalization. We have demonstrated biosensing capability of the sensor by attaching biotin to the NHC functionalized group via click chemistry and then detecting streptavidin.

References:

2:30 PM SB07.12.04
Benchmarking the Role of Additives on the Electrochemical Performance of an Ethylenedioxythiophene Based Copolymer Georgios Nikiforidis, Shofarul Wustoni, Cyril Routier, Victor Druet and Sahika Inal; KAUST, Saudi Arabia

Poly(3,4-ethylenedioxythiophene), PEDOT, has been widely used in an array of applications spanning from energy storage to biomedical devices due to its high conductivity, good chemical stability, biocompatibility, and feasibility of functionalization. Herein we present a new strategy to copolymerize PEDOT, and its hydroxyl terminated counterpart (PEDOT-OH) through electropolymerization in the presence of different additives. A fixed amount of the monomers is introduced in the presence of ClO₄⁻ or PSS⁻ anions. The range of additives spans from MXene, CNTs, Au nanoparticles to ionic liquids such as 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. We study the impact of these components on the physicochemical and electrochemical properties of the resulting films. The roughness and topography amongst the various electrodes are compared by AFM and SEM-FIB and correlated with the results stemmed from electrochemical impedance spectroscopy, cyclic voltammetry and galvanostatic charge-discharge cycling performed in an aqueous environment (0.1 M NaCl). The best performing copolymers are further used to build state-of-the-art electrodes for oxygen reduction and electrodes for neural recordings.

2:45 PM OPEN DISCUSSION

3:00 PM BREAK

SESSION SB07.13: Sensors at Cell Interface
Session Chairs: Tzahi Cohen-Karni, Anastasia Elias, Sahika Inal and Christoph Tondera
Thursday Afternoon, December 5, 2019
Hynes, Level 3, Ballroom B

3:30 PM SB07.13.01
Precise Attachment of Living Cells to Electroactive Surfaces Ariel L. Furst; Massachusetts Institute of Technology, United States

The ability to control the interaction between living systems and electroactive surfaces has been a longstanding goal of many scientific disciplines, ranging from healthcare to clean energy. For bioelectric applications, maintaining the specificity of cell placement while facilitating electron transfer between cells and the surface remains a challenge. DNA is capable of both imbuing specificity through self-recognizing hybridization and wire-like behavior, making it ideal to address key issues with the interfacing of cells with electroactive surfaces. Through DNA hybridization-based cell adhesion, we have captured and monitored non-adherent mammalian cells, yeast, and microbes on DNA-modified electrodes. Importantly, we have applied this method to the rapid assembly of low-density monolayers of current-producing cells. Through DNA-based immobilization, we have found that these cells maintain their electron transfer abilities prior to biofilm formation. We attribute this feature, at least in part, to the conductivity of DNA. This DNA-based technique to interface cells with inorganic surfaces has broad applications, including diagnostic tools and biofuel cells.

3:45 PM SB07.13.02
Supported Biomembranes on Electronic Devices for Sensing Pathogen Interactions That Occur at the Cell Surface Susan Daniel; Cornell Univ, United States

The cell membrane is the first point of contact for pathogen entry. It is the interface that defines the inside of the cell from the environment and a surface that presents an array of biological moieties that pathogens can use to recognize
a specific host cell target. Pathogens or pathogenic material, such as viruses or bacterial toxins, target these surface moieties, which are often specific proteoglycans or glycolipids. Binding occurs first, then various mechanisms are used to gain entry into the cell by crossing the membrane barrier. Bacterial toxins poke holes in membranes, which causes catastrophic leakage of ions and nutrients from the cell, while allowing external materials enter. Viruses can inject genetic material across the plasma membrane directly or get endocytosed into the cytosol to later release their genetic code after membrane fusion. With the constant evolution of resistant bacteria and viruses that can evade the immune system, being a step ahead of them by defining new ways to disarm them is progressively more difficult. Here we present a new biomembrane sensing platform that mimics host cell membranes and takes advantage of the natural propensity of these pathogens to want to interact with these surfaces. Binding, membrane disruption, or membrane fusion can be sensed using an electroactive polymer film that supports the biomembrane as an element in an electronic circuit that monitors the electrical properties of the membrane when pathogens attack.

Bio-Hybrid Membrane for Solid-State Devices

Bio-Hybrid Membrane for Solid-State Devices Xingyao Feng, Teng Ma, Daisuke Tadaki and Ayumi Hirano; Tohoku University, Japan

Bilayer lipid membranes demonstrates an ultrathin thickness (3–5 nm) and ultrahigh ionic resistivity (>100 GΩ). Here, we propose that by utilizing the outstanding properties of bilayer lipid membranes, functional bio-hybrid membranes can be formed by doping the lipid membrane with organic molecules. In this work, organic molecules Copper (II) 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine (CuPc), which has been widely used in the fields of catalysis, solar cells, and transistors, were used to dope the lipid membranes. It is supposed that hydrophobic CuPc molecules can be inserted into the hydrophobic tails of bilayer lipid membrane, forming a sandwiched binary hybrid membrane structure. Therefore, these nano-scale hybrid membranes can be functionalized by inserting nanoparticles, without disturbing the natural ordered membrane structure. Since the lipid membrane have good insulativity and ultrathin thickness, this hybrid membrane can be used as a basic framework of bio-hybrid devices. The bio-hybrid membranes composed of lipids and CuPc molecules were formed by using self-assembly at water/air interface. Lipid molecules DPhPC and CuPc were dissolved in organic solvent. At room temperature, the prepared solution was dropped onto water surface. As the solvent evaporated, hybrid membranes immediately formed on the water surface. Finally, the self-assembled hybrid membranes were transferred onto Si substrate by gradually lowering water level.

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To investigated the surface morphology, atomic force microscope (AFM) was used. By measuring 74 samples, it is concluded that all the thicknesses of membranes are very close to multiples of 5 nm, such as 10 nm, 15 nm, 20 nm and so on. Therefore, it is highly possible that the hydrophobic CuPc molecules combined hydrophobic tails of two lipid molecules to form a hybrid sandwich structure. X-ray diffraction (XRD) measurement were used to examine the structure of hybrid membranes. The patterns did not show any peak representing the CuPc packing. This result indicated that CuPc molecules did not aggregate to form small crystals in the hybrid membrane. Furthermore, an experiment was designed based on fluorescence resonance energy transfer (FRET) theory by adding fluorescent labeled lipids into hybrid membranes. The experimental results indicated that the CuPc molecules are closer to the tails rather than heads of lipid molecules in the membranes, which is corresponding to former speculation. And these hybrid bilayer membranes can stack up to form multilayer structures whose thicknesses are integral multiples of 5 nm. With this insulator-semiconductor-insulator structure, the hybrid membrane can be used as a framework for novel nano-devices.

Carbon Nanotube Fibers for Neural Stimulation and Recording

Carbon Nanotube Fibers for Neural Stimulation and Recording Noe T. Alvarez, Elke Buschbeck, Ilya Vilinsky, Sydney Miller, Vandna Agrawal, Chethani Ruhunage and Anh D. Le; University of Cincinnati, United States

Recordings and stimulations of neuronal electrical activity is a topic of great interest in neuroscience. Multiple neurological disorders can benefit from a microelectrode that is flexible, chemically inert, electrically conducting, and preferentially transfers electrons via capacitive charge-injection. Commercial electrodes that currently exist and other electrodes that are being tested with the purpose of facilitating and improving the electron transport between solid electrode materials and biological tissue still have some limitations. This paper discusses a carbon nanotube-based microelectrode from its synthesis, fiber assembly, polymer coating and application as microelectrode for neural recording and stimulation. We compare electron transport capabilities of carbon nanotube fibers to noble metals Au and Ag wire microelectrodes to biological tissue. The recording ability of microelectrodes is demonstrated through Electroretinography (ERG) on Sarcophaga bullata fly eyes, where light stimulation generates
potential changes that were detected by our microelectrodes. Stimulation is demonstrated through Au wire and carbon nanotube fiber implants in Madagascar hissing cockroach (Gromphadorhina portentosa) antennas to control their locomotion directions. A comparison of their impedance, charge injection capacity and electrical conductivity demonstrates that carbon nanotube fibers have great potential as microelectrodes in neuroscience.

4:45 PM SB07.13.05
Pseudo 3D Graphene for Enhancing Cell-Chip Coupling Laura Matino1,2, Sahil Rastogi1, Michele Dipalo1, Francesco de Angelis1, Tzahi Cohen-Karni1,3,3 and Francesca Santoro1; 1Istituto Italiano di Tecnologia, Italy; 2University of Naples, Federico II, Italy; 3Carnegie Mellon University, United States

Bioelectronic devices interact directly with biological systems to monitor cellular electrical activity and promote cell reaction to electrical stimulation. The capabilities of such devices, in terms of recording and stimulation, are affected by the effective cell-platform coupling. Therefore, during the last years, the development of engineered 3D micro and nanostructures has improved the effectiveness of biosensors using protruding structures to achieve a more intimate contact between cells and substrates. In parallel, the rising of carbon-based materials for bioelectronics has gained attention during the last years because of their outstanding chemical properties which allow improved cell-device interface. Given this scenario, 3D out-of-the-plane graphene structures has been designed and grown on planar platforms, exploiting the electrical, mechanical and optical features of this promising material. 3D fuzzy graphene (3DFG) and nanowire-templated 3DFG (NT-3DFG) were realized as electrode surface (1). Here we report a comprehensive study of the interface by using fluorescence and electron microscopy for characterizing cell-materials interactions at micro and nanoscale. First, we investigated the biocompatibility and the adhesion effect (cell stretching) of the diverse graphene-based pseudo-3D surfaces. Then, we examined the membrane deformation and the actual cell-device coupling via scanning electron microscopy/focused ion beam sectioning (2,3). Finally, as outlook we will present preliminary results on how the material surface can affect the recording of spontaneous action potentials from electrogenic cells. We found out an enhanced cells adhesion on the substrates, suggesting that out-of-the-plane platform could improve the coupling between cells and sensors.

References

SESSION SB07.14: Biosensor Interfaces
Session Chairs: Tzahi Cohen-Karni and Sahika Inal
Friday Morning, December 6, 2019
Hynes, Level 3, Ballroom B

8:30 AM SB07.14.01
Mixed-Conducting Particulate Composites for Soft Electronics Patricia Jastrzebska-Perfect1, Georgios Spyropoulos1, Claudia Cea1, Zifang Zhao1, Omri Rauhala1, Ashwin Viswanathan2, Sameer Sheth2, Jennifer Gelinas1 and Dion Khodagholy1; 1Columbia University, United States; 2Baylor College of Medicine, United States

Bioelectronic devices should optimally merge a soft, biocompatible tissue interface with capacity for local, advanced signal processing. Here, we introduce an organic mixed-conducting particulate composite material (MCP) that can form functional electronic components by varying particle size and density. We created MCP-based high performance anisotropic films, independently-addressable transistors, resistors, and diodes that are pattern-free, scalable, and biocompatible. MCP enabled facile and effective electronic bonding between soft and rigid electronics, permitting recording of neurophysiological data at the resolution of individual neurons from freely moving rodents and from the surface of the human brain through a small opening in the skull. We also acquired high spatiotemporal
resolution electrophysiological signals non-invasively by directly interfacing MCP with human skin. MCP provides a single material solution to facilitate development of bioelectronic devices that can safely acquire, transmit, and process complex biological signals.

8:45 AM SB07.14.02
Case Studies of Bio-Iontronic Devices for Detecting the Concentration of Glucose and Monovalent Ions John A. Selberg, Chunxiao Wu and Marco Rolandi; University of California, Santa Cruz, United States

The control of ion concentration gradients and ionic currents is ubiquitous in tissue-level and cell-level processes such as enzyme activation, oxidative phosphorylation, neuronal excitation, and immune response. Bioelectronic devices with functional materials that can transduce between electronic and ionic signals allow researchers to use existing knowledge of electronics to perform unique tasks with ions in solution. Devices of this nature are well-suited to these biological ion-driven applications. Here, I report on recent progress towards developing and using iontronic devices for activating metal oxide catalysis in aqueous solutions with the application of glucose sensing.

9:00 AM *SB07.14.03
Interfacing Human Cell Membrane Models with Bioelectronics for Ion Channel Monitoring Walther Traberg-Christensen1, Anna-Maria Pappa1, Han-Yuan Liu2, Quentin Thiburce3, Alberto Salleo3, Susan Daniel2 and Roisin Owens1; 1University of Cambridge, United Kingdom; 2Cornell University, United States; 3Stanford University, United States

Cellular membranes represent an obvious, yet relatively neglected target for fundamental understanding of the mechanisms of disease and for therapeutic optimization. Existing membrane models suffer from incompatibility at the biotic/abiotic interface and lack molecular complexity, compromising their reliability. To address these issues we have developed human membrane models by fusing native extracellular material on top of conducting polymer transducers. This unique platform rises above the state of the art by providing a physiologically relevant biomimetic environment close to that of native membranes, as well as by providing integrated functionality to transduce biological events at the molecular level. The use of conducting polymers and in particular poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), overcomes the issue of the commonly used solid substrates (ie., glass, Au) for signal transduction, by facilitating mobility of the transmembrane proteins, enhancing the native structural and functional properties of the membrane. Simultaneously, it allows for the electrical characterization of the membrane properties and its interactions, by transducing the ionic flux to an electronic signal. In this work, we demonstrate the formation of native cell membranes from human embryonic kidney 293 cells (HEK) in the form of supported lipid bilayers (SLBs) on top of PEDOT:PSS electrodes and transistors. We monitor the formation of the native SLBs and characterize them using both optical and electronic methods. We show dynamics of membrane fusion by electrically monitoring the changes on the membrane properties. Finally, we show that the h-TREK-1 potassium ion channel overexpressed in HEK cells can be monitored within its native membrane context. We show that our devices can transduce the action of clinically important molecules that are able to open or block these channels. Our results suggest that this platform could be an excellent in vitro assay for drug testing, providing a scalable and cost-efficient alternative to using whole cells e.g. patch clamp assays.

9:30 AM BREAK

10:00 AM SB07.14.04
Direct Printing of Transparent and Substrate-Free PEDOT:PSS Fibre Arrays Yan Yan Shery Huang and Wenyu Wang; University of Cambridge, United Kingdom

Ultra-thin conducting fibres possess unique mechanical, optical and electrical properties due to the high aspect-ratio, low bending stiffness and transparency. Those fibre arrays made with different conducting materials could enable a variety of novel applications, ranging from transparent textile-based circuits to bio-sensors. Current fibre fabrication techniques usually deposit fibres onto substrates, and the optomechanical properties of substrates largely compromise the advantages of ultra-thin fibres. Herein, we present an efficient fibre printing method to produce conducting and substrate-free sub-micron fibres arrays. The fibre printing and fibre to circuit connection are completed in one step under a sub-80°C mild temperature, without needing post processing steps such as annealing. With this printing method, we demonstrate the capability to print conducting polymer based (PEDOT:PSS, (poly(3,4-ethylenedioxythiophene) polystyrenesulfonate)) fibres. The high resolution fibres can span across a
freestanding distance up to 10mm, having both ends attached to outer circuit with negligible contact resistance. Floating electronics are demonstrated where small electronics such as LEDs and photodiodes can be mechanically supported and electrically connected by suspended fibre arrays. Cell attachment and viability results with the PEDOT:PSS fibre arrays also show their potential use as biosensors.

10:15 AM SB07.14.05
Δ9-THC Sensing for Cannabis Detection Using 3D Printed Organic Electrochemical Transistors Darren R. Majak, Jiaxin Fan and Manisha Gupta; University of Alberta, Canada

Traditional electronics is based on the silicon transistors for a number of decades. However, the emergence of organic, conductive polymers leading to organic transistors has allowed for research into non-traditional electronic devices that combine organic and inorganic material. Organic transistors [3,4] have shown many benefits and applications, by using organic semiconductors, devices can be flexible, solution processable, 3D printable and economical. Organic Electrochemical Transistors (OECTs)- a specific subset of organic transistors - are perfectly suited for biological sensing. OECTs have specifically been used to sense dopamine, DNA, pH, lactate, glucose, ion concentration and more. OECTs operate in a similar manner to traditional silicon transistors but the channel is made of an organic polymer and uses the ions in an electrolyte as part of the gate contact. OECTs operate with both electrical and ionic current, meaning they can be driven at lower voltages and have lower power consumption. In addition, they have built-in amplification, which means higher sensitivity and lower power consumption. By operating with ionic current, OECTs can be used for bio-sensing as they can detect ions present in biological environments.

Canada is the first nation in the G7, and the second in the world to legalize the recreational use of cannabis. However, despite legalization, a number of challenges remain that need to be solved. One of the main issues is the detection, and quantization of impairment. The psychoactive cannabionoid, Δ²-Tetrahydrocannabinol (THC), is the cause of impairment, however the extent of it is difficult to determine because THC remains in blood, urine and other bodily fluids long after exposure and therefore does not correlate to impairment. Currently, all the Δ9-THC detection techniques are based on either utilising mass spectroscopy or gas chromatography (GC) for oral fluids. Both of these techniques are accurate but require extensive measurement equipment and are not cheap. The other Δ9-THC measurements are based on blood or urine pathological measurements which also require more sampling equipment along with the issues of hygiene and can take several hours to obtain results. A better approach is to test the concentration of THC present in the saliva [1, 2] of the user, as THC concentrations in saliva can more closely be correlated with cognitive and motor impairment. OECTs are perfectly suited for this application, due to the high transconductance and sensitivity. Our 3D printed OECTs [6-8] can detect concentrations down to 0.05 nM, in DI water, without functionalization of the OECT. This limit of detection is well within the required level to be able to detect the THC levels present in cannabis users’ saliva. These sensors are entirely 3D printed, which means that they can be easily and cost effectively fabricated, as compared to traditional nano and micro fabrication methods. These sensors show repeatable results with low drift (~3.6%), as well as a fast response (163s average). The next step is to improve the detection capability of the sensors in saliva rather than water and this can be achieved by functionalization of the gate electrode to detect only the Δ9-THC. Results from this study will be presented.


10:30 AM SB07.14.06
Label-Free Aptamer-Based Detection of Amyloid Beta Proteins on SiO2 Covered Silicon Structures Hanna Hlukhova¹, Yuriy Kutovyi², Marcus Menger², Andreas Offenhäusser² and Svetlana Vitusevich¹; ¹Forschungszentrum Jülich, Germany; ²Fraunhofer Institute for Cell Therapy and Immunology, Germany

Neurodegenerative processes in the brain became an important challenge with increased age of the population.
Usually, relatively bulky optical methods are used to detect Amyloid β peptides, which are linked to the pathogenesis of Alzheimer disease. To prolong effective and healthy memory and thinking capability as well as to stop the factors resulting in Alzheimer’s disease new high-sensitive and direct methods for the early detection of peptides involved in Alzheimer’s disease have to be developed. In this contribution, we report on successful demonstration of a new label-free approach for detection of amyloid beta proteins by high-selective aptamers immobilized onto the SiO₂ surface. A nucleotide aptamer was synthesized to detect the target Amyloid beta-40 sequence. Functionalized structures based on thin SiO₂ dielectric layer has been developed to detect ultra-low concentrations of the target protein. The detection technique utilizes high-efficient aptamer immobilization on the SiO₂ surface of the sensor system configured with a liquid-gate. The introduction of amyloid beta protein of different concentrations in a wide range from 0.1 pM to 1 μM to the surface of the sensor results in a change of surface potential. Obtained experimental data demonstrate high-sensitive and reliable detection of ultra-low concentrations of the amyloid beta protein, which opens the perspective for the development of real-time electrical sensors for studies and understanding of different stages of Alzheimer’s disease utilizing nanostructures fabricated on the basis of cost-efficient CMOS-compatible technology.

SYMPOSIUM SB08

Advanced Neural Materials and Devices
December 2 - December 4, 2019

Symposium Organizers
Mohammad Reza Abidian, University of Houston
Rylie Green, Imperial College London
Mahiar Hamedi, KTH
Laura Poole-Warren, University of New South Wales

* Invited Paper

SESSION SB08.01: Materials and Devices for Neural Interfaces I
Session Chairs: Mohammad Reza Abidian and Laura Poole-Warren
Monday Morning, December 2, 2019
Hynes, Level 3, Room 301

9:00 AM *SB08.01.01
Large-Scale Neural Interface Devices Dion Khodagholy; Columbia University, United States

As our understanding of the brain’s physiology and pathology progresses, increasingly sophisticated technologies are required to advance discoveries in neuroscience and develop more effective approaches to treating brain disease. There is a tremendous need for advanced materials solutions at the biotic/abiotic interface to improve the spatiotemporal resolution of neuronal recording. Organic electronic devices offer a unique approach to these challenges, due to their mixed ionic/electronic conduction, mechanical flexibility, enhanced biocompatibility, and capability for drug delivery. We designed, developed, and characterized conformable organic electronic devices in the form of transistors and electrodes to efficiently interface with the brain and acquire neurophysiological activity not previously accessible with recordings from the brain surface. These devices have facilitated large-scale rodent neurophysiology experiments and uncovered a novel hippocampal-cortical oscillatory interaction. The biocompatibility of the devices allowed intra-operative recording from patients undergoing epilepsy surgery, highlighting the translational capacity of this class of neural interface devices. In parallel, we are developing the high-speed electronics and embedded acquisition and storage systems required to make high channel count, chronic
neurophysiological recording from animals and human subjects possible. This multidisciplinary approach will enable the development of new devices based on organic electronics, with broad applicability to the understanding of physiologic and pathologic network activity, control of brain-machine interfaces, and therapeutic closed-loop devices.

9:30 AM BREAK

10:00 AM *SB08.01.02
OPEN SLOT

10:30 AM OPEN DISCUSSION

10:45 AM SB08.01.04
High-Speed Enhancement Mode Ion Driven Transistors for Bioelectric Device Claudia Cea¹, Georgios Spyropoulos¹, Jennifer Gelinas² and Dion Khodagholy¹; ¹Columbia University, United States; ²Columbia University Medical Center, United States

Technological leaps to improve brain-machine interface devices require sophisticated integrated circuits based on ion driven transistors. These devices should be capable of forming complementary logic and analog circuits to allow acquisition, processing and manipulation of a biological environment. However, the lack of readily available p-type polymers for use in enhancement mode transistors and their complicated synthesis significantly limits the investigation and application of such devices in bioelectronics. To address this challenge, we propose a simple route for creation of enhancement mode Ion Gated Transistors (IGT) by combining a highly conductive poly(3, 4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS) and a reducing agent polyethyleneimine (PEI) to enable doping of the polymer in an aqueous environment. The protonated PEI bonds with the PSS- and dedopes the PEDOT:PSS chain resulting in an initial off-state of the transistor. A subsequent application of negative gate voltage dopes the PEDOT:PSS switching the channel on. Furthermore, we introduce a novel operation mode of these organic transistors by utilizing contained mobile ions within the conducting polymer channel to permit shortened ionic transit time and high transconductance. The embedded ions within the channel are obtained through the addition of D-sorbitol, a biocompatible hydrophilic sugar alcohol, which uptakes water molecules keeping the channel hydrated through the generation of ion reservoirs. The distance ions have to travel to modulate the transistor is shorter compared to the one of electrolyte-based transistor resulting in substantially faster devices (time constant of 2.6 μs). To determine an optimal transistor configuration and material composition, we microfabricated transistor arrays of varying geometrical parameters. In doing so, we were able to extract conductivity, contact resistance, and electrochemical impedance values for all the critical interfaces of various composites. The resulting high-transconductance, high-speed enhancement-mode transistors were realized in the form of conformable depth probes fabricated on thin film plastics to enable in vivo electrophysiological recording of cortical activity from neonatal rats and conformable surface devices to be utilized for electrocardiography, electroencephalography and electromyography from human subjects. The ultra-high speed, improved transconductance and stability of these arrays were demonstrated by recording biosignals covering a full biological frequency band varying from single unit activity to local field potentials, cardiac and muscular activity, (0-1000 Hz) paving the way for use as a reliable neural interface device.

11:00 AM SB08.01.05
A Flexible IrOx-Based Microneedle Electrode Array with Integrated Electrically Driven Drug Delivery Hsiang-Ping Liao, Fu-Erh Chan and Pochun Chen; National Taipei University of Technology, Taiwan

Implantable neurostimulation devices have been attracted considerable attention recently since neural disordered disease can be treated by electrostimulation. Microneedle electrode arrays have high aspect ratio that can sufficiently penetrate to the depth of target without causing any damage. Additionally, electrically controlled drug release has been particularly attractive for bioelectronics because the electrical signal is portable and controllable on-demand, without the requirement of large or special equipment. However, protein-based bioactives such as growth factors or antibodies are easily denatured to lose their bioactivity in response to external stimulation. It is challenging to develop a bio-electrode system that permits the electrically responsive drug release without damage. In this study, we designed and fabricated an IrOx-based microneedle electrode array on a flexible Parylene C
substrate. Then, the microneedle electrode array has been treated by a facile method to form a hybrid film of iridium oxide and bovine serum albumin (BSA). We carried out a cyclic voltammetry approach to co-electrodeposit iridium oxide and plasma protein on the microneedle electrode array. We characterized and evaluated the hybrid electrolytes and deposited films for bio-electrode applications. We also demonstrated the electrically controlled release triggered by pulse current stimulation. In addition, the biocompatibility of the microneedle electrode array was also investigated by testing the cell viability.

SESSION SB08.02: Materials and Devices for Neural Interfaces II
Session Chairs: Rylie Green and Mahiar Hamedi
Monday Afternoon, December 2, 2019
Hynes, Level 3, Room 301

1:30 PM *SB08.02.01
Interfacing with the Brain Using Organic Electronics George G. Malliaras; University of Cambridge, United Kingdom

One of the most important scientific and technological frontiers of our time is the interfacing of electronics with the human brain. This endeavour promises to help understand how the brain works and deliver new tools for diagnosis and treatment of pathologies including epilepsy and Parkinson’s disease. Current solutions, however, are limited by the materials that are brought in contact with the tissue and transduce signals across the biotic/abiotic interface. Recent advances in organic electronics have made available materials with a unique combination of attractive properties, including mechanical flexibility, mixed ionic/electronic conduction, enhanced biocompatibility, and capability for drug delivery. I will present examples of novel devices for recording and stimulation of neurons and show that organic electronic materials offer tremendous opportunities to study the brain and treat its pathologies.

2:00 PM SB08.02.02
High Throughput Evolution of Near-Infrared Serotonin Nanosensors Sanghwa Jeong, Darwin Yang, Abraham Beyene, Anneliese Gest and Markita Landry; University of California, Berkeley, United States

Release and reuptake of neuromodulator serotonin is central to mood regulation and neuropsychiatric disorders, whereby imaging serotonin is of fundamental importance to study the serotonin signaling system. Herein, we present a reversible near-infrared optical probe for serotonin that reports physiologically-relevant serotonin concentrations on relevant spatiotemporal scales, and is compatible with pharmacological tests. The probe responds with ΔF/F₀ of up to 194% in the near-infrared fluorescence emission window of 1000-1300 nm, and is constructed from semiconducting single-walled carbon nanotubes (SWNT), which have shown utility for non-invasive through-skull imaging in rodents. Synthetic molecular recognition for serotonin was conferred by evolving molecular recognition between single stranded DNA (ssDNA) and SWNT. To do so, we developed a high-throughput screening platform for evolution of serotonin molecular selectivity, in which systematic evolution of ligands by exponential enrichment is implemented on carbon nanotube surfaces, a process we’ve termed SELEC. 10¹¹ unique SWNT-ssDNA constructs can be screened for their ability to bind a target analyte and provide a selective near-infrared fluorescence signal. Iterative selection of analyte-binding polymers that form a SWNT-surface-adsorbed phase for serotonin recognition are identified through ionic desorption of sub-optimal polymers, and exponential amplification of nucleotides that recognize serotonin. The best-responding serotonin nanosensor is shown to bind serotonin with a K_d of 6.3 µM, is shown to be reversible, and exhibits unaltered performance in artificial cerebrospinal fluid. We show that our serotonin nanosensor does not respond to serotonin metabolites 5-hydroxyindoleacetic acid (HIAA), 5-hydroxytryptophan (HTP), and 5-methoxytryptophan (MTP) and of importance to understanding pharmacology in the context of serotonin signaling, we additionally show serotonin receptor-targeting drugs fluoxetine, MDMA, 25I-NMOMe, and quetiapine do not interfere with nanosensor performance. Lastly, nIRHT can be introduced into the brain extracellular space in acute brain slices, and can be used to image exogenous serotonin reversibly. Our results suggest evolution of nanosensors could be generically implemented to rapidly develop other neuromodulator probes, and that these probes can image neuromodulator dynamics at spatiotemporal scales compatible with endogenous neuromodulation. While we’ve implemented SELEC to develop an optical probe for serotonin herein, the platform
is fundamentally generic for generating other optical probes of neurological relevance.

2:15 PM SB08.02.03
Ultra-Thin, Flexible, Inkjet-Printed Neural Probes with Mechanically Gradient Structure Toshinori Fujie\textsuperscript{1,2,3}, Nana Kokubo\textsuperscript{1}, Kento Yamagishi\textsuperscript{1}, Shinji Takeoka\textsuperscript{1} and Hiroyuki Ohta\textsuperscript{1}; \textsuperscript{1}Tokyo Institute of Technology, Japan; \textsuperscript{2}Japan Science and Technology Agency, Japan; \textsuperscript{3}Waseda University, Japan; \textsuperscript{4}National Defense Medical College, Japan

Flexible materials are important for the development of insertable neural probes for recording stable signals (spikes) \textit{in vivo}. However, conventional neural probes such as silicon probes have several drawbacks, including high rigidity compared with soft brain tissues and poor mechanical properties during manipulation. In addition, the operator must handle the probe carefully because its tip is extremely small, sharp, and brittle, so it can be easily damaged if touched by a finger or dropped on the floor. To overcome these problems, here, we show inkjet-printed, flexible neural probes for spike recording by using polymeric ultra-thin films (nanofilms). The neural probes were constructed from 400 nm-thick poly(D,L-lactic acid) nanofilms, inkjet-printed lines consisting of Au and poly(3,4-ethylenedioxythiophene):polystyrenesulfonate nanoinks, and insulating fluoropolymer layers. The neural probe was prepared as following steps: i) 50-µm-wide conductive lines were inkjet-printed on the nanofilm, which was dip-coated with a fluoropolymer solution to make insulating layers. ii) The tip of the insulated nanofilm was trimmed with a razor, exposing the microelectrodes. iii) The resulting 6-µm-thick flexible electrode was twisted from a 2D sheet into a 3D needle, allowing it to be inserted into brain tissues. The electrode was also integrated into an optical fiber (i.e., optrode) to enable optogenetic recording. iv) To connect the electrode to the external amplifiers, the stiffness was gradually increased from the flexible nanofilm to the rigid device and fabricated pre-assembled connection. The nanofilm-based probe with a needle shape recorded not only \textit{in vivo} neuron spikes from mouse thalamus, but also spontaneously and optogenetically evoked individual spikes from rat hippocampus with the optrode. The flexible and robust structure of the present neural probes will allow for tailor-made customization for various research requirements, such as changing the complex geometry, increasing the number of electrodes for spike signal sensing, and segmenting the electrode tips to precisely record \textit{in vivo} neuronal activity.

2:30 PM SB08.02.04
Breaking Longitudinal Symmetry of Fiber-Based Neural Probes via In-Fiber Photolithography Youngbin Lee\textsuperscript{1,1}, Andres Canales\textsuperscript{1,1}, Gabriel Loke\textsuperscript{1,1}, Yoel Fink\textsuperscript{1,2} and Polina Anikeeva\textsuperscript{1,1,1}; \textsuperscript{1}Massachusetts Institute of Technology, United States; \textsuperscript{2}Advanced Functional Fabrics of America, United States

Thermal drawing has been applied to produce flexible, microstructured polymer fibers integrating diverse functionalities. Because of their small size, flexibility, and biocompatibility of the component materials, these multifunctional fibers are attractive for applications in neuroscience to probe and modulate neural activity. Despite the advantages of thermal drawing, including simplicity of materials integration and high device yield, the functionality of thermally drawn fibers is constrained by the symmetry of the fiber along its axial direction. In the present work, we suggest two hybrid fabrication methods combining thermal drawing and photolithographic process to break this symmetry and enable interactions of fiber-based probes with multiple neural populations along their shaft following implantation into the brain.

We employed thiol-epoxy/thiol-ene click chemistry to produce a novel photoresist with low polymerization shrinkage stress and low oxygen inhibition during polymerization. The system is polymerized via two steps - thermal and photo curing. Thermal polymerization yields formation of linear chains through a reaction between thiol and epoxy functional groups resulting in a thermoplastic compatible with fiber drawing. In contrast, photo curing occurs only at areas exposed to ultraviolet light, generating an insoluble network structure through the thiol-ene reaction, allowing for the development of desired patterns. The reported photoresist can be applied either prior to or following fiber drawing allowing for the design of functional features along the fiber shaft.

In addition to offering greater utility of fibers for neuroscience and neural engineering, our technique will likely find broader applications in fields of optoelectronics, sensors and smart textiles.

2:45 PM SB08.02.05
Transparent Organic Electrochemical Transistor Array toward Flexible Multielectrode Dish Yasutoshi Jimbo\textsuperscript{1}, Daisuke Sasaki\textsuperscript{2}, Sunghoon Lee\textsuperscript{1}, Takashi Ohya\textsuperscript{2}, Masaya Nishinaka\textsuperscript{1}, Tomoyuki Yokota\textsuperscript{1}, Tatsuya Shimizu\textsuperscript{2} and Takao Someya\textsuperscript{1}; \textsuperscript{1}The University of Tokyo, Japan; \textsuperscript{2}Institute of Advanced Biomedical Engineering and Science, Tokyo Women’s Medical University, Japan
We fabricated a transparent organic electrochemical transistor (OECT) using ultrathin Au (14 nm), and successfully recorded extracellar potential of induced pluripotent stem cell-derived cardiomyocytes.

OECT has attracted interests in both material engineering and biological engineering fields because its high transconductance and simple structures enable versatile applications by combined with other flexible materials. Monitoring electrophysiological activity of cells is one of those applications[1]. By using OECT instead of conventional electrodes, we could expect better data quality and high density measurement without lack of flexibility, which is usually realized on gel and provides bio-tissues with free movement and better maturity. Although transparency is also an advantage of OECT, cell monitoring with transparent OECT have never been reported as far as we know. OECT usually consists of three layers other than substrates: metal source and drain electrode, organic semiconductor as channel, and passivation. Unlike other organic transistors, the channel of OECT can be made from poly(3,4-ethylenedioxy- thiophene):poly(styrenesulfonate) (PEDOT:PSS), which is a transparent semiconductor. Therefore, by replacing metal source and drain electrode for transparent conductors, you can make the whole device transparent. It enables the support of imaging technologies including fluorescence imaging or image based force mapping.

Transparent OECT for in vivo optogenetic experiment was previously reported[2], but its grid structured metal electrode may bother imaging in micro-meter scale cell monitoring. Thus in our previous report, we used Indium-tin-oxide/Au/Indium-tin-oxide (ITO/Au/ITO) structure as highly conductive transparent electrode instead[3]. Here we further optimized its structure. ITO/Au/ITO structure was replaced by simple ultrathin Au supported by polyimide coated parylene substrate. The photoresist used as passivation layer was also replaced for parylene to ensure its biocompatibility. Owing to the small total thickness, which is less than 5 µm, it can be used as highly flexible, foldable device. The mechanical robustness was limited so far due to the ITO layer. The ultrathin Au showed stable operation under bending test which is equivalent to 1.25 % tensile strain whereas ITO/Au/ITO started failing at 0.9 %. The sheet resistance was 8.6 ohms/sq. so that you can achieve sufficiently low parasitic resistance against channel resistance (~500 ohms). Owing to the simplified structure and low sheet resistance, transparent active matrix fabrication and extracellar potential recording were successfully demonstrated.


3:00 PM BREAK
Our ability to treat neurological disease is severely limited by the complexity of the nervous system and the quality of the information derived from recording devices. A device that holds great potential for recording high quality electrophysiology signals is the organic electrochemical transistor (OECT). OECTs are transistors in which the output current is regulated by the injection of ions from an electrolyte. They are fabricated from biocompatible materials and have been shown to provide higher signal-to-noise ratio compared to electrodes. Their unique properties pave the way for enhanced performance neural interfaces while minimising the invasiveness of the recording method. We report on how different parameters such as device geometry and bias conditions affect the noise characteristics of OECTs. These results show how to minimise noise and boost signal-to-noise ratio. We further show how these new design rules are applied to reduce the footprint of OECTs and drastically improve their recording capability when used in neural interface applications.

4:15 PM SB08.02.08
Nanofluidic Sampling Platform for Micro-Invasive Membrane-Free Tracking of Neurochemical Biomarkers
Ritu Raman, Erin Rousseau, Michael Wade, Allison Tong, Max Cotler, Alejandro Lugo, Forest White, Michael Cima and Robert Langer; Massachusetts Institute of Technology, United States

Introduction: Neural pathology is characterized by electrical and chemical dysregulation in distinct brain circuits. Chemical dysregulation can be monitored by measuring the local composition of interstitial fluid (ISF). The current state-of-the-art in neurochemical sampling, microdialysis, enables the collection of small, highly concentrated neurochemicals from ISF via diffusion across a semipermeable membrane. Large probe sizes (> 150 μm) limit spatial resolution, which can lead to tissue scarring and limit chronic recording. Moreover, relying on diffusion limits spatiotemporal resolution and increases detection limits. Membranes particularly limit measuring neuropeptides, which are prone to non-specific absorption (average recoveries < 20%) and are present at very low concentrations in ISF, and preclude measuring dense core extracellular vesicles (EVs), which play a critical role in cell-cell signaling. We have built a novel micro-invasive membrane-free sampling platform that enables direct sampling of ISF. This is a fundamental shift from microdialysis, which tracks small and abundantly present neurotransmitters, to a device that samples the complete biochemical milieu with pinpoint spatiotemporal resolution. We anticipate this will enable a deeper understanding of the onset and progression of neural pathologies.

Methods: We have manufactured a sampling platform composed of micro-invasive probes (80 μm outer diameter, 50 μm inner diameter) coupled to a custom-made nanofluidic pump (nanopump). Fluid flow within custom tubing (100 μm inner diameter) in the pump is driven by the sequential contraction of nitinol wires (shape memory alloy), and back flow is prevented by a nitinol powered valve. The nanopump is capable of bidirectional flow control with single nanoliter precision and negligible dead volume, a capability not demonstrated by the current state-of-the-art, and is fully portable for in vivo use. Flow is controlled via the electrically-triggered contraction of nitinol wires (Fig. 1A) and flow rates (1 nL/s) and sampling volumes (100-1000 nL) safe for in vivo operation in the brain were used. Sampled fluid is analyzed via liquid chromatography-tandem mass spectrometry (LC-MS/MS) to detect neuropeptides at physiological concentrations (1-20 femtomolar).

Results & Discussion: We have shown that our micro-invasive probes minimize gliosis when chronically implanted in rodent brains, and retain fluidic functionality for 12 mos. post-implantation. Extensive characterization of nanopump-driven infusion into and sampling from agarose brain phantoms in vitro has enabled optimization of platform performance in response to a variety of parameters including wire number and pre-tension, tube diameter and length, capillary size, and flow control algorithm. Ex vivo infusions into rodent striatum have been characterized using both histology and 3D fluorescence imaging, showing bolus volume control as a function of infusion time. Nanopump-driven sampling from ex vivo and in vivo brains has also been performed, with confirmed presence of proteins specific to neural extracellular space, including brain acid soluble protein 1, myelin basic protein, and gamma enolase. Sample stability in different cryo-storage/processing conditions has been thoroughly characterized. Ongoing in vivo sampling studies will enable chronic tracking of covariant neuropeptides and EVs in physiological and pathological states. A first step will be long-term tracking of the spatiotemporal dynamics of dynorphin, a neuropeptide associated with stress, anxiety, and substance use disorders, a capability that is not possible with current tools.

Conclusions: We have developed a novel tool for biomedical engineers and neuroscientists to investigate the biochemical basis for neural pathology. Our micro-invasive ISF sampling platform has the potential to generate new fundamental knowledge and enable more accurate diagnosis and treatment of neural disorders in the future.
SB08.03.01

*Induction of Calcium Elevations in Hippocampal Neural Networks by Intracellular Stimulation*  
Juyoung Kwon¹, Sukjin Ko², Jaejun Lee¹, Jukwan Na¹, Hyojung Lee¹, Seonghyeon Lee¹, Seungsoo Chung² and Heon-Jin Choi¹; ¹Yonsei University, Korea (the Republic of); ²Yonsei University College of Medicine, Korea (the Republic of)

Recent advances in the field of neural interfaces have been developed to improve the precision with high resolution and specificity of stimulation to the level of individual cells. To activate neurons with enhanced selectivity, the efficient coupling between the cell membrane and electrodes is required. Here, we demonstrate a vertical nanowire multi-electrode array (VNMEA) with feature sizes and densities comparable to neural circuits which enable the individual stimulation by forming tight junctions with cell membranes. This study demonstrated stimulation-induced Ca²⁺ elevations in individual primary hippocampal neurons by direct intra-neuronal stimulation with a vertical nanowire multi-electrode array (VNMEA). VNMEA-mediated stimulation showed superior properties of peak amplitude of Ca²⁺ elevation and kinetics of recovery than those through field stimulus. Moreover, tight physical/electrical coupling with the individual neuron enables targeted stimulation of a specific neuron without activation of nearby neurons, and localization of spiking neurons in response to depolarization due to intra-neuronal stimulation, which is considered the connection and activation pathway of the neurons. From the results of simulation models, we demonstrate the spatial and temporal confinement of intracellular stimulation by 6.9-fold higher current density built in intracellular space compared to extracellular space. Considering the activation modalities of separate neurons are essential for a complete understanding of neural circuit dynamics, the VNMEA platform could further provide a versatile tool for both manipulating single neurons and probing the functional connectivity of specific neural networks.

SB08.03.02

*Conducting Polymer Nanofibers for Articulating Artificial Muscles*  
Mohammadjavad Eslamian, Fereshtehehsadat Mirab, Vijay K. Raghunathan, Sheereen Majd and Mohammad Reza Abidian; University of Houston, United States

Conducting polymer actuators are promising materials for biomedical applications ranging from artificial muscles to drug delivery devices. These devices rely on bulk volume changes of conducting polymers (CPs) which arise from electrochemical redox processes. The changes in polymer chains conformation combined with the transportation of ions and solvent in and out of the polymer matrix are responsible for the micro and macro-scale expansion/contraction of the CPs. Construction of bilayer/trilayer bending devices is a very common strategy to convert the reaction-driven volume changes into macroscopic motions, where electrical energy is transduced into mechanical energy via electrochemical redox reactions in the active CP layer. In such devices, the CP layer is adhered to a passive thin layer to convert the in-plane actuation strain generated in the CP layer into macroscopic bending movements. Prior works have focused on the actuation of bilayer/trilayer actuators based on polypyrrole (PPy) films. We have previously proposed a novel structure for PPy:polystyrene sulfonate (PSS) in the form of randomly-oriented nanotubes and studied their ion transport behavior during cyclic voltammetry (CV) via electrochemical quartz crystal microbalance. Here, we report a bilayer actuator based on PPy nanofibers doped with PSS and constructed on a passive layer of Au-coated polypropylene (PP) film (length= 20 mm, width= 1 mm, PP thickness= 30 μm, Au thickness= 180 nm, PPy thickness= 12 μm). The PPy nanofibers were fabricated using electrochemical deposition of PPy (charge density 3.6 C/cm²) around electrospun poly-L-lactide nanofibers with the average diameter of 140±4 nm. The average diameter of the resultant PPy nanofibers was 626±16 nm. The bending behavior of the PPy nanofibers was investigated by measuring the tip deflection of actuator in both liquid and agarose gel (0.2%) electrolytes containing 0.1 M NaPSS. The PPy nanofibers were subjected to CV in the potential range of −0.8 V to +0.4 V at various scan rates of 10, 50, 100, and 200 mV/s for 20 cycles. The actuator showed a
reversible bending movement during each potential cycle. The maximum deflection of actuator decreased in both liquid and gel electrolytes by increasing the scan rate. The maximum deflection in liquid was 7.89±0.08 mm, 5.38±0.04 mm, 3.81±0.01 mm, and 2.52±0.01 mm, respectively at the scan rates of 10, 50, 100, and 200 mV/s. The maximum deflection in gel was 432±11 µm, 301±2 µm, 222±1 µm, and 148±1 µm, respectively at the scan rates of 10, 50, 100, and 200 mV/s. Ultimately, the actuation moment generated during cycling at various scan rates was calculated using linear bending beam theory and Bernoulli’s equation for fluid drag force. The findings in this study may have a great impact on the utilization of CP nanofibers for development of bioactuators.

SB08.03.03
Spatial Modulation of Conducting Polymer Surface Properties—Template-Free Preparation of Variable-Surface Roughness Gradients of Conducting Polymer Film for Neural Interfaces
Anthony M. Kisucky, Martin Antensteiner and Mohammed R. Abidian; University of Houston, United States

Peripheral nervous system injuries are a common accessory to trauma, constituting tens of thousands of cases per year. Without intervention, these injuries can compound into a permanent reduction or loss of limb function. Clinical treatments are limited to performing an autograft to close the gap. While effective, this method has some drawbacks, primarily nerve-tract mismatch in the host area and dysesthesias in the donor region. Artificial conduits have been widely studied as an additional intervention, but outcomes are not yet on par with autografts. Conducting polymers (CPs) have garnered much interest in neuroprosthetic applications due to their combination of unique electrical, physical, and chemical properties. Due to their biocompatibility, CPs can guide growing or regenerating axons, but the quantitative relationships between CP surface properties and axonal outgrowth are not yet clear. Characteristic feature size is known to be a crucial element in biomaterial substrates, enhancing, hindering, or entirely blocking the growth of cells cultured upon the biomaterial. Studies have demonstrated the effect of various substrate morphologies on neuron behavior and morphology, but the effect of spatially-variant surface features remains an unstudied realm.

Here we have investigated poly(pyrrole) (PPy) films fabricated using galvanostatic (GSTAT) electrodeposition at 0.5mA/cm² current density and poly(styrene-sulfonate) (PSS) dopant. An agarose gel was incorporated into the electrodeposition circuit to selectively apply Py:PSS monomer solution to controlled areas of an Au substrate. By positioning the gel on a computer-controlled motion stage, different regions of the substrate could be sequentially polymerized upon. Additional control software permits precise and variable control of the stage velocity; by changing the movement speed, residence time of the monomer liquid bridge may be adjusted. Increases in residence time caused increases in layer thickness and surface roughness. For example, by sequentially decreasing the stage velocity from 10.42µm/s to 3.21µm/s over 25 minutes, the PPy surface roughness (Rq) increased linearly from 2.75±0.69nm to 7.52±1.73nm, and the thickness increased from 318.5±75.9nm to 1,199.0±129.3nm. Various stage-velocity profiles allowed fabrication of multiple surface morphologies; constant-thickness, linear-increase (wedge-shaped), exponential-increase, and increase-decrease (hill) velocity profiles were successfully applied to 10 millimeters of Au substrate. Materials confocal microscopy was used to characterize film thickness and surface roughness as a function of substrate position.

SB08.03.04
Electropolymerized Poly(3,4-ethylenedioxythiophene) Coatings for Implantable Stimulating Microelectrodes
In Vivo
Jo‘Elen R. Hagler1, Côme Bodart1, Nicolò Rossetti1, Bénédicte Amilhon2 and Fabio Cicoira1;
1Polytechnique Montreal, Canada; 2University of Montréal, Canada

Implantable neural electrodes are important tools for recording and manipulating functions of the nervous system. Neural network interfaces, such as electrodes, have been used to better understand neural network plasticity through recording brain signals, and stimulating neural electrodes have been used clinically for therapeutic and assistive purposes in people with disease and injury. The challenges facing neural interface engineering is to develop materials that can seamlessly interface with the biological environment of the brain over long time periods, consistently provide the desired therapeutic results, and mitigate health risks associated with chronic implantation. Coating electrodes with conductive polymers such as poly (3,4-ethylenedioxythiophene) (PEDOT). PEDOT has shown to enhance the performance of metal electrodes by decreasing the impedance and increasing the charge storage capacitance. PEDOT is an excellent candidate for interfacing with the brain because of its mixed ionic-electronic conductivity, biocompatibility, and electrochemical stability.

Here, stimulating platinum-iridium (PtIr) neural microelectrodes were coated with PEDOT:tetrafluoroborate through
electrodeposition in the solvent propylene carbonate. Coated and uncoated stimulating electrodes along with tungsten recording electrodes were implanted in the hippocampus of mice. The coated/uncoated PtIr electrodes were stimulated daily, the recording electrodes measured the local field potentials generated by the stimulation, and the impedance before and after stimulation was measured at each electrode. The coated electrodes were able to effectively stimulate neuronal activity in the brain, thus demonstrating that PEDOT-coated electrodes are a viable alternative to bare PtIr recording electrodes.

SB08.03.05
Porous Boron Doped Diamond Based MEAs / Microprobes for Dual Mode Neural Recording
Andrew Taylor¹, Petr Ashcheulov¹, Ladislav Klimša¹, Jaromír Kopeček¹, Vincent Mortet¹, Silvia Sedláková¹, Jan Krášek², Ivan Dittert², Václav Petrák³, Veronika Benson¹,³, Silvana Baluchová¹,³, Mariola Brycht³, Karolina Schwarzoňová-Pecková¹,³, Alexandr Laposa⁴ and Vladimíra Petráková³;¹FZU - Institute of Physics of the Czech Academy of Sciences, Czechia; ²Institute of Physiology of the Czech Academy of Sciences, Czechia; ³Faculty of Biomedical Engineering, Czech Technical University in Prague, Czechia; ⁴Institute of Microbiology of the Czech Academy of Sciences, Czechia; ⁵Charles University, Faculty of Science, Czechia; ⁶Czech Technical University in Prague, Czechia

In this presentation we focus on fabrication pathways established for development of a system for dual recording of neuroelectrical and electrochemical signals based on porous boron doped diamond (pBDD) microelectrode arrays (MEAs) and microprobes, enabling alternate, or even simultaneous, recording of two types of information from one biological sample during one measurement session, i.e. detection of action potentials and neurotransmitters. pBDD based MEAs were fabricated via a novel combination of ink-jet printing and microwave linear antenna plasma enhanced chemical vapour deposition (MW-LA-PECVD) techniques. Nanodiamond seeded SiO₂ nano-spheres in a dispersion of ethylene glycol were ink-jet printed onto a Ti/quartz MEA with 20 electrode pads. Following seeding the MEA substrate was loaded into a MW-LA-PECVD system for layer deposition. The selected growth conditions enabled co-deposition of conductive pBDD on seeded areas and insulating silicon carbide (SiC) on unseeded areas, and thus matching the functionality requirements of layers for in-vitro MEAs. This novel combination of techniques negates the need for complicated and time consuming lithography/masking/etching steps. Fabricated pBDD/SiC MEAs were then used to culture hippocampal neurons and record their activity using a MEA amplifier USB-MEA64. Regular measurements revealed neuronal activity on day 10 -12 in-vitro. Activity was maximal 19-22 days in vitro, later declined and after 40 days disappeared. Comparison of electric activity between neurons grown on commercial TiN MEAs and pBDD MEAs showed a 2x lower standard deviation of voltage noise recorded for pBDD MEAs.

For electrochemical recording, we aim to employ pBDD based microprobes positioned in close proximity to a firing neuron on a pBDD MEA electrode in order to record neurotransmitter (e.g. dopamine) activity. pBDD µprobes were fabricated following anisotropic chemical etching of metallic wires (W or Ti) and then coated with BDD using the same MW-LA-PECVD system. Electrochemical characterization of model planar and porous BDD electrodes has been performed by recording cyclic voltammograms (CVs) of the inner-sphere [Fe(CN)₆]⁴⁻/³⁻ and the outer-sphere [Ru(NH₃)₆]³⁺/²⁺ redox markers. The acquired ΔEp values approach 59 mV (a value for reversible one-electron system), thus confirming fast electron transfer kinetics as well as the high quality of the fabricated electrode materials. In addition, the electrochemical behaviour of 0.1 mmol L⁻¹ dopamine was investigated by CV. Results indicate that both BDD materials can be applied for dopamine detection in media used for neuron culturing, e.g. HEPES.

In conclusion, we have demonstrated a simplified fabrication regime for the preparation of BDD based MEAs and microprobes with enhanced surface area. Functionality of the developed electrodes is shown by electrical recordings from firing neurons along with detection of neurotransmitters.

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SB08.03.06
Control of a Microfluidic Three-Ring Chemical Oscillator Network
Maria Eleni Moustaka, Michael M. Norton, Chris Simonetti and Seth Fraden; Brandeis University, United States

We study synchronization patterns in microfluidic networks containing Belousov-Zhabotinsky (BZ) chemical oscillators. In our experiments, the auto-catalytic, light-sensitive, BZ reaction is confined to micro-fabricated wells constructed from the elastomer PDMS. Using soft lithography, PDMS networks are arranged into wells with
controlled topology. Each well can be regarded as a single network node that sends and receives inhibitory signals. Here we present the dynamics of a 3-node ring network. This network has two equivalent circular traveling waves of excitation. Control over the chirality of the wave can be achieved by exploiting the light sensitivity of the BZ catalyst, which can modulate the frequency of an individual node. In experiment, we perturb the network by changing the light intensity and duration of each of the three BZ wells. This network provides a model of gait switching in central pattern generators and a dynamic method of information storage.

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**SB08.03.07**

High-Resolution Organic Electrochemical Transistors Defined by Mould-Guided Drying of PEDOT:PSS Liquid Suspension Xin Chang1, Jin Li1, Shunpu Li2 and Daping Chu1; 1Centre for Photonic Devices and Sensors, University of Cambridge, United Kingdom; 2Shenzhen Technology University, China

Ion-sensitive transistors with nano- or micro-scale dimensions are promising for high-resolution electrophysiological recording and synaptic transistors. Technologies that are capable of patterning polymer functional materials directly from solution can effectively avoid any chemical damage induced by conventional lithography techniques. We report a method and process to pattern PEDOT:PSS-based transistors directly from their water-based suspension with high resolution. Gold electrodes with nanoscale channel width were also fabricated by firstly creating high-resolution polymer lines with mould-guided drying and subsequent pattern transferring, and PEDOT:PSS lines were then created through mould-guided drying on the predefined electrodes. The small devices with both nanoscale channel length and width exhibited good performance in electrical amplifying, high-frequency and multiple-frequency response. In addition, the assembled PEDOT:PSS lines showed anisotropy in electrical conductivity due to modified polymer chain alignment during drying.

**SB08.03.08**

Novel Nanostructured Scaffold for Neural Tissue Guidance and Regeneration Walaa Abbas and Nageh K. Allam; American University in Cairo, Egypt

Neural regeneration treatment after spinal cord injury (SCI) is still unsatisfactory despite the advances made in the field. One of the main challenges in neural tissue engineering is axonal growth and directionality. Cell and molecular therapies can enhance the axonal attachment and growth, however, axons may be unsuccessful to maintain their native organization and may grow in a disorganized fashion. Nanofiber scaffolds represent a potential solution for the problem of neural regeneration and axon guidance, as they can mimic the neural tissue extra cellular matrix (ECM) and combine the advantages of the combinatorial therapy for nerve injury in SCI cases. In this work, we aimed to fabricate a nanostructured scaffold that can be used as a physical support for maintaining axonal growth and regeneration in the lesion site. In addition to providing a suitable environment for the axonal extension to reconnect with their target neural tissues and restore their functional recovery. Anodized TiO2 nanotube powder incorporated into Chitosan and Poly Vinyl Alcohol (PVA) nanofibers with different percentages as 0.5, 1 and 3%. The composite scaffold was fabricated using rapid break down anodization and electrospinning techniques for TiO2 nanotubes and polymeric composite respectively. Characterization techniques such as Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR) in addition to the viability assessment test using MTT assay with neural cell line were conducted. The results revealed that the scaffold with 0.5 and 1 % showed high biocompatibility material with neural cells which mimic the properties of the neural tissues in terms of biological and architectural properties and can be considered a regenerative treatment for axonal neural guidance of SCI.

**SB08.03.09**

Free-Standing Artificial Synapse Based on Ferroelectric Organic Field-Effect Transistor for Wearable Neuromorphic Computing Systems SeongHoon Jang1, Sukjae Jang2, Minji Kang2, Tae-Wook Kim2 and Gunuk Wang3; 1KU-KIST Graduate School of Converging Science and Technology, Korea University, Korea (the Republic of); 2Applied Quantum Composites Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology, Korea (the Republic of)

Recently, the field of neuromorphic electronic system for mimicking diverse functionalities of biological synapse
and massively parallel neural network found in human brain has been emerging as a promising approach toward energy-efficient computing technology1. For wearable electronic technology, an ultra-flexible neuromorphic device platform could be envisioned as an on-body intelligent integrated circuits to instantly and proactively interact with a wearer for general or specific information and sensing technology purposes. Here, we introduce a new class of artificial synapse as a basic unit for flexible and wearable intelligent device applications2. We fabricated a large scale of ferroelectric organic field-effect transistor memory (~ 500 nm total thickness) in a free-standing form using a pentacene and a ferroelectric copolymer, PVDF-TrFE, and utilized it as a free-standing artificial synapse. The device exhibits the reliable switching properties even in free-standing form, and it can also properly operated on various corrugated surfaces such as a thermal-shrink plastic film, a jelly, a textile, a candy, a teeth brush, and a brain mold. By applying diverse electrical pulses with modulated relative time correlation between pre-synaptic (gate electrode) and post-synaptic neuron (drain electrode), diverse synaptic activities such as STP, LTP, LTD, and STDP have been implemented. Furthermore, it features sustainable synaptic functions for more than 6,000 times of input signals under extreme conditions such as transferred on the corrugated brain-like mold and completely folded with very small banding radius (R = 50 µm). Our demonstration suggests that the ultrathin conformable organic artificial synapse platforms are considered as one of key technologies for realization of wearable intelligent electronics in the future.


SB08.03.10
Wireless Optogenetics with Multifunctional Integrated Fibers Atharva Sahasrabudhe1,1, Tural Khudiyev1, Tomo Tanaka1,2, Sirma Orgue1, Marc-Joseph Antonini1,3, Jimin Park1,1, Andres Canales1, Yoel Fink1,1, Anantha Chandrakasan1 and Polina Anikeeva1,1,1; 1Massachusetts Institute of Technology, United States; 2NEC Corporation, Japan; 3Harvard-MIT Division of Health Science and Technology, United States

Reliable operation of neural probes over time scales ranging from minutes to years is essential to longitudinal studies of development, aging, and chronic neurological diseases. Recently developed fiber-based neural probes offer a promising platform for integrating multiple functions in a miniature, flexible form factor that is also biocompatible with the soft neural tissue.

In this presentation, I will describe strategies for further expanding the array of functions delivered by fiber-based neural probes by outfitting them with programmable, wireless optogenetics capability. The traditional approach to light delivery into the brain for optogenetics studies relies on tethering implanted fibers to external sources via optical cables, which limits the range of possible experiments, particularly those involving complex motor functions or social interactions among multiple animals. Here we present multifunctional fiber-based neural probes capable of complete wireless and programmed optical neuromodulation using integrated microscale LEDs for control of complex behaviors in freely moving untethered animals. The same fibers incorporate conducting electrodes that enable chronic extracellular electrophysiology and microfluidic channels for delivery of drugs and genes to the target neural tissue. The devices still maintain a miniature footprint (~270×200 µm²). A detachable wireless transponder with an on-board battery for power and low-energy Bluetooth for data transmission permit straightforward application of these probes in a multitude of behavioral assays.

SB08.03.11
Biomaterials for iPS Cell-Derived Sensory Neurons—Biocompatibility and 2D/3D Patterning Minoru Hirano1,2, Daniel V. Jarquin1, Rosakaren Ludivina De la Garza Hernández1, Yasamin Aliashrafi Jodat1, Yike Huang1 and SuRyon Shin1; 1Brigham and Women's Hospital, United States; 2Toyota Motor North America, Inc, United States

Ever since stem cell technologies were developed several decades ago, researchers have produced a variety of cells without ethical issues which arise in obtaining cells from animal. Since embryonic stem cells (ESCs) and induced pluripotent stem cells (iPSCs) can proliferate rapidly and infinitely, and possess multipotency, they are promising cell sources for bioengineering and regenerative medicine. Recently, efficient sensory neurons (SNs) differentiation methods from ESCs and iPSCs have been developed by using small chemicals and growth factors. The engineered
SNs could be used to develop sensible neuroprosthetic devices and regenerated skin tissues for treating severe traumatic injuries or congenital malformations. However, there are still many issues remaining for current stem cell technologies regarding differentiation efficiency and controlling the structures and alignment of SNs. For example, matured SNs interconnected via dendrites were not amenable to enzymatic dissociation for reseeding due to the inevitable cell damage during dissociation process. Although immature SN progenitor cells (SNPCs) can be reseeded, they still possess stemness, resulting in differentiation into non-neuronal cells. To solve the issue, at first, we investigated the optimal seeding method of SNPCs on a two-dimensional (2D) substrate. SNPCs reseeded onto a crude laminin-coated dish survived and elongated with neurites but a small amount of non-neuronal cells selectively proliferated and dominated to the culture space over the time. DAPT[11] was used to efficiently inhibit the non-neuronal differentiation and the proliferation. Besides, subtypes of recombinant laminin were screened, revealing that specific subtypes of recombinant laminins retained SNPC as a neuronal progenitor cell and selectively induced matured SNs. Second, we compared the biocompatibility of several hydrogels for SNs such as gelatin methacryloyl (GelMA), collagen type I, and Matrigel. Although GelMA is well-known as an appropriate biomaterial for creating various 2D and 3D tissue constructs, SNPCs showed less viability and no-elongated neurites in the GelMA hydrogel. On the other hand, SNPCs were able to elongate neurites in both collagen type I hydrogel and Matrigel and then they matured and connected to the adjacent neurons forming dense neuronal networks in 3D hydrogels. Next, we performed 2D patterning of SNs using bioprinting techniques. Laminin solutions were printed onto conventional plastic tissue culture plates, SNPCs were then seeded, and specifically attached and elongated with neurites on the printed lines. However, the weakly attached neurons on the printed line were easily destroyed by mechanical stress such as medium replacement, and the patterned SNs couldn’t be sustained for a long time. [12] In order to overcome this situation, SNPC patterns were embedded into collagen type I hydrogel. To do this, a sacrificial bioprinting technique was used, so SNPCs suspended in gelatin bioink were printed on the laminin-coated tissue culture plate and then physically crosslinked on ice. The printed SNPCs-laden gelatin lines were covered by collagen type I solution and solidified at 37°C. The printed gelatin was then gradually dissolved into the culture medium and hollow microchannels were left. The SNPCs originally suspended in gelatin bioink were attached on the laminin-coated plate. SNPCs were elongated with neurites following the hollow microchannel structures and connected to each other, forming straightforward lines at the centimeter level. Now, we are developing and improving this method to form 3D neuronal wiring with printing SNPCs-embedded gelatin bioink in hydrogel bath constructs and connecting them to electrical devices like CMOS sensors to record the action potential of SNs later. These techniques above are expected to be applicable in generating 3D sensible prosthetics or skin tissues with complex wired sensory neuron networks in the future.

**SB08.03.12**

**Needle-Based Electrochemical Sensors on Flexible Substrates with Bio-Compatible Coating** Wonryung Lee¹, Young-Woo Lim¹, Hyunjae Lee², Injun Lee¹, Shingo Kobayashi³, Masaru Tanaka³ and Byeong-soo Bae²; ¹Korea Advanced Institute of Science and Technology, Korea (the Republic of); ²Samsung Electronics Semiconductor R&D Center, Korea (the Republic of); ³Kyushu University, Japan

Recently, flexible electronic devices have shown their ability as tools for in vivo electrophysiological or electrochemical recordings of organs due to their conformability and biocompatibility [1]. However, flexible devices only can make contact on the surface of biological tissue. In general, the ability to insert sensors into the precise location of biological tissue also yields important capability to get signals from origins. Accessing the origins of the complex signal landscape over the organs of larger mammals will require conformal substrates, insert sensors, and biocompatibility simultaneously. Here we present electrochemical and physiological needle based sensors on integrated substrates between rigid microneedle and soft flexible substrates. The microneedle (300-μm- caliber and 700-μm-height) is fabricated by epoxy hybrid materials on the 40-μm-thick PDMS substrate and passivation. The electrode channel is formed by Au/Ti which has a 35nm/5nm thickness, respectively. The electrode on the microneedle is coated by polyaniline through the electrochemical deposition. Polyanieline is formed well on the microneedle, which can be confirmed by scanning electron microscope (SEM) image. And their electrode shows low site impedance as 800Ω (1kHz) due to their porous structure, when the surface area is 0.5 mm². Additionally, the ability of pH detecting of flexible microneedle electrode is demonstrated by open circuit potential (OCP). As an analyte, phosphate-buffered saline (PBS) which has different pH controlled by hydrochloric acid, is used. The OCP measurement is performed between silver chloride and polyaniline microneedle, and it shows the 30 mV/pH. Finally, we successfully made 5×5 large areas flexible electrochemical needle array with 4.5 mm spacing. To enhance the biocompatibility of the
microneedle, poly(3-methoxypropyl acrylate) (PMC3A) which has ion-permeability [1,2] is deposited by dip-coating. Such integration of rigid and soft materials as one substrate could make the device to have the flexibility and insert sensors at the same time. This electrochemical and physiological sensor arrays hold great promise for medical applications including local field potential (LFP) measurement on the complicated organs of mammals.


SB08.03.13
Nanotopological Effects of Collagen-Based Fiber Patterns on Neurite Outgrowth and Axon Guidance JR Kim and Juhea Kim; Korea Institute of Industrial Technology, Korea (the Republic of)

Most animals have the nervous system consisting of the central nervous system and the peripheral nervous system. Damage or malfunction of the nervous system causes serious diseases such as spinal cord injury, Alzheimer’s disease, and neurodegenerative disorders. Current in vitro nervous systems such as microarray have a limited ability to mimic a single cell-cell connection of neural networking and do not enable control over diverse aspects of the neural microenvironment.

In this study, we developed collagen-based various nanofibrous patterns (uniaxial, perpendicular, diagonal patterns) to mimic the extracellular matrix (ECM) and investigated neurite outgrowth and axon guidance depending on the patterns and the density of nanofibers. In general, neurons displayed the accelerated outgrowth and synaptic connection on fibrous patterns and showed nanofiber-guided growth of cell body. However, in this system, axon growth showed various directions and the interaction between nanotopography and neurons. Calcium imaging also showed different rate and intracellular calcium signals released from neuronal activity depending on arrangement and density of nanofibrous patterns.

This paper will discuss how nanotopological cues of collagen-based fibrous patterns to regulate neurite outgrowth and axon guidance, and optimize the neural activity within this system. The patterned nanofibrous system developed by our group could be extended to serve as a model for pathophysiological study of the nervous system and artificial 3D neural tissue engineering. Furthermore, our findings offer new insights into the design of nanofiber-based scaffolds for nerve injury repair and will provide new guidelines for the construction of neuronal network architecture.

SB08.03.14
Biocompatible Electrode Materials for Electrophysiological Sensor and Stimulation Pochun Chen and MingTing Hsieh; National Taipei University of Technology, Taiwan

ITO coated mica has been a promising flexible substrate for implanted electrochemical sensor of in situ sensing, monitoring of biological conditions (i.e. pH) and detect multiple species simultaneously. (i.e. glucose, dopamine and uric acid). Minimizing the pH sensor for implanting and long-term record could minimize the local tissue damages and improve the special resolution. Study the sheet resistance and curvature of substrate also discussed in this study. Iridium oxide has been an attractive material due to its advantages of electrochemical applications and electrophysiological sensing due to its excellent chemical stability, sensitivity, electrochemical catalytic activity and good biocompatibility. We developed a flexible iridium oxide based on ITO coated mica electrode for application in electrophysiological sensing by chemical bath deposited iridium oxide film. The characterization of thin film was investigated by SEM, XRD, XPS and XAS. Three-electrode system was selected as the sensing stimulation with pH varying from 1 to 11. The sensitivity was up to 80 mV/pH with an accuracy of 0.1 mV/pH. Moreover, the as-deposited sensor had an attractive properties of detecting multiple species of uric (AA) and dopamine (DA). The stability test was demonstrated by 1000 cycles of CV scanning. After finishing stability test, the charge storage capacity (CSC) and the charge injection capacity (CIC) maintained 96.3 % and 92 % of efficiency, respectively. Great electrochemical properties, high sensitivities, wide pH ranges, fast response time and great reversibility presented that the chemical bath deposited iridium oxide film presented well in electrophysiology electrodes.
8:30 AM *SB08.04.01
NIH/NINDS Funding Opportunities for Technology Development and Translation Eric Hudak, Kari R Ashmont, Brooks A. Gross and Nick B Langhals; NIH, United States

The mission of the NINDS Division of Translational Research (DTR) is to accelerate basic research findings towards patient use for neurological disorders and stroke by providing funding, expertise, and resources to the research community. DTR provides funding and resources through grants, cooperative agreements, and contracts to academic and industry researchers to advance early-stage neurological technologies, devices, and therapeutic programs to industry adoption (i.e. investor funding and corporate partnerships). We have created a variety of programs that support the design, implementation, and management of research activities critical to translational challenges in the treatment of neurological disease. In addition, DTR plays an active role in the NIH BRAIN Initiative, SPARC Program, and HEAL Initiative. NINDS DTR is actively managing programs that support small molecule, biologic, and neural device therapeutics, biomarkers, and training through grants, contracts, and consultants. These programs cover all stages of translational research from early assay/biomaterial/device development and optimization to preclinical development and early clinical development. Funding opportunities and resources are actively supporting translational research in preclinical discovery and development of new therapeutic interventions for neurological disorders and stroke, as well as neuropsychiatric disorders and neurotraumatic injuries (BRAIN Initiative) and pain (HEAL Initiative). An overview of NIH/NINDS translational programs and resources will be presented.

9:00 AM SB08.04.02
Towards Full Colour Artificial Retina via Inkjet-Printed Conjugated Polymers Devices Maxim Shkunov1, Manuela Ciocca1,2, Pavlos Giannakou1 and Thomas M. Brown2; 1University of Surrey, United Kingdom; 2University of Rome - Tor Vergata, Italy

Photo-sensitive conjugated polymers provide highly promising platform for visual prosthesis offering novel retinal biocompatible devices. Their high absorption coefficients, chemically tuneable bandgaps, the ability to be processed at room temperatures on flexible substrates, and signal transduction mechanisms that do not require external power sources make them ideal materials for retinal prosthetic applications. Despite ongoing research efforts in artificial retina field with organic semiconductor materials, full-colour sight restoration remains very challenging. We demonstrate tri-colour optoelectronic devices based on three different band-gap conjugated polymers with absorption in red, green and blue spectral regions, mimicking absorption of human retinal cones responsible for full colour vision, as well as high-sensitivity broadband absorption polymer/small molecule blend imitating rods absorption. Photo-response of these devices, interfaced with biological electrolyte solution, is demonstrated with long-pulsed excitation from monochromator-filtered light source, and spectral response is shown to deviate from optical absorption of dry polymeric films. We compare polymers’ films response with retinal photoreceptors colour sensitivity and discuss the role of polymer-electrolyte interface for photo-transduction mechanisms, identifying the role of capacitive charging, and ions interactions with the polymer layers during light excitation process. Ink-jet printed devices are fabricated in the form of an array of semiconducting 50 to 90 micron diameter polymeric round pixels-photoreceptors with specific red, green and blue colour sensitivity. The devices do not require wiring or external bias to operate, and are stable in aqueous physiological conditions. Due to biological compatibility of organic semiconductors, high absorption and wide spectral tuneability, this device technology is expected to find medical applications as retinal bio-engineered prosthesis towards the restoration of human vision lost due to common eye diseases, including Age Related Macular Degeneration and Retinitis Pigmentosa.

9:15 AM SB08.04.03
Melt Electrowriting (MEW) of Novel Conductive Polymer Composites for Electroactive Fibers Julian Heck1, Robert Luxenhofer2, Paul Dalton1, Josef Goding1 and Rylie Green1; 1Imperial College London, United Kingdom; 2University of Würzburg, Germany

Current scaffolds for soft tissue regeneration and rehabilitation are limited in that they are commonly fabricated from non-conductive polymers or have low-conductivity due to poor percolation of conductive components within
an insulating polymer. When electroactive particles such as carbon nanotubes or metal nanoparticles are suspended within a polymer matrix, the conductive path is inadequate as the particles must be in close proximity to maintain conduction. This necessitates high concentrations of particles to facilitate sufficient conductivity, which in turn can be detrimental to the mechanical properties of the polymer system.

Conductive polymers (CPs) can have high conductivity, but are often stiff and friable, with typical moduli of 20 to 100 MPa. These poor mechanical characteristics have driven the need for new electroactive materials with softer, more robust mechanics. In addition, thermal processing of CPs, including MEW has not been achieved due to the thermal breakdown of CPs prior to reaching a melt phase. To achieve flexibility, conduction and thermal processability in a CP system, it is necessary to develop new CP based building blocks that can retain the CP chains in close apposition, while enabling movement and fabrication into devices.

New macromers of melt processable poly(2-oxazine) (POx) functionalized with thiophene have been developed. Using the synthesis strategy of Seeliger and Wittig et al. several thiophene-oxazoline/oxazine monomers were produced with a range of properties. The first isolated crystal structures of 2-oxazoline were observed. Using ring-opening polymerization (ROP) it was possible to polymerize homopolymers, copolymers and block copolymers. This broad variation is expected to enable control over material properties such as glass transition temperature (Tg) and fiber flexibility.

These new polymer building blocks were shown to retain the processability of the POx and enable the printing of a CP monomer using MEW for the first time. Specifically, poly(2-thiophene-2-oxazine) can be printed in continuous fibres with ~200 µm diameter. The MEW printing temperature was 160 °C, with voltages ranging up to 4kV. This molecule can polymerized to obtain a product with conductive properties reflective of a CP chain formation. Free PEDOT chains can be added to the co-polymer to improve conductivity, however, future work will focus on developing co-polymers where CP chain alignment can be facilitated during the printing process.

9:30 AM BREAK

10:00 AM SB08.04.04

Direct Writing of Soft and Bioactive Conducting Polymer Microstructures for Organic Bioelectronics Applications Milad Khorrami, Vijay K. Raghunathan and Mohammad Reza Abidian; University of Houston, United States

Fabrication of 3D conductive microstructures is a great of interest in the field of bioelectronics and biosensors. However, the main challenges are (1) inability of the commercially available 3D-printers to precisely control the spatial architecture and failure to maintain a high resolution and (2) incompatibility of the printing inks to fabricate functionalized and biocompatible structures. To overcome these challenges, we introduced a novel electronically conductive and biocompatible ink for fabrication of sub-micron resolution 3D-structures using two photon polymerization technique. The ink is consist of poly(ethylene glycol) diacrylate (Mn=700) as a crosslinker, ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate as a photoinitiator, and high conductive grade conductive poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) dispersion in water. The 3D conductive microstructures were fabricated using a Laser uFAB Microfabrication Workstation (Newport, USA) at wavelength 800 nm with laser power 3.5 mW. Electrical conductivity of bar-shaped (800 µm length, 20 µm width and 1 µm height) structures with PEDOT:PSS concentration of 0 wt%, 0.1 wt%, 0.2 wt%, 0.3 wt%, 0.4 wt% and 0.5 wt% were 3.1 ± 0.6 S/m, 137.8 ± 11.9 S/m, 5502.9 ± 586.2 S/m, 13857 ± 927.9 S/m, 19042 ± 1302.1 S/m, and 25034 ± 886.3 S/m, respectively. These results showed the significant improvement of conductivity of 3D-structures up to 4 orders of magnitude (P<0.001). Furthermore, laminin protein was incorporated within conductive microstructure during fabrication process to enhance the cell attachment. Atomic Force Microscopy results revealed that the young modulus conductive microstructures was in the range of 200-500kPa. The development of conductive and bioactive 3D microstructures can be utilized in the field of bioelectronics and can be potentially utilized for neural interfaces. The future work will be focused on 3D-printing of organic neural microelectrode for recording brain signals.

10:15 AM *SB08.04.05

Functionalized Polythiophene Copolymers for Electronic Biomedical Devices David C. Martin, Samadhan Nagane, Yuhang Wu, Vivek Subramanian, Shrirang Chhatre, Peter Sitarik and Quintin Baugh; University of Delaware, United States
We continue to investigate the design, synthesis, and characterization of electrically and ionically active conjugated polythiophene copolymers for integrating a variety of biomedical devices with living tissue. This talk will focus on our most recent results, including the development of several new monomers that be used to tailor the surface chemistry, adhesion, and biointegration of these materials with neural cells. Our recent efforts have focused on copolymers of 3,4-ethylenedioxythiophene (EDOT), functionalized variants of EDOT (including EDOT-acid and the trifunctional EPh), and dopamine (DOPA). The resulting PEDOT-based copolymers have electrical, optical, mechanical, and adhesive properties that can be precisely tailored by fine tuning the chemical composition and structure. We have also been investigating the ability of these materials to be deposited directly around living tissue, particularly peripheral nerves. We will present results on EDOT-dopamine bifunctional monomers, including EDOT-dopamide and EDOT-dopimine and their corresponding polymers. We will also introduce an EDOT-aldehyde monomer and show how it can be used as the starting point for a wide variety of functionalized monomers and polymers.

10:45 AM SB08.04.06
Polymeric Memristors from Poly(n-Alkyl Methacrylate) as an Artificial Synapse Benjamin T. Grant, Stephen Foulger and Yura Bandera; Clemson University, United States

Memory devices based on organic materials are a promising alternative towards the next generation of nonvolatile nanoelectronics. The memristor is defined as any two-terminal electronic device that alters its conductivity based on its electronic history. In this effort, a methacrylate polymer is derivatized with an electronically active carbazole. Under an applied electric field, the carbazole groups rearrange their alignment, thus facilitating easier electron carrier delocalization and charge transport through molecular conformational changes. By tuning the structure of the polymer, the flexibility of the chain and the number of conductivity states can be further modified. The ability to have a multitude of conductivity states according to applied voltage makes the memristor a major candidate for emulating synapses in artificial neural networks – offering both the high connectivity and the high density required for efficient computing. Memristors, with a simple sandwich device architecture of ITO/poly(n-(9H-carbazol-9-yl)n-alkyl methacrylate)/Al, exhibit essential synaptic plasticity and learning behaviors, including short-term plasticity and spike-timing-dependent plasticity, through programmed waveforms inspired by neuronal action potential. Variations to the length of side chains that attach the carbazole moiety to the polymer backbone were studied for their effects on the optical and electrical properties of these materials.

11:00 AM SB08.04.07
Softening Polypyrrole-Coated Cryogel Electrodes for Deep Brain Stimulation in Mice Taylor J. Morrison¹, Elana Sefton¹, Milos R. Popovic¹,², Cindi M. Morshead¹,²,¹, Hani E. Naguib¹,¹,¹ and Tianhao Chen¹; ¹University of Toronto, Canada; ²University Health Network, Canada

Deep brain stimulation (DBS) is a well-established tool that is widely used in the clinical treatment of neurological disorders such as Parkinson’s disease and depression. However, treatment advances can be limited by not fully understanding how the brain is affected, and thus animal studies in vivo are needed to investigate the mechanisms involved. In vivo studies using DBS require one or more electrodes be implanted in the brain so that an electric field can be applied across the targeted area. As these electrodes may stay implanted for several days to months, it is crucial to the success of the trial that the electrode materials are fully compatible with the brain. However, the electrodes currently available to scientists are rigid, causing significant inflammation and damage to the contrastingly soft brain tissue. While research is ongoing to develop soft electrodes capable of replacing their rigid counterparts, meeting the many requirements of stimulating electrodes, including biocompatibility, high electrical conductivity, low Young’s modulus, and a functional insertion mechanism, has posed a significant challenge to researchers.

To address this challenge, we have developed novel electrodes that are biocompatible, conductive, stiff during insertion, but soft once placed in the brain. The polyvinyl alcohol (PVA), cellulose nanocrystal (CNC), and carbon nanotube (CNT) composite is repeatedly frozen and thawed in fiber form to produce a soft, highly elastic, conductive cryogel material, which is then coated in polypyrrole to further increase conductivity and reduce excess swelling of the electrode that could damage surrounding tissue. When dry, the fiber can be made as thin as 90 microns diameter, and with a compressive modulus of 1.8 MPa, can apply enough force without bending to penetrate tissue (>1 mN). Once saturated, the Young’s modulus reduces to 3 kPa, approximately matching that of
the brain (1-2 kPa). With wet conductivity as high as 150 S/m, we demonstrate that these electrodes can effectively stimulate mice in vivo. Furthermore, this material is shown to be 3D printable, with potential to print more complex electrode designs for advanced stimulation experiments.

11:15 AM SB08.04.08
Biocompatible Materials for Memory and Neuromorphic Applications Min-Kyu Kim, Youngjun Park, Dongshin Kim and Jang-Sik Lee; Pohang University of Science and Technology, Korea (the Republic of)

Biopolymers have been utilized as a matrix for filamentary resistive switching memory due to its abundant, inexpensive, and biodegradable properties. Resistive switching characteristics can be governed by diverse factors, and ionic conductivity of the matrix is one of the most critical factors in filament formation. Here, we report biocompatible memory and synaptic devices based on the biopolymer matrix [1-2]. Filament formation dynamics are controlled by modulating the ionic conductivity of biopolymer matrix. In biopolymer matrix with low ionic conductivity, the volatile resistive switching behavior is observed. Synaptic characteristics such as short-term plasticity, paired-pulse facilitation and transition from short-term to long-term plasticity are emulated by exploiting the similarities between the volatile filament formation dynamics in the biopolymer matrix and Ca^{2+} dynamics in biological synapse. The devices also exhibit good non-volatile memory characteristics such as fast switching speed, low operation voltage, and high on/off ratio by improving ionic conductivity via chemical modification. This study may provide a new possibility for biomaterials to be used as biocompatible memory and artificial synapse devices. In this presentation, resistive switching behavior in biopolymer for memory and neuromorphic applications will be presented in detail.

**Biographene and Neural Communications** Gordon Wallace; University of Wollongong, Australia

Graphene has been shown to exhibit an extraordinary range of tunable properties. High electrical and thermal conductivity coupled with exceptional mechanical properties and tunable chemical/biological activity has the materials science community enthralled. This combination of properties has led to the use of graphene to form electrodes for use in energy conversion and storage as well as in medical bionics.

We have been particularly interested in the processing of graphene from graphite in such a way that the above properties are retained but also the materials produced are amenable to a range of fabrication protocols. One approach to fabrication that has had a marked impact on the bionics area is our ability to produce long lengths of micron dimensional fibers with high electrical conductivity and exceptional mechanical properties. Our latest version of this is a fiber that can be sutured around individual nerves to enable stimulation and recording with unprecedented spatial resolution and sensitivity (1).

Here we will present the impact of these developments on the emerging field of electroceuticals - the use of electrical stimulation to treat disease.

**Reference**


**2:15 PM SB08.05.03**

**Ionic Communication for Implantable Neural Interface Devices** Zifang Zhao and Dion Khodagholy; Columbia University, United States

High-speed, low-power, and biocompatibility are the main requirements of neural implantable devices at can acquire electrophysiological signal at high spatiotemporal resolution. However, the high ionic conductivity of biological tissue limits effective transmission of conventional electromagnetic based waves from inside of the body. In addition, such approaches often require complex implantable electronic components and circuits that increase the size and power consumption of the implanted device.

Here, we introduce a novel ion-based high-speed, low power consumption communication.

Three forms of ionic communication including capacitive, galvanic, and RF coupling were evaluated and characterized for their bandwidth, cross talk and scalability. Physical and geometrical factors of ion transport and movement including the distance between electrode pairs, implantation depth, electrode size, electrode material, ion concentration were determined to establish optimal high-speed ionic communication. To further increase the communication bandwidth, we investigated the feasibility of multiple parallel communication lines through manipulation of the spatial extent of ionic waves in the medium. Conducting polymer-based hexagonal electrodes were fabricated on conformable substrates to improve flexibility and maximize the electrode density. We evaluated the error rate of the ionic communication at different speeds and established four ion-based communication lines for validating the efficacy of this transmission in animal experiments.

We have performed in vivo electrophysiological recordings of heart cells and neurons in anesthetized and freely moving rats. High-resolution electrophysiological signals were transmitted via ionic communication across the animal’s body without any extruding element, creating an imperceptible communication path between inside and outside the body. The proposed ionic communication scheme has broad applicability to implantable bioelectronics that require data exchange with external elements such as deep brain stimulators, pacemakers, implantable pumps, and brain machine interfaces. It will also enable development of novel implantable bioelectronic devices, with the potential to improve the care of patients who rely on medical devices to diagnose and treat disorders.

**2:30 PM SB08.05.04**

**Photoswitchable Spiropyran-Calmodulin Mimicked Peptide for Calcium Brain Imaging** Zinah H. Al Hammad, Do Hyun Bae, Soo-Yeon Lee and Yong Ho Kim; Sungkyunkwan University, Korea (the Republic of)
Calcium ions (Ca\(^{2+}\)) plays an important role in neuronal signaling, challenges to analyze various neuronal calcium sources is that they are not active one at a time, overlapping activity with strong interactions. An advance in this field would come from the development of selective, reversible fluorescent chemosensors, capable of repeated measurements. To this end, the rational design and fluorescence-based photophysical characterization of calmodulin calcium binding motif spiropyran-based chemosensors for Ca\(^{2+}\) are presented. Incorporation of spiropyran-based sensors into a peptide conjugation system in a crown shape has a promising results to yield significant signal to background changes with minimal sample volumes, a real advance in biological sensing that enables measurement on subcellular scale samples. In order to demonstrate chemo-peptide sensor compatibility within the light intense microenvironment photoswitching and photostability, revealing reversible Ca\(^{2+}\) binding with improved photostability compared to the non-photoswitchable calmodulin calcium binding motifs. The spiropyran-based peptide chemosensor reported here highlight untapped opportunities for a new class of photoswitchable Ca\(^{2+}\) probe and present a first step in the development of a light-controlled, reversible sensor for Ca\(^{2+}\) .

2:45 PM SB08.05.05

**Diamond as a New Encapsulating Material for Neuronal Implants**

Lionel Rousseau\(^1\), Emmanuel Scorsone\(^2\), Gaelle Lissorgues\(^1\), Blaise Yvert\(^3\) and Serge Picaud\(^4\); \(^1\)ESIEE Paris, ESYCOM, UPEM, France; \(^2\)LIST/LCD, France; \(^3\)BrainTech Laboratory U1205 Inserm, France; \(^4\)Institut de la vision UMR 7210, France

Today Brain Computer Interface (BCI) offers a way to restore neuronal dysfunction due to degenerative diseases or accidents. Thus it becomes possible to restore vision with retinal implant or to offer tetraplegic a way to control a robotic tool by thought with electrodes implanted in the cortex. One major limitation of these systems is their insufficient stability. After several months of implantation, some modification can appear such as swelling of the passivation polymers thus inducing current leakage, or degradation of the electrode material. Moreover neuronal prostheses are poorly accepted by tissues and a glial reaction may appear at the vicinity of the implant. Hence for future generation of implants it will be crucial to limit glial reactions and fabricate a full hermetic implant. Several research teams proposed to protect the metallic tracks by encapsulating them in multilayers of in-organic materials like AL2O3 or TiO2 obtained by ALD. But in case of pin holes or adhesion problems between each layer, metallic parts will not be well protected. To overcome these issues we propose to fabricate a full hermetic diamond implant. Diamond properties are very attractive for medical applications. Indeed diamond is a biocompatible material and it has no native oxide, so there is no degradation when the structure is placed in water or harsh environment. Being also a high density material, there are no species that can migrate inside diamond. Conductive diamond obtained by introduction of Boron dopants, called boron doped diamond (BBD) has a wide electrochemistry window compare to classical metallic electrodes. In parallel CVD growth diamond reactor offers a way to achieve a thin diamond film on silicon or glass wafer. This technology is compatible with classical micro fabrication process and offers an elegant way to achieve a full diamond implant. Using the same material for passivation and electrodes offers a way to achieve a full hermetic structure compatible with long term in vivo usage.

To validate this technology we started with the fabrication of a full diamond strip composed of Boron doped diamond for the electrodes and intrinsic diamond for the encapsulation. We have also produced several strips with more conventional encapsulating materials used for implants such as parylene, AL2O3 or Si3N4 and with several electrode materials like platinum, gold, PEDOT or black Pt. To compare both electrode and encapsulation materials, we designed strips with 3 electrodes (of diameter 60 µm or 30 µm) covered with same protective material. Two electrodes were continually stimulated during all the experiments while one was used as a reference (no electrical stimulation). To follow the evolution of the electrode and encapsulating materials, impedance spectroscopy was used periodically in buffer media (PBS) over several weeks, and first results clearly showed the advantage of diamond over the classical materials.

In parallel of these developments we have also achieved a preliminary version of a soft full diamond implant which will be used to test the surgical implantation procedure and to optimize the total thickness.

3:00 PM BREAK

3:15 PM SB08.05.06

**Immobilized Laminin Gradients on Conducting Polymer Films for Axonal Regeneration**

Omid Dadras Toussi,
Axons navigate along specific pathways based on the gradients of guidance cues. Following substantial neural injury, axons may fail to fully regenerate without external intervention due to limited intrinsic axonal growth capacity and/or interference from scar tissue. Hence, development of platforms capable of providing gradients of guidance cues to facilitate axonal regeneration is crucial in the field of neural tissue engineering. Even though numerous technologies have already been established, effective axonal guidance over long distances is still challenging.

Here we report a novel method for creation of gradient of laminin on conducting polymer film. Conducting polymers (CPs) such as Poly(3,4-ethylenedioxythiophene) (PEDOT) have been widely used for neural interfaces, owing to their excellent biocompatibility, soft mechanical properties, relatively high conductivity and outstanding chemical stability. Laminin is a major substrate-bound molecule for axonal growth, known as a chemoattractant. In an effort to mimic the extra-cellular environment, this study aims to provide different gradient shapes of laminin such as linear, hill, and exponential to modulate axonal regeneration in the nervous system. First, using micro-scale motorized X-Y-Z stages and nano-syringe pump, lines of laminin have been printed with various concentrations (based on the gradient profile) ranging from 20-100 ug/ml on the surface of a 2% agarose hydrogel slab (hydrogel thickness was 10 mm). The laminin concentrations can be accordingly adjusted to create different gradient shapes. Processing parameters including injection flow rate and stage velocity have been optimized to create minimum line widths (i.e. 200 um) which leads to generation of high-resolution 10mm-long laminin gradients on 10 mm length of agarose gel. The whole pattern is then transferred onto the surface of a Poly (L, Lysine)-treated PEDOT film. PEDOT was previously electropolymerized on the surface of gold coated silicon substrate using galvanostatic mode with charge density of 0.18 C/cm². Immunohistochemistry was used to quantify various immobilized laminin gradients on the PEDOT surface.

We aim to culture dorsal root ganglion explants and cortical neurons on top of CP substrates printed with laminin gradient patterns. This will allow us to assess the neurite response to various gradients and compare these responses to find the optimum gradient type and concentration range for effective axonal regeneration. The outcome of this project will pave the way towards development of more effective engineered conduits for nerve regeneration and will help us unravel fundamental questions of axonal regeneration in the nervous system.

3:30 PM SB08.05.07
Patterned Semiconducting Multi-Electrode Arrays for the Optical Stimulation of Neuronal Cells
Frano Milos1, Maria Rosa Antognazza2, Gabriele Tullii2, Maria Cecilia Pasini3, Francesco Galeotti3, Dirk Mayer1 and Andreas Offenhäusser1; 1Forschungszentrum Juelich, Germany; 2Istituto Italiano di Tecnologia, Italy; 3ISMAC-CNR, Italy

Photoconductive organic polymers are attracting considerable interest in tissue engineering and bioelectronics due to their remarkable light absorption along with tunable optical and mechanical properties. Moreover, these materials can be easily processed into precisely defined topographical patterns with large area coverage and low fabrication costs. We present a novel photoconductive biointerface which combines a multi-electrode array (MEA) functionalized with a semiconductive conjugated polymer patterned into defined microscale topographical features. In previous studies, photoexcitation of a light-sensitive semiconductive polymer, poly(3-hexylthiophene-2,5-diyl) (P3HT), was used to induce variations in the membrane potential of HEK-293 cells and the occurrence of capacitive charging was observed at the P3HT/electrolyte interface that could potentially lead to photo-capacitive stimulation of the cell membrane. Our aim is to further this approach by developing a functional non-invasive tool for the optical and topographical modulation of primary cortical neurons in vitro. Poly(3-hexylthiophene-2,5-diyl) was deposited on MEAs and patterned into conical micropillars to improve the cell-electrode coupling. Since P3HT is excited by visible light, the presented device can be easily implemented in any electrophysiological set-up without requiring complex optical systems. We observed that polymer photoexcitation leads to a significant decrease in the electrode impedance. Furthermore, we cultured primary cortical neurons and observed that microscale pillars significantly promote neurite growth and their alignment to the underlying topography in comparison to flat substrates commonly used in cell culture. Since light treatment did not result in significant detrimental effects on cell viability, we aim to optically stimulate primary cortical neurons using the presented device and further investigate whether polymer photoexcitation influences neuronal development on flat and patterned P3HT substrates.

In conclusion, the presented system is a step towards light-controlled manipulation of neuronal development and network activity which could have considerable implications for neural regeneration and the design of neuro-
prosthetic devices.


3:45 PM SB08.05.08
Neuritogenic Potentiating Effects of Controllable Electrically-Induced Polarization of Poly (L-lactic) Acid
Paula Maria Vilarinho, Nathalie Barroca, Ana Marote, Sandra Vieira, Odete Silva and Maria Helena Fernandes; Univ de Aveiro, Portugal

Electrical stimulation is known to be beneficial for neuronal function, particularly on neurite growth. Electroactive materials as conductors and piezoelectrics are known to provide extra stimulatory signals for neural repair and have shown promising results. Poly (L-lactic) acid (PLLA) is a biodegradable and piezoelectric polymer studied as a scaffolding material and drug delivery system. It demonstrates and FDA-approved biocompatibility and biodegradability for particular applications, as screws for fixing fractures in orthopaedics [20] or in injectable filling for lipotrophy.

In our work, we are exploiting the feasibility of combining electrical polarization in PLLA films and aligned nanofibers and investigate the biological outcome of these electrically-induced poled PLLA platforms on neuronal relevant *in vitro* models. Here we report on the production of electrically polarized PLLA aligned nanofibers along with a precise quantitative analysis of their polarization and stability. We advocate that electrical poling causes C=O dipoles orientation, which brings tensile piezoelectricity, and results in charged surfaces. Our results show the neuritogenic potentiating effects of this controllable electrically-induced polarization on human SH-SY5Y neuroblastoma cells and rat embryonic cortical neuronal differentiation.

4:00 PM SB08.05.09
Transparent, Flexible, Penetrating Microelectrodes Arrays with Capabilities of Single-Unit Electrophysiology
Kyung Jin Seo¹, Pietro Artoni², Michela Fagiolini² and Hui Fang¹; ¹Northeastern University, United States; ²Boston Children's Hospital, United States

Accurately mapping neuronal activity across brain networks is critical to understand cortical phenomena, yet it is challenging due to the need of tools with both high spatial and temporal resolutions. Here, penetrating arrays of flexible microelectrodes made of low-impedance nanomeshes are presented, which can record single-unit electrophysiological neuronal activity and at the same time, are transparent, allowing to bridge electrical and optical brain mapping modalities. These 32 transparent penetrating electrodes each with a small site area, 225 μm², have a low impedance of ~ 149 kΩ at 1 kHz, an adequate charge injection limit of ~ 0.76 mC cm⁻², and 100% yield. Mechanical bending tests reveal that the arrays are robust up to 1,000 bending cycles, and their high transmittance of 67% at 550 nm makes them suitable to combine with various optical methods. A temporary stiffening using polyethylene glycol allows the penetrating nanomesh arrays to be inserted into the brain minimally invasively, with in vivo validation of recordings of spontaneous and evoked single-unit activity of neurons across layers of the mouse visual cortex. Together, these results establish a novel neurotechnology—transparent, flexible, penetrating microelectrode arrays—which possesses great potential for brain research.

4:15 PM SB08.05.10
Soft, Flexible and Conductive Elastomers for Bioelectronics
Estelle Cuttaz, Alexey Novikov, Christopher Chapman, Josef Goding, Catalina Vallejo Giraldo and Rylie Green; Imperial College London, United Kingdom

Flexible, polymeric-based electronics have the potential to fundamentally change the design, fabrication and performance of bioelectronic devices. Contemporary bioelectronic devices are restricted to metals for charge transduction and injection in the body. The use of metallic conductors hinders the design and fabrication of truly stretchable and flexible electronics. The mechanical mismatch between metals and insulative polymers such as
polydimethylsiloxane (PDMS) used in bioelectronic devices can lead to device failure due to issues such as mechanical failure and fluid ingress. Furthermore, the mechanical mismatch between metallic conductors and soft tissues contributes to chronic inflammatory responses upon implantation of bioelectronic devices.

Carbon-based conductors such as carbon nanotubes and conducting polymers provide a potential avenue for the synthesis of fully organic electrical conductors. In this study several approaches for the fabrication of soft, flexible organic conductors have been investigated and the resultant materials have been used in the fabrication of fully polymeric electrode arrays. Two key approaches for fabrication of conductive elastomers were explored. The first approach is the fabrication of a poly(ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) hydrogel which is impregnated with PDMS resulting in a bulk composite of an embedded PEDOT network within a PDMS matrix. The second approach entails dispersion of PEDOT fibres and nanowires within a polyurethane (PU) matrix to produce films via solvent casting. The effect of PEDOT loading on electrochemical and mechanical characteristics were investigated. Elastomers with 15 wt% PEDOT loading were identified as ideal for device fabrication, having conductivity of 4.15 S.cm⁻¹, young’s modulus of 20.5 MPa, an ultimate tensile strength of 7.4 MPa and strain at failure of approximately 265%. Cytocompatibility of conductive elastomers was assessed in vitro using ReNcell VM human neural precursors. Cultures on conductive elastomers were found to have an increased neural cell population compared to neat PU (33% compared to 53% of the cell population) due to increased surface roughness. However this was accompanied with a decrease in average neurite length due to the accompanied increase in Young’s modulus (298.4 ± 16.9 µm for PU versus 45.2 ± 1.5 µm for CE).

Flexible, fully polymeric electrode arrays were fabricated from conductive elastomers using conventional laser micromachining techniques. Methods to connect the polymeric arrays to traditional electronics were also developed. Arrays were comprised of nine, 900µm electrode sites in a hexagonal array. Charge injection limits (CIL) of the CE array were determined using biphasic stimulation with a phase length of 0.2 ms. CE electrodes were found to have a CIL of 0.020 ± 0.002 mC.cm⁻² compared to 0.013 ± 0.001 mC.cm⁻² for platinum electrodes of the same geometry. CE arrays were also found to have high charge storage capacity, 205 ± 55 mC.cm⁻² but also a high track impedance of 0.41 ± 0.16 Ω. Electrode arrays were demonstrated to maintain charge conduction and injection under strain and flexural deformation.

The formation of PEDOT networks within elastomeric polymer matrices has been demonstrated as a promising approach for the fabrication of soft, flexible bioelectronic materials. CEs facilitated the fabrication of a fully polymeric, flexible electrode array using conventional laser fabrication techniques. CE arrays were found to have favourable charge injection properties compared to platinum electrodes, however track conductivity is a current limitation which needs to be addressed in order to open up the application of CEs in the next generation of flexible bioelectronics.

4:30 PM SB08.05.11
Modular Peptide Hydrogels for Tissue Regeneration after Brain Injury Biplab Sarkar, Xiaotang Ma, James Haorah and Vivek Kumar; New Jersey Institute of Technology, United States

Traumatic brain injuries (TBI) affect more than 2 million people in the US annually. Major causes include falls, motor-vehicle crashes, and assault/self-harm. Sports-related injuries suffered by athletes and blast injuries affecting soldiers are also notable contributors to the TBI patient population. Native brain microenvironment has low intrinsic regenerative capability and such injuries may lead to long-term effects such as dementia.

We describe a class of injectable materials that can manage and possibly reverse the harmful biological responses to TBI. These hydrogels, with material properties similar to native matrix in the brain, can liquefy during injections and be reconstituted in the brain after injection. We apply lessons learned from self-assembly of short peptides to create materials that can promote blood vessel formation, modulate the immune microenvironment, and facilitate survival and reconstitution of the functional neuronal circuit in and around the injury site. Our multi-disciplinary approach bridges chemical principles with neurobiological insights to set up a modular neuroprotective therapeutic platform with both stationary and diffusive biologic signals. This integrative approach will increase our understanding of the response of injured brain microenvironment to implanted biomaterials and solve a major problem in clinical management of injured brain tissue without complicated surgical intervention. The biomaterial scaffolds are based on functional self-assembling peptide hydrogels.
There are three distinct post-TBI responses that we can control with such implantable biomaterials: (a) enhanced angiogenesis, (b) immunomodulation, and (c) improved neuronal survival, recruitment of neural progenitor cells, neural sprouting, and synaptic restoration. Following implantation in the injured site in the brain, the peptides disassociate from the bolus, inducing angiogenesis, immunomodulation, and neuronal survival. The biocompatibility, tunable biodegradability, and facile material properties of the biomaterial platform complement the therapeutic efficacy of the peptide formulations. We compare the in vivo efficacy of the hydrogels in the injury site in a rodent model of TBI (fluid percussion injury) and determine the biodistribution of the hydrogels away from the injection site in a time-dependent fashion.

Self-assembled peptide hydrogels with covalently attached bioactive epitopes and sequestered immunomodulatory agents are promising materials for promoting neuro-regeneration after debilitating brain injury. Such injectable scaffolds that can create a neuroprotective niche after being injected in vivo have great potential for treatment of TBI, non-TBI stroke, and other ischemic conditions of the central nervous system.

4:45 PM SB08.05.12
Bioinspired Neuron-Like Electronics for Minimally Invasive Brain Probes Xiao Yang, Tao Zhou, Theodore Zwang, Guosong Hong, Yunlong Zhao, Robert Viveros, Tian-Ming Fu, Teng Gao and Charles M. Lieber; Harvard University, United States

As an important application of functional biomaterials, neural probes have contributed substantially to studying the brain. Bioinspired and biomimetic strategies have begun to be applied to the development of neural probes, although these and previous generations of probes have had structural and mechanical dissimilarities from their neuron targets that lead to neuronal loss, neuroinflammatory responses and measurement instabilities. Here, we present a bioinspired design for neural probes—neuron-like electronics (NeuE)—where the key building blocks mimic the subcellular structural features and mechanical properties of neurons. Full three-dimensional mapping of implanted NeuE–brain interfaces highlights the structural indistinguishability and intimate interpenetration of NeuE and neurons. Time-dependent histology and electrophysiology studies further reveal a structurally and functionally stable interface with the neuronal and glial networks shortly following implantation, thus opening opportunities for next-generation brain–machine interfaces. The NeuE subcellular structural features are shown to facilitate migration of endogenous neural progenitor cells, thus holding promise as an electrically active platform for transplantation-free regenerative medicine. Finally, I will discuss the potential application of NeuE to facilitate the recovery of brain injury.

8:30 AM *SB08.06.01/SB07.07.01
Are Conducting Polymer Electrodes Capacitive or Faradaic? George G. Malliaras; University of Cambridge, United Kingdom

Organic electrochemical devices, which use conjugated polymers in contact with an electrolyte, have applications in bioelectronics, energy storage, electrocatalysis, and sensors. Their operation relies on the oxidation (electron loss) or reduction (electron gain) of the polymer, which are traditionally described as Faradaic processes that transfer charge. However, recent evidence from various devices based on poly(3,4-ethylenedioxythiophene) chemically doped with poly(styrene sulfonate) (PEDOT:PSS) is consistent with a purely capacitive process that stores charge. To clarify whether PEDOT:PSS is an exception or the rule and determine which processes are capacitive and which are Faradaic, solid-state physics methodology developed to understand the operation of organic light-emitting diodes can be used. Such studies can pave the way for device optimization.

9:00 AM *SB08.06.02/SB07.07.02
Fiber-Based and Nanomagnetic Neural Interfaces Polina Anikeeva; Massachusetts Institute of Technology,
Within 1.3L of human brain billions of neurons connected by trillions of synapses are continuously exchanging signals. These signals govern the inner workings of the nervous system, and the aberrations in communication between neurons and other cells within the brain are manifested as the neurological and mental conditions that increasingly affect our aging society. While clinically available devices lack the finesse of the neural circuits and drugs often come with unwanted side effects, our team leverages the principles of optoelectronics and magnetism to develop tools matching the signaling complexity of the nervous system and cause minimal disruption to natural physiological function.

My talk will discuss how multimaterial fiber technology can be leveraged to produce compliant and miniature devices capable of electrical and optical recording and stimulation of neural activity, and delivery and sensing of neurochemicals. I will further highlight how multimaterial fibers can be employed for neural repair following traumatic injury as well as the potential candidates for artificial muscles with future applications in prosthetics. The second half of my talk will focus on using iron-containing nanomaterials as transducers of magnetic fields to biologically relevant stimuli such as heat and force. By tuning magnetic nanomaterials properties in conjunction with magnetic field conditions, it is possible to independently control multiple heat- or force-dependent biological processes. Finally, iron-containing nanomaterials can be used to aid minimally-invasive delivery of neurochemicals via magnetothermal and electrocatalytic means.

**9:30 AM *SB08.06.03/SB07.07.03***

*Microfabricated, Conformable Auditory Brainstem Implants—Materials and Technology Advances towards Clinical Translational*  
Nicolas Vachicouras¹, Christina Tringides², Osama Tarabichi³, Vivek Kanumiri³, Yohann Thenaisie¹, Florian Fallegger¹, Chris Brown³, Daniel Lee³ and Stephanie P. Lacour¹; ¹Ecole Polytechnique Federale de Lausanne, Switzerland; ²Harvard University, United States; ³Massachusetts Eye and Ear Infirmary, United States

The auditory brainstem implant (ABI) is a neuroprosthesis that provides sound awareness to deaf individuals who are not candidates for the cochlear implant. The ABI electrically stimulates the surface of the cochlear nucleus (CN) in the brainstem. The complex anatomy and physiology of the CN together with the poor spatial selectivity of electrical stimulation and inherent stiffness of contemporary implants lead to only modest auditory outcomes in ABI users.

We propose a soft conformable ABI electrode array to improve the biomechanical match of the man-made implant to the curved CN surface. The conformable implant provides stable positioning of the implant in vivo and enables higher selectivity of electrical stimulation. The soft neurotechnology leverages miniaturization, high performance thin-film materials, and engineered mechanical compliance to produce implants compatible with the demanding ABI surgical insertion and conformability to the curvature of the brainstem. We developed elastic micro-structured multilayers, a soft electrode coating, and transient surgical features that allowed the fabrication of a scalable ABI from miniaturized mouse implants to human-size arrays.

This talk will report on the microfabrication and scaling process, mechanical and electrochemical characterization of the compliant ABIs. The soft electrode specifications are very similar to those measured in clinical ABIs with average impedance at 1 kHz of 5.78 ± 0.62 kΩ (electrodes of 0.385 mm² surface area). In a mouse model, we show that soft neurotechnology can be implemented to reliably activate auditory neurons in vivo for up to 4 weeks, a mandatory step before evaluating longer, chronic use of the technology. In a human cadaveric model, we demonstrate that the soft ABI is robust to surgical manipulation and insertion into the lateral recess of the IVth ventricle, and displays improved electrochemical performance compared to current clinical devices.

**10:00 AM BREAK**

**10:30 AM SB08.06.04/SB07.07.04***

*Conductive Hydrogel-Coated Cochlear Implants Improve Electrical Performance In Vivo*  
Ulises A. Aregueta Robles¹, Mario Huynh², Ashley Dalrymple², Bryony Nayagam³, James Fallon², Rob Shepherd², Rylie Green² and Laura Poole-Warren¹; ¹UNSW Sydney, Australia; ²Bionics Institute, Australia; ³The University of Melbourne, Australia; ⁴Imperial College London, United Kingdom

Aim: This study aimed to compare the chronic in vivo charge transfer properties of conductive hydrogel (CH) coated cochlear implant (CI) electrodes to traditional platinum (Pt) CI electrodes.
Background: CIs can improve quality of life in profoundly deaf people by restoring sound perception. Ideally, bionic devices should safely operate for a lifetime; however, host responses such as protein adsorption, inflammation and fibrosis can impact electrode impedance. These host responses can lead to inefficient stimulation and formation of toxic byproducts. CH coatings, based on poly(vinyl alcohol) (PVA) anti-fouling polymers modified with conductive polymers (CPs), can provide enhanced electrical properties, superior to those of traditional Pt electrodes. This technology can be directly coated onto metallic substrate of state-of-the-art bionic devices. This study tested the hypothesis that PVA conductive hydrogels can enhance safe charge injection and improve the quality of neural recordings.

Methods: CIs with 4 electrodes specifically designed for the rat cochlea were implanted for up to 5 weeks. The CH coating was fabricated using PVA hydrogel modified with 20 taurine groups for electrical doping and 5 methacrylate groups for crosslinking. The CP poly(ethylene dioxythiophene) (PEDOT) was galvanostatically grown through the hydrogel and arrays were ethylene oxide-sterilized (ETO) prior to implantation. Electrochemical impedance (EI), charge injection limits (CIL) and charge storage capacity (CSC) of electrodes was compared before and after implantation using a 3-electrode cell (vs Ag/AgCl). Sprague Dawley rats were unilaterally implanted with CH coated or uncoated Pt CIs. The animals were chronically stimulated using charge balanced biphasic pulses for ~20 hrs/week over the implantation period. To evaluate electrode performance in vivo, voltage transient impedance was measured 5 days/week, and EI, CIL and CSC was also recorded over the implantation period. Explanted electrodes were imaged using scanning electron microscopy (SEM) for evaluation of the CH attachment and for signs of Pt oxidation.

Results: Before implantation, EI of CH coated electrodes over a frequency range of 10Hz-50kHz was more than 3 times lower than uncoated Pt implants. CSC and CIL of CH-coated electrodes was over one and two orders of magnitude higher than Pt electrodes, respectively. During implantation periods, common ground impedance of CH-coated electrodes increased from ~4kW in the first week, and stabilized thereafter at ~6kW. In contrast, the impedance of Pt electrodes was approximately double that of CH immediately after surgery at ~8kW and after 2 weeks at ~13kW. Following implantation electrochemical impedance was maintained at close to pre-implantation levels in CH coated electrodes, which was significantly lower than in Pt. CSC and CIL remained stable, and ~60% in CH coated electrodes following implantation, but both were still ~10 times higher than the Pt CSC and CIL. Preliminary observations of SEM images (n=2) showed that the CH coat remained intact and did not cause any damage or signs of Pt oxidation were observed.

Conclusion: CH-coated cochlear arrays maintained enhanced electrical properties during and after implantation. These results support the potential of CH as an advanced electrode coating for cochlear implants with superior electrochemical performance than Pt electrodes.


10:45 AM *SB08.06.05/SB07.07.05 Towards Seamless Neural Implants/Tissue Integration Xinyan T. Cui; University of Pittsburgh, United States

Microelectronic devices placed in the nervous system present tremendous potentials for mapping neural circuits and treating neurological disorders. Currently, these devices often experience failures in part due to the electrical, mechanical, and biochemical, mismatch between the artificial device and neural tissue. Quantitative histology and 2 photon imaging have revealed neuronal damage and degeneration, inflammatory gliosis, blood brain barrier leakage and oxidative stress at the site of implants which may compromise the intended recording/stimulation/neurochemical sensing function. We use several biomaterial strategies to minimize these mismatches in order to achieve seamless and stable device-tissue interface. First, various conducting polymer based nanocomposites have been investigated as electrode coatings and facilitate the signal transduction/charge transfer between the ionically conductive tissue and the electrical device. Nanostructuring is employed to improve the adhesion, stability and charge injection and drug delivery capability of the conducting polymers to meet the material challenges in chronic interface. Secondly, to minimize the mechanical mismatch at the device-brain tissue interface, novel soft and elastomeric electrode materials have been developed with Young’s modulus approaching that of neural tissue (less than 1 MPa). Soft implants demonstrated reduced inflammatory tissue response in both CNS and PNS compared to stiff implants of
similar geometry and surface chemistry. Thirdly, bioactive approaches are being developed to modulate the biological responses. One approach is to modify the implant surface with biomolecules or biomimics. Surface immobilization with these bioactive molecules significantly improved neuronal health and inhibited the inflammatory tissue response around the implants. Alternatively, therapeutics that control inflammation, neurodegeneration and oxidative stress have been delivered systemically or locally. These bioactive approaches have demonstrated significant benefit in neural recording quality and longevity. The ultimate solution to a seamless device/tissue interface may be a combinatorial approach that takes advantage of multiple biomimetic strategies discussed above and beyond.

11:15 AM SB08.06.07/SB07.07.07
Design and Fabrication of Tissue-Mimicked Parylene C Based Neural Microelectrode Arrays Yu-Chih Chiu and Pochun Chen; National Taipei University of Technology, Taiwan

In recent years, implantable bioelectronics has raised huge interest, especially for neural diseases. Among them, devices with a nerve guidance to guide neuron growth can enhance neural regeneration for traumatic peripheral nerve injury. However, the commonly used nerve conduit cannot provide a spatiotemporal regulation and in-situ monitoring for localized neurons. Accordingly, in this study, an implantable neural device that is built with microelectrode arrays on transparent and flexible substrate was developed to enhance cell growth through applying electrical stimulation and neural signals recording in a tissue-mimicked microenvironment. A new type of flexible substrate, nanoporous Parylene C, was designed and fabricated to exhibit tissue-mimic structural and mechanical properties. The microelectrode array, iridium oxide electrode for both neural stimulation and recording, was pre-deposited on a water-soluble sacrificial layer of poly acrylic acid (PAA) prior to the transfer print process. Such transfer printed tissue-mimic neural microelectrode array enabled conformable adhesion on a curvilinear nerve surface and electrical signals transduction from the microelectrode site, which is expected to provide higher performance of peripheral nerve regeneration. In addition, we characterized and evaluated the microelectrode array of iridium oxide film, including charge storage capacity, charge injection capability, and electrochemical impedance.

SESSION SB08.07: Poster Session II: Materials and Devices for Neural Interfaces II
Wednesday Afternoon, December 4, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB08.07.01
Membrane Nanomaterials with Controllable Mechanics for Delivery Applications Fereshtehsadat Mirah, Yifei Wang, Mohammad Reza Abidian and Sheereen Majd; University of Houston, United States

Lipid vesicles, also known as liposomes, present simple yet highly versatile nanocarriers for delivery of therapeutic and diagnostic agents. Composed of one of the most abundant biological molecules, lipids, these carriers have similarities to biological membranes and are thus, biocompatible, biodegradable, and easy to decorate on the surface. The lipid membrane in a liposome encloses an aqueous volume and therefore, liposomes are soft and highly deformable. Recent studies on delivery nanomaterials have suggested a prominent role for the mechanical aspects of these materials in their delivery performance (e.g. biodistribution). To enable variation of mechanical properties in liposomes, here we incorporate hydrogel materials in the lumen of liposomes. In this study, we present a straightforward and reliable technique for fabrication of nano-scale liposomes filled with photo-crosslinkable hydrogel, poly(ethylene glycol diacrylate) (PEG-Da). This technique relies on the lipid film hydration, extrusion, and proper incorporation of the photoinitiator into the liposomes followed by UV exposure to form a cross-linked hydrogel within the lumen of liposomes. We assess the resultant gel-filled liposomes for size and morphology using dynamic light scattering and scanning electron microscopy and confirm the presence of PEG hydrogel in the lumen of liposomes. We demonstrate that the present approach can successfully produce gel-filled liposomes with size range of 150-300 nm size. These gel-filled liposomes show good colloidal stability under physiological condition for at least 6 days. We demonstrate that this method allows for (i) changing the lipid composition of membrane and (ii) changing the hydrogel volume percentage. Mechanical testing of bulk hydrogels with various PEG-Da volume
percentages revealed that increasing the PEG-DA volume percentage (10-40%) results in a significant increase in the elastic modulus of the hydrogel (0.1-6 MPa). The resultant gel-filled liposomes can, therefore, offer various levels of mechanical elasticity. Such membrane nanomaterials provide exciting and controllable platforms for delivery of therapeutic and/or diagnostic agents for different medical or biomedical applications.

SB08.07.02
Investigating Neurogenic Differentiation of Dental Pulp Stem Cells Using PLA and Graphene Thin-Film and Electrospun Fiber Scaffolds in Vitro Dipen Mehta, Michael Stabile, Nicholas Stabile, Daniel Luo, Kuan-Che Feng, Marcia Simon and Miriam Rafailovich; Stony Brook University, United States

Dental pulp derived cells are pluripotent stem cells which can be differentiated along odontogenic, osteogenic, adipogenic, or neurogenic lineages. Odontogenic and osteogenic differentiation, in the absence of dexamethasone, have been shown to be highly dependent on substrate morphology and mechanics. Here we focus on neurogenic differentiation, using the protocol described in [1], and its dependence on substrate nature. DPSCs were cultured on PLA, a biodegradable polymer approved for internal use. The upregulation of genetic markers was compared with that of cells plated on standard TCP. The role of substrate morphology was investigated by plating on electrospun fibers approximately 2.0 ± 1.0 μm in diameter and on spin-cast thin films. The influence of electrical conductivity was investigated through the addition of 3% and 10% graphene nanoparticles to the films and fibers respectively. The aspect ratio of the cells was measured using confocal microscopy. Cells grown on graphene containing substrates had larger aspect ratios than their non-graphene counterparts, and cells grown on microfibers were longer than their counterparts on the flat films. But the cell aspect ratio did not necessarily correlate with genetic differentiation. The results after 21 days of incubation indicated that early markers (TBP, β-III tubulin), decreased uniformly on all substrates relative to day 0, with the largest decrease occurring on the PLA flat film with graphene. The late stage marker, NEFM, which indicates differentiation, was upregulated to a significantly larger extent on all PLA substrates. No difference was observed between the fibers and the flat film in the absence of graphene, thus morphology did not play a significant role on this polymer. Addition of graphene did not affect the outcome on the fibers, but significantly suppressed the gene expression on the flat films. These results indicate that PLA is a promising scaffold material for neurogenic differentiation.


SB08.07.03
Development of Novel Cerebral Aneurysm Embolization Method via Injection of Pluronic® F-127 Multiblock Copolymer Hydrogel Ikshu Pandey1, Divya Rai-Gersappe1, Rithu Paramesh1, Kevin Yang1, Finnur Christianson1, Aaron Sloutski2, Daniel Cohn2, Dennis Galanakis1, Chandramouli Sadasivan1, Juyi Li1 and Miriam Rafailovich1; 1Stony Brook University, The State University of New York, United States; 2The Hebrew University of Jerusalem, Israel

Intracranial aneurysms are a serious condition, affecting approximately 6 million people annually. The current method of treatment, endovascular coiling, utilizes a catheter to release platinum coils directly into the aneurysm which promotes diversion of blood flow. However, coiling is reported to be thrombogenic, and induces recanalization[1]. In order to circumvent these problems, we propose an alternative approach, where polymer gels are directly injected into the aneurysm. In this manner, the polymer can be engineered to occlude blood flow, while promoting endothelialization and minimizing thrombogenesis. A silicone model was 3-D printed from a cone CAT scan of a goat aneurysm. The model was connected to a peristaltic pump which simulated the pulsatile blood flow in the carotid artery. The polymer gels were then injected directly into the model, maintained at 37°C, via a Stryer Catheter, under radiological imaging. Two types of gels were tested. A physical gel composed of F127 Pluronic micelles was injected at 4°C, but warmed above the gelation temperature immediately after reaching the aneurysm. The retention time of the gels was then probed by x-ray imaging with induced contrast. Mixtures of F127 copolymer with multipblock (n=6), PF127 were tested in order to optimize retention time and injection viscosity. The F127 group of polymers are non cell-adhesive, and may need further modification to promote endothelial migration. Gelatin, was mixed with matri-gel or fibrinogen, injected, and gelled 37°C, using MTG. Endothelization was found to be successful on this surface. In this case, retention times in excess of 76 hours were determined. Even though both gelatin and Pluronic copolymers are presumed to be minimally thrombogenic, thrombus formation in both cases will be probed directly by circulation of platelet rich plasma across the aneurysm.
**SYMPOSIUM SB09**

Interfacing Bio/Nano Materials with Cancer and the Immune System  
December 2 - December 4, 2019

**Symposium Organizers**

SJ Claire Hur, The Johns Hopkins University  
Shana Kelley, University of Toronto  
John Slater, University of Delaware  
Ian Wong, Brown University

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* Invited Paper

**SESSION SB09.01: Cancer Diagnostics**

Session Chairs: Rong Fan, SJ Claire Hur, Ian Wong and Alexander Xu  
Monday Morning, December 2, 2019  
Hynes, Level 3, Room 304

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**8:30 AM *SB09.01.01**

SNAPflex—A Paper-Based Nucleic Acid Preparation, Storage and Shipping Device for Molecular Diagnostics  
Catherine Klapperich1, Nikunja Kolluri1, Mario Cabodi1, Nikolas Albarran2, Jose Gomez-Marquez2 and Anna Young2;  
1Boston University, United States; 2Makerhealth, Inc, United States

One strategy to decrease the cost and increase the use of nucleic acid amplification tests is developing sample collection technologies that reduce or eliminate the need for a cold chain for storage and transport. Blood is usually collected at a satellite collection site (SCS) via venipuncture and shipped to the testing laboratory. The cost of sample preparation steps are borne by the central lab, and the cost per test varies per result delivered to the patient depending on the local health system. The cost of transport and associated sample preparation is about 80% of the total cost per result for many important tests in low resource settings. Removing the cold chain for blood sample transport would greatly reduce costs of blood testing for the patient, the SCS and the central lab. Without a cold chain requirement, sample collection can be carried out closer to the patient, reducing travel and opportunity costs. If the SCS does not have to maintain special storage on site, samples can be collected, batched and sent on a regular schedule to the central testing facility, thus reducing costs. If the sample collection method also prepares the sample for direct input to a NAAT, significant costs can be offset at the central lab.

We translated our three dimensional microfluidic blood sample preparation technology (SNAP) into a two dimensional flexible blood sample nucleic acid (NA) sample preparation card (SNAPflex). The final prototype uses commodity grade self-laminating plastic sheet for the top cover, heat sealing thermal plastic (5 mil) for the waste pad cover and base layers, Ahlstrom 320 thick chromatography paper for the waste pad, and a Millipore 0.7um glass fiber filter without binder for the nucleic acid capture membrane. Everything except the capture membrane was cut on Trotec Speedy 100 laser cutter. The capture membrane was cut on Graphtec FCX200-60VC cutter plotter. The design allows for roll-to-roll processing with two pick and place steps to add the waste pad and the sample capture filter. These parts can be die cut from separate materials in another roll-to-roll process.

We demonstrate the utility of SNAPflex in extracting HIV RNA from whole virions spiked into whole blood. Our
results indicate consistent recovery across four logs of input virion concentrations. An initial comparison with QIAGEN QIAamp viral extraction kit shows that SNAPflex has superior recovery. QIAGEN extraction requires an initial plasma separation prior to viral RNA extraction requiring centrifugation while SNAPflex can process whole blood using passive wicking only, indicating not only performance improvement but also simplified sample processing. In stability experiments, in vitro transcribed RNA for the HIV gag gene was prepared. Samples were processed on the SNAPflex devices. For Day 0 and no template control conditions, samples were immediately eluted and analyzed by RT-qPCR analysis. For extended time point samples (Days 1 – 14), after drying, the sample capture membranes were transferred to mylar zip-top bags containing silica packets that were sealed using a heat sealer. At the appropriate time points (1, 7, or 14 days post sample processing), the samples were eluted and analyzed by RT-qPCR. In vitro transcribed RNA for the HIV gag gene was used for standard curve analysis with input concentration ranging from $10^4$ cp/mL to $10^7$ cp/mL. These data indicate that RNA extracted by SNAPflex remains stable on the capture membrane for 14 days, demonstrating its potential for use in a field-based HIV viral load monitoring program without the need for a cold-chain.

9:00 AM *SB09.01.02
**Single-Cell Functional Profiling of CAR-T Cell Activation States** Rong Fan; Yale University, United States

The activation of CAR-T cells is through the binding of CAR to a surface marker such as CD19 expressed on the tumor cells and the subsequent signal transduction to its intracellular domain such as CD28/CD3z to elicit effector responses, which is independent of the conventional T-cell receptor (TCR) and peptide major histocompatibility complex (p-MHC) pathway. Therefore, the mechanism of CAR-T activation could differ substantially from that of classic T cells, which still remains inadequately studied but essential to the quality control of CAR-T products and the design of future CAR therapies. In this talk, I will present single-cell level transcriptional and cytokine profiling of anti-CD19 CAR-T cell activation states upon antigen-specific stimulation. We found that the predominant response is a highly mixed $T_{HL1}/T_{HL2}$ functional state in the same cell and the regulatory T cell ($T_{reg}$) activity, although observed in a small fraction of activated cells, emerges from this hybrid $T_{HL1}/T_{HL2}$ population. Surprisingly, the cytokine response is largely independent of differentiation status. This explains in part the functional proteomics data generated through collaborations with Novartis and Kite Pharma, showing that ‘polyfunctional’ CAR-T cells correlate with antigen-specific activation as well as the objective response of patients in clinical trials. Our work provides new insights to the mechanism of CAR activation and implies the necessity for cellular function assays to characterize the quality of CAR-T infusion products and monitor therapeutic responses in patients.

9:30 AM SB09.01.03
**Increasing the Dimensionality of Single Cell Transcriptomics to Address Systems Biology—Proteins, Imaging and More** Alexander Xu1,2, Qianhe Liu1, Kaitlyn Takata1, Sarah Jeoung1, Yapeng Su2, Sisi Chen1, Igor Antoschechkin1, Matthew Thomson1 and James R. Heath1; 1California Institute of Technology, United States; 2Institute for Systems Biology, United States

Systems biology is concerned with the complex interactions within and between cells that animate biology and create organisms that are more than the sum of their parts. This is currently exemplified in the field of single cell transcriptomics, where thousands of cells are analyzed with thousands of degrees of freedom, revealing novel cell types and interactions in heterogeneous tissues and diseases like cancer. One caveat however, is that single cell transcriptomics addresses a single class of molecules, poly-A-tailed mRNA, while systems biology has proven that proteins, lipids, metabolites, and more all play important roles. Here we demonstrate new methods to extend the functionality and dimensionality of single cell transcriptomics methods to address the concurrent biology of single cells beyond transcriptomics. This addresses the critical question of how different classes of molecules interact in single cells, and how this multi-modal heterogeneity manifests in biology. Current methods of multi-modal single cell analysis require interconversions of measurements, resulting in inevitable signal losses. Here we show that a microfluidic chip can integrate proteomic and transcriptomic measurements by embedding location information within transcriptomic measurements. The transcriptome is sequenced, while proteins are measured by fluorescent immunoassays. This is done with a location encoding strategy and microfluidic flow patterning, linking single cell transcriptomics captured by Dropseq-style bead based methods to single cell protein measurements made using DNA-Encoded Antibody Libraries. With this method, we measure full transcriptomes as well as proteins localized to the cytosol, mitochondria, and nucleus within the same single cells. We then show how this generalized strategy
can be extended to augment single cell transcriptomics with completely orthogonal measurements, such as fluorescent measurements of glucose uptake and imaging analyses, to extend the reach of multi-modal single cell measurements in new directions.

9:45 AM SB09.01.04
A Standalone, Reusable and Portable Microfluidic Device for Single-Cell Transcriptomic Analysis of Breast Cancer in Hypoxic Tumor Microenvironment Yanxiang Deng and Rong Fan; Yale University, United States

We present a standalone, reusable, and portable microfluidic device for single-cell transcriptomic analysis. The microchip platform is designed for performing single-cell capture and lysis directly toward 3’ mRNA sequencing. The presented approach offers format flexibility with a simplified, widely adoptable workflow that reduces the number of preparation steps and hands-on time, with the quality of data and cost per sample matching that of the state-of-the-art scRNA-seq platforms. Through this approach, we profiled thousands of single cells from mouse whole breast tumor and successfully identified different cell types from tumor microenvironment (e.g. tumor cells, tumor-associated macrophages, fibroblasts, B cells, and T cells). In addition, we studied the heterogeneity in tumor hypoxia in human breast cancer cells both in vitro and ex vivo and found a unique cell subset in the ex vivo model.

Single-cell RNA-sequencing (scRNA-seq) is becoming a popular tool in biology research to examine the heterogeneity of complex samples, identify distinct cell subsets, and dissect cell differentiation processes and lineage commitment. While many platforms are now available utilizing various approaches, one of the most commonly used techniques involves co-isolating each single cell with a uniquely barcoded mRNA capture bead as the enabling step for preparing barcoded libraries. Droplet-based microfluidic techniques and microwell arrays have been one of the widely used approaches to achieve such cell-bead co-isolation, however, they require major capital, peripheral equipment, and complex fabrication process, which limits their wide-spread adoption. Therefore, a more accessible method should be developed to be practically used for potential applicability in numerous cell biology and clinical applications.

Our platform is composed of three components: (1) PDMS microwell array, in which single cells and mRNA capture beads are co-isolated; (2) parafilm flow channel, which is to introduce cells and reagents using a laminar flow profile; and (3) acrylic clamp, which is to create a closed environment. This format is particularly advantageous due to increased consistency, higher cell loading efficiency (~50%), reduced cell consumption (~500 cells total), and high beads loading efficiency with minimal waste of barcoded beads (>99% bead loading efficiencies). It also should be noted that the easier fabrication and assembling process can facilitate the wide-spread adoption of this platform across different laboratories.

To validate the device’s overall workflow and its technical performance in resolving populations of cells in complex primary samples, we profiled thousands of cells from a mouse breast tumor. After sequencing and alignment, unsupervised graph-based clustering was implemented, revealing unique subpopulations in the breast tumor microenvironment, including tumor cells, tumor-associated macrophages, fibroblasts, B cells, and T cells.

Finally, the heterogeneity in tumor hypoxia in human breast cancer was studied both in vitro and ex vivo. Single cells from normoxia and hypoxia conditions were processed by this platform separately, and the downstream data analysis revealed heterogeneous cellular responses under hypoxia environment and found a unique cell subset in the ex vivo model.

10:00 AM BREAK

10:30 AM SB09.01.05
Developing Upconverting Nanoparticles as a Novel Tool to Probe Mechanical Forces of the Immune Synapse Claire A. McLellan, Stefan Fischer, Chris Siefe, Alice Lay, Abhinav Parakh, Vincent Van Unen, Mark M. Davis, Miriam B. Goodman, Wendy Gu and Jennifer A. Dionne; Stanford University, United States

Mechanical forces play a prevalent role in the immune system, particularly during the formation and duration of an immune synapse. During the synapse, a T-cell must latch onto a pathogen-primed antigen-presenting cell (APC) while enduring shear flow forces. These mechanical forces, which range from 10 pN to 100 nN, are thought to be crucial to immune cell-to-cell interactions but directly measuring them remains an open challenge. Traditional
methods of measuring cellular forces such as traction force microscopy (TFM) and FRET sensors have limitations when measuring the immune synapse. TFM cannot be employed in vivo or between cells, while FRET sensors generally bleach over the multi-hour-long duration of the synapse.

Here, we present a novel mechanical force sensor based on upconverting nanoparticles (UCNPs), which can detect inter-cellular forces throughout the formation and duration of an immune synapse. These nanoparticles absorb near-infrared light and emit visible light, with a ratiometric color response that depends on the applied force. Using solvothermal techniques, we synthesize ~11 nm diameter UCNPs comprised of alkaline-earth rare-earth fluoride host lattices (CaLuF, SrLuF, and BaLuF) doped with 30% Yb\(^{3+}\) and 2.9 % Er\(^{3+}\). As a control, we also synthesize cubic-phase NaYF\(_4\) host lattice particles doped with 28% Yb\(^{3+}\) and 2.8% Er\(^{3+}\). X-ray diffraction and transmission electron microscopy confirm that the synthesized nanoparticles are all phase-pure (cubic) and monodisperse. We record upconversion spectra as a function of applied pressure using a diamond anvil cell. When excited at 980 nm, the nanoparticles emit predominately at 550 nm (green) and 660 nm (red), with a red-to-green intensity ratio (I\(_{R}\)/I\(_{G}\)), and hence color that depends on pressure. For the four materials, CaLuF, SrLuF, BaLuF, and NaYF\(_4\), we measure a percent change in (I\(_{R}\)/I\(_{G}\)) per pressure response. The pressure responses for the particles are 38 ± 4, 16.3 ± 0.6, 12.8 ± 0.9, and 40 ± 4 %IR/IG/GPa for CaLuF, SrLuF, BaLuF, and NaYF\(_4\) respectively. The response of all particles measured remains consistent over three pressure cycles, demonstrating their cyclability. Upconversion quantum yield was also studied to determine the brightness of the particles. The upconversion quantum yields for the CaLuF, SrLuF, and BaLuF particles are 0.18%, 0.53%, 0.19% at 80 W/cm\(^2\) respectively \[1\]. We find that SrLuF particles are our most sensitive particles with the highest quantum yield of 0.53% at 80 W/cm\(^2\) and the lowest noise force response at 16.3 ± 0.6 %IR/IG/GPa. We can detect mechanical pressures down to 37 MPa corresponding to 27 nN of force, a value within the range useful for the immune synapse.

Furthermore, we are exploring how to integrate UCNPs into an immune synapse between T-cells and APCs. Through charge stabilization and adding amino-functionalization groups to our UCNPs we are working towards functionalizing UCNPs to attach to the cell membrane of APCs. We will also investigate the cytotoxicity of our particles. With our highly force sensitive UCNPs, we are working towards unraveling the mechanisms of the immune synapse.

\[1\]S. Fischer et al., Nano Lett. 19, 3879–3885 (2019).

10:45 AM SB09.01.06
Magnetic Isolation and Identification of Exosomes Using Magnetic Nanowires Zohreh Nemati Porshokouh\(^{1,1}\), Javier Alonso Masa\(^{2}\), Mohammad Reza Zamani Kouhpanji\(^{1}\), Joseph Um\(^{1}\), Yali Zhang\(^{1}\), Lucía Gandarias\(^{3}\), David Gandia\(^{4}\), Alicia Muñal\(^{5}\), Maria Luisa Fdez-Gubieda\(^{4,3}\), Rhonda Franklin\(^{1}\), Jaime Modiano\(^{1,1}\) and Bethanie Stadler\(^{1,1}\); 1University of Minnesota, United States; 2Universidad de Cantabria, Spain; 3Universidad del País Vasco, Spain; 4BCMaterials, Spain

We are developing segmented magnetic nanowires (MNWs) as a new platform for highly specific biolabels. We found that cancer cells internalize MNWs and package them into exosomes, which are then secreted for several days. These MNWs thus enable magnetic isolation of exosomes, which could prove useful in future diagnosis. Our immediate goals are to study how cells internalize MNWs, to determine the timing and reproducibility of exosome secretion, and to improve the magnetic isolation of exosomes. Following this work, we aim to use ferromagnetic resonance (FMR) to identify specific MNW biolabels, similar to radio frequency identification (RFID). In addition, we can compare the isolation efficiency we have employed high quality magnetite nanoparticles synthesized by magnetotactic bacteria (magnetosomes).

In this study, we incubated osteosarcoma (OSCA-8) cells with Fe/Au segmented MNWs with and without PEG coating for 48 hours. Internalization of MNWs as a function of concentration (5-40 μg/ml) was followed by fluorescence and transmission electron microscopy (TEM). We obtained quantitative estimates of MNW internalization by magnetic measurements. Our experiments indicated better internalization of the MNWs using PEG as a capping agent. As we increased the concentration of MNWs, both the number of cells with MNWs and the number of MNWs per cell increased. TEM images show that after uptake by cancer cells, MNWs were predominantly located within lysosomes, and they appeared to be fragmented into small segments of similar size as exosomes. These segments were mostly composed of either Fe or Au, suggesting that fragmentation occurred at or near the boundary of segments. In the case of magnetosomes, we also observed that they were internalized inside lysosomes, but their morphology remained intact.
We used two different methods for exosome isolation: non-magnetic isolation (centrifuge and ExoQuick TC) as a control and magnetic isolation. We incubated OSCA-8 cells with different concentrations of MNWs (0 to 35 μg/ml), and exosomes were isolated for up to 11 days. We analyzed the exosome size distribution using a nanoparticle tracking analyzer (NanoSight) and found that exosomes isolated magnetically, both with MNWs and magnetosomes, had similar size distributions as those isolated non-magnetically. A minimum concentration of 25 μg/ml MNWs in 3×10⁵ cells was required for appreciable magnetic isolation. Increasing the concentration of MNWs progressively; however, isolated microvesicles that had wider and more heterogeneous size distributions. TEM images of exosome isolated magnetically show that these exosomes packaged small pieces of MNWs.

Next, we successfully identified two different types of MNW biolabels by FMR. MNWs were fixed in a polymer that was placed onto an RFID chip. Each type of MNW exhibited a unique RF signature as the sample was exposed to an external magnetic field.

Our preliminary data show that MNWs appear to allow fast, inexpensive magnetic exosome isolation and is our future goal is MNW identification of exosomes. The methodology developed in this study should be transferable to develop comparable approaches to isolate and identify exosomes from virtually any type of cell.

11:00 AM SB09.01.07
Aptasensor-Encoded DNA Flowers for Monitoring ATP Dynamics in Living Cancer Cells
Nayoung Kim, Eunjung Kim, Hyemin Kim, Michael R. Thomas and Molly Stevens; Imperial College London, United Kingdom

There is a fundamental interdependence of adenosine triphosphate (ATP) dynamics and cancer development, given that ATP is required for a range of biosynthetic pathways during cancer cell proliferation, migration, and invasion. As a facile tool to monitor the ATP dynamics, biologically-deliverable nanoprobes have drawn increasing attention as an alternative to protein-based biosensors that require extensive genetic engineering for sensor-encoded cells. Nonetheless, challenges have remained with in vitro stability and toxicity issues of the nanoprobes, false positive signals that derive from cellular autofluorescence, and difficulties in normalisation of the intensimetric signals. Here, we present a programmable DNA-inorganic hybrid composite (termed as DNA flower, DNF) as a conjugation-free nanoprobe, enabling imaging of ATP dynamics in living cells upon the selective receptor-mediated internalization. The aptasensor-encoded DNF with two dye pairs achieved FRET-based ratio-metric imaging, where ATP recognition events trigger conformational changes of the aptamer within the composites and change the two fluorescence emission profiles. To the best of our knowledge, this system represents the first example of intracellularly deliverable probes that allow ratio-metric, spatial and temporal measurements of ATP levels in living cells. Capitalising on the structural stability of the DNF against nuclease degradation [1, 2], the developed probes achieved reliable and sensitive detection of changes in cytosolic ATP levels under exposure to various therapeutic agents over the time period. Given the versatility and robustness of the proposed DNA-based nanoprobes, it paves the way for facile, semi-quantitative tool-kits to monitor abundance of intracellular biomolecules during biological processes in cells.

References

11:15 AM SB09.01.08
Molecular Recognition and Sub-Cellular Detection of Temozolomide and 4-amino-5-imidazole-carboxamide for Glioblastoma Using Fluorescent Nanosensors
Manki Son, Freddy Nguyen, Punit Mehra, Michael A. Lee, Naveed Bakh and Michael Strano; Massachusetts Institute of Technology, United States

The efficacy of chemotherapeutics such as temozolomide and its decomposition, active product 4-amino-5-imidazole-carboxamide is often affected by the timing, quantity and frequency of dosages. There is strong interest in facilitating the ability to monitor efficacy in individual patients for specific subtypes of cancer. Real-time, dynamic measures of potency may also supplement or in some cases replace reliance on bio-imaging. Towards this end, in this work we develop new, synthetic molecular recognition sites for temozolomide, and its decomposition product AIC, grafting them onto near infrared fluorescent nanoparticles capable of forming optode or other biosensor interfaces to monitor drug efficacy in real-time. Infrared fluorescent single-walled carbon nanotubes, which have a specific DNA wrapping, are encapsulated with poly(ethylene glycol) diacrylate hydrogels and enable the selective recognition of an anti-cancer drug, temozolomide, on U-87 MG human glioblastoma cells. In both solution phase and hydrogel form, the sensors were responsive to temozolomide and show detection limit of 30 uM. Furthermore,
cells exhibited no changes in viability for 7 days when in interfaced with the hydrogel. The sensors were used to track the progression of glioblastoma death following temozolomide administration. By providing real-time information of local chemotherapeutic concentration, our technology has the potential to increase the efficacy of cancer treatments.

11:30 AM SB09.01.09
Tumor-Specific Extracellular Vesicles Unveiled by Size-Specific Single-Vesicle Analysis Yoon-Kyoung Cho1,2, Dongyoung Kim1, Hyun-Kyung Woo2, Chaehee Lee2 and Yoo-hong Min1; 1Institute for Basic Science, Korea (the Republic of); 2UNIST, Korea (the Republic of)

Extracellular vesicles (EVs) are nano-sized vesicles that carry complex cargoes of lipids, proteins, and nucleic acids depending on the biogenesis and the cell origin. Tumor-derived EVs have emerged as a promising circulating biomarker for liquid biopsy application. However, finding tumor-specific EVs among a heterogeneous population of EVs remains as a major challenge. Here, we extend our EV isolation disc to enrich EVs in three different size fractions; large EVs (L-EVs; 200–1,000 nm), medium EVs (M-EVs; 100–200 nm), and small EVs (S-EVs; 20–100 nm). This centrifugal microfluidic platform allows not only enriching EVs in three size portions but also fluorescently staining for the protein profiling of individual EVs. Combining single-particle localization techniques in super-resolution microscopy and machine learning-based classification analysis, we visualize and analyze the biomarker contents in individual EVs. As a proof-of-concept, we analyzed the presence of human epidermal growth factor receptor 2 (HER2) or prostate-specific membrane antigen (PSMA) in breast cancer cell- or prostate cancer cell-derived EVs, respectively, using the three different size fractions at the single-EV level. By reducing the complexity of EV heterogeneity in each size fraction, we found that HER2-positive breast cancer cells showed the greatest expression of HER2 in S-EVs, whereas PSMA expression was the highest in L-EVs derived from prostate cancer cells which were further confirmed using plasma-derived EVs obtained from prostate cancer patients. Our study suggests the EV heterogeneity will be broken down in several populations in specific size fraction, cell type, and biomarker using the size fraction disc with single EV analysis. Our study demonstrated that single-EV analysis could successfully identify potent subpopulations of cancer type-specific EVs, which has promising translational implications for cancer theranostics.
samples, computational approaches, and decellularized ECM models we found that breast adipose tissue contains more M2-biased than M1-biased macrophages across all body mass index (BMI) categories. Obesity further increased M2-biased macrophages but did not affect M1-biased macrophage density. Gene Set Enrichment Analysis (GSEA) suggested that breast tissue macrophages from obese women are more similar to tumor-associated macrophages (TAMs) than macrophages from lean women. These changes positively correlated with adipose tissue interstitial fibrosis, and in vitro experiments indicated that obese ECM directly stimulates M2-biased macrophage functions. Importantly, however, mammographic density cannot be used as a clinical indicator of these changes. Collectively, our data suggest that ECM microarchitecture can be an independent driver of obesity-associated fibrosis, but may also promote tumorigenesis by stimulating a macrophage phenotype similar to TAMs. These studies suggest a novel, ECM-driven link between obesity and breast cancer.

Acknowledgements: This work was performed in collaboration with Vivek Shenoy, University of Pennsylvania, Andrew Dannenberg and Olivier Elemento, Weill Cornell Medicine, Neil Iyengar, Memorial Sloan Kettering Cancer Center, and Delphine Gourdon, University of Ottawa, Canada. Funding by the Center on the Physics of Cancer Metabolism through Award Number 1U54CA210184-01 from the National Cancer Institute.

2:00 PM *SB09.02.02
A 3D Bone Marrow Hydrogel to Study Metastatic Cancer Cell Drug Resistance and Dormancy Shelly Peyton; Univ of Massachusetts Amherst, United States

Three-dimensional (3D) synthetic hydrogels have recently emerged as desirable in vitro cell culture platforms capable of representing the extracellular geometry, elasticity, and water content of tissue in a tunable fashion. Hydrogels are typically decorated with 1-3 peptide moieties to direct cell behavior, which vastly underrepresents the proteins found in the extracellular matrix (ECM) of real tissues and provides a critical limitation in their biological functionality. Further, peptides chosen are ubiquitous in ECM and are not derived from specific proteins. We developed an approach to incorporate the complex protein signature of specific tissues into biomaterial design. Our hydrogel mimics the elasticity of marrow and has 20 marrow-specific cell-instructive peptides. Compared to generic PEG hydrogels, our marrow-inspired hydrogel improves stem cell differentiation and proliferation. Additionally, this hydrogel can be easily tuned to probe ECM-mediated cell signaling. Here, we made a collagen-null marrow hydrogel, and show that prostate cancer cell growth is dependent on this peptide in a nutrient depleted, marrow-like environment. We propose this tissue-centric approach as the next generation of 3D hydrogel design for applications in tissue engineering.

2:30 PM SB09.02.03
Engineering Oxygen-Depleting Cryogel Scaffolds for Anti-Cancer Drug Screening Thibault Colombani¹, James Sinoimeri¹ and Sidi Bencherif²,¹; ¹Northeastern University, United States; ²Harvard University, United States

Hypoxia, defined as low oxygen tension, is a characteristic feature of solid tumors and a hallmark of aggressive cancers. Metabolic adaptation to hypoxia leads to tumor cell growth and invasion, resistance to apoptosis, and multidrug resistance. For decades, a number of solid tumor models have been engineered to emulate key aspects of tumor biology such as hypoxia. However, challenges with tumor formation and reproducibility, inadequate biomechanical cues provided to cells, and uncontrolled oxygen depletion among other limitations led to non-physiological tumor cell responses and inaccurate clinical predictions to anticancer drugs. To model solid tumors more accurately, we have recently developed an innovative approach using porous cryogel scaffolds inducing rapid oxygen depletion while enabling cellular rearrangement into spherical-like cell aggregates within a three-dimensional (3D) polymer network. Our main objectives were: (1) to engineer hypoxia-inducing cryogels to induce cellular hypoxia; (2) to provide a biophysical support enabling tumor cell attachment, proliferation, and remodeling, and (3) to evaluate acquired resistance of hypoxic B16-F10 melanoma cells to anti-cancer drugs. Engineered oxygen-depleting scaffolds are capable of inducing local hypoxia while promoting tumor cell remodeling and aggressiveness, leading to anti-cancer drug resistance. Our preliminary data suggest that the tumor-cell laden hypoxia-inducing cryogels mimic key aspects of the native tumor microenvironment, making these advanced cellularized scaffolds a promising platform for drug screening in 3D and potentially improving anti-cancer drug development and discovery.

2:45 PM SB09.02.04
In Vitro Models for Design of Novel Cancer Metastasis Markers Kalpana Katti, Sumanta Kar, Haneesh Jasuga,
Bone tissue engineering is a promising technology for next generation regenerative medicine based therapies. In addition, these tissue engineered scaffolds can be used as testbeds to create humanoid cancer tumors at primary site and at metastatic site. In particular, breast and prostate cancer have the propensity to metastasize to bone at which point the disease is incurable. The design of in vitro testbeds is particularly attractive due to lack of availability of human samples at this stage of metastasis and failure of animal models (since animals die before metastasis to bone).

We have designed an amino acid modified nanoclay based polymeric scaffold for bone tissue engineering. This scaffold uses biomimetic mineralization of hydroxyapatite inside nanoclays galleries mimicking remodeling human, characterized by low Ca/P stoichiometry bone, a niche to which cancer cells migrate. On seeding the tissue engineered bone scaffolds with prostate and breast cancer cell lines led to the creation of tumoroids of cancer. The tumoroids exhibited a late stage metastasis as indicated by the gene expression and protein expression. Tumors were extracted from scaffolds and we conducted FTIR experiments as well as nanomechanical experiments at cancer metastasis progression from 0 to 20 days. Softening of tumors as well as increase in plastic deformations were captured at metastasis. In addition unique spectral markers of DNA, RNA, proteins and lipids were obtained that indicate progression of metastasis. Unique bone-biomimetic scaffolds provide new opportunities as testbeds to evaluate cancer metastasis.

3:00 PM BREAK

3:30 PM SB09.02.05
Cancer Extracellular Vesicles Derived Supported Bilayers as a Cell Culture Platform to Understand Surface Interactions between Stem Cells and Extracellular Vesicles

Cancer is the second leading cause of death in the US and 92% of such casualties are due to metastasis. Thus, discovering mechanisms employed by cells to promote metastasis and developing strategies to stop them, are the main targets of cancer research. In particular, extracellular vesicles (EVs) shed from cancer cells, have been recently implicated as important mediators of cellular communication and are suspected to play an important role in metastasis. EVs are membrane-encapsulated vesicles known to shed from several types of eukaryotic cells. Extensive research has shown the existence of two major EVs subtypes, exosomes and microvesicles (MVs). Exosomes are vesicles generated from multivesicular bodies and secreted to the extracellular space by fusing with the plasma membrane. Exosomes are between 20 -120 nm in diameter. The second type, MVs, has a larger size range between 120 nm - 1μm in diameter. MVs are directly shed from the plasma membrane into the extracellular space, preserving native properties from the mother cell. EVs of both types contain different cargo including mRNA, DNA, proteins, and receptors. MVs and exosomes differ in biogenesis, cargo, and surface makeup. Research findings suggest that they have different intracellular routes and functions in cell communication. Therefore, it is imperative to distinguish between them since their functions and communication pathways may have different effects on cells. Both populations have been highlighted in research due to their capacity to facilitate intercellular communication. In that manner, interactions between EVs and host cells have been shown to lead to modifications in cellular behavior of the recipient cell. In the context of cancer, EVs are known to influence proangiogenic activity and transformation on adipose derived stem cell (ADSC) leading to cancer progression. How these interactions occur in the molecular level is not clear. Cues most certainly come from both membrane components on EVs, as well as their internal cargo. Yet, there is a lack of techniques to study those interactions in vivo. Hence, we developed an in vitro platform that allows the isolation and study of interactions between EVs surface and ADSCs. Using hybrid supported lipid bilayer techniques developed by our group and EVs derived from cancer cells, MDA-MB-231, we originated an EVs derived supported bilayer (ESB) as a model of EVs membrane. ESB is a planar, tunable platform that can serve as a cell culture substrate to study the effects and insights of interactions between EVs surface and ADSCs. To assure preservation of EVs membrane materials in our generated ESBs, TIRF microscopy was employed to detect expression of EVs markers specific to each EV population. Furthermore, ADSCs were cultured on ESBs and cell adhesion and spreading, cell viability, and cell VEGF production were analyzed. Our results showed that ADSCs cultured on ESBs displayed higher cell spreading, stronger focal adhesions, and higher VEGF production than cells on synthetic supported lipid bilayers. Therefore, we observed that EVs surface interactions with ADSCs enhances cell adhesion, spreading, viability, and proangiogenic activity.
related to high VEGF production. In all cases, the influence of ESB from both EVs populations followed the same pattern with MVs derived ESB having a larger effect on ADSCs behavior compared to exosomes derived ESBs. Consequently, we present our developed ESB, containing native composition of EVs membranes, as a cell culture platform to study interactions between EVs and stromal cells. Our method allows the production of different EVs populations derived ESBs to study individually the interactions of EVs and stromal cells and to decouple the biological outcomes produced by each of the EVs population. It could be utilized as a method to investigate cell to cell interactions, and extracellular particles to cell interactions for different types of cells and for several disease scenarios.

3:45 PM OPEN DISCUSSION

4:00 PM SB09.02.07
Polymer Nanoparticles for Detection and Ablation of Colorectal Cancer Tumor Organoids Bryce D. McCarthy1,1,2, Amit Cudykier1, Shay Soker1,2 and Nicole Levi-Polyachenko1,2; 1Wake Forest University, United States; 2Virginia Tech, United States

Our group has recently developed Hybrid Donor-Acceptor Polymer Particles (HDAPPs), nanoparticles composed of the fluorescent polymer poly[(9,9-dihexylfluorene)-co-2,1,3-benzothiadiazole-co-4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole] (PFBDTB10) and the heat-generating polymer poly[4,4-bis(2-ethylhexyl)cyclopenta[2,1-b;3,4-b']dithiophene-2,6-diy-alt-2,1,3-benzoselenadiazole-4,7-diyl] (PCPDTBSe) to create a theranostic platform. HDAPPs can be activated via 450 nm laser exposure for fluorescent imaging within the NIR tissue absorption minimum by exploiting an amplified energy transfer between the PFBDTB10 and PCPDTBSe polymer components, emitting at 825 nm. Additionally, HDAPPs can be activated by 800 nm laser exposure for photothermal ablation of colorectal cancer (CRC). To actively target CRC, HDAPPs were functionalized via hyaluronic acid (HA) coating of the NP surface to exploit overexpressed CD44 receptor on CRC. A major hurdle for the clinical translation of NPs is their interaction with the 3D tumor microenvironment, where NP transport and photothermal heat dosing may be isolated to the outermost shell of the tumor that maintains direct exposure to the nanotherapeutic. To study the targeted fluorescent detection and heating potential of HDAPPs in the 3D tumor microenvironment, we investigated the encapsulation of tumor cells in a specialized hydrogel (3D organoid) in vitro. Further, to monitor HDAPPs-mediated ablation in real-time within organoids, we demonstrated the utility of a unique fiber-optic-based (FOB) imaging system capable of laser-induced point excitation and fluorescent image reconstruction in opaque media. HDAPPs were first synthesized using the nanoprecipitation technique, where an aqueous phase consisting of Pluronic F127 surfactant is interfacial via sonication with an organic phase of the polymer constituents to create HDAPPs nanoemulsions. HDAPPs were then coated with chitosan and further targeted to CD44 receptor via coupling of HA to the surface. Selective binding and ablation of CT26 CRC cells in 2D was demonstrated with HA-targeted NPs under photothermal activation with 800 nm stimulation, where HA-targeted NPs displayed increased binding relative to non-functionalized NPs and, upon photothermal activation with laser, CT26 cells incubated in 2D with HA-targeted NPs demonstrated a respective decrease of viability by 40%. Photothermal ablation of CT26 cells expressing green fluorescent protein (CT26.GFP) and encapsulated in 3D organoids was next assessed. HA-targeted NPs decreased cell viability in organoids by 60%, though ablation in 3D organoids occurred only under increased laser fluences in comparison to 2D culture, demonstrating decreased efficiency of photothermal therapy in 3D-tumor like conditions. A major therapeutic hindrance in therapy is diffusion limitation in tumors, where HDAPPs diffusion was measured by exposing HDAPPs to the outer surface of organoids and monitoring via confocal microscopy for up to 24 hrs. Diffusion studies showed that at least 12 hours exposure to therapeutic concentrations is necessary to achieve ablative potential. Finally, to demonstrate FOB imaging compatibility with the 3D tumor environment, organoids with CT26.GFP cells and non-functionalized HDAPPs were imaged by FOB laser excitation and fluorescent images were successfully reconstructed that map to control images. The results of this work demonstrate the performance of a unique NP platform capable of detecting and ablating CRC within the tumor microenvironment. Coupling of organoids with the FOB imaging device demonstrates a preclinical system that can simultaneously assess CRC detection and ablation with NP therapeutics, where we aim to both develop an organoid platform for proper preclinical translation of photothermal nanotherapeutics while investigating the properties of our own HDAPPs.

4:15 PM SB09.02.08
Breast Cancer Cells Transition from Mesenchymal to Amoeboid Migration in Tunable 3D Silk-Collagen
Hydrogels Amanda S. Khoo, Thomas M. Valentin, Susan E. Leggett, Dhananjay Bhaskar, Elisa M. Bye, Blanche C. Ip and Ian Y. Wong; Brown University, United States

Invading cancer cells adapt their migration phenotype in response to mechanical and biochemical cues from the extracellular matrix. For instance, mesenchymal migration is associated with strong cell-matrix adhesions and an elongated morphology, while amoeboid migration is associated with minimal cell-matrix adhesions and a rounded morphology. However, it remains challenging to elucidate the role of matrix mechanics and biochemistry, since these are both dependent on protein concentration. Here, we demonstrate a composite silk fibroin and collagen I hydrogel where stiffness and ligand density can be independently controlled. Using an overlay assay geometry, we show that the invasion of metastatic breast cancer cells exhibits a biphasic dependence on silk fibroin concentration at fixed collagen I concentration, with an optimum occurring at intermediate stiffness. Indeed, mesenchymal morphology exhibits a similar biphasic dependence on silk fibroin concentration, while amoeboid morphologies were favored when cell-matrix adhesions were less effective. We used exogenous biochemical treatment to perturb cells towards increased contractility and a mesenchymal morphology, as well as to disrupt cytoskeletal function and promote an amoeboid morphology. Overall, we envision that this tunable biomaterial platform in a 96-well plate format will be widely applicable to screen cancer cell migration against combinations of designer biomaterials and targeted inhibitors.

4:30 PM SB09.02.09
Programming Cellular Mechanophenotype Using Magnetically-Aligned Nanofiber Architectures Alex Hruska, Michelle Adler and Ian Y. Wong; Brown University, United States

Introduction: Cell polarity, morphology, and migration are regulated bidirectionally by nanotopographical cues from the extracellular matrix (ECM). In particular, ECM architecture may become dysregulated during wound healing or tumor progression with highly aligned and crosslinked fibrillar nanostructures. However, these fibrillar architectures are biophysically coupled to ligand density, stiffness, and other ECM properties, making it challenging to elucidate their individual contributions. Here, we elucidate how cells respond to 3D nanotopography using a composite hydrogel consisting of magnetically aligned ECM-coated nanoparticles embedded within a background hydrogel of gelatin methacryloyl. We show that by systematically varying the biophysical parameters of the fibrillar nanostructures or the background matrix, cell protrusions and morphology can be tuned to direct cell polarization and migration.

Materials & Methods: ECM-coated 300nm magnetic nanoparticles were dispersed in gelatin methacryloyl (GelMA) precursor solution and exposed to a magnetic field gradient, inspired by previous work from Tanner et al (Biomaterials, 197, 101-118, 2019). Nanoparticles assembled into chain-like fibrillar structures under optimized field gradients, which mimicked the dimensions of ECM fibers observed in vivo. Next, the GelMA was photocrosslinked using UV light with LAP as the photoinitiator. Various cell lines (e.g. MDA-MB-231 overexpressing GFP in the cytoplasm) were then cultured in this composite hydrogel and imaged using spinning disk confocal microscopy with environmental control. Time-lapse images were then analyzed using Bitplane Imaris and custom MATLAB code.

Results & Discussion: Nanoparticle assembly and GelMA hydrogel polymerization were optimized using a custom magnetic apparatus to uniformly disperse fibrillar nanostructures over millimeter scales in 3 dimensions. We optimized the length and diameter of these fibrils based on magnetic field gradient, and further characterized GelMA as a “blank slate” with amorphous topography, tunable stiffness, pore size, and RGD-binding sites. Finally, we show that by systematically tuning either the fibrillar topography or the background matrix, cell protrusive activity as well as migration velocities can be altered. For instance, highly metastatic MDA-MB-231 cells exhibit directed migration along fibers, where providing no magnetic alignment yields a uniform dispersion of particles and yields slow, random migration with short protrusions. In comparison, a stiff background matrix of highly cross-linked GelMA limits protrusive activity and migration, while softer more porous background matrix allows cells to extend long protrusion along engineered fibers and enables higher migration velocities. These migratory behaviors were perturbed by biochemical inhibition of integrins and the cytoskeleton, which were profiled using computer vision and machine learning.

Conclusion: We demonstrate a composite 3D biomaterial with orthogonally tunable fibrillar architecture, hydrogel chemistry, and stiffness to elucidate bidirectional interactions between cells and the ECM. We find that cell protrusions, morphology, and migration are biased by varying degrees of magnetic nanoparticle chaining, which dominate over the mechanochemical cues from the surrounding GelMA hydrogel. We implement this in a scalable...
format that is compatible with multiwell plates, which could be extended for high content screening. Thus, we envision that this technology could be utilized to systemically characterize mechanotransduction of ECM cues in the context of targeted drug perturbations.

**Acknowledgments:** This work was funded by the NCI Innovative Molecular Analysis Technologies Program (R21CA212932) and Brown University through the Karen T. Romer Undergraduate Research and Teaching Award.

**4:45 PM SB09.02.10**

**A General-Purpose 3D Printed Organ-on-Chip System—Fabrication and Validation of Use in a Tumor-on-Chip Application Scenario**

Itzel M. Lara-Mayorga¹, Brenda G. Flores-Garza¹, David Choy-Buentello¹, Mariana García-Corrál¹, Valeria Perales-Salinas¹, Christian C. Mendoza-Buenrostro¹, Juan Yee-de León², Yu S. Zhang³,¹, Grissel Trujillo-deSantiago¹,¹ and Mario M. Alvarez¹,¹; ¹Tecnologico de Monterrey, Mexico; ²DeLee Co., Mexico; ³Brigham and Women’s Hospital, Harvard Medical School, United States

Organ-on-chip systems are useful tools to fundamentally study the physiology of organs and tissues, to evaluate the efficacy or toxicity of drug compounds, or to study the effect of tensors on human tissues. However, to design and fabricate an organ-on-chip system is not a trivial task. Here we present an example of a step-by-step fabrication and validation of a 3D-printed microfluidic system that can be generically used to culture cells, micro-tissues, and organoids under well-controlled environments. The system is conformed by three compartments. The left and right compartments have one inlet and one outlet each, providing means to continuously feed liquid streams to the system. The central compartment is designed to host a cell-laden hydrogel where a microtissue can be confined and culture. A transparent lid and bottom can be adapted to enable visual inspection under a microscope.

We conducted fluorescent and saline tracer experiments to characterize the hydraulic performance of the system. In addition, we cultured MCF7-spheroids embedded in a cell-laden hydrogel construct (placed in the central chamber), to illustrate the use of this system to sustain long term micro-tissue culture experiments. We present experimental results that illustrate the flexibility and robustness of use of this 3D-printed device for tumor-on-chip experiments. This “open-source” organ-on-chip system is intended to be a general-purpose resource to facilitate democratize the development of new organ-on-chip applications.

**SESSION SB09.09: Poster Session I: Interfacing Bio/Nano Materials with Cancer and the Immune System I**

**Monday Afternoon, December 2, 2019**

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

**SB09.03.01**

**Microfluidic Imaging Windows for the Study of Cancer Metastasis with Intravital Imaging**

Tristen Head¹, Suhasini Gattu¹, Rojin Jafari², Xianjun Ye², Natalya Tokranova¹, John Condeelis², David Entenberg² and Nathaniel Cady¹; ¹SUNY Polytechnic Institute, United States; ²Albert Einstein College of Medicine, United States

Simultaneous observation and induction of biomolecular changes in the tumor microenvironment are challenging to accomplish over extended periods of time. The effect of therapeutics on the target site is often obfuscated by systemic on- and off-target effects inherent in drug administration. Thus, localized delivery and high-resolution imaging are necessary to assess cellular response to changes in the tissue microenvironment. Here, we report on the design, fabrication and testing of a novel microfluidic imaging window (MFIW) using glass and SU-8 photoresist microfabrication techniques to actively deliver agents (e.g. drugs, antibodies, inhibitors, etc.) to underlying living tissue. Microfluidic channels were fabricated using multi-layer SU-8 patterning techniques on 12 mm glass coverslips. Point spread functions were compared between standard glass windows and MFIWs and optical performance of the MFIWs was validated with 2-photon microscopy (at 880nm) on transgenic MMTV-PyMT Dendra2 fluorescent tumors, which confirmed device applicability for biological studies. Microfluidic delivery and diffusion of fluorescent dye into tissue surrogates was measured via confocal microscopy and then compared to COMSOL simulations to characterize agent delivery depth and concentration profile. These results demonstrate the ability of the device to deliver sub-microliter quantities of fluid, and the ability to control the depth and diameter of the diffusion profile. Ongoing studies are focused on insertion and testing of devices in mice, including validation of...
drug delivery to the tumor microenvironment, *in vivo.*

SB09.03.02
**A Scalable 3D Printed Spheroid Capture Device for Rapid Immunotherapy Cancer Diagnostics**  
Alex W. Markoski¹ ², Ian Y. Wong² and Jeffrey T. Borenstein¹; ¹Draper Laboratory, United States; ²Brown University, United States

Immunotherapies such as immune checkpoint inhibitors (ICI) show great promise as more efficacious treatments for various cancers compared to current methods such as chemotherapy. However, preclinical evaluation of immunotherapies typically relies on mouse models that have limited relevance to human responses, or on *in vitro* culture methods that suffer from small sample sizes, limited cell viability, a lack of physiologically relevant stimuli such as flow, and an absence of tumor-immune cell interactions. To address these limitations with current models, we have developed a scalable 3D printed microfluidic devices capable of capturing multicellular tumor spheroids and perfusing them in the presence of circulating tumor infiltrating lymphocytes (TILs). Finite element modeling was first used to optimize flow conditions for capturing spheroids as well as for extended viability. Next, we experimentally characterized how T cells interacted with multicellular tumor spheroids in varying flow conditions, as well as after anti-PD-1 immune checkpoint treatment. Ultimately, these microfluidic devices will enable researchers and clinicians alike to test various immunotherapies in a scalable, rapid, and *in vivo* relevant manner.

SB09.03.03
**Peptide Self-Assembly into a Three-Dimensional Scaffold for Cell Growth and Encapsulation**  
Michael Jorgensen and Jean Chmielewski; Purdue University, United States

Self-assembling peptides have been used in recent decades for a variety of medical applications, including but not limited to tissue engineering, drug delivery, and biosensing. One peptide of particular interest, the leucine-zipper of the transcription factor GCN4, can exist in multiple oligomeric states based on the hydrophobic interface. Through functionalizing these GCN4 peptides with metal-binding ligands on the hydrophilic faces of the coiled coil, metal ion-mediated self-assembly can be promoted radially, and by altering the C- and N-termini of the peptide, self-assembly can be facilitated linearly. A design which merges these two modifications to create crosslinked coiled coil biomaterials will be reported.


SB09.03.04
**Selective Capture and Identification of Liver Cancer Related microRNAs and Intracellular Proteins through Antisense-Vectorized Magnetic Nanobeads**  
Isabel Gessner¹, Xiaojie Yu², Christian Jüngst³, Annika Klimpel¹, Lingyu Wang² ³, Thomas Fischer¹, Ines Neundorf⁴, Astrid Schauss², Margarete Odenthal² ³ ⁵ and Sanjay Mathur⁶; ¹University of Cologne, Germany; ²University Hospital Cologne, Germany; ³Cluster of Excellence - Cellular Stress Responses in Aging-Associated Diseases (CECAD), Germany; ⁴Center for Molecular Medicine (CMMC), Germany; ⁵Center of Integrative Oncology, Germany

MicroRNAs (miRNAs) are small non-coding nucleotides playing a crucial role in posttranscriptional expression and regulation of target genes in nearly all kinds of cells. In this study, we demonstrate a reliable and efficient capture and purification of miRNAs and intracellular proteins using magnetic nanoparticles functionalized with antisense oligonucleotides. For this purpose, a tumor suppressor miRNA (miR-198), deregulated in several human cancer types, was chosen. Magnetite nanoparticles carrying the complementary sequence of miR-198 (miR-198 antisense) on their surface were delivered into cells and subsequently used for the extracellular transport of miRNA and proteins. The successful capture of miR-198 was demonstrated by isolating RNA from magnetic nanoparticles followed by real-time PCR quantification. Our experimental data showed that antisense-coated particles captured 5-fold higher amounts of miR-198 when compared to the control nanoparticles. Moreover, several proteins that could play a significant role in miR-198 biogenesis were found attached to miR-198 conjugated nanoparticles and analyzed by mass spectrometry. Our findings demonstrate that a purpose-driven vectorization of magnetic nanobeads with target-specific recognition ligands is highly efficient in selectively transporting miRNA and disease-
relevant proteins out of cells and could become a reliable and useful tool for future diagnostic, therapeutic and analytical applications.

**SB09.03.05**

*Non-Thermal Atmospheric Pressure Plasma as an Effective Tool to Activate the Expression of Cytokines and Growth Factors to Induce Proliferation of Various Mesoderm-Derived Adult Stem Cells*  
*Kwon Song1, Jeongyeon Park1, Hyunyoung Lee2 and Hae June Lee2; 1Yonsei University, Korea (the Republic of); 2Busan National University, Korea (the Republic of)*

Non-thermal atmospheric pressure plasma (NTAPP) is described as a partially ionized gas containing charged particles and radicals at atmospheric pressure. Recently, some studies have reported the application of NTAPP to regenerative medicine for wound healing and activation of immune responses. In this study, we demonstrate that NTAPP activates the proliferation of various mesoderm-derived adult stem cells including adipose tissue-derived stem cells (ASCs), bone marrow-derived stem cells (BM-MSCs) and hematopoietic stem cells (HSCs) to develop NTAPP as an efficient tool for adult stem cell therapy. In our study, NTAPP induced the proliferation of these adult stem cells by 1.5 to 2-fold, compared with unexposed cells. Also, NTAPP exposure increased the expression of stem cell-specific surface markers, CD44 and CD105, by 5-fold in BM-MSCs, compared with that in unexposed cells in a low glucose medium with a low concentration of basic fibroblast growth factor (b-FGF), and augmented the expression of well-known pluripotent genes including Oct4, Sox2 and Nanog in ASCs and BM-MSCs compared to that in unexposed control cells, suggesting that NTAPP activated the proliferation of various adult stem cells without affecting the stem cell properties. The whole genome expression profiles of ASCs whose proliferation is highly activated by NTAPP showed that NTAPP upregulated genes for cytokines and growth factors, while it downregulated genes functioning in the intrinsic apoptotic pathway. With genes that showed more than two-fold increase or decrease in NTAPP-exposed ASCs by whole RNA-sequencing, we also confirmed the increased mRNA expression of leukemia inhibitory factor (LIF), heparin-binding epidermal growth factor (HBEGF), interleukin-6 (IL-6), IL-11, fibroblast growth factor 16 (FGF16), and IL-1β by 2 to 12-fold and decreased expression of bel-2-binding component 3 (BBC3), death-associated protein kinase 1 (DAPK1), caspase 10 (CASP10), tumor protein p53 (TP53), and receptor interacting serine/threonine kinase 3 (RIPK3) by 2 to 4.5-fold by real-time PCR, compared with the unexposed control. The increased expression of various cytokines and growth factors was highly declined comparing with NTAPP-treated ASCs in the presence of a nitric oxide (NO) scavenger, indicating that NO generated from NTAPP is mainly responsible for the enhanced expression of cytokines and growth factors by NTAPP. Collectively, these results strongly demonstrated that NTAPP would be an excellent tool to control the expression of cytokines and growth factors to trigger the activation of adult stem cells *in vitro* for stem cell therapy.

**SB09.03.06**

*A Nanoparticle-Enabled Focused Ultrasound-Stimulated Magnetic Resonance Imaging Spotlight*  
*Tian Deng, Le Zhang, Holden Wu and Jeffrey I. Zink; University of California Los Angeles, United States*

High-intensity focused ultrasound (HIFU) guided by Magnetic Resonance Imaging (MRI) is used as a therapeutic technique in clinical practice. To improve its efficacy, it is essential to accurately identify, or spotlight, target tissues for treatment. In this talk, we present a novel contrast enhancement method based on MRI-guided HIFU and mesoporous silica nanoparticles (MSNs). HIFU modulation was applied to MSNs modified with a thermo-responsive and biocompatible polymer to generate MRI T1 relaxivity changes in regions of interest. A modulation enhancement map (MEM) was reconstructed to spotlight the region of interest with almost two orders of magnitude increase in contrast compared to conventional enhancement methods. HIFU provides a 1.5 mm³ focal point that is spatially controllable in three-dimensions. The data acquisition time for the experiments in our study was 100 s, and it is practical for imaging during clinical applications. The small (2 °C) temperature change would cause minimal tissue damage. This non-invasive method can be applied in improving the identification of target tissues, such as delineation of tumor margins, for MRI-guided HIFU therapies.

**SB09.03.07**

*Downconversion Luminescent Nanoparticles Harnessing Changes in the Surface Dipole as a Novel Approach for Small Molecule Detection*  
*Khashayar R. Bajgiran, James A. Dorman and Adam T. Melvin; Louisiana State University, United States*

Traditional sensing techniques such as enzyme-linked immunosorbent assay (ELISA) offers limits of detection
(LOD) in the pM-fM range, however, it is labor-intensive, require multiple washing steps, and most importantly utilize expensive antibodies for analytical detection which limits their utility for point of care (POC) applications. To address these issues, colloidal nanoparticle (NP) biosensors can be designed to provide precise analytical detection without requiring antibodies and extensive post-processing steps. Optical NPs offer a wide range of biosensing applications such as ultrasensitive detection of cancer biomarkers in human serum, multiplexed, point of care (POC) detection of analytes, and in vivo sensing of reactive oxygen species. Optical nanoparticles, such as quantum dots (QDs) have exhibited comparable LOD to ELISA in some cases with high signal to noise ratios (SNR>10). However, the heavy-metal content of QDs results in high cytotoxicity prohibiting the wide-scale use of QDs particularly in clinical applications. Luminescent upconversion NPs have been introduced as biocompatible alternatives with comparable LODs (~6 nM). However, they require expensive, high energy infrared lasers and are limited in their ability for multiplexing. We have recently developed a Bi³⁺-doped YVO₃:Eu³⁺ core-shell nanoarchitecture that can utilize the changes in surface dipole moments as a novel mechanism for detection. It was found that the downconversion luminescent signal of the NPs can be modulated with respect to the dipole moment. The developed NP sensor was then functionalized with D-biotin to be used for label-free detection of avidin. Decorating the surface of the NPs with D-biotin generated a positive dipole moment (i.e., electron withdrawing) resulting in a decreased luminescent signal. The surface coverage of the biotin decorated NPs was evaluated using thermogravimetric analysis (TGA) to perform by time and concentration-dependent studies into how avidin binding further altered the luminescent properties of the NPs. Exposure to avidin resulted in a further decrease in the luminescent signal of the NPs suggesting that the interaction of avidin with biotin resulted in a positive dipole moment with a larger magnitude. This decrease in luminescent signal was found to be specific and concentration-dependent with respect to the free avidin concentration in solution. The downconversion NPs exhibited a similar SNR to upconversion NPs (SNR~15) with a LOD comparable to those of the QDs. This novel approach in biosensing can be expanded to the label-free detection of disease biomarkers or pathogens at low limits of detection in bulk fluid which is paramount for POC applications.

SB09.03.08
Dual-Gel Dual-Porosity Metamaterial as 3D Cell Culture Matrix for Studying Effects of Interstitial Flow on Cell Migration Jing Fan and Alimohammad Anbari; City College of New York, United States

Interstitial flow, the slow fluid flux occurring in the interstitial space of extracellular matrix (ECM), is mostly negligible in normal soft tissues, yet it could play crucial roles in regulating cellular behaviors in some pathological tissues or bone tissue. With the speed up to a few microns per second, the interstitial flow not only provides direct mechanical cues to the resident cells through shear stress and normal stress, but also couples with biomolecular diffusion to induce biochemical cues to the cells. Previous in vitro and in silico studies have implied that interstitial flow can regulate individual cell migration through at least two mechanisms: autologous chemotaxis and integrin-mediated focal adhesion activation [1-2]. The effectiveness of the former depends on interstitial fluid velocity; the effectiveness of the latter depends on both interstitial fluid velocity and ECM permeability. However, even in vitro, these two mechanisms cannot be rigorously examined due to the inevitable inverse correlation between permeability and stiffness of hydrogel matrices. Specifically, stiffness is another important mechanical cue that influences cell migration. Therefore, developing a thorough understanding of cellular behaviors regulated by interstitial flow requires an ability to independently control permeability and stiffness of the matrix, interstitial fluid velocity, as well as other relevant properties, such as ligand composition and density in the matrix; this independent control is still an unmet challenge in existing 3D in vitro models.

To address this challenge, we developed a dual-gel dual-porosity metamaterial integrating with a microfluidic platform for studying the effects of interstitial flow on cellular behaviors. This novel in vitro model, consisting of GelMA-PEGDA microgels and collagen, allows for independently controlling stiffness, cell-binding cites, permeability, and interstitial flow, as well as live imaging of migrating dynamics. We will present our preliminary results showing the effectiveness of our dual-gel metamaterial based cell culture model by characterizing the migration of breast cancer cells under different flow conditions and ECM properties.

References:
SB09.03.09
Agarose Beads with Controlled Pore Structures for High Precision Clinical Diagnostics in Biosensing
Deniz Vurmaz¹ and John T. McDevitt²,¹; ¹NYU Tandon School of Engineering, United States; ²NYU college of dentistry, United States

Increasing the precision and reliability in biosensing is critical for accurate clinical disease diagnosis and rapid implementation of relevant treatment modalities. A key factor in high precision detection is the reduction of the coefficient of variation in a biosensing platform. A variety of polymer-based microbeads have been used as the medium to immobilize probes for a wide range of targets. Microbeads have been an attractive platform for diagnosis of diseases by targeting specific biomarkers in body fluids such as serum, saliva and urine, that are complex media with a large background of large variety of non-specific biomolecules, including proteins, peptides, mRNA and other small and large biopolymers. Among the several problems associated with the bead-based systems, the key issues are related to bead-to-bead signal variation because of the size and the surface versus internal bead structural variations. These limitations also include the variability and inefficiency of immobilization approaches as well as the formation and mechanical properties of the beads.

We have developed a mechanical methodology by which to mass produce agarose gel-based nanoporous microbeads with controlled internal and surface structures which facilitates a closer control over the surface functionalization. We demonstrate herein a covalent biofunctionalization of disease-specific probes and show high signal-to-noise ratio biomarker detection. For proof-of-concept demonstration, two key biomarkers were used, CRP and CTNI, that raise substantially after injury for multiple organ failure, respectively. Specifically, using gloxylation method we biofunctionalized the agarose beads with a capturing antibody protein both on the surface and throughout the porous internal structure to systematically analyze the capture of disease-specific antigens with significantly enhanced signal-to-noise ratio. The ease of manufacturing and performance characteristics of agarose microbeads demonstrated herein show a significant promise in the rapid and high precision diagnostic of disease-specific biomarkers paving the way for potential clinical implementations where the detection of the disease-specific antigens rapidly and with high efficiency is of prime importance. Funding was provided by the NIH through the National Institute of Dental and Craniofacial Research (NIH Grant Nos.3 U01 DE017793-02S1 and 5 U01 DE017793-2) and the ARO - contract No. W911NF-16-P-0030.

SB09.03.10
Cancellous Bone Characterization Using Ultrasonic Spectroscopy
Alina Karki¹, Xiaoman Shen² and Junru Wu¹; ¹The University of Vermont, United States; ²Beijing Institute of Technology, China

Ultrasound spectroscopy has evolved as a great potential non-invasive tool in the osteoporosis diagnosis and bone assessment since ultrasonic parameters such as normalized broadband ultrasound attenuation (nBUA) and speed of sound (SOS) have been used to characterize cancellous bone. However, the bone characterization is limited to the study of their relations to bone mineral density (BMD). An understanding of the underlying mechanisms responsible for the ultrasound propagation in cancellous bone is still lacking. There is also no evidence on the feasible frequency range for the assessment of bone. We have used the ultrasonic spectroscopy technique in transmission geometry to measure nBUA and speed of longitudinal ultrasonic waves in twenty-two beef cancellous bones at frequencies ranging from 2.25-7.5 MHz, with the goal of finding suitable frequency range for bone assessment. Bone porosity is another important parameter which greatly affects interaction or scattering of ultrasound in cancellous bone, which in turn affects ultrasound speed and influences the elastic properties of bone. In our study, bone porosity of each bone specimen is determined using x-ray micro CT scan and the relationships between bone porosity and ultrasonic parameters like nBUA and SOS are explored in the above-mentioned range of ultrasonic frequencies. We have utilized a systematic approach, beginning with the investigation of a polyethylene disk, moving on to the investigation of bone specimens.

SB09.03.11
Chimeric Solid-Binding Peptide-PNA Probes towards Cancer Bionanosensors
Richard V. Lee, Hadi Zareie and Mehmet Sarikaya; University of Washington, United States

Key aspects of designing effective biosensors include i) Tethering probes onto the sensing substrate while maintaining their proper orientation to appropriately bind target molecules, ii) Efficient signal transduction across
soft bio/nano interfaces of the sensing surface, and iii) Reusability of the sensor chip. Solid-binding peptides (SBPs) present a viable method for non-covalent immobilization of probes onto single-atomic layer substrates—providing unprecedented prospects for sensor design. This approach delivers functionalization while eschewing the challenges posed by covalent modification, such as the introduction of lattice defects that could adversely affect sensing properties, and is therefore especially relevant to sensors based on two-dimensional materials like graphene and MoS2. In addition, nucleic acid biomarkers, e.g., microRNA, cell-free DNA, etc., hold great potential for disease diagnosis and prognosis. Herein we design and construct heterofunctional chimeric PNA-SBP biomolecules that facilitate hybridization of nucleic acid targets onto the sensor surface. Using surface plasmon resonance spectroscopy (SPR), we demonstrate detection of DNA with these chimeric probes against a complex biological fluid, e.g., fetal bovine serum, in aqueous environment. We interrogate the effect of steric hindrance on optimal probe assembly using fluorescence microscopy and atomic force microscopy (AFM) imaging techniques, which reveal that lesser probe packing density results in greater target capture. We also demonstrate the sequential biomolecular assembly of the modular PNA-SBP system on the sensor surface and assess its performance under variety of solution conditions. These results provide a highly effective methodology for defect-free functionalization of 2D material-based bionanosensors through non-covalent means while enabling probe immobilization onto the sensing substrate. The latest results include design criteria of the chimeric probes, immobilization/biofunctionalization protocols, sensor architectures, and data acquisition and analysis procedures.

Technical help by Rebekah Khajehpour and Jessica Ahrens-Tran were appreciated. The research is supported by NSF-DMREF program through the grant DMR-1629071 as part of Materials Genome Initiative (MGI).

SESSION SB09.04: Immunotherapy
Session Chairs: Zhen Gu and Gabe Kwong
Tuesday Morning, December 3, 2019
Hynes, Level 3, Room 304

8:30 AM *SB09.04.01
New Single Cell Methods for Oncology and Immuno-Oncology James R. Heath1,2, Yapeng Su1,2 and William Chour1,2; 1California Institute of Technology, United States; 2Institute for Systems Biology, United States

In this talk I will discuss new algorithms and analytical technologies associated with single cell analysis, with an emphasis on capturing and analyzing multiple levels of information (i.e. multi-omic analysis) from the same single cells. In one instance, I will discuss how single cell methods can resolve cancer cell adaptive responses to therapy, and reveal that even isogenic cells can exhibit multiple, independent adaptive responses, each of which can be independently drugged. I will also discuss large library approaches designed for sampling and single cell characterization of antigen-specific T cell populations, with the goal of identifying matched antigen-TCRa/b pairs for T cells that are circulating in the blood, but are tumor-antigen (or neoantigen) experienced.

9:00 AM *SB09.04.02
Enhancing Chimeric Antigen Receptor (CAR) T Cell Cancer Immunotherapy through Lymph Node-Targeted CAR Ligands Darrell J. Irvine; Massachusetts Institute of Technology, United States

We recently developed a strategy to target peptide vaccines to lymph nodes, by linking peptide antigens to albumin-binding phospholipid-polymers. Small peptides are normally rapidly dispersed in the bloodstream following parenteral injection, but binding of amphiphile-peptides to endogenous albumin, which constitutively traffics from blood to lymph, retargeted these molecules to lymph nodes. However, these lipid-polymer conjugates bind to albumin with a relatively low affinity, and these molecules can also partition into cell membranes. We hypothesized that by attaching a small molecule, peptide, or protein ligand for a chimeric antigen receptor (CAR) to the same polymer-lipid tail (forming an “amph-vax” molecule), CAR ligands could be delivered efficiently to lymph nodes by albumin and subsequently partition into membranes of resident antigen presenting cells (APCs), thereby co-displaying a CAR T cell ligand from the cell surface together with native cytokine/receptor costimulation. In syngeneic mouse models of adoptive cell therapy, we demonstrated that this approach effectively concentrates CAR T ligands on the surfaces of dendritic cells in lymph nodes, leading to profound expansion of amph-vax-boosted CAR T cells in vivo. Amph-vax boosting safely increased the polyfunctionality of CAR T cells in parallel with T
cell expansion. In a syngeneic model of melanoma, this converted a CAR T treatment that had no impact on tumor progression to a therapy that strongly delayed tumor outgrowth and enhanced survival. We have reduced to practice three different strategies to generalize this approach to any CAR of interest. This concept provides a strategy to regulate the expansion and function of CAR T cells directly in vivo to enhance adoptive cell therapy of cancer.

9:30 AM SB09.04.03
High Throughput Microwell Assay for T Cell-Cancer Cell Interaction in Cancer Immunotherapy Qingxuan Li, Thibault Colombani, Sidi Bencherif and Ming Su; Northeastern University, United States

Cell-cell interaction is of fundamental importance for immune system to mediate abnormal stimuli and eliminate pathogens. Understanding the mechanism of cytotoxic T cells in eliminating cancer cells in tumor immunotherapy requires a quantitative analysis of the interaction between T cells and cancer cells. Given the heterogeneity of cancer cells, it is imperative to evaluate the killing efficiency at single cancer cell level. This project uses a microwell device as a high-throughput platform to assess co-cultured OT-1 cells (T cells) and OVA-expressing B16 cells (cancer cells) and evaluate the cytotoxic efficiency based on different T cell numbers. Each micro-well defines the interaction area, to the point where the same group of T cells with the specific single cancer cell are tracked continuously in each well. The cell activity during attacking process is quantified by fluorescence intensity, which indicates the cytotoxic efficiency is proportional to the number of T cells which have communication with cancer cells, and reversely proportional to the cancer cell size. This precise control, high-throughput method, longitudinal observation using micro-well platform can give a new idea to evaluate therapeutic dosage, reduce the cost and at the same time with the same efficacy of immunotherapy.

9:45 AM SB09.04.04
Biomimetic Molecular-Scale Devices for the Spatial Control and Study of Activating-Inhibitory Balance in Natural Killer Cells Esti Toledo, Guillaume Le Saux, Avichai Edri, Uzi Hadad, Angel Porgador and Mark Schwartzman; Ben-Gurion University of the Negev, Israel

The cytotoxic activity of lymphocytes is regulated by a gentle balance between activating and inhibitory signals. Understanding the molecular mechanism of this balance is of fundamental importance, and is essential for the rational design of the future based immunotherapies. For this purpose, the exact function of each receptor must be investigated individually and in combination with each other. In particular, to understand the mechanism of the spatial integration of activating and inhibitory receptors, individual receptors should be manipulated and controlled. Spatial control of receptor with molecular resolution has been possible by exposing cells to arrays of patterned nanodots functionalized with the ligands for the studied receptors\(^1\)\(^-\)\(^3\). Such state-of-the-art arrays, however, could only control receptors of one type, and therefore could not be used to study how different receptors with complementary function integrate their signals. An experimental platform that allows simultaneous spatial control of two or more different receptors within the cell membrane has not been demonstrate up to date. Here, we developed a novel nanochip approach that allows simultaneous spatial control of individual transmembrane receptors of two types. We applied this nanochip approach to reveal how the nanoscale segregation between NKG2D and KIRDL1, which are the activating and inhibitory receptors in Natural Killer (NK) cells, respectively, regulate the cytotoxicity of NK cells. Our nanochips are based on tunable arrays of paired 10 nm nanodots of different metals, which are selectively functionalized with activating and inhibitory ligands for NK cells. The functionalized arrays, in turn, are used as a stimulation platform for NK cells, which encodes the arrangement of the two receptors within the cell membrane, and allows to monitor the cytotoxic response of NK cells the variations in this arrangement. To realize the nanochips, we first fabricated heterogeneous arrays of Ti and Au nanodots by nanoimprint lithography, followed double angle evaporation of two metals, and liftoff. Here, the spacing between the nanodots, which was ranged from zero to a few tens of nm, is precisely controlled by the metal evaporation angle. We then selectively functionalized Ti and Au nanodots with (i) MHC class I polypeptide-related sequence A (MICA) – a ligand for NKG2D, and (ii) monoclonal antibody for KIR2DL1, using biotin-avidin and Nitriltriactice acid (NTA)-Histidine conjugations, respectively\(^4\). We stimulated NK cell on the chip surfaces, and assessed their degree of activation through the expression of CD107a – a commonly used degranulation marker. We found that KIR2DL1-regulated inhibition of NKG2D signaling indeed depends on the spacing between the two receptors, and is mostly effective when the two receptors are separated by 30 nm. Our results shed the light on the way by which the innate immune function is spatially regulated by the activating and inhibitory signaling crosstalk. Furthermore, our novel nanochip technology opens a general pathway to complex, multifunctional nanomaterials which can be used as experimental platforms for the nanoscale study of the function and structure of immunological synapse, as well as other interfaces between cells.

Final Program 1/13/2020 2767
and their environment.


10:00 AM BREAK

SESSION SB09.05: Drug Delivery I
Session Chairs: Emily Day and Daniel Heller
Tuesday Morning, December 3, 2019
Hynes, Level 3, Room 304

10:30 AM *SB09.05.01
Platelet-Delivered Immunotherapeutics Zhen Gu; University of California, Los Angeles, United States

Platelets play a vital physiological role in hemostasis, inflammation and tissue regeneration, which are associated with wound healing as well as cancer development and metastasis. Inspired by this intrinsic ability of platelets and the clinical success of immune checkpoint inhibitors, we have demonstrated that conjugating anti-PDL-1 antibodies (aPDL-1) to the surface of platelets can reduce post-surgical tumor recurrence and metastasis. Using mice bearing partially removed primary melanomas (B16-F10) or triple-negative breast carcinomas (4T1), we found that anti-PDL1 was effectively released on platelet activation by platelet-derived microparticles, and that the administration of platelet-bound anti-PDL1 significantly prolonged overall mouse survival after surgery by reducing the risk of cancer regrowth and metastatic spread. Furthermore, we have shown that systemically delivered blood platelets decorated with anti-PD-1 antibodies (aPD-1) and conjugated to hematopoietic stem cells (HSCs) suppressed the growth and recurrence of leukemia in mice. This cellular conjugate also promoted resistance to re-challenge with leukemia cells. In addition, we genetically engineered platelets from megakaryocyte progenitor cells to express the programmed cell death protein 1 (PD-1). The PD-1 platelet and its derived microparticle could accumulate within the tumor surgical wound for eradication of residual tumor cells. Cyclophosphamide was further loaded into PD-1-expressing platelets to deplete regulatory T cells, enhancing inhibition of tumor recurrence after surgery.

11:00 AM *SB09.05.02
Proteases as Biological Bits for Programmable Medicine Gabe A. Kwong; Georgia Tech & Emory, United States

Biological systems endowed with engineered biocircuits have the capacity to augment and reprogram living functions. We create biological bits (bbits) using proteases – a family of pleiotropic, promiscuous enzymes – to construct the biological equivalent of Boolean logic gates, comparators and analog-to-digital converters. We use these modules to assemble a cell-free bioprogram that can combine with bacteria-infected blood, quantify infection burden, and then calculate and unlock a selective drug dose. Inspired by quantum computing, we leverage protease promiscicity as the biological analog of superposition to program three probabilistic bbits that solve all implementations of the two-bit oracle problem, Learning Parity with Noise. Treating a network of dysregulated proteases in a living animal as an oracle, we use this algorithm to resolve the probability distribution of complement and coagulation proteases in vivo, allowing diagnosis of pulmonary embolism with high sensitivity and specificity (AUROC = 0.92) in a mouse model of thrombosis. Our results demonstrate that proteases can be programmed in cell-free systems to carry out classical and probabilistic algorithms for programmable medicine.

11:30 AM SB09.05.03
Erythrocyte Leveraged Chemotherapy (ELeCt) for Lung Metastasis Treatment Zongmin Zhao, Anvay Ukidve, Yongsheng Gao, Jayoung Kim and Samir Mitragotri; Harvard University, United States
Due to its unique physiological features like high blood throughput and high density of narrow capillaries, lung is one of the major organs into which the evaded tumor cells from primary tumor sites can spread. In fact, 30-55% of advanced cancer patients have lung metastasis. In spite of being the mainstay of cancer treatment, chemotherapy has shown limited efficacy for the treatment of lung metastasis due to ineffective targeting and poor tumor accumulation. Here we report a highly effective Erythrocyte Leveraged Chemotherapy (ELeCt) platform, consisting of biodegradable drug nanoparticles assembled onto the surface of erythrocytes, to enable chemotherapy for lung metastasis treatment. The ELeCt platform significantly extended the circulation time of the drug nanoparticles and delivered 10-fold higher drug content to the lung compared to the free nanoparticles. In both the early- and late-stage melanoma lung metastasis models, the ELeCt platform enabled substantial inhibition of tumor growth that resulted in significant improvement of survival. Further, the ELeCt platform can be used to deliver numerous approved chemotherapeutic drugs. Altogether, the findings suggest that the ELeCt platform offers a versatile strategy to enable chemotherapy for effective lung metastasis treatment.

11:45 AM SB09.05.04
Biomimetic Membrane-Wrapped Nanoparticles for Targeted siRNA Delivery to Hematopoietic Stem Cells
Jenna Harris, Samik Das, E. Terry Papoutsakis and Emily Day; University of Delaware, United States

Delivery of therapeutic cargo to hematopoietic stem and progenitor cells (HSPCs) is a challenging problem whose solution would transform the treatment of a wide variety of diseases.[1] To target HSPCs, nanoparticles (NPs) must not only enter the bone marrow, but also specifically bind and deliver cargo to HSPCs, which are extremely difficult to transfect. To date, only a single NP formulation has achieved this goal.[2,3] It consisted of nucleic acid-loaded poly(lactic-co-glycolic acid) (PLGA) NPs, and while it represents a novel advance, the level of HSPC gene modification it achieved was <1%.[2] There exists a substantial need for a more potent delivery system that will overcome physiological barriers to efficiently deliver cargo to HSPCs. Here, we report the development of biomimetic membrane-wrapped PLGA NPs that meet this need. We show that PLGA NPs wrapped with megakaryocyte (Mk)-derived membranes and loaded with model cargo have preferential binding to, and can enter, HSPCs in vitro. Additionally, we show that these Mk membrane-wrapped NPs (MkNPs) can deliver functional siRNA cargo to HSPCs to elicit gene regulation.

DiD fluorophore-loaded PLGA NPs were prepared by a single-emulsion solvent evaporation process [4] and siRNA-loaded PLGA NPs were prepared following a double-emulsion solvent evaporation process. [5]. siCD34 and siNeg were used as proof-of-concept cargo to allow for measurable silencing of CD34 in early-stage HSPCs. For siRNA-loaded NPs, the encapsulation efficiency (EE) was measured by comparing the amount of siRNA remaining in the filtrate after purification to the total added. The EE was >99%, indicating the siRNA is contained in the NPs and not lost during fabrication.

To create Mk membrane-wrapped NPs (MkNPs), the PLGA NPs and Mk membranes extracted from Mk cells were co-extruded with an Avanti Mini Extruder. Membrane wrapping was confirmed by measuring NP size and zeta potential before and after wrapping with dynamic light scattering (DLS), nanoparticle tracking analysis (NTA), and transmission electron microscopy (TEM). These measurements showed that the NPs were monodisperse and spherical, with the wrapped NPs having a diameter 10-20 nm larger than bare NPs and a complete membrane coating. The preferential interaction of DiD-loaded MkNPs with HSPCs as compared to non-targeted HUVECs (human umbilical vein endothelial cells) and MSCs (mesenchymal stem cells) was evaluated by flow cytometry and confocal microscopy. HSPCs internalized DiD-loaded MkNPs within 24 hr of incubation at a much higher rate than the other two cell types, confirming the Mk membrane coating can facilitate HSPC-specific binding.

To evaluate gene silencing, siCD34-MkNPs and siNeg-MkNPs were cultured with early-stage HSPCs, which express CD34. After 24, 48, 72, and 96 hr incubation, CD34 expression was analyzed by exposing the samples to anti-CD34 antibodies and performing flow cytometry. Since HSPCs acquired from different donors have variable CD34 expression, the percent deviation from control was calculated by comparing CD34 expression in siCD34-MkNP and siNeg-MkNP treated cells to that of the untreated donor control cells in each trial. MkNPs containing siCD34 significantly decreased CD34 expression in HSPCs over a 96 hr time period by >15%, while MkNPs loaded with siNeg had no impact on CD34 expression. These data indicate MkNPs have substantial potential as tools for targeted gene regulation of HSPCs.

In conclusion, MkNPs can be successfully loaded with, and deliver, siRNA cargo to HSPCs in vitro, eliciting gene knockdown. This exciting advance paves the way for further optimization of the system to induce greater levels of HSPC gene regulation, as well as for further examination of their targeting specificity in vivo.

Antibody Nanocarriers for the Treatment of Triple-Negative Breast Cancer

Emily Day; University of Delaware, United States

Antibodies that antagonize cell signaling pathways specific to their targeted receptors are invaluable tools to treat cancer, but their utility is limited by high production costs and treatment dosages. We and other researchers have shown that antibodies conjugated to nanoparticles display increased affinity for their target relative to freely delivered antibodies due to multivalent binding. In this presentation, I will discuss how my group has exploited this capability to create antibody nanocarriers that are drastically more effective than freely delivered antibodies at suppressing oncogenic signaling. Specifically, we have developed nanoparticles coated with Frizzled7 antibodies and Notch-1 antibodies to suppress Wnt and Notch signaling, respectively, in triple-negative breast cancer cells. Wnt and Notch are developmental signaling pathways that are overactive in triple-negative breast cancer and drive its progression and metastasis. We have shown that our Wnt inhibitory and Notch inhibitory nanoparticles can reduce cell viability, invasion, and stem-like behavior \textit{in vitro} and hinder primary tumor growth and metastasis \textit{in vivo}. These exciting observations warrant further investigation of antibody nanocarriers to manage triple-negative breast cancer and other malignancies that suffer from lack of available targeted therapies.

Delivery of Monoclonal Antibodies to the Central Nervous System for Brain Tumor Therapy

Yunfeng Lu; University of California, Los Angeles, United States

As an essential component of immunotherapy, monoclonal antibodies (mAbs) have emerged as a class of powerful therapeutics for treatment of a broad range of diseases. For central nervous system (CNS) diseases, however, the efficacy remains limited due to their inability to enter the CNS. I'll discuss about a platform technology that enables effective delivery of mAbs to the CNS for brain tumor therapy (Advanced Materials, 1805697, Nature Biomedical Engineering, in press). This is achieved by encapsulating the mAbs within nanocapsules that contain choline and acetylcholine analogues; such analogues facilitate the penetration of the nanocapsules through the brain-blood barrier and the delivery of mAbs to tumor sites. This platform technology uncages the therapeutic power of mAbs for various CNS diseases that remain poorly treated.

Nanomedicines to Improve the Therapeutic Index of Precision Medicines

Daniel A. Heller\textsuperscript{1,2}; 1Memorial Sloan-Kettering Cancer Center, United States; 2Weill Cornell Medicine, United States

Therapy based on personalized medicine—the genomic context of a patient’s disease—has become a leading strategy to treat cancer. Small molecule drugs such as kinase inhibitors, which target key effectors of cancer signaling pathways, constitute a major component of this strategy. However, such drugs can affect the same signaling pathways in healthy tissues, which often leads to dose-limiting toxicities. Increasing the therapeutic index of targeted therapies would greatly improve their effectiveness. We are investigating new targets to localize precision drugs to the microenvironment of primary and metastatic tumors. We developed nanoparticle drug carrier platforms to localize targeted therapies in tumor-associated vasculature and away from healthy tissues to obviate dose-limiting toxicities and concomitantly improve therapeutic index. We targeted MEK and PI3K inhibitors, pan-kinase inhibitors, and sonic hedgehog pathway inhibitors to tumor sites in both primary and metastatic models, resulting in superior anti-tumor efficacy and the striking reduction of toxicities. Moreover, measurements of tumor tissue show prolonged inhibition of downstream effectors in the signaling pathways, constituting a significant modulation of drug pharmacokinetics.
Chiral Supraparticles for Controllable Nanomedicine Jihyeon Yeom¹, Pedro Guimaraes¹, Hyomin Ahn², Kevin McHugh¹, Michael Mitchell¹, Chae-Ok Yun², Ana Jaklenec¹ and Robert Langer¹; ¹Massachusetts Institute of Technology (MIT), United States; ²Hanyang University, Korea (the Republic of)

Chirality is ubiquitous in nature that is hard-wired into every living biological system. Despite the critical role, the nexus of chirality engineering on biomaterials has not been explored. Here we designed chiral supraparticles (SPs) that react distinctively to cells and proteins depending on their handedness. SPs coordinated with $D$-chirality showed at least three times more efficient cell membrane penetrations and anti-cancer properties. We carried out quartz crystal microbalance with dissipation (QCM-D) and isothermal titration calorimetry (ITC) measurements to understand the mechanism, which confirmed that $D$-SPs had more effective adhesion on lipid layers where most of the phospholipids in nature has $D$-chirality. The stronger affinity of $D$-SPs over $L$-SPs to lipids was because interactions between the same optical isomeric structures are thermodynamically more stable than that of opposites. When it comes to in vivo environments that contain a large, heterogeneous population of proteins, $D$-SPs showed superior stability and longer biological half-lives due to the incompatible chirality with endogenous proteins including proteases. This study shows that incorporating $D$-chirality into nanosystems enhances cellular uptake and in vivo stability in blood providing support for the importance of chirality in biomaterials. Chirality engineering will provide “smart” platforms for drug delivery systems, tumor detection markers, biosensors, and many other biomaterial devices.

Novel Nanolipogels for In Vivo Genome Editing of Triple Negative Breast Cancer Peng Guo¹, Jiang Yang¹, Jing Huang¹, Debra Auguste² and Marsha Moses¹; ¹Boston Children's Hospital, United States; ²Northeastern University, United States

Triple negative breast cancer (TNBC), which represents 15-20% of all breast cancers, is a devastating breast cancer subtype that occurs more frequently in women under 50 years of age, in African American women and in individuals carrying a breast cancer early onset (BRCA1) gene mutation. To date, TNBC holds the highest mortality rate among all breast cancer subtypes, and a central problem for TNBC therapy is the lack of effective therapeutics that can hinder the growth and spread of breast cancer cells. To address this challenge, here we report the development of a novel non-cationic, deformable and tumor-targeted nanolipogel system (tNLG) for CRISPR genome editing in TNBC tumors. CRISPR genome editing is a revolutionary biotechnology that may potentially provide a cure for many genetic diseases including TNBC. We have demonstrated that tNLGs can be used to encapsulate CRISPR genome editing plasmids in a highly facile and efficient manner. Then we showed that tNLGs mediate a potent CRISPR knockout of Lipocalin 2 (LCN2), a known breast cancer oncogene, in human TNBC cells in vitro and in vivo. The loss of Lcn2 significantly inhibits the migration and the mesenchymal phenotype of human TNBC cells and subsequently attenuates TNBC aggressiveness. Furthermore, we performed in vivo CRISPR genome editing of orthotopic TNBC tumors by systemically administering tNLGs, resulting in significant tumor growth suppression (>77%). Our proof-of-principle results provide the first experimental evidence that tNLGs can be used as a safe, precise and effective delivery approach for in vivo CRISPR genome editing in TNBC.

Genomic-DNA Coated 3D Printed Materials for Drug Capture Daryl Yee, Robert H. Grubbs and Julia R. Greer; California Institute of Technology, United States

Since the discovery of chemotherapy in the beginning of the 20th century, researchers around the world have been actively developing new and more effective chemotherapeutic agents to better treat cancer. Traditionally, chemotherapeutic agents work by interfering with cell division. However, by virtue of their mechanism of action, healthy normal cells can also be targeted and destroyed. As a result, while chemotherapy is an effective way of managing cancer, the resulting side effects limits its use. One approach currently taken to reduce these side effects is to deliver the chemotherapy drugs directly to the tumor via transarterial chemoembolization, or other similar procedures. While this has been effective in reducing systemic toxicity, more can be done to improve this. Ideally, a device that could sequester any unreacted chemotherapy agents could be installed "downstream" of the tumor prior to them entering systemic circulation. Such drug-capture materials have only just started to be realized due to the
difficulty in achieving materials that have the right surface chemistry and geometry for blood flow.

Working together with medical doctors, computational fluid dynamics experts, chemists, and materials scientists, we report the fabrication of DNA coated 3D printed porous materials that can be used to capture doxorubicin, a commonly used DNA-targeting chemotherapy agent. We discuss the concept behind the device, the use of 3D printed materials as an ideal substrate, and the chemistries considered in drug binding. To achieve scalability of these devices, we developed a method of attaching cheaply available genomic DNA to these materials, a departure from commonly used synthetic DNA. The efficacy of these functionalized materials were demonstrated, where we observed a >70% reduction in doxorubicin concentration over a period of 10 minutes, highlighting the viability of this as a method of drug capture.

3:45 PM SB09.06.07
Conductive Elastomer-Based Active Drug Delivery Platform for Targeted Chemotherapy in Glioblastoma Multiforme
Christopher Chapman, Estelle Cuttaz, Josef Goding and Rylie Green; Imperial College London, United Kingdom

Glioblastoma multiforme is an aggressive untreated brain cancer with a 14.6-month median survival time and a 2% 5-year survival rate after diagnosis. The current best practice for treatment is surgical resection followed by radiotherapy and systemic chemotherapy. However, many tumours cannot be removed surgically leaving only the nonspecific treatments of radiotherapy and systemic chemotherapy, further reducing survival rates. Currently the primary chemotherapeutic agent used to treat these tumours is the alkylating agent temozolomide (TMZ). The success of this drug stems from its limited ability to cross the blood brain barrier. Attempts to mechanically cross the blood brain barrier with an implanted device to deliver liquid drug cocktails directly to the tumour have seen limited efficacy due to increasing the intracranial pressure, which can produce oedema and additional brain damage. Recently, ionic drug delivery has been a subject of increased focus using both drug eluting electrodes or electronic ion pumps as the delivery vehicle. Because these devices can deliver drug molecules without a liquid carrier (termed ‘dry delivery’) they cause no increase in the volume to the surrounding tissue. Therefore, this mode of delivery is a strong candidate for the targeted delivery of high concentrations of chemotherapeutic agents deep in the brain, as the side effects associated with the liquid delivery are avoided.

Recently, fully polymeric conductive elastomers fabricated using dispersions of a doped conducting polymer poly(3,4-ethylenedioxythiophene):polystyrene-sulfonate (PEDOT:PSS) in polyurethane, have shown significant promise for applications in bioelectronic interfaces. These materials present a unique platform for the voltage controlled dry release of drug molecules as the elastomer enables the encapsulation of small molecule drugs, and the conductive polymer enables on-demand electronically controlled offloading of the drug. Here we demonstrate the ability for this system to actively release a model drug (fluorescein) in clinically relevant concentrations ranging from 1 µM to 1 mM through the application of a negative electrical potential. Similarly, a positive electrical potential can be applied to stop the release on-demand. Using the same method, we show that the common chemotherapeutic agent doxorubicin can also be released in the same concentrations ranges. Additionally, by tuning multiple material parameters such as the weight percent of PEDOT:PSS in the polyurethane as well as material thickness, further control of the drug release profiles can be achieved. Finally, the translatability of this technology is shown through the fabrication and implantation of a doxorubicin loaded device into an agar tissue phantom using traditional stereotactic methods.

Through the coupling of material parameters with applied electrical potential, we demonstrate a high degree of customizability for the device to be tuned toward patient specific needs. Moving forward, experiments are underway to confirm the active anti-cancer effect of the device in vitro through implantation of the doxorubicin loaded device into rat glioblastoma spheroids, actively releasing doxorubicin, and tracking of the toxic effects through spheroid size reduction over a period of weeks. Ultimately, this technology constitutes a significant step forward in biomaterials-based cancer treatments and shows promise for ease of translation into clinical use to improve the outcome of patients with non-operable glioblastoma multiforme.

Coaxially Electrospun Three-Dimensional Disc for Long-Term Local Therapy Against Brain Tumors

Daewoo Han¹, Riccardo Serra², Noah Gorelick², Henry Brem²,²,² Betty Tyler² and Andrew J. Steckl¹; ¹University of Cincinnati, United States; ²Johns Hopkins University School of Medicine, United States

Glioblastoma multiforme (GBM), the most aggressive brain cancer, has an incidence of ~3.2 cases/100,000 persons/year, with a recurrence rate > 90%, a 5-year survival rate of 5.1%, and a mean survival of < 15 months. GBM treatment relies mainly on the combination of maximally safe surgical resection followed by radiation therapy (RT) and concomitant chemotherapy with temozolomide (TMZ). Local chemotherapy for GBM treatments is the most attractive approaches by enhancing drug biodistribution to the tumor and avoiding systemic toxicities. GBM recurrence mostly within 2 cm of the original lesion makes it local therapy very attractive. Also, it overcomes the limitation posed by the blood-brain barrier. Gliadel®, a carmustine (bis-chloroethyl-nitrosourea (BCNU))-impregnated polyanhydride poly-(1,3 bis[p-carboxyphenoxy] propane-co-sebacic acid) 20:80 polymeric (p(CPP):SA) wafer, is currently the only FDA-approved local therapy device. Although Gliadel releases most of drugs within a week, the triple therapy paired with RT and systemic TMZ administration improved the median survival up to 21 months. Obviously, the use of local chemotherapy is very effective for GBM treatments. Therefore, the use of new polymer structures extending a release time period can further improve the survival and prevent the recurrence while minimizing side effects from cytotoxic agents.

We have developed discs formed from multi-layered core-sheath fiber membranes (‘NanoMesh’) to provide controlled and sustained drug release for long-term periods, leading to excellent in vivo performance in an animal model. Drug encapsulated core-sheath fibers have been fabricated using pCPP:SA / BCNU core and PCL sheath. SEM images show uniform fiber formation with average diameter of ~2.3 µm (sheath of ~0.46 µm). Three-dimensional discs were formed from coaxially electrospun fiber membranes by a simple fold-and-punch process and consistent long-term release with no initial burst release was observed in vitro for up to 160 days. NanoMesh discs provide fairly uniform diffusion lengths over time, because aqueous media gradually wets the disc from the outside due to the hydrophobic nature of fiber surfaces. Therefore, consistent long-term release of encapsulated drugs with minimized initial burst release is obtained. This benefit is significant when targeted to long-term release with hydrophilic drugs. NanoMesh reported here can provide long-term release kinetics regardless of the nature of the encapsulated drug.

In vivo survival was assessed following implantation of NanoMesh discs either concurrently with or five days after intracranial implantation of 9L gliosarcoma to F344 rats. Concurrent implantation of NanoMesh and 9L gliosarcoma resulted in statistically significant long-term survival (>150 days). Control (drug-free) NanoMesh confirmed the safety of these novel implants. Similarly, Day 5 studies showed significant median survival, and long-term survival rates of 50%. Brain histology shows no evidence of malignant cells even at Day 150. Animals in all control groups died very early (~12-14 days).

In addition, we have evaluated the release kinetics of multi-drug incorporated NanoMesh to mimic the current systemic ‘cocktail’ chemotherapy with multiple anti-cancer drugs. Different anti-cancer drugs can be incorporated into different layers within the NanoMesh to be released either in concurrent or sequential manner. Local chemotherapy using NanoMesh implants provides promising means for GBM treatment. Drug delivery with coaxial core-sheath structures benefits from high drug loading, controlled long-term release kinetics, and slow polymer degradation. This represents a promising evolution for the current treatment of GBM. Furthermore, controlled ‘cocktail’ local therapy may bring a new paradigm to the GBM therapy.

Harnessing Sustained Release Technologies to Produce Robust and Durable Immunity

Eric A. Appel; Stanford University, United States

Vaccines can take one of several forms, but those based on subunit antigens (representative subunits of the pathogen for which immunity is desired) offer the greatest safety profile and scalability, but elicit weaker, less durable immune responses. Failure to elicit a sufficiently strong response likely arises from inappropriate temporal control over antigen/adjuvant presentation and immune cell activation. Either short-term presentation of these signals, or misalignment of their presentation along different timelines, results in poor affinity maturation of antibodies and poor immune memory responses. When considering the iterative selection process occurring during somatic hypermutation and antibody affinity maturation in B lymphocytes, it is intuitive that prolonged lymphocyte activation and antigen exposure would lead to the generation of higher-affinity antibodies. In this work we exploit a
novel injectable hydrogel platform providing unique drug delivery capabilities for the long-term co-delivery of antigen and adjuvant in subunit vaccines and investigate impact of this altered delivery behavior on the humoral immune response and the development of ultra-high-affinity antibodies. We demonstrate that prolonged hydrogel-based immunizations greatly enhance the magnitude and duration of the primary antibody response, enhance and prolong germinal responses, and lead to 1000-fold enhancement in antibody affinity maturation when compared to the same vaccine delivered in bolus. These advanced materials technologies, therefore, have the potential to provide vastly superior vaccine performance through the precise and sustained delivery of subunit vaccines that take advantage of natural immune mechanisms for building long-lasting and potent immunity.

4:30 PM SB09.06.10
A Facile Approach to Augment DNA Vaccine Efficacy by Injectable Mesoporous Silica Microrods for Cancer Immunotherapy Thanh Loc Nguyen, Yue Yin, Youngjin Choi, Ji Hoon Jeong and Jaeyun Kim; Sungkyunkwan University, Korea (the Republic of)

DNA cancer vaccine is one of the potential strategies in cancer immunotherapy. In order to provoke robust antigen-specific adaptive immune response against tumor, DNAs coding tumor antigen are desired to be engulfed by host antigen-presenting cells (e.g. dendritic cells) which subsequently become antigen-activated for T cell priming. However, therapeutic efficacy of this approach is still restricted due to insufficient DNA transfection to host dendritic cells (DCs) and lack of immunogenicity. Herein, we introduce an injectable 3-demensional macroporous scaffold constructing of high aspect ratio mesoporous silica microrods (MSRs) and antigen-coded DNA complexes (designated as MSR-DNA vaccine) for augmenting the efficacy of DNA vaccine. Release of chemotactic and immune adjuvant from MSRs initiate the migration and maturation of huge amount of host DCs into MSRs scaffold where DNA complexes are present in the interparticle space, thus enhance cellular uptake of DNA complexes by recruited DCs. Subcutaneous immunization of MSR-DNA vaccine elicits more robust host DCs activation and maturation in comparison to the bolus DNA vaccine counterpart, consequently triggers antigen-specific CD8+ T cell response in draining lymph node. Interestingly, MSR-DNA vaccine induces Th1-biased immune response through significant secretion of TNF-α and IFN-γ by CD4+ and CD8+ T cells along with high production of anti-OVA IgG2a in blood serum. In prophylactic study, MSR-DNA vaccine significantly prevents melanoma growth by the generation of CD8+ effector memory T cells. Impressively, established lung metastasis can be inhibited with a single injection of MSR-DNA vaccine. Our findings suggest that MSRs could be a novel platform for delivering DNA vaccine to DCs for the effective cancer immunotherapy.

4:45 PM SB09.06.11
Solid-Phase Synthesis for Molecularly Imprinted Polymer Nanocomposites—Synthetic Antibody Mimics for Cell Targeting and Imaging, Diagnostics and Theranostics Alicia Alejandra Mier Gonzalez; Universite de Technologie de Compiegne, France

Abnormalities in the expression of cell surface proteins or receptors are promising biomarkers of human diseases, notably cancer. However, the detection and quantification of these biomarkers are often challenging. Molecularly imprinted polymers (MIPs) are tailor-made synthetic receptors (antibody mimics), able to specifically recognize target molecules. They are synthesized by copolymerization of functional and cross-linking monomers in the presence of a template molecule, resulting in the formation of binding sites with affinities and specificities comparable to those of antibodies.

In the present project, we demonstrate the targeting of a cancer protein biomarker with MIP nanoparticles. MIPs were synthesized using a solid-phase approach in which a fragment of the protein was selected as epitope and immobilized on glass beads (solid support) via click chemistry. This configuration allows an oriented immobilization of the template upon which thermoreponsive MIP nanoparticles are synthesized. The binding sites of the resulting MIPs all have the same orientation, thus MIPs synthesized by the solid-phase approach can be considered analogous to monoclonal antibodies.

MIPs were found to bind the epitope with high (nanomolar) affinity and selectivity as demonstrated by equilibrium binding assays with the peptide fluorescently labeled. Fluorescent MIPs were used for cell imaging to reveal the recognition of the target protein on cancer cells. When control cells not expressing the protein were used, the staining was dramatically decreased. In addition, very similar staining patterns were obtained at immunostaining with monoclonal antibodies. The application of MIPs as therapeutic agents is being studied.
SESSION SB09.07: Poster Session II: Interfacing Bio/Nano Materials with Cancer and the Immune System II
Session Chairs: John Slater and Ian Wong
Tuesday Afternoon, December 3, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB09.07.01
Drug-Loaded Titanium Dioxide Nanoparticle Coated with Tumor Targeting Polymer as a Sonodynamic Chemotherapeutic Agent for Anti-Cancer Therapy Seonil Kim and Won Jong Kim; POSTECH, Korea (the Republic of)

Sonodynamic therapy utilizes ultrasound (US)-responsive generation of reactive oxygen species (ROS) from sonosensitizer, and it is a powerful strategy for anti-cancer treatment in combination with chemotherapy. Herein, we designed drug-loaded nanoparticle which could release drug by ultrasound-mediated ROS generation. Doxorubicin (DOX)-coordinated titanium dioxide nanoparticle (TNP) are encapsulated with polymerized phenyboronic acid (pPBA) via phenyl boronic ester coupling between pPBA and DOX. Phenylboronic ester bonding is cleavable by ROS generated from TNP under ultrasound stimulus. The size of nanoparticles is 200 nm, and DOX was released by generated ROS through ultrasound irradiation. In addition, this nanoparticle can target tumor by interaction between PBA and sialylated epitopes of tumor surface. Tumor targeting capability, intracellular ROS generation, and combined therapeutic effect against tumor cells were confirmed in vitro. Furthermore, this nanoparticle showed high tumor accumulation of and efficient tumor growth when treated by intravenous injection, which have potential as a multi-functional agent for sonodynamic chemotherapy. The nanoparticles have outstanding therapeutic effects owing to several advantages: 1) An appropriate size of the NP makes an effective cancer-specific accumulation through the EPR effect in vivo; 2) Negative charge of remaining carboxylic acid group can increase circulation time in vivo by preventing unnecessary interactions with serum proteins; 3) PBA moieties also have a high affinity to tumors; 4) Since DOX is released in response to US stimulation, it is possible to reduce the non-specific release of DOX and improve the delivery efficiency; and 5) The dual therapeutic effect of generated ROS and released anti-cancer drug by US can reveal combinatorial synergistic anti-cancer effect. In this study, we investigated the physicochemical properties of nanoparticles, tumor targeting ability, US-responsive behavior and its anti-cancer effect in vivo as well as in vitro.

SB09.07.03
In Vivo Fluorescence Imaging of Genetically Engineered Oncolytic Apoptin Nanoparticles for the Assessment of Targeted Cancer Therapy Dong-Eun Lee1 and Joong-jae Lee2; 1Korea Atomic Energy Research Institute, Korea (the Republic of); 2Kangwon National University, Korea (the Republic of)

Targeted delivery of pro-apoptotic proteins with tumor-selective properties, including oncolytic virus-derived proteins and other human tumor suppressors has been considered an ideal platform to achieve high therapeutic efficacy and negligible side effects in cancer therapy. Despite notable therapeutic efficacy, however, the facile production and combination of efficient targeted delivery system remain a challenge. Here, we present genetically engineered oncolytic protein nanoparticles comprising a tumor-selective protein and a targeting moiety as a direct protein delivery system for the targeted cancer therapy. Apoptin, which is a 13.6 kDa protein from the chicken anaemia virus (CAV), has attracted considerable attention as a promising anti-cancer therapeutic because it triggers tumour-selective cell death, while leaving normal cells unaffected. Interestingly activity of apoptin proceeds independently of tumor suppressor p53, and its biological function is stimulated by various intracellular oncoproteins. An EGFR-specific repebody, which is composed of LRR (Leucine-rich repeat) modules, was employed to play a dual role as a tumor-targeting moiety and a fusion partner for production of apoptin nanoparticles, respectively. The repebody was genetically fused to apoptin, and the resulting construct (repebody-apoptin, Rb-Apo) was shown to self-assemble into supramolecular apoptin nanoparticles (Rb-Apo-NP) with high homogeneity and stability as a soluble form in E. coli. We examined the whole-body distribution and EGFR specific uptake of the Rb-Apo-NPs, particularly after intravenous administration. Near-infrared fluorescence dye (Cy5.5) was conjugated to the Rb-Apo-NPs and MBP-Apo-NPs, and their distribution in vivo and ex vivo was analyzed
through optical imaging in xenograft mouse models with EGFR-overexpressing MDA-MB-468 cells. The Rb-Apo-NPs were shown to be preferentially localized around the tumor cells at 24 h after intravenous administration, and the tumour regions could be clearly distinguished from the normal surrounding tissue. On the other hand, relative low intensity was observed in EGFR-negative MCF7 xenografts. The Rb-Apo-NP showed a remarkable tumor regression in xenografts mice through a targeted delivery by the EGFR-specific repebody and tumor-selective apoptosis by apoptin.

SB09.07.04
Colloidal Motors for Autonomous Motion and Cargo Delivery in Extracellular Matrices

Shrishti Singh,
Delaram Dastan, Parag Chitnis, Remi Veneziano and Jeffrey L. Moran; George Mason University, United States

Most nanometer-size drug delivery systems fail to reach their target site (e.g. tumors), largely due to the action of the immune system or elimination by liver or kidney. Furthermore, the drug delivery nanosystems that do reach the tumor are inefficient at killing cells in the tumor neoplasm due to the formidable barrier posed by the tumor microenvironment. The tumor microenvironment limits diffusion of the nanocarriers' cargo (i.e. chemotherapeutics) due to high interstitial pressure and the presence of a dense stroma surrounding the cells. This extracellular environment (stroma) has a plethora of cells like fibroblasts, macrophages, T and B-cells embedded in a network of collagen, fibrin and other protein fibers. This network of fibers, known as the tumor extracellular matrix (ECM), can be remodeled by the tumor cells to their advantage, making it a dynamic obstacle for the drug delivery system to overcome. As a result, the overall delivery efficiency of nanoparticles to tumor cells is less than 1% on average.

Colloidal motors are synthetic particles roughly between 10 nm - 100 μm in size that can propel themselves in an aqueous environment by converting energy stored in their surroundings (chemical, electric/magnetic fields, sound, etc.) into propulsive forces. Steering these colloidal motors is challenging and requires clever engineering, but guidance systems based on magnetic fields have been developed and show promise for navigation in biological environments. Colloidal motors have been shown to carry and deliver cargo (including anticancer drugs) to targeted sites (including cancer cells). However, previous studies have demonstrated these feats in vitro, and successful drug towing and delivery in tumor ECM has yet to be demonstrated.

In this study, we experimentally demonstrate the movement of magnetic helical motors driven by rotating magnetic fields in two in vivo ECM mimics. The first ECM model/mimic used is Matrigel, a commercially available basement membrane commonly used for 2D and 3D cultures. The second is low-molecular weight PEG hydrogels modified with different molar ratios of DTT (dithiothreitol) for tunable pore-sizes. The pore size, shear and storage modulus are measured for both ECM models. The speed is dictated by the rotational frequency of the field and the orientation of the motors depends on the orientation of the field. Using glancing angle deposition (GLAD), helices 70 nm in diameter, 400 nm in length, and 120 nm wide can be fabricated. These are small enough to potentially be able to navigate between the openings in ECM. Fluorescent dyes and quantum dots enable external tracking of helices in both ECM models. The trajectory of the helices and their velocity is determined for different magnetic field properties and ECM parameters. Finally, we explore the viability of these colloidal motors to be tracked using photoacoustic imaging, which has the potential to image and track these particles in vivo. This work takes the first steps toward enabling targeted drug delivery by self-propelled nanocarriers a possibility.

SB09.07.05
Fabrication of Drug Loaded Poly (γ-glutamic acid)-Based Hydrogel and Its Application in Pancreatic Cancer Model

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Poly (γ-glutamic acid, PGA) is a poly (amino acid) naturally produced by Bacillus subtilis. It is made of glutamate units connected by amide linkages between α-amino and γ-carboxylic acid groups. As an FDA GRAS material, it is widely used in food and cosmetic industries. In the biomedical field, PGA has been widely studied due to its excellent muco-adhesion, biocompatibility, and biodegradability. In this study, a novel PGA-based hydrogel as a local anti-cancer drug delivery matrix for treatment of pancreatic cancer. It is important that drug loaded matrix is stably sufficiently retained on the surface of the tumor to be effective. To achieve this key property, an in situ forming adhesive hydrogel was designed by modifying the carboxyl group of PGA to NHS (N-hydroxysuccinimide) activated ester applying carbodiimide chemistry. Then the
NHS activated PGA was mixed with a multi-functional nucleophile (i.e. multi-arm PEG) to form the hydrogel. The hydrogel quickly formed a crosslinked 3-D network structure within 2 sec and showed good adhesive property as well as high burst pressure. Subsequently, anticancer drugs (e.g. paclitaxel, or gemcitabine, etc.) were loaded into the hydrogel (PTX: 0.97%(w/v), GEM: 5.18%(w/v)) and the anti-tumor efficacy was tested in vivo in murine orthotopic pancreatic tumor model. Briefly, the tumor growth was inhibited and the metastasis of pancreatic cancer cells was reduced, without bodyweight loss. Current results demonstrated that local delivery of anticancer drug enhanced an antitumor efficacy. We expect that this hydrogel system as a promising platform to enhance the efficacy of cancer drugs by increasing the therapeutic index.

References

SB09.07.06
Organic-Inorganic Bio-Hybrid Nanoparticle for Systemic Targeted siRNA Delivery for Simultaneous Treatment of Primary and Metastatic Melanoma Min Sang Lee and Ji Hoon Jeong; Sungkyunkwan University, Korea (the Republic of)

Although primary melanoma would be easily removed by surgical resection, it could be developed to metastatic melanoma spreading tumor cell from primary melanoma to other tissue, which leads to significant decrease of five-year survival rate of patient. In addition, detection of melanoma at an early stage is difficult due to lack of appropriate tumor markers and absence of symptoms, which causes that the majority of patients with melanoma experience metastasis. Therefore, considering therapeutic aspects of metastatic melanoma, simultaneous treatment of primary and metastatic melanoma would be suitable therapeutic strategies. To achieve desired therapeutic effect, delivery carrier encapsulating anticancer drug should be sufficiently accumulated not only in primary tumor but also in metastatic melanoma that was not detected in early stage of diagnosis, which could completely cure melanoma and increase overall survival rate for patient.

Small interfering RNA (siRNA) has attracted a lot of attention as an alternative anti-cancer drug reducing side effects of chemotherapy owing to their anti-cancer potency and selectivity via tumor-specific RNA interference. Despite their therapeutic potential, the application of siRNAs is limited due to their rapid enzymatic degradation, non-specific accumulation in tissue, and poor cellular uptake in vivo. Thus, successful tumor treatment via siRNA delivery requires the development of a systemic delivery carrier that provides efficient siRNA protection, tissue-targeting ability and enhanced intracellular uptake.

In this study, we prepared a targeted small interfering RNA (siRNA) delivery platform using organic-inorganic hybrid materials capable of specific tissue targeting and efficient target gene silencing. dopa-hyaluronic acid conjugate (d-HA) successfully formed stabilized calcium phosphate (CaP) nanoparticle, which effectively protect siRNA from enzymatic degradation, enhance colloidal stability and provide targeting ability for tumor cell overexpressing CD44. Cellular uptake of the nanoparticles was enhanced via HA receptor-mediated endocytosis in B16F10 melanoma cells, which leads to enhanced gene silencing efficiency. In vivo biodistribution and therapeutic effect demonstrated that the systemically injected nanoparticles formulated with VEGF siRNA was simultaneously accumulated in primary melanoma and metastatic lung tumor, resulting in an improved therapeutic effect by reducing VEGF expression. These results suggested that the systemic targeted nanoparticle formulated with therapeutic siRNA can be considered as a prospective candidate for simultaneous targeted therapy for primary and metastatic melanoma.

SB09.07.07
Membrane Wrapping Efficiency of Elastic Nanoparticles During Endocytosis—Size and Shape Matter Zhiqiang Shen and Ying Li; University of Connecticut, United States

Using coarse-grained molecular dynamics simulations, we systematically investigate the receptor-mediated endocytosis of elastic nanoparticles (NPs) with different sizes, ranging from 25 to 100 nm, and shapes, including sphere-like, oblate-like, and prolate-like. Simulation results provide clear evidence that the membrane wrapping efficiency of NPs during endocytosis is a result of competition between receptor diffusion kinetics and thermodynamic driving force. The receptor diffusion kinetics refer to the kinetics of receptor recruitment that are affected by the contact edge length between the NP and membrane. The thermodynamic driving force represents the amount of required free energy to drive NPs into a cell. Under the volume constraint of elastic NPs, the soft
spherical NPs are found to have similar contact edge lengths to rigid ones and to less efficiently be fully wrapped due to their elastic deformation. Moreover, the difference in wrapping efficiency between soft and rigid spherical NPs increases with their sizes, due to the increment of their elastic energy change. Furthermore, because of its prominent large contact edge length, the oblate ellipsoid is found to be the least sensitive geometry to the variation in NP’s elasticity among the spherical, prolate, and oblate shapes during the membrane wrapping. In addition, simulation results indicate that conflicting experimental observations on the efficiency of cellular uptake of elastic NPs could be caused by their different mechanical properties. Our simulations provide a detailed mechanistic understanding about the influence of NPs’ size, shape, and elasticity on their membrane wrapping efficiency, which serves as a rational guidance for the design of NP-based drug carriers.

SB09.07.09
Dual Probe Imaging of Tumors Using Cadmium-Free NIR-Emitting Quantum Dot
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When nanoparticle-based imaging agents are used for targeted tumor contrast, only a fraction of the dose is specifically delivered; the remaining material circulates, passively accumulates in the tumor due to the enhanced permeation and retention (EPR) effect, or accumulates in off-target organs. When multiple contrast agents with near identical chemical and physical properties, yet distinct spectral emissions, are used, dual-probe imaging can be used to discern between the background and target signal. This can be achieved by removing the contribution of the untargeted probe from the image leaving only the signal from the targeted probe. NIR-emitting quantum dots (QDs) provide an excellent opportunity to improve targeted imaging of tumors in murine models for the study of cancer biology, as multiple QDs emitting discrete tissue-penetrating wavelengths can be prepared such that their size and surface properties are perfectly matched except for the presence or absence of a tumor-specific targeting ligand. We have synthesized multiple near infrared (NIR) emitting cadmium-free quantum dots (QDs) as bright and photostable contrast agents for multiplexed imaging in tissues. These indium phosphide-based QDs have tunable emission across most of the visible wavelength regime and the first near infrared (NIR) tissue imaging window. Our Inverted-Type I structure comprising InP shells on a ZnSe core, capped with ZnS for stability, exhibit extended tunability beyond that of a traditional InP Type-I QD. By controlling the thickness of the InP shell, we can tune the emission peak from 530 nm to 868 nm (2.34 – 1.43 eV). The full width half maximum (FWHM) of the emission peak remains constant as monolayers are added, indicating regular and high-quality shell growth. To confer water solubility, long circulation times, and chemical handles for bioconjugation, the QDs were encapsulated in PEGylated phospholipid micelles functionalized with terminal azido groups. The QDs retain their high quantum yield and monodispersity following encapsulation. Using click chemistry, the terminal azido groups are conjugated to tumor targeting ligands, including anti-HER2 or anti-CXCR4 peptides, as well as a clickable BCN-ethylenediamine modified folic acid. Dual probe imaging of tumors using targeted and untargeted fluorophores improves the imaging contrast of the specific cancer biomarker of interest.

For dual probe imaging to be successful, the signal contributions from each of the fluorophores has to be well resolved and the contribution from autofluorescence accounted for. To accomplish this, we evaluated multiple spectral unmixing algorithms to determine which generates the most accurate representation of true fluorophore concentration at tissue depth. This is done by covering well plates, where wells contain varying ratios of QDs, with skin-mimicking PDMS phantoms of varying thicknesses, and then imaging these well-phantoms using an IVIS sytem. This algorithm is then applied to the in vivo targeted tumor imaging experiments.

This method is being used to determine the biomarker status of two distinct biomarkers in tumor xenografts of BT-474 and MCF-7 cells in nude mice. Excitingly, the number of distinct biomarkers in a tumor that can be probed per imaging session is only limited by the full width half maximum of the emitters and the number of distinct emitters in the first optical tissue window.

SB09.07.10
Silica Coated Gold Nanorods for Target Tumor Specific Localization and Delivery of Therapeutic Molecules
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With a size smaller than a living cell, nanoparticles became one of the most promising therapeutic tools in a variety of biomedical application fields. In particular, the new optical, physical and chemical properties of nanomaterials offer a new pathway of treating cancer without affecting healthy cells. Thereby, the hyperthermia properties of
magnetic or optical active nanoparticles can be used to induce specifically natural cell death. In this context, gold nanoparticles came into the main focus of cancer research over the last decades by showing high surface plasmonic resonance leading to optothermal behavior in the near infrared area. Furthermore, gold is chemical inert and nontoxic to the human body.

Nevertheless, an immense challenge for using nanoparticles in cancer therapy is to ensure a highly specific uptake of nanoparticles for cancer cells. Therefore, we present monodispersed and highly selective nanoconjugates for example iron oxide (Fe3O4 with a size of 5 nm) and gold nanorods (mSiO2@Au with a length of 40 nm and a width of 20 nm), which were vectorized by attaching estrogen molecules at their surface by chemo specific reactions. The as-vectorized nanoconjugates were also loaded with therapeutic agent to investigate its drug loading and drug release capacity. The nanoconjugates showed enhanced cellular uptake for MCF breast cancer cell lines, which was quantified by FACS analysis. The functionalized nanoprobes showed promising accumulation at the tumor side as compared to the healthy organs. Our data shows, that as-prepared nanoconjugates holed potential to be used as targeting specific drug delivery nanoprobes.

SB09.07.11
Regulate Hippo Signalling via Lipid-Raft-Targeted Molecular Assembly for Ovarian Cancer Treatment
Guanying Li, Xunwu Hu and Ye Zhang; Okinawa Institute of Science and Technology, Japan

Hippo signalling pathway controls multiple cellular functions that are central to tumorigenesis. Its importance in cancer cell proliferation and metastasis has been well recognized. Here we created polypyridyl ruthenium conjugated peptide complex for lipid-raft-targeted molecular assembly. Via hydrolyzation by ovarian cancer biomarker, glycosylphatidylinositol-anchored placental alkaline phosphatase (ALPP), molecules assemble into nanostructures adhere to lipid rafts restricting their dynamics and spatial distributions. Through actin cytoskeleton, the regulation of lipid rafts stimulates Hippo signalling pathway deactivating the core oncogene YAP in cancer cells suppressing cancer cell migration and inducing cancer cell apoptosis.

SB09.07.12
Harnessing Immunological Synapse Formation as Trigger for Highly Regulated Stimuli-Responsive Drug Delivery
Sooseok Im, Donghyun Jang and Won Jong Kim; Pohang University of Science and Technology, Korea (the Republic of)

Despite of an outstanding therapeutic effect, direct administration of chemotherapeutics still involves diverse side effects and lowers its efficacy. Although, nanoparticle-based drug delivery system (DDS) has been a promising strategy to resolve the problems, continuous controversies about the efficiency of EPR, active targeting, and stimuli-responsive delivery have been suggested. Therefore, rather than relying on man-made targeting system, we focused on natural and intrinsic tumor targeting system in our body, natural killer (NK) cells. The anti-cancer effect of NK cells are known to be innate, immediate and cancer specific, yet insufficient to induce complete regression of tumor. Once circulating NK cells approach to tumor tissue along chemokines from tumor microenvironment, a NK cell would encounter a target cell and initiate the formation of immunological synapse (IS). IS is a pivotal part where panels of activating and inhibitory receptors are binding whose the signals are integrated, thus NK cell decide whether to release its lytic granules. Inspired by the fact the acidic lytic granules are released toward the IS cleft, we hypothesized that the local acidification of the IS cleft would be a stimuli for controlled behavior of drug delivery. To reinforce the cytotoxic killing effect of NK cells as well as to deliver chemotherapeutics in highly regulated manner, IS formation-responsive drug delivery system was developed.

Herein we propose a NK cell decorated by functional nanoparticle with embedded therapeutic cargo. These nanoparticles are composed of acid degradable polymers in micellar formation which contains Doxorubicin. Micelle disassembly will only occur when local pH lowered by release of lytic granules from the NK cell towards cancer cell during immunological attack, therefore minimizing the non-specific release of cytotoxic DOX. Hence, the anti-cancer activity is enhanced through combination of NK-cell-induced tumor-specific homing and potent chemotherapeutic efficacy. The advantages in its therapeutic efficacy and targeting precision will benefit further trials in development and clinical translation of NK cell mediated immunotherapy of cancer.

SB09.07.13
Effect of Hollow Manganese Oxide and Surface Modification for T1 Relaxivity Enhancement
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Magnetic resonance imaging (MRI) has attracted increasing interest because of its nonradiative and noninvasive character in addition to providing anatomic images with striking spatial resolution and depth. Positive contrast or proton MR images are produced by T1-based contrast agents such as gadolinium (Gd^{3+}) or manganese oxide (MnO) nanoparticles, which increase the signal from protons by reducing the spin-lattice relaxation time of nearby water leading to the brightening of the voxel. Through decades of research, various approaches have been developed for the synthesis of manganese oxide nanoparticles. Despite growing interest, T1-based MR imaging remains comparatively limited because of ratiometric complications and low signal intensities. Also, in order to impact their relaxation times, T1 contrast agent need to directly interact with the surrounding water protons. In case of nanospheres, only ions at the surface are effective. Decreasing the particle size could provide larger surface area. Also, by converting the particles to the hollow nanostructures, nanoparticle surface percentage could be increased which will in turn provide higher relaxivity. Hollow nanoparticles can provide a high specific area and, excellent penetration and permeation abilities. Hollow nanoparticles have significantly higher volumetric capacity to access water molecules, thereby, enhancing the MR contrast. Furthermore, ligand exchange can lead to added enhancement of contrast by making the surface hydrophilic as compared to the bilayer coated nanoparticles as, hydrophobic inner coating may inhibit water penetration leading to a lower spin effect. Until now, a few hollow MnO-based nanoparticles have been developed, including MnO nanoparticles loaded with iron oxide nanoparticles or drug molecules. Despite this, hollow MnO nanoparticles have not been optimized for low relaxivity and maximum contrast enhancement.

We have developed various solid and hollow manganese oxide (MnO) nanocubes for T1-weighted MR imaging (MnOEn, MnOEx, MnOEnHo and MnOExHo). The as-synthesized MnO nanocubes were rendered water soluble by ligand exchange and ligand encapsulation. Moreover, particles were further treated with phthalate buffer leading to formation of hollow MnO nanocubes. Further characterizations found that hollowed out-ligand exchanged nanostructures (MnOExHo) exhibit maximum enhancement of the longitudinal relaxation by allowing more exposure of Mn ions to water protons. We confirmed the T1 MRI contrast effect of the balb / c nude mice gastric orthotopic xenograft cancer model using MnOExHo nanocube. In this study, we suggested that these hollow ligands exchanged nanocubes (MnOExHo) could be used for biomedical research as effective T1 contrast agents.

SB09.07.14
Self-degradable Graphene Nanomedicine Operated by DNAzyme for Cancer Therapy and Clearance
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DNA has been utilized as a building block for the formation of a specific structure as well as a fascinating biomaterial for delivery system due to high biocompatibility and the favorable interactions with several biomolecules. Moreover, recent studies have revealed that the DNA can transform the conformation dynamically depending on stimuli such as pH, ion, and biomolecules, suggesting the use of DNA as a functional domain as well. In particular, the G-quadruplex (G4), a guanine-rich sequence which forms the stacked G-quartets structure, can interact with hemin [iron (III)-protoporphyrin] with high specificity, and exhibits a remarkable catalytic property that mimics peroxidase. Owing to the high structural stability and easier handling, DNAzyme has been extensively studied for biosensing, DNA/RNA cleavage, and catalytic reactions.

Graphene oxide (GO) have attracted much attention in biomedical applications due to mechanical and chemical stability, abundant oxygen functional groups on large surface area, and photothermal effect. Although GO possesses many functionalities as itself, modification of GO with several polymers and/or protein is inevitable for the use of nanomedicine because of the fact that the modification increases physiological stability, decreases systemic toxicity, and improves gene/drug loading capability. However, such a modification severely prohibits the degradability of GO by catalytic enzymes including peroxidases due to the steric hindrance of modified materials on the surface of GO.

In this present study, we introduce the G4/hemin complex to take advantage of these modified GOs and induce degradation in the body after the therapy. By applying unique features of catalytic DNAzyme and GO, we propose an ingenious self-catalytic GO nanomedicine for cancer therapy operated by multifunctional DNAzyme and controlled by photo-switch. The surface of GO is decorated by DNA double strand of G4 and its complementary sequence with mucin1 (MUC1) aptamer for targeted delivery. An anticancer drug, doxorubicin (DOX), is loaded on the DNA double strand, while hemin is loaded on the surface of GO. After cellular internalization and turning on the
photoswitch, loaded DOX is released by the DNA melting triggered by the photothermal effect of GO. The remained single stranded G4 sequence conjugated on the GO surface forms quartet structure and subsequently the hemin on GO surface binds on the quartet, inducing catalytic peroxidase effect. Due to the high local concentration of H2O2 in cancer cells, G4-hemin generated efficient amount of strong oxidant, hypochlorous acid (HOCl), inducing the degradation of GO into the small fragments for potential clearance.

**SB09.07.15**

**Singlet Oxygen Generation in Graphitic Carbon Nitride Quantum Dots for Photodynamic Therapy of Cancer**

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Photodynamic therapy (PDT) is an anticancer therapy based on special drugs/ photosensitizers. The three basic elements of photodynamic therapy are the excitation laser, photosensitizer molecule, and oxygen in tissue. After irradiation, the photosensitizer responds to specific light thus generating reactive oxygen species (ROS) killing cancer cells. Being a potential photocatalyst, g-CNQDs are able to create more electron-hole pairs under visible light illumination thereby resulting in the production of large amount of ROS which is helpful to cause severe cellular damage. Graphitic carbon nitride (g-C₃N₄) has been used for various biomedical applications due to its small sheet size, high dispersity, hydrophilicity and non cytotoxicity. g-C₃N₄ also have the ability to generate ROS towards cancer killing under very low-intensity light irradiation. In this study, the g-CNQDs are synthesized by two step thermal polymerization of melamine and EDTA. The QDs are small in size ranging from 2-7nm and demonstrate no visible cytotoxicity against fibroblast cells (L929 cells) and HuVEC cells upto a concentration of 5mg/mL. The optical absorption lies in the UV region at ~250 nm which is due to π-π* electronic transitions. The CNQDs exhibit broad emission peaks shifting towards red region when excited at different wavelengths. The g-CNQDs show excellent singlet oxygen generation capacity that makes them a suitable photosensitizer. In vitro ROS studies reveal that CNQDs were able to generate 370% ROS as compared to control dark. The photocotoxicity of g-CNQDs was assessed using MTT assay and Lactate Dehydrogenase (LDH) assay. In presence of blue light, the g-CNQDs were able to kill almost 75% of C6 glioblastoma at a concentration of 1.25 mg/mL as revealed by MTT assay. This data was supported by LDH assay showed release of 582% of LDH with respect to control. The photosensitized cells were stained with Fluorescein Diacetate (FDA) and Propidium Iodide (PI) in order to determine the percentage of live and dead cells. The cells treated with CNQDs in presence of light exhibited almost 99%. Cell death via apoptotic pathway was observed from Annexin V/FITC PI assay confirming 93.6% of necrotic and apoptotic population. In addition, caspase 3/7 detection assay was performed to detect the caspase mediated apoptosis corresponding to 88% of apoptotic population in light sensitized cells. These data imply blue light irradiated CNQDs exhibited considerable photodynamic effect against cancer cells by caspase activation through the modulation of apoptosis.

**SB09.07.16**

**Thermoresponsive Polymeric Micelles with Enhanced Loading Efficiency Through a Co-Loading Approach**

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Chemotherapy is one of the most effective treatments for cancer, but it has always faced some challenges such as multi-drug resistant (MDR) effect, poor aqueous solubility, and cardiotoxicity of the drug. In the past few decades, micellar drug delivery systems were used to encapsulate anticancer drugs for better therapeutic effects, but they have poor drug loading content. To address this problem, we designed a micellar drug delivery system using benzyl-substituted poly(caprolactone) (PBnCL) as the hydrophobic block for better interaction with anticancer drug Doxorubicin (Dox). Another approach is the co-loading of Dox with other hydrophobic molecules. Quercetin (Que) is a polyphenolic plant-derived flavonoid which has cardioprotective and chemosensitizing properties. Thus, the co-loading of Dox and Que not only enhances the loading capacity of Dox in micelles but also decreases the adverse side effects of anticancer drug and overcomes the MDR effect. Our other approach to improve conventional chemotherapies is developing thermoresponsive micelles. Thermosensitive nanocarriers ideally will retain their load at physiological temperature and release the drug within a tumor once the external temperature is applied to induce local hyperthermia. Polymers exhibiting lower critical solution temperature (LCST) or upper critical solution temperature (UCST) are used as polymers for thermoresponsive drug delivery systems. Herein, we report the synthesis of thermoresponsive polycaprolactones (PCLs) having LCST close to physiological temperature with the advantage of biocompatibility and biodegradability.
Ring-opening polymerization of benzyl- and oligoethylene glycol-substituted ε-caprolactone monomers was performed using tin octanoate as a catalyst and benzyl alcohol as an initiator to generate amphiphilic block copolymers. The synthesized PME_n-CL-b-PnBL polymers were characterized by 1H NMR analysis. To make a comparison between amphiphilic copolymers, a 50:50 ratio of hydrophilic to hydrophobic block were synthesized. The critical micellar concentration (CMC) that evaluates the thermodynamic stability of micelles in the aqueous solution was measured using the fluorescent hydrophobic probe, pyrene. All polymers have CMC values in the order of 10^{-5} g L^{-1}, which indicates high thermodynamic stability of micelles. The particle size distribution of micelles in aqueous solution was measured by dynamic light scattering. All polymers formed micelles with sizes lower than 100 nm, which is the ideal size for passive targeting of tumor cells. LCST measurements will be performed using a temperature-controlled UV-Vis spectrometer. Que and Dox were loaded in micelles through solvent evaporation method, and the drug loading capacity and encapsulation efficiency were measured using UV-Vis spectroscopy. We are expecting that the co-loaded micelles will demonstrate higher drug loading for both drugs in comparison to individual loading of drugs in micelles due to hydrophobic interactions between drugs.

SB09.07.17
Iron-Catalyzed poly(methyl methacrylate) Oligomers for Vaccine Adjuvants Cordula Hege1,1, Amy Stimpson1,1, Kathy Belt2, Chris Fox2 and Derek Irvine1,1; 1University of Nottingham, United Kingdom; 2IDRI (Infectious Disease Research Institute), United States

Adjuvants increase the efficacy of vaccines and can reduce the number of needed immunizations to achieve protection. Mainly aluminium salts are the most used adjuvants, however their immune response is not broad enough (only Th2 response, not Th1 response). For example, aluminium adjuvants are not useable against influenza or malaria. Therefore, it is favourable to search alternative adjuvants. Poly(methyl methacrylate) is useable for medicine-related applications, for example hip replacements or bone cements. Therefore, it is attractive to analyse if it is a possible adjuvant. Previous studies showed that PMMA has good adjuvant activity.1 The previous works did not mention the molecular weight of the polymer. To allow renal clearance, adjuvants should have a molecular weight below 20 kg/mol. To achieve that, one needs to produce reproducible and controlled polymers with a low molecular weight, so oligomers.

Catalytic chain transfer polymerization (CCTP) is a valuable method to synthesize oligomers. However, mainly cobalt catalysts are used. This is disadvantageous for the use as adjuvant. To create a more biocompatible method, iron catalysts were analysed for CCTP. Four-coordinate (diimine)iron catalysts containing aryl substituents proved successful as CCTP catalysts.2 Related to that, four-coordinate iron-diimine complexes with disopropylphenyl (DIPP) and trimethylphenyl (TMP) as substituents were explored. Also we tried, to produce the catalyst in situ, so without additional synthesis of the catalyst. For that dimethyl glyoxime and diphenyl glyoxime were used as ligands. Iron(II)bromide and iron(II)chloride were used to generate the iron complexes.

The reactions were performed with conventional heating and microwave heating (MH), both in bulk and in solvent solution at a reaction temperature of 80°C.

Both methods display chain-transfer behaviour, noting that molecular weight of polymer products was lower than uncontrolled free radical polymerisations. In case of bulk polymerization one has to take care about the reaction conditions to avoid uncontrolled reactions and the Trommsdorff-Norrish effect. With the right conditions, it can lead to lower molecular weight than the solution polymerizations. Microwave heating proved rewarding for the iron-catalysed CCTP.

On the whole, iron catalysed CCTP is demonstrated to be a favourable way to produce MMA oligomers to be used as adjuvants.


SB09.07.18
Development of Near-Infrared Fluorescence Dye and Astaxanthin Loaded Hyaluronic Acid Micelle for
**Photothermal Therapy** Subin Kim¹, Myeong Ju Moon², Suchithra Poilil Surendran¹, In-Kyu Park¹ and Yong Yeon Jeong²; ¹Chonnam National University Medical School, Korea (the Republic of); ²Chonnam National University Hwasun Hospital, Korea (the Republic of)

Recently, researches on the relation between anti-oxidant activity and cancer have been much attracted. Astaxanthin (ATX) has been regarded as an strong anti-oxidant that is several hundred times stronger than vitamin C. Photothermal therapy (PTT) is the usage of heat produced by electromagnetic radiation for cancer treatment. PTT is utilized to maximize the synergistic effect of anticancer drug. Near-infrared fluorescent dye, IR780 iodide (IR), was utilized for performing PTT. In regarding to lipophilic property of both ATX and IR, there are limitation for bio-applications. Hyaluronic acid (HA) is widely used hydrophilic polymer to overcome the this limitation. HA based micelles are beneficial for cancer treatments owing to their biocompatibility and tumor targeting ability to CD44-overexpressing tumors.

In this study, we fabricated HA micelles by self-assembly method and co-loaded with IR and ATX (IR-ATX-HA) for selective tumor targeting in CD44 overexpressed mouse head and neck squamous carcinoma cell line (SCC7). The physicochemical characterization of IR-ATX-HA micelles showed that the IR and ATX were successfully co-loaded into HA micelles. Furthermore, IR-ATX-HA micelles were destabilized upon laser irradiation and were able to release ATX to be utilized for cancer therapy. Intracellular uptake analysis of IR-ATX-HA micelles in SCC7 demonstrated CD44-based targeting. Moreover, cytotoxicity studies proved the improved anti-tumor activity aided by both ATX and PTT therapies compared to without NIR laser irradiation. In conclusion, IR-ATX-HA based micelles were effective in targeting SCC7 cancer cell and able to elicit enhanced cancer therapy effect of ATX and PTT.

**SB09.07.19**

**Solid State Diffusion Controlled Dissolution of Iron-Doped Copper Oxide Nanoparticles Opens a Therapeutic Window for Cancer Therapy In Vitro and In Vivo** Hendrik Naatz¹,², Bella B. Manshian³,³, Suman Pokhrell¹,², Stefaan J. Soenen³,³ and Lutz Mädler¹,²; ¹University of Bremen, Germany; ²Leibniz Institute for Materials Engineering IWT, Germany; ³KU Leuven, Belgium

The therapeutic use of copper oxide nanoparticles (CuO NPs) as effective anti-cancer drug is a promising alternative to conventional treatments. In contrast to insoluble carrier nanoparticles, e.g. iron oxide, copper oxide readily dissolves in cellular nutrient-rich environments, even at physiological pH. Intracellular released Cu²⁺ leads to a redox imbalance and binds to available reaction partners such as amino acids, polypeptides or proteins. At the same time, lattice oxygen will result in the formation of reactive oxygen species causing oxidative stress. Regulatory mechanisms to maintain copper homeostasis involve transport and excretion of copper via Cu-ATPase. If the Cu²⁺ release kinetics are too fast for a regulation, elevated copper levels cause severe damage such as proteasome inhibition leading to apoptosis of cancer and peripheral cells.

Due to differences (i.e. metabolism and pH) between maleficent and peripheral cells determining the release kinetics, we postulated that finely tuned release kinetics of CuO NPs can open a therapeutic window for cancer treatment. To test our hypothesis, we synthesized a library of pure and iron-doped CuO NPs using our in-house flame spray pyrolysis process. The incorporation of iron resulted in a bond-length variation and a strong Jahn-Teller distortion with a decreasing release of copper in biotical environments¹. The Cu²⁺ release kinetics of pure and Fe-doped CuO NPs were investigated on the long-term (250 hours, in agreement with the cell and mice studies) in biological test media containing amino acids present in common growth media, e.g. RPMI or DMEM. In contrast to the fast burst-like release of pure CuO, the iron doping resulted in a two-step dissolution: (1) an initial release on the time scale of hours and (2) a long-term release on the time scale of weeks. Material characterization of the as-prepared particles and the remaining particles after long-term dissolution showed that only copper is released from the particle, while iron remains on the surface. Based on these findings, a release kinetic model was developed to explain the two-step dissolution. The model includes the release of copper until all surface available copper is released, followed by a solid state diffusion limited long-term release.

Three materials (pure, 6% and 10% Fe-doped CuO NPs) with a fast, an intermediate and a slow release kinetic, respectively, where chosen to investigate our hypothesis in-vitro and in-vivo. While the cell viability of tumor and peripheral cells was affected in case of pure CuO, 6% Fe-doped CuO NPs only reduced the cell viability of tumor cells, even for doxorubicin (conventional chemotherapy) resistant cell types. In a combined treatment with an immune activator (IDO1), the 6% Fe-doped CuO NPs were successfully tested in-vivo, resulting in complete tumor
remission in a syngeneic subcutaneous mouse model (KLN-205).


**SB09.07.20**

**Hollow Silica Capsules as Transporters for Sustained Delivery of Anticancer and Antimicrobial Drugs** *Eva Krakor*¹, *Isabel Gessner*¹, *Astrid Schauss*¹, *Silke H. Christiansen*², *Uwe Ruschewitz*¹ and *Sanjay Mathur*¹;

¹University of Cologne, Germany; ²Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

The field of nanoparticles for biomedical applications has become one of the most promising and most studied topics in the last years. In terms of therapeutic applications, especially drug delivery vehicles have been intensively studied. In this case, hollow mesoporous silica capsules (HMSC) have aroused tremendous interest due to their unique properties such as high biocompatibility and stability in biological milieu, large surface areas, low densities and high loading capacities due to a protected hollow core.

HMSC were synthesized through a hard template-based method. For that purpose, ellipsoidal hematite particles were synthesized in a solvothermal process, coated with silica in a sol gel process and subsequently the iron oxide core was etched resulting in HMSC. The porosity of as-prepared particles was analyzed using nitrogen adsorption-desorption method revealing a pore size of circa 4 nm and a high surface area of 308.8 m²/g. Cytotoxicity was determined using cell viability test (MTT) towards human kidney cells (HEK293) which clearly demonstrates that no reduction of cell viability was observed even at high concentrations of 100 µg/ml. Uptake studies using confocal microscopy were carried out using human cervical cancer cells (HeLa) which could show the successful internalization over a period of 24 hours. For testing their capability as drug delivery vehicle, a hydrophilic antibiotic (ciprofloxacin) and a hydrophobic anticancer (curcumin) compound were loaded and a pH dependent release under physiological conditions at 37°C was monitored via UV-Vis spectroscopy. Ciprofloxacin-loaded HMSC with a concentration of 10 µg/ml were also tested towards gram negative bacteria (E.coli) revealing a complete growth inhibition over 18 hours. This study demonstrates the suitability of as-prepared hollow silica capsules as drug delivery vehicles for a broad range of drugs.

**SB09.07.21**

**Adhesion of Gold Nanoparticles to Triple Negative Breast Cancer Cells** *Vanessa Uzonwanne*¹, *John Obayemi*¹, *Jingjie Hu*², *Arvand M. Navabi*¹, *Nima Rahbar*¹ and *Winston Soboyejo*¹; ¹Worcester Polytechnic Institute, United States; ²Mayo Clinic, United States

The need for the development of nanoparticles for the early detection and treatment of cancer provides the motivation for specific targeting of cancer. This paper presents results of an atomic force microscopy and molecular dynamics study of the adhesion between Triple Negative Breast Cancer Cells (TNBC) (MDA-MB-231 and MDA-MB-468) cells and biosynthesized gold nanoparticles (BGNP). The BGNPs are conjugated with Luteinizing Hormone Releasing Hormone (LHRH), which is known to target LHRH receptors that are over–expressed on the surfaces of breast cancer cells. The adhesion forces between the LHRH-conjugated gold nanoparticles and the breast cancer cells are found to be about 4-5 times greater than those between normal breast cells and LHRH-conjugated gold nanoparticles. The increase in the adhesion of LHRH to breast cancer cells is shown to be associated with an increase in the LHRH receptor density, which is revealed via confocal microscopy. The implications of the results are then discussed for the development of ligand-conjugated gold nanoparticles for the detection and treatment of cancer.

**SB09.07.22**

**FRα-Targeted Gold Nanobipyramids for Fluorescence-Enhanced Imaging and Multimodal Therapy of Triple Negative Breast Cancer Cells** *Ioannis G. Theodorou* and *Triantafyllos Stylianopoulos*; University of Cyprus, Cyprus

Despite significant advances in cancer therapeutics, breast cancer (BC) remains a leading cause of cancer-related death in women worldwide. This could be partly due to the lack of early detection required for improved prognosis, while treatment complications (*e.g.* high systemic toxicity of anticancer drugs or drug resistance) often lead to treatment failure. In particular, triple-negative breast cancers (TNBCs) are highly aggressive, lack validated
therapeutic targets and have high risk of metastasis, representing an urgent unmet clinical need for new treatment options [1]. Here, a novel multifunctional theranostic nanostructure for TNBC is presented, combining for the first time metal-enhanced fluorescence (MEF) imaging with multimodal cancer treatment, through hyperthermia and chemotherapeutic drug delivery.

This integrated theranostic platform comprises a gold (Au) nanobipyramid (AuNBP) core as the MEF amplification component. MEF is an optical process in which the near-field interaction of fluorophores with metallic nanoparticles (NPs) can, under specific conditions, produce large fluorescence enhancements [2]. Efforts are underway to exploit this light amplification to considerably increase detection sensitivity in fluorescence bioimaging, particularly in the biological near-infrared (NIR; wavelengths 650-900 nm) window [3], where bright and biocompatible fluorophores are lacking. In the present work, we focus on AuNBPs, a type of elongated Au nanoparticle (NP) with two sharp tips, equipped with several features that make them attractive candidates for MEF. For instance, their high monodispersity compared to other anisotropic NPs, affords lower inhomogeneous spectral broadening of their localized surface plasmon resonance (LSPR) peaks, while their sharp edges allow significant enhancements of the local electric fields. Here, AuNBPs with tunable sizes are synthesized, allowing LSPRs tunable in the NIR window. We show that NIR fluorophore conjugation to AuNBPs through a mesoporous silica (MS) spacer allows several times fluorescence enhancement in the NIR window. Using time-resolved fluorescence measurements to semi-quantitatively deconvolute excitation enhancement from emission enhancement, as well as electric field modeling, we provide important insights into the mechanism of MEF from AuNBPs.

We then explore the in vitro chemotherapeutic efficacy of doxorubicin, loaded within the pores of the MS layer as a strategy to facilitate local drug delivery to BC cells. In parallel, the AuNBP core is applied for photothermal therapy via NIR laser irradiation, as a synergistic treatment modality. Our results demonstrate that hyperthermia amplifies the potency of doxorubicin against BC cells. Finally, we use folate functionalization of the MS-coated AuNBPs for active targeting of the folate receptor alpha (FRα). FRα is a protein overexpressed in 86% of metastatic TNBC patients, and its expression is associated with poor clinical prognosis, making it a good candidate for TNBC targeting [4]. Using fluorescence imaging, we show that folate functionalization enables selective detection of TNBC cells over cells with low FRα expression. We also show that folate targeting enhances NP accumulation in TNBC cells and potentiates TNBC cell killing.

In summary, the insights gained through this work could guide further development of bright NIR-MEF nanoprobes. Our study also demonstrates the potential clinical utility of folate conjugation to enable selective detection and targeted treatment of aggressive BC subtypes.

References:
3. (a) Theodorou, I.G. et al., Nanoscale, 2019,11, 2079-88. (b) Theodorou, I.G. et al., Nanoscale, 2018, 10, 15854-64.

SB09.07.23
Fabrication and Evaluation of High-Dispersive Gadolinium-Complexed Nanodiamond Particles for MR Lymphatic Imaging
Kosaku Yano1, Tomohiro Matsumoto1,2, Takako Nakamura3, Yutaka Okamoto1, Terumitsu Hasebe1,2 and Atsushi Hotta1; 1Keio University, Japan; 2Tokai University Hachioji Hospital, Japan; 3National Institute of Advanced Industrial Science and Technology, Japan

Nanodiamond (ND) particles are nano-scale materials that have recently been attracting major attention for biological purposes, owing to their high biocompatibility and chemical stability. ND particles, however, have their disadvantage to form micro-scale aggregates, which could lead to the loss of the advantageous properties of nanoparticles. An ND-based MRI contrast agent is an example of the material that holds such a problem as mentioned above. Nano-sized contrast agents were fabricated in our previous studies by the complexation of ND particles and gadolinium chelates (Gd-DTPA). The primary size of the gadolinium-complexed ND (Gd-DTPA-ND) particles was set at around 5 nm to achieve the selective imaging of the lymphatic system. This was because MRI contrast agents with a diameter of 3–10 nm could be selectively ingested through lymphatic vessels and filtered in...
Fabrication of Gadolinium-Complexed Carboxylated Nanodiamond Particles for MR Imaging of the Lymphatic System

Kosaku Yano1, Tomohiro Matsumoto1,2, Takako Nakamura1, Yutaka Okamoto1, Terumitsu Hasebe1,2 and Atsushi Hotta1; 1Keio University, Japan; 2Tokai University Hachioji Hospital, Japan; 3National Institute of Advanced Industrial Science and Technology, Japan

The structure and the role of the lymphatic system in the human body have not yet been fully explored in the medical field. This is mainly due to the microscopic diameter of lymphatic vessels, which makes it highly difficult to inject contrast agents directly into vessels. However, it has recently been reported that a macromolecular contrast agent can be uptaken selectively by lymphatic vessels through simple subcutaneous injection to perform high-resolution imaging of the lymphatic system. This is because particles larger than 3 nm in diameter can be drained by lymphatic vessels, but are difficult to penetrate through venular endothelia, resulting in selective lymphatic drainage. Particles smaller than 10 nm in diameter would be uptaken by vessels and filtrated in the kidney for the final excretion. Therefore, fabricating MRI contrast agents with 3–10 nm in size could be a major pathway to address this problem. Previously, we fabricated MRI contrast agents of a few nanometers in diameter with the condensation of gadolinium complexes and ND particles (Gd-DTPA-ND). The primary particles of these contrast agents possessed a diameter of approximately 5 nm, which was considered to be an adequate size for contrast agents to be selectively uptaken by the lymphatic vessels before the excretion in the kidney. However, these particles formed tight aggregations in water, resulting in micro-scale aggregates. The aggregates were too large to be well uptaken and excreted, and the agents could not be used for lymphatic imaging. In this work, the dispersity of the Gd-DTPA-ND particles was analyzed, which was improved by employing ND particles with abundant hydrophilic carboxyl groups on their surface by a pre-oxidation step (CND). The carboxyl groups introduced by oxidation induced hydrophilicity and hence negative charge to the ND surface, resulting in the high dispersity of the gadolinium-complexed CND particles. The dispersity of Gd-DTPA-CND particles in distilled water was evaluated by the dynamic light scattering, revealing higher dispersity for the fabricated particles than for the Gd-DTPA-ND particles. The MRI visibility of the Gd-DTPA-CND particles in distilled water was also evaluated by the 1.5T MRI. It was found that high contrast imaging could be established by the Gd-DTPA-CND particles, showing that the Gd-DTPA-CND particles possessed high MRI visibility in distilled water. Furthermore, the Gd-DTPA-CND particles also possessed high dispersity and MRI visibility even in human serum, suggesting that the particles could be used intravitally. Finally, Gd-DTPA-CND particle solution was injected in a tail vein of a rat to investigate the MRI visibility of the Gd-DTPA-CND particles in vivo. As a result, the injection of the Gd-DTPA-CND particles produced a strong contrast in the blood circulatory system. A bladder was eventually imaged, suggesting successful filtration of particles in the kidney and assembly in the bladder. The results revealed that Gd-DTPA-CND particles could realize high contrast imaging in living bodies and the particles could be filtered in the kidney for the final excretion in the bladder. It was, therefore, concluded that Gd-DTPA-CND particles could be promising MRI contrast agents for the imaging of the lymphatic system through subcutaneous injection.
Protein-Templated Raspberry Gold Nanostructures for Intracellular Plasmonic Imaging and Photothermal Therapy
Animesh Pan, Muzahidul Islam Anik and Geoffrey D. Bothun; University of Rhode Island, United States

Gold-based nanomaterials have shown outstanding physicochemical properties in biomedical applications due to their inherent low toxicity, and their tunable localized surface plasmon resonance (LSPR) wavelength from the visible to near-infrared (NIR) “biological window” region by simply adjusting the size and shape of the nanoparticles. This has enabled the building of fascinating gold-based nanostructures theranostic nanoplatforms for cellular imaging and photothermal therapy (PTT). Herein, we report the synthesis of raspberry gold nanostructures using a polyelectrolyte coated protein (albumin) nanoparticles templates. Albumin nanoparticles were synthesized by desolvation technique using conventional cross-linker (glutaraldehyde) for stable and uniform albumin nanoparticles and then were coated with positively charge poly-L-lysine to enrich the interface with gold anion, exposed to a reducing agent to form raspberry gold nanoshell. The protein templated nanostructures were characterized by dynamic light scattering, filed-emission scanning electron microscope, transmission electron microscopy and visible-near-infrared spectroscopy. The critical parameters for photothermal efficiency, including the concentration and irradiation time, were evaluated. Moreover, the good biocompatibility and the low cytotoxicity of raspberry nanostructures, together with their superior photothermal ablation effect on A549 cancer cells have also been confirmed. Furthermore, we also report the nanostructures for surface-enhanced Taman scattering (SERS) detection of cancer cells with the bioconjugation of different Raman tags. Our study indicates that the protein-templated gold nanoplatform could be a potential candidate PTT and plasmonic sensing in future.

SB09.07.26
Investigation of the Immunological Properties of Cationic Lipid Nanoparticles
Tianshu Li and Shinji Takeoka; Waseda University, Japan

Cationic lipid nanoparticles (LNPs) are well known as drug delivery system (DDS) of nucleic acids and proteins owing to their easy preparation and high cellular uptake efficiency. Many researches have shown various designs of the lipid component to enhance the cellular internalization in different types of cells and meanwhile reduce the cytotoxicity. However, there still lacks the investigation on whether or how cationic LNPs interact with the immune cells.

The NLRP3 inflammasome senses danger signals such as pathogens to alert the immune system by releasing interleukin (IL)-1β. Some cationic NPs and conventional adjuvant alum are reported to have the potential in stimulating the NLRP3 inflammasome. To study the rational of lipid structure in stimulating immune cells, we have investigated a series of cationic LNPs with lysine or arginine head groups but varied lengths of hydrophobic chains and spacers in between in terms of the NLRP3 inflammasomes activation. We found a preferable lipid backbone, ie, ditetradecyl fatty acids with propyl spacer, in either lysine- or arginine-based liposomes that showed high potency in the NLRP3 inflammasome activation in both human and murine macrophages. In addition, these liposomes also exhibited much enhanced antigen presentation in murine dendritic cells when they loaded the ovalbumin antigen on the surface in comparison with other liposomes. The antigen presentations were mediated by both major histocompatibility complex (MHC)-I and MHC-II molecules without interfering co-stimulatory molecules such as CD40, CD80 and CD86. Therefore, OT-I and OT-II lymphocytes (T cells) were sufficiently activated in vitro with significantly increased IL-2 secretion and cell division.

In summary, we have investigated the structure effect of cationic lipids in activating the innate immune cells and further verified their efficiency as antigen carriers in promoting antigen presentation.

Reference:

SB09.07.27
Zinc Oxide as Enzyme Mimics for Nitric Oxide Delivery
Tao Yang1, Alexander N. Zelikin2 and Rona Chandrawati1; 1University of New South Wales (UNSW Sydney), Australia; 2Aarhus University, Denmark

Nitric oxide (NO) is a signalling molecule produced by endothelial cells that serves important biological functions in immune system, cardiovascular system, and central nervous system. However, radical NO species are short-lived.
For this reason, controlled delivery of precise amounts of NO with spatiotemporal resolution is highly challenging. Zinc oxide (ZnO) particles offer unique properties that make them excellent tools in biomedical diagnostic and therapeutic fields. In this study, we discovered enzyme-mimicking activities of ZnO and their ability to catalytically decompose endogenous NO prodrugs to generate NO (nM - µM) at physiological conditions. We report a simple approach to synthesize ZnO particles via a chemical precipitation method using poly(vinylpyrrolidone) as the directing agent to control ZnO morphology. We showed that NO can be locally synthesized and the amount generated can be up-/down-regulated simply by tuning the concentration of ZnO (enzyme mimics) and NO precursors. The catalytic approach enables NO delivery on demand, which can be initiated when needed by external administration of the precursors or prodrugs. ZnO preserved their catalytic activity for at least 6 months and enabled sustained delivery of NO. The present study offers opportunities to overcome current challenges of NO delivery in tissue engineering and regenerative medicine.

References:

SB09.07.28
Cell Mimicking Microparticles to Tune the Immunity
Mohammad Mahdi Hasani-Sadrabadi1, Fatemeh Sadat Majedi1, Song Li1 and Manish Butte2; 1University of California, Los Angeles, United States; 2UCLA, United States

Diseases may arise if there is a physiological inability to make enough key protective factors when most needed. Nano-bio-manufacturing affords the opportunity to synthesize specific factors \textit{in situ} and deliver to cells while employing controls on timing and spatial delivery that cannot be achieved by biological systems. Our main objective here is to develop an on-demand production and release of therapeutic proteins at the site of immunological action. Here, we have developed a nano-bio-manufacturing platform that safely augments the immune response to cancers. As a proof of concept, we chose cytokine interleukin 2 (IL2) as our synthetic target which well known to help activate cytotoxic T cells to fight infections and cancer. Here, the microfluidic platform was used to make a library of monodisperse nanoliposomes of variable sizes that can encapsulate IL2 plasmid DNA and extracts of prokaryotic or eukaryotic cells with a high yield. DMPC and DOPC were used as lipid sources. Incorporation of fluorescent GreenLys or GFP-expressing plasmids were used to monitor protein production in real time. Activated caged ATP (DMNPE-caged ATP) was used to block the expression. UV exposure at 360–480 nm wavelength (OmniCure S2000) for 10 s and 80 mW/cm2 at pH 7.4, 37 °C uncaged the ATP, and IL2-GFP was successfully synthesized. We then first fabricate artificial cells that mimic the size, shape, and mechanics of lymphocytes like T cells. Then we contain the synthetic machinery for transcription and translation of functional IL2 protein and elements that allow for precisely controlled activation and release of the cytokine. The biosynthesis of proteins \textit{in vivo} from artificial cells allows for the production of cytokines with number of features not attainable by conventional biological systems: tunable initiation to eliminate basal expression and systemic toxicity; controlled release to locally focus the site of the cytokines’ activity; and targeting to attach the artificial cells to T cells or cancer sites. Here we optimize \textit{in vitro} synthesis of IL2 cytokine in order to tune T cell fate. First, we encapsulated cell-free protein biosynthesis systems into liposome nanoparticles to make IL2 cytokine. We have established a microfluidic platform to generate monodisperse nanoparticles of various sizes. By controlling the flow rates, we tuned the size of liposomes over a broad range of size (50 - 400 nm). These nanoparticles encapsulated the cell-free synthesis extract and desired plasmids with efficiency dependent on the DNA size of the cargo. 340 nm particles were selected as the optimized size of nanoliposomes and were loaded inside alginate-based microgels. Stimuli-responsive production and sustain release of IL2 showed improve activation and performance of CD4 and CD8 T cells both \textit{in vitro} and in B16 melanoma cancer model \textit{in vivo}. We have developed the \textit{de novo} design of synthetic immune cells to eliminate systemic toxicities through the local manufacture and sustained release of target cytokines (e.g. IL-2), and eliminating basal production by initiating the synthesis specifically upon an external stimulus.

SB09.07.29
Engineering T Cell Activation for Solid Tumor Immunotherapy
Fatemeh Sadat Majedi, Mohammad Mahdi Hasani-Sadrabadi, Manish Butte and Louis S. Bouchard; University of California, Los Angeles, United States
Despite the many promising results that adaptive T cell therapy has offered to cancer therapy the major hurdle that exists in its clinical translation is the difficulties associated with delivery of trained lymphocytes to tumor sites, along with lack of presence of a support for cells to allow their proper expansion in the immunosuppressive environment of tumor. To bring adaptive T cell therapy one step closer to clinical translation we seek to improve three aspects of current therapies. The first step is to improve capacity and efficiency of adaptive T cells. To tackle this here we have proposed a 3D biopolymer implant as an artificial niche that provides a support for better expansion of pre-trained T cells. We have developed biopolymer-based scaffolds based on the biocompatible Alginate and to further encourage cell trafficking within these structures we have decorated Alginate with RGD peptides. The porosity of scaffolds then modified to creates micro-pores within these implants that both allows for maximizing the loading capacity for delivering T cells and facilitates their expansion as well. To pursue proliferation which for that we have improved this artificial niche by embedding mesoporous silica microparticles within this scaffold to present cytokine (here IL-2) signal in order to improve T cell proliferation. Surface of these particles also decorated with anti-CD3/anti-CD28 to provide T cells with activation signals. One of the main reasons for immunosuppressive environment of tumors in the abundance of TGFβ signal that pursues formation of regulatory T cells (Tregs) which then results in suppression of T killer cells. To overcome this issue, we have empowered our artificial niche with PLGA nanoparticles that engulf TGFβ and suppresses formation of Tregs and gives the trained CD8 T cells a better chance to engage and fight cancer cells. Overall, these bioimplants can be most useful to treat inoperable tumors or in situation were it is near to impossible to remove the whole tumor.

SESSION SB09.08/SB06.10: Joint Session: Mechanics of Cancer Invasion
Session Chairs: Ming Guo, Jan Lammerding, Susan Leggett and Ian Wong
Wednesday Morning, December 4, 2019
Hynes, Level 3, Room 304

8:30 AM *SB09.08.01/SB06.10.01

Cell-Matrix Interactions in Cancer and Fibrosis—Multiscale Chemo-Mechanical Models Vivek Shenoy;
University of Pennsylvania, United States

Cell invasion into the surrounding matrix from non-vascularized primary tumors is the main mechanism by which cancer cells migrate to nearby blood vessels and metastasize to eventually form secondary tumors. This process is mediated by an intricate coupling between intracellular and extracellular forces that depend on the stiffness of the surrounding stroma and the alignment of matrix fibers. A multiscale model is used to elucidate the two-way feedback loop between stress-dependent cell contractility and matrix fiber realignment and strain stiffening, which enables the cells to polarize and enhance their contractility to break free from the tumor and invade into the matrix. Importantly, our model can be used to explain how morphological and structural changes in the tumor microenvironment, such as elevated rigidity and fiber alignment prior to cell invasion, are prognostic of the malignant phenotype. The model also predicts how the alignment of matrix fibers can recruit macrophages, which are among the first responders of the innate immune system following organ injury and are crucial for repair, resolution, and re-establishing homeostasis of damaged tissue. I will discuss how the deformation of the nucleus during migration can lead to changes in the spatial organization of chromosomes and their intermingling which can result in genetic mutations and genomic instability. I will also discuss how targeting extracellular matrix mechanics, by preventing or reversing tissue stiffening or interrupting the cellular response in cancer and fibrosis, is a therapeutic approach with clinical potential.

BIO: Vivek Shenoy is the Eduardo D. Glandt President’s Distinguished Professor in the School of Engineering and Applied Sciences at the University of Pennsylvania. Dr. Shenoy’s research focuses on developing theoretical concepts and numerical methods to understand the basic principles that control the behavior of both engineering and biological systems. He has used rigorous analytical methods and multiscale modeling techniques, ranging from atomistic density functional theory to continuum methods, to gain physical insight into a myriad of problems in materials science and biomechanics. Dr. Shenoy's honors include a National Science Foundation CAREER Award (2000), the Richard and Edna Solomon Assistant Professorship (2002-2005) and the Rosenbaum Visiting Fellowship from the Isaac Newton Institute of Mathematical Science, University of Cambridge and the Heilmeier award for excellence in faculty research (2019). He is the principal investigator and director of the NSF-funded
Science and Technology Center for Engineering Mechanobiology established in 2016. He also serves the editor of the Biophysical Journal and is a fellow of the American Institute for Medical and Biological Engineering.

9:00 AM *SB09.08.02/SB06.10.02
Biomechanical Imaging of Cancer Cells and Tumor Development in 3D Ming Guo; Massachusetts Institute of Technology, United States

Sculpting of structure and function of three-dimensional multicellular tissues depend critically on the spatial and temporal coordination of cellular physical properties. Yet the organizational principles that govern these events, and their disruption in disease, remain poorly understood. Here, I will introduce our recent progress performing biomechanical imaging to quantify cell and extracellular matrix (ECM) mechanics, as well as their mechanical interaction. By integrating confocal microscopy with optical tweezers, we have developed a platform to map in three dimensions the spatial and temporal evolution of positions, motions, and physical characteristics of individual cells throughout a growing mammary cancer organoid model. Compared with cells in the organoid core, cells at the organoid periphery and the invasive front are found to be systematically softer, larger and more dynamic. These mechanical changes are shown to arise from supracellular fluid flow through gap junctions, suppression of which delays transition to an invasive phenotype. Together, these findings highlight the role of spatiotemporal coordination of cellular physical properties in tissue organization and disease progression.

9:30 AM SB09.08.03/SB06.10.03
3D Traction Force Microscopy of Multicellular Invasion in Biomimetic Silk-Collagen Hydrogels Susan E. Leggett¹, Mohak Patel¹, Thomas M. Valentin¹, Christian Franck² and Ian Y. Wong¹; ¹Brown University, United States; ²University of Wisconsin–Madison, United States

Epithelial tumors exhibit dysregulated cell-cell and cell-matrix adhesions as they invade into the surrounding extracellular matrix. In particular, the epithelial-mesenchymal transition (EMT) is associated with weakened cell-cell adhesions and strengthened cell-matrix adhesions, resulting in multicellular dissemination. Traction force microscopy enables new insights into the cell-generated forces that mediate these behaviors, but has primarily been applied to individual cells in 3D. Here, we elucidate the collective tractions of multicellular clusters in 3D matrix after induction of the EMT master regulator Snail. We find that multicellular clusters exhibit characteristic spatial signatures that can be used for mechanophenotypic profiling. In particular, EMT results in highly localized “hotspots” of strong cell-matrix adhesion, associated with high contractility and front / back polarization. We further show that chemotherapeutics and targeted inhibitors can perturb clusters towards more epithelial or mesenchymal-like mechanophenotype. We envision that this 3D culture assay will enable high content preclinical screening of targeted anticancer compounds as well as to predict the clinical response of human patient samples.

9:45 AM SB09.08.04/SB06.10.04
Unjamming and Collective Migration in MCF10A Series of Breast Cancer Cell Lines Jae Hun Kim and Jeffrey Fredberg; Harvard University, United States

Carcinoma cells tend to migrate in collective strands, ducts, sheets or clusters (Friedl, & Gilmour, Nat. Rev. Mol. Cell. Bio. 2009). To migrate collectively, the epithelial collective has been argued to overcome geometric constraints attributable to cell jamming (Atia et al., Nat. Phys. 2018). If so, then the greater is the degree of cellular jamming, then the more would be the extent to which each individual cell becomes caged by its neighbors, and therefore, the less rapidly it would be able to migrate (Park et al., Nat Mat. 2015). The jamming hypothesis, however, has never been tested in the context of cancer cell invasiveness. Using classical in vitro cultures of six breast cancer models, here we investigate structural signatures of jamming, dynamical signatures of jamming, and the relationship between them. In order of increasing invasiveness, the cell lines examined included MCF10A, MCF10A,vector; MCF10A.14-3-3z; MCF10.Erb2, MCF10AT; and MCF10CA1a. Across all models tested, cell shape and shape variability from cell-to-cell conformed well to structural signatures of cell layer jamming. In all cases but one, migratory dynamics changed roughly in concert with expectations based on structural signatures –as the strength of structural signatures of unjamming increased, the rapidity of migratory dynamics tended to progressively increased. The exception was the case of MCF10CA1a, wherein structure signified a moderately jammed state whereas migratory dynamics were excessively rapid and therefore discordant with structure. Closer
examination of migratory dynamics of MCF10CA1a showed anomalously large migratory persistence, but the mechanism of discordance in this case remains unclear. A hallmark of cancer is multiple dimension of heterogeneity. Nevertheless, each of the diverse cases examined here reveals that cell jamming imposes an overriding geometric constraint.

10:00 AM BREAK

10:30 AM *SB09.08.05/SB06.10.05
Mechanical Forces, the Microenvironment and Metastasis of 3D Microtumors Joe Tien¹, Celeste Nelson² and Bryan A. Nerger²; ¹Boston University, United States; ²Princeton University, United States

Progression to metastatic breast cancer requires cancer cells to invade from a solid tumor into the surrounding stroma and escape into a lymphatic or blood vessel. To understand the biophysical and biochemical parameters that define the kinetics of invasion and escape, we engineered a three-dimensional model of human breast microtumors embedded within native extracellular matrix. We previously found that interstitial fluid pressure (IFP) determines the invasive response of human breast microtumors: specifically, interstitial hypertension (i.e., elevated IFP) prevents invasion, whereas interstitial hypotension (i.e., lowered IFP) promotes invasion. We have now used this system to examine the effects of matrix density, proteolysis, proliferation, and IFP on the kinetics of tumor cell escape into an empty cavity. Our data suggest that the physical microenvironment of a tumor dictates the rates of two early steps in the metastatic cascade, namely, invasion of the surrounding interstitium and escape into an open space. These physical features dictate whether escape results from a ballistic or diffusive invasion process. Furthermore, acute changes in interstitial pressure can suppress tumor cell escape after invasion has already occurred. Our results point to the possibility of using physical therapies to delay or prevent metastatic progression in breast cancer.

11:00 AM *SB09.08.06/SB06.10.06
Engineered Microfluidic Environments to Study the Role of Nuclear Mechanobiology in Cancer Progression Jan Lammerding; Cornell University, United States

Cancer metastasis, i.e., the spreading of cells from the primary tumor to distant organs, is responsible for more than 80% of all cancer deaths. During cancer cell invasion and metastasis, tumor cells migrate through interstitial spaces and transendothelial openings substantially smaller than the diameter of the cell. Recent research has made it apparent that cells migrating in such confined three-dimensional (3D) environments face substantially physical challenges. In particular, the cell nucleus is the largest and stiffest organelle, making nuclear deformation a rate-limiting factor in the passage of cells through confined 3D environments. We have used micro- and nano-fabrication approaches to generate microfluidic devices that closely mimic the physical constraints of physiological interstitial environments, while providing precise control over the constriction geometry and enabling live-cell imaging at high spatial and temporal resolution. Using these devices, we demonstrated the importance of available pore size and nuclear deformability on the ability of cells to move through 3D environments. We combined these devices with fluorescent reporters for nuclear envelope rupture and DNA damage to assess the functional consequences of the physical forces exerted on the nucleus during confined migration. In addition, we developed a microfluidic micropipette aspiration device to rapidly measure nuclear stiffness in large numbers of cells. We found that highly metastatic breast cancer cells had decreased levels of the nuclear envelope proteins lamin A/C, which determine nuclear deformability, compared to less aggressive tumor cells, and that the increased nuclear deformability promoted migration through tight spaces. Increasing expression of lamin A in breast cancer cells with normally low levels of lamin A/C significantly impaired their invasive properties, while depletion of lamin A/C increased invasive potential through micron-scale microfluidic constrictions and dense collagen matrices. Importantly, analysis of human breast tumor tissue microarrays showed that low levels of lamin A/C correlated with reduced disease-free survival, demonstrating the clinical relevance of our findings. Taken together, these studies indicate that downregulation of lamin A/C could promote both cancer cell invasion and metastasis in breast cancer while highlighting the appeal of engineered materials and microenvironments to study tumor cell mechanobiology. Insights gained from this work could improve prognostic approaches; ultimately, targeting regulator pathways associated with altered lamin expression may offer novel therapeutic avenues to control metastatic disease in breast cancer.

11:30 AM *SB09.08.07/SB06.10.07
The National Cancer Institute’s Support for the Interface of Bio/Nano Materials with Cancer Research

Nas Zahir; National Cancer Institute, United States

The U.S. National Cancer Institute (NCI) leads, conducts, and supports cancer research across the nation to advance scientific knowledge and help people live longer, healthier lives. Many advancements in cancer research in areas of progression, metastasis, and treatment response have been enabled by the development of innovative technologies, including novel biomaterials, microfluidics, and biomimetic engineered technologies. Several programs at the NCI have helped foster cancer technology development in these areas as well as the overall convergence of approaches and perspectives from the physical sciences and engineering into cancer research. Over the past decade, the NCI has supported the NCI Physical Sciences – Oncology Network (PS-ON), which is comprised of nearly 30 transdisciplinary teams that integrate physical sciences perspectives with cancer research to complement and expand on our current understanding of cancer across many biological length- and time-scales. Thematic areas under investigation in the PS-ON include transcriptional dynamics and genomic architecture, modeling evolutionary dynamics of treatment response, cancer mechanobiology and the physical microenvironment, and multi-scale computational modeling approaches to integrate data across length scales. PS-ON investigators and those in the affiliated Cancer Tissue Engineering Collaborative (TEC) research program are utilizing biomaterials and biofabrication for experimental model systems of cancer that recapitulate the tumor microenvironment and tumor-stromal interactions. There is also sophisticated incorporation of bioreactors and microfluidic culture to mimic perfusion, lymphatics, interstitial pressure, and molecular gradients. Other research initiatives supported by the NCI to promote convergent, cross-disciplinary research that include projects incorporating novel biomaterials are the Cancer Systems Biology Consortium (CSBC) and the Innovative Molecular Analysis Technologies (IMAT). The NCI demonstrates its interest in supporting materials science and engineering in cancer research by investment in these areas through investigator-initiated research and the targeted programs. The continued investigation of the physical dynamics of cancer and incorporation of novel biomaterials and biomimetic engineered technologies will be important, focusing on understanding the complex and dynamic multiscale interactions of the tumor, host, and immune system. Innovative technology development will continue to be critical for unprecedented measurements and discoveries in cancer research.

SESSION SB09.09/SB06.11: Joint Session: Cancer Cell—ECM Interactions
Session Chairs: Sidi Bencherif, Matthew Paszek, John Slater and Nas Zahir
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Room 304

1:30 PM *SB09.09.01/SB06.11.01
Nuclear Rupture at High Curvature and High Rates Upsets DNA Repair to Affect Cell Cycle, Differentiation and Genome Variation
Dennis E. Discher; University of Pennsylvania, United States

The nucleus links physically to cytoskeleton, adhesions, and extracellular matrix – all of which are subject to stresses and strains. We have taken various materials-intensive approaches to study nuclear rupture in tumors [1], embryonic organs [2], and various in vitro models, and we find rupture results from high nuclear curvature, leading to cytoplasmic mis-localization of multiple DNA repair factors and transcription factors that impact cell fate and function. Curvature is imposed by external probe [1], by migrating quickly (not slowly) through constricting micropores [3,4], or by cell attachment to either aligned matrix or stiff matrix [1], and theory indicates rupture pores from by a heterogeneous nucleation mechanism [5]. Mis-localization of nuclear factors is greatly enhanced by nucleoskeleton depletion (soft nuclei), requires many hours for nuclear re-entry, and correlates with pan-nucleoplasmic foci of DNA damage and with electrophoretic breaks. Excess DNA damage is rescued in ruptured nuclei by co-overexpression of multiple DNA repair factors as well as by soft matrix or inhibition of either actomyosin tension or oxidative stress – with combination treatments needed to rescue a cell cycle checkpoint [4]. Increased contractility has the opposite effect, and stiff tumors with softened nuclei indeed exhibit increased nuclear curvature, more frequent nuclear rupture, and excess DNA damage. Normal differentiation processes of myogenesis and osteogenesis are also affected by migration through constricting pores, suggesting general effects on cell fates [6]. Mis-repair of DNA is further suggested by two cancer lines that, after constricted migration, exhibit greater genome variation [1,3]. References: [1] Y Xia, … DE Discher. Nuclear rupture at sites of high curvature

2:00 PM *SB09.09.02/SB06.11.02
The Dynamic and Reciprocal Relationship between Tissue Tension and Pro Tumor Immunity Valerie Weaver; University of California, San Francisco, United States

Tumors show increased tissue level forces and a present with a chronically stiffened extracellular matrix (ECM), and transformed cells exhibit a perturbed oncogene-stimulated and ECM-tuned mechanophenotype. We have been studying how these aberrant cell and tissue level forces promote malignant transformation and drive tumor metastasis, and how they modulate tumor recurrence and treatment resistance in breast and pancreatic cancer and glioblastoma. We use two and three dimensional culture models with tuned extracellular matrix stiffness, as well as transgenic and syngeneic mouse models, human PDX models and human biospecimens, in which ECM crosslinking and stiffness and integrin mechanosignaling can be quantified and modified. Our studies have thus far revealed that the ECM in all tumors is progressively remodeled and stiffened by stromal fibroblasts and that this occurs prior to malignant transformation. We determined that ECM remodeling and stiffening is mediated very early during malignancy by stromal fibroblasts that are activated by factors including TGFβ that are secreted by infiltrating pro inflammatory macrophages. The stromal-fibroblast stiffened ECM disrupts tissue organization, promotes cell growth and survival and drives cell invasion. A chronically stiffened tissue stroma drives angiogenesis, and activates STAT3 to induce key cytokines and chemokines that promote pro-tumor immunity to foster tumor growth and dissemination and impede tumor treatment. The stiffened ECM also drives an epithelial to mesenchymal transition and primes the metastatic niche to foster metastasis. I will discuss the dynamic and reciprocal interplay between tissue tension and innate and acquired immunity and how this can not only force tumor aggression and metastasis but may also initiate tumor progression.

2:30 PM BREAK

3:30 PM *SB09.09.03/SB06.11.03
Biosynthetic Hydrogels for Islet Engraftment and Immune Acceptance Andres Garcia; Georgia Institute of Technology, United States

Hydrogels, highly hydrated cross-linked polymer networks, have emerged as powerful synthetic analogs of extracellular matrices for basic cell studies as well as promising biomaterials for regenerative medicine applications. A critical advantage of these synthetic matrices over natural networks is that the biophysical and biochemical properties of the material can be tuned with high control and precision. For example, bioactive functionalities, such as cell adhesive sequences and growth factors, can be incorporated in precise densities. We have engineered poly(ethylene glycol) [PEG]-maleimide hydrogels that support improved pancreatic islet engraftment, vascularization and function in diabetic models. Two biomaterial strategies will be discussed. We have developed proteolytically degradable synthetic hydrogels, functionalized with vasculogenic factors, engineered to deliver islet grafts to extrahepatic transplant sites via in situ gelation. These hydrogels induce differences in vascularization and innate immune responses among subcutaneous, small bowel mesentery, and epididymal fat pad transplant sites with improved vascularization and reduced inflammation at the epididymal fat pad site. This biomaterial-based strategy improves the survival, engraftment, and function of a single pancreatic donor islet mass graft compared to the current clinical intraportal delivery technique. In a second application, we have developed a localized immunomodulation strategy using hydrogels presenting an apoptotic form of Fas ligand (SA-FasL) that results in prolonged survival of allogeneic islet grafts in diabetic mice. A short course of rapamycin treatment boosts the immunomodulatory efficacy of SA-FasL-hydrogels, resulting in acceptance and function of allografts over 200 days. Survivors generate normal systemic responses to donor antigens, implying immune privilege of the graft, and have increased T-regulatory cells in the graft. Current studies focus on evaluating this immunomodulatory strategy in a large animal model of type 1 diabetes. This localized immunomodulatory biomaterial-enabled approach may provide an alternative to chronic immunosuppression for clinical islet transplantation.
4:00 PM *SB09.09.04/SB06.11.04
Viscoelasticity and Cancer David J. Mooney; Harvard University, United States

It has long been recognized that tissue mechanical properties are altered in cancer, and this can serve as the basis for early diagnosis. While the impact of changes in tissue stiffness has been the focus of research to date, the role of tissue viscoelasticity has not been widely explored. We have developed hydrogels which allow for independent control over elastic moduli and stress relaxation/creep, and can mimic the fibrillar architecture of native collagenous matrices. These material systems are being utilized in 3D cell culture models of cancer and immunotherapy, and demonstrate that the gene expression of various cell types present in tumors, including cancer cells, mesenchymal cells, and immune cells is profoundly impacted by the viscoelastic properties of their matrix.

4:30 PM SB09.09.05/SB06.11.05
Integrin-Specific Hydrogels Direct Mesenchymal Stem Cell Immunomodulation and Bone Regeneration
Karen E. Martin1, Amy Y. Clark1, José R. García1, Christopher T. Johnson1,2, Hannah S. Theriault1, Woojin M. Han1, Dennis W. Zhou1, Edward Botchwey1,2 and Andres Garcia1; 1Georgia Tech, United States; 2Emory University, United States

Mesenchymal stem cells (MSCs) are a promising cell source for regenerative medicine applications due to their ability to self-renew, capacity for multipotent differentiation and secretion of a diverse array of cytokines and growth factors (the MSC secretome). These cells are frequently utilized in conjunction with biomaterial scaffolds designed to encourage cellular retention and direct the cells’ regenerative properties. However, hydrogel carriers have not yet yielded significant results in the clinic in part due to a lack of understanding of how hydrogel biophysical and biochemical properties impact cellular function. Although many synthetic hydrogels incorporate short peptides (e.g. RGD) to support integrin-mediated cell adhesion, the impact of hydrogel adhesive properties on transplanted cell function remains unknown.

We engineered integrin-specific hydrogels for the delivery of MSCs by tethering either the ubiquitous RGD cell adhesion motif or the type-1 collagen derived GFOGER adhesion motif into synthetic poly(ethylene) glycol (PEG)-based hydrogels. Integrin-specificity was confirmed using blocking antibodies and a custom spinning disk platform in which cells attached to hydrogel disks are exposed to well-defined hydrodynamic shear forces allowing for sensitive measurements of the force required to detach the cell from the substrate. The effects of integrin-specific adhesive peptide presentation on MSC secretome and MSC-macrophage interactions were evaluated in vitro using Luminex multiplex technology. Finally, integrin-specific hydrogel directed MSC bone tissue regeneration was assessed over the course of 8 weeks in a critical size radial bone defect in an NSG mouse model.

Spinning disk analysis shows that cell adhesion to hydrogels presenting the adhesive peptides RGD and GFOGER are specific to αvβ3/β1 and α2 integrins respectively. Luminex data shows that the secretome of MSCs encapsulated in integrin-specific hydrogels cluster distinctly based on peptide and secretion of IL-6, IL-8, and VEGF is increased in GFOGER functionalized gels compared to RGD and non-adhesive controls. Further, in a co-culture assay, we show that macrophage cytokine secretion is differentially modulated by MSCs encapsulated in integrin-specific hydrogels, including an increase in IL-10 secretion by macrophages interacting with GFOGER encapsulated MSCs. Finally, MSCs delivered in GFOGER functionalized hydrogels significantly enhance repair of critical size bone defects in vivo compared to RGD and non-adhesive controls. Taken together, our results demonstrate that integrin specificity can be engineered into synthetic hydrogel systems resulting in modulation of the MSC secretome, differential MSC-macrophage interactions and improved tissue healing.

4:45 PM SB09.09.06/SB06.11.06
Designing Biomaterial Vaccines to Generate Tumor-Specific Immunotherapy
Nisarg Shah1,2, Alexander Najibi1, Angelo Mao1, Ting-Yu Shih1 and David J. Mooney1; 1Harvard University, United States; 2University of California, San Diego, United States

Acute myeloid leukemia (AML) is a malignancy of hematopoietic origin with limited therapeutic options. The standard-of-care cyto-reductive chemotherapy can rapidly induce an apparent remission but relapse occurs in the
majority of patients, highlighting the difficulty in eradicating all AML cells. A highly immunosuppressive AML microenvironment in the bone marrow and a paucity of suitable cell surface immunotherapy targets on AML cells precludes the induction of an effective endogenous adaptive immune response, which contributes to disease relapse. AML cells generally have a relatively low mutational load, are weak stimulators of host immune cells and often possess mechanisms that prevent induction of an effector T cell response. However, the anthracyclines used for treating AML induce cell death and promote dendritic cell (DC) cross-priming of tumor-associated antigens for T cell by the release of damage-associated molecular patterns. This effect is broadly associated with stimulating an antitumor T cell immune response and may partially contribute to the efficacy of the treatment. The susceptibility of AML to effector T cells is supported by the finding that AML, like many other types of cancer cells, displays tumor antigens that have the potential to trigger immune responses. Therefore, therapeutic vaccines have the potential of achieving a lasting AML-specific immune response capable of eradicating the residual disease that remains following chemotherapy. The development of cancer vaccines requires T cell activation resulting from effective presentation of one or more tumor antigens in the context of co-stimulation. To promote a robust and durable immune-response against AML, we developed a biomaterial-based vaccine which provided a sustained release of GM-CSF to concentrate dendritic cells (DCs), TLR agonist CpG-ODN and one or more leukemia antigens in the form of a peptide antigen, cell lysates or sourced from in vivo recruited AML cells. The vaccine induced local cell infiltration and activated DCs to evoke a potent anti-AML immune response. Prophylactic vaccination alone prevented the engraftment of AML cells. Moreover, mice were able to overcome a re-challenge, indicating the potential of these vaccines to establish a long-term immunity. Combining induction chemotherapy (iCt) and the biomaterial vaccine maximized efficacy to eradicate established disease, even without exogenous delivery of a defined vaccine antigen. We found that by recruiting DCs and sustaining their activation in an otherwise immunosuppressive AML environment, the biomaterial vaccine can harness a broad range of tumor antigens arising from chemotherapy-induced AML cell death, including those not delivered through the vaccine. Furthermore, iCt in combination with the biomaterial vaccine transiently decreased bone marrow FoxP3+CD25+ Tregs and enhanced tumor-specific T cells. The CD8+ T cell/Treg ratio was higher in the bone marrow of mice treated with iCt and the antigen-free vaccine, compared to the antigen-free vaccine alone. The combination treatment depleted AML cells and generated durable long-term effector T cell responses, and immunized transplanted mice against AML. The biomaterial vaccine treatment was well-tolerated and promoted AML rejection without the indication of pancytopenia or autoimmunity in the studies. Our findings suggest that induction of a potent anti-AML immune response in such a setting might prevent the life-threatening evolution of this disease. In contrast to neoantigen-based vaccination, a scaffold generating tumor specific immune responses in situ can be an off-the-shelf approach for treating patients post-iCt. The results from this experimental mouse model of AML demonstrate the capacity of a biomaterial-based vaccination approach to induce a potent immune response to deplete AML and prevent relapse.
SESSION SB10.01: Smart Textiles  
Session Chairs: Beatrice Fraboni, Alon Gorodetsky, Esma Ismailova and Martin Kaltenbrunner  
Monday Morning, December 2, 2019  
Hynes, Level 3, Room 300

8:30 AM *SB10.01.01  
Smart Textiles for Next-Generation User Interface Solutions Michael Haller¹, Martin Kaltenbrunner², Roland Aigner¹, Sara Mlakar¹, Patrick Parzer¹, Andreas Pointner¹, Thomas Preindl¹ and Reinhard Schwoediauer²; ¹Media Interaction Lab, Austria; ²Johannes Kepler Universität Linz, Austria

The beginning of the 1990s marked the dawn of research into smart textiles. At this time, Mark Weiser and his colleagues at Xerox PARC introduced their vision of a computational environment embedded seamlessly into our lives. The vision of Ubiquitous Computing proposed a world in which “computers disappear into our everyday environments and weave themselves into our daily lives without being noticed”. While smart textiles were initially mainly influenced by the military and existing wearable technologies, consumer and healthcare markets have since become major driving forces. Today, textiles make up an essential and indispensable part of our daily lives. Since they are generally lightweight and highly flexible, they are applicable in a wide range of applications. In combination with electronic components, textiles can be enhanced with several additional capabilities ranging from sensing and actuation to lighting and information display. This opens the door to many novel application areas. As stated by Ivan Poupyrev, the leader of the Project Jacquard team at Google, “if you can hide or weave interactivity and input devices into the materials, that will be the first step to making computers and computing invisibly integrated into objects, materials and clothing”.

Within the project TextileUX, we aim to take the next step in realizing Mark Weiser’s vision. We strongly believe that smart textiles can thoroughly augment any object and provide new and exciting features that are difficult or impossible to realize with other solutions. The goal is to create an interactive textile sensor capable of sensing touch gestures and deformation input in real-time. The underlying principle is similar to a Force Sensing Resistor (FSR) that has been used for over thirty years. A typical FSR device is a continuous electrical switch whose electric conductance gradually increases as external force is applied. In one common configuration, two conductors are placed into mutual contact via a semi-conductive material. Most of these sensors, though common, generally detect only a single touch. Resistive array-based multi-touch sensors have a flat form factor, are inherently inexpensive, use little power, and can continuously measure applied force. Researchers have transferred this basic principle into the field of pressure-sensitive fabrics in the form of textile materials that include an array of vertical and horizontal conductors separated by a semi-conductive layer. We reduce the layer stack to one single layer by transferring the same pressure-sensing principle right into the yarn itself. Our novel yarn comprises a conductive metallic thread with a resistive coating consisting of an organic polymer solution containing conductive carbon-based particles. Once an external force is applied to the resistive yarn, the coating gets compressed, which increases the density of conductive particles in the coating and corresponds to a change in resistance of the coating. In the case where two coated yarns overlap each other, the change in resistance can be measured by applying voltage to one yarn and measuring the voltage drop across the other one. The same principle can also be achieved by overlapping a resistive-coated yarn with an off-the-shelf conductive yarn. This simple principle opens up a wide array of possibilities for the design of interactive textiles.

9:00 AM SB10.01.02  
Flexible Magnetoelectronics for Interactive Wearables Gilbert Santiago Canon Bermudez and Denys Makarov; Helmholtz-Zentrum Dresden-Rossendorf e.V., Germany

The recent rapid advance and eagerness of portable consumer electronics stimulate the development of functional elements towards being lightweight, flexible, and wearable. Next generation flexible appliances aim to become fully autonomous and will require ultra-thin and flexible navigation modules, body tracking and relative position monitoring systems. Key building blocks of navigation and position tracking devices are magnetic field sensors. Although there is a remarkable progress in the field of shapeable magnetoelectronics [1], there is no technology available that can enable sensitivities to geomagnetic fields of 50 µT and, ultimately, magnetic fields of smaller than 1 µT in a mechanically compliant form factor. If available, these devices would contribute greatly to the realization of high-performance on-skin interactive electronics [2-5] and point of care applications [6,7]. Here, we will present technological platforms allowing to realize not only mechanically imperceptible electronic
skins, which enable perception of the geomagnetic field (e-skin compasses) [8], but also enable sensitivities down to ultra-small fields of sub-50 nT [9]. We demonstrate that e-skin compasses allow humans to orient with respect to earth’s magnetic field ubiquitously. Furthermore, biomagnetic orientation enables novel interactive devices for virtual and augmented reality applications. We showcase this by realizing touchless control of virtual units in a game engine using omnidirectional magneto-sensitive skins.


9:15 AM  SB10.01.03
Foundation for Textile Electronics—Self-Patterned Fibers Mehmet Kanik, Michael Tarkanian, Sirma Orguc, Anantha Chandrakasan and Polina Anikeeva; Massachusetts Institute of Technology, United States

Stable and reliable textile electronics require precise tools for the integration of active electronic components. Most printed circuit boards are manufactured using hard materials such as metals, glasses, and semiconductors, which often fail to provide a flexible foundation for textile applications. Polymer-based fibers, which exhibit flexible mechanical properties provide a promising alternative material choice for flexible electronics. Electronic textiles produced from multimaterial fibers could be designed to integrate multiple functionalities while providing the required mechanical stability owed to built-in packaging and insulation. Electronic fabrics based on such fibers can further be integrated into apparel or used for medical or situational monitoring.

As a flexible analog to a breadboard, we demonstrate self-patterned planar fiber structures with push-in electrical connectors. Self-patterned fibers contain 24 to 1000 electrodes (5 µm in thickness), for straightforward assembly of on-fiber electronics. While the thickness of these self-patterned fibers is < 50 µm, they can be drawn as long as 500 meters. The patterns along the fiber can be engineered prior to fiber drawing of the macroscopic preform using conventional machining. After deposition of the electrodes on the self-patterned preform, the fibers can be cut to various lengths and stacked to create complex electronic circuits or used as a continuous fiber-electronic board. In addition, the design allows the integration of on-chip connectors similar to USB ports. The electrodes on the self-patterned fiber can be thermally deposited metals (Au, Pt or TiN), and the impedance can be optimized by tuning the metal thickness. After surface mounted electronic components have been placed onto the fiber circuits, these devices can be encapsulated by depositing high-density dielectrics and parylene C or polymeric coatings. Such fibers are expected to find a broad range of applications in textile electronics, sensors, and structural health monitoring.

9:30 AM BREAK

10:00 AM *SB10.01.04
Tailoring Multi-Scalar Material Behavior for Sensorimotor Movements and Social Interactions Sean Ahlquist; University of Michigan, United States

The design and control over bespoke means of advanced manufacturing has become ubiquitous within the field of architecture. A designer’s proficiency in orchestrating the means of production, through crafting design-specific fabrication techniques, links directly to the level of technical specificity that is possible for the assembly, form and responsivity of an architectural system. In the most experimental cases, this approach is deployed in order to finely tailor the ambient relationships between the architectural system and its environment – embedding responsivity to atmospheric factors such as light, temperature and humidity. The on-going research discussed here, titled Social Sensory Architectures, looks to further such access to advanced manufacturing by exploring the influences of architectural environment on human behavior. Particularly, the research addresses architecture’s imposition on social function for individuals with the neurodevelopmental disorder of autism, where a sensorial hyper-awareness can commonly drive anxiety and maladaptive behavior.
In this research, novel uses of industrial knit manufacturing are leveraged to create sensorially-reactive architectural environments intended to access an individual’s beneficial spectrum of hyper-awareness towards sensory stimuli. The common immutability of an architectural environment poses a diminished capacity for an individual’s development due to their lack of adaptability towards stressful scenarios – typical for those with autism. Alternatively, proffering an environmental adaptability, particularly towards the tactual modes of stimulation, creates the potential for enhancement of learning, motor and social outcomes. This is done so through tailoring degrees of elasticity across the entire hierarchy of constitutive properties for a manufactured knit textile – fiber, stitch, pattern, interface and structure. As part of a tent-like assembly, which affords a macro-scale degree of deformation and elasticity, the textile serves as a reactive tensile interface. Its operative nature utilizes (i) elastic filaments and the ability to straighten coiled inelastic fibers tailored for responsiveness at the scale of the hand, (ii) the conformable nature of varying stitch types to produce areas of differential pre-stress, and (iii) 3D geometry through which volumetric spatial organizations emerge and manage loading at the scale of the body.

Two key capacities were exhibited: (i) the adaptiveness of the responsive environment towards a diversity of sensorial interests across the neurodiverse population that was observed, and (ii) a sustained interest in the exploration, practice and mastery of new movement behaviors allowing for generalization beyond the specific site in which it was mastered. This unfurls the overarching potential for the research, in providing a template for exploration, practice and mastery of new movement behaviors allowing for generalization beyond the specific site in scales of movement patterns taking place across the entirety of the environment.

For those with autism, the development of motor skills is commonly delayed and the ability to engage in physical activities increasingly limited with age. The acquisition of motor skills on the same timetable as with peers is critical to social engagement, particularly when centered around play. This linkage between sensorimotor and social behaviors is core to this research, enabling individuals to shape patterns of tactile, proprioceptive and vestibular movement. Through field studies with the sensory-responsive environments, in venues with elementary-age children such as schools, science museums and specialized therapy centers, observational data showed such variability in scales of movement patterns taking place across the entirety of the environment.

Two key capacities were exhibited: (i) the adaptiveness of the responsive environment towards a diversity of sensorial interests across the neurodiverse population that was observed, and (ii) a sustained interest in the exploration, practice and mastery of new movement behaviors allowing for generalization beyond the specific site in which it was mastered. This unfurls the overarching potential for the research, in providing a template for sensorimotor accommodations necessary within more normative architectural conditions. To afford social opportunity within the responsive environment enables the acquisition of the critical adaptive behaviors that allow for more successful engagement in adjacent environments and activities – ones that pose more inflexible sensory and social demands.

10:30 AM SB10.01.05
Wearable Textile Platform for Selective Sensing in Healthcare Luca Possanzini, Isacco Gualandi, Marta Tessarolo, Federica Mariani, Erika Scavetta, Francesco Decataldo and Beatrice Fraboni; Bologna University, Italy

Nowadays, the ubiquity of smart technologies and wireless communication networks is stimulating the development of sensing systems able to continuously monitor the human health state and physiological parameters. Local point-of-care medical units or monitoring systems for athletic training performance are two possible examples that would directly profit from such a technology. The crucial bottleneck to establish robust wireless biological sensor networks is the development of new transducer materials capable to effectively convert the biological event (for example concentration changes of chemical markers or a bioelectronic current) into the electronic domain. Semiconducting polymers, such as PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate)) are widely employed in bioelectronic and biosensing applications as they combine two main advantages: (i) they offer electronic as well as ionic conductivity; (ii) they exhibit excellent bio-compatibility and good mechanical properties.

Here, we report a new fully textile biosensing platform that can be directly integrated into fabric, for continuous monitoring of ion chloride concentration and the pH value in biofluids, such as sweat, thus limiting the invasiveness for the wearer. Human sweat contains abundant information about a person’s health status and representing an excellent biofluid for portable, non-invasive chemo-sensing. For instance, chloride content is a precious index for hydration status as well as a consolidated hallmark in newborns diagnosis of cystic fibrosis, while sweat pH is related to hormonal unbalance and lactic acid secretion during physical activity. Our platform consists of PEDOT:PSS-coated threads whose functionalization determines their selective sensing. The ion chloride thread sensor exploits Ag/AgCl nanoparticles that act as a gate electrode embedded into the conductive polymer channel, thus combining an intrinsically amplified response with a simple two terminal electrical connection [1]. The sensor is validated in standard electrolytes and in artificial sweat showing high sensitivity and selectivity demonstrating the reliability of our device.

On the other hand, we synthesize a pH-sensitive composite of PEDOT doped with pH dye Bromothymol Blue to convert pH variation into an electrical signal. The simple two terminal thread sensor gives results similar to the one
observed for the devices fabricated onto planar substrates, providing the proof of principle for a wire-shaped sensor that can be easily sewed on clothes for monitoring pH level in sweat.

In conclusion, we demonstrate selective and real-time monitoring of bioanalytes in artificial sweat, validating the implementation of our biosensors in a fully textile electronic device. This approach paves the way for a new generation of smart wearable sensors for medical point of care, effectively fabricated onto non-conventional substrates, such as textiles or single fibres.


10:45 AM SB10.01.06
Advanced Textile-Based Hybrid Energy Harvesting/Storage System Lu Yin, Jian Lyu and Joseph Wang; University of California, San Diego, United States

Next generation wearable electronics hinges on the development and integration of emerging technologies that can further advance the functionality, user comfort and runtime of devices. Flexibility, conformity and stretchability are commonly addressed in individual textile-based electrochemical devices such as sensors, supercapacitors and batteries, but few works has been reported on the device-level integration of electrochemical energy harvesters and energy storage units. Addressing this issue, we report for the first time of a device-level energy-harvesting and energy-storage hybrid system based on textile-based flexible and stretchable wearable biofuel cells and supercapacitors. The reported all-in-one epidermal device can harvest energy from enzymatic reaction fueled by the abundant lactate from human perspiration. Furthermore, the energy is directly stored into capacitive/pseudocapacitive materials to deliver enhanced and stable output over long period of time. Simple, low-cost and high-throughput screen-printing fabrication is used to deposit customized, screen-printable and stretchable ink composites that exhibit outstanding stability under rigorous mechanical deformations. The continued development of such integrated wearable energy system represents a vital step towards self-powered wearable electronics for healthcare, fitness, security and environmental monitoring applications.

11:00 AM *SB10.01.07
Rubbery Electronics - Electronics Fully Made out of Rubber Materials Cunjiang Yu; University of Houston, United States

Owing to the merits of mechanical softness and stretchability, stretchable electronics holds promise in many applications including health monitors, medical implants, artificial skins and human-machine interfaces. In general, electronic materials, especially semiconductors, are non-stretchable. Structural designs with special mechanical architectures have been widely adopted to enable the stretchability in those materials. An alternative route to eliminating the burden of constructing dedicated architectures and the associated sophisticated fabrication processes is to build stretchable electronics from rubbery electronic materials, which have potential toward scalable manufacturing, coherent material and device integration, and large-strain tolerance. Here, I would like to present our recent progress on developing rubbery electronics fully made out from intrinsically stretchable, rubbery composite materials of semiconductors and conductors, which can be scalably manufactured from common and commercial available materials without dedicated and complicated synthesis. Specifically, we build nanofibril organic semiconductor and metallic nanowires percolated in the elastomeric polymer matrix in a composite format for the rubbery semiconductors and conductors, respectively. Employing these rubbery electronic materials, we have achieved fully rubber format devices, including transistors and sensors, logic gates, active matrices, and elastic sensory skin systems etc. The rubbery stretchable electronics holds a wide range of applications, such as artificial skins, biomedical implants, and wearable applications.
1:30 PM *SB10.02.01
Materials and Processing in E-Textiles: Challenges to Marketplace Jesse S. Jur, Amanda C. Myers, Inhwan Kim, Braden M. Li, Elizabeth Cobarrubias, Caitlin Knowles and Boemjun Ju; North Carolina State University, United States

Strategies for the selection of materials and manufacturing overwhelmingly dictate e-textile product cost and acceptance into a specific marketplace. Challenges are presented due to the uncertainty in materials selection and then the subsequent need to matching that material within a process to manufacture, which often results in delays in the product development cycle. The goal of this presentation is to outline current best practices and future advancements in materials and manufacturing of e-textiles. From a materials perspective, particular focus will be made on yarn-level design and use of printing strategies, which allow for ‘in process’ formation of e-textile systems. The implication on materials selection and the impact on fabric formation processes will be made based on traditional cut and sew strategies and the evolving whole garment as well as flatbed knitting techniques. Finally, testing strategies will be reviewed for understanding the e-textile at the component and system levels. The future prospective toward more complex e-textile systems will be presented.

2:00 PM SB10.02.02
Coaxial Electrospinning of Core-Shell PEDOT:PSS – PVP Nanofibers Doped with Different Solvents and PbS Quantum Dots for Optoelectronic Applications Domingo Ixcoatl Garcia Gutierrez, Maria I. Mendoza-Diaz and Diana F. Garcia-Gutierrez; Universidad Autonoma de Nuevo Leon, Mexico

Conductive polymers (CPs) display an exceptional set of electrical and optical properties, which in many cases can be tuned to mimic those of inorganic semiconductors and/or metals. Therefore, they have found numerous applications in different technological arenas, such as transparent and flexible conductors in optoelectronics, and as biomaterials, biosensors and tissue engineering substrates in biomedical applications. The fabrication of CPs nanostructures has been investigated comprehensively in recent years, in particular the synthesis of CPs in the form of nanofibers. Unfortunately, producing nanofibers of such CPs has been a challenge faced by several research groups due to the rigid backbone they display. Coaxial electrospinning has been reported as one of the possible approaches that allow the formation of CPs nanofibers. Additionally, recent studies have reported that doping the CPs with certain solvents can improve their charge carriers transport properties; moreover, recent reports have indicated that the addition of metallic and semiconductor nanoparticles into CPs thin films and nanofibers not only improves the electrical charge transport properties of the composite nanofibers, but also bestows on them the property of photocurrent generation when illuminated with the proper light source. In the present study core-shell PEDOT:PSS – PVP nanofibers were synthesized by coaxial electrospinning. These fibers were doped with different solvents (dimethylsulphoxide, isopropyl alcohol, and ethylene glycol) and PbS nanoparticles at different concentrations; additionally, the coaxial electrospinning setup process was inverted in order to exchange the phases comprising the core-shell morphology. The synthesized samples displayed an increment in the conductance of the composite nanofibers, based on a more conjugated structure of the PEDOT:PSS phase, and a better dispersion of the PbS nanoparticles within the nanofibers; this increment was, under certain synthesis conditions, up to three orders of magnitude higher than in the case of the nanofibers with no solvent, nor nanoparticles, added. Photoresponse also showed a clear increment in the value of the photogenerated current as the concentration of the nanoparticles increased. Inverting the arrangement of the core-shell phases in the nanofibers increased the conductance and the photogenerated current in the cases analyzed. These results show novel evidence on the capability of tuning the conductance and photoresponse of composite core-shell nanofibers, based on the doping of the PEDOT:PSS phase with different solvents and PbS nanoparticles, and the arrangement of the core-shell phases.

2:15 PM SB10.02.03
A Cephalopod-Inspired Thermoregulatory Material for Clothing Erica Leung; University of California, Irvine, United States

Abstract not available.

2:30 PM *SB10.02.04
Highly Durable Elastic Conductors for Electronic Textiles Tomovuki Yokota, Hanbit Jin and Takao Someya; The University of Tokyo, Japan
In this talk, we will report recent progress of elastic conductors for electronic textile. First, we have fabricated a metal–elastomer composite with a nanofiber reinforcement. By embedding randomly aligned polymer nanofibers into a silver–fluoroelastomer composite, the elastomer matrix was reinforced and the stress was dissipated by the nanofiber scaffolds. Moreover, combined with the buckled structure, high cyclic durability against repeated stretching was achieved. As a result, a stretchable electrode made from nanofiber-reinforced elastic conductors and wrinkled structures has both excellent cyclic durability and high conductivity, and is stretchable up to 800%. The cyclic degradation (ΔR/R0) remains at 0.56 after 5000 stretching cycles (50% strain), while initial conductivity and sheet resistance are 9903 Scm$^{-1}$ and 0.047 Ωsq$^{-1}$, respectively. Finally, we demonstrated a skin-tight multimodal physiological sensing suit using a highly conductive and durable elastic conductor as electrodes and wirings. By wearing the suits, we successfully demonstrated continuous long-term monitoring of electrocardiogram, electromyogram, and motions during weight-lifting exercises without significant degradation of signal quality.

3:00 PM BREAK

3:30 PM *SB10.02.05
Flexible Elastomeric Materials and Sensors via 3D Printing Rigoberto C. Advincula; Case Western Reserve University, United States

Flexible electronics and wearable textiles are of high interest for functional devices including health monitoring and other display applications. Haptics technology enables the appreciation of functional surfaces for interfacing with the human sensory function. The use of 3D printing to create prototypes and devices from elastomeric and polymeric materials has appended the design functionality for new materials including uses in biomedical devices enabling rapid development. New opportunities for multi-materials and composites are possible. The processability and functionality of thermosets and elastomers make it a challenge to employ using most 3D printing methods for polymer additive manufacturing. This is more evident with the choices of 3D printing methodologies (fused deposition modeling - FDM, stereolithographic apparatus - SLA, selective laser sintering- SLS, and viscous solution printing - VSP) which can make use of blended or formulated compositions. We have demonstrated the 3D printing of biomedical grade thermoplastic polyurethanes (TPU), epoxy, silicones, and rubberized epoxies to demonstrate flexible and wearable objects and devices. 4D printing allows the design of new materials and applications based on integrating the chemistry of conversion with the printing mode. In this talk, we will demonstrate the fabrication of multi-materials including thermosets and thermoset elastomers with concept objects and elastomeric actuators. This is based on the use of biomedical grade TPU melts and extruded viscous solutions. Other works based on the use of SLA, SLS, FDM, towards high strength epoxy, silicones, and nanocomposite materials will be discussed.

4:00 PM SB10.02.06
Thermal Drawing of Stretchable Triboelectric Fibers for Efficient Energy Harvesting Chaoqun Dong, Andreas Leber, Tapajyoti Dasgupta, Qu Yunpeng, Tung Nguyen, Wei Yan and Fabien Sorin; École Polytechnique Fédérale de Lausanne, Switzerland

Fibers that are capable of harvesting various mechanical energy via triboelectric effect are excellent power units for wearable electronics, especially for smart textiles. However, the fabrication of highly stretchable and soft fibers for the realization of truly conformal, elastic and durable textiles with high triboelectric outputs remains still challenging. Here, a large-scale fabrication of inherently stretchable and soft triboelectric fibers with engineered architectures, for a dual function of energy harvesting and self-powered mechanical sensing, is demonstrated. We take advantage of the rheological behavior of the selected thermoplastic elastomer and employ the one-step thermal drawing process for the large-scale production of uniform triboelectric fibers (Advanced Materials 2018, 30, 1707251). The resulting fibers can sustain large strains of up to around 560% and maintain high electrical outputs, regardless of long-term extreme deformations and extended environmental exposure. By exploiting the particular attributes of the thermal drawing process, we optimized the outputs by introducing textured pattern to the triboelectric fiber surface (Advanced Functional Materials 2017, 27, 1605935). The versatility of this unique fiber enables its facile integration into a soft, elastic and machine-washable triboelectric textile with excellent electrical outputs of ~490 V (triggered by hand tapping), which are even higher than two-dimensional planar triboelectric nanogenerators with similar dimensions. With the drawing process being simple and scalable, it opens the possibilities for the practical implementation of self-powered multi-functional smart fibers and large-area textiles.
Photo-Actuated Fiber-Based Artificial Muscles

Mehmet Kanik, Sirma Orguc, Anantha Chandrakasan, Yoel Fink and Polina Anikeeva; Massachusetts Institute of Technology, United States

Advances in artificial muscles have demonstrated high power-to-mass ratio, work capacity, energy density, and work efficiency, challenging traditional actuators. Recently, thermally actuated fiber-based artificial muscles, capable of lifting more than 650 times their weight, have demonstrated strain programmability and the ability to transduce electrical signals in response to contraction and relaxation, similar to biological muscles. Expanding the palette of the suitable driving stimuli to include electrical, thermal, photonic, hydraulic, and pneumatic will pave way for applications of these fiber-based devices in smart textiles, implantable sensors, wearable electronics, and prosthetics.

Here, we report on a class of fiber-based artificial muscles that can be actuated by a broadband illumination with wavelengths spanning 10-400 nm. These photo-actuated artificial muscles are manufactured using thermal-drawing process, and consist of polymer bimorph structures of cyclic olefin copolymer elastomer (COCe) and carbon loaded polyethylene (CPE) as the low and high thermal expansion materials, respectively. CPE further serves as a UV absorbing material. To amplify the actuation capacity of the thermally drawn fibers, we transformed them into coiled structures via cold drawing, arriving at cross-sectional dimensions of 300×470 µm². We demonstrate the weight lifting capacity of the photo-actuated fibers using a 324 nm light emitting diode with an energy density of 1 mW/mm². Photo-actuated fiber muscles can be actuated using a single LED, potentially enabling the remotely controlled operation and further expanding the domain of utility of these miniature devices.

A Dynamic Stretchable and Self-Healable Composite Conductor Enabled Electrical Self-Boosting

Hyunseon Seo¹, Zhenan Bao² and Donghee Son¹; ¹Korea Institute of Science and Technology, Korea (the Republic of); ²Stanford University, United States

The phenomenon of self-healing, an intrinsic nature of human skin, has inspired those who focus on interdisciplinary field of biomimetics, robotics, and wearable electronics to pursue humanlike electronic skin systems that offer the opportunity to realize future healthcare and wearable robotics. Specifically, developments of intrinsically stretchable and self-healable conductors are significantly desirable for interfacing with active electronic modules with taking advantages of reliable reuse and low power consumption even after mechanical damages. However, it is still difficult to simultaneously achieve high stretchability and high conductivity and autonomous self-healability, due to limited materials strategies.

Here, we describe electrically and mechanically self-healable composite conductor with ultra-stretchability, fabricated by simply mixing conducting nano-/micro-materials (Ag flakes) with a tough self-healing polymer (SHP, PDMS-4,4’-methylenbis(phenyl urea) (MPU)_0.4-isophorone bisurea units (IU)0.6). The conductivity of our self-healable composite conductor is as high as 1137 S cm⁻¹ even under 3500% tensile strain, and more interestingly, it gradually increased to 3086 S cm⁻¹ over 60 hrs under 3500% strain. Such unprecedented phenomenon, termed “electrical self-boosting”, result from a synergy effect: an efficient strain energy dissipation of SHP and self-alignment and rearrangement of Ag flakes with spontaneously assembled AgNPs in response to dynamic nature of the strained polymer matrix. This dynamic behaviors of Ag flakes-AgNPs in a stretch mode is confirmed by using micro computed tomography (μ-CT), in-situ scanning electron microscope (SEM), and transmission electron microscope (TEM).

Furthermore, we found that a double-layered conducting structure formed using a self-bonding process shows extremely reliable stretching endurance performances over 1000 cycles at 50% strain owing to its homogeneous conducting interface located on the neutral mechanical plane. Finally, we successfully demonstrated that electromyogram (EMG) signals can be measured in real-time by a flexible wireless bio-integrated system using our conductor and transmitted to a prosthetic robot hand to control various hand motions after making a complete cut and self-healing. Our dynamic stretchable and self-healable composite conductor is highly applicable to the robust interactive human-machine interfaces.

Highly Elastic Conductive Polyamide/Lycra Fabric Treated with PEDOT:PSS and Polyurethane

Desalegn Alemu Mengistie¹,², Melkie G. Tadesse³,⁴, Yan Chen⁵, Lichuan Wang⁶, Carmen Loghin⁷ and Vincent Nierstrasz²; ¹Chalmers University of Technology, Sweden; ²California Polytechnic State University, San Luis Obispo, United States

4:45 PM SB10.02.09

Highly Elastic Conductive Polyamide/Lycra Fabric Treated with PEDOT:PSS and Polyurethane

Desalegn Alemu Mengistie¹,², Melkie G. Tadesse³,⁴, Yan Chen⁵, Lichuan Wang⁶, Carmen Loghin⁷ and Vincent Nierstrasz²; ¹Chalmers University of Technology, Sweden; ²California Polytechnic State University, San Luis Obispo, United States
Conductive elastic fabrics are desirable in wearable electronics and related applications. Here, we report a highly elastic conductive polyamide/lycra knitted fabric using intrinsically conductive polymer poly (3, 4-ethylenedioxythiophene) (PEDOT) blended with polyelectrolyte poly (styrene sulfonate) (PSS) by easily scalable coating and immersion methods. We investigated the effects of these two methods of treatments on uniformity, electromechanical property, stretchability, and durability. Different grades of waterborne polyurethanes (PU) were employed in different concentrations to improve the coating and adhesion of the PEDOT:PSS on the fabric. The immersion method gave better uniform treatment, higher conductivity, and durability against stretching and cyclic stretching than the coating method. The surface resistance increased from ~1.7 and ~6.4 Ω/sq at 0% PU to ~3.7 and ~12.6 Ω/sq at 50% PU for immersion and coating methods, respectively. The treatment methods as well as the acidic PEDOT:PSS did not affect the mechanical properties of the fabric and the fabric showed high strain at break of ~650% and remain conductive until break. The resistance increased only by a small amount when samples were stretched for 10 cycles at 100% strain and the samples show good durability against 10 domestic laundry washing cycles.

SESSION SB10.03: Poster Session I: Electronic Textiles I
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB10.03.01
3D Braided Textile Structures as Low Cost Microfluidic Platforms for Electrophoretic Separation of Chemical and Biological Analytes Jawairia U. Khan1,2,3, Sepidar Sayyar1,2, Brett Paull4,2 and Peter Innis1,2;
1University of Wollongong, Australia; 2ACES, ARC Centre of Excellence in Electromaterials Science, Australia; 3University of Agriculture, Pakistan; 4University of Tasmania, Australia

In recent decades, microfluidics has emerged as a game changer in the field of clinical diagnostics. These in-situ, on-site microfluidic portable devices have a great potential to substitute traditional analytical labs. However, the complex fabrication techniques (photolithography, etching and printing) used to make microchannels, as well as complex pumping system to drive fluids, are a potential barrier for the development of practical microfluidic devices. In a simpler approach, textile substrates (in the form of fibres, yarns or fabric) which have an inherent ability to create microchannels and wicking properties that facilitate fluid movement provides the potential for a far simpler approach than the microfluidic chip. In this work multi-yarn textile assemblies, that are either knitted or braided, have been investigated as a potential electrofluidics separation platforms. These provide an open surface accessible separation platform, which contrast conventional closed glass capillaries or chips, where direct access to sample zone during separation is nearly impossible. In this work, braided structures made from a range of commercially available fibers have been investigated for; the electrophoretic separation of different analytes through capillary zone electrophoresis; the preconcentration of analyte through Isotachophoresis and selective delivery of analyte through their transport and separation in bifurcated and trifurcated braided structures. This channelled textile platform can be successfully used for the separation of complex mixtures of chemical and biological samples. The developed technology will provide significant new inverted-microfluidic capabilities in bioanalysis, proteomics and rapid clinical diagnostics.

SB10.03.02
All Textile-Based Tactile Pressure Sensor Array Kuni Takei1,2, Satoko Honda1, Takayuki Arie1 and Seiji Akita1;
1Osaka Prefecture University, Japan; 2JST PRESTO, Japan

Macroscale, flexible electronics are now of great interests in the human-interactive application. In fact, low-cost device fabrications such as printing technique have been proposed. For the practical applications as human-interaction devices, reliability and washability as well as economic fabrication method are key parameters. However,
most of reports have not covered all important requirements due to difficulties to fabricate the devices. To address this challenge, we demonstrate textile-based tactile pressure sensor sheet with high reliability and washability as well as the sensitivity and threshold pressure analyses. To simplify the fabrication method and structure, Ag threads or printed conductive polymer (PEDOT:PSS) are used for the resistive sensing materials.

Ag thread and standard thread were sewn in the two linen textiles by using a commercial sewing machine. After sewing the threads, a mesh sheet was sandwiched by the linen sheets. For the electrical connection between the textile sensors and measurement equipment, Ag coated Velcro strap was used. One side of the Velcro strap was sewn on the linen sheets using the Ag thread continued with the sensor area. Another side of Velcro strap was sewn on a PET film, where Ag electrodes were screen-printed. Using this Velcro strap, textile sensor sheet and read-out circuit can be readily connected and disconnected, which allows it to wash the sensor sheets without having special water-proof coating over the equipment. For the sensing mechanism, by applying tactile pressure, Ag threads are contacted through the mesh holes. After contacting the electrodes, then contact resistance changes as a function of applied pressure due to rough surface of Ag thread.

Mesh thickness and diameter size dependences for the pressure sensor were characterized to control the detectable tactile pressure range. Detectable threshold pressure was varied from 1 kPa to 1 MPa depending on the number of mesh sheets (i.e. thickness: 1 – 5 sheets) and diameter (0.5 – 3.0 mm) of mesh. This indicates that this can detect the pressure difference by monitoring the resistance change, and the threshold pressure can be tuned by mesh sheet thickness and diameter of mesh size. It is also confirmed that real-time pressure can be measured with relative fast response less than 0.5 s.

Next, reliability and washability were analyzed. The results indicate the limitation of repeatable measurement cycles. Depending on the applied pressure, this limitation is varied. However, it is found that the limitation can be estimated with line fitting of the results. For human body pressure monitoring on a bed, the pressure distribution is ~5 kPa. For this body pressure monitoring, the sensor sheet shows high reliability >250,000 cycles. Without using any water-proof coating or packaging, this sensor sheet can be washable using a standard washing machine with detergent. Output resistance does not change even after 2 times washing processes.

Finally, as proof-of-concepts, real-time monitoring of derriere and foot pressure distributions and respiration were conducted by placing the sheet under body. Based on the results, this simple device structure can be used for the tactile pressure sensor sheet with high reliability and washability.

This study proposes the high reliable and washable tactile pressure sensor textiles. We confirmed that this platform can be used for the pressure distribution monitoring including respiration.
Textile electronics are increasingly becoming an important field of research. One of the key features of smart textiles is the ability to control core body temperature in different weather conditions. Particularly, the idea of battling cold weather conditions using self-heated textile is intriguing. It can be done in for various applications like in jackets for military personnel who fight in cold climate conditions, in hand gloves for skiers [1], for heat therapy for certain medical conditions and so on. A power supply, bus bars for sending the currents, heating elements and a carrier to assist the heating elements are needed for such heated wearable textiles [2]. Another important aspect is that the heating element needs to be flexible and stretchable since it is used in textiles. This work presents the idea of using space-filling fractal curves based heating elements in textiles. Because heating elements are based on metal coils, they are the most large-area and expensive component of a self-heating wearable. However, decreasing metal spacing or metal length in coils leads to non-uniform temperature distribution. Hence, a cost-effective and efficient heater should have uniform temperature distribution while having minimum metal consumption. The geometry of the heater plays a crucial role in its uniformity and average temperature ($T_{av}$). We modelled space-filling fractal curves as geometries for heaters and observed that they are on par with the typical double-spiral heat-pad in terms of temperature uniformity, while being cost-effective due to optimal distribution of metal. This work presents modelling of fractal curves based on Peano curve, Hilbert curve and Moore curve of different orders, as micro-heaters. To make the metal coil designs stretchable, sharp edges in the geometries were modified into smooth arcs. Further, to compare them in an efficient way, a constant power of 2 W was maintained across all the geometries and the heating elements were restricted to an area of 30 mm x 30 mm. Finite element analysis (FEA) results showed that heating elements based on Hilbert & Moore curves of order-4 and Peano curve of order-3 outperformed double-spiral heating element in terms of temperature uniformity while being cost-effective, i.e., using lesser metal coil length (all the curves were assumed to have the same metal width and thickness). Heaters based on Hilbert & Moore curves of order-4, Peano curve of order -3 were observed to have a temperature non-uniformity (%) of 4.4%, 4.3% and 2.2% respectively, whereas double-spiral had non-uniformity of 5.8%. The average temperature was lower by 10 K for Hilbert and Moore order -4 and 50 K for Peano order -3. Further, heaters one fractal order lower than these, i.e., Hilbert & Moore of order -3 and Peano of order -2, gave the same average temperature as double spiral heaters, while using only half the length of the double-spiral, thus promising significant reduction in metal consumption. Hilbert and Moore order -3, Peano order-2 were observed to have a non-uniformity of 11.7%, 11.6% and 7.24%, respectively, which makes them slightly more non-uniform compared to the double-spiral heater, but with only half the metal consumption. With many fractal patterns to choose from, space-filling fractal curves can provide very good performance heating elements for smart, self-heating textile applications.

References

SB10.03.05
Flexible Photodetector Based on Reduced Graphene Oxide Electronic Yarns Hee Yeon Yang, Hyun Joo Lee and Yong Ju Yun; Kunkuk University, Korea (the Republic of)

Graphene-based electronic textiles have recently been recognized as a promising flexible materials and devices for smart fabrics and next-generation wearable electronics due to their many advantages such as good electrical conductivity, mechanical strength, chemical stability, softness, light weight. In addition, they can be produced at low cost, easily cut, and assembled into diverse flexible substrates in various form by simple approaches such as sewing and weaving. In these reasons, a variety of wearable devices have been developed including textiles transistors, thread like solar cells, fabric type nanogenerators, yarn like chemical and physical sensors, etc. Among these devices, threat and fabric type photodetectors have gained importance for applications in biomedical imaging, environmental sensing, fire monitoring, etc. However, processing challenges for improving their poor performances and complicated fabrication process have so far precluded the realization of diverse wearable electronic devices. Here we report a facile solution strategies to fabricate the high performance graphene electronic textiles composed of reduced graphene oxide (RGO) and commercial cotton yarns by simple dipping and chemical reduction and investigate the broadest photoresponses from the ultraviolet upto the infrared in various deformations such as bending and stretching. The as-prepared RGO yarns showed good basic properties including including electrical conductivity (~1.0 S/cm) and mechanical stability (1,000 cycles), as well as a UV photoresponsivity of 1.31 mA/W.
(flat) and 1.0 mA/W (bent) and response times of 5 s/6 s (flat) and 6 s/7 s (bent). Using our high-performance RGO textiles, we successfully fabricate wearable optoelectronic systems that can be integrated with garments for continuous ultraviolet radiation.

SB10.03.06
**Stretchable Micro-Wavy Structured Cu Interconnects Fabricated by Using a Micro-Corrugation Machine and a Pre-Stretched Rubber Substrate** Shinji Okuda, Michitaka Yamamoto, Ryu Karasawa, Seiichi Takamatsu and Toshihiro Itoh; The University of Tokyo, Japan

Wearable IoT devices and sensors have been featured recently, therefore stretchable interconnects and devices are required to develop. In this research, we have developed an advanced fabrication method of stretchable interconnects that corrugated copper (Cu) foil attaches to a pre-stretched elastomer substrate. Fabricated interconnects applying our method showed >200% stretchability stably. We also applied our method to stretchable electrical circuits.

There are two types of methods to fabricate stretchable interconnects: using conducting inks such as a mixture of metal nanowires or carbon nanotubes with thermoplastic polyurethane resin (TPU) or fluorine rubber, and processing metal film into a wavy shape (vertical or horizontal wavy structure). Stretchable vertical-wavy-shaped metal interconnects are getting attractive because the conductivity is smaller by one order of magnitude to that of the above mentioned inks. Wagner et al. (2004) made stretchable thin-film conductors by metallizing a pre-stretched elastomer membrane with Au, and reported that fabricated conductors showed 10-100% stretchability. But the stretchability was unstable, that is, it varied widely in the fabricated samples. Although vertical-wavy interconnects are preferred since they can achieve high density wiring and electrical stability, vertical-wavy-structured interconnects are hard to fabricate in terms of manufacturing stability.

Thus, we propose a new method of bending a Cu film by corrugate process in advance and then attaching it on a pre-stretched substrate in order to shrink corrugated Cu foil further. The proposal method is as follows:

1. Corrugating a strip of copper (Cu) foil by a pair of gears to create vertical-wavy structure
2. Adhering the above processed Cu foil on a pre-stretched Polydimethylsiloxane (PDMS) substrate
3. Relaxing the pre-stretched PDMS substrate into its initial length to compress the vertical wavy structure
4. Covering the whole interconnect with PDMS and peeling it off

The elongation rate of a pre-stretch substrate was changed to 0, 25, 50 and 75%, and each sample was prepared. The thickness of Cu foil was 5um. The fabricated samples showed 220% stretchability in the case where pre-stretch rate was 75%, while 102% stretchability in the case where a PDMS substrate was not stretched in advance. The resistances of all samples were <1 ohm/cm and these fluctuations during stretching were ±0.1 ohm/cm.

In order to consider possibility of higher stretchability if Cu foil thickness is different from 5um, an effect of Cu foil thickness on stretchability was investigated when a PDMS substrate is not stretched beforehand. Cu foil thickness was varied from 2um to 40um. Stretchability of vertical-wavy interconnects can be predicted by measuring a wavy shape (pitch, height and angle) of corrugated Cu foil. The actual shapes of fabricated samples were measured and stretchability was predicted from prediction equations. It was assumed that the thinner Cu foil is, the larger stretchability gets because height of waves also is getting high. On the other hand, as the result of the break tests of fabricated samples, the stretchability became the highest (73%) when the thickness was 10um. The reason is considered that thinner Cu foil has not enough strength so it broke before it gets flat.

In this study, higher stretchability and lower resistivity than those of previous studies were achieved, so our fabricated interconnects can be useful as stretchable interconnects with high conductivity. Finally, we demonstrated stretchable LED circuits with our proposal technique. LEDs can be lit in the manufactured circuit with about 50% stretch. Therefore, it is assumed that our proposal technique can be applied to stretchable circuits.

SB10.03.07
**Impact of Fabric Properties on Textile Pressure Sensors Performance** Luca Possanzini, Marta Tessarolo, Enrico Campari, Laura Mazzocchetti and Beatrice Fraboni; Bologna University, Italy
In recent years, the field of wearable technology and Internet-of-Things has attracted a great attention and a large variety of sensors has been developed. Wearable electronics sensors are becoming extremely attractive for several application fields such as medical, healthcare, wellness, sport, entertainment and safety. A very promising platform to realize fully wearable and imperceptible sensors is the “smart textile” one, as fully textile physical or chemical sensors offer unique features in terms of comfort and fitting features.

In this framework, we focused our attention on developing wearable textile pressure sensors operating in a wide linear pressure range. Pressure sensors with high sensitivity in the low pressure range (<10kPa) allow touch detection, very relevant for human-computer interaction and for the development of artificial hands for handling object. Conversely, pressure sensors that operate in high pressure range (up to 100 kPa), can be used to monitor the foot pressure distribution, the hand stress during the movement of heavy weights or to evaluate the cyclist’s pressure pattern on a bicycle saddle.

In this presentation, we report on a new promising class of fully textile pressure sensors based PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate)) [1]. The sensor can be easily fabricated directly on textile fabric by processing from solution and sewing. We report and discuss the sensor working principles, investigated by comparing the effects of macroscopic to nanoscopic variation in the sensor performance [2]. We quantitatively discuss (by analyzing static and dynamic operation mode) how the mechanical properties of several fabrics and the piezoresistive properties of different ink formulations impact on the sensor response. Our results highlight the complexity of the whole system, due to the active role of multiple parameters (e.g. the fabric composition, structure, the polymer formulation, the targeted pressure range, etc.) and suggest a protocol to optimize and tune textile pressure sensors to every kind of application.

Electrically Conductive Silver/Polyimide Fabric Composites Fabricated by O2 Plasma Pretreatment and Spray-Assisted Electroless Plating

Fangbing Lin, Jinhua Jiang and Nanliang Chen; Donghua University, China

Functional flexible fabrics with both excellent electrical conductivity and high-performances are increasingly attractive in modern industries. In this study, we report a silver/polyimide fabric (Ag/PIF) composite with high conductivity, heat-resistance, mechanical and fastness properties, which is fabricated by combining an O2 plasma pretreatment and a spray-assisted electroless plating (SAELP) technique. The O2 plasma pretreatment can firstly roughen the surface of PIF, induce the oxygen functional groups on PIF and rearrange the imide groups in PIF, which results in a great improvement in the wettability of PIF. The silver nanoparticles (Ag NPs) are deposited on the plasma-treated PIF by the SAELP technique to obtain the Ag/PIF composites. The effects of O2 plasma treatment and SAELP duration on the Ag/PIF composites are investigated and discussed. The results demonstrate that the Ag NPs are coated on PIF uniformly and densely with surface resistance of 0.1 Ω/sq. The first decomposition temperature of Ag/PIF composites is up to 600 °C, indicating the excellent thermal stability of Ag/PIF composites. This work gives a new strategy for fabricating electrically conductive functional fabrics with high-performance properties.

Textile-Fiber-Array-Embedded, Stretchable Alternating-current Electroluminescent Device—Utilization of In-Plane Electric Field

Seongkyu Song and Soon Moon Jeong; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

To date, although there has been significant progress in the development of new techniques for emerging EL devices, enabling soft robots, actuators, flexible/stretchable/wearable electronics, and self-healable devices, most of these reported devices require planar electrodes with high transmittance and mechanically durable characteristics as well as stable electrical conductivity, even in the deformed state. Here, we present a textile-fiber-array–embedded flexible composite system capable of producing multiluminescence (electroluminescence (EL) and mechanoluminescence (ML)) on the application of electromechanical stimulus [1]. In our work, we embed a conducting fiber array into a mixture of PDMS and ZnS EL phosphors with parallel orientation, to act as electrodes. Because the EL is generated by the in-plane field, there is no requirement for the light to be transmitted to the electrode, thereby eliminating the requirement of high transmittance. We also found radially distributed electric/optical fields arising from the unique fiber-array configuration, which are beneficial for applications as a uniform plane light source. Furthermore, a patterned device was realized by controlling the embedding depths of fibers, utilizing the vertical and in-plane electric fields simultaneously. We believe that these results can provide a basis for the development of emerging soft display systems.


Textile Strain Sensor Knitted with Conductive Aluminum Coated Yarn, for Wearable Electronics

Junhyeok Jang, Kangmin Lee and Mijung Lee; Kookmin Univ., Korea (the Republic of)

E-textile is a representative technology used in smart clothing, which is an integrated type of fabrics with electronic components to realize wearable computers. In early stage, it was realized by attaching various kinds of electronic devices on clothes. Recently, research is active on inherently textile-like devices such as fiber transistors, piezoelectric temperature sensors, and fiber displays based on yarn-type conductive fibers.[ref] In our previous research on e-textile using conducting yarns, we have succeeded to develop the resistance switching memory devices with normal yarn, coated with aluminum using solution process, and carbon fiber.[ref] This study focuses on change of resistance at the contact between fibers along the strain, and a strain sensor was developed that can be used in smart clothing. The contacts between different yarns for the resistance change were achieved with all in one yarn, comprising aluminum coated yarns, carbon fibers and normal yarns. In this knitted textile, the resistance switching characteristics was shown as confirmed in previous studies. Then, the samples were stretched in both the horizontal and vertical directions to demonstrate a change of on / off resistance ratio. This variation of on/off ratio was verified by the physical and chemical mechanism and a dependence on the contact area was also investigated. On / off resistance ratio decreased when stretched, and restored to the ratio before stretch when the sample was recovered. This characteristic is maintained when stretching and recovery are repeated along the cyclic test. We
expect that the textile-type resistance strain sensor developed in this study can be used as a strain sensor/motion sensor by applying to the joint part of clothing.

SB10.03.12
A Textile Design Study Informed by the Exploration of New Surface Materials—Is 'Calm' Technology the Future of Wearables? Raymond Oliver and Jacob B. Goff; Northumbria University, United Kingdom

The concept of wearable technology is currently concerned with products that are more 'attachable' than truly wearable. Over the past decade the world’s biggest consumer-product focused corporations have found varying levels of success from their experiments within the industry. These devices generally exist to quantify, socialise or record. They are ‘outward facing’ and share data that contributes to ‘The Internet of Things’. Intuitive interfaces, further development of responsive materials and a deeper understanding of unobtrusive human-centred design or ‘calm’ technology (Weiser, 1993) are all central to the concept of an authentically wearable device.

Using practice-led 2D and 3D design:STEM activities, this research explores the triangular relationship between the user, the device and the environment it exists in, on both a physical and emotional level. Key to this exploration is the understanding that human bodies are kinetic and their needs therefore differ from that of static entities. As identified, these three factors contribute to the development of effective ‘wearable’ materials used in, on or around the human body. Although the study of ergonomics, anthropometrics and human-centeredness are well explored, challenging them within the context of materials that possess intrinsically responsive behaviours reveals new areas of research. This work describes results of research undertaken at Northumbria’s bio-design STEM Lab to investigate interactive materials with intrinsically responsive behaviours that can be applied to soft stretchable fabrics potentially resulting in artefacts that work in harmony with its user and/or surrounding space to benefit living. The basis for this work and the results of the sensing and response to external stimuli will be highlighted including progress with Weiser’s concept of ‘calm technology’ which is not a burden on the user.

SB10.03.13
Piezo-Enhanced Triboelectric Generator Using Carbon Fiber Yarns Raquel Barras, Andreia dos Santos, Elvira Fortunato, Rodrigo Martins, Rui Igreja, Pedro Barquinha and Luis Pereira; Universidade NOVA de Lisboa, Portugal

With a forecasted market value higher than 27 billion dollars by 2022, the amount of wearable devices sales will double by that time and obviously continuing to grow. As consumers interest pursues more and more portable electronic devices such as wearables, batteries dimensions and capacity of such devices is a common limitation of their size, weight and life time between charging cycles. Off the grid standalone power harvesting systems that can convert kinetic energy from human motion through piezoelectric and triboelectric effects will soon be a reality capable to meet the requirements of such low power electronics.

In this work, carbon fiber stretch-broken yarn is used as inner electrode for a piezo enhanced triboelectric generator (PETG). The carbon yarn was functionalized with nanostructured ZnO rods grown by a simple solvothermal method and covered with a layer of Polydimethylsiloxane rubber (PDMS) by a novel method that was, to the extent of the authors knowledge, not ever reported in literature and named “in-situ PDMS curing”. The use of a fiber-shaped system and the selection of such materials and methods intends to meet a lightweight, bendable, ecological and sustainable power converter for the widely available and unused energy from body motion, in which the enhancement of power output, as well as the energy conversion mechanisms, were subject of study.

SB10.03.14
A New Device Architecture with Double-Stranded Assembly of Electrode Microfibers for High-Performance Fibrous Organic Transistors in Electronic Textile Applications Jung Ah Lim1, Soo Jin Kim1,2 and Hyoung Jun Kim1; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

With the increasing importance of electronic textiles as an ideal platform for wearable electronic devices, organic thin-film transistors (OTFTs) comprised of organic or polymeric electronic components have been shown to be a promising component for e-textile applications on account of their flexibility, light weight, and ease of implementation. While the realization of fibrous OTFTs have been demonstrated so far, several critical issues including a low drain current, unstable contact between the semiconductor and source/drain electrodes, and a high operation voltage remains to be addressed. We report herein is a demonstration of high performance fibrous organic transistors with a new device architecture that exceeds the current limitations of fiber OTFTs. A key feature of this
work is that the semiconductor channel of the fiber transistor comprises a twist assembly of the source and drain electrode microfibers that are coated by an organic semiconductor. This architecture allows us to not only facilely control the channel dimension of the device by varying the thickness of the semiconductor layer and the twisted length of the two electrode microfibers, but also passivate the device without affecting interconnections with other electrical components. The resulting fibrous organic transistors based on the twist assembly of the microfibers showed a high output current of over -5 mA at a low voltage of -1.3 V and a good on/off current ratio of 10^5. The electrical properties of the device were maintained even after repeated bending deformation and washing with a strong detergent solution. In this presentation, discussions on a holistic process for the fabrication of this fiber OTFTs and the correlation between the nano-crystalline structure of semiconductor films and the device performance will be included.

SB10.03.15
Mechanical Modeling of Stretchable Conductive Paste Kazuki Hiraoka, Seiichi Takamatsu and Toshihiro Itoh; University of Tokyo, Japan

To fabricate stretchable electronics devices, wiring parts to connect power supply and devices such as sensors and IC chips is important. There are two types of stretchable wiring: metal thin film and electrically conductive paste. Electrically conductive paste made by dispersing conductive fillers such as silver particles and CNTs into insulating polymer matrices are widely used because it can be fabricated by simple printing method. The recent papers reported a successful strategy to effectively improve electrical conductivity by using multiple CNTs with different shape. On the other hand, research and development of stretchable conductive paste have mainly been conducted based on discovery and empirical rules. If the modeling of stretchable paste is developed, further research and development of new stretchable can be expected to be promoted.

In this study, to develop a modeling method of mixing multiple types of conductive particles, a mechanical and electrical model to calculate the conductivity of the stretched silver paste mixing micro-flake particles and nano-spherical particles at different blending ratios was suggested. Here, micro-flake particles and nano-spherical particles are treated as multi-sphere and hypothetical sphere models, respectively.

The calculation steps are described below.

(1) Generate multi-sphere and hypothetical sphere models in a cubic area. In this paper, volume fraction of silver particles, blending ratio of micro-flake particles and nano-spherical particles, and dimensions of area can be changed. In case of three-dimensional model, the three-dimensional particle distribution was generated by stacking the two-dimensional particle distribution in the normal direction. Moreover, in order to avoid the calculation of the distance between silver particles, the region is divided into small regions to be able to determine the particle distribution without volume intersection.

(2) Update the position of particle distribution following the stretch force to the silver paste, which was calculated by using the finite element method (COMSOL).

(3) Calculate the electrical resistance between each particle: If the spherical particles obtained by the finite element method are adjacent to each other, it is 1Ω, otherwise ∞Ω.

(4) Calculate the electrical resistance of the entire composite between two parallel plate electrodes by inverse matrix calculation.

In this paper, volume fraction of silver particles was set to 50%, and three-dimensional model was selected. Blending ratio of micro-flake particles and nano-spherical particles was varied from 0 % to 100 % every 10 %. In calculation, the size of the particles in model was set to Φ 3.5 to 5.5 μm for micro-flake particles and 200 nm for nano silver particles, which was determined from measurement result of real silver particles.

From the above calculation of conductivity, the optimum blending ratio of small particles and large particles when stretch force was applied to silver paste was estimated. As a result of blending large and small particles, the volume resistivity became lower than the result of small or large single silver particle, and the lowest result was obtained when the blending ratio of nano-particles was 50%. The contact between the particles is classified two types: contact in the conduction direction and contact in the normal direction of the flake particles. In this model, the resistance of contact in the conduction direction was calculated as the same electrical resistance regardless of the particle shape. Therefore, the increase in the volume resistivity of the nano-spherical particles was considered to be caused by the increase in the number of contact points in the conduction direction between the flat plate electrodes sandwiching the particle distribution. On the other hand, the high resistivity in case of using only flake particles seems to be caused by the high resistance value...
in the normal direction of the flake particles.

SB10.03.16
Silver Nanowire Modified Fabrics for Wearable Triboelectric Nanogenerators Doga Doganay, Mete Batuhan Durukan, Melih Ogeday Cicek, Merve N. Guven and Husnu E. Unalan; Middle East Technical University, Turkey

Functional textiles received considerable attention both in scientific field and in the market since late 2000s. Thanks to the developments in nanotechnology, functional textiles have been evolving into smart textiles. In addition to powering the smart textiles, improvement of their washing stability has utmost importance. Currently, batteries are used as the energy sources of smart textiles. However, there are cases where batteries do not fulfill the consumer needs. Moreover, integration of batteries onto the conventional clothes without reducing the consumer comfort is almost impossible. As a consequence, self-powered systems using triboelectric nanogenerators (TENGs) are evolved as strong alternatives to battery powered smart textiles. Silver nanowires are known to impart antibacterial activity [1] and heatability [2] to the textiles. In this study, silver nanowire (Ag NW) decorated fabrics are used as current collectors for the realization of wearable TENGs. Thermoplastic polyurethane (TPU) was deposited onto Ag NW decorated textiles and used as both the dielectric and protection layer. Simple dip and drying method was used for the deposition of both Ag NWs and TPU. The overall structure was used as a single electrode for wearable TENGs, where an open circuit voltage and short circuit current of 30 V and 4 µA were measured, respectively. TENGs were connected in series to further improve the output power. TPU overcoating was also demonstrated to enhance the washing stability of the Ag NW decorated fabrics. While the fabrics without TPU coating lost their conductivity after 10 washing cycles, TPU overcoated fabrics kept their conductivity up to 20 washing cycles.


SB10.03.17
Channel-Dimension Controllable Fibriform Organic Field-Effect Transistors by Hydrogel-Supported Transferring of Printed CNT Microelectrodes Hyoung Jun Kim, Tae-Hyung Kang, Hyunjung Yi and Jung Ah Lim; Korea Institute of Science and Technology, Korea (the Republic of)

With the extensive research of electronic textiles for wearable devices, fibriform organic field-effect transistor is a one of the key components for organizing the electronic circuit into the fabric by weaving the fiber. However, fiber type field-effect transistors have disadvantage of channel dimension since the resolution of printing or deposition techniques on microfibers is primarily restricted by the dimension of the microfibers. Here, we report a new strategy to improve the performance of fibriform OFET where the channel dimension can be readily controllable. Key technology of this work is that single-walled carbon nanotube source and drain (S/D) electrodes with desirable geometry are printed at hydrogel substrate first, then directly transferred to the semiconductor-insulator layer coated Au microfiber. Fine geometry of CNT electrodes was successfully transferred to the microfiber by special rolling process and resulting transistors with wrapped CNT S/D electrodes exhibited a high on/off ratio of ~ 10^5 and good field effect mobility of 0.73 cm^2 V^-1 s^-1. It was confirmed that the fibriform transistors demonstrated on the flexible polyurethane thread also exhibited good electrical performance which was maintained even after bending deformation at different bending radius.

SB10.03.18
The Optical and Structural Properties of Melt-Spinning Nanocomposite Fibers of UHMWPE/HDPE Blended Fibers Yassine Ait-El-Aoud1, Richard Pang1, Elizabeth A. Welsh1, Ihsan Uluturk1, Sean Dinneen1, Stephen A. Giardini1, Peter Stenhouse1, Michael Okamoto1, Luis M. Lozano2,3, Yi Huang2, Seongdong Hong4, Alkim Akyurtlu5, Svetlana V. Boriskina2 and Richard M. Osgood1; 1US Army CCDC-SC, United States; 2Massachusetts Institute of Technology, United States; 3Tecnologico de Monterrey, Mexico; 4Defense Agent for Technology and Quality, Korea (the Republic of); 5University of Massachusetts Lowell, United States

Recently, some forms of polyethylene compounded with nano-particles/micro-particles promise to absorb less infrared radiation by enhancing the forward scattering in the long-wave infrared. By developing such as fibers containing special materials that are infrared transparent and visibly opaque, textiles could be made for clothing which actively cool the body and provide thermal comfort. This technology could have potential in civilian and
In this study, the nanocomposite fibers comprised of blended ultrahigh molecular weight polyethylene (UHMWPE) and high density polyethylene (HDPE) with different mass ratios were successfully prepared using a microcompounder/twin-screw extruder via a two-step process. The first step involved melt-blending UHMWPE powder with TiO2 nanoparticles at 250°C for a residence time of 3 minutes; then HDPE pellets were added and mixed with the melt blended TiO2/UHMWPE at 220°C for a residence time of 5 minutes. The fibers were produced via melt-spinning through a controllable diameter spinneret and collected on a motorized spool at various speeds. The morphology and thermal properties of the samples were characterized by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) techniques. The total reflection and transmission of the blended fibers were measured using the FTIR coupled to an IR integrating sphere. This study showed that the crystallinity and melting temperature of nanocomposites of the blended fibers were found to be significantly increased by decreasing the blended fiber diameter and the IR-transparency of samples was remarkably improved by increasing the draw ratios.

**SB10.03.19**

**Simultaneous Submicron IR+Raman Analysis of Inkjet Printed Flexible Electronic Textiles** Curtis Marcott¹, Frank Weston², Eoghan Dillon², Debra Cook², Jay Anderson², Inhwan Kim³, Ying Zhou³ and Jesse S. Jur³; ¹Light Light Solutions, United States; ²Photothermal Spectroscopy Corp, United States; ³North Carolina State University, United States

Inkjet printing of functional inks on textiles to embed passive electronics devices and sensors is a novel approach in the space of wearable electronic textiles. Achieving functionality such as conductivity by inkjet printing on textiles is challenged by the porosity and surface roughness of textiles. A novel reliable and conformal inkjet printing process is demonstrated for printing particle-free reactive silver ink on uncoated polyester textile knit, woven, and nonwoven fabrics. The particle-free functional ink can conformally coat individual fibers to create a conductive network within the textile structure without changing the feel, texture, durability, and mechanical behavior of the textile. It is noteworthy that the electrical conductivity of the inkjet-printed conductive coating on pristine polyethylene terephthalate fibers is improved by an order of magnitude by in situ heat-curing of the textile surface during printing as the in situ heat-curing process minimizes the wicking of the ink into the textile structures. A new approach which combines simultaneous collection of submicron spatial resolution infrared (IR) and Raman spectra was used to help characterize the structures produced. These two complimentary vibrational spectroscopy techniques provide key insights into the identification and distribution of chemical entities on the surface of these textile fibers as a function of deposition and heat curing conditions.

**SB10.03.20**

**Design of Highly Durable and Flexible Electrodes for Wearable Supercapacitors** Nasim Anjum, Jun Li and Caiwei Shen; University of Massachusetts Dartmouth, United States

Flexible supercapacitors have been intensively studied as promising power sources for next-generation flexible electronics in many consumer, medical, and military applications, because they are safe, mechanically stable and durable compared with current batteries. However, flexible supercapacitor devices reported so far have not demonstrated mechanical properties that can withstand critical deformations including folding, twisting, and machine washing, which are required for real-world applications. Multifunctional materials that can provide not only mechanical flexibility and strength, but also energy storage capability are desired for practical flexible supercapacitors.

Here we present the design of composite electrodes with exceptional mechanical properties for foldable, twistable, and machine-washable supercapacitors. The composite materials consist of polymer electrolyte as matrix and carbon-based materials as fillers. The polymer electrolyte acts as both ion conductor and binder. The combination of activated carbon fibers and particles serves as both high-surface-area electrodes and reinforcement materials. Calculations and simulations show that proper volume ratio of the polymer, fibers, and particles results in optimized flexibility, strength, as well as high areal capacitance. The use of carbon fiber with proper length also enables the composite to survive critical mechanical deformations which particle-based electrodes cannot.

The supercapacitor prototypes are constructed using thin composite electrodes and ion-conducting separators. The separator is composed of randomly distributed glass fibers in polymer electrolyte matrix. The electrochemical and
mechanical tests demonstrate that the activation of the carbon fiber surface has not only improved the mechanical properties of the laminates, but also greatly increased the surface area of electrodes, which leads to two orders of increase in their electrical double-layer capacitance. The prototypes show adjustable areal capacitances of over 10 mF/cm² with thickness and flexibility (flexural rigidity) comparable to wearable fabrics. The electrochemical performance has remained unchanged after repeated folding and twisting tests. Moreover, we sewed the devices onto fabrics and washed them in a washing machine, after which we observed no mechanical damage or capacitance degradation.

In conclusion, we believe that the excellent electrochemical performance, flexibility and mechanical durability make the composite-based flexible supercapacitors promising to power various flexible and wearable electronics. The design rules and results are also applicable to developing other multifunctional devices that require high performance without sacrificing mechanical properties.

SB10.03.21
Electrically Conducting and Mechanically Strong Fibers for Flexible Electronics and for Joule Heating
Mingxuan Lu1, Jiawei Xu1, Prabhakar V. Gulgunje1, Kishor Gupta1, Pedro J. Arias-Monje1, Narayan Shirolkar1, Adam Maffe1, Edward DiLoreto1, Yudhisthira Sahoo2, Sandip Agarwal2 and Satish Kumar1; 1Georgia Institute of Technology, United States; 2Vuronyx Technologies, Inc, United States

Polyacrylonitrile (PAN)/carbon nanotube (CNT) composite fibers have been processed by gel spinning with combined good tensile properties and electrical conductivity. These fibers can potentially be used for smart textiles, electromagnetic interference (EMI) shielding, electrical heating of fabrics, and for making stabilized fibers and carbon fibers via Joule heating. High CNT loading leads to high materials cost. To address this issue, further studies have been done to reduce CNT content in the fiber while also achieving good electrical conductivity and mechanical properties.

Bi-component spinning has been successfully conducted to produce fibers with 100% PAN in the core and 90:10 PAN:CNT weight ratio in the sheath. The overall CNT content in the fiber is about 5 wt%. The processing steps, structure and properties of the fibers will be presented. One important application for these composites fiber is to make carbon fibers. Polyacrylonitrile (PAN)/carbon nanotube (CNT) fibers can be stabilized by applying electric current (Joule heating process), rather than by external heating. Thus, stabilization of PAN/CNT fibers by application of electric current provides a pathway for making carbon fibers with reduced energy consumption. The innovation, opportunity, as well as the scale up challenge for Joule heating, and for flexible electronic applications of this PAN/CNT bi-component fiber technology will be presented and discussed.

SB10.03.22
Reel-to-Reel Production of Sub-Micron Diameter Metallic Wires over Meter Scale Lengths through Contactless Electroplating onto Electrospun Nanofibers
Heena K. Mutha1, Alex Couch1, Aykut Aydin2, David Adler1, Ernest Kim1, Peter H. Lewis1, Vinh Nguyen1, Terrell Williams1, Didier Rusangiza1, Roy Gordon1, David J. Carter1 and Kasey J. Russell1; 1The Charles Stark Draper Laboratory, United States; 2Harvard University, United States

Sub-micron diameter metallic wires of long lengths would enable a wide range of applications including electronic textiles, woven batteries to power wearables, sensitive neural electrodes, and low-loss conductors for microwave electronics, among many others. Existing synthesis methods for developing nanowires are often limited to sub-millimeter lengths, or long length fine wires are extruded at high cost. Instead, we use a low-cost, scalable, bottoms-up approach to fabricate small wires by metallizing long lengths of electrospun polymer (PMIA) nanofibers. While we have demonstrated that a wide variety of metals can be deposited onto the PMIA nanofibers by sputter or vapor deposition, electroplating would provide a more cost-effective and scalable deposition approach. Traditional reel-to-reel electroplating is done by connecting electrical leads to the drum that a metalized wire sits on and driving it through a plating solution that has a platinum electrode immersed in it also connected to electrical leads, thus closing the circuit. However, polymer nanofibers in air can easily be disturbed by forces exerted by convection and electrostatic charging, and can also break under low tensile loads, which can make handling the fibers challenging and prevent making an electrical connection through physical contact. Therefore, we developed a contactless electroplating method comprised of at least two isolated fluid streams of plating solution and conductive salt solution which are used to tension and guide the nanofiber. A potential drop across electrodes immersed in the fluids drives current to flow through the bridging conductive nanofiber allowing for contactless electroplating. Using a
commercial gold electroplating bath, we demonstrate metallized wires with lengths that are $10^3$ to $10^6$ times greater than the core diameter. This work was sponsored by the Air Force Research Laboratory (AFRL) and the Defense Advanced Research Agency (DARPA).

**SB10.03.23**

**Electrospun Microfibers with Embedded Thermochromic Material for Textile and Energy Storage Applications**
Sharan K. Indrakar$^1$, Keon Sahebkar$^3$, Sylvia Thomas$^1$, Sessa Srinivasan$^2$ and Elias Stefanakos$^1$; $^1$University of South Florida, United States; $^2$Florida Polytechnic University, United States

Electrospinning is an inexpensive and versatile technique for fabricating micro and nano scaled fibers for varied applications. There have been limited attempts to employ it for the fabrication of a thermochromic device however, and the fabrication for a three component (dye, developer, and solvent) thermochromic system has required the use of a more complicated coaxial electrospinning technique. Herein, we will employ a simple and novel method for creating thermochromic fibers by electrospinning single strands of poly(methyl methacrylate) (PMMA) with embedded thermochromic powder of polymer encapsulated three-component system. Unlike past thermochromic fibers, an unmodified syringe tip can be used for the spinning process and only one flow rate needs to be determined. A solution of solvent (either N-dimethylformamide or chloroform), PMMA, and commercially available black thermochromic powder was created and spun using a custom-made electrospinning apparatus. The effects of solvents, polymer concentration, and thermochromic powder concentration on morphology and thermochromic performance were also investigated to determine the composition for an electrospinning solution with the most consistent structure and most visible color change from black to translucent. These as-developed micro- or nano-fibers will be characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM) imagery to determine surface/interface morphology, energy dispersive X-ray (EDS) spectroscopy to determine the elemental composition, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to analyze thermal properties and Fourier Transform Infrared Spectroscopy (FTIR) to determining the chemical environment. The thermochromic color change behavior with respect to temperature of these electrospun fibers will be observed by modified Ocean Optics’s UV-Vis/CIE spectrophotometer.

**SB10.03.24**

**Wearable Sensor Enabled by Carbon Nanoink**
Changyu Wang and Ming Su; Northeastern University, United States

Wearable sensors with various sensing functions and lower costs are necessary for practical application. Sensors based on carbon materials with unique physical and chemical properties can be considered alternatives to relatively expensive electronic devices. This project uses a quick and effective dip-dry method to make carbon nanoparticle wearable sensors on cotton fabric, silk, and sponge. The sensors are responsive to various physical stimuli like relative humidity, temperature, strain, and pressure. The sensor can be properly designed to isolate each stimulus from others, allowing precise determination of each property through resistance measurement. The composites formed by carbon nanoparticles and sponge are found to have high sensibility and fast response to pressure and strain, showing potential for wearable sensors.

**SB10.03.25**

**Silver Nanowire–Cobalt Hydroxide Textile Electrodes for Flexible and Wearable Energy Storage**
Mete Batuhan Durukan, Farzaneh Hekmat, Doga Doganay and Husnu E. Unalan; Middle East Technical University, Turkey

While the future developments are emphasized towards thinner, lighter and cheaper solutions, flexible electronics are highly promising and expanding the areas of use almost daily. In this manner, smart textiles are considered to be the next generation of textiles with added functions like sensing, controlling, computation etc [1]. Regarding the key role of energy storage systems for wearable electronics, the actual interest of the researchers will be allocated for developing high performance wearable energy storage systems—receiving benefit from foldability and flexibility. In this work, polyol synthesized silver nanowires are used as conductive additives to fabricate conducting textiles via a simple dip and dry method [2]. Cobalt hydroxide (Co(OH)$_2$) is decorated onto conducting textiles via electrodeposition [3]. A detailed morphological, structural and chemical analysis was performed on the fabricated textile-based electrodes. Electrochemical characteristics of the fabricated textile-based electrodes were investigated through cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy. During
electrochemical measurements, 3 M KOH aqueous electrolyte was used. Preliminary results showed that the fabricated Co(OH)₂ decorated Ag NW smart textiles have a capacity of 33.7 C.cm⁻² at a current density of 3 mA.cm⁻² within a potential range of -0.2 - 0.6 V. Moreover, an energy efficiency of 65% and a Coulombic efficiency of 87% was obtained. Improved electrochemical stability of the Ag NWs was also noteworthy. Numerous bending cycles were used to determine the mechanical stability of the fabricated textile-based electrodes. Gravimetric analysis is underway to determine the gravimetric capacity of the electrodes.


SB10.03.26
CuS/Au-Coated Velour Fabric Composite Electrodes—A New Architecture for Stretchable and WearableEnergy Storage Yunyun Wu and Tricia B. Carmichael; University of Windsor, Canada

The future of textiles is electronic, with new wearable devices integrated into "smart clothing" systems that will incorporate sensors to detect biometric data, light-emitting devices to display data, and integrated wiring. Powering this next generation of smart clothing is of key importance, making the development of flexible and stretchable energy storage devices that are compatible with textiles particularly urgent. Lithium-ion batteries (LIBs) are one of the most promising power sources because of their high energy density and long cycle life. As a core component, the battery electrode largely dictates the mechanical properties of the entire battery. The electrodes of conventional LIBs are typically fabricated by depositing brittle composite materials on metal foils. These electrodes are vulnerable to mechanical strain, which can cause the delamination and cracking of active materials, and ultimately device failure. Previous work has relied elastomeric materials to improve the mechanical properties of these active materials. Depositing active materials onto a prestrained elastomer to form wavy electrodes, coating 3D porous elastomers, or mixing active materials with elastomers to form stretchable composites are all leading approaches. However, active materials in these systems still experience strain to some extent, which can be problematic for practical use. There is therefore an urgent need to explore new ways to fabricate electrodes with good mechanical properties and that retain functionality under strain for use in stretchable LIBs. In this presentation, we report a new approach that uses textile structures to protect the active materials from strain and subsequent damage. We use a warp-knitted velour fabric structure, which consists of a warp-knitted trellis and a cut pile. Metallizing the fabric using solution-based electroless nickel-immersion gold plating renders it conductive, preparing it for use as a current collector. We then electrolessly deposit copper selectively on the cut pile fibers, and convert the resulting copper film into CuS by reaction with elemental sulfur. This unique preparation method integrates the active material and the current collector into a single piece of velour fabric in a way that protects the CuS from strain when the fabric electrode is elongated. The CuS/Au-coated velour fabric electrode shows stable conductivity to 130% strain, and the conductivity also remains stable through 1000 cycles of 50% strain. We demonstrate its application in LIBs. The electrode exhibited a specific capacity of ~400 mAh/g at 0.5 C with no obvious sign of capacity decay for at least 300 cycles. After 1000 cycles of 50% strain, the electrode still exhibited stable electrochemical performance.

SB10.03.27
Analysis of Heat Releasing Engineered Fibers and Films for Thermal Comfort via a Simulated SkinTemperature Device Michael Okamoto¹, Yassine Ait-El-Aoud¹, Ihsan Uluturk¹, Elizabeth A. Welsh¹, Svetlana V. Boriskina², Luis M. Lozano², Yi Huang² and Richard M. Osgood¹; ¹US Army Combat Capabilities DevelopmentCommand - Soldier Center, United States; ²Massachusetts Institute of Technology, United States

Radiative cooling and heating can play a role in influencing and controlling the temperature of things like shelters, solar cells, and the human body. Personal thermal comfort is an important consideration for helping to maintain optimum physical and cognitive performance in an individual. It has been shown that thermally transparent polymeric films and fibers can theoretically transmit metabolically-generated heat from the body to the environment via passive radiative cooling [1].

In order to compare the heat-trapping or heat-releasing properties of engineered films and fiber swatches, a
simulated device for skin temperature was designed. The device consists of a heater operating at constant power output to mimic the heat produced by human skin which is at roughly 34°C. High density polyethylene (HDPE) fibers and/or films will be compared to commercially available ones. The fabric and/or film of interest is placed over the “skin” and the temperature differential, delta-T, across the elemental material or monolayer fiber array or film/membrane is measured. This unique capability can directly measure two test samples simultaneously thus allowing for direct comparison under identical environmental conditions to control for changes in factors like air temperature, wind, and humidity. Finally this device can be operated in a vacuum thus removing conduction and convection as cooling or heating pathways.

While the textile industry community employs standardized test methods and instruments for measuring larger end-item textile products, this measurement capability will enable better analysis of early-stage research materials instead of just finished textiles thus allowing for better control, prediction, and understanding of inherent material properties.

**SB10.03.28**  
**Textile-Based Capacitive Pressure Sensors** Saki Tamura¹², Justin K. Wyss¹¹, Mirza S. Sarwar¹, Addie Bahi¹, John D. Madden¹ and Frank K. Ko¹; ¹University of British Columbia, Canada; ²Kyoto Institute of Technology, Japan

Capacitive pressure sensors (CPS) have long been recognized to be an effective component for interaction with electronic devices. The growing interest in the development of flexible and wearable electronics has prompted the interest in flexible sensors. A number of sensor arrays have been demonstrated on bendable and stretchable substrates. In order to enhance design flexibility and scalability in the manufacture of the CPS, we demonstrate orthogonally woven CPS integrated into elastomer substrates. A further advantage of using a combined elastomer and textile structure is the ability to shape the elastomer to maximize change in capacitance in response to proximity, pressure, touch and shear. In this work we focus on proximity and pressure detection. Specifically, 4x4 cross array woven structure consisting of Ag coated Nylon yarns (diameter 0.54 mm, 0.438 Ω/cm) have been developed that cover an area of 5.5 x 5.5 cm. The woven structure was embedded into Ecoflex™. Each electrode is composed of 5 parallel Ag coated Nylon yarns, with 4 electrodes interlaced in each direction to form an array of 16 intersection, each sensitive to pressure and proximity. The woven composite assemblies were subjected to light touch and pressure loads. The corresponding capacitances were measured and are similar in response to those of the orthogonal non-interlaced/non-textile structure, including good proximity detection (> 1 cm), pressure detection (0.23 %/kPa) and spatial resolution ~1 cm). The devices operate in bending and during stretch. Next steps include integration in clothing and bedding to enable health monitoring.
speech, ambulatory gait, body orientation and others, of wide applicability in health monitoring and clinical care. Demonstrations include comparisons to clinical gold standards for various individual indications, and to full-night polysomnography (PSG) results captured in a hospital sleep lab.

9:00 AM SB10.04.02
Washable ECG Electrodes from Sewn High Performance Carbon Nanotube Fibers Lauren W. Taylor1, Steven M. Williams1, J S. Yan1, E A. Bengio1, Oliver S. Dewey1, Flavia Vitale2 and Matteo Pasquali1,1,1; 1Rice University, United States; 2University of Pennsylvania, United States

Commercially available electrocardiogram (ECG) electrodes are rigid and require a gel electrolyte to obtain a clear signal. This electrolyte can dry over time leading to a degradation in signal to noise ratio. Furthermore, the lack of airflow to the skin and adhesive can be irritating to the user. This can pose issues for individuals that require continuous monitoring. Here, we present ECG electrodes made with high performance carbon nanotube (CNT) fiber that are suitable for long-term use. The high conductivity of the fiber and low contact impedance between the fiber and skin allow for good transmission of the ECG signal without the use of a gel. Additionally, the CNT fiber has excellent tensile strength and flexibility so it can be sewn into fabric with a standard sewing machine. The woven structure and softness minimizes the irritation caused by recording ECGs. Furthermore, the CNT fiber is robust and chemically inert so that it can be machine washed without losing performance.

9:15 AM SB10.04.03
Sensing Human Behavior with Smart Garments Trisha L. Andrew; University of Massachusetts Amherst, United States

Smart apparel with embedded self-powered sensors can revolutionize human behavior monitoring by leveraging everyday clothing as the sensing substrate. The key is to inconspicuously integrate sensing elements and portable power sources into garments while maintaining the weight, feel, comfort, function and ruggedness of familiar clothes and fabrics. We use reactive vapor coating to transform commonly-available, mass-produced fabrics, threads or premade garments into a plethora of comfortably-wearable electronic devices by directly coating them with uniform and conformal films of electronically-active conjugated polymers. By carefully choosing the repeat unit structure of the polymer coating, we access a number of fiber- or fabric-based circuit components, including resistors, depletion-mode transistors, diodes, thermistors, and pseudocapacitors. Further, vapor-deposited electronic polymer films are notably wash- and wear-stable and withstand mechanically-demanding textile manufacturing routines, enabling us to use sewing, weaving, knitting or embroidery procedures to create self-powered garment sensors. We will describe our efforts in monitoring heartrate, breathing, joint motion/flexibility, gait and sleep posture using loose electronic garments and highlight collaborative endeavors to combine signal processing, machine leaning and human factor integration to predict behavior in selected at-risk populations.

9:30 AM BREAK

10:00 AM *SB10.04.04
Smart Textiles for Personalized Health Care Jun Chen; University of California, Los Angeles, United States

There is nothing more personal than healthcare. Health care must move from its current reactive and disease-centric system to a personalized, predictive, preventative and participatory model with a focus on disease prevention and health promotion. As the world marches into the era of Internet of Things (IoT) and 5G wireless, technology renovation enables industry to offer a more individually tailored approach to healthcare with more successful health outcomes, higher quality and lower costs. However, empowering the utility of IoT enabled technology in personalized health care is still significantly challenged by the shortage of cost-effective and wearable biomedical devices to continuously provide real-time, patient-generated health data. Textiles have been concomitant and playing a vital role in the long history of human civilization. In this talk, I will introduce my research on smart textiles for biomedical monitoring and personalized diagnosis, textile for therapy, and textile power generation as an energy solution for the future wearable medical devices. Lastly, I will briefly introduce an autonomous self-powered textile body area network that seamlessly integrates wearable power sources, self-powered sensors, microcontrollers, and internet connection for revolutionary applications in the future personalized health care and body computing.

References (* Equal contribution author; * Corresponding author)
Integration of smart devices into textiles is a key challenge for tomorrow-wearable technologies. On one hand, the electronics should perform diversified computational operations, such as data processing and transmission, with high performances for responsive smart systems. These conditions are only met today by rigid silicone-based systems. On the other hand, clothes are soft, closely fit to the skin and adapt to the human body. The mismatch in mechanical properties between soft substrates and rigid components induces specific reliability issues, especially for wearable systems, as they are subjected to wearing and washing.

In this work, we present a fabrication process of soft and ultra-thin circuit for imperceptible systems, integrating microelectronic silicon-based components. We use a customized stack of thin decorative copper leaf on polymer, which can be assembled and connected through vias for multilayered systems. We consider and study the aforementioned aspects of imperceptibility (wearability), and mechanical robustness through specifically designed bending tests. We investigated the optimization of electrical connection between ultra-soft substrates and rigid components, and the influence of the stack composition in multilayer electronic systems on the overall reliability of the device.

The combination of optimized stack layout and compliant interconnections allow the fabrication of robust and ultra-conformable, imperceptible devices.

An Ultrasoft Graphene Network-Based Stretchable Sensor for Full-Range of Human Bodily Motions Detection

Zijun He1,2, Ling Qiu3,1 and Dan Li2,1; 1Monash University, Australia; 2The University of Melbourne, Australia; 3Tsinghua-Berkeley Shenzhen Institute, China

Human bodily activities are complex that consists of dynamic motions of different body parts with broad frequency ranges. Despite it has been widely exploited in human bodily motion detections, the possibility of using soft rubber-based stretchable sensors in the detection of full-range of bodily motions from muscle functions up to mass movements have not been well explored. Here, we demonstrate that controlled interfacing of an ultralow modulus graphene network with rubber can lead to a stretchable hybrid elastomer with performance combinations of high sensitivity, large stretchability, similar modulus compliance to the skin and good durability. The resultant sensor allows resistive detection of subtle dynamic skin stretches induced by muscles and large deformation caused by joints motions, which fills the gap for sensing the whole spectrum of human bodily motions via soft flexible electronics.

Wearable and More—Biopotential Recording by Ultraconformable Devices

Piero Cosseddu, Danilo Pani, Andrea Spanu and Annalisa Bonfiglio; Università di Cagliari - UniCa, Italy

The recent rise of the so-called flexible electronics has paved the way for the development of flexible systems that can be easily integrated and also directly fabricated onto textiles, and be employed for the monitoring of a different
bio/physical parameters. In this presentation we will introduce different technological solutions for the realization of smart wearable systems specifically engineered for biopotential recordings and on-skin sensing applications. The first proposed approach is based on screen printed PEDOT:PSS electrodes which are seamlessly integrated directly onto commercial garments, for the measurement of the ECG signal, coupled with respiration. These 2 measurements allow evaluating the physiological status of patients and subjects as athletes and workers under stressful conditions, in several applications ranging from rehabilitation to the monitoring of athletes performance or subjects at work.

Moreover, we will also show the employments of similar electrodes for EMG applications. These recordings can be used to evaluate muscle performance and fatigue, by means of simple commercial garments where recording electrodes have been seamlessly integrated. Examples of applications in rehabilitation and gesture recognition will be shown.

Textile sensing systems are part of a broader area of devices that, thanks to their mechanical conformability, can be successfully used for the human body monitoring. Also tattoo electronics can offer interesting solutions for this kind of applications. In this presentation, we will discuss comparatively their advantages and drawbacks for the recording of biopotentials and/or different physiological parameters.

11:30 AM SB10.04.08
New Generation of Flexible Energy Storage Devices and Humidity Sensors on Reinforced Carbon Fiber Textile
Karen R. Pearson¹, Kasra Sardashti¹, Shi Fu² and Vladimir Samuilov²; ¹Fashion Institute of New York, United States; ²State University of New York at Stony Brook, United States

Carbon fiber textile has been utilized as flexible supercapacitor electrodes with cost-effective graphene nanoplatelete (GNP) composite as model material for coating the electrodes. This composite is considered to be a new class of carbon nanomaterial with very high intrinsic electrical conductivity in plane and accessible surface area. Carbon nanotubes (CNT) at the concentration 50:50 of CNT to GNP were added to take advantage of the high surface area of the composite of these two carbon nano-materials. Perfect shape of the voltammetric curves indicates excellent ion transport behavior, good charge propagation and low losses in supercapacitors with GNP/CNT coated electrodes. The first experimental results without optimization showed promising supercapacitor behavior of the carbon fiber textile with bare pads, better than in the state-of-the art reference [1]. Graphene nanoplatelete – carbon nanotube (50:50) electrode material has improved the capacitance density approximately 10 times. Carbon fiber textile is promising material for fabrication of electrodes for high-capacitance high-energy density flexible supercapacitors [2].

We have also developed flexible carbon nanotube sensor for applications of moisture detection. A cost-effective sensor that could detect and measure humidity/moisture levels has been developed. Prototype sensor have demonstrated an extremely high sensitivity to water.


1:30 PM *SB10.05.01
Textile-Based Wearable Robots Conor Walsh; Harvard School of Engineering, United States

The rapidly emerging field of soft robotics presents a new opportunity to develop wearable assistive technology optimized for the needs of individuals with residual capacity as well as for augmenting human performance. Unlike their rigid counterparts, soft wearable robots are lightweight, intimately conformal to the body and can more easily
fit a range of sizes. The hierarchical structure and flexible/conformal nature of textiles provide an ideal platform to construct these wearable robotic systems. The ability to tune mechanical properties for use in inflatable actuation profiles or to anchor to the body and distribute and route forces through attachment points in cable driven systems. Looking forward, additional functionalities will be embedded into the textile beyond structural needs including sensing, and flexible electronic routing.

2:00 PM SB10.05.02
Electromagnetic Textiles with Novel Thermal and Reconfigurable Properties Richard M. Osgood1, Michael Okamoto1, Yassine Ait-El-Aoud1, Ihsan Uluturk1, Elizabeth A. Welsh1, Sean Dinneen1, Justin Murphy1, Danielle Froio-Blumsack1, Svetlana V. Boriskina2, Luis M. Lozano2, Alkim Akyurtlu3, Guinevere Strack3, Leila Deravi4, Amrita Kumar4 and Camille Martin4; 1US Army Combat Capabilities Development Command - Soldier Center, United States; 2Massachusetts Institute of Technology, United States; 3University of Massachusetts Lowell, United States; 4Northeastern University, United States

The field of electronic textiles (“e-textiles”) is currently growing rapidly, impacting by research and development activities in multiple fields, from physics and mathematics to textiles and power engineering to health, safety, and social sciences. Combining multiple functionalities – from basic warmth and comfort to harvesting power to more focused monitoring and/or protection – is of great interest, but has so far found only limited success. We report on our research to analyze and experimentally demonstrate both heat-releasing and heat-trapping polymer films and simple 1-d arrays of fibers, and discuss enabling both functionalities in different scenarios for both heating and cooling applications, such as for the human body. We discuss the use of a thermally transparent film in some hot weather applications, when it is critical to release heat, and also where it is essential, for cold weather applications, to trap heat at an extremity. We build on earlier results that highlighted the importance of polyethylene, especially high- and ultra-high –weight polyethylene, for heat release and improved thermal conductivity [1] and light-scattering bio-particles in melt-extruded polymer fibers [2]. Using our thermally transparent materials, we observe small decreases (few degrees C) in the temperature of artificial ‘skin’ when constant power density, emulating an exercising person, is applied to a novel system for characterizing both power density and artificial skin temperature, compared to control samples of standard, commercial polymers. Similarly, we report on heat-trapping experiments when the outside temperature is much lower than the temperature of the artificial skin. We discuss how such ‘electromagnetic textiles’ – purely passive but electromagnetically responsive materials – can be controlled actively, using 1) electrical voltage with conductive particles in the fibers 2) magnetic fields using magnetic particles and 3) thermoelectric materials that generate a voltage in response to an engineered thermal differential 4) light-activated scattering. These active controls will enable the fiber’s or film’s heat-trapping or heat-transmitting states to be reconfigured actively (voltage control) or passively (due to temperature or electromagnetic field alone). We predict how future textiles, containing polymer materials with particles similar to those we have studies, will perform, and discuss new applications for electromagnetically-responsive polymers, including protection and color.


2:15 PM SB10.05.03
Stretchable Ultrasheer Fabrics as Transparent Electrodes—A Textile-Centric Approach to Wearable Light-Emitting e-Textiles with Changeable Display Patterns Yunyun Wu, Sara Mechael, Cecilia Perez-Lerma, R. Stephen Carmichael and Tricia B. Carmichael; Univ of Windsor, Canada

Research on smart clothing aspires to seamlessly integrate electronic devices with textiles to add exciting new functionality without losing softness and wearability. In particular, light-emitting e-textiles are an emerging technology with applications in fashion design, interior design, visual merchandizing, and healthcare. At present, light-emitting textiles are mainly realized by sewing discrete, rigid elements like light-emitting diodes (LEDs) or optical fibers into clothing, which reduces softness, stretchability, and wearability. Better integration of device functionality into clothing requires the incorporation of intrinsically stretchable functional materials into the textile structure; however, this fabrication is challenging due to the porous, 3D structures of textiles that present a non-planar surface for fabrication and readily absorb and wick solutions of functional inks. In this presentation, we show...
that textile structures can instead be exploited to form the basis for a new, textile-centric design approach. We use the open structure of a low-denier nylon and spandex ultrasheer fabric as the framework for a highly stretchable transparent electrode in wearable and stretchable light-emitting devices. We coat the fibers of the ultrasheer fabric with a conformal gold coating using solution-based electroless nickel immersion gold plating, producing a semitransparent, conductive, and highly stretchable textile electrode. Adhering these new textile-based electrodes to a stretchable emissive material produces lightweight, wearable, and washable light-emitting e-textiles that function to 200% strain. Combining the metallization of the ultrasheer textile with low-cost stencil printing of a wax resist provides patterned electrodes to create patterned light-emitting displays; furthermore, incorporating soft-contact lamination in the device fabrication produces light-emitting textiles that exhibit, for the first time, readily changeable patterns of illumination.

2:30 PM SB10.05.04
Towards the Smart Fabrics—Rollable Metamaterial as a New Paradigm Chun-Che Wang, Yang-Fang Chen and Hung-I Lin; National Taiwan University, Taiwan

Since the development of photonics, towards optoelectronic devices of flexible, rollable, wearable, user-friendly, and robust to improve human-machine interfaces have been progressed rapidly. To integrate these devices onto human body, they are designed to be biocompatible and can withstand mechanical deformation. A large number of demonstrations have been proven for the promising market of wearable photonics and optoelectronics such as flexible photodetectors, stretchable laser systems, artificial electronic skins, and paper-based memory devices. Biocompatibility, high sensitivity, low energy loss, and long-term endurance, are the features to successfully integrate with wearable photonic systems, the flexible and rollable optoelectronic devices. Certainly, there remains a great challenges to achieve the above mentioned benefits with considering the practical applications.

On the other hand, photonic metamaterials provide a large number of potential functionalities that can be used for wearable optoelectronic devices. Metamaterials are designed with sub-wavelength geometries for controlling or tailoring the electromagnetic waves for a variety of functionalities. A distinct class of metamaterials is hyperbolic metamaterial (HMM), which is defined by its hyperbolic iso-frequency curve in momentum space. For light-matter interactions, HMMs have been proven to boost the transition rates for both of the spontaneous and stimulated emission dynamics. Owing to the increased transition rate of the optical gain media, stimulated emission (e.g., laser action) comes along with a strong output power and a reduced lasing threshold. However, these demonstrations have primarily been done on rigid substrates. To fully explore the excellent functionalities of HMM, large degree of flexibility and even rollability are highly desirable, which remains as a challenge issue.

To realize the usefulness of our new design, we demonstrate that the flexible and rollable HMM is able to enhance random laser action, in which light suffers from multiple scattering in between disordered media, thereby strongly enhancing its optical gain. We choose low-dimensional organic-inorganic perovskite nanocrystals (PNCs) as the gain material, which is composed of methyl-ammonium lead bromide (MAPbBr3) with a bandgap of ~2.3 eV that can achieve a high quantum efficiency up to ~90.5%. Interestingly, the enhanced laser action based on our flexible and rollable HMM maintains superior stable performance even under cyclic bending to curvatures below 1mm. The intensity of laser action is enhanced by 2.5 times as compared to the flat surface. By tuning the thickness of the HMM structure, we have achieved a large enhancement of the density of states and the scattering efficiency. Simulation results based on the scattering efficiency and the dipole-like dynamics confirm an efficient out-coupling. We anticipate that this flexible and rollable HMM structure can serve as a diverse platform for flexible photonics technologies, such as light-emitting devices, wearable optoelectronics, and optical communication.

Acknowledgments
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2:45 PM SB10.05.05
Multifunctional Triboelectric-Nanogenerator Fabric for Universally Harvesting Energy from Rain Drops, Winds and Human-Motions, and as Self-Powered Sensors Ying-Chih Lai, Yung-Chi Hsiao and Hsing-Mei Wu; National Chung Hsing University, Taiwan
Developing nimble, shape-adaptable, conformable and widely-implementable energy harvesters with the capability to scavenge multiple renewable and ambient energy sources is highly demanded for distributed, remote, and wearable energy uses to meet the needs of internet of things. Here, we present the first multifunctional and waterproof triboelectric-nanogenerator fabric that can produce electricity from both natural tiny impacts (rains and winds) and body movements, which can not only serve as a flexible, adaptive, wearable, and universal energy collector but also act as a fabric-based self-powered active sensor. The working principle comes from a conjunction of contact triboelectrification and electrostatic induction during contact/separation of internal soft fabrics. The structural/material designs of the smart textile are systematically studied to optimize its performance, and its outputs under different conditions of rains, winds and various body movements are comprehensively investigated. Its applicability is practically demonstrated in various objects and working situations to gather ambient energy. Lastly, a self-powered human-system interface is demonstrated on a garment for remotely controlling a music-player system. The multifunctional yet nimble energy fabric can not only address the long-lasting challenge of waterproof, adaptive, deformable, and universal energy devices for locally accessible energy but also bring a new class for wearable energy and smart articles.

[Ref]
[1] Demonstration video: https://www.youtube.com/watch?v=Py-Gib1VDqQ

[News]
https://www.advancedsciencenews.com/energy-harvesting-raincoats/?fbclid=IwAR1kb5La8dmDIFEN02Efu5jt5PTjUfjaN2Aaa02HRB3LPnscKYAWvMVMis


3:00 PM BREAK

3:30 PM *SB10.05.06*
Engineering Flexible Multi-Scale Materials for Sustainable Multi-Functional Clothes and Wearables Svetlana V. Boriskina; Massachusetts Institute of Technology, United States

The ever-growing demand for lightweight portable high-tech devices is evolving into an even more challenging demand for fully wearable devices integrated into clothes. To meet this demand, the emerging wearable optical technologies must combine multiple functionalities, including visual effects, communications features, thermoregulation to maintain personal comfort level, and even self-cleaning and microbial treatment by sunlight. These technologies often require portable or renewable power sources to operate—and the lack of cheap, long-lasting and lightweight sources has proved a big hurdle to wider adoption. Finally, new technologies must meet the global demand for tighter environmental standards to reduce energy and water use and waste during the fabrication process as well as throughout the garments life cycle. They must also provide a clear pathway for recycling and re-using the materials into new fabrics and wearables. We develop multi-functional materials for wearable technologies, which combine a variety of optical, thermal, mechanical, and biological functionalities, and meet high standards for energy and water saving and sustainability. I will discuss the engineering approaches used in designing and fabricating woven and knitted fabrics out of polyethylene fibers to achieve either passive cooling without breaking a sweat or passive heating without the use of uncomfortable metal films. I will then show how the fiber micro-structuring can be combined with nano-scale engineering via embedding a variety of nano-inclusions to combine thermoregulation-by-radiation-control functionality with structural coloring, unique lateral heat conduction properties, and anti-microbial resistance of new textiles. We embed colorants and anti-microbial agents into fibers and films during their fabrication, which does not require significant water usage, in stark contrast with the standard industrial processes that use 200 liters of water to produce 1 kg of textile, and create large amounts of wastewater contaminating the environment. The new textiles also offer excellent water wicking, dirt-resistant, and fast drying functionalities, offering significant energy and water savings for their maintenance, and can be easily recycled at the end of their lifetime. Finally, I will discuss how the new fabrics can be further enhanced by incorporating other functional wearable elements, including fibers for optical communication, photo-detectors, and flexible, lightweight, round-the-clock energy harvesters capable of operating in the self-powered regime.
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4:00 PM SB10.05.07
Two-Dimensional Field-Effect Heterostructures for Wearable and Textile Electronics Tian Carey1, Stefania Cacovich1, Giorgio Divitini1, Jiesheng Ren2, Jong Min Kim1, Chaoxia Wang2, Roman Sordan3 and Felice Torrisi1,4; 1Cambridge Univ, United Kingdom; 2Jiangnan University, China; 3Politecnico di Milano, Italy; 4Imperial College London, United Kingdom

Solution processing of graphite and other layered materials provides low-cost stretchable inks enabling electronic textile devices [1]. However, the limited quality of the two-dimensional (2d) material inks, the complexity of the layered arrangement, and the lack of a suitable dielectric 2d material ink [2] has impeded the fabrication of active field effect devices on fabric based on fully-printed 2d heterostructures. In this work we demonstrate fully inkjet printed 2d material active heterostructures with graphene, MoS2 and hexagonal-boron nitride (h-BN) inks, and use them to fabricate all inkjet printed flexible and washable ambipolar, n- and p-type field effect transistors (FETs) on textile, reaching a field effect mobility of μ ~ 105 ± 29 cm2 V-1 s-1 on polyester fabric, at low operating voltages (< 5 V). The devices maintained their performance even under ~ 4% tensile strain and showed stable operation for periods up to 2 years, indicating the two-fold role of the h-BN layer as a flexible dielectric and encapsulant. Our 2d material textile FETs are washable up to 20 cycles, which is ideal for textile electronics. The viability of our process for printed and textile electronics is demonstrated by fully inkjet printed electronic circuits, such as reprogrammable volatile memory cells, complementary inverters, and OR logic gates with graphene/h-BN FETs.

References

4:15 PM SB10.05.08
Superelastic Sputtered TiNiCuCo Thin-Film Serpentine Interconnects for Wearable Electronics Sabrina M. Curtis1,2, Lars Bumke1, Prasanth Velvaluri1, Ohuwaamilola Ajibuwa1 and Eckhard Quandt1; 1Kiel University, Germany; 2University of Maryland, United States

The next generation of wearable sensors, actuators, and power microsystems must maintain a large area density while recovering reversible elastic deformation of at least 30 - 100% macroscopic strain, to match the elasticity of human skin. To achieve this, wearable devices are often fabricated through the “island-plus-bridge” method where an array of active rigid device micro-islands are separated by stretchable serpentine metal interconnects. Serpentines are advantageous for integration into textiles as interconnect structures since they can undergo geometrical reconfigurations to relieve stress under applied strain. Traditional metals with low intrinsic tensile strains (i.e Cu) configured into serpentine with a large amplitude and narrow wavelength are able to achieve large macroscopic strains of tens to hundreds of percent. Replacing these traditional metals with materials that have a larger elastic intrinsic strain may offer a route to create higher area density devices by requiring less serpentine interconnect material to achieve the same macroscopic strains.

Freestanding magnetron sputtered Nickel – Titanium (NiTi) based shape memory alloys (SMA) are attractive for
textile and wearable interconnect technologies. They can reversibly recover from unusually large elastic strains (up to 6%) through a temperature induced solid-to-solid phase transformation, compared to 1% for traditional metals like Cu. When a SMA’s transition temperature is below room temperature, the material is considered to be superelastic, where elastic strain recovery occurs purely upon unloading. Previously, superelastic TiNiCuCo thin-films were demonstrated to be ultra-low fatigue, reversibly deforming through 10 million cycles at a 2% strain [1]. Additionally, superelastic and SMA materials exhibit exceptional mechanical strength and efficient electrical conductivity, making them ideal stretchable electrode material candidates for active serpentine interconnects in various wearable devices.

Here, we present a MEMS compatible fabrication process to fabricate and characterize the stretchable mechanical performance of novel superelastic TiNiCuCo serpentines [2]. Fabricated devices have a serpentine amplitude of 1 mm, wavelength of 1 mm, width (w) between 25 – 75 μm, and film thickness (t) between 20 – 80 μm. We evaluate different mechanical deformation modes for our serpentines where < 1 results in buckling deformation and > 1 results in scissoring deformation [3]. We demonstrate large single strain-to-rupture testing of all devices ranging between 97 - 156% macroscopic strains, superior than those modeled for a Cu system of the same geometry. Preliminary cyclic fatigue testing has demonstrated these serpentine interconnects can survive up to 8000 cycles at a 100% macroscopic strain, with minimal structural and functional fatigue. Future fatigue testing will explore electropolishing of the serpentine structure to exclude any residual defects which is likely to improve the fatigue resistance even further. Overall, our results show superelastic metals may offer a route to increase the stretchability of wearable devices while simultaneously reducing the size and cost of device production.


4:30 PM SB10.05.09

Graphene Nanoplatelets-Based Membranes for Thermal Comfort Enhancement in Textiles Lorenzo Bonetti1, Andrea Fiorati1,2, Andrea Serafini1, Francesca Tana1, Agnese D'Agostino1, Guido Masotti1,3, Lorenza Draghi1,2, Roberto Chiesa1,2, Silvia Farè1,2, Massimiliano Bianchi1, Laura Giorgia Rizzi1 and Luigi De Nardo1,2; 1Politecnico di Milano, Italy; 2National Interuniversity Consortium of Materials Science and Technology (INSTM), Italy; 3DIRECTA PLUS S.p.A. c/o ComoNExT - Science and Technology Park, Italy

Composite materials incorporating carbon allotropes are emerging as a powerful technology to manufacture membranes able to impart advanced functions to textiles [1,2]. Body temperature increases under physical effort, and an excessive body warming negatively affects the comfort feeling and the physiological performances [3]. Here, we report an innovative family of advanced nanocomposite membranes for thermal comfort enhancement in functional textiles, based on a thermosetting aliphatic polyurethane (PU) and graphene nanoplatelets (GNPs).

A thorough chemico-physical characterization of GNPs was performed to provide an insight of the thermal properties obtained for the composite materials. The highly crystallographic quality of GNPs, obtained via physical-mechanical processes, was revealed by Raman spectroscopy (ID/IG = 0.127) [4]. TEM and AFM analyses assessed that about 85% of the analyzed GNPs possessed a thickness lower than 10 graphene planes. These results confirmed the suitability of the produced GNPs for the fabrication of highly performant membranes in terms of thermal conductivity.

The GNPs were then loaded into the PU matrix (5 and 10% w/w) by conventional industrial mixing process. The obtained composites were characterised after coupling with cotton fabrics, via hot-melt process. SEM micrographs showed that graphene nanoplatelets were homogeneously distributed in the PU matrix, with a preferential alignment parallel to the matrix plane, maintaining the original dimensions. Crystalline phases present in the composites were evaluated by X-ray diffraction: two peaks around 2θ = 26.48° and 54.78°, corresponding to the characteristic peaks of GNPs, were clearly present in the diffraction patterns of PU-GNPs composites. Moreover, the intensity of these peaks increased by increasing the GNPs loading [5].

Thermal characterization was performed on the composite membranes as a function of the filler percentage. In-plane thermal conductivity of the pristine PU membranes and PU-GNPs membranes was measured, showing that thermal...
conductivity improved (up to 471 %) by increasing the percentage of GNPs. An appropriate designed forearm manikin device was used as phantom to evaluate the thermal conductivity and thermal dissipation of the developed membranes, mimicking the possible in vivo condition [6]. PU-GNPs membranes were demonstrated to improve the thermal dissipation, lowering the internal temperature of the phantom compared to pristine PU membranes (-1.2 °C for 10% GNPs-loaded membranes).

This study provides a new approach for the design of innovative membranes suitable for sport and technical textiles, with significant performance improvement in thermal comfort.

References:

4:45 PM SB10.05.10
Monitoring Joint Motion Using Knitted Fabric Strain Sensors S. Zohreh Homayounfar, Hannah Meeran, Alfred J. Crosby and Trisha L. Andrew; University of Massachusetts Amherst, United States

Smart apparels capable of tracking the wearer’s gait and motion have the potential to revolutionize human behavior sensing and personalized health monitoring by transforming everyday clothing into sensors. The ability to measure motion at individual joints can enable many applications. For example, the knee and ankle joints are important to monitor gait disorders that can occur due to neurological causes like Dementia and Parkinson’s, as well as non-neurological causes such as Osteoarthritis, intoxication, and medications (e.g. sedatives). However, existing sensing techniques typically rely on sewing or inserting traditional hard sensors (such as inertial measurement units and piezoelectric buttons) into tight-fitting garments to obtain sufficient signal to noise, making it uncomfortable to wear and limiting the technology to niche applications in lab settings.

Here, we describe an approach to leverage the unique properties of textiles and garments themselves to enable entirely new ways to sense motion using clothing. Specifically, a garment folds, compresses, twists, and stretches as a wearer moves, and, by conformally applying an imperceptible electronic polymer coating directly onto the textile surface, we demonstrate the ability to transduce these mechanical deformations into an electrical signal. We use a solvent-free vapor coating technique developed in our lab to conformally deposit an electronic polymer film followed by an insulating polymer encapsulant onto mass-produced fabrics or garments. Vapor coated samples retain the weight, feel and flexibility of the starting fabrics and garments. Our polymer coatings simply impart electronic functionality to a previously insulating substrate, thus providing a handle to detect changes as the fabrics/garments bend, compress or twist during movement. Notably, vapor deposited polymer coatings are sweat repellent and stable to machine washing, ironing, and mechanical abrasion.

Vapor coated compression socks and elbow sleeves, in particular, serve as resistive strain sensors that produce a unique signal pattern (resistance change) for each specific joint motion. The special knitting pattern of these garments imparts multiaxial strain sensitivity to the sensor, and their tight fitting design maintains constant body contact during motion, limiting spurious noise. The high stretchability of the commercial fabric used in compression socks and elbow sleeves allows for a large range of dynamic motions (axial, bending and torsional strain) to be captured without the need for adaptive circuitry or sophisticated signal processing routines. Because vapor-deposited electronic polymer films are conformal and pinhole-free, a linear resistance change is created while a subject is wearing the compression sock or elbow sleeve, even at large strains (>100%), which is a notable advance over reported movement sensors. Moreover, since vapor deposited coatings are automatically grafted onto the surface of the fabric, repeated and varied mechanical deformations do not deadhere, delaminate or realign the electronic polymer coating over time, meaning that signal hysteresis and stretching fatigue are not observed. Lastly, due to the direct and tight-fitting contact of the vapor coated compression sock with skin, this structure also boasts the ability to record ECG data, which can be correlated with joint motion. All these prominent properties empower wide-spread applications in gait detection and human performance monitoring.
Developing new textile devices is a sequence of trial and error. This iterative process is largely due to a lack of modeling tools that are paramount for predicting properties like electronic conductivity and mechanical performance. In comparison, other industries, such as automotive and aerospace, rely on a digital design environment before fabrication to study the effects of geometry and architecture on device performance. As this kind of engineering system does not exist for textiles, studying the effects of these parameters, including knit architecture, geometry, and loop pattern, on device performance has been underexplored.

We have developed a novel bicontinuous helicoid lattice system for modeling yarn pathways within the knit structure that can begin to address this challenge. This lattice is based on established principles, with the surfaces of the lattice mathematically defined. This allows the path of the yarn to be known at each distinct point throughout the structure, defined by its relationship to the lattice surface, providing an understanding of the complex three dimensionality of the knit textile structure. With the helicoid lattice, we can model how stitch pattern changes lead to loop deformations in the resulting fabric structures. This includes the effects of knit and purl stitch combinations and the deformations these patterns can create, leading to variable surface geometries. The model was originally developed to understand the deformation mechanisms that occur within the knit structure and produce a self-folding effect. Through this understanding, we can see how loop architecture informs device performance in a variety of textile applications, including electronic textiles, where design of non-planar structures can be used to enhance functionality.

Specifically, in the design of textile supercapacitors we explored the effect of knit structure on device performance. Recent literature on the development of fiber and yarn supercapacitors demonstrate high capacitance and energy density at short lengths only (<4 cm), with reduced performance at longer lengths due to high resistance. For this reason, knitted electrodes are a promising new architecture of textile energy storage devices; yarn electrodes are manipulated into interconnected loop structures, providing multiple pathways for electron transport. One of the inherent challenges of knit supercapacitors is that the spacing between electrodes is significantly larger than that of planar microsupercapacitors, and it is well known that the narrower the spacing between electrodes, the better the rate capability, power response, and energy density of a device.

In this work, methods to minimize the electrode spacing were explored by exploiting the fundamental loop structure of knitted textiles. Using the bicontinuous helicoid lattice model to inform design decisions, specific loop structures were chosen to control the device geometry and optimize electrochemical performance. By tuning the knit structure, the spacing between electrodes decreased by more than a factor of 4 and the capacitance increased by almost a factor of 2 at low scan rates.

Photolithographic defined films play an important role in modern optoelectronics and are crucial for the development of advanced organic thin-film transistors (OTFTs). Here, we explore a facile photosist-free photopatterning method for natural carbohydrates and their use as OTFT gate dielectrics and passive for flexible transistors. The effect of the cross-linkable unit chemical structure on the crosslinking chemistry and dielectric strength of the corresponding films was explored by investigating cinnamate-functionalized carbohydrates from monomeric (glucose) to dimeric (sucrose) to polymeric (cellulose) backbones. UV-illumination of cinnamate ester of these carbohydrates leads to [2+2] cycloaddition and thus the formation of robust crosslinked dielectric films in the irradiated areas. Using propylene glycol monomethyl ether acetate as solvent/developer, patterned dielectric films with micrometer size features can be fabricated. P- and N-type OTFTs were successfully demonstrated using unpatterned/patterned crosslinked films as the gate dielectric and pentacene and N,N'-1H, 1H-perfluorobutyl

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**Beyond Materials—Knit Architecture to Improve Textile Device Performance** Chelsea Knittel, Ariana S. Levitt, Yury Gogotsi, Randall Kamien, David Breen and Genevieve Dion; Drexel University, United States; A.J. Drexel Nanomaterials Institute, United States; University of Pennsylvania, United States

**Natural Carbohydrates as Crosslinkable Dielectric Materials for Flexible Dielectric and Passive Applications** Antonio Facchetti; Northwestern University, United States; Flexterra Corp, United States
dicyanoperylenecarboxydiimide (PDIF-CN2) as the p- and n-channel semiconducting layer, respectively. Furthermore, implementation of these materials on elastomers enable good performance and mechanical flexibility. Our results demonstrate that natural-derived polymer gate dielectrics, which are soluble and patternable using biomass derived solvents, are crucial for the realization of a more sustainable flexible OTFT technology.

9:15 AM SB10.06.03
Fiber-Based Highly Efficient Phosphorescent Organic Light-Emitting Diodes and Addressable Structure for Textile Displays Yong Ha Hwang, Seon Il Kwon, Jeong Bin Shin, Hyun Cheol Kim and Kyung Cheol Choi; KAIST, Korea (the Republic of)

Textile-based light-emitting devices, one of the more promising approaches for cutting-edge wearable electronics, have been developed in a variety forms. They can be fabricated directly on fabric, or on individual strands of the fiber itself. Among these approaches, fiber-based light-emitting devices possess many structural advantages including flexibility, breathability and light weight, that make them promising candidates for future wearable displays.[1-2]

So far, most fiber-based light-emitting device studies have focused on fabricating a single device. However, it is essential that light-emitting devices are capable of displaying composite information. High efficiency is also a very important characteristic for functional textile displays. Here, we introduce fiber-based phosphorescent organic light-emitting diodes (fiber phOLEDs) which exhibit the impressive current efficiency (CE) of over 20 cd/A, the highest CE value ever reported. This work also proposes an addressable structure which allows multiple emitting-cells to emit light from a strand of fiber.

The fiber phOLEDs are based on a dip-coating process strategy developed in our previous work proposing organic light-emitting fibers.[2] First, to obtain a higher CE than achieved in our previous work [2], we used a phosphorescent dopant material, tris(2-phenylpyridine)-iridium(III) (Ir(ppy)3), which can achieve 100% internal quantum efficiency (IQE). However, Sophisticated structures to control the excitons were needed to take advantage of the 100% IQE because the exciton lifetime is so long. The Ir(ppy)3 based emitting layer (EML) was therefore designed to not only take charge balance into consideration, using co-host materials, but also the appropriate concentration for avoiding aggregation of the solution. Also, a high triplet energy hole transport layer (HTL) was inserted between the EML and Al anode layer for exciton confinement. These sophisticated structures on the thin fiber resulted in the outstanding CE value of over 20 cd/A, along with a sufficient level of luminance, over 3000 cd/m². Next, to make them addressable, an array structure composed of the fiber phOLEDs and Al-deposited fibers was prepared. The layer next to the dip-coated EML was deposited by vacuum thermal evaporation as a series of striped patterns on one side of the fiber, to form multiple emitting–cells on a strand of fiber. Then, each Al-deposited fiber was contacted to the patterned layer. Initially, when we simply placed the fibers on this array structure, there were problems with short circuits and instability. To solve these problems, we introduced contact regions that were inserted between the EML and the patterned layers. No incidental damage was observed in this array structure. As a result, each emitting-cell of the high efficiency fiber phOLED can be reliably addressed.

The resulting fiber phOLED is addressable and highly efficient and exhibits the characteristics required for textile displays, including flexibility, weavability and a reasonable level of brightness. We expect that these strategies will take us a step closer to functional textile displays that can provide visual information.

Acknowledgments
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References

9:30 AM BREAK

10:00 AM *SB10.06.04
Merging the Lines between Fashion, Material Science and Engineering Galina Mihaleva; Nanyang Technological University, Singapore

Leaving in the era of the Fourth Industrial Revolution provides the opportunities of taking wearable technology and
design to a whole new level. The increase in reliance on creativity across industries and interdisciplinary creative work in fields such as fashion, science and technology, sets the balance and the boundaries, used as a metaphor to describe "creativity in terms of crossing or pushing out a ..." Bogartz (1994). The fusion of smart textile materials and wearable computing technology are introducing a shift in textile, from a passive to a dynamic behaviour: active smart textiles and ultra-smart textiles. The ultra-smart textiles perform similarly to a human brain, with reasoning, cognition, and activating capabilities or a second smart skin.

The recent urge in the design and development of biosensors for health care and wellness engineering is pushing the boundaries of material and technological processes for new kinds of material modification and manipulation, with emphasis on sustainability. The aim of this research is to propose and to open up new opportunities and challenges of the next-generation e-healthy monitoring, in collaboration with one of the most forward moving field: Fashion. Also to push the boundaries of what makes smart fabric technology revolutionary based not only on its ability to communicate, transform, but also to grow or naturally fabricate. Proposing another fold of opportunities - one where technology meets craft and craft meets science and art, while sustainable materials are also a key factor. To propose the next generation of wearables by implementing electrophysiology interfaces by mechanically Interlocking of conducting polymer and silk fibroin to develop new applications for monitoring, diagnosing, displaying and preventing.

Textiles of today are materials with applications in almost all everyday activities. Fibres, yarns, and other structures with added-value functionality have been developed for a range of applications textile materials and the textile has become an important platform for high-tech innovations. The projects developed and introduced in this paper followed a design approach by fusing technology, science and nature, introducing new innovative hybrid fabrics explorations that requires the understanding of: the what (the purpose of the concept); the how (the used bio and tech); the where (the context in which the product is used) and finally the wearability issues connected to the role of trans materials and technology in human body, changing and perception.

Keywords: wearable technology, textiles, bio, science, nature, Silk Fibroin

10:30 AM SB10.06.05
A Yarn-Based Microbial Fuel Cell Yang Gao and Seokheun Choi; State University of New York at Binghamton, United States

We demonstrated an innovative, flexible yarn-based biobattery that generates green electricity from bacterial respiration. The battery can be easily scaled up by controlling the length of the yarn of a single battery or connecting multiple yarns in series. Bacterial cells in the yarn break down the organic fuels (e.g. glucose and lactic acid) and transfer the produced electrons to the electrode, providing power for external applications. The yarn-based biobattery was knotted into a bracelet by connecting three battery units in series, generating the current density of 0.33mA/cm². Furthermore, this proposed biobattery can be woven or embroidered into a large smart fabric, potentially providing hundreds of milliampere for powering actual wearable electronics. The ever-increasing worldwide efforts in developing renewable energy sources and reducing environmental footprint are among the greatest challenges faced by mankind. Although there are great potential and innovations in large-scale alternative energy technologies (e.g., wind and solar), the small-scale applications are still powered by batteries that may cause environmental and economic burdens with their recycling and replacement. In addition, electronic products such as wearable devices are becoming more powerful and smaller in size, and work in closer contact with the human body. The conventional energy storage and harvesting devices (e.g., lithium-ion batteries and photovoltaic cells) fail to meet flexible and environmental requirements for the next generation of electronics and micro-/nanosystems (MNSs). Hence, various emerging energy-harvesting techniques have been proposed as a power source by using organic-photovoltaic, thermoelectric, electromagnetic, and piezoelectric/triboelectric principles. The biochemical energy harvesting devices (or biobatteries), notwithstanding being the least explored, have three major advantages. First, the biofuels that can be utilized for electricity generation are readily available in sweat, saliva, urine, and even in common beverages. Second, they are capable of continuously generating electricity independent from lights or motions. Last, the devices are easily disposable and cost-effective. However, significant challenges remain in the making of flexible, green and scalable biobattery for the energy conversion. The biobattery developed here can not only be readily integrated into wearable electronics or smart textiles, but also be scaled up to revolutionize the power performance for real-world applications. The proposed battery was made by wrapping the functionalized yarns onto
a non-conductive cord. Both the anodic and cathodic yarns were treated with the poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), making its own yarn conductive while retaining its porosity and hydrophilicity. Furthermore, the cathodic yarn was loaded with a low-overpotential Ag2O solid electron acceptor and coated with Nafion as a proton exchange membrane (PEM).

10:45 AM SB10.06.06

The goal of this research was to realize a textile display that could sustain 3 dimensional deformation such as bending, wrinkling, and stretching. We developed a multifunctional next-generation display technology with commercial-level driving voltage, brightness and efficiency characteristics, and a new form factor. There were three fundamental technical components used to fulfill the goal of the research, a Platform, the Display and Encapsulation layer.

(1) Platform: A study of an elastic clothing platform with a flat surface and a stress lowering structure
[Planarization] A planarization study was conducted to form a flat surface on a textile. A sacrificial layer, a planarization layer, an adhesive layer and the textile were formed on the glass, and then the sacrificial layer was simply removed by deionized water. Previous studies have performed planarization by attaching a plastic film to the textile, and used a very thick planarization layer of several tens of, hundreds of micrometers.[1, 2] However, the planarization layer in this work was only 0.5 micrometers.
[Stress-lowering structure] Flexible and stretchable features of textiles produce very high strain and stress as well. Accordingly, this work studied a platform between the planarization layer and the textile by introducing a ‘stress–buffer’ layer. The stress–buffer also functioned as the adhesive layer, and significantly reduced mechanical strain and stress, and had the advantage of enhancing durability.
[Improvement of applicability] A stress–buffer that was capable of hardening at room temperature was used to prevent any deformation and distortion by heating. This research developed a fabrication process that can be applied to any textile including cotton, linen, wool, leather, etc.

(2) Display: Low temperature process (below 150 degrees Celsius) OLED display
[Textile-based OLED] To realize the clothing-shaped full-color display, red, green and blue OLEDs were fabricated on the textile platform. The textile–based R, G, B OLEDs had almost the same luminance and efficacy as glass-based OLEDs.
[Low temperature processed display backplane] Thin film transistors (TFTs) typically require a high temperature heating. This causes serious damage to the textile such as twisting and burning. Since a heat treatment is necessary to repair interface damage on the insulator produced by plasma during sputtering, a TFT fabrication method was investigated to avoid plasma damage and chemical deposition of the insulator.

(3) Encapsulation: Washable encapsulation with water-blocking ability and flexibility
[Nano-stratified and washable encapsulation] A study using a nano-stratified structure was performed to improve the gas barrier property and mechanical flexibility of the encapsulation. The nano-stratified encapsulation was composed of ultra-thin sub-layers (less than 3nm) fabricated using the ALD(atomic layer deposition) process. The multi-interface system blocked the growth of defects, and as a result, WVTR(water vapor transmission rate) was lowered. The porous structure also contributed to improved flexibility. In addition, the encapsulation layers were formed on a passivation film to block liquids, and then it was integrated with the textile display.[3]

(4) Practical application study of the textile display
[Smart fashion] The developed textile display combines aesthetic elements with smart functions, which means that it not only has functional capability, but can be attractive in the fashion industry. The proposed approach permits OLED displays on shirts, hats, shoes etc.

References
After more than 20 years of development, e-textiles for various applications are gaining increasing attention worldwide. Industry driven application oriented developments are superseding the research oriented projects. This leads to changes in the technological approaches. Manufacturability becomes a more important aspect which leads automatically to a simplification of components and processes. On the other hand the overall systems reach a new complexity in order to be useful in a real life environment.

In order to enable industrial manufacturing of wearable e-textiles it is necessary to develop modular concepts as well as integration processes suitable for high volume production. Only with modules dedicated for textile integration with standardized interfaces it will be possible to realize new systems in short development cycles. These smart modules have to be compatible to allow fast design of new functionalities and even flexible adaptation.

Approaches to integrate electronics on textile ribbons with conductive bus structures instead of aiming to assemble the modules directly on large area textiles are very promising. They reduce complexity and footprint of the assembly equipment while simultaneously reducing the process time. New interconnection processes like thermoplastic non conductive adhesive bonding and ultrasonic welding will allow to reduce cycle times additionally.

From the early stages of smart textile development the monitoring of physiological parameters plays the most important role. Smart textiles for medical applications can cover various aspects: prevention, diagnosis, therapy and rehabilitation. Derived from rehabilitation concepts a new generation of wearable systems which will support patients but also healthy subjects are now aiming at combining the monitoring of movement, muscle activity and other parameters with actuators for active assistance. For most applications sensors can be textile or polymer based but also miniaturized conventional sensors can be required. A broad range of measurement principles can be realized and integrated. In most cases only the combination leads to the data required for optimum control.

The scope of the presentation is the overview and evaluation of technologies for conductor-, electronics-, sensor- and actuator-integration in textiles to meet the requirements of different wearable applications together with manufacturing and reliability aspects.

The development of new composite materials exhibiting both high infrared (IR) emission and good electrical conduction represents a challenging task for those applications where efficient radiative properties and electrical conduction are simultaneously needed as for instance for heat dissipation in conductive yarns and conductive textiles or for the realization of IR thermal detectors.

To this aim, a set of polymeric fibers composed of randomly oriented carbon nanotubes (CNTs) dispersed into a poly(ethylene terephthalate) (PET) matrix host was prepared and investigated [1]. Among the different carbon materials, CNTs were chosen for the uniqueness of their emissive properties in the IR wavelength range. Besides electrical conductivity, in fact, the inclusion of CNTs offer the possibility to increase of the IR emissivity which is usually not straightforward.

The amount of CNTs in the investigated set of samples ranges between 1 and 10 wt%. The effects of the inclusions on electrical and morphological properties were studied by means of electric conductance, scanning electron microscopy and white light interferometry investigations, respectively. Finally, the IR emissivity was characterized in the 3.5-5.1 micron spectral range by using the infrared thermography technique under heating regime [2]. The electrical conductivity showed a percolation-like behavior with increasing CNTs content. In particular, an exponential conductivity growth from the pure PET value (~ 10^-18 S/cm) to about 2×10^-3 S/cm was obtained by dispersing 1 wt% of CNTs as the percolation threshold is passed while an almost linear increase was observed in the samples with a larger CNTs concentration. Concerning with IR characterization, experimental results show that emissivity is gradually growing with the amount of dispersed CNTs.

In order to analyze the obtained experimental results, a model based on the Maxwell Garnett mixing rules was
adopted to calculate the dielectric permittivity of the polymeric matrix with randomly oriented inclusions. The effective medium data have then been employed to retrieve the absorption cross section for infinitely long cylinders by means of the Mie scattering theory. The experimental data show higher emissivity values with respect to numerical ones, particularly for larger CNTs concentrations. The large values of the experimental emissivity has been ascribed to the emerging of surface roughness when CNTs are included, as evidenced by SEM images and mean surface roughness measurements carried out by WLI analysis. Indeed, the emerging of surface roughness may lead to an increase in the specific surface and, consequently, gives rise to an increase of the IR emissivity due to the larger value of the radiating sample surface.

Concerning with mechanical properties, in order to preserve the flexibility of the bare PET fibers along with the ability to use these fibers to form textures or fabrics, CNTs values should be kept lower than 4-5 wt%. However, experimental results demonstrate that limiting the CNTs content to 5% still allows good electrical conductivity ($1.5 \times 10^{-3}$ S/cm) along with IR high emissivity (>0.90).

In conclusions, this study highlights the possibility to get high electrical conductivity values associated to high values of IR emissivity. Such unconventional properties encourage their use for the realization of conductive yarns displaying both high IR emissivity/absorbance and good electrical conduction.


SESSION SB10.07: Textile Devices and Smart Systems
Session Chairs: Beatrice Fraboni and Esma Ismailova
Wednesday Afternoon, December 4, 2019
Hynes, Level 3, Room 300

1:30 PM *SB10.07.01
Microsystem Packaging and Integration Technologies for Electronic Textiles Toshihiro Itoh; The University of Tokyo, Japan

Electronic textiles (e-textiles) are fabrics that are integrated with electronic elements including sensors, actuators and microcontrollers, and are expected to be applied to not only wearables but also smart sheets, for instance. In order to realize high function e-textiles, we have been developing integration and packaging technologies to integrate silicon or compound semiconductors based microdevices into textiles, such as stretchable interconnect, flexible interposer and spring contact technologies. Continuous manufacturing processes for these have been developed. Stretchability is frequently required for e-textiles. For instance, since human skin around the elbow or knee joints can be stretched to more than 30%, interconnects of wearable devices need stretchability of 30% or above. Although stretchable interconnects on textile substrates are often realized by printing horseshoe-patterns with use of “stretchable” inks, printing patterns cannot cover stretch as large as 30% and require large surface areas. To realize fine interconnects with stretchability of 30% or above, we have developed vertical wavy Cu stretchable interconnects utilizing micro-corrugation process of Cu foils and embedding in silicon rubber. When Cu foils are shriveled to -30% by micro-corrugation, the interconnects should be stretched to 30% without electric resistance change. The micro-corrugation process is based on the metal foil forming technique where a flat Cu foil is continuously deformed into wavy shape of interconnects between the upper and lower gears. After the process, the wavy machined Cu foils are embedded in silicone rubber to protect them and improve the interconnects’ elasticity. The fabricated wavy Cu interconnects showed stretchability of more than 40%. Using the 0.5-mm-wide interconnects, FPC(flexible printed circuit)-compatible stretchable electric circuit integrated with LEDs was successfully demonstrated.

It could be difficult to integrate “hard” devices such as ICs, optical devices, MEMS sensors and passive elements as they are into “soft” textile substrates. In addition, inflexibility of hard devices causes breaks of e-textiles during use including washing. To overcome the problems, we have developed an interposer of miniature FPC board on which hard devices are mounted. The flexible interposer can be easily integrated on soft textiles. Using the interposer
technology, we prototyped large area (1.2 m x 1.2 m) LED array fabric. The interposers with LED and passives can be continuously mounted and soldered on ribbon textiles woven with polyester fibers copper wires. The large area fabric is realized by weaving the LED integrated ribbons and polyester fibers together. These interposers are necessary for re-distribution of interconnects, because it is often difficult to form fine interconnects and bonding pads on textile substrates.

Even though both interconnects and devices are flexible, solid electrical contacts between them may cause breaks of breaks of e-textiles during use. We have developed reel-to-reel continuous fabrication process of flexible contact structures on fibers (cables). The contact structures are hemisphere or bell shaped elastomers coated with PEDOT:PSS. The fabrication process consists of dispensing suitable silicon elastomer and both hydrophilic and hydrophobic PEDOT:PSS coating. It was found that the structure has life time of more than a million deformation cycles. Although the contact structure was developed for the contact between the fibers (cables), it could be effective that this type of flexible spring structure is introduced into joints between interconnects and devices on textile substrates.

2:00 PM SB10.07.02
Compressible and Electrically Conducting Fibers for Large-Area Mapping of Pressures Andreas Leber, Alexis Page, Dong Yan, Qu Yunpeng, Shahrazad Shadman Yazdi, Pedro Reis and Fabien Sorin; École Polytechnique Fédérale de Lausanne, Switzerland

The integration of conductive elements in soft material constructs provides attractive opportunities for the realization of diverse electromechanical devices. Flexible pressure sensors, in particular, offer a wide application range in health monitoring and human-machine interaction. However, their implementation in functional textiles is limited because existing devices are usually small, 0-dimensional elements, and pressure mapping is only achieved through arrays of sensors that are difficult to integrate and include many failure-susceptible connections. Here, we demonstrate compressible and electrically conducting fibers for the detection, quantification, and localization of kPa-scale pressures over m²-size surfaces.[1, 2] The scalable thermal drawing technique is employed to co-process polymer composite electrodes within a soft thermoplastic elastomer support into long fibers with customizable architectures. Exerting pressures on the fibers results in the selective and reversible contacting of the electrodes within the fully enclosed structure, thereby generating electrical signals at distinct pressure levels. Moreover, resistance measures can be directly related to pressure positions along the fibers, enabling pressure localization. The fibers act as accurate and robust 1-dimensional pressure sensors, functional over large cycle numbers, variable frequencies of mechanical stimulation, and in humid environments. Their potential in health care is demonstrated by mapping pressures on a gymnastic mat for the monitoring of body posture and motion. The fibers represent a simple, cost-effective, and reliable strategy towards the functionalization of large, flexible surfaces.

References:

2:15 PM SB10.07.03
Making Soft Optical Sensors More Wearable Cindy K. Harnett; University of Louisville, United States

This presentation will discuss new materials and components that enable our intrinsically stretchable optical fibers [1] to measure strain while meeting the power and washability requirements of wearables. These threadlike sensors work with high-throughput fabrication methods designed for textiles. However, for wearables, practical requirements must be taken into account.

Coated [1], molded [2], and extruded [3] elastomeric optical fibers are a new low-cost, all-polymer sensor material for measuring wearer activity. They can be applied to fabrics by sewing or adhesives. After their light intensity signals are transformed into electronic signals using optoelectronic sensors, the activity data can be sent over a wireless link for analysis. Because washable, battery-free radios are still under development, a battery/processor/radio communication module that separates from the textile is a popular approach that lets the communication module skip the laundry. Resistive strain sensors and conductive-fiber electrodes for sensing the electrical activity of skeletal muscles (electromyography or EMG) rely on conductive connections to the communication module. For reversibly connecting the communication module to these electrical signal sources, a common solution is a metal snap fastener. Fabric-integrated optical fibers need a similar rugged, quick-connect
solution for practical applications. This presentation will cover our approach to making reversible optical
counters specifically for wearables using all-polymer components.
All-polymer optical sensors are heat-bondable to synthetic fabrics and do not corrode during washing, in contrast to
conductive fibers that corrode in water. However, power consumption for light emitting diode (LED)-driven optical
fiber strain sensors is significantly higher (~10 mW) than for resistive strain sensors made from conductive fibers
(~0.1 mW). Because the power resources for wearables are so limited, both optical and resistive sensors are turned
off when not in use. Even so, the peak power requirements of optical sensors may still prevent their use in
lightweight, battery-free energy-harvesting wearables.
Differential absorption in a mismatched fiber pair removes the effect of changing light conditions for optical strain
sensors, making it possible to drive them with unknown-intensity ambient light. We have previously investigated
process-based methods for modifying the light attenuation coefficient of fibers [4]. Control over optical transmission
means one can compare the signal intensity from two parallel fibers with known optical transmission differences and
thus subtract out the unknown source light that leaked into the fibers along their path over a surface. This approach
will be discussed in the presentation. When sufficient external light is available to make measurements, the LED can
be turned off, cutting out the main power-consuming component. The optoelectronic sensor brings power
consumption to the resistive sensor level. Unlike resistive sensors, no signal return path is required for textile-
embedded fiber pairs that use ambient light. Since textiles increasingly form the skins of soft robots in addition to
wearables, new developments here will lead to sensorized surfaces in a wide range of applications.


2:30 PM BREAK

3:30 PM *SB10.07.04
Design and Development of Wearable Textile Materials on an Industrial Scale Arnaldo Usai; Let's Web-earable
Solutions, Italy

The development of objects of sensorized clothing in the previous years has been the subject of experiences of
affixing sensors extraneous to the textile nature of the fabric, maintaining as a principle of stability of the sensors on
the skin the containing effect of the pressure of the fabric on the body; compromising the effective wearability,
comfort and usability of the sensorized clothin'objects.
In this framework we present a new method of developing a range of fully textile sensorized clothing items,
completely wearable, washable and usable in different contexts: work, sport, defense and health.
The use of a new method and the new materials for the production of fully wearable sensorized clothing items
changes the scope of application of the monitoring materials of bio-vital parameters in use, from a purely episodic
and professional use, to a continuous widely use.
The industrialization of this technology makes it possible to apply these materials to different sectors of clothing:
technical, formal and specialist, expanding the concept of clothing from a need for purpose and function, creating a
new and different awareness of users with respect to clothing materials and individual well-being.
The classic prerogatives of clothing materials in covering, decorating, protecting and distinguishing the human body
and its social function are changed by the use of these materials, in which the functions of the body's purpose (its
own performances) are measured and evaluated, analyzing the basic parameters of organized action no longer on
time shifts but by introducing indicators of safeguard and individual well-being.

In the framework we will present concrete cases of the application of these materials and wearable technologies in
the industrial, health and sport fields.
We developed 5 μm thick ultrathin film MEMS piezoresistive strain sensor for wearable human motion sensors. We made the 5 μm thick ultrathin film MEMS sensor on polyurethane film and detected human finger motion. Thin microelectromechanical systems (MEMS) sensors which is made of very thin (< 5 μm thick) have been expected for the application to healthcare monitoring, infrastructure monitoring, structural health monitoring of infrastructure, automotive, aircrafts, and other transportation equipment. The advantages of thin (<5 μm thick) MEMS devices are highly flexible, long-term stability, high sensor sensitivity and mass productivity because thin film exhibits smaller bending strain than conventional thick MEMS films and silicon-based devices have not be affected by the atomosher without packaging in compared with organic semiconductor devices.

Thin MEMS sensor assembly of releasing thin MEMS film and transferring thin film onto flexible substrate has been, however, difficult. Previous studies on thin MEMS sensor assembly report the surface machining MEMS structure as a thin MEMS film releasing structure with PDMS stamp. But the adhesive force of PDMS is not stable or applicable to industrial use because vacuum suction type chip mounter is commonly used.

In this paper, we developed the mechanical model of ultrathin MEMS sensor separation and optimize the design of MEMS sensors and connection parts to achieve high yield of thin MEMS sensor chip mounting with commercially available chip mounter. In detail, we analyze plastic-scale-model-like assembly of ultrathin MEMS piezo-resistive strain sensor theoretically and experimentally in order to find an optimal design of MEMS sensor chip for high yield assembly. In the plastic-scale-model-like assembly of ultrathin MEMS sensor, MEMS sensor chip consists of ultrathin piezo-resistive sensor parts, disconnect part, and outer frame and its structure is similar to the plastic scale model. The plastic-scale-model like MEMS sensor chip is fabricated through conventional MEMS process. By using commercially available chip mounter, the MEMS sensor is cut and picked up from the outer frame in the similar manner of plastic-scale-model assembly. Then, the MEMS sensor film was placed and released on the desired area of substrate.

In the chip-mounting mechanical model analysis and experiment, if the number and the width of the disconnection parts are decreased to four and 20 μm, the successful rate of the chip mounting increased to 100 % because the shear stress on those parts are concentrated for ease of cutting and the resultant small load on sensor body reduces bending stress on sensor body for avoiding crack of sensor body. Therefore, in case of 1 mm x 5 mm sensor film, the four connecting parts with 20 μm width are optimal design for high successful plastic-model like MEMS sensor assembly.

Finally, we made human finger motion sensor by ultrathin MEMS sensors. The stretchable silver paste is patterned on the Polyurethane film (PUfilm) to make electrode. Then, ultrathin MEMS sensor is placed on the electrode and the edge of the MEMS sensor and electrode is connected by silver paste. Then the hot-melt PU film covers the MEMS sensor for avoiding the break of the sensors. The fabricated MEMS sensor on PU film is attached on the glove and the bending of the human finger was detected.

Recently, emerging technologies like 3D-printing has doped the development of flexible electronics to design foldable displays, bioprosthesis, wearable devices, etc.1,2 Particularly, stretchable microelectronics able to adopt easily complex shapes like emulating the human body have attracted attention for smart textiles3,4. To achieve the fabrication of such devices, innovative technologies and new designs involving the use of materials with advanced mechanical properties are required5. In this work, the fabrication of lithium nickel manganese oxide (LNMO) micropillar electrodes on Al serpentine interconnects that can be stretched up to 70% without structural damaging has been achieved by laser patterning technique6. Unlike compact and continuous electrode thin-films, we show that under mechanical strains, arrays of vertical micropillar supported on serpentines are carrying empty spaces that can prevent the formation of cracks and the electrode delamination.

This innovative approach has been used to fabricate a flexible micro-battery for powering a smart contact lens7 and garments. The innovative micro battery approach relies on two flexible substrates assembling consisting of polydimethylsiloxane (PDMS) supporting 1 cm² surface area disk of LNMO and LTO serpentine electrodes separated by a gel polymer electrolyte.
Interestingly, the micro battery shows in the first reversible cycle a charge and discharge areal capacities of 1.22 mAh cm\(^{-2}\) and 1.196 mAh cm\(^{-2}\), respectively. The coulombic efficiency for the first reversible cycle corresponds to 96.17%. Regarding the cycling performance, the LTO/polymer/LNMO micro battery has been assessed at fast kinetics for 30 cycles. The micro battery delivers 73.5 µAh cm\(^{-2}\) at 6C, 47 µAh cm\(^{-2}\) at 12C and 32 µAh cm\(^{-2}\) at 20C with a remarkable stability.

**REFERENCE**

monitoring of health conditions. The sensing part is typically made into a thin film that guarantees high flexibility with different sensing materials as functional units at different locations. However, a thin-film sensor easily breaks during use because it cannot adapt to the soft or irregular body surfaces, and, moreover, it is not breathable or comfortable for the wearable application. Herein, a new and general strategy of making electrochemical fabric from sensing fiber units is reported. These units efficiently detect a variety of physiological signals such as glucose, Na⁺, K⁺, Ca²⁺, and pH. The electrochemical fabric is highly flexible and maintains structural integrity and detection ability under repeated deformations, including bending and twisting. They demonstrate the capacity to monitor health conditions of human body in real time with high efficacy.

SB10.08.02
Development of Solution-Processed Polymer Light-Emitting Diodes on a Plastic Fiber and Its TFT-Driven Operation for Textile Displays

Hyungsoo Yoon, Taehoon Kim, Sujin Jeong and Yongtaek Hong; Seoul National University, Korea (the Republic of)

Electronic textiles have integrated life of human being with highly developed electronic devices in an innovative way, enabling wearable electronics for displaying bio-medical information and illuminative textiles for smart fabric or internet-of-things applications. Light-emitting devices on textiles can display bio-medical signals immediately via integrating with health-monitoring devices or notify information using a luminous carpet. Although, in order to realize “real” textile displays, flexibility, lightweight, and breathability are necessary for skin-conformal electronic devices, various prototypes of commercial products still have been focused on rigid silicone-based devices. Recently, many research groups have reported flexible light-emitting devices directly implemented on the fabric or fiber. The alternating current electroluminescent (EL) devices on fiber substrate have been reported, whose device configuration is quite simple compared to other EL devices, however, low power efficiency demands high driving voltage up to hundreds volts, which limits practical use. Organic light-emitting diodes on fabric substrate showed good mechanical properties based on its ultra-thinness, but they have low breathability because of additional planarization layers for evaporation process. In addition, high process temperature in the fabrication causes inevitable deformation in the textile substrate. While, polymer light-emitting diodes (PLEDs) has good advantages of low-voltage operation and low temperature process available. And, since the light-emitting polymer is compatible with solution processes, fiber-shaped PLEDs and the corresponding woven structure can be developed without any breathability loss. Although some papers have already reported fiber-shaped PLEDs, a practical integration with thin-film transistor (TFT) has not been reported yet. Some technical challenges such as low device performances should be also addressed.

In this work, we report development of solution-processed PLEDs on a plastic fiber substrate and its TFT-driven operation for textile displays. Specifically, we fabricated the fiber PLEDs on polyethylene terephthalate (PET) fiber, which is flexible and weavable for textiles. By controlling the condition of dip coating of PET fibers, such as withdrawal speed and coating number, we can obtain poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) anode, which has resistance of 200 ohm/mm for 5 times dip coating. Then, PEDOT:PSS hole-injection layer and SPG-01T emissive layer are successively dip coated. After then, lithium fluoride and aluminum are thermally evaporated for an electron-injection layer and cathode, respectively. The device shows a turn-on voltage of 4.8 V at 1 cd/m², a current efficiency of 4.58 cd/A at 1000 cd/m², and luminance of ~4000 cd/m² at 10 V, enabling low-voltage operation for highly luminous display applications. Finally, we integrated fiber PLEDs with fiber TFTs that are also fabricated by a solution process on a PET fiber, showing the feasibility of our devices in textile displays. The detailed fabrication process and experimental results will be discussed at the conference.

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SB10.08.03
Investigation of Thermo-Regulating Properties of Textiles with Incorporated Microencapsulated Phase Change Materials

Maria Cristina Larciprete¹, Stefano Paoloni², Concita Sibilia³, Vitalija Rubeziene³ and Audrone Sankauskaitė³; ¹SBAI Sapienza, Italy; ²Università degli Studi di Roma Tor Vergata, Italy; ³State research institute, Lithuania

Thermal regulating textiles play a very important role in providing thermal comfort for human beings in temperature
changing environments. The level of thermal comfort depends on the heat exchange between the human body and the surrounding environment. The thermoregulatory effect can be achieved by dispersing microcapsulated phase change materials (PCMs) into the textiles. As these materials have ability to lower the temperature of the body, besides wearing comfort they can improve thermal concealment properties of nowadays defence personnel military camouflage clothing.

Various types of phase change materials (PCM) are currently used in the production of smart materials capable to actively control the temperature of the body. Studying the thermoregulatory effects of PCM treated textiles and their multi-layer assemblies is fundamental for the effective use of such smart thermal functional textiles [1, 2].

In the present work two types of commercially available microcapsules of organic phase change materials were investigated in order to improve the thermo-regulating properties of textile fabric. The first type of PCMs, namely type PCM-A (PCM microcapsules –Mikrathermic P, developed by DEVAN® Chemicals NV, Belgium), demonstrates chemical activity to all kinds of fibres without the use of a binder. The second type of PCMs, type PCM-B (Ito finish PCM microcapsules, LJ Specialities LTD, UK) was embedded into the textile by means of an acrylic binder as cross linking resin.

For samples preparation, the knitted fabric, produced from cotton/PES, intended for contacting layer near the skin, were treated by PCM microcapsules using pad-dry-cure method. After sample preparation, melting point and latent heat storage capacities (enthalpy ΔH, J/g) of PCM microcapsules and the corresponding treated knitted fabrics were characterized, using differential scanning calorimeter equipped with a nitrogen-based refrigerated cooling system.

The IR emissivity of the PCM-based textiles has been characterized by means of Infrared Thermography according to the ASTM E1933-99a standard method [3] in the contact-free configuration. In the adopted method, a small portion of sample is covered with a thin layer of a reference paint with known emissivity. The textiles samples were placed onto a heating stage, which is also equipped with a Peltier modulus in order to set their temperature below and above phase transition temperature of PCMs. During measurements samples and reference paint were simultaneously imaged by the IR camera, operating in the 3.5-5.1 μm range, and from the resulting thermographic images the infrared (IR) emissivity was characterized before and after PCMs phase transition. Experimentally obtained data show an emissivity increase with increasing temperature, as a consequence of additives’ phase transition. Furthermore, the emissivity dynamic range (εhot-εcold) for the three samples containing type-A additives show anti-correlation with melting enthalpy values, i.e. the higher enthalpy corresponds to lower emissivity variation, along the phase transition. The observed features open the way to potential applications such as tunable emissivity smart textiles and pave the way to the design of customized IR shielding textiles, by proper selection of the suitable additives type and amount.

8:30 AM *SB11.01.01
The Adaptive Design of an Image Pre-Processing Step for Classifying Materials Design Experiments Paul Clegg; University of Edinburgh, United Kingdom

Ideally, the outcome of materials design experiments would be determined automatically based on a limited quantity of readily obtainable data. This task is often possible for an experienced practitioner. Here we automate this classification step for the case of soft materials design. We want to know whether a particular attempt to create a bijel has been successful or not based on a single confocal micrograph. Our most effective classification approach is based on shape descriptors of the co-continuous fluid domains in the image. Here, I will show how adaptive design can be used to optimize the pre-processing of the confocal image to improve our classification performance.

9:00 AM SB11.01.02
Active Liquid Colloids and Their Application as Transducers in Liquid-Sensing Applications Lukas Zeininger1,2, Markus Antonietti1 and Timothy M. Swager2; 1Max Planck Institute of Colloids and Interfaces, Germany; 2Massachusetts Institute of Technology, United States

Dynamic multiphase complex emulsions formed from two or more immiscible solvents offer a unique platform for the generation of new triggerable materials. In designing our methods, we make use of solvent combinations that are immiscible at room temperature but exhibit a lower (LCST) or upper critical solution temperature (UCST). Emulsification of the mixture below LCST or above UCST enables a simple one-step fabrication of complex multicomponent emulsions as well as structured soft-matter particles with highly uniform morphology via temperature-induced phase separation. The morphology of these dynamic liquid colloids is exclusively controlled by interfacial tensions and the droplet geometries can be controllably altered after emulsification. Dynamic liquid colloids can selectively invert morphology in response to external stimuli such as the presence of specific analytes, small pH changes, light or high energy irradiation, and the presence of an electric or magnetic field and thus provide a new active element for novel and existing applications of emulsions including chemotaxis, the fabrication of optical metamaterials, and chemical/biological sensing.

We explore the potential of our dynamic micro-colloids to manipulate the pathway of light in response to chemically triggered morphology changes. Dynamic morphological reconfiguration of microscale refractive components in combination with the potential to incorporate a variety of active optical media as well as stimuli-responsive elements enables the application of these purely liquid-based or solidified micro-colloids as new transduction materials for chemo- and bio-sensing. Here, we will demonstrate a series of optical transduction methods that are based on having control over the total internal reflection of light from outside and inside multicomponent colloids. An associated understanding of the unique chemical-morphological-optical coupling inside chemically functionalized active soft matter colloids creates a solid foundation for the development of sensing paradigms targeting a series of chemical and biological analytes, including a rapid and sensitive method for the detection of common foodborne pathogens Escherichia Coli and Salmonella enterica bacteria.

9:15 AM SB11.01.03
How Wettability Controls Nanoprinting Joel De Coninck; University of Mons, Belgium

Using large scale molecular dynamics we study in detail the impact of nanometer droplets of low viscosity on at substrates and the effect of the wettability between the liquid and the plate. We show the maximal contact diameter during the nanodroplet impact (Dmax) as well as the time required to reach it (tmax) are in agreement with experimental data at the macroscale showing similarities between droplet impacts at the nano and the macro scales. The comparison between the MD simulations and different models reveals that most of these models do not take into
account all the effects we observe at the nanoscale. Moreover, most of their predictions for the impact at the nanoscale do not correspond to the simulation results. Because of this, we have developed a simple model for Dmax which is in agreement not only with the simulation data but also the experimental observations and it also takes into account the effects of the liquid-solid wettability. We also propose a new scaling for tmax with respect to the impact velocity which is also in agreement with the experimental observations. With the new model for Dmax plus the scaling found for tmax, we present a new way to collapse in a master curve the evolution of the micro to nanometer drop contact diameter during impact for different wettabilities and different impact velocities. We believe our results may help to design better nanoprinters since they provide an estimation of the maximum impact velocities required to obtain a smooth and homogenous coverage of the surfaces without dry spots.

9:30 AM *SB11.01.04  
Bicontinuity is Easy with Fumed Silica—A Morphology-Composition Map for Particle-Filled Blends of Immiscible Polymers  
Derrick Amoabeng1, Andrew Tempalski2, Brian Young2; Bernard Binks3 and Sachin Velankar1; 1University of Pittsburgh, United States; 2The Pennsylvania State University, United States; 3University of Hull, United Kingdom

In ternary mixtures of two immiscible liquids and one particulate species, capillary forces are a strong driving force for particle aggregation. In such mixtures, a rich variety of microstructures appears from a coupling between interfacial tension, particle wetting phenomena, and viscous forces of mixing. For the simplest case of spherical particles, it is possible to construct a non-equilibrium state diagram based on rational considerations of the various phenomena. This talk will discuss the situation with a far more complex type of particle: fumed silica.

We examine melt-blended mixtures of two molten plastics, polyisobutylene (PIB) and polyethylene oxide (PEO), and fumed silica particles which have strong affinity for the PEO. The unusual structure of fumed silica – which comprises 15-30 nm primary particles permanently bonded together into highly porous, fractal-like aggregates – strongly influences the morphology at all compositions. At relatively low PEO loadings, the PEO is absorbed into the pores within the fumed silica aggregates. The morphology consists of a network of interlocked particle aggregates bonded together by PEO. At higher PEO loadings, the PEO and the particles form a combined phase that is solid-like even at low fumed silica loadings. The morphology somewhat resembles a conventional co-continuous morphology where one phase is PIB and the other is a fumed silica-filled PEO. What is most interesting and potentially useful is that morphologies with two percolating phases appear across almost the entire composition range examined. We construct a composition-microstructure map for mixtures containing fumed silica and contrast against the simpler case of spherical particles.

10:00 AM BREAK

10:30 AM SB11.01.05  
Epoxy-Based Bicontinuous Nanocomposite Monoliths  
Molla Hasan and Jonathan P. Singer; Rutgers University, United States

Epoxy-phenolic resins, valued for their ease of processing into various shapes and coating thicknesses, have been widely used as base materials for a wide variety of applications, such as integrated circuit packages, laminating resins, adhesives, binders, surface coatings, and impregnants. Here we report a simple method to make bicontinuous epoxy-based porous nanocomposite monoliths. We begin with a bijel comprised of immiscible mixtures of two fluids: epoxy and vegetable oil, stabilized by epoxidized soybean oil (ESO) as a surfactant and a means to improve the interfacial bonding between the epoxy resin and vegetable oil. By adding nanofillers and mixing at high shear, interfacial jamming occurs, which arrests the fluids in a bicontinuous configuration. During the evolution of the emulsion, the configuration maintains, creating an interconnected porous structure, which length scale is determined by the selection of particle. Our rheology results reveal the role of ESO in this process, with low quantities not participating in the epoxy curing due to interfacial segregation and high loadings modifying the curing kinetics and mechanical properties as a plasticizer. Through this fabrication method, we can produce porous monoliths at a wide range of feature length scales that shrink less than 2% after curing and removal of the oil porogen, and due to the non-volatile nature of the oil, have uniform porosity through the bulk of the structures. In addition, the surface of the porous monolith can be functionalized by selectively altering the nanofillers.

10:45 AM SB11.01.06
3D Printed Porous Structures of 2D Materials Using Capillary Suspensions Hui Ding, Suelen Barg and Brian Derby; University of Manchester, United Kingdom

Capillary suspensions of particles in immiscible fluid mixtures are stabilised by pendular drops of the minor liquid phases forming bridges between the solid particulate phase, a structure distinctly different from that of a Pickering emulsion.[1] This behaviour requires two immiscible fluids one of which strongly wets the solid phase (the secondary liquid which is usually a relatively small volume fraction of the suspension), while the other shows a relatively high contact angle. Capillary suspensions have a distinct rheology with a transition from a rigid gel to a fluid emulsion occurring above a yield stress and the gel reforming if the fluid strain rate drops below a critical value. This rheological behaviour is similar to that found with particle suspensions in tri-block copolymer solutions (e.g. Pluronics) but can be achieved with immiscible small molecules, e.g. water and octanol. The rheology of capillary suspensions is ideal for 3D printing by direct write extrusion and has the advantage over current methods by not requiring large quantities of polymers that may need removal by secondary post-processing.

Here we demonstrate a printable graphene ink produced by adding a small amount (1-2 vol%) of the secondary liquid, in this case octanol, to an aqueous graphene suspension (GS). Octanol is immiscible with the primary liquid, water, and strongly wets the graphene flakes in the suspension, forming the graphene capillary suspension (GCS). Rheological studies show that the storage modulus of GCS is three orders of magnitude larger than that of the original GS with a yield stress of 95 Pa. Beyond the yield stress the GCS shows shear thinning behaviour with the viscosity decreasing as the shear rate increases. The GCS materials were used as inks for Robot-assisted direct writing to fabricated simple graphene structures. These show a relatively high porosity of 81% and a corresponding bulk density of 426 kgm⁻³. The printed structures show a crushing strength of 1.4 MPa and high electrical conductivity of 2370 Sm⁻¹ after heat treatment. Computed X-Ray tomography and SEM are used to explore the internal structure of the extruded filaments. Comparing the X-Ray tomography images of GCS and GS filaments, it shows a shear aligned graphene plate structure with the GS ink and a more disordered flake distribution with the GCS ink. This is consistent with the flake alignment in the GCS occurring after extrusion has arrested and the capillary suspension gels. Similar behaviour is found using BN as the 2D particulate material but not with MoS₂, despite both materials showing similar surface energetics when dispersed in water and octanol. Reasons for this discrepancy are explored.

Reference

11:00 AM SB11.01.07
Electrohydrodynamic Bridging for Scalable Thermal Oscillators Tianxing Ma¹, Matthew Signorelli¹, Darrel Dsouza¹, Kyrsten M. Ryerson², Yang Zhao³, Chinedum Osuji³ and Jonathan P. Singer¹; ¹Rutgers, The State University of New Jersey, United States; ²Biola University, United States; ³University of Pennsylvania, United States

Pyroelectric materials are emerging as an alternate to thermoelectrics for waste heat harvesting due to their potential for higher efficiency. The desire to maximize scenarios compatible with pyroelectric waste heat harvesting introduces the challenge of inducing temperature oscillations in a pyroelectric material based on near-constant temperature, or constant flux, heat sources. Prior efforts in this area have utilized electrowetting on dielectric (EWOD) and microelectronic mechanical systems (MEMSs) to fabricate compact waste-heat harvesting devices for testing. However, for large-scale applications, a compromise must be made between device efficiency, cost, and device miniaturization. In this presentation, we demonstrate a method using electrohydrodynamic (EHD) force to actuate a capillary bridge from a liquid droplet between a heat source and heat sink which serves as a proxy for a pyroelectric material. Enhancement of heat transfer is derived from the capillary bridge. Through EHD thermal experiments with different thermal fluids, we found the enhancement of heat transfer is achieved by different dominant mechanisms depending on the viscosity of the formulation, with high viscosity formulations relying on thermal conductivity and lower viscosity relying more on the convection induced by the EHD and Marangoni flow. Through periodically forming and breaking the capillary bridge, temperature oscillations were successfully established due to the resulting differences in the heat transfer rate. Employing this approach, a laminate device is built to turn a steady thermal field to an oscillating thermal field, showing a scalable method compatible with the roll-to-roll fabrication of sheet devices.
Multiphase fluid systems are strongly influenced by gravitational phenomena that affect everything from transport dynamics to the self-assembly of ordered systems. Buoyancy-driven convection drives heat and mass transport, providing a source of mixing. Density-driven segregation leads to inhomogeneities and phase separation including sedimentation. One byproduct of the sedimentation is the occurrence of stratification phenomena in self-assembled multiphase fluid systems such as foams and emulsions. The removal of gravity as a force provides opportunities for the investigation of discrete phenomena such as diffusion or viscosity in isolation. For example, in a persistent microgravity environment, the interfacial energies in self-assembled structures can be studied in isolation from sedimentation and stratification effects.

The International Space Station (ISS) U.S. National Laboratory offers a unique environment in persistent microgravity that enables the decoupling of physical phenomena such as buoyancy-driven convection from diffusion. Areas of investigation onboard the ISS have included droplet formation, colloid interactions (emulsions, nanoparticles, biomolecules, etc.), foam formation and stability, gel formation (aerogels, hydrogels, etc.), and self-assembled structures. For example, microgravity provides the opportunity to study “wet” foams in the absence of drainage—a result that is difficult to replicate terrestrially.

We will introduce the underlying physical phenomena of multiphase liquids in microgravity. We will present case studies of multiphase liquid system investigations conducted onboard the ISS, including studies of droplet formation, gel and foam stability, and the self-assembly of hydrogels and aerogels, and compare results with those from terrestrial experiments. We will also discuss translational lessons learned from microgravity experiments that inform and direct terrestrial research and manufacturing. Finally, we will present opportunities for future microgravity experiments and access to ISS facilities through the ISS U.S. National Laboratory.
the production of structured hydrogels whose conformation changes over 10s of micrometer length scales. This is achieved using drops with well-defined sizes and compositions that are produced with microfluidics. I will demonstrate microfluidic devices that offer a tight control over the arrangement of the drops. These assembled drops are subsequently converted into macroscopic structured hydrogels possessing compositions with well-defined, locally varying compositions. I will show how the local composition of hydrogels influences their macroscopic mechanical properties.

2:15 PM SB11.02.03

Self-Ejection of Crystal Structures from Evaporating Droplets on Superhydrophobic Surfaces Samantha McBride, Henri-Louis Girard and Kripa Varanasi; Massachusetts Institute of Technology, United States

Crystal fouling due to saline spray leads to corrosion and degradation of many materials, including metals, stones, and organics. This degradation is visible in many coastal cities, where buildings and other structures degrade faster than their non-coastal counterparts due to salty ocean spray. Implementation of superhydrophobic surfaces is one strategy that may help prevent crystal fouling, but is only successful when no crystals are able to form at the surface, as any amount of nucleation will seed additional crystal formation at that surface and degrade the hydrophobicity. In this work, we demonstrate an unusual phenomenon in which sodium chloride crystals grown from a drop placed on a heated superhydrophobic surface self-eject from that surface. This phenomenon is related to the plastron (a thin film of air) layer within the texture of the superhydrophobic surface, which creates a channel for water vapor to escape from the evaporating drop. A large temperature gradient across the drop leads to enhanced vaporization at the surface, and escaping vapor creates crystalline micro-tubules which continue to grow as salt crystallizes at the tips. These tubules grow into "legs," causing the entire salt structure to lift off from the surface. We find that the self-removal of the crystals keeps the surface clean, and observe no degradation of the anti-fouling performance over extended use. This phenomenon could be useful in cooling towers using water spray heat exchange, where water typically must be very pure to avoid salt corrosion. By implementing substrates that cause self-ejection of crystals, it may be possible to use salt water rather than ultra pure water, and thus preserve fresh water resources while also cutting down on costs associated with water treatment.

2:30 PM SB11.02.04

Jammed Films of 2D Materials Assembled at Liquid/Liquid Interfaces Joe Neilson and Brian Derby; The University of Manchester, United Kingdom

2D materials are being widely explored for use in the fabrication of large area flexible, transparent electronic devices such as: field-effect transistors (FETs), sensors, and light emission devices. The assembly of large area films from a 2D material dispersion is a key step in the manufacture of electronic devices. Close packing and edge to edge contact is believed to be crucial in order to ensure high carrier mobilities through the 2D material film. However, widely used film assembly methods such as spin coating and spray coating result in low transfer efficiency, flake restacking and loose random packing of flakes in the film. Here, we present a thin film assembly method which overcomes these issues using a molecularly flat assembly plane; the interface of two immiscible liquids.

In this work, dispersions of exfoliated 2D material are deposited at the liquid/liquid interface and are compressed laterally by an interfacial tension gradient away from the point of injection. The resulting thin film is a 2D jammed monolayer of flakes which has minimal overlap and predominantly edge to edge contact between flakes. The packing density of the resulting film is high (87 %) and the transfer efficiency is over 100 m² per gram of exfoliated 2D material. The method described has the additional benefit that the bulk liquid phases help to wash contaminants from the thin film. We demonstrate how the resulting large area films, which can coat the entire surface of a 4 inch wafer, are highly pristine and simple to produce.

FETs were manufactured using the aforementioned film deposition method with a dispersion of electrochemically exfoliated MoS₂. The mobility and on/off current ratio of the back gate and bottom contact FETs were 7 cm² V⁻¹ s⁻¹ and 10⁵ respectively; comparable to chemical vapour deposition grown MoS₂ FETs. This work demonstrates the use of liquid/liquid interfaces as a tool for self-assembly of high performance monolayer thin film devices made from dispersions of ultrathin 2D material.

Cellulose-Based Membranes for Effective Capture of Oil Microdroplets in Water

Ana C. Trindade¹, Ana P. Almeida², João Oliveira², João Canejo², Susete Fernandes², Jon O. Fossum¹ and Maria Helena Godinho²; ¹Norwegian University of Science and Technology, Norway; ²Faculty of Science and Technology, Universidade NOVA de Lisboa, Portugal

Disasters are sometimes associated with the transportation of oil across big distances using oil tankers. When an accident occurs large volumes of oil are spilled into the ocean and have to be collected from the water. However, the traditional oil-removing methods fail to collect the micro-sized droplets of oil originated by the mechanical action of the waves.[1] Oil/water separation is an important field, not only for scientific research but also for practical applications aiming to resolve industrial oily wastewater and oil-spill pollution, as well as environmental protection[2,3].

This work focusses on the recovery of oil microdroplets suspended in water, using a manufactured cellulose acetate (AC) non-woven electrospun membrane coated with different patterns of cellulose nanocrystals (CNCs). Efficiency tests show that these membranes can remove up to 80% of the oil microdroplets present in a water emulsion. The imprint the different designs of the CNCs layer was performed using screen-printing and the adhesion of the CNCs with the fibers of AC was promoted by a thermal treatment. The removal of the oily micro droplets is achieved when a water/oil emulsion flows through the membranes, due to the hydrophilic character of the AC fibers, and the CNC-coated regions collect micro droplets of oil, due to its oleophilic character.

This work demonstrates that it is possible to produce efficient all-cellulosic composite membranes for the capture of micro-oil droplets dispersed in water, with easy tailoring of the ratio AC membrane and annealed NCC allowing to maximize the micro-droplet oil collection and at the same time the water flow. More, the combination of annealed NCC with non-woven electrospun membranes opens the door to a low-cost environment-friendly method of treating polluted ocean and waste-oily waters.

References:

3:00 PM BREAK

3:45 PM SB11.02.06
OPEN SLOT

4:00 PM *SB11.02.07
Large-Scale Production of Microfluidic Emulsions and Particles via Parallelization Daeyeon Lee; University of Pennsylvania, United States

The advent of microfluidics has led to remarkable advances in the synthesis of functional particles and microcapsules for a variety of applications. The ability to precisely manipulate the flow of multiphase fluids in microchannels enable production of highly uniform liquid droplets and gas bubbles with complex morphology. Despite these exciting developments, there remains some key challenges that must be addressed to enable successful commercialization of these technologies. In this talk, I will discuss our recent contributions in producing “designer” microparticles for drug delivery, diagnostics and regenerative medicine applications. The importance of understanding and harnessing the fundamental interfacial phenomena to engineer the structure and functionality of these particles will be described. I will also discuss our recent efforts to scale-up the production of particles via parallelization in solvent-resistant microfluidic devices.

4:30 PM SB11.02.08
Lipid Droplet Microarrays Steven Lenhert, Troy Lowry and Aubrey Kusi-Appiah; Florida State University,
United States

If micro-wells were the size of biological vesicles, there would be room for $10^{17}$ compartments in one cubic centimeter. In contrast, the state of the art in high-throughput screening uses 1536 well plates and about 3 ml of solution per plate. Motivated by a desire to understand biological compartmentalization and to use it for biotechnology, this presentation will describe the fabrication and applications of arrays of micrometer and nanometer scale lipid droplet microarrays. Arrays are fabricated by nanointaglio, which involves the transfer of fluid inks from the recesses of a microstructured stamp onto a substrate.[1] Thousands of different materials can be integrated into the droplets using pin spotting technology. Lipophilic small molecules can be encapsulated into the oil droplet, and cell cultured over the arrays for phenotypic screening with pharmaceutical applications.[2] Furthermore, exposure of these droplet arrays to lipid binding analytes such as proteins while observing scattered light from the arrays allows label free detection of remodeling events in the lipid droplet nanostructure.[3] Droplet size, shape, and composition are central to these applications. Recent progress in the use of these multiphase fluids to investigate and control biological systems will be presented.


4:45 PM *SB11.02.09
Emulsions and Heterogeneous Materials for Fabricating Oscillatory Chemo-Mechanical Networks Seth Fraden; Brandeis University, United States

A simplified theoretical model treats neurons as non-linear oscillators that when coupled together through excitatory and inhibitory connections give rise to complex spatio-temporal patterns. When organized, these patterns are capable of processing and storing sensory information, and actuating musculature. Extrapolating from this general definition of a neuronal network, we posit these dynamics can be captured on an abiologic reaction-diffusion platform. We reported advances in soft lithography that allow the engineering of synthetic reaction-diffusion networks capable of producing the same spatiotemporal dynamics of the eel’s CPG². The network is natural in the sense that the oscillators and couplings are physical-chemical processes that, once initiated, proceed without any external intervention. Our experimental model system uses the oscillatory Belousov-Zhabotinsky (BZ) reaction with which we created diffusively coupled networks over which we designed (i) the topology of the network, the (ii) boundary and (iii) initial conditions, (iv) the volume of each reactor, (v) the coupling strength, and (vi) whether the coupling is of an inhibitory or excitatory nature. In particular, Central Pattern Generators have been modeled theoretically as being networks of identical oscillators²-⁴. With this BZ experimental system we will probe a number of fundamental questions addressing the suitability of chemical oscillators networked into CPGs for control of soft robotics. It is important to note that the engineering principles we identified are general and can be applied to other oscillatory reaction-diffusion systems besides BZ.

Network symmetry imposes constraints on dynamics in both expected and surprising ways²-⁴. First, the impact of network symmetry is completely independent on the underlying chemical nature of the oscillator. When wiring together identical oscillators, symmetry imposes significant constraints on the dynamics. These constraints create invariant manifolds, privileged subspaces in phase space that are impenetrable to the dynamical flow of the system. Invariably, real systems are not strictly symmetric. Oscillators and their connections have heterogeneities. How much variability does a system need in order to break the rules arising from symmetry?

A related question arises in regards to control of a network. Optimal control theory asks what is the minimum effort required to move as system from one stable attractor to another. Because dynamics is constrained to move on invariant manifolds, symmetries influence control protocols. We can test the theoretical role of symmetry and the protocols of optimal control theory in an experimental system. As specific examples of the role symmetry plays in network dynamics, we consider the simple cases of a ring of 3 and 4 identical oscillators and study how the dynamics changes as we break symmetry by changing the natural frequency of oscillation. The ring of 3 oscillators has two stable attractors. Moving to a ring of 4 oscillators leads to richer dynamics corresponding to the gaits of quadrupeds²-⁴. The general questions we ask are: How to optimally switch from one gait to another? Can one control the entire network by manipulating a subset? How robust is the stability of the attractors to noise?
References


SESSION SB11.03: Poster Session I
Session Chairs: Esther Amstad and Paul Millett
Monday Afternoon, December 2, 2019
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

SB11.03.02
Porous Liquid Infused Surfaces in Microfluidics for Fluid Delivery—Pressure and Heat Transfer Measurements
Reginald Goodwin, Bolaji Sadiku and Jeffrey R. Alston; North Carolina A&T State University, United States

Porous liquid infused surfaces, commonly referred to as SLIPS (slippery liquid infused surfaces), can be fabricated from any nano/microstructured porous solid material with a lubricating liquid film used to create surfaces that exhibit liquid repellency, self-healing, optical transparency, pressure stability, and self-cleaning. If designed properly these surfaces can repel many fouling challenges including bacteria, ice, water, oil, dust, barnacles, or other contaminants, and have been proposed as coatings on industrial and medical surfaces. These surfaces are robust even under high temperature and pressure conditions which also positions them as a viable treatment for the walls of microelectronic cooling channels or on fuel lines to reduce coking in high-temperature fuel delivery. To establish this use case, we present the development of a microfluidic device incorporating a porous liquid infused surface, and we measure the pressure drop and heat transfer across this surface while tailoring the chemistry, porosity and infusing liquid on the surface.

SB11.03.02
Are Contact Angle Measurements Useful for Oxide-Coated Liquid Metals?
Ishan D. Joshipura1,2, K. A. Persson2, Hong Zhao3 and Michael Dickey2; 1Lawrence Livermore National Laboratory, United States; 2North Carolina State University, United States; 3Virginia Commonwealth University, United States

Liquid metals are useful soft and fluidic conductors for electronics, composites, and microfluidics. In the presence of oxygen, these metals form a thin (~3 nm) surface oxide that acts as a deformable solid shell and adheres to many surfaces. The first portion of the talk will address the unusual wetting behavior of oxide-coated liquid metals (in comparison to water) on smooth, non-reactive substrates using conventional tools for measurement contact angles. These experiments demonstrate the unusual contact angle hysteresis behavior due to pinning of the oxide. Next, this talk will discuss the effect of surface roughness and surface chemistry on oxide adhesion, including strategies to prevent oxide adhesion. Overall, we find that the contact angle can be manipulated mechanically to be any value from 0° to >140° depending on the hysteresis. Thus, for oxide-coated liquid metals, conventional wetting measurements may be relatively uninformative and subject to different interpretations. Accordingly, the results provide fundamental insights on the adhesion of the oxide to substrates, which is important for additive manufacturing of metals, soft and biocompatible electrodes and interconnects, and reconfigurable electronics.

2. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. IM Release #: LLNL-ABS-777669

SB11.03.03
Liquid-Based Resistive-Switching Memory with Synaptic Functions Using Ion Dynamics in Liquid Dongshin Kim, Min-Kyu Kim, Youngjun Park and Jang-Sik Lee; POSTECH, Korea (the Republic of)

Liquid materials have emerged as a promising material in neuromorphic devices and energy storage devices because of the high ionic mobility of the liquid. We report liquid-based resistive-switching memory (LRSM) devices, exploiting the formation and rupture of silver filaments in the solution [1]. The devices are designed to have a metal-solution-metal structure, consisting of an Ag electrode and an inert electrode that together sandwich a solution. The switching behaviors of the LRSM devices occur at a very low operating voltage, similar to the action potential in biological synapses because the movement of silver ions does not need much energy to migrate under the electric field in the AgNO₃ solution. Furthermore, we also evaluate the potential use of LRSM devices in neuromorphic devices. The LRSM devices have neuromorphic characteristics including potentiation, depression, excitatory postsynaptic current (EPSC), and paired-pulse facilitation (PPF). Silver filaments that are formed in solution lead to changes in the conductivity of the device and provide neuromorphic characteristics. Also, LRSM devices have flexibility due to using a liquid as the main component. This study will offer the potential for the development of flexible and highly energy-efficient brain-mimicking devices. In this presentation, liquid-based resistive-switching memory characteristics will be presented in detail.


SB11.03.04
Microfluidic Patterning of Liquid-Mediated Materials through Liquid Foam Control Juyeol Bae and Taesung Kim; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Appropriate external forces or physicochemical constraints can reshape liquid into desired morphologies. Historically, early strategic techniques for shaping liquid (e.g., brushing and printing presses) have significantly affected civilization. Recently, numerous micro- and nanofluidics has substantially enriched applicable micro- and nanodevices made of functional liquid-processible materials (i.e., liquid-mediated materials) by enabling spatiotemporal manipulation of fluids at the micro- and nanoscale, simultaneously offering cost-effectiveness, simplicity, flexibility in choice of materials and substrates, and scalability. In the micro- and nanofluidic liquid-mediated patterning (MNLP), nanowires particularly have been studied to meet increasing demands for transparent and wearable electronics. However, the state-of-the-art methods have required expensive preparation steps for nanostructured templates, otherwise they have shown low-resolution spatial control of liquid. Though nanoscale liquid-air interface control by microstructured templates have been a compromise between the cost and resolution issues in the nanopatterning, it is limited to unidirectional wire patterns. To this end, liquid foam pervasive in nature can be useful in comparison to the reported approaches for patterning networked high-resolution nanowires, though it involves certain challenges such as their unmanageable drying, complex topological changes, and dynamic fluidity.

Herein, we report a MNLP technique to engineer 2D liquid foam, motivated by its potentials in micro- and nanoscale material patterning. The main idea is the design of micropost and microhole arrays in a hexahedral liquid space. The evaporative microholes allow the fast generation of discretized liquid–air interfaces and directed receding of the interfaces toward micropost. Then the microposts pin the generated interfaces in predefined locations to make them form networked-line pattern of liquid. The generated liquid pattern could be used as molds for evaporatively structuring of the target materials in liquid, enabling material patterns of several micrometers or hundreds of nanometer width, showing results that cannot be easily achieved by using conventional patterning technologies. First, multiple heterogeneous materials could be self-aligned respectively into multiple different patterns precisely without cumbersome high-resolution alignment. Second, conventional photolithography technique could be combined with our MNLP method. From the demonstration of microscale UV writing on the bottom-up nanoscale prepatterned uv-curable poly(ethylene glycol) diacrylate (PEGDA), we can do mask-less nanopatterning in a low-
cost and high-through manner. Third, our suspended nanowire was made in a single step without any conventional fabrication process, otherwise the 3D structure is made commonly using relatively laborious multi-step top-down fabrication techniques. Furthermore, it is no doubt that other useful materials like organic-inorganic hybrid perovskite, functional nanocrystals, graphene will be patternable. Therefore, our foam-based MNLP technique shows high potential in field of micro-/nanopatterning for various applications such as micro-/nanofluidic, optoelectronics, and multi-functional electronic devices.

SB11.03.05
The Strange Case of Coexisting Isotropic Phases in Liquid Crystal Solvent Mixtures Catherine G. Reyes¹, Jörg Baller¹, Takeki Araki² and Jan P. Lagerwall¹; ¹University of Luxembourg, Luxembourg; ²Kyoto University, Japan

Though the dynamics of phase transition in many multi-phase liquid mixtures have been thoroughly investigated, there is still more to explore with mixtures containing common liquid crystalline (LC) compounds and low molar mass solvents. Especially now that much LC research has been devoted to the development of soft devices and composites [1-3], where the preparation of LC-solvent emulsions may be necessary for processing using microfluidics [4-5] or ink-jet printing [6], for instance, it is essential that experimentalists consider the phase equilibria of LCs in solvents. While numerous studies already exist on 4-cyano-4′-pentylbiphenyl (5CB), a low molar mass room temperature nematic, we now experimentally find that binary mixtures between this LC and anhydrous ethanol show a broad miscibility gap that leads to phase separation between two distinct isotropic phases. More surprisingly, contaminating the ethanol-5CB mixtures with water (3 vol.% suffices) dramatically raises the temperature range of the miscibility gap and the critical temperature at which phase separation by spinodal decomposition occurs to higher than 50°C. The phase diagrams presented here describing these phenomena, experimentally analyzed using temperature-controlled polarized optical microscopy and differential scanning calorimetry (DSC), corroborated by theory and numerical simulations, emphasize the often overlooked practical consequences that mixing LCs with common laboratory solvents can have in the formation and stabilization of future LC-composites.

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SB11.03.06
In Situ Templating for Faster Protein Crystal Nucleation Caroline McCue, Henri-Louis Girard and Kripa Varanasi; Massachusetts Institute of Technology, United States

Slow protein crystal nucleation is a major barrier to using crystallization as a separation and purification strategy in protein drug manufacturing. This work demonstrates the use of functionalized nanoparticles in solution to act as in situ templates for initiating crystal nucleation. We used lysozyme, a protein with well-characterized crystallization conditions, to evaluate the nucleation rates of crystals grown on the functionalized particles. On a microfluidic chip, a supersaturated solution of lysozyme is mixed with a stream containing precipitants and functionalized nanoparticles. The nucleation rates are measured using an emulsion based technique. Nanoparticles functionalized with groups that covalently bind with proteins demonstrate up to four times faster crystal nucleation than controls, and faster nucleation than bare nanoparticles or nanoparticles with other types of functionalizations. Surface adsorption measurements on larger flat surfaces with the same functional groups are used to examine the mechanism by which the functional groups enhance crystal nucleation.

SB11.03.07
A Dry Bacterial Cellulose-Carboxymethyl Cellulose Formulation as Stabilizer for Pickering Oil-in-Water Emulsions Daniela Martins, Fernando Dourado and Miguel Gama; Centre of Biological Engineering - University of Minho, Portugal
Hydrocolloidal microcrystalline cellulose (MCC) from plant sources, is already widely used in industry to regulate the stability, texture, rheology and organoleptic properties of many food and cosmetic formulations. Bacterial cellulose (BC) is produced biotechnologically by different microorganisms, but most efficiently by acetic acid bacteria from the genera *Komagataeibacter*. This biomaterial is a prominent alternative to the already marketed celluloses, being more pure, crystalline, and having nanoscale fibres with high aspect ratio which account for excellent mechanical properties. BC has already been used in its hydrated form for the stabilization of oil-in-water (o/w) Pickering emulsions (particle-stabilized systems, as an alternative for the conventional surfactant-stabilized). For the sake of storage, economy and practicality, additives for industries are preferentially provided in a dry or powder form. Co-drying cellulose fibres or crystals with water soluble polysaccharides helps maintaining the rheologic and structuring properties after rehydration.

The main objective of this study was to assess the stabilizing properties of BC in Pickering o/w emulsions. For this, an equimassic formulation of BC and 90 kDa carboxymethyl cellulose (BC:CMC) was prepared and spray dried. Isohexadecane-in-water emulsions (10:90) were prepared in the presence of 0.10%, 0.25% and 0.50% of the BC:CMC formulation. Visual and microscopic aspect of the emulsions was registered over time. Samples were also visualized in Cryo-SEM. Rheological tests were performed to assess the emulsion’s viscosity profile, storage and loss moduli. Interfacial tension between the immiscible phases was measured with the Pendant Drop and Du Noüy Ring methods. For benchmarking purposes, the same emulsion preparation and analysis protocol was made with several different commercial cellulose products and xanthan gum.

Microscopic analyses showed large oil droplets, but stable over time. Despite a visible creaming in the emulsions with lower BC:CMC concentrations, there was no evident separation of the oil phase; with 0.50% BC:CMC, the emulsions were effectively stabilized against agglomeration, coalescence and creaming for up to 90 days without the need of any other emulsifying agents. The same did not happen for the commercial celluloses at the same concentration. Cryo-SEM images showed the entangled and disordered three-dimensional networks formed by BC fibres structuring the water phase and surrounding the dispersed oil droplets. The BC:CMC emulsions showed a characteristic viscoelastic and shear-thinning behaviour. An increase in BC:CMC concentration results in higher emulsion viscosity, higher than the emulsions prepared with other cellulose products. IFT measurements showed that the presence of the BC:CMC formulation actually diminishes the interfacial energy between the immiscible phases, more than the other cellulose products. The results of our dry BC:CMC formulation were only comparable to the ones with xanthan gum.

In short, BC:CMC showed formation of a three-dimensional network and viscosity increasing (thickening) properties, crucial characteristics for emulsion stabilizing formulations. BC has technically superior properties that will allow it to compete with, or even replace, plant celluloses in industry.

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**SB11.03.08**

**Acoustic Bubble Suppression by Constructing a Hydrophilic Coating on HDPE Surface**

Junjie Niu; University of Wisconsin--Milwaukee, United States

Due to the serious reflection/scattering of sound waves, the acoustic bubbles on the surface that are generated during the sonication are posing a critically detrimental effect on the signal resolution of sonochemical devices such as various sensors for water-based liquid detection and sonobuoys for underwater acoustic study and anti-submarine warfare applications (*Adv. Mater. 2011, 1922*). In parallel, a large variety of high-density polyethylene (HDPE) polymers are extensively used in different devices particularly with sensors due to the high chemical and mechanical stability (*Polym. Degrad. Stab. 2007, 1219*). This outstanding stability also poses a challenge on modifying the surface with designed functional groups. The original HDPE surface shows a contact angle large than 60°, which generates plenty of bubbles when it suffers the ultrasound agitation. Even though there are a few reports about the hydrophilic coating created using versatile nanoparticles and polymers, forming a controllable hydrophilic coating on HDPE surface is not studied yet.

The ultrasonic bubbles on the solid surface of various sonochemical devices largely affect the signal resolution due to the serious reflection/scattering of sound waves. The Laplace pressure of the cavitation bubble can be tuned by constructing an ultra-thin hydrophilic layer, which leads to the solvation or pinching off of the bubbles from the surface. In this talk, we will introduce a polydopamine polymer layer coated on the HDPE surface (*Ye et al.* *ACS*...
The formed hydrophilic layer with contact angle less than 45 degree almost completely eliminates the bubbles in both water and 32.5 vol% diesel exhaust fluid (DEF) solutions upon sonication, which results in the operation of the piezoelectric sensor over 500 hours while the sensor with pure HDPE only ran less than 2 hours. Further, the coated sensors showed a high stability under the temperatures of 60-80 °C. An improved mechanical property was confirmed via abrasion test, enabling a long-term stability in harsh environments including acidic urine and ultrasonic agitation. The acoustic bubble suppression via the hydrophilic polymer coating on HDPE surface displays broad applications particularly with acoustic sensors, sonobuoys and non-destructive surface detection in sonochemistry.

**SB11.03.09**

**Multicomponent Phase Separation During Thin Film Formation** Eleni P. Hughes and Edward Van Keuren; Georgetown University, United States

Recently, phase separations in multicomponent solutions have attracted attention due in part to their potential usefulness in understanding biological systems. Living cells possess membrane-less organelles, formed by liquid-liquid phase separations with the cell. Multicomponent phase separations of polymers in solution may occur under certain thermodynamic conditions of temperature and concentration. Here we present studies of the phase separation of two immiscible polymers during film formation. By taking real-time optical microscopy video of the blade coating process, we are able to observe the multicomponent polymer system as it transforms from solution to thin film. Additionally, we use Raman mapping to confirm localized regions of polymer components. Finally, we present results showing the effect of additional components on the system.

**SB11.03.10**

**Droplet-Based Magnetofluidic Platforms for Detection and Analytics** Larysa Baraban¹ and Denys Makarov²; ¹Dresden University of Technology, Germany; ²Helmholtz-Zentrum Dresden-Rossendorf, Germany

The development of next-generation biosensing technologies has picked up momentum in the past decade. Particularly, among a variety of biosensing principles, magnetic biosensing technologies based on magnetic particles and magnetic field sensors have attracted growing attention due to the unprecedented advantages brought by this unique sensing format. Our contribution to this exciting field of research and technology includes the development of a compact droplet-based magnetofluidic platform encompassing integrated novel functionalities, e.g. analytics in a flow cytometry format [1-3], magnetic barcoding [4] and sorting of magnetically encoded emulsion droplets [5,6]. We put forth a novel high-capacity indexing scheme based on multiphase microfluidic networks for large-scale screening applications [5,6] and realized flexible microfluidic platform with integrated magnetoresistive sensors [4]. The technology on how to integrate high-performance magnetic field sensors into multi-functional self-assembled tubular architectures [7-9] for lab-in-a-tube concept [10] will be discussed. These features are crucial to address the needs of modern medical research, e.g. drug discovery [11].

In recent years, numerous innovative methods have been developed to meet the increasing demand for high throughput production of monodisperse droplets. These methods can be either passive, such as dripping, or active, such as acoustophoretic printing. However, both often require elaborate fine-tuning or cost-heavy equipment, which inhibits the field’s growth as it poses an entrance barrier for new researchers.

As a cheap and simple alternative to these methods, we have explored the use of commercial inkjet printers for the production of picoliter droplets; thereby, benefitting from decades of optimization in their speed, precision, and miniaturization. Nowadays, a 300$ office printer can produce >10k droplets per second from nozzles spaced 80 µm apart and a size down to 1.5 picoliter. In addition, many modern inkjet printers allow for variation of the droplet size, which makes their versatility even more pronounced. Despite the clear advantages, challenges related to backlash induced printing repeatability and printer-roller introduced sample contamination have limited the exploration of the many possibilities.

Through simple hardware adjustments to the office printer, we have made it possible to print multiple times without smearing and improved the between-print positioning repeatability from millimeter range to below 50 µm. This improvement enables a manifold of new utilities for the inkjet system. The low-cost inkjet printer has six ink lines; thereby, immediately allowing for droplet production with six different liquids. We demonstrate simultaneous printing with both polar and non-polar liquids containing fluorescent dyes, drugs, bacteria, and colloids. In particular, we have focused on using the inkjet printer to load drugs into microcontainers for targeted delivery and personalized treatment. This new loading method is superior to its predecessor due to its possibility of easily customizable drug content.

References:

SB11.03.11
Hacking Office Printer for Multipurpose Droplet Production Nikolaj K. Mandsberg, Jesper Højgaard, Shreya S. Joshi, Line H. Nielsen, Anja Boisen and En T. Hwu; DTU Health Tech, Denmark

With the emergence of additive manufacturing technologies, such as “in-air microfluidics”, compound drops are attracting an increasing attention. One of the critical challenges 3D printing applications is to control the deposition process of the impacting drop and therefore its spreading, potential rebound and splashing. By studying the dynamics of compound drops consisting of immiscible liquids, we identified the mechanism of self-lubrication of water-in-oil compound drops impacting on a solid surface. The presence of an oil shell encapsulating a core water drop acts as a lubricating layer promoting water rebound even on a hydrophilic substrate, on which water deposition is typically expected. We define the mechanisms and the conditions that lead to deposition or rebound of the inner water drop, as such providing design guidelines for the printing of compound drops to be used in additive manufacturing.

SB11.03.12
Self-Lubrication of Immiscible Compound Drops upon Impact Carlo Antonini¹,², Nathan Blanken³, Muhammad S. Saleem² and Marie-Jean Thoraval³; ¹University of Milano-Bicocca, Italy; ²Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; ³Xi’an Jiaotong University, China

With the emergence of additive manufacturing technologies, such as “in-air microfluidics”, compound drops are attracting an increasing attention. One of the critical challenges 3D printing applications is to control the deposition process of the impacting drop and therefore its spreading, potential rebound and splashing. By studying the dynamics of compound drops consisting of immiscible liquids, we identified the mechanism of self-lubrication of water-in-oil compound drops impacting on a solid surface. The presence of an oil shell encapsulating a core water drop acts as a lubricating layer promoting water rebound even on a hydrophilic substrate, on which water deposition is typically expected. We define the mechanisms and the conditions that lead to deposition or rebound of the inner water drop, as such providing design guidelines for the printing of compound drops to be used in additive manufacturing.

SB11.03.13
A New Paradigm on Minimal Adhesion at Solid-Bio/Species Interface Bahareh Eslami, Peyman Irajizad and Hadi Ghasemi; University of Houston, United States
Interfacial characteristics of a material play a key role in its interaction with foreign species. Low adhesion of the deposited materials provides the advantage of their easy removal from the surface. Different approaches have been developed to reduce solid-bio/species adhesion by modifying chemical and physical atomic forces, tailoring polymer chains, micro/nano structuring of a surface and so on. Here, we developed the underlying physics of the stress-localization concept to minimize adhesion of a solid on a surface. The fundamental underpinnings of this concept are elucidated and a simple formulation that could be used to characterize solid adhesion on various surfaces is derived. Using this concept, we developed a new bio-polymer material system with superior characteristics while exhibiting long-term mechanical, chemical and environmental durability. This polymeric material contains dispersed organogels in a high shear modulus matrix. In this study, we focused on the interaction of bio-species including both soft and hard organisms with this biopolymer material. Interfacial cavitation induced at the interface of bio-species and organogels particles lead to stress-localization and detachment of bio-species from these surfaces with minimal shear stress. In a comprehensive study, the performance of these surfaces is assessed for both soft and hard-biofouling including Ulva, bacteria, diatoms, barnacles, and mussels and is compared with state-of-the-art surfaces. These surfaces show Ulva accumulation of less than 1%, minimal bacteria biofilm growth, diatom attachment of 2%, barnacle adhesion of 0.02 MPa and mussel adhesion of 7.5 N. These surfaces promise a new physics-based route to address the biofouling problem and avoid adverse effect of biofouling on environment and relevant technologies.

SB11.03.15
Temperature Effect on Fluid Behavior for Crystal Growth and Material Assembly Yan Li, Yitan Li, Yuguang Chen and Hao Wang; Peking University, China

The behaviors of fluid have shown great importance in crystal growth and material assembly on various substrates. Herein, we studied the temperature dependence of the fluidic behavior of several organic solutions on both solid and liquid substrates. On solid substrates, we focused on the liquid wedge near the air-liquid-solid contact line. The temperature gradient of the liquid wedge was manipulated by using a top-heating-bottom-cooling (THBC) setup. A steady Marangoni flow with a single vortex was created in the thin liquid film which benefits the material patterning. We also studied the behavior of volatile organic droplets on the water surface. The liquid-liquid-air contact lines are tunable by varying the temperature. A spontaneous self-division process of the droplets was observed. By thus tuning the fluid behaviors, the crystal growth and material assembly processes were manipulated and CH$_3$NH$_3$PbI$_3$ crystal arrays and dumbbell-shape C$_{60}$ aggregates were prepared.

References

SB11.03.16
The World’s Largest ‘Ink Jet Printer’—From the Lab to Full-Scale Implementation Raymond Oliver$^1$ and Robert Munro$^2$; $^1$Northumbria University, United Kingdom; $^2$Institute for Manufacturing, United Kingdom

Laminar flow cylindrical inviscid and viscous jet break-up by capillary instability has been observed, measured and modelled many times since Lord Rayleigh’s initial physical insights, from Rutland and Jameson to Lafrance using both analytical and numerical solutions to predict linear and non-linear jet break-up. The driver has been the prediction of droplet size, satellite formation and overall size distribution as these provide printing quality or , in our case, allow us to investigate new opportunities from solutions to suspensions to melts for the creation of near monodisperse particulates. In our work, we had the additional challenge to create an environmentally beneficial industrial process for the creation of agrochemical products that had to have an extremely narrow size distribution in order to generate monodispersions. These would then undergo multiple phase transitions that resulted stable particulates for agricultural use on a grand scale of approx. 1 Te/ min or in excess of 1000tes/day! The work carried out will describe in detail the experimental and numerical work carried out over a two year period from single jet studies, through bench-scale investigation to pilot plant optimisation and finally full-scale production. In carrying out this work, we will describe a novel means of perturbing cylindrical liquid jet break—up allowed us to simultaneously control 2800 jets, the evolution of which was modelled using a 3rd order perturbation method considering amplitude effects to predict and validate the final size distribution outcome.
Gait Engineering—Studies of Small Synthetic Neural Networks
Ian Hunter, Michael M. Norton, Chris Simonetti, Bolun Chen and Seth Fraden; Brandeis University, United States

Living beings have evolved to use coupled neurons to perform autonomous functions, from breathing to walking. Local, often small, clusters of neurons known as central pattern generators (CPGs) perform these essential functions in the absence of constant guiding input from the brain. This modular method of control of whole organisms may present advantages over centralized, computational robotic control. An experimental platform, composed of diffusively-coupled PDMS microreactors each containing the oscillatory, light sensitive Belousov-Zhabotinsky (BZ) chemical reaction forming CPG-like patterns has been studied. Understanding experimental observations of quadruped gaits, and an explanation of a systematic method making synthetic CPGs with desired steady state gaits will be the focus of the presentation.

Microfluidic Biochip Platform Incorporating Hydrogel-Based Differential Coulter Counting Technology for Rapid, Multiplexed Detection of Biomolecules
Thomas Cowell, Enrique Valera, Aaron Jackelow, Joonhyuck Park, Alex Schrader, Ruihua Ding, Rashid Bashir and Hee-Sun Han; University of Illinois at Urbana Champaign, United States

Rapid, multiplexed quantification of biomarkers in patient samples is a critical step for effective diagnosis and prognosis. Recently, we have developed a new microfluidic biochip platform integrating a differential coulter counter and an immuno capturing chamber. This platform enables rapid quantification of a specific cell type and plasma proteins without involving expensive apparatus. Despite their immense potential as a cheap, simple, point-of-care diagnostic device, the current platform suffers from its inefficiency in simultaneous quantification of multiple targets. This limitation is due to the non-optimal properties of solid microparticles used for biomolecule capture. Using droplet microfluidics, we have created multiple monodisperse populations of magnetic hydrogel beads (MHBs), which address all the limitations presented by solid microparticles. In particular, each MHB population exhibits distinct electrical signal while having similar sizes and densities, a key requirement to achieve uniform capture efficiencies across different MHB populations at a given flow condition. The magnetic properties of our new hydrogel beads enable facile manipulation and separation of the beads from a complex mixture. The additional advantages of the new MHBs include easily tunable surface chemistry, highly monodisperse size, and density close to dispersing aqueous solutions. Using a differential counting microfluidic device and the newly synthesized MHBs, we confirmed the simultaneous and selective detection of target DNA molecules. The dependence of capture efficiency on the concentration of target molecules is also demonstrated. The size of our newly synthesized MHBs is similar to the size of cells, thereby enables researchers to use the same chip to analyze both cell counts and biomarker concentrations. We aim to use this technology for rapid quantification of multiple biomarkers from fluid samples in a point-of-care device.

Wrapping of Drops and Nanoparticles in Clay Nanosheets
Osvaldo Trigueiro Neto¹, Ville Liljeström², Koiti Araki³, Lina Mayr³, Josef Breu³, Jon O. Fossum¹ and Paul Dommersnes⁵; ¹Norwegian University of Science and Technology, Norway; ²Universidade de São Paulo, Brazil; ³University of Bayreuth, Germany

We have investigated synthetic clay mineral nanosheets of different lateral sizes. The clay nanosheets have mechanical properties similar to graphene oxide or graphene sheets, which already have been proven to be capable of wrapping at different lateral length-scales. It is known that clays (e.g. mica) can also wrap magnetic nanoparticles, which might lead to improved control of magnetic particle transportation in porous media, e.g. for medical, or for oil-reservoir diagnostic purposes.

To achieve wrapping of liquid droplets, very dilute oil-in-water emulsions (0.01–1%) and exfoliated clay colloidal suspensions have been prepared separately and subsequently mixed. The oil drops have diameter 10-25 μm, and the exfoliated clay (synthetic sodium fluorohectorite) have thickness 1 nm, and lateral dimensions 10-100 μm. Our results demonstrate wrapping of droplets by the clay nanosheets.
Furthermore, we have probed clay sheet deformation characteristics by depositing exfoliated clay particles on solid substrates with various curvatures. This forms the base for ongoing work of establishing protocols for nanosheet clay wrapping of magnetic nanoparticles.

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SB11.03.20  
Reduction in Contact Time of Bouncing Droplets on Dense Nanostructured Superhydrophobic Surfaces Lin Wang and Tak-Sing Wong; The Pennsylvania State University, University Park, United States

Many plants and insects have developed intriguing wetting properties that enable them to thrive in their natural habitats [1, 2]. Lotus leaf, which is one of the most well-known biomimetic examples, has served as the blueprint for designing superhydrophobic surfaces for over two decades. Specifically, the water repellency of lotus leaves mainly stems from the hydrophobic epicuticular wax coating and low fraction of solid surface (Φs) that is in direct contact with water [2]. As shown by the classical Cassie-Baxter equation (1944), superhydrophobicity can be achieved by a surface with solid fraction (Φs) less than 0.05 [3]. However, some insect surfaces exhibit exceptional water repellent characteristics at solid fractions (Φs) much greater than 0.05. For example, superhydrophobic mosquito eyes, springtails, and cicada wings possess solid fractions (Φs) as high as 0.25 – 0.64 [4 – 6]. In addition, the texture size on these insect surfaces is typically on the order of 100 – 300 nm. To understand why both high solid fraction and nanoscale textures are important on these superhydrophobic insect surfaces, we systematically designed and fabricated a series of synthetic textured surfaces with feature size ranging from 100 nm to 30 µm with solid fractions (Φs) of 0.25 and 0.44, and investigated their static and dynamic wetting behaviors. We discover that nanoscopic textures (i.e., ~100 nm) at high solid fraction (i.e., Φs ~ 0.44) enable reduced droplet contact time (the duration that an impacting droplet is in contact with the solid) by as much as ~2.6 ms, which is ~14% of contact time reduction as compared to those of microscopic counterparts. The amount of contact time reduction is significant, as it is comparable to the timescale for a mosquito to escape from a lethal raindrop collision [7]. Detailed analysis of the results will be presented in the meeting. Our discovery may provide a new physical insight to the design of new superhydrophobic materials for highly dynamic environments.

Keywords: nanostructures | insects | superhydrophobic surfaces | drop impact | contact time


SB11.03.21  
Microfluidic Device for Optical Screening of Droplets Kouta Taniuchi1,2, Takasi Nisisako3 and Satoru Shoji1,2; 1The University of Electro-Communications, Japan; 2Japan Science and Technology Agency, Japan; 3Tokyo Institute of Technology, Japan

The sorting and separation techniques of microscopic droplets have been progressed with the aid of microfluidic
device. At present, various methods had been reported for the manipulation of droplets based on electric, acoustic, magnetic, hydrodynamic control[1]. In this presentation, we introduce a method utilizing optical radiation pressure. The magnitude of the optical radiation pressure depends upon the optical property (refractive index, scattering cross section and absorbance) of the materials. Therefore, the method will be able to distinguish the droplets by not only size-dependence but also color-dependence. We developed a micro fluidic device for screening droplets by optical radiation pressure. The device we developed is simple construction only irradiating laser beam to micro fluidic channel. Micro fluidic channel we designed contains inlet, main and outlet channels. The inlet section consists of three 50µm-width and 20µm-height channels crossing by 90 degree. The main channel has its width of 150µm and height of 20µm along 10mm. The main channel is branched out into two 75µm-width and 20µm-height outlet channels. The channel was made of poly(dimethylsiloxane) and fabricated by soft lithography. In our experiment, oil in water emulsion was infused to a center inlet channel. Aqueous solution without droplets was infused to the two side branched channels as sheath flow. The structure of three crossing channels caused hydrodynamic focusing, hence a line of flowing droplets was created at the main channel. A line shaped focused laser beam with 532 nm wavelength was irradiated to the main channel orthogonally. Flowing droplets in the main channel were irradiated by the laser beam. Depending on their optical property, only the droplets experienced strong optical radiation pressure were changed their flowing position. Eventually, they were introduced to one of outlet channels, however, the rest flew into the others. In the presentation, we will show experimental results showing screening droplets by their size and color.


SB11.03.22
Chemically Patterned Surfaces and Their Use as a Component in Liquid Molding Processes Takamichi Shimosaka and Thomas J. McCarthy; University of Massachusetts Amherst, United States

Wetting-controlled surfaces are typically hydrophobic/hydrophilic patterned surfaces that can be wet rapidly to create a matrix of precisely aligned and shaped sessile liquid droplets. 2D wetting controlled surfaces have attracted much interest for both fundamental issues and applications that include the creation of small droplet arrays of proteins and cells for analysis and screening purposes. Wetting controlled surfaces are also applicable to generate effective solution separating walls for precise ink deposition or conductive layer deposition in producing electronic devices. A potentially beneficial attribute of this process is that the two-dimensional patterned surfaces create, along with the liquid, three-dimensional shaped features. These features can be used in molding processes that are versatile because of the flexibility of the 2D pattern, the liquid identity and the liquid volume (contact angle).

We present a novel 3D structure fabrication technique using 2D hydrophilic / hydrophobic patterned wetting surfaces. The preparation of controlled wetting surfaces and the subsequent liquid coating processes create reproducible sessile droplet arrays. The patterned surfaces show sufficient liquid trapping capability with a wide range of liquids with surface tension values ranging from 72.8 (water) to 18.8 mN/m (octamethylcyclotetrasiloxane). These droplet arrays can be covered with controlled thickness silicone prepolymers which are cured catalytically. The array serves as a mold, and the liquid is retained in the more hydrophilic regions due to a hydrophilic / hydrophobic confinement effect. The velocity of liquid application using a flow coating system affects the volume of coated liquid yielding molds with varying feature height while maintaining the width of droplets. Several types of liquid, including ionic liquids, glycerol, and water were studied to confirm the versatility of this molding process. Immiscibility between the silicone and certain ionic liquids permitted precise molding. A molded silicone resin showed light scattering behavior that was predicted by the 2D droplet array structure, indicating the successful replication of the array to the silicone resin. The shape of resulting molded silicones when water was used was a function of relative humidity, because of the significant water vapor permeability of silicones. Due to the finite vapor pressure of glycerol, we could control the height (and shape) of features using controlled condensation/evaporation after flow coating. In this presentation, we will present our work on the preparation of wetting controlled surfaces, the creation and effect of the liquid droplet as a mold, and subsequent molding processes.

SB11.03.23
Wettability at Picodrop Levels—Analysis of Ink and Substrate Surface Properties under Inkjet Conditions Paul Simutis1, Peter Oberschachtsiek2, Martin Gruesser2 and Michaela Laupheimer2; 1DataPhysics Instruments USA Corp., United States; 2DataPhysics Instruments GmbH, Germany
Compatibility of ink and substrate is crucial for an optimal printed image. Currently in inkjet printing, the ink must be adjusted to each printer head and then precisely formulated for the printing process. Consequently, the only degree of freedom for desired print image lies in the properties of the substrate’s surface. By choosing a proper substrate or modifying it, according to its surface free energy, the required wettability and adhesion properties can be obtained; sometimes even without any primer or additional sealing process, which reduces production costs. In addition to wetting and adhesion, the absorption process on absorbent substrates has an influence on the final image quality. Using a goniometer capable of delivering ink droplets to a volume as low as 30 picoliters, the wettability of different raw and modified substrates was determined by contact angle measurements and the surface free energy of the substrates was calculated. With this knowledge it becomes possible to estimate wetting and adhesion behavior of inks. Using picodrop-level dosing with the goniometer, the ink-substrate interaction directly under inkjet drop dispensing conditions is observed. Contact angle changes due to absorption and wetting can be determined with a speed of up to 1 ms. This picodrop delivery technique can be used for early-stage printing tests of newly developed ink formulations with conditions similar to the inkjet process without the risk of printer head blockage. These measurements enable fast and reliable determination of the surface properties of substrates and inks which simplifies the choice of substrate-ink combination for ideal image printing. Selected examples will be presented.

SB11.03.24
New Force Tensiometer Development for Adhesion Force Measurement of Liquids on Solid Surfaces

Paul Simutis¹, Daniel Scholz² and Michaela Laupheimer²; ¹DataPhysics Instruments USA Corp., United States; ²DataPhysics Instruments GmbH, Germany

The measurement of contact angles and surface free energy is a well-known method to study and understand adhesion properties of liquids to solid surfaces. Work of adhesion between liquid and substrate can be estimated by determination of surface energy of a substrate, measurement of surface tension of a liquid and calculation of adhesion work between them using Young-Dupre equation. This methodology is therefore commonly used in the development of coatings, paints and varnishes, for example, as well as to characterize surfaces and the effects of surface treatments. In this lecture a new, more direct approach to measurement of adhesion using a tensiometer will be presented. This new method uses small platinum ring to hold a droplet of the test liquid, software-controlled movement of the substrate to attach the droplet to the test substrate and measure the force between the liquid and the substrate while the droplet is being pulled off from the substrate. An integrated camera records the process of the drop detachment and allows calculation of the contact area as well as contact angle between the drop and the substrate. With this novel technique it is now possible to directly observe and measure the liquid’s behavior when in contact with a solid surface. Several examples will be presented including biosurfaces and membranes to test the adhesion of water droplets to them. The droplets are brought in contact with, pressed onto and then pulled off the biosurfaces and various membranes. During this process force distance curves were recorded and later compared to each other. An analysis of the maximum adhesion force shows good correlation to contact angles which can also be analyzed combining the tensiometer with this video system.

Furthermore liquid transfer to or into the material can be analyzed and different compression rates can be used to simulate different drop behavior.

SB11.03.25
Correlating the Structure of Ferrocene-Loaded Microemulsions near Surfaces to Their Electrochemistry

Luke Heroux¹,², Brian Barth¹, McKensie Nelms¹, Nelly Cantillo¹, Jing Peng¹, Thomas Zawodzinski¹,², Douglas Hayes¹ and Mark Dadmun¹,²; ¹University of Tennessee, United States; ²Oak Ridge National Laboratory, United States

Structured liquids are of interest as possible electrolytes for energy storage and other electrochemical applications, where one focus is the electrochemical behavior of oil-in-water microemulsions. Stable microemulsion systems consisting of water (plus salt), toluene (oil phase) and a Polysorbate 20/butanol surfactant/cosurfactant system with ferrocene, a model redox active agent, loaded into the toluene phase is the focus of our studies. Electrochemical results indicate remarkably reversible (fast) electrochemical kinetics in the region in which oil-in-water droplets or bicontinuous microemulsions are present. To understand this process further, we have examined the structure of the microemulsion in the bulk with x-ray and neutron scattering and near a surface with neutron reflectivity. The near surface studies will provide insight into the interaction and ordering of the microemulsion at an electrode surface.
This talk will focus on the structure of this microemulsion near surfaces with well controlled hydrophobicity using neutron scattering, where initial results indicate a layering of the components near these surfaces.

SB11.03.26  
**Fabrication of Electromagnetic Interference Shielding Sheet with Stretchable Using Ga Based Liquid Metal Powder**  
Chan-Geun Song, Hyeunseok Choi, Sungbok Kang and Jongseok Kim; Korea Institute of Industrial Technology, Korea (the Republic of)

Gallium based liquid metal (LM), Eutectic gallium indium (EGaIn) exists in liquid form at room temperature. EGaIn has high electrical conductivity and thermal conductivity in liquid phase. Many kinds of way to make stretchable electrode pattern with LM and study of its properties have been published in research papers. These researches show several applications such as microfluidic systems, soft electronics and wearable devices. In the recently, micro-nano sized LM droplet or powders have received significant focus in fabrication methods, applications and its natural material properties. LM powders are a type of biphasic materials which have an inner core in liquid state and an outer shell of Ga oxide, is reported to be a 30-50A thickness. LM powder has been of interest as this is able to show high interesting characteristics coming from the difference material properties (electrical, mechanical) between core and shell. The shell is electric insulation material, and the core is conductive. In this study, we propose a fabrication process of micro-nano size liquid metal (LM) powder. For showing application example, we implemented a stretchable EMI shielding sheet using LM powder and silicone resin. This sheet has electric insulation that reason why the shell of LM powder is the insulating oxide layer, and it has enough EMI shield property because the core of LM powder in the sheet is conductive metal.

At first step, we make ethanolic micro-nano scale LM colloids using sonication, ultrasonic homogenizer make high oscillating shear forces in vial with LM and to form LM particles. The LM is a eutectic gallium–indium (Ga 74.5% and In 25.5%, Melting point 16°C). During the sonication process, LM particle is exposed to oxygen. Gallium oxide continuously forms on LM particles. We can control size of the LM particle by sonication time. The longer time of sonication, the smaller size of LM particle is. When sonication time is 15min, we can produce LM particle size 100nm~150nm. After sonication, Precipitation makes LM particle separation in vial by its size. We extract the LM particles from vial using a syringe. Finally evaporating the ethanol, we can get dried LM powder.

The sheet of EMI shield is made by silicone resin (Dragon skin™ 10NV) and fabricated LM powder. We mix the LM powder with the silicone resin, and add the hardening agent. After curing 2hours, we fill off the EMI shield sheet applied LM powder from a substrate (Si wafer)

Generally, EMI shielding materials use conductive materials and there is a risk of electric short circuits. We have confirmed the possibility of liquid metal powder as EMI shielding materials with non-conductive properties. This study used LM powder as EMI shielding material while preventing electric short circuits on the surface. Silicone resin is easy to form and have a stretch, which is advantageous for applying a composite sheet to various fields. We measured the electromagnetic shielding using a network analyzer and measured the insulation performance using an insulation resistance tester withstand voltage insulation resistance tester. The EMI shielding performance of LM powder, insulation was evaluated via experiment results of developed the LM powder shield sheet. In the future work, we will study the theoretical relationship between the size of LM powder and the EMI shielding performance. We expect the performance of the sheet depending on the volume ratio of silicone resin and LM powder.

SB11.03.27  
**Controlling the Jet-Mode Break-Up of Multiphase Emulsions for High-Throughput Fabrication of Structured Microparticles Using Microfluidic Devices**  
Seung-Kon Lee and Jin-Hee Kim; KAERI, Korea (the Republic of)

There has been intense and longstanding interest in the use of biocompatible microparticles for a variety of applications such as bio-imaging, drug delivery, medical diagnostics, photonics, optical data storage, and display pigment. Batch synthesis has been the method of choice for preparing polymer particles due to practical advantages in productivity and accessibility, despite disadvantages in controllability and efficiency. In batch synthesis, multiple separated steps of synthesis, purification, loading and washing are required to prepare the particles. During this process, the amount and size of loadable materials is limited. Furthermore, an excessive portion of loading materials is wasted, which is especially problematic when expensive loading materials are used (ex. Quantum dots, biomaterials, drugs and etc.).

Compared to the batch processes, the microfluidic drop breakup scheme allows predominant production of uniform
emulsions with highly controlled size in continuous manner. Combined with photopolymerization scheme, those emulsions can be instantly converted into crosslinked particles containing various functional materials. Even infinitesimal amount of precious materials can be handled without any loss, since the emulsions are prepared from shear induced breakup of one phase into another immiscible fluid. In this scheme, there is no additional washing step or development step which causes material dissipation. Furthermore, this scheme allows easy loading of relatively large dispersion materials up to several micrometers. Most of the microfluidic particle synthesis is operated in a dripping mode regime which allows precise size distribution control. However, dripping mode operation has limited production rate since the breakup occurs one by one, with relatively low frequency. In addition, the controllable size range is limited because the emulsion sizes are more dependent on the nozzle diameter and interfacial properties rather than the flow conditions. To get smaller emulsion sizes, dimensions of the microfluidic channels around the breakup junction must be decreased, causing unstable flow and significant pressure build up in the system. Viscous monomers used for the particle preparation creates even larger pressure accumulation and can lead to device failure. By applying multiphase flow in the microfluidic system, structural emulsions, such as janus or eyeballs, snowman and hemispheres can be fabricated.

In this study, we presented production of highly uniform emulsions with various structures using harmonic breakup of co-flowing jet with high Weber number system. In jet mode breakup, axisymmetric laminar jet of inner fluid is broken into a train of uniform tiny emulsions. Ideal harmonic fluctuation formed by a well-defined microchannel leads to series of disconnection with regular interval from the periodic modal points. Since the jet diameter is relatively small and widely variable for given nozzle diameter, the jet mode allows low pressure drop, high production rate and wide range of controllability, simultaneously. Here, biocompatible microspheres with various shapes were synthesized throughout a controllable size range of 10 ~ 100 μm and 3% of uniform size distribution using jet breakup. The production speed can be ranged from 400 Hz to 100,000 Hz, according to the microfluidic chip material.

SESSION SB11.04: Emulsions/Capsules
Session Chairs: Esther Amstad and Alberto Fernandez-Nieves
Tuesday Morning, December 3, 2019
Hynes, Level 3, Room 306

8:30 AM *SB11.04.01
Advective Flow in Nanostructured Bijels via Electroosmosis Martin F. Haase; University of Utrecht, Netherlands

Particle stabilized bicontinuous emulsions (bijels) have been introduced over 10 years ago.[1] Soon after their discovery, their future use as continuously operated crossflow reactors for chemical reactions between immiscible reactants was proposed. This potential yet remains to be demonstrated. Here, we take a significant step towards realizing this vision by introducing advective flow in bijels via electroosmosis. Recently, we have introduced Solvent Transfer Induced Phase Separation (STrIPS), a straightforward technique for generating bijel fibers with asymmetric oil/water channels of micrometer dimensions.[2] Our current work has advanced STrIPS to generate bijel fibers with submicron sized oil/water channels of high uniformity. Surface tension and contact angle measurements are employed to rationalize the structure formation mechanisms. The uniform channels are found to enhance the mechanical strength and elasticity of STrIPS bijels, as determined by microfluidic in-situ mechanical testing.[3] Last, we investigate electroosmotic flow by monitoring dye propagation within the bijel fibers. Electroosmotic flow with speeds of up to 1 cm per minute is observed in the bijels by increasing the voltage and the nanoparticle surface charge. We report our research as a major step towards employing bijels as media for multiphasic processes with potential applications in Pickering interfacial catalysis and as cross-flow microreactors.

References

9:00 AM SB11.04.02
Optical Sorting of Droplets and Particles by Optical Radiation Pressure Runa Sugimoto1,2 and Satoru Shoji1,2;
Recently, centrifugation and chromatography are commonly used to sort micro/nano particles. These methods allow us to sort particles by mass difference or size difference. In this presentation, we propose another particle separation method, in which particles are sorted by the difference of optical properties. For this purpose, we use optical radiation pressure. When laser light is launched onto small particles, the particles scatter the light, the particles are received impulse exerted as reaction. This optical force is usually very small, in the order of a few pN, and this force is called optical radiation pressure. Since the cause of the pressure is scattering of light, the magnitude of optical radiation pressure depends on optical scattering efficiency of particles. To utilize this dependence to sort particles, we built a simple optical system, consisting of a glass microcapillary and laser. First, we filled the glass capillary with an aqueous suspension of particles. Then we focused laser light from the tip end. The laser light traveled into the tube by waveguide mode toward the opposite end. The particles floating in the capillary were pushed by optical radiation pressure. The particles moved in the capillary with different speed. In the experiment, we used Nd:YVO4 laser light emitting at 1064 nm. The inner and outer diameter of the capillary are 20 µm and 25 µm, respectively. To prevent temperature rising, we used heavy water for the dispersant. The motion of these materials was observed by a bright field optical microscope from the side of the capillary. We investigated 3 types of micro/nano particles, milk fat/water emulsions, polystyrene microspheres, and multi-walled carbon nanotubes. We observed the transport speed varied in material. We also show experimental results of sorting milk fat/water emulsions and polystyrene sphere.

9:15 AM *SB11.04.03
Sequential Bottom-Up Assembly of Synthetic Cells Joachim P. Spatz and Oskar Stauffer; Max Planck Institute for Medical Research, Germany

The evolution of cellular compartments for spatially and temporally controlled assembly of biological processes was an essential step in developing life by evolution. Synthetic approaches to cellular-like compartments are still lacking well-controlled functionalities, as would be needed for more complex synthetic cells. With the ultimate aim to construct life-like materials such as a living cell, matter-to-life strives to reconstitute cellular phenomena \textit{in vitro} – disentangled from the complex environment of a cell. In recent years, working towards this ambitious goal gave new insights into the mechanisms governing life. With the fast-growing library of functional modules assembled for synthetic cells, their classification and integration become increasingly important. We will discuss strategies to reverse-engineer and recombine functional parts for synthetic eukaryotes, mimicking the characteristics of nature’s own prototype. Particularly, we will focus on large outer compartments, complex endomembrane systems with organelles and versatile cytoskeletons as hallmarks of eukaryotic life. Moreover, we identify microfluidics and DNA nanotechnology as two highly promising technologies which can achieve the integration of these functional modules into sophisticated multifunctional synthetic cells.

9:45 AM BREAK

10:15 AM *SB11.04.04
From Long-Term Stability to Ultrafast Dynamics of Pickering Bubbles Valeria Garbin; Imperial College London, United Kingdom

Solid particles can adsorb at fluid-fluid interfaces, much like molecular surfactants. Unlike molecular surfactants, however, the adsorption of solid particles can be considered to be irreversible, due to a large capillary energy associated with adsorption. As a result, solid particles can be used to stabilise drops and bubbles. Remarkably, particle-stabilised bubbles (Pickering bubbles) are found to be indefinitely stable, because the particle monolayer can arrest bubble dissolution, which is otherwise driven by the Laplace pressure. I will present two phenomena, discovered in our laboratory, which occur when particle-stabilised bubbles are subjected to changes in temperature or pressure. We found that a decrease in temperature destabilises particle-coated microbubbles in water beyond dissolution arrest. A simple model describing the effect of the change in temperature on mass transfer suggests that the dominant mechanism of destabilization is the increased solubility of the gas in the liquid. We can also drive particle-stabilised bubbles into periodic compression-expansion at 10-100 kHz by ultrasound forcing. This causes ultrafast deformation and microstructural changes in the particle monolayer. For large-amplitude forcing, the compression of the interface leads to particle expulsion, and we have uncovered different expulsion scenarios depending on the mode of bubble deformation, including highly directional patterns of particle release during non-spherical oscillations. For small-amplitude driving, we have observed the formation of a transient microstructure -- a
network of strings -- which is consistent with anisotropic interparticle interactions. By comparing the experimental results with the predictions of particle-based simulations, we have found evidence of dynamic capillary interactions resulting from the deformation of the interface due to the non-negligible inertia of the colloidal particles at the extreme accelerations caused by ultrasonic forcing.

10:45 AM SB11.04.05
The Vibration Behavior of Submicron Gas Vesicles in Response to Acoustic Excitation as Determined via Laser Doppler Vibrometry An Huang¹, Shuai Zhang¹, Avinoam Bar-Zion², Jiaying Wang¹, Oscar Mena¹, Mikhail Shapiro² and James Friend¹; ¹University of California San Diego, United States; ²California Institute of Technology, United States

Gas vesicles (GVs) are remarkably stable nano-sized gas-filled protein shells proven effective in ultrasonic imaging, especially in traditionally difficult, small-scale vasculature and interstitial spaces around tumors. The many potential benefits of GVs arise from their strong gas equilibrium at a submicron size as produced by bacteria or algae from a known genome, producing significant contrast in ultrasound imaging. The actual vibration behavior of GVs, including buckling and collapse, is poorly understood since the GVs are too small for observation methods of sufficient speed to produce details of the GV deformation during exposure to ultrasound. Traditional optical or acoustic microscopy methods are, in any case, not useful, and ex-situ transmission electron microscopy produces useful images but without sufficient time resolution.

We propose to instead use laser Doppler vibrometry (LDV) to observe the vibration behavior of GVs. Employing interferometry, LDV offers a far better spatiotemporal resolution, in our case up to 2.4 GHz in frequency and as little as 200 fm in surface displacement over a spot size of 1 µm. While the typical GV is smaller than 1 µm, an agglomeration of GVs may be used with the LDV to produce a measurable displacement response from a controlled, acoustically-delivered pressure. In this talk, we report the fundamental and first harmonic resonance frequencies of GVs at 1.02 GHz and 1.70 GHz, interparticle resonances at ~300 MHz, and vibration to buckling and collapse at the clinically relevant frequency of 6.5 MHz. We also compare these results with predictions from classic theories of bubble and particle oscillations and finite difference-based computations.

11:00 AM SB11.04.06
Closed Cellular Structure from Monodispersed Graphene Bubbles for Ultralight, Strong and Superelastic Materials Min Jun Oh¹, Seon Ju Yeo², Hyun Min Jun¹, Minhwan Lee³, Jung Gun Bae³, Yeseul Kim¹, Kyung Jin Park⁴, Seungwoo Lee⁵, Daeyeon Lee⁶, Byung Mook Weon¹, Won Bo Lee¹, Seok Joon Kwon⁷ and Piljin Yoo¹; ¹Sungkyunkwan University, Korea (the Republic of); ²North Carolina State University, United States; ³Seoul National University, Korea (the Republic of); ⁴Kyung Hee University, Korea (the Republic of); ⁵Korea University, Korea (the Republic of); ⁶University of Pennsylvania, United States; ⁷Korea Institute of Science and Technology, Korea (the Republic of)

The design of well-controlled three-dimensional (3D) structures from individual building blocks such as graphene nanosheet or carbon nanotube has technological and scientific importance since it can provide advanced physical properties compared to their bulk counterparts. In particular, for a number of practical applications including electrode, supercapacitor, sensor, fluid absorber, energy damping, thermal insulator and catalysis, it is essential to fabricate well-defined 3D graphene structures with high surface area. While progress toward creation 3D porous graphene materials, previous efforts have placed severe restrictions on their wide-spread utilization because it is hard to create regularized and ordered structures with controlled dimensions, shapes, and morphologies. To overcome these challenges, we investigated multiphasic fluid mixtures such as emulsions droplets as alternative templates for generating well-defined 3D structures. This study uses a hierarchical design approach starting from the functionalized graphene oxide nanoplatelets at the molecular- and nanoscale, leading to the microfluidic fabrication of solid bubbles at the microscale. Then, generated graphene microbubbles are assembled into centimeter-scale 3D structures. Importantly, these assembled structures are self-interconnected into completely space-filled and reinforced closed-cellular structure. The 3D graphene structure exhibits the Young’s modulus above 177 kPa with a light density of 4.67 mg cm⁻³ and structurally stable up to 87% of the compressive strain benefiting from systematic stress dissipation through the complete space-filled closed-cellular structure. The method opens a new horizon for designing lightweight, strong, and superelastic properties.

11:15 AM SB11.04.07
Tuning the Properties of Infrared-Absorbing Nanofluids for Microfluidic Applications Urice Tohgha¹,² and
The transport and actuation of droplets in microfluidic-based devices strongly relies on the properties of the fluids. Nanofluids (fluid-containing nanomaterials) offer an appealing approach to modulate key fluid properties such as conductivity, viscosity and interfacial tension which directly impact the wettability on various surfaces. This approach also has the added advantage of utilizing the optical properties of the nanomaterial for microfluidic-based optoelectronic applications such as reflective displays as well as photodetectors. Nanofluids comprising IR-absorbing nanofluids have been less explored and also pose colloidal stability challenges. We will present our results on the engineered properties of nanofluids comprising Ag$_2$Se, PbS and SnTe semiconductor nanoparticles in different solvent systems. The study highlights the synthesis of nanoparticles with surface ligands capable of significantly altering the conductivity and interfacial tension of nanofluids. This work uses electrowetting (droplet actuation through voltage application) in a biphasic system to probe the wettability of the different nanofluids by evaluating the changes in droplet contact angle on a dielectric surface. We show unique spreading characteristics of nanofluids in non-aqueous (Dimethyl sulfoxide and Dimethylformamide) and aqueous dispersion media. The work presented will certainly shed more light on the use of nanofluids in microfluidic-based devices and the properties of nanoparticles in aqueous and non-aqueous media.
phase behaviors and mechanical properties. We demonstrate that this gelation platform is general and robust over a wide range of composition, colloid size and component chemistry. By carefully characterizing the colloids and obtaining a mechanistic understanding of their response, we construct the interparticle potential and explain trends in material behaviors. This stimulus-responsive gelation platform is general and offers new strategies to engineer complex viscoelastic soft materials.

2:15 PM SB11.05.03
Connecting the Viscoelastic Response of Nanosheet Gels to the Elastic Properties of the Particles  
Sebastian Barwich and Matthias Möbius; Trinity College Dublin, Ireland

Micron-sized nanosheets such as graphene or MoS₂ platelets can be used to make conducting inks or as fillers in composites to enhance their mechanical properties. At high concentrations beyond rigidity percolation, nanosheet suspensions become yield stress fluids with a finite storage modulus. In this regime the elastic response of nanosheet suspensions appears to be universal. The storage modulus plateau of few-layer graphene in NMP solvent [1] and aqueous graphene oxide gels [2] exhibit a power law exponent close to 3 as a function of packing fraction.

We present a new analytical model that explains this behaviour and connects the bulk response to the elastic properties of single nanosheets and their size. We infer the bending stiffness of single nano-sheets from our rheological data which agrees well with previous AFM experiments on single sheets and simulations. This model opens up the possibility to infer elastic properties of different nanosheets from rheological data of the suspension rather than performing AFM experiments on single nano-sheets. Furthermore, this model may explain the mechanical enhancement of nanosheet composites where a similar exponent can be observed [3].


2:30 PM SB11.05.04
Anomalous Compliance of Structured Liquids  
Yu Chai¹,²,³, Alysia Lukito³, Jaffar Hasnain³, Anju Toor³, Wenqian Feng¹,², Yufeng Jiang¹,³, Joe Forth², Yanhui Tang¹, Honghao Hou², Teresa Williams¹, Ravi C. Chintala¹, Dong Li¹, Philip Geissler³, Brett A. Helms¹,², Thomas Russell²,⁴,⁵ and Paul Ashby¹,²; ¹Lawrence Berkeley National Lab, United States; ²Lawrence Berkeley National Laboratory, United States; ³University of California, Berkeley, United States; ⁴University of Massachusetts Amherst, United States; ⁵Beijing University of Chemical Technology, China

The jamming of nanoparticle surfactant assemblies at liquid-liquid interfaces enables the generation of persistent liquid in liquid structures or Structured Liquids. In general, increasing the binding strength of the individual nanoparticles to the interface leads to an increase in the stiffness of the assemblies. However, we observe a region of anomalously low compressive stiffness as nanoparticle binding energy is increased. We use a combination of tensiometry and in-situ AFM to reveal that the mechanism of anomalous stiffness is surfactant molecules surrounding nanoparticles at the interface without phase transfer which facilitates nanoparticle-nanoparticle interactions normal to the plane of the interface leading to facile multilayer formation. This region of anomalous stiffness expands the parameter space for the creation of complex shapes of structured liquids.

2:45 PM OPEN DISCUSSION

3:00 PM BREAK

3:30 PM SB11.05.06
Smart Microcapsules with Molecular-Polarity-Selective and Temperature-Dependent Permeability  
Ji-Won Kim¹, Sang Seok Lee², Jinho Park³, Minhee Ku³, Jaemoon Yang³ and Shin-Hyun Kim¹; ¹Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of); ²Korea Institute of Science and Technology, Korea (the Republic of); ³Yonsei University, Korea (the Republic of)

Cells, the building blocks of life, are enclosed with semi-permeable membranes. The membranes protect important genetic materials from surroundings while selectively allowing the transmembrane transport of molecules. This
molecule-specific permeation is of great importance in cell growth and cell-to-cell communications. Inspired from the cell membrane, microcapsules with molecular size- or charge-dependent permeability have been developed using the membranes with consistent pore sizes and surface charges. Beyond these simple regulations of transmembrane transport, here, we suggest a new microcapsule with molecular polarity-selective permeation whose rate is further adjustable with temperature. Highly monodisperse microcapsules are produced using a microfluidically-prepared template of water-in-oil-in-water (W/O/W) double-emulsion drops. As the middle oil phase of the double-emulsion drops, we use a ternary mixture of photocurable triacrylate monomer, phase change material (PCM), and molecular compatibilizer. Upon UV irradiation on the drops, the monomer forms a polymeric shell and the liquid PCM fills the voids of the polymeric framework. The molecular compatibilizer, composed of acrylate group and PCM-like moiety, prevents the macrophase separation between the polymer and PCM, maintaining a homogenous shell at sub-10 nm scale. As the PCM forms the continuous nanochannels across the shell, the molecules that are soluble in the liquid PCM can diffuse through the channels above the melting point of PCM. By contrast, the molecules insoluble in the PCM are rejected from the microcapsules. The rate of permeation through the shell depends on the partition coefficient of the molecules in the PCM relative to water. As a less polar molecule has a higher partition coefficient, it shows faster permeation. The rate of permeation can be further adjusted by temperature. When the temperature drops below the melting point of PCM, the solubility dramatically decreases, resulting in the significant retardation of permeation. Therefore, the microcapsules provide molecular polarity-selective and temperature-dependent permeability whose threshold values are adjustable by the selection of PCM. As the polymeric framework and PCM form a homogeneous shell in the presence of molecular compatibilizer, PCM is preserved in the shell during temperature swing below and above the melting point, enabling the reversible change of permeability. This advanced transmembrane regulation provides a new opportunity for microcapsules as drug carriers, microsensors, and microreactors. For example, the microcapsules can be used as an injectable and implantable drug carrier that releases relatively hydrophobic drugs in a sustained fashion when the body temperature rises above the melting point of PCM as we verified through in-vitro and in-vivo experiments.

3:45 PM SB11.05.07
New Materials for Spatiotemporal Control of Jamming via Photo-Actuation Nicholas Vishnosky and Rachel Steinhardt; Syracuse University, United States

Many materials consist of soft particles at or below the jamming transition. However, we incomplete understanding of the relationship between material properties—such as rheology— and microstructure. To aid in this study of soft materials, we have created an experimental tool that enables spatiotemoral control over jammed microstructure. The composite has a photo- triggered jamming transitions, so we can direct what micro-regions of the materials are jammed. We have characterized the properties of this material on multiple length scales. This tool assists in the quantitative assessment of individual microstructural elements to the bulk material rheology, and may aid in the design of new soft materials.

4:00 PM SB11.05.08
Structural Coloration from Multiple Total Internal Reflections at Complex Emulsion Concave Interfaces Amy Goodling1, Sara Nagelberg2, Bryan Kaehr3, Caleb Meredith1, Seongik Cheon1, Ashley Saunders1, Mathias Kölle2 and Lauren D. Zarzar1; 1The Pennsylvania State University, United States; 2Massachusetts Institute of Technology, United States; 3Sandia National Laboratories, United States

Structural color is created by the interaction of light with physical structures and is most commonly seen in hard materials with high refractive index contrast and nanoscale periodicity such as diffraction gratings or photonic crystals. Developing methods to harness structural color in soft materials at larger length scales, such as in droplets, would enable use of such coloration mechanism for more diverse applications such as sensors, camouflage, or displays. Recently, we have observed tunable structural coloration from microscale concave interfaces of oil-oil complex droplets suspended in an aqueous surfactant solution. We were able to model the observed color and found that this effect was from light propagating by TIR along the interface can have different numbers of reflections and thus different path lengths which leads to interference and iridescent color. The requirements to achieve this effect include a transition from a high to low refractive index and a microscale geometry to support multiple TIR, allowing generation of structural color in a multitude of different materials and geometries and by diverse fabrication methods. For example, we have generated this effect in complex liquid droplets, solid particles, water drops condensed on substrates with low wettability, and solid elastic surfaces. With a light responsive surfactant, we were able to pattern reflective colored images in complex emulsions by stabilizing droplets of varying shape. These
simple geometric requirements provide new opportunities for fabricating, designing, and controlling structural color, enabling use of such structural coloration in materials where it previously would have not been possible.

SESSION SB11.06: Active Matter
Session Chairs: Damien Baigl and Alberto Fernandez-Nieves
Wednesday Morning, December 4, 2019
Hynes, Level 3, Room 306

8:30 AM *SB11.06.01
Anisotropy in Action—Harnessing Emergent Dynamics in Flowing Anisotropic Matter Anupam Sengupta;
University of Luxembourg, Dept. of Physics and Materials Science, Luxembourg

Anisotropy, the ability of partially ordered materials to respond directionally to a stimulus, is key to the dynamics and functions in living systems. From transporting signalling molecules within cells to transmitting mechanical stresses within growing bacterial colonies, anisotropy underpins the physics of living matter. Outside biological systems, liquid crystals (LCs) – formed typically by locally oriented low-molecular-weight rod-like molecules – offer an experimentally tractable system within which the fundamentals of anisotropic interactions can be precisely tuned and studied. In my lab, we harness this setting to, on the one hand, understand the fundamentals of anisotropic cross-talks between bio-relevant fluids and cues, and on the other hand, apply this knowledge to uncover the dynamics of real living systems. During this talk, I will allude to this iterative learn-apply-n-learn strategy to showcase how topological defects emerge within biological systems, regulate their micro-environment, and thereby tune the local material, transport, and mechanical attributes. Analysing living matter as emergent systems where anisotropy mediate evolutionarily well-timed biological functions, introduces a novel, yet general, mechanistic framework applicable for disparate biological systems. I will conclude by discussing how our ability to harness anisotropy – in action across disparate material fields – could have meaningful implications, from designing novel materials to exploring open questions in biology and translational medicine.

9:00 AM SB11.06.02
Nonreciprocal Chasing Interactions in Active Emulsions Caleb Meredith1, Pepijn Moerman2,2, Yu-Jen Chiu1, Jan Groenewold2, Willem Kegel2, Alfons van Blaaderen2 and Lauren D. Zarzar1; 1The Pennsylvania State University, United States; 2University of Utrecht, Netherlands

Emulsions stabilized with surfactants above the critical micelle concentration undergo solubilization as oil from droplets is transferred into the micellar phase. Concentration gradients of solubilize species can create interfacial tension differences across droplets leading to their movement via the Marangoni effect. We explore how long-ranged interactions between solubilizing oil droplets occur due to the overlap of their continually maintained solute profiles to generate active behavior. Mixing droplets of different oils under various surfactant conditions we observe unique nonreciprocal interactions which lead to chasing between droplets and drive their self-assembly into clusters with dynamic but predictable motions. We show how the underlying interactions are caused in part by oil exchange between droplets via oil-filled micelles. Control over droplet interactions and the directional exchange of chemical components can be utilized in the design of tunable active multiphase fluid systems with the ability to self-organize, adapt to environmental stimuli, or carry out self-regulated reactions.

9:15 AM SB11.06.03
Self-Propulsion of Small Droplets on Thin Oil Films Victor Leon and Kripa Varanasi; Massachusetts Institute of Technology, United States

Surfaces that prevent the adhesion of and remove droplets have received significant attention in the context of self-cleaning, anti-icing, and anti-fouling surfaces. Superhydrophobic surfaces offer a passive solution; however, they are susceptible to Cassie-to-Wenzel transition and depend on gravity to move the droplets. Active droplet manipulation has also been explored using electric, magnetic, and vibrational fields, but such technologies have difficulties with surface pinning and viscous liquids. In this context, systems in which droplets self-propel are promising avenues to remove contaminants from surfaces.
Here, we investigate the self-propulsion of small droplets of radii at and below the capillary length on heated thin oil films. At film temperatures above the boiling point of the droplet and low film viscosities, we observe that droplets can propel at velocities up to 16cm/s. The propulsion of the droplet originates from the asymmetric release of vapor from beneath the boiling droplet, propelling the droplet towards the edges of the substrate. Studies of film parameters, such as film oil, temperature, viscosity, and thickness, were conducted. Additionally, the effects of surface geometry and texture were explored. The droplet velocity was found to have the greatest dependence on film oil, temperature, and viscosity. We predict the droplet velocities using a model that balances the viscous dissipation in the oil film with the momentum of the vapor ejected from beneath the boiling droplet. Within our experimental range, the simple model accurately predicts droplet velocities at a variety of oil film thicknesses, oil viscosities, oil temperatures, and droplet radii.

9:30 AM *SB11.06.04
Understanding Sperm Navigational Mechanisms to Improve Assisted Reproductive Technologies Alireza Abbaspourrad; Cornell University, United States

The fertilization process in mammals as sperm traverse towards the fertilization site where the oocyte has been released. In the case of marine animals and plants, which release gametes into the sea, the motion of sperm occurs in a vast aquatic environment. In contrast, the fertilization process of mammals happens inside a complex environment known as the “female reproductive tract”. The intriguing, multifaceted question is, how do healthy sperm naturally navigate the correct path towards the fertilization site? And concurrently, how does the female reproductive tract select for the best sperm while they move towards the oocyte. Since performing in vivo studies to answer these questions is difficult and faces many technical and ethical issues, designing in vitro environments that mimic at least one facet of female reproductive tract is vital.

In the last two decades, “microfluidics”, with its high and unprecedented precision of preforming studies on microswimmers and active matters in microenvironments, has enabled us to study the navigation strategies of mammalian sperm. Although the journey of mammalian sperm is many-sided and includes complex biological and chemical processes, studying the motion of sperm in microfluidic geometries, and under fluid flows that mimic the biophysical aspects of the sperm swimming channel in vivo, is critical. These studies will reveal new insight about the physical and fluid-mechanical clues provided by the female reproductive tract to facilitate sperm navigation towards the fertilization site.

The fluid-mechanical clues that enable mammalian sperm to swim along a correct path towards the fertilization site include the upstream swimming of the sperm in a simple, shear flow known as “rheotaxis”. Furthermore, the hydrodynamic interactions of sperm with nearby rigid boundaries is another navigation mechanism that is referred to as “boundary-dependent navigation”. We have performed studies on the fluid-mechanical navigation of the mammalian sperm as well as the influence of specific, geometrical features on the sperm locomotion. To study the sperm navigation in a geometry that mimics the shape of “uterotubal junction”, which is a narrow junction at the beginning of fallopian tube, we designed a microfluidic stricture and studied the sperm locomotion under a simple shear flow. We discovered that such junctions select for highly motile sperm that can pass through the stricture while the slower sperm accumulate before the stricture. Therefore, a microfluidic stricture functions as a fluid-mechanical gate. The accumulation before stricture occurs in a hierarchical manner so that the competition is fiercest among sperm with the highest motility. To study the role of flagellar beating pattern on the sperm navigation, we first studied the flagellar beating pattern of sperm discovering a zeroth harmonic in the spatially asymmetric beating of the flagellum. This asymmetric beating creates a net torque and, thus, rotational components in the motion of sperm. We discovered that this zeroth harmonic, and asymmetric beating, impairs the boundary-dependent navigation while rheotaxis is less dependent on flagellar beating pattern.

To use our basic understanding of the sperm locomotion for such medical applications, we also have designed a microfluidic, rheotaxis-based sperm separation method. The microfluidic sperm separation techniques are sought-after for assisted reproductive technologies and infertility treatment as they are passive and operate without exertion of external forces. These efficient methods, accordingly, provide sperm with less DNA fragmentation. Our “microfluidic corral system” is a passive technique that only isolates progressively motile sperm with motilities higher than a tunable cut-off value.

10:00 AM BREAK
We will present a number of strategies for using multiphasic liquid-liquid-polymer systems to make a rich variety of colloidal structures and materials. The capillary forces originating at the liquid/liquid interfaces can serve for reconfigurable binding in soft matter systems, including Pickering emulsions, novel responsive capillary gels, and compositions for 3D printing. We will first present responsive structures made of filaments from lipid-coated magnetic nanoparticles suspended in water-oil systems. The nanocapillary binding results in ultra-high filament flexibility. As an example of the application of such structures, we will discuss the development of new 3D printing inks consisting of water, crosslinked PDMS microbeads and liquid PDMS phase. These Homocomposite Thixotropic Pastes (HTPs) can be directly extruded and shaped on a 3D printer. The curing of the PDMS bridges yields remarkably elastic, flexible and biocompatible structures. The HTP-3DP inks enable the 3D printing of “active” and magnetically reconfigurable structures. In alternative materials synthesis approach the liquid/liquid droplet interfaces can template the formation of a variety of polymer nanomaterials, including nanoparticles, nanofibers, nanoribbons, microrods, and microsheets. This allowed us to introduce a new class of soft dendritic polymer microparticles (“dendricolloids”) with hierarchical morphology similar to molecular-scale polymer dendrimers, but two orders of magnitude larger in scale. The polymer particles with branched and fractal morphology are fabricated by a simple and scalable process of interfacial polymer precipitation in turbulently sheared liquid media. The dendricolloids combine the properties of two of the most fascinating and studied soft matter systems – the freely-suspended dendritic particles have very large excluded volume, while in contact their nanofiber corona possesses the highly adhesive abilities of the nanofiber-padded gecko legs. The fractal branching and contact splitting phenomena of the dendricolloids enable a range of highly unusual properties – gelation at very low volume fractions, strong adhesion to surfaces and to each other, and ability to bind strongly and form coatings, nonwoven sheets, and ultrasoft membranes.

Visible light driven nano/micro swimmers are promising candidates for potential biomedical and environmental applications. However, the previously reported mean squared displacement (MSD) values are low, typically in the range of up to 200 µm² (when measured over 10 s), even under the favourable UV light illumination.[1,2] This is a severe drawback for the applications where the efficient transport of micromotors within a vessel is demanded.

Here, we demonstrate Ag/AgCl-based spherical Janus micromotors that reveal an efficient propulsion under visible blue light illumination.[3] The proper design of an Ag/AgCl-based micromotor can boost the MSD to a remarkable value of 3000 µm² (over 10 s) in pure H₂O, even when activated with blue light (excitation λ = 450-490 nm). The revealed propulsion of micromotors owns a dependence of the intensity of visible light, which is contributed by the couple plasmonic light absorption of Ag/AgCl and the efficient photochemical decomposition of AgCl. With the motion comparisons of individual Janus particle, small cluster, and large cluster, the effect of suppressed rotational diffusion has been revealed experimentally and in numerical simulations. Furthermore, we show that Ag/AgCl-based Janus micromotors reveal efficient exclusion effect to their surrounding passive polystyrene (PS) beads in pure H₂O.[4] The exclusion efficiency is controlled by the number of single Janus PS/Ag/AgCl particles that compose a cluster. Using numerical simulations of the Langevin equations, we gain a fundamental understanding not only the diffusion constants, but also the system-specific interaction parameter between Janus motors and passive beads.
Tuning Synthetic Active Matter—From Living Clusters to Liquid Swarms Paul Dommersnes and Jon O. Fossum 1,2; 1Norwegian University of Science and Technology, Norway; 2Institut Pierre-Gilles de Gennes (IPGG), ESPCI, France

Biological active matter, such as populations of cells and animals, often change between different swarming states. One example is shoaling, milling and schooling fish. Synthetic active matter consist of self-propelled inanimate units and emulates biological active matter. We combine electric field induced attraction with electro-rolling propulsion [1] in a population of granular beads. A variety of swarming regimes is realized: living crystals and clusters, a stripe phase of clusters, and polar liquid swarms, reminiscent of transitions in active matter simulations [2,3,4]. Remarkably, the crystal to liquid transition occurs at a different velocity threshold than the local to global polar order transition. The stripe phase is reminiscent of those in quasi two-dimensional matter with competing interactions. The system links universal patterns in biological and synthetic active matter, and can open new routes for tuning self-assembly in soft matter technologies.

controlled topologies, as vesicle templates. In particular, we show the utility of water-in-oil-in-water (W/O/W) double emulsion drops with ultrathin middle oil layers as templates to fabricate vesicles exhibiting either phase separations in the vesicle cores or domains in the vesicle membranes [1,2]. We also show the utility of W/O/O/W triple emulsion drops with two ultrathin middle oil layers as templates to fabricate vesicles with asymmetric membranes [3]. Both approaches have high encapsulation efficiency and yield vesicles with monodisperse sizes, owing to the size monodispersity of the emulsion drops used as templates. Furthermore, coupling microfluidic vesicle production techniques to confocal fluorescence microscopy observations enables the accurate determination of both the composition of phase-separated compartments in the vesicle cores and the degree of asymmetry in the vesicle membranes.


2:30 PM BREAK

3:30 PM SB11.07.03
Engineering Compartments in Cells Using Complex Coacervation of Supercharged Proteins Jouwen Wang, Vivian Yeong and Allie Obermeyer; Columbia University, United States

Complex coacervation is a well-studied liquid-liquid phase separation phenomenon between oppositely charged polyelectrolytes. Recently, it has been appreciated that complex coacervation likely plays a role in the formation and function of membraneless organelles in eukaryotic cells. For example, polyanionic RNA can condense with cationic intrinsically disordered regions of proteins to form membraneless organelles such as nuclear bodies. Here we investigate how liquid-liquid phase separation via complex coacervation can be engineered from the ground up. Using protein engineering the overall charge and charge distribution on model fluorescent proteins was systematically varied. In particular, this study explores the impact of GFPs with different supercharged tags on the formation of protein complex coacervates in vivo. GFP variants with the same net charge but different charge distributions were expressed and their intracellular localization was monitored by optical microscopy. We found that GFP variants with positively charged tags can form a condensed phase in E. coli, and this condensed phase has many of the properties of a complex coacervate. In summary, we have identified several supercharged amino acid tags that can promote liquid-liquid phase separation of proteins of interest intracellularly. This finding can be applied to engineer intracellular complex coacervation to form artificial membraneless organelles.

3:45 PM SB11.07.04
Marangoni Flows Drive the Alignment of Cell-Laden Collagen Hydrogels During Self-Assembly Bryan A. Nerger, Pierre-Thomas Brun and Celeste Nelson; Princeton University, United States

Type I collagen is a self-assembling protein that generates fibrous viscoelastic networks. In the body, cell-laden networks of collagen are remodeled to generate anisotropic fiber networks that can impact biological processes as diverse as cancer cell invasion and vascular network formation. Despite this ubiquity, fabricating cell-laden networks of aligned collagen fibers ex vivo remains challenging. Here, we use Marangoni flows in evaporating sessile droplets of monomeric collagen to fabricate cell-laden networks of aligned type I collagen fibers. Using time-lapse confocal reflection microscopy, we find that Marangoni flows give rise to radial flow in the evaporating droplet, which orients collagen fibers radially over mm-scale areas. Our data suggest that the resulting collagen fiber alignment depends on the relative humidity and the rate of collagen fiber self-assembly. Moreover, we found that the pattern of collagen fiber alignment can be tuned by changing the geometry of the droplet. By incorporating mammalian cells into evaporating droplets, we generate cell-laden collagen hydrogels that can be used for cell culture. We observe that cells collectively orient in the direction of collagen fiber alignment. Marangoni flow is a simple, rapid, and scalable approach that can be used to generate fibrillar cell-laden collagen hydrogels with broad applicability.
Molecular Communication between Synthetic Cells Friedrich Simmel; TU Munich, Germany

Exchange of molecular signals is essential for the coordination of cell behaviors in cellular consortia and tissues. This, in turn, enables the development and organization of large multicellular structures of higher complexity than typical single-celled organisms.

In recent years, a variety of attempts have therefore been made to emulate such communication processes in the context of artificial cells – e.g., to divide tasks between specialized synthetic organelles or for the creation of artificial tissue-like materials.

In this talk, we will present several examples, in which compartments containing chemical reaction systems and gene circuits communicate with each other via the exchange of molecular signals – e.g., on-chip gene expression, gel-based organelles that exchange RNA molecules, or emulsion droplets that communicate via small molecules.

SB11.08.01
Electrochemical Generation of Supercooled Microdroplets Nian Liu and Po-Wei Huang; Georgia Institute of Technology, United States

Since the first discovery of supercooling in 1724, the study of supercooled matter has been mainly limited to varying temperature or pressure. Early this year we have demonstrated an electrochemical approach to generate supercooled sulfur and observe the dynamic process in situ (see Publication 1 below). Our methodology combines dark-field optical microscopy, a transparent electrochemical cell, and a fast camera to visualize the process at single microdroplet with millisecond time resolution. This platform may open up opportunities for studying supercooled liquids as the droplets approach either homogeneous nucleation to the crystalline state or enter into the glass transition. The sulfur droplets remain liquid at 155 °C below sulfur’s melting point (Tm = 115 °C), with fractional supercooling change (Tm − Tsc)/Tm larger than 0.40. In operando light microscopy captured the rapid merging and shape relaxation of sulfur droplets, indicating their liquid nature. Micropatterned electrode and electrochemical current allow precise control of the location and size of supercooled microdroplets, respectively. Using this platform, we initiated and observed the rapid solidification of supercooled sulfur microdroplets upon crystalline sulfur touching, which confirms supercooled sulfur’s metastability at room temperature.

In a follow-up work (see Publication 2 below), we expanded the above methodology to generate polybromide droplets, which is the charge product in zinc-bromine flow batteries, a promising technology for stationary energy storage. The liquid behavior was also confirmed by rapid merging and shape relaxation. The results provide insights into the future design of zinc-bromine flow batteries.

This presentation is based on the following two recent publications from my lab:
   https://doi.org/10.1073/pnas.1817286116
   https://doi.org/10.1002/ange.201906980

SB11.08.02
Controlling Shape Changes and Interactions within Nanogel Arrays at Liquid-Liquid Interfaces Vaibhav A. Palkar, Chandan K. Choudhury and Olga Kuksenok; Clemson University, United States

Nanogels at liquid-liquid interfaces are used for applications ranging from emulsion stabilization to interfacial catalysis and enhanced oil recovery. We present herein a dissipative particle dynamics (DPD) approach to model dynamics of polyacrylamide (PAAm) hydrogels at the oil/water interface. To develop the model, we first compare hydrogel swelling dynamics to continuum theory. We compare the distribution of end to end distances of polymer
chains within a swollen hydrogel network to the Gaussian model predicted for polymers in a theta solvent. Next, we compare equilibrium swelling volume fraction of gels measured from the DPD simulations to continuum Flory-Rehner theory. Using this equilibrium swelling volume fraction, we estimate the elastic moduli of our model hydrogels to be within the range observed in experiments. Having established these comparisons, we next focus on the shape changes of the hydrogel as it adsorbs from the aqueous phase onto the oil/water interface. The nanogel undergoes reshaping and adopts several morphologies from spherical to pancake. We highlight the competition between interfacial energy (which tends to deform the gel) and the gel’s elastic energy (which opposes this deformation). We also investigate spreading dynamics and interactions of nanogel arrays initially placed in the aqueous phase. We investigate conditions at which saturation of the interface with these gels forces protrusion of gels into the aqueous phase. These findings provide data for optimizing the design of PAAm-based nanogels for various applications.

SB11.08.03
Droplet Manipulation for the Synthesis of Anisotropic Nanoparticles with Controlled Morphology Abhiteja Konda1,1, Ryan Dohn2, Rebecca Back2, Tijana Rajh1 and Anindita Basu2,1; 1Argonne National Laboratory, United States; 2The University of Chicago, United States

Anisotropic nanoparticles have gained significant interest in the past decade due to their enhanced properties (both physical and chemical). These properties can be tuned and are dependent not only on their size and morphology, but also on their composition. The use of anisotropic nanoparticles for enhanced surface plasmon resonance (SPR) effect is widely studied. In the present work we use droplet-based microfluidics for the synthesis of anisotropic gold nanoparticles (a-AuNPs) for applications in biology based on its SPR effect. Specifically, we use the Pico injection (a technique of introducing picolitre volume reagents into droplets by the application of electric field that destabilizes the surfactant in the droplets and thereby allowing the addition of the new solution) for the controlled synthesis of a-AuNPs. While there are several other potential applications for these a-AuNPs, we are interested in using these for the lysis of microbial cells in single-cell sequencing experiments. The current single-cell techniques predominantly focus on multicellular organisms and cannot be readily transferred to unicellular organisms due to the differences in their size and composition. The microbial cells are small (~1 μm) with concomitantly small amount of RNA and have a tough, adaptive cell wall that permits their survival in harsh environments (extreme pH or temperatures, anti-microbials, etc.); these characteristic features of the microbes together make their lysis challenging. Here, we use the a-AuNPs and their SPR effect (induced by laser irradiation) to achieve micron-scale heating when attached to the cell wall and thereby its lysis by disrupting the cell wall. Once lysed, the single-cell lysates will be sent for high-throughput single-cell RNA sequencing. Single-cell sequencing of microbial cells is critical in addressing some of the challenges in medicine and other environmental engineering applications.

SB11.08.04
Temperature-Dependent Pattern Formation in Drying Aqueous Drops of Lysozyme Anusuya Pal1, Amalesh Gope2 and Germano Iannacchione1; 1Worcester Polytechnic Institute, United States; 2Tezpur University, India

Drying bio-colloidal drops have a wide range of applications from medical diagnostics to industries as the patterns at the dried state can be linked to the nature of the constituent particles. The drying process and the resulting patterns are found to be affected by the atmospheric conditions including temperature, humidity, and so on. It, therefore, demands a detailed investigation to understand the nature of atmospheric conditions on the drying states. Lysozyme is a well-known globular protein, and preparations of lysozyme in de-ionized water make the simplest bio-colloid which could be used to explore the atmospheric effects on the drying states. During the drying process, a drop containing lysozyme particles gets pinned to the substrate and undergoes a convective flow. In the next stage, a fluid front recedes in a stick-slip manner and deposits particles from the periphery to the central region of the drop. The particles get redistributed during the fluid front movement; form a "coffee-ring", and finally result in crack patterns like other bio-colloids. A mound-like structure which forms in the central region is believed to be the leftover lysozyme particles flowed along with the fluid front. It is considered as a fingerprint for any aqueous lysozyme drop. In this experimental work, the time evolution and the resulting morphology during the drying process at different initial concentrations (1-20 wt%) and temperatures (25-55 °C) are investigated using bright-field optical microscopy. The captured images are then analyzed by various image processing techniques in ImageJ. The initial concentrations of lysozyme solutions are divided into three regimes, diluted (1 wt%), concentrated (5-13 wt%) and ultra-concentrated (17-20 wt%) regimes. During the drying process, initially, the fluid front moves slowly and linearly and then shows a fast, non-linear movement in both dilute and concentrated regimes. With the increase of...
Initial lysozyme concentration, this movement in the non-linear region slows down as the front carries and deposits more particles at each step. However, in the ultra-concentrated regime, the fluid front moves linearly throughout the drying process. The deposition of particles by the fluid front creates the “coffee-ring” and is found to increase with every initial concentration. A dimple is observed in the existing mound-structure, and both structures grow with the increase of the initial concentration. The width of the ring also increases monotonically with the concentration. The cracks which are only observed in the ring at dilute regime, are spread throughout the drop at concentrated and ultra-concentrated regimes. Besides these concentration effects, the temperature increases the drying rate at every regime. It provides almost no time for the convective flow of the particles during the early stage of the drying process. The dimple in the mound structure changes to an inflamed spot in the diluted and concentrated regimes, whereas, it diminishes in the ultra-concentrated regime when the temperature rises. Both concentration and temperature gradient within the drop leads to a surface tension gradient, affecting the drop morphology. Due to the presence of a large number of particles in the ultra-concentrated regime, the drop forms thickest film and experiences high mechanical stress resulting in smaller and delaminated crack domains. This study sets an example to the diverse assays of biocolloidal drops and has the versatility and applicability for machine learning algorithms.

**SB11.08.05**

**Evaporation of SiO2 Colloidal Droplets on a Hydrophobic Surface in the Presence of Saturated Wax-Esters**

Rudra Dev Mandal and Saumendra Bajpai; Indian Institute of Technology Madras, India

Differential evaporation of a sessile droplet containing small particles leaves a ring-like deposit, called the coffee ring effect (CRE). However, an inward flow, also known as the Marangoni flow, can also occur due to a surface tension gradient. In this investigation, we study the evaporation of a 1 ul droplet of a suspension containing low molecular weight Wax Esters (WEs, about 0.48 KDa) and silicon dioxide nanoparticles (NPs, about 15 nm) of varying concentrations (null to 5 mg/ml) and wettability (unmodified silica or PDMS-coated silica NPs) on a hydrophobic glass substrate (modified using FOTS) at room temperature (about 25 C). We observe that for hydrophobic NPs/WE droplet, the residual pattern after complete evaporation shows a single ring exhibited in all conditions and that the ring-thickness increases with increase in the WEs concentration. In contrast, the residual pattern for hydrophilic NPs/WE droplets showed a transition from ring-like deposits to uniform deposits, as we increase the WEs concentration. Concurrently, measurement of surface tension (pendant-drop method) reveals a bipartite change in surface-tension with varying NP: WE ratio under all conditions. In the light of these results, we propose that polar attractions between hydrophobic NPs and WEs ensure localization of WEs at the periphery of the droplet, thereby increasing the local surface tension and giving rise to inverse Marangoni flow. This results in a thicker ring as observed before. On the other hand, hydrophilic NPs and WEs do not exhibit a strong polar attraction, thus forming a Marangoni eddy and subsequently suppressing the ring-formation. Together, these results provide us with a closer insight into the evaporation of volatile solvents while spiked with oils and NPs. Finally, these findings can be used in applications that require a uniform particle deposition, such as printed electronics and ink-jet printing.
12:15 PM *X.01.01  
**Ghost in the Machine—Translating New Technologies into Next Generation Neurodevices**  
Brian Litt; University of Pennsylvania, United States

Modern neurodevices are rapidly expanding their footprint in research and clinical care. As science and technology advance, so is device complexity: hardware, software, and the systems that unite them. In this lecture I review the current state of neuro and bioelectronic devices, and provide a vision for how new materials and hardware will seamlessly integrate with state of the art algorithms and systems to improve quality of life. Cost, complexity, robustness and “plasticity” are themes we will discuss, as we envision devices of the future and their role in modern healthcare.

**Biography:**
Brian Litt, M.D., is Professor of Neurology, Neurosurgery and Bioengineering at the University of Pennsylvania. A clinician and scientist, he divides his time equally between Penn’s Schools of Medicine and Engineering, Directing the Penn Epilepsy Center, Penn’s Center for Neuroengineering and Therapeutics and a new cross campus medical technology initiative called Penn Health-Tech. Dr. Litt has an A.B in Engineering from Harvard, completed an M.D and Neurology training at Johns Hopkins, and has held faculty appointments at Johns Hopkins, Emory, Georgia Tech and for the past 20 years, Penn. His research translates NeuroEngineering - hardware, algorithms, machine learning, and high speed computing for implantable devices into clinical systems and devices, with a focus on improving the lives of people with Epilepsy. Dr. Litt has received many awards, created over 20 patents, contributed to or co-founded several device med-tech companies including Blackfynn, NeuroPace, MC10, NeuroVista, EpilepsyCo and the Rothberg family of companies.

12:15 PM *X.02.01  
**Nanoengineered Materials for Advanced Energy and Water Technologies**  
Evelyn N. Wang; Massachusetts Institute of Technology, United States

Nanoengineered materials have exciting, untapped potential to improve energy and water technologies. In this talk, I provide a few examples of how we leverage nanoscale manipulation capabilities to develop advanced thermal management, solar thermal energy conversion and water harvesting devices. First, I discuss our recent work that harnesses novel surface designs to control and manipulate wettability and liquid-vapor phase-change processes. We demonstrated high flux evaporation from ultra-thin nanoporous membranes and nanostructured surfaces that can repel liquids even during condensation. Next, I discuss how nanoengineered materials can also be used to increase the efficiency of solar thermal devices. Specifically, I share our work on nanophotonic solar thermophotovoltaics and optically transparent thermally insulating aerogel solar receivers. Finally, I present a water harvesting device that leverages the unique properties of metal organic frameworks and other adsorbents to address water scarcity.
challenges in arid climates.

**Biography:**
Evelyn N. Wang is the Gail E. Kendall Professor and Department Head in the Mechanical Engineering Department at MIT. She received her BS from MIT, and MS and PhD from Stanford University in Mechanical Engineering. From 2006-2007, she was a postdoctoral researcher at Bell Laboratories. Her research interests include fundamental studies of micro/nanoscale heat and mass transport and the development of efficient thermal management, solar thermal energy conversion, and water harvesting systems. Her work has been honored with awards including 2008 DARPA Young Faculty Award, the 2011 Air Force Office of Scientific Research Young Investigator Award, the 2012 Office of Naval Research Research Young Investigator Award, the 2012 ASME Bergles-Rohsenow Young Investigator Award, the 2016 ASME EPPD Women Engineer Award, and the 2017 ASME Gustus L. Larson Award. She was recognized as one of Foreign Policy’s Global Re-Thinkers in 2017. She is an ASME Fellow.

SESSION Session X.03
Wednesday Afternoon, December 4, 2019
Sheraton, 2nd Floor, Grand Ballroom

12:15 PM *X.03.01
Using Materials Science Concepts to Design New Drugs  
Francesco Stellacci; Ecole Polytechnique Fédérale de Lausanne, Switzerland

Viral diseases kill millions of people every year, mostly in developing countries. We need efficient drugs to fight them when vaccines fail. To date, only a handful of antivirals have been developed. I will show that it is possible to use Materials Science concepts to design a whole new class of antiviral drugs. Viruses can be viewed as the self-assembly of many biological components. It is possible to design nanoparticles, macromolecules, and simple molecules that target specific parts of the viruses (the viral attachment ligands). I will show that, in these materials, the presence of long hydrophobic, flexible arms induces irreversible damages to the self-assembled virions upon binding, rendering them non-infective permanently. The design principle underlying this effect is the hydrophobic contact between the drugs and the virions that results in a locally applied pressure. Results in vitro, ex-, and in-vivo against a number of viruses will be discussed.

**Biography:**
Francesco Stellacci is a full professor in the Institute of Materials and in the Bioengineering Institute at EPFL where he also founded and heads the Integrative Food and Nutrition Center. Stellacci graduated in Materials Engineering at the Politecnico di Milano, in Italy, where he studied photochromic polymers. He moved to the Chemistry Department of the University of Arizona as a post-doc and worked on two-photon microfabrication techniques to produce three-dimensional metallic structures embedded in polymeric matrices. He was an assistant and associate professor in the Department of Materials Science and Engineering at the Massachusetts Institute of Technology. There he worked on the characterization of the ligand shell of nanoparticles, on DNA-based microfabrication techniques, and invented the concept of super-hydrophobic materials that remove oil from water. He is a fellow of the Royal Society of Chemistry, the European Academy of Sciences, and the Academia Europaea.

SESSION Session X.04
Thursday Afternoon, December 5, 2019
Sheraton, 2nd Floor, Grand Ballroom

12:15 PM *X.04.01
Engineering 2D Heterostructures with a Twist  
Alessandra Lanzara1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States
The past few years have seen exciting new opportunities emerging from simply stacking and/or twisting together atom tick layers of same or different materials. The lattice mismatch or rotational misalignment introduced by such stacking give rise to long range Moire patterns that leads to modification of the electronic band structure. This leads to the appearance of unexpected properties, such as Mott like behavior and superconductivity, even in weakly interacting systems such as graphene. In this talk I will present some recent efforts in my group on twisted and strained graphene and TMD heterostructures as a function of twisting angle and gating. By using angle resolved photoemission spectroscopy I will discuss the effect of such misalignments on their electronic structure and discuss what are the key parameters that lead to the onset of strong correlation and novel behavior in these materials.

Biography:
Alessandra Lanzara is the Charles Kittel Professor of Physics at the University of California Berkeley since 2002. She is the Elected Chair of the American Physical Society (APS) Far West Section, and the Director of the International School of Non-Equilibrium Phenomena at the Majorana Institute in Italy. She is the founder of QuAD - Quantum Advanced Detection, a company that enables breakthrough research in quantum computing. Lanzara has made groundbreaking contributions in quantum materials from discovery of spin momentum locking and electron-phonon interaction in high-temperature superconductors, symmetry breaking in graphene, to optical control of spin photocurrents in topological insulators. She has received several prizes such as Fibonacci Prize, Goepert Award, and Elected Fellow of APS. Lanzara received a Bachelor in Physics in 1995 from University of Rome La Sapienza, a Ph.D. in Physics and Materials Science from the same university in 1999 and was a post-doctoral fellow at Stanford University.